Effect of CaO on Leaching Kinetics of Boehmite from Middle Timan Deposit Bauxites

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Abstract

The addition of lime has a positive effect on many aspects of alumina production, but its effect on the kinetics of the leaching process is not fully understood. This paper describes the investigation of the influence of lime on the kinetics of leaching of boehmite from Middle Timan bauxite deposits. It was found that the extraction of 80 % alumina in the presence of lime is achieved only after 1.5 – 2 hours of leaching, whereas in the absence of lime the same degree of extraction is achieved after 1 hour of leaching. The addition of lime in the leaching of currently processed bauxite of Middle Timan deposit leads not only to a decrease in the rate of the process but also to an almost twofold increase in the apparent activation energy. This indicates that the rate-limiting step is the chemical reaction. The cause of the limitations, apparently, is the formation of hydrogarnet, the presence of which in the red mud is confirmed by x-ray diffraction analysis.

Keywords: bauxite, alumina, leaching, lime, kinetics.

1. Introduction

More than 90 % of alumina is produced from bauxite by the Bayer method [1], which consists of leaching alumina-containing minerals with an alkaline recycling solution. The solution, enriched with aluminum, is then sent to the deposition of aluminum hydroxide, which is calcined to produce alumina. The decomposed solution is recycled on the leaching of new portions of the bauxite. The solid residue from leaching (red mud), is sent to the sludge fields for storage [2]. The yield of the red mud is more than 50 % of the weight of the original bauxite

The output of red mud is strongly dependent on the quality of the used bauxite and the processing technology itself. Most harmful impurity in the bauxite is silica, which inevitably goes into solution and then precipitates in the form of desilication product. The number of generated red mud is also dependent on the method of desilication (the type of desilication product) [3]. In addition, the output of red mud depends on additional chemicals that are added with the purpose of intensification of extraction of alumina in solution.

For example, when using bauxite containing titanium in the form of anatase, it was shown that the addition of lime can significantly intensify the process of extraction of alumina by eliminating the formation of a film of sodium titanate on the surface of alumina-containing minerals [4]. In the presence of the titanium ii bauxite in the form of rutile, the necessity of Ca addition disappears, but the lime continues to be added to reduce the loss of alkali from red mud in the form of cancrinite. Because of the presence of lime, the silicon is bound in hydrogarnet, which is confirmed by x-ray diffraction analysis [5].

In addition, as shown in the recent work of Arikan et al. [6], the addition of lime contributes to a faster thickening of red mud, as well as obtaining better quality alumina by reducing the content of impurities in the aluminate solution. However, in their paper, the influence of lime on the

degree of extraction of alumina was shown only in terms of the final extraction of alumina into the solution after 2 hours of leaching. And, as far as we know from the open literature, at the moment a little amount of works has been carried out to study the effect of lime on the kinetics of the leaching process of boehmitic bauxites.

Based on the above, this paper attempt to study the effect of lime on leaching kinetics of boehmitic Middle Timan bauxites at different temperatures of the process and to explain observed phenomena.

2. Experimental

The bauxite of the Middle Timan used in our experiments had the following chemical composition, mass. %: Al_2O_3 – 50,27; SiO_2 – 8,31; Fe_2O_3 – 24,60; S – 0,05; CO_2 – 0,30; CaO – 0,42; TiO_2 -2,90; H_2O. – 15,50; M_s = 6,06. Chemical analysis of raw materials and obtained red mud was carried out using the XRF-2000 spectrometer. Theoretical extraction of alumina from bauxite of this composition is 85% [7]. This parameter takes into account the losses of alumina with a complete transfer of the silica out of solution in insoluble desilication product. According to the X-ray difraction (XRD) in figure 1, the phase composition of Middle Timan bauxite is mainly represented by boehmite, hematite, rutile, kaolinite and chamosite.

