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Evolution of the Technology for the Production of Alumina from Bauxites

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Abstract

This article covers the description and systematization of different technologies for the production of alumina from bauxites and the substantiation of the advantage in the application of “Bayer-hydrochemistry, hydro-garnet version” technology for the processing of low-quality bauxites and red muds.

Introduction

As of 2012 the world alumina production output is estimated to be at the level of 100 million tons per year [1] Approximately 98.7 million tons alumina from this quantity is produced from bauxites and about 1.3 million tons – from nephelines.

As of 2012 bauxite mining is estimated to be 220 million tons (average content of $\text{Al}_2\text{O}_3 = 48\%$, $\text{SiO}_2 = 4.5\%$), and geological reserves of bauxite in the world make up 29 billion tons [2].

The trend of last decades is a permanent degradation of bauxites: decrease of silica ratio, increase of impurities content, and occurrence of hard Al_2O_3 forms in raw materials.

Large part of quality bauxites is available in the regions with difficult access from the geographical point of view as there is no developed industry and/or social infrastructure in these regions.

At the same time, alumina refineries that were in operation earlier or are still in operation today are surrounded by large mud lakes which store industrial waste in form of dump red muds with average content of $\text{Al}_2\text{O}_3 = 10.5\%$ and $\text{Na}_2\text{O} = 3.1\%$.

The total quantity of stored harmful industrial waste (red mud) is approximately 2 billion tons, which contain about 210 million tons alumina and about 62 million tons of caustic, significantly impairing the environmental situation at the areas of mud lakes' location.

Besides high-quality bauxites low-quality bauxites are available in different regions of the world (silica ratio < 4.0 , Al_2O_3 content $< 45\%$); their geological reserves being estimated at ~ 100 billion tons. These bauxites are not yet involved in alumina production.

All these factors determine the need in carrying out a classification of the existing situation by technologies for bauxite processing on which base it could be possible to define the most efficient methods for bauxite processing from the technological, environmental and economic points of view [3, 4, 5].

Classification of the technologies for the alumina production from bauxites

Austrian scientist Karl Joseph Bayer (1847-1904) worked at chemical plants in Russia in 1885-1892 and had made two

important discoveries in the technology of alumina production from bauxites, on which he obtained two patents in Germany. The first patent (1889), describes the process of spontaneous decomposition of sodium aluminate liquors in the presence of freshly precipitated seeds of aluminium hydroxide. This discovery was made at the Tenteleyev plant (now “Krasnyi Khimik”) in Saint Petersburg, Russia.

The second patent dated 1892 claims the possibility to dissolve aluminium oxide from bauxites and generate sodium aluminate by processing bauxites with strong caustic solution under pressure in autoclaves. Spent liquor, resulted from the sodium aluminate decomposition as per first patent was used as the source of strong caustic. The discovery was tested in 1890 at Bonduzhskiy chemical plant, Elabuga, Russia.

In 1893 Karl Joseph Bayer became director and built in France the first refinery for alumina production from bauxites as per method, patented in 1889-1892. Further, this method was implemented in many countries and named “*The Bayer Method*”. Now we can designate it as “*Classical Bayer*” method [6,7].

The lack of high-quality bauxites with silica ratio higher than 15 in USSR necessitated the search for alternative approaches to enhance the “Classical Bayer” method. As a result, the Soviet scientists developed a combined method that was called “*Bayer-sintering, parallel version*” [8,9,10].

In 1939 the Ural aluminium smelter was put in operation in Kamensk-Uralskiy in the Soviet Union. This smelter had alumina production plant, where the technology of “*Bayer-sintering, parallel version*” was used. The same technology was used in 1949 at the Bogoslovsk alumina refinery in Krasnoturinsk.

The essence of the improvement, implemented at these enterprises, consists in that together with the Bayer branch in which low silica mono-hydrate bauxites of quality are digested, a parallel line for high-silica bauxite processing based on bauxite sintering with limestone and soda, is also operational. In this line the thermal causticization of the mixture of fresh soda ash and recycled “red soda” occurs.

Aluminate liquors from Bayer branch and sintering branch are jointly processed into alumina in accordance with the first Bayer's patent. The capacity of sintering area is determined by the need in soda that was subjected to the causticization, which is much lower than the capacity of Bayer branch. Red muds from both branches are discharged to a common mud lake.

In 1965 an alumina refinery was put in operation in Pavlodar, Kazakh Republic of Soviet Union, for the processing of bauxites with SiO_2 content higher than 12.0 % according to the method of “*Bayer-sintering, successive version*” [11,12,13,14].

