Light Metals 2014
Edited by: John Grandfield
TMS (The Minerals, Metals & Materials Society), 2014

HYDROCHEMICAL METHOD OF LOW-QUALITY RAW MATERIALS PROCESSING TO ALUMINA

Vladimir G. Kazakov[1], Vadim A. Lipin[2]
[1]St. Petersburg State Technologic University of Plant Polymers
4, Ivana Shernykh st., St. Petersburg, 198095, Russia
[2]St. Petersburg State Polytechnical University
29, Polytechnicheskaya st., St. Petersburg, 195251, Russia

Keywords: Low-quality bauxite, Nepheline, Coal fly ash, Alumina, Hydrochemical method

Abstract

The technological substantiation of the process flowsheet for low-quality bauxite, nepheline, coal fly ash and other kinds of raw materials with high silica content processing by hydrochemical method is presented. According to this process, silica changes to calcium hydrosilicate in autoclave conditions at the low concentration of the caustic. This allows conducting the alumina production at low consumption of energy resources, high regeneration of the heat and at the low vapor consumption for the liquor evaporation. Besides the hydrochemical method may be used to different kinds of alumina content processing solid waste. Thus the ecological problems are solved. Besides the hydrochemical method processing may be used to various kinds of alumina content processing solid waste. Thus environmental problems may be solved.

Introduction

Alumina production in its practical implementation is the technological scheme in the form of closed circulation fluid flow alkali-aluminate liquor. At the beginning of the cycle, the feedstock is putted to expense, and in the end is brought out into the open in the form of finished products as alumina.
Main in determining the technical and economic performance and, as a result, in the numerical value of the cost is the quality of the aluminumcontent material. The basic criterion of feedstock is the content of SiO_2 in it. The quality of feedstock tends to worsen with each passing year.

With increasing in feedstock of SiO_2 content the stream of materials per unit of produce increased, the productivity of equipment for alumina decreased, all technical and economic performance of the process have become worse, and the cost of alumina increased.
High quality bauxites with low SiO_2 content are processed only by Bayer process. For low-grade bauxite and nepheline and other aluminum-containing raw materials with a high content of silica known several possible ways of processing to alumina:

- sintering method with limestone and soda;
- Bayer-sintering method as parallel version;
- Bayer-sintering method as serial version;
- Hydrochemical method.

In the practical use of these methods are far from achievable by uneven economic and environmental indicators.
Disadvantages of the method of sintering are significantly exceed the Bayer process energy requirements for the process mainly during the sintering of charge, carbon dioxide emissions into the environment, mud discharge. Sintering method is also associated with high operating costs of managing complex technological scheme and the cost of protecting the environment.

The processing of the nepheline concentrate to alumina is carried out by sintering method. This method is characterized by high consumption of the energy, mainly in the form of fuel, during the charge sintering. The alumina production by this method is cost-efficient only provided the complex processing of nepheline concentrate to alumina, soda, potash, cement, etc. takes place [1,2]. Therefore the sintering method for high silica raw materials finds limited application.

Creating of new object working by sintering method causes the high one-off investment costs. Those shortcomings characterize and processing of bauxite in parallel Bayer-sintering method. Sequential Bayer-sintering method is characterized by acceptable economic performance of processing of bauxite raw materials with Al_2O_3/SiO_2 weight ratio 3,8÷4,5 units, but retains all the negative characteristics inherent in sintering method.

The hydrochemical method is an alternative to the sintering method at the nepheline and other kind of aluminiumcontent raw materials processing to alumina [4,5]. For example the use of hydrochemical method for the nepheline processing allows lowering the energy consumption for the nepheline processing to alumina more than twice.

Hydrochemical method of processing the aluminum material in a classical form provides highly alkaline leaching of raw concentrated liquors in autoclave conditions followed by separation in solid phase of sodium calcium hydrosilicate - $Na_2O{\cdot}2CaO{\cdot}2SiO_2{\cdot}H_2O$. Hydrochemical method in its traditional form has the following disadvantages:

1). the need for rapid separation of autoclaved mud (otherwise the liquid phase is cooled and hydrolysis occurs with precipitation in solid phase of aluminum-containing compounds);
2). difficulties of working with highly alkaline concentrated liquors (the need for expensive equipment and operational complexity).
3). absence of corrosion-resistant high-pressure equipment, necessary for high temperature leaching in concentrated aluminate liquors. The high cost of the equipment for the leaching process, as well as deep evaporation aluminate liquors, and high consumption of thermal energy in excess of 10.0 Gcal per 1 ton of alumina.