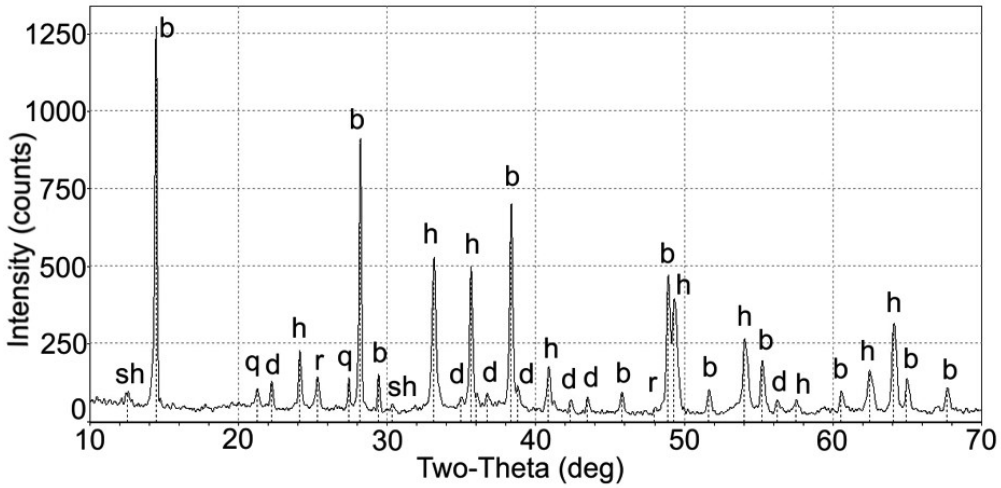

Figure 1. XRD pattern of the phase composition of Middle Timan bauxite: b – boehmite; h – hematite; d – diaspore; q – quartz; r – rutile; sh – chamosite.

For the experiment, bauxite was previously ground to a size of 75 μm more than 90%. As a reagent, a factory circulating solution of the branch of JSC RUSAL Ural in Kamensk-Uralsky with the Na_2O_k concentration 260 g\L and α_k module 3.55 units was used. The dosage of the solution during leaching of the bauxite sample was carried out to obtain a final α_k module equal to 1.64 units. Experiments with lime were carried out by adding the CaO of the chemical purity in an amount of 3 % of the mass of the initial bauxite.

Leaching of bauxite was carried out in an autoclave of Parr company with a volume of 1000 ml. The pulp after leaching was diluted to Na_2O_k concentration 130 g\L with distilled hot water and then filtered with subsequent repeated washing of the resulting red mud, which, after drying at 80 °C to a constant mass, was subjected to various physical and chemical methods of analysis.

3. Results and Discussion

The temperature at which bauxite leaching is carried out depends on the form of alumina in it [8]. In the studied bauxite, according to figure 1, alumina is mainly contained in the form of boehmite.

Boehmite is located in the middle in a series of the persistence of aluminum hydroxides and its leaching requires a temperature of more than 180-190 °C. Leaching of bauxite of Middle Timan at the branch of JSC "RUSAL Ural" in Kamensk-Uralsky is carried out at a temperature of 220-230 °C, so the temperature range from 190 to 230 °C was chosen to study the kinetics of leaching of this raw material. The leaching time was limited to 2 hours, as according to the factory data this time is enough to complete the process. Kinetic curves of leaching (dependence of the degree of extraction of alumina into the solution on the time and temperature of the process) of bauxite in the presence of lime are shown in figure 2.

