Conference Paper

Prospects of Chlorine Method of Aluminum Production in Modern Conditions

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Abstract

The results of the feasibility study of the complete aluminum chlorine production cycle in comparison with the conventional method, namely, the extraction of alumina by the Bayer method and subsequent electrolysis of cryolite-alumina melts are reported in this paper. The advantages of the proposed method are: using low-quality Al-containing raw materials and less scarce and aggressive chlorides instead of fluorides; reduction of specific electric power consumption by about 30%; elimination of high-quality carbon-containing materials consumption and harmful emissions into the atmosphere; reduction of capital investments; labor productivity improvement.

Keywords: aluminum-containing raw material chlorination, electrolysis of aluminum chloride, electricity savings.

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Aluminum industry is the classic example of international division of labour with a focus on mining and primary "dirty" process stages of raw materials in developing countries. In developed countries, where the main consumption of aluminum is concentrated, "finishing" process stages with high added value are located. Developing countries currently account for more than 50% of bauxite mining, about 1/3 of alumina and primary aluminum production and as many as 25% of its consumption [1].

The modern process of aluminum smelting is mainly based on alumina production according to the Bayer method followed by electrolysis of cryolite-alumina melts (Hall–Héroult process). Despite the long-standing application this method has a number of significant disadvantages: high specific energy consumption; low specific metal output (~ 1 kg/m^2·h), and the cell life; high labour and capital inputs. Aluminum smelters off-gases contain carbon dioxide, nitrogen, oxygen, gaseous and solid fluorides, and alumina dust particles, creating significant environmental damage.

Alternative methods for producing aluminum could be as follows: carbothermal, low-temperature electrolysis of chloride melts, improvement of the existing electrolysis process through the use of inert anodes, the development of wettable carbon cathodes and new compositions of electrolytes [2]. Actually the chlorine method is the closest to industrial development.

The IMET RAS laboratory for physicochemistry of aluminum conducted research and conduct pilot testing of chlorination within the conditions of fluidized bed of various types of aluminum raw materials: kaolin clay, North-Onega bauxite, alumina, rough alumina, separated using alkaline or acid enrichment of aluminum-containing raw materials. As a result of these studies the technological and energy balance indicators of chlorination process, to give anhydrous aluminum chloride, were obtained [3].

Objective is the feasibility study of the complete aluminum chlorine production cycle in comparison with the conventional method, namely, the extraction of alumina by the Bayer method and subsequent electrolysis of cryolite-alumina melts.

Technological and qualitative comparisons. Physico-chemical benefits of aluminum chloride electrolysis before electrolytic decomposition of aluminum oxide are: the lower process temperature, the lower $AlCl_3$ decomposition potential, carbon anode inactivity in relation to chlorine - provide savings at the process stage. However, the aluminum chloride electrolysis is more particular about quality of raw materials, and thus there is a need for additional chlorination costs. High purity of raw materials and lack of anode ash ensure commercial aluminum purity, similar to the super-purity aluminum (SPA).

Ratio evaluation of the energy savings on aluminum electrolysis and additional cost of the raw materials preparation is the methodological framework for subsequent calculations.

Comparative evaluation of operating costs. Raw materials. Raw materials for electrolyzer - metallurgical alumina GOST 305558–98. Consumption per 1 ton of aluminum is 2 tons of alumina. The price of 1 ton of metallurgical alumina is $400 or on per 1 ton of metallic aluminum basis - $800. Middling product for the aluminum chloride electrolysis must contain at least 99.97% of the main component - $AlCl_3$. Consumption per 1 ton of aluminum is 5 tons of aluminum chloride; per 1 ton of aluminum chloride - 0.4 tons of Al_2O_3. The cost of the alumina chlorination process is $63 per ton of $AlCl_3$.

Direct chlorination of natural or technology-related raw materials is inefficient, since the additional amount of chlorine go to chlorination of impurities in the material used. Cleaning of the resulting aluminum chloride from fractional condensation impurities is expensive operation. In addition, the issues of utilization of produced chlorides need to be addressed [3].