Physico-chemical basis of the modified hydrochemical method

From a technological point of view disadvantages hydrochemical technologies can be largely mitigated by using a modified version

of it, including the precipitation in solid phase at the leaching of aluminum-silicon compounds in raw form $2CaO{\cdot}SiO_2{\cdot}nH_2O$.
In the system $Na_2O–Al_2O_3–CaO-SiO_2–H_2O$ at temperatures above 280 °C, molar ratios of $CaO:SiO_2$ = 2:1 and $Al_2O_3:SiO_2$ = 1:1 and Na_2O more than 200 g/l depending on the α_{ku} the equilibrium solid phases are phases described in Table. 1.

Table 1
The equilibrium solid phase in the system $Na_2O–Al_2O_3–CaO-SiO_2–H_2O$

N	$\alpha_{ку}$, unit	The equilibrium solid phase	N	$\alpha_{ку}$, unit
1	0-1,2	$3CaO{\cdot}Al_2O_3{\cdot}mSiO_2{\cdot}(6–2m)H_2O$; AlOOH	1	0-1,2
2	1,2-5,0	$3CaO{\cdot}Al_2O_3{\cdot}mSiO_2{\cdot}(6–2m)H_2O$	2	1,2-5,0

From the presented data in Table 1 follows what the hydrodicalcium silicate is in equilibrium with the aluminate liquor having caustic module higher than 5 units.
The interaction of silica and lime to produce $2CaO{\cdot}SiO_2{\cdot}nH_2O$ can occur in low concentrations liquors in autoclave conditions.

Processing of low-grade bauxite by the modified hydrochemical method

For the processing of low-grade bauxite into alumina in the current practice used combined methods including Bayer branch and sintering branch. Hydrochemical method allows to get rid of sintering branch and, thus, to cut energy costs. In addition, the hydrochemical method is suitable for processing of bauxite with any ratio Al_2O_3/SiO_2 them.
The specificity of a number of bauxite is also a presence of chamosite - $(Fe^{2+},Mg,Fe^{3+})_5Al(Si_3Al)O_{10}(OH,O)_8$. Even within the same deposit the chamosite is characterized by unstable chemical composition, different conditions of mineralization, uneven distribution.

The presence of chamosite as siliceous minerals at autoclave leaching of bauxite in Bayer process negatively influences a commodity output of alumina. So in the aluminate liquor with molar ratio of Na_2O/Al_2O_3 1.7 and leaching temperature 240 ºC pure the chamosite composition, wt %.: 23,28 Al_2O_3, 24,10 SiO_2, 17.33 Fe_2O_3, 18,3 FeO expanded by only 30%. However, with the reduction of aluminate ions in the liquor increases the degree of decomposition. At the same temperature and molar ratio of Na_2O/Al_2O_3 3.6 the chamosite expanded by 55%. In pure alkaline liquors chamosite completely decomposes to sodium hydroalumosilicate and magnetite.

Given the characteristics of the modified hydrochemical method namely low alumina content in liquor, high temperature of leaching, molar ratios of Na_2O/Al_2O_3 from 4 to 7÷8, a full leaching of chamosite can expect.

For the processing of bauxite with high content of chamosite to alumina the Bayer-Hydrochemistry sequential method is represented expedient. In hydrochemical part provides dressing of red mud, autoclave processing of aluminumcontent component after dressing, precipitation and regeneration of three-calcium hydroaluminate – TCAH (Figure 1).

As result of this method implementation the energy and capital costs for processing of low-grade bauxite in comparison with the combined Bayer-sintering method considerably decrease and the rise of alumina commercial yield at processing of bauxite with high content of chamosite is reached.

Nepheline processing by the modified hydrochemical method

According to hydrochemical method, nepheline is processed with caustic liquor at the temperature exceeding 230 ºC in presence of lime [4,5]. According to one of the options of hydrochemical method silica from nepheline gets fixed in calcium hydrosilicate as per overall reaction:

$$(Na,K)_2O{\cdot}Al_2O_3{\cdot}mSiO_2 + nCa(OH)_2 = nCaO{\cdot}mSiO_2{\cdot}(n\text{-}p)H_2O + 2(Na,K)AlO_2 + pH_2O,$$

and aluminium passes into liquor.