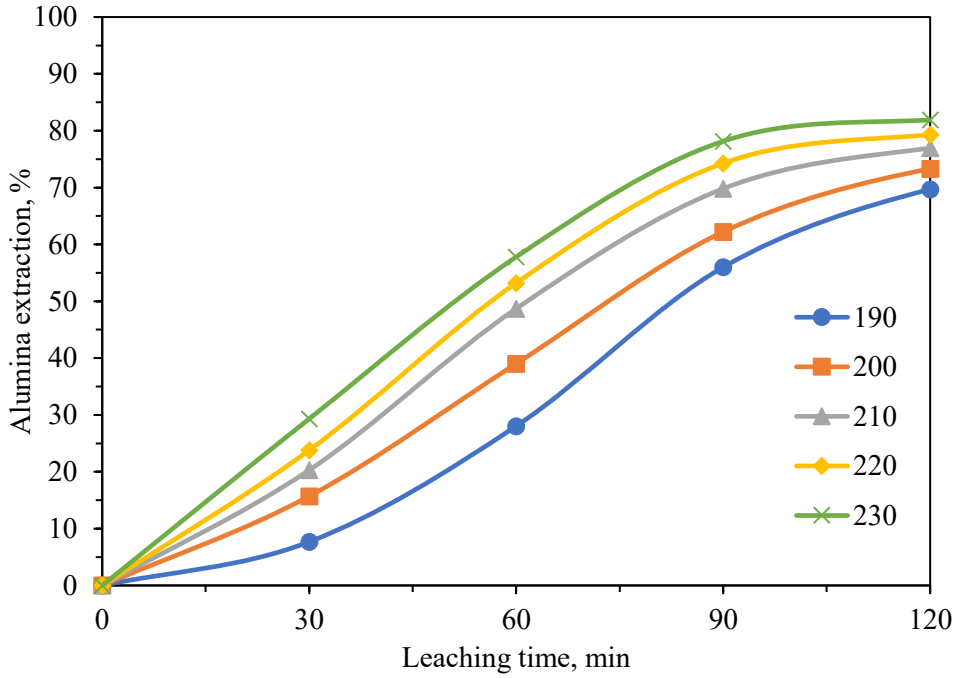

Figure 2. Dependence of the degree of extraction of alumina into the solution on the time and temperature of the process in the presence of lime.

According to figure 2, the leaching temperature and duration have a significant effect on the leaching of alumina from bauxite in the presence of lime, for 2 hours the maximum extraction of alumina from bauxite was 82.10%, which is close to theoretical. At temperatures below 200 degrees, the extraction rate did not exceed 73.3 %, indicating possible kinetic limitations of the process. Figure 3 shows the effect of temperature and duration on the recovery of alumina from bauxite during lime-free leaching.

It is obvious that the leaching of bauxite in the absence of lime is much more intense, especially in the first 30 minutes, and the degree of extraction of alumina reaches 80% after 1 hour of leaching, the maximum degree of extraction was 83.9 %, which is almost 2 % higher than in experiments with lime. At the same time, the influence of temperature is not as great as in the case of leaching bauxite in the presence of lime, which indicates the possible presence of diffusion limitations.