The essence of this method consists in additional treatment of Bayer red mud by sintering with limestone and soda liquor. After the digestion of produced sinter in recycled caustic-aluminate liquor, silicon dioxide turns completely into dump mud, mostly as part of two-calcium silicate. Such flowsheet of high-silica bauxite processing allows reducing the losses of Na_2O and Al_2O_3 considerably in comparison with traditional Bayer method. Aluminate liquors from both branches are also processed together in accordance with the first Bayer's patent.

In 1958 and 1980 two alumina refineries were built in Zaporozhie and Nikolaev (Ukraine), respectively, that used the Classical Bayer method for processing high-quality bauxites that were supplied from the overseas, but in which SiO_2 content was higher than 4.0%.

Different mineral forms of aluminium-bearing rock-forming phases of bauxite (gibbsite, boehmite, diaspore) required some modifications to be introduced into the Classical Bayer technology [15]. The distinguishing features relate to the Process Flow Diagram, PFD, and Process & Instrumentation Diagram, PID, for the autoclave area, the temperature level in the reaction zone, and the need for controlling scale formation on the heating surface of untreated bauxite slurry.

This resulted in appearance of classical Bayer method versions that could be classified as follows:

1. Classical Bayer, low-temperature version ($T_{\text{digest.}} = 100\div 115^\circ\text{C}$; gibbsite bauxites).
2. Classical Bayer, medium-temperature version ($T_{\text{digest.}} = 210\div 235^\circ\text{C}$; boehmite bauxites).
3. Classical Bayer, high-temperature version ($T_{\text{digest.}} = 260\div 280^\circ\text{C}$; diaspore bauxites).

Figure 1 shows classification of methods for the production of alumina from bauxites using the Bayer technology.

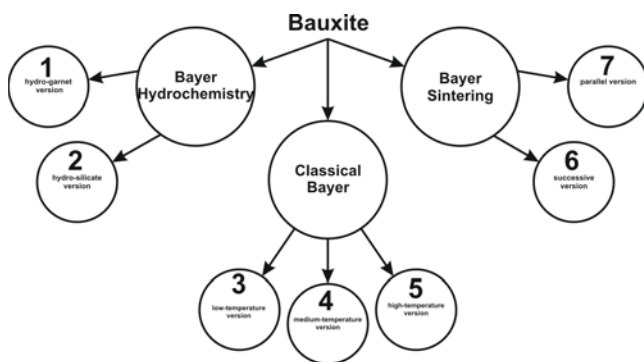


Fig. 1. Methods for alumina production from bauxites:

1-hydro-garnet version, 2- hydro-silicate version, 3-low-temperature version, 4-medium-temperature version, 5-high-temperature version, 6-successive version, 7-parallel version.

In 1970s, the Institute of Metallurgy and Concentration of the Academy of Sciences of Kazakhstan (Alma-Ata, USSR) developed the method of "Bayer-hydrochemistry, hydro-silicate version" for the processing of high-silica bauxites. This method was tested at the pilot plant LOZ VAMI (Saint Petersburg) in the 80s. According to the proposed technology all silica from Bayer red mud is combined into sodium-calcium hydro-silicate

$\text{Na}_2\text{O}\cdot 2\text{CaO}\cdot 2\text{SiO}_2\cdot \text{H}_2\text{O}$, which does not have any aluminium oxide in its composition [16,17].

In order to implement this process, a high-temperature (280°C) hydro-chemical digestion red mud and quick lime mixture is required. The concentration of $\text{Na}_2\text{O}_{\text{caustic}}$ in caustic-aluminate liquor is around 450 g/dm^3 and the caustic make-up ratio is ~ 35 .

Sodium hydro-silicate mud, produced during the digestion, is subjected to intensive washing with water for caustic regeneration. As a result of this washing the significant quantity of hydroalumosilicate is formed along with monocalcium hydro-silicate, $\text{CaO}\cdot \text{SiO}_2$, in the washed phase, which substantiates the losses of both caustic and alumina. The mineral composition of hydroalumosilicate phase is $n\text{Na}_2\text{O}\cdot a\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\cdot c\text{CO}_2\cdot s\text{SO}_3\cdot h\text{H}_2\text{O}$.

High-active dump mud, having the mineral composition, similar to that of sintered mud, is dumped to the mud lake.