Inexpensive raw materials (active with relation to low impurities chlorine) for chlorination can be obtained by hydrochloric acid enrichment of high silicon aluminum-containing raw materials with the rough alumina release [4]. For the achievement the high degree of chlorination the part of the stream could be split in traditional alumina refineries, and rough alumina could be extracted by low-temperature carbonization, without deep desiliconization, at low (up to 800°C) calcination temperature. Due to this simplification, by our calculations, the resulting rough alumina used as the starting material for chlorination may be 5–25% cheaper than commercial alumina obtained in accordance with GOST 30558–98.

As a result, the estimated cost of aluminum chloride per 1 ton of metallic Al will be: (0.4 × 400 × 0.85 + 63) × 5 = $995 per ton Al (during chlorination of rough alumina). Thus, the cost of raw materials for aluminum chloride electrolysis is higher by $195 per ton Al than that of for the alumina electrolysis.

The use of electricity. On modern electrolyzers with baked anodes at amperage of 275–350 kA and anode current density of 0.85–0.88 A/cm^2 current output is ~ 95%, specific energy consumption is ~ (13200 kW·h) per ton Al, anode consumption being 550/420 kg per ton Al (gross/net). When using the bipolar electrodes system, the electrolytic decomposition of aluminum chloride can reduce the specific energy consumption up to (8800 kW·h) per ton Al (at power yield of 86%), i.e. by 35%, and increase the power of a single bath by 4–8 times. With electricity cost of $0.05/kW·h, the comparative savings will be $220 per ton Al.

Cut-down costs for anode output. Anode consumption in the process of electrolysis of aluminum oxide: carbon consumption with 100% CO_2 will be 333.5 kg, and with 100% CO - 667 kg per ton aluminum; calculated average plant-performance figure of anode consumption is: net 420 kg per ton Al and gross 550 kg per ton Al; the raw materials cost in the anodes manufacture is 350 $ per ton Al; manufacturing charges - $150 per ton Al. Therefore, the total cost of the anodes per 1 ton of Al: net - total: (350 + 150) × 0.420 = $210 per ton Al; gross - manufacturing cost: 150 × 0.130 = $20 per ton Al; total: cost of the anodes: 210 + 20 = $230 per ton Al.

Additional manufacturing costs related to the anodes quality: cracking - $30 per ton Al; scumming, CO_2 burnout in air stream; roughness; sparkwear - $63 per ton Al; reequipment cycle and height - $13 per ton Al. Anodes quality total costs: $106 per ton Al. Overall spendings on anodes during the aluminum oxide electrolysis: 230 + 106 = $336 per ton Al. Non-consumable anodes are used in electrolysis of chloride aluminum and are recognized in capital expenditures.

Process losses of raw materials and electrolyte. During electrolysis of cryolite-alumina melts irrecoverable losses of AlF_3 electrolyte are 15–25 kg per ton. Alumina losses in the dust form due to entrainment by anode gases depend mainly on granulometric size composition (from amount of fines under 10–20 microns), as well as the electrolysers processing technique, the tuning of automatic alumina feed control and frequency of anode effects. The total loss of mealy alumina is 17–25 kg per ton of aluminum, that is ~ 10–15 kg per ton higher as compared with the results for sandy alumina. Total cost of process losses per 1 ton of aluminum is $5. Electrolyzers of aluminum chloride are leak-free, and the losses of such nature are practically absent.

Operation costs cutout. Nonsumable anodes in electrolysis of chloride aluminum can reduce personnel for their maintenance and cut operating labor effort to $33 per 1 ton of aluminum produced.

The quality of commodity aluminum. Due to fewer impurities, when chloride aluminum is electrolysed, the cleaner metal can be obtained than during the aluminum oxide electrolysis; and given raw materials tertiary treatment by fractional condensation at chlorination, it is possible to obtain super-purity aluminum. Saleable materials price difference is 10% for this calculation.

Environmental impact - reduced greenhouse gas emissions. When introducing production method of aluminum from its chloride the essential beneficial effect will be eliminating the release of polyfluorocarbons into the atmosphere and CO_2 overall lowering by 40% due to the sealing of electrolyzers.