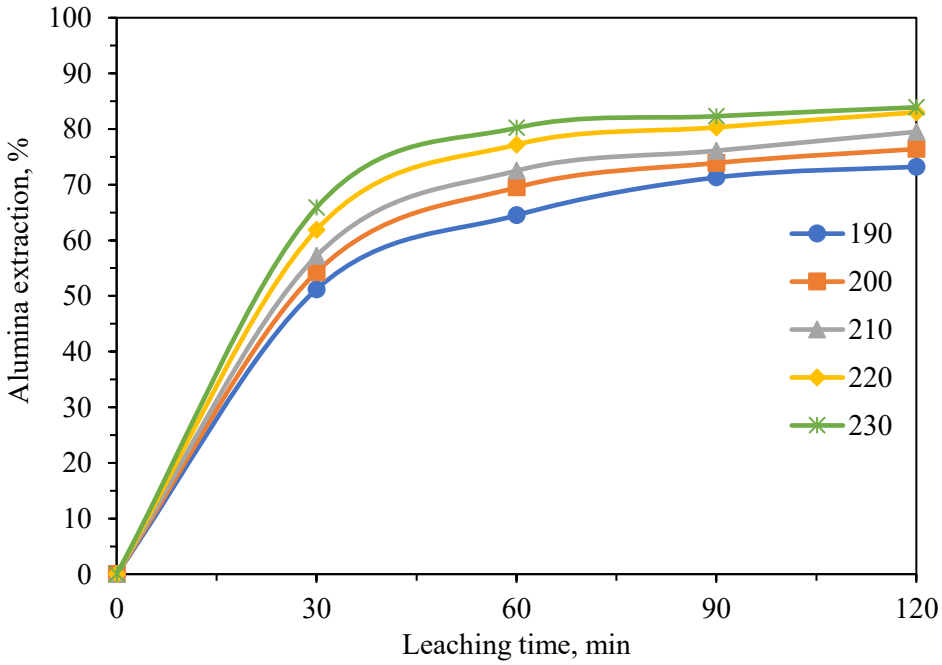

Figure 3. Dependence of the degree of extraction of alumina into the solution on the time and temperature of the process in the abscence of lime..

Thus, it can be seen that the addition of lime changes the leaching mechanism. To confirm the findings, calculations of the apparent activation energy were performed using the method described by Zelikman et al. [9], which is based on the Arrhenius equation $k=k_0e^{-E_a/RT}$.

According to the obtained kinetic curves, the apparent activation energy of the bauxite leaching process was calculated at the alumina extraction rate of 30%, the results of processing the curves are presented in tables 1 and 2.

Table 1. Results of processing of kinetic curves of extraction of alumina in the presence of lime.

T, K	1/T, 1/K	dα/dt, %/min	ln(dα/dt)
473	0.00211	0.62	-0.48
483	0.00207	0.76	-0.28
493	0.00203	0.86	-0.15
503	0.00199	0.98	-0.02

Table 2. Results of processing of kinetic curves of extraction of alumina in the abscence of lime.

T, K	(1/T), 1/K	dα/dt, %/min	ln(dα/dt)
473	0.00211	2.06	0.72
483	0.00207	2.20	0.79
493	0.00203	2.41	0.88
503	0.00199	2.60	0.96

The angle of the slope of the line in the coordinates ln(da/dt) - (1/T) (figure 4) allow to calculate the value of the activation energy by the equation (1):

$$E = -Rtg\alpha, \quad (1)$$

where E – the activation energy (kJ/mol),
R – universal gas constant (J/mol·K),
tgα – the angle of the slope of the straight line drawn through the experimental points in the coordinates ln(dα/dt) - (1/T).

Study of the leaching kinetics and calculation of the apparent activation energy showed that the extraction of alumina in solution most likely occurs in the diffusion mode, regardless of the presence of lime, as the resulting values of the apparent activation energy were 30.0 kJ/mol with lime and 15.7 kJ/mol without lime. This is also confirmed by the literature data [9], according to which at temperatures below 180 ° C the rate-limitins step of leaching of diaspore and boehmite is the chemical reaction, and at temperatures above 180 ° C – the diffusion of ions.

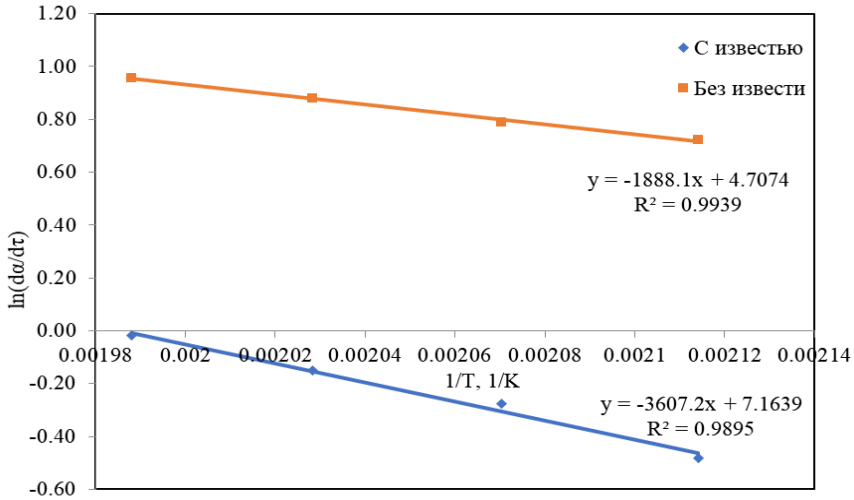

Figure 4. Results of processing of kinetic curves in coordinates ln(dα/dt) – (1/T).