In the 80s – 90s VAMI institute proposed an alternative method for processing of alumosilicate materials that was tested on bench- and pilot-plant scale.

Later, during the period of 2001-2012, ALCORUS Co Ltd (Saint Petersburg, Russian Federation), formulated theoretical foundations, related to the development of PFD and PID, the selection of equipment and development of civil engineering solutions that could be used for semi-industrial tests and introduction of a new method to process bauxites and red muds. New technology was named "Bayer – hydro-chemistry, hydro-garnet version".

The essence of this method consists in that the autoclave digestion of red mud from Bayer branch is carried out in high-ratio liquor with $\text{Na}_2\text{O}_{\text{caustic}}$ concentration of 210 g/dm^3 and caustic ratio of 32 at the temperature of 240°C in presence of activated additive, - the mixture of calcium hydroxide with sodium ferrite.

During red mud digestion all silicon dioxide passes from caustic phase of hydroalumosilicate to brand new mineral form, which does not have any sodium oxide and contains minimum of aluminium oxide. This form is represented by iron- and aluminium-calcium hydro-garnets - $3\text{CaO}\cdot \text{Fe}_2\text{O}_3\cdot 2\text{SiO}_2\cdot 2\text{H}_2\text{O}$ and $3\text{CaO}\cdot \text{Al}_2\text{O}_3\cdot \text{SiO}_2\cdot 4\text{H}_2\text{O}$. The final caustic-free solid product of red mud utilization is removed from the cycle as *iron-calcium concentrate* without any additional treatment; this concentrate having high application potential.

Sodium oxide and aluminium oxide, being regenerated from red mud, are recycled into the Bayer branch without any losses or they could be transformed into commercial products – soda, sodium hydroaluminate, fine-dispersed white aluminium hydroxide [18].

ALCORUS Co Ltd developed the mathematical model for calculating mass balances for different versions of Bayer technology. This model was used for the calculation of mass balances for all the versions of bauxite processing shown in Figure 1. In particular, the calculations for "Classical Bayer" technology used characteristics of tri-hydrate African bauxites; the calculations for "Bayer-sintering, parallel version" technology were based on monohydrate bauxites from Russian Federation

deposits, located in the Urals and in Komi Republic. The calculations for “Bayer-sintering, successive version” and “Bayer-hydro-chemistry, hydro-silicate version” technologies used the actual composition of Kazakh bauxites that are processed in Pavlodar. The calculations for “Bayer-hydro-chemistry, hydro-garnet version” technology used the characteristics of blended hypothetical bauxite composition, inherent to monohydrate bauxites from the Urals and Cisurals regions. The comparative analysis of the parameters of bauxite processing by different Bayer technologies is shown in table 1.

Based on the data presented in table 1, some conclusions are made and discussed below.

Particular features of “Classical Bayer” technology

High-quality tri-hydrate bauxites which are usually used by the “Classical Bayer” technology, have some physical-chemical and mineralogical differences (e.g., presence of alumogothite and hard forms of $Al_2O_3 \cdot H_2O$) that determine the need for modifications in processing parameters of the digestion stage. In particular, they require the increase of digestion temperature from 105°C to 280°C, as well as the increase in total lime to be used from 54 kg/t to 134 kg/t alumina. The increase of digestion temperature results in the increase of fuel consumption at the thermal power plant and in the increase of electric power consumption.

Table I. Computer model calculation of bauxite processing parameters using the Bayer technology