Similar reactions are possible at the following parameters: concentration of the liquors used for the nepheline decomposition is 113÷124 g/l NaOH as Na_2O, temperature - 270÷300 ºC, molecular ratios - $(Na,K)_2O/Al_2O_3$ = 6÷7, CaO/SiO_2 = 2, leaching time - 0,5÷2 hours. Under these parameters the alumina and caustic recovery should exceed 80 %. In addition, these conditions make it possible to conduct the process at the high heat regeneration of autoclave slurry and at the low vapor consumption for the liquor evaporation [6].

The use of hydrochemical method of nepheline processing (Figure 2) allows compared with sintering method to cut down the energy consumption for processing of nepheline to alumina more than twice. The best results for the yield of alumina from nepheline at dose of lime on the molecular ratio SaO/SiO_2 = 2 units obtained with the following parameters: concentration of caustic liquor in 120 g/dm^3, leach temperature 317 ºC, leaching duration 80 minutes.

Processing of anorthosite kaolinite, coal fly ash and other low-quality raw aluminumcontent raw materials

The predominant minerals in anorthosite are albite - $Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2$ and anorthite - $CaO{\cdot}Al_2O_3{\cdot}2SiO_2$, in kaolinite - $CaO{\cdot}Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$. Coal fly ash are obtained in tremendous quantities at heat and power plant and have designated as the main chemical components CaO,$\cdot Al_2O_3\cdot$and SiO_2, in various combinations [7].

Processing of anorthite, kaolinite, and coal fly ash by sintering method [2,5] due to their high content of silica is associated with high energy consumption (more than 60 GJ/t Al_2O_3) and large material flows.
Hydrochemical technology (figure 2) allows essentially to reduce the energy costs for processing these types of high-silicon raw materials, and to use of industrial waste for alumina production.