Capital expenditures. Assessment of capital investments in aluminum production [5] varies considerably, it is determined not only by the factory location, but also by the original technological requirements for equipment, degree of mechanization and automation, and environmental requirements.

Capital investments in the complete process cycle of aluminum production according to traditional technologies compared with the chlorine method are approximately the same and has been estimated at $6500 per 1 ton capacities for metal A1. In the chlorine method, the most part, 65%, of capital expenditure is accounted for receiving impure alumina and its chlorination, and a smaller part (35%) - for electrolysis. Aluminum smelting conventional technology has inverse ratio of capital investment: alumina production accounts for 35%, and cryolite-alumina melts electrolysis - 65%. However for the chlorine manufacturing practice, due to closed chlorine cycle, chlorination and electrolysis processes should be located in close proximity to each other and the complete cycle must be invested at a time. Aluminum plants operating under the traditional aluminum production scheme can enter into long-term contracts for the supply of alumina and not build new plants of their own. Alumina contract prices include all associated capital costs with its manufacture and delivery. The price of alumina as a product of the world economic system is liable to sizeable variation, that fact creates additional risks in aluminum production.The cost of alumina is approximately 50% of that of aluminum produced by electrolysis of cryolite-alumina melts. Availability of in-house facilities for aluminum chloride production protects the chlorine process from above-mentioned fluctuations in raw material prices.

TABLE 1: Comparative indicators of aluminum production processes by chlorine technology and by traditional one, production of alumina by the Bayer method followed by electrolysis of cryolite -alumina melts.

Technological indicators	Chlorine method of aluminum production	Conventional Bayer alumina production process and electrolysis of cryolite-alumina melts in AR-30-type baths	Δ, $ per ton, (+/-)
Anode type	bipolar (carbon)	carbon	
Current efficiency	86.0	95	
Current density	1.3	0.8	
Electric energy consumption	8800	13200	
Bath voltage (V)	2.63	4.3	
Raw material cost	995	800	-195
Cost of electricity, $ per ton Al	440	660	220
Cost of anodes	22	336	314
Other operating costs			5
Overall operational costs			33
Quality of commodity Al			190
Total greenhouse gas emissions (equiv. ton CO_2/ton Al)	9.57	15.89	

Toth Aluminum Corporation (TAC) tested its own “Clay-to-Aluminum” technology of chlorination and purification at a pilot plant with a capacity of 25 tons per day. In the company report Fluor Daniel concludes that TAC Chlorination Technology is ready for commercialization. The chlorine method of aluminum production can be implemented on the basis of qualitative restructuring of technology and equipment of enterprises. Doing so, to meet the target, namely, to create a waste-free technology for processing aluminum-containing raw materials, chlorine method of aluminum production is the most effective. This method consists of two main process stages - the production of aluminum chloride and its electrolysis.

1. Conclusions

Advantages of method of aluminum production by electrolysis from its chloride compared to electrolysis of cryolite-alumina melts are as follows:

- possibility of using low-quality aluminum-containing raw materials;

- reduction of specific electric power consumption by about 30% (electrolysis of aluminum chloride takes place at temperature 700°C, and electrolysis of cryolite-alumina melts - at 950-960°C);

- elimination of high-quality carbon-containing materials consumption (graphite non-consumable electrodes are used in electrolysis of aluminum chloride);

- the use of less scarce and aggressive chlorides instead of fluorides;

- labor productivity improvement;

- reduction of capital investments, given expenses, cost of end-use products and harmful emissions into the atmosphere [6].

The special feature of the chlorine technological process is requirement to place the production on a single site while investing in the complete cycle, this is a deterrent to the construction of plants that use this technology. Electrolysis of aluminum chloride in modern conditions has development potential not as mass technology, but as an effective process for the HPA production in minor workshops.

References

[1] Maksakovsky, V. P. (2009). *General Economic and Social Geography: Course of Lectures*. Moscow: Humanitar. prod. Vlados Center.

[2] Poljakov, P. V., *et al*. (2008). Electrolysis of Thickened