| No. | Parameter | Unit | Bayer process flow diagram version | | | | | | |
|-----|---|----------------|------------------------------------|-----------------------------------|---------------------------------|------------------|--------------------|------------------------|----------------------|
| | | | Classical Bayer | | | Bayer-sintering | | Bayer-hydrochemistry | |
| | | | Low-temperature version, 105°C | Medium-temperature version, 235°C | High-temperature version, 280°C | Parallel version | Successive version | Hydro-silicate version | Hydro-garnet version |
| 1 | Commercial output of Al_2O_3 | % | 82.30 | 87.40 | 88.00 | 82.32 | 85.43 | 86.00 | 93.36 |
| 2 | Na_2O losses with waste, per 1t bauxite | kg | 13.48 | 14.08 | 13.90 | 35.30 | 19.87 | 10.89 | 3.84 |
| 3 | Consumption rates for producing 1t of alumina | | | | | | | | |
| | 3.1. Bauxite (dry) | t | 2.61 | 2.45 | 2.43 | 2.33 | 2.71 | 2.70 | 2.19 |
| | 3.2. Soda ash (Na_2CO_3 -100%) | kg | 0 | 0 | 0 | 70.65 | 105 | 0 | 23.07 |
| | 3.3. Caustic soda (NaOH-100%) | kg | 52.10 | 51.23 | 43.59 | 60.82 | 0 | 56.00 | 0 |
| | 3.4. Total need in Na_2O | kg | 40.38 | 39.70 | 33.78 | 88.46 | 61.42 | 43.40 | 13.49 |
| | 3.5. Quick lime (CaO = 91,17%) | kg | 54 | 125 | 134 | 171 | 439 | 388 | 246 |
| | 3.6. Thermal energy, total | Gcal | 2.08 | 2.30 | 2.50 | 3.92 | 3.18 | 14.00 | 2.30 |
| | 3.7. Equivalent fuel in technology | kg equiv. fuel | 128 | 128 | 128 | 232 | 450 | 128 | 158 |
| | 3.8. Equivalent fuel at power plants | kg equiv. fuel | 386 | 427 | 464 | 728 | 592 | 2605 | 428 |
| | 3.9. Electric energy | kWh | 256 | 275 | 285 | 275 | 399 | 250 | 252 |
| | 3.10. Technical water | m ³ | 6.86 | 6.86 | 6.86 | 6.56 | 5.06 | 5.00 | 4.08 |
| 4 | Red mud to mud lake per 1 t of alumina | t | 1.16 | 1.10 | 1.09 | 1.36 | 1.75 | 1.79 | 0 |
| 5 | Output of iron-calcium concentrate ($Fe_2O_3 + CaO \geq 70\%$) per 1 t of alumina | t | 0 | 0 | 0 | 0 | 0 | 0 | 1.10 |
| 6 | Cost of raw materials and energy for production of 1t of alumina | % | 100 | 99.3 | 98.9 | 119.2 | 111.2 | 130.7 | 76,6 |
| 8 | Bauxite composition | | | | | | | | |
| | Al_2O_3 | % | 46.17 | 46.17 | 46.17 | 51.64 | 42.6445 | 42.64 | 47.40 |
| | SiO_2 | % | 2.29 | 2.29 | 2.29 | 6.63 | 10.19 | 10.19 | 6.52 |
| | Fe_2O_3 | % | 22.22 | 22.22 | 22.22 | 24.57 | 19.80 | 19.80 | 22.04 |
| | H_2O_{kr} | % | 24.50 | 24.50 | 24.50 | 11.46 | 19.97 | 19.97 | 18,52 |
| | Silica ratio | | 20.16 | 20.16 | 20.16 | 7.79 | 4.18 | 4.18 | 7.27 |
| | Theoretical Al_2O_3 recovery | % | 95.78 | 95.78 | 95.78 | 89.09 | 79.69 | 79.69 | 88.31 |

The growth of energy costs within the total production expenses in the high-temperature version of Classical Bayer process is only partially compensated by the increase in commercial output of alumina – from 88.3 to 89%, and by reduction of dry bauxite consumption – from 2.61 t/t Al₂O₃ to 2.43 t/t Al₂O₃.

At the same time the increase of bauxite treatment temperature requires considerable increase of investment and operating costs because of the use of bauxite digesting units and high pressure water steam generators.

Finally, the use of medium-temperature and high-temperature versions of the “Classical Bayer” technology in those investment projects, in which mines and refineries are located in the areas with undeveloped transport, industrial, energy and social infrastructures, makes them economically unattractive.

Particular features of “Bayer-sintering” technology

The “Bayer-sintering” technology is usually used for the processing of low-quality bauxites. As a rule, its successive version uses one kind of bauxite, in which silica ratio varies within the range of 3.8-4.4. Its parallel version usually processes two kinds of bauxites with different silica ratios. As a rule, low-silica bauxite is supplied to the Bayer branch (82% of alumina production), and high-silica bauxite together with limestone and soda is supplied to the sintering branch. Average weighed silica ratio of mixed bauxite materials is in the range between 7.5 and 8.

The successive version, according to which red mud from Bayer branch is subjected to sintering, achieves the lower consumption of raw materials and energy resources as well as provides higher commercial output of alumina in comparison with parallel version of “Bayer-sintering” technology.

The vast experience in “Bayer-sintering” technology application in Russia and Kazakhstan shows that these technologies are economically unattractive for the development of alumina production facilities. From the environmental point of view they are inefficient largely due to harmful emissions to the environment at the sintering areas where rotary kilns are in use.