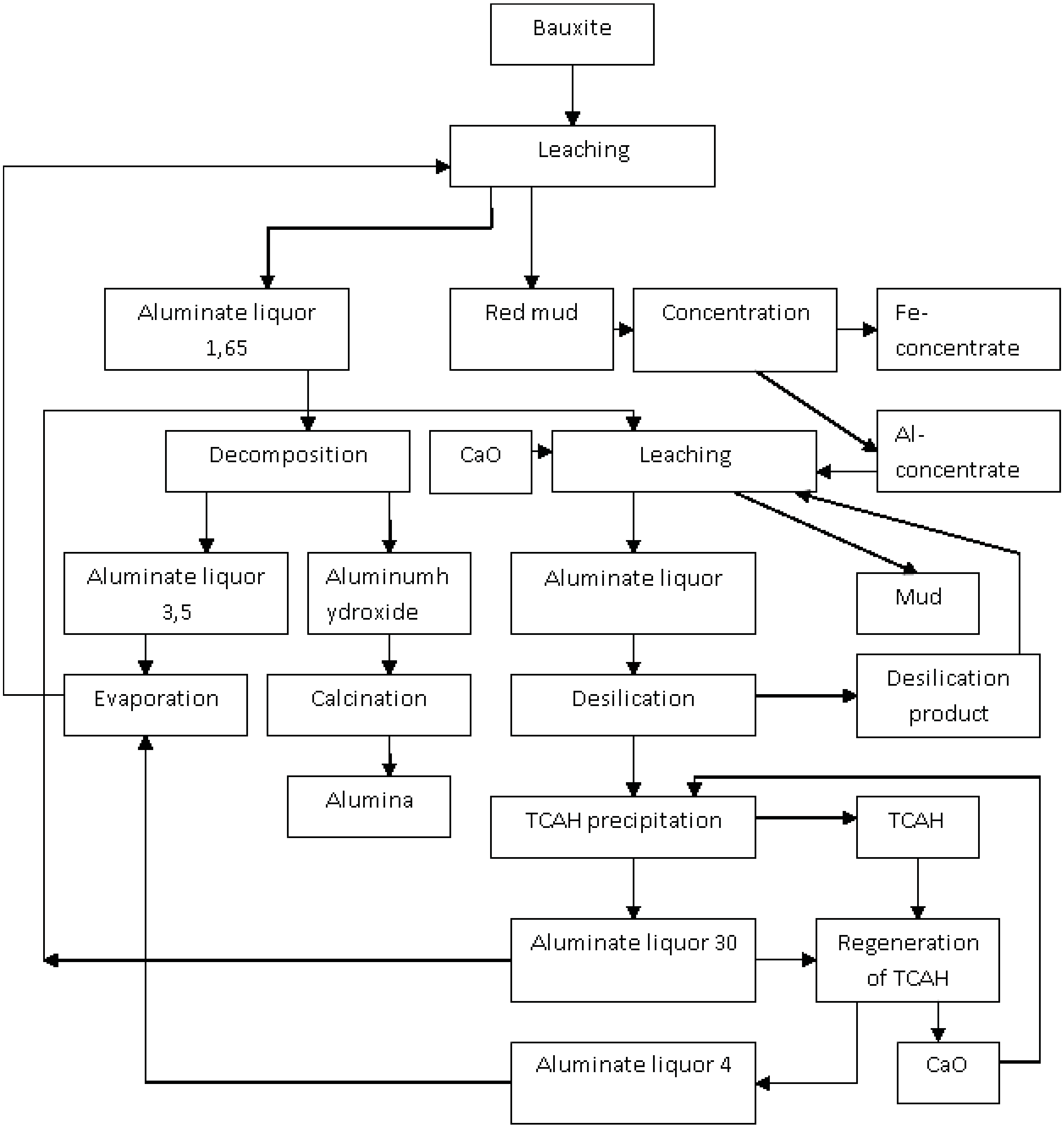

Figure 1. Scheme for processing of bauxite by the modified hydrochemical method.