However, the value of the apparent activation energy of leaching of Meddle Timan bauxite in the presence of lime is almost two times higher, indicating that there are difficulties in the chemical reaction of dissolution of boehmite by caustic alkali. It is possible that these difficulties are associated with the formation of hydrogarnets, which can be seen on the XRD of red mud in figure 5.

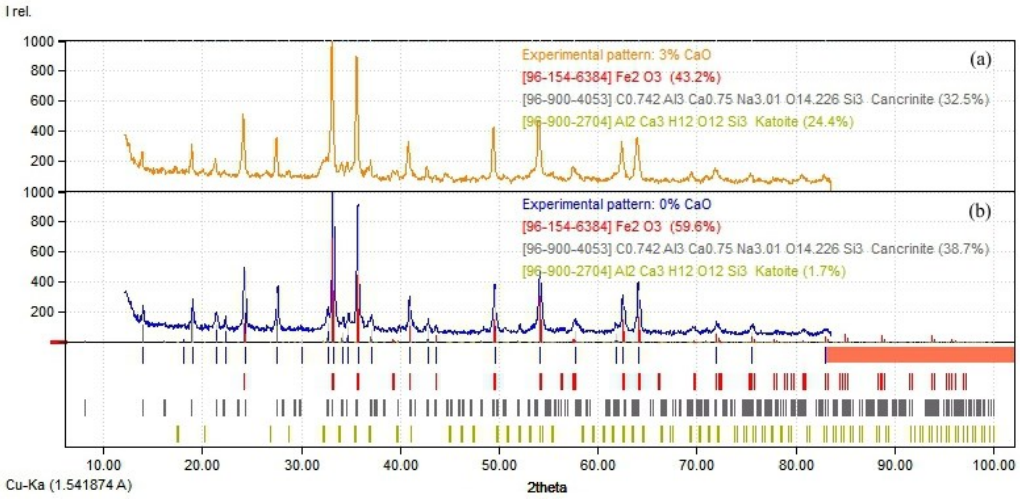

Figure 5. XRD pattern of red mud obtained with the addition of lime (a) and in the absence of lime (b).

The XRD in figure 5 shows that the addition of 3 % lime by weight of the starting bauxite decreases the amount of cancrinite (desilication product), and significantly increased the number of katoite (hydrogarnet), which reduces losses of caustic alkali, however, increases the loss of alumina. Also at the initial moment, the formation of tricalcium aluminate is possible, and the addition of lime, among other things, can affect changes in the structure of the aluminate solution, which is confirmed by almost complete inhibition of the decomposition process with a large amount of lime in the pulp.

4. Conclusions

As a result of the experiments and the study of the kinetic features of the leaching of bauxite of Meddle Timan deposit in the presence and without lime additives, it was found that even a small addition of CaO (3 %) leads to a change in the mechanism of dissolution of boehmite with caustic alkali. Extraction of 80 % alumina in the presence of lime is achieved only after 1.5 – 2 hours of leaching, whereas in the absence of lime the same extraction is achieved after 1 hour of leaching. According to the calculations of the apparent activation energy, both processes apparently proceed in the diffusion regime, since the apparent activation energy was 30 and 15.7 kJ/mol for the dissolution of boehmite with caustic alkali in the presence and without lime, respectively. However, the value of the apparent activation energy in the presence of lime was almost two times higher, which indicates the appearance of difficulties in the chemical reaction itself, which causes a slowdown in the leaching process. The mechanism of slowing, apparently, associated with the formation of hydrogarnets in the initial time of the process.

5. References

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