In addition, these technologies result in the storage of large amounts of high-active red and sintered muds in the mud lakes. These muds are harmful to the eco-systems at the areas of alumina refineries’ waste storage.

Particular features of “Bayer-hydrochemistry” technology

Economic advantages of “Bayer-hydrochemistry” technology relative to “Classical Bayer” technology and some versions of “Bayer-sintering” technology are determined by high commercial output of Al₂O₃, low consumption of Na₂O and reduced consumption of energy.

The important advantage of “Bayer-hydrochemistry, hydro-garnet version” method consists in the possibility to utilize low-quality bauxite in the production and to completely transform dump red mud into new types of products that could have consumer benefit. Consequently, environmental advantages become obvious, consisting in that mud lakes around alumina refineries would be eliminated and, when compared to versions of “Bayer-sintering”

technology, the emissions of harmful matters from sintering kilns to the environment would be eliminated as well.

The specific feature of “Bayer-hydrochemistry, hydro-garnet version” technology is the hydro-chemical digestion of the red mud, lime and sodium ferrite mixture in high-caustic aluminate liquor (caustic molar ratio Na₂O/Al₂O₃ = 32) at the temperature of 235°C, caustic and aluminium oxide being passed to the medium-caustic liquor (caustic molar ratio Na₂O/Al₂O₃ = 10). Sodium oxide, recovered from red mud and the recycled soda liquor, returns back to the Bayer branch as part of high-caustic liquor component.

Aluminium oxide, recovered from red mud, is converted into solid aluminium hydroxide that is sent to the Bayer aluminate liquor precipitation area as active additive. Solid waste of red mud processing is removed from the cycle as iron-calcium concentrate to be sold on the market [19,20,21,22].

As is evident from table 1 (category 3), raw materials consumption for alumina production according to the “Bayer-hydrochemistry, hydro-garnet version” technology is lower than that for “Bayer-sintering, successive version” technology with respect to all components: bauxite, soda, limestone, thermal energy, equivalent fuel. This result is produced by high commercial output of aluminium oxide, low losses of caustic and by excluding the stage of thermal processing of initial raw material mixture.

Main advantages of the “Bayer-hydrochemistry, hydro-garnet version” technology in comparison with “Bayer-sintering, successive version” technology when processing low-quality bauxites consist of the following:

1. no discharge of dump sodium-bearing waste to mud lakes (~1.75t per 1t alumina);
2. possibility to build an autonomous hydro-chemical installation for processing of precipitated red muds according to hydro-garnet technology at existing alumina refineries; This would allow step-by-step utilization of accumulated red muds in parallel with main production operations;
3. red mud, stored in mud lakes, would be used as iron-bearing component for the causticization of soda flows and for liquidation of organic impurities via most efficient thermal method which is implemented through sodium ferrite synthesis. The quantity of red mud to be utilized would make up to 300-400kg per 1t alumina produced, depending on the composition of bauxite and red mud precipitated;
4. sodium oxide and aluminium oxide, recovered from dump red muds are recycled back to the production in amount of 15-16kg Na₂O and 23-25kg Al₂O₃ per 1t alumina;
5. solid residue, generated after the processing of red mud, is transformed into a new commercial product in the form of iron-calcium concentrate having high consumer properties. The output of new commercial product achieves 1.1-1.2t per 1t alumina.

Conclusions

Annual growth of aluminium consumption volumes in the world requires the increase in alumina production output, involving not only bauxites of quality but also low-quality bauxites as well.

The advantage of “*Bayer-hydrochemistry, hydro-garnet version*” technology consists in the possibility to use this technology at alumina refineries operating according to the “Classical Bayer” technology. This could be done by construction of additional areas for processing both fresh red muds and old ones being stored in mud lakes.

These additional production facilities would be closely integrated into the existing facilities of alumina production that would increase output both due to the increase in commercial aluminium oxide generation and due to return of Al_2O_3 recovered from processed red mud.

The “*Bayer-hydrochemistry, hydro-garnet version*” technology allows building new plants for the processing of low-quality bauxites, technical-economic parameters of these new plants would be better than those of “Classical Bayer” and “Bayer-sintering” technologies.

The “*Bayer-hydrochemistry, hydro-garnet version*” technology could be defined as environmentally-friendly technology as it excludes red mud storage and transforms alumina production waste into the product that could make profits. This would significantly improve the investment attractiveness of alumina refineries construction.

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