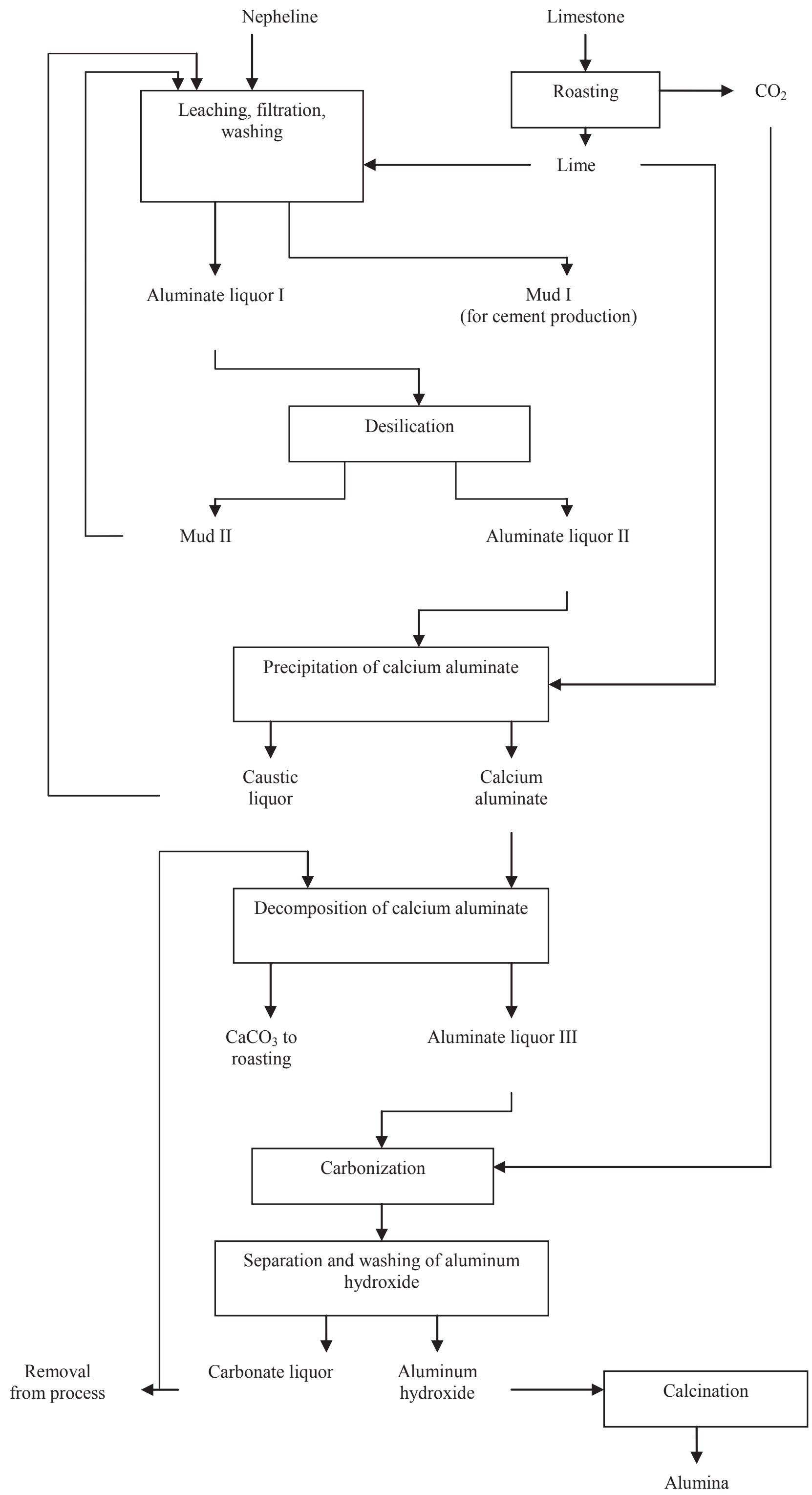

Figure 2. Scheme for processing of nepheline raw materials by hydrochemical method.

Future Trends

Active processing of high quality bauxite, inevitably and quickly lead to the need of processing of raw materials with lower ratio in it aluminum and silicon oxides. Under the circumstances, the classic Bayer method will not provide an acceptable cost of the final product. The sintering method applied to the aluminum-containing low-quality raw materials will have limited use. Hydrochemical method for processing low-grade aluminum-containing materials in various combinations with the Bayer process or without is only one alternative at this level of technology.

In addition, the hydrochemical method of processing can be turned to different types of industrial wastes, which, for example, are the ash from the combustion of coal et al. Thus the use of this method allows solving the rather serious problem of solid waste of thermoelectric power stations. As the result an environmental problem is solved.

The realization of hydrochemical method for processing of aluminiumcontent raw materials should be organized primarily using standard processing methods at traditional equipment of alumina production. Thermal circuit of raw materials refining shall be a minimum consumption of primary energy.

References

1. M. N. Smirnov, "Physical-chemical fundamentals of alumina production from nepheline", Proceedings of the Second International Symposium of ICSOBA. Budapest, 3 (1971), 337-345.
2. B. I. Arlyuk, "Comparative evaluation of efficiency of using bauxite and nepheline ores for production of alumina", Light Metals 1995 (Edited by J. Evans, The Minerals, Metals & Material Society, 1995), 121-131.
3. V. A. Lipin and N. N. Tikhonov, "Features of alumina production technology from alumosilicate raw material with potassium's high contain", Light Metals 1997 (Edited by R. Huglen, The Minerals, Metals & Material Society, 1997), 137-141.
4. V. S. Sazin, "New Hydrochemical Procedures for Complex Processing of Aluminum Silicates and High-Silicon Bauxites", Metallurgiya: Moscow, USSR, 1988, 212 p. (Russ); "Chemical Abstract", 1988, 109 (54), # 194357j (English)
5. V. I. Rayzman and S. A. Shcherban, "Recovering alumina, silica and byproducts from coal ash through the use of process for silicon pre-extraction", Light Metals 1997 (Edited by R. Huglen, The Minerals, Metals & Material Society, 1997), 133-136.
6. V. G. Kazakov, V. A. Lipin, V. A. Matveev, D. V. Mayorov and V. N. Korovin, "Joint Effect of Parameters of Hydrochemical Nepheline Processing on Alumina", Russian Journal of Applied Chemistry, (1) (86) (2013) 1-5.
7. Laishi Li, Xinqin Liao, Yusheng Wu and Yingying Liu, "Extracting Alumina from Coal Fly Ash with Ammonium Sulfate Sintering Process", Light Metals 2012 (Edited by C. E. Suarez, The Minerals, Metals & Material Society, 2012), 215-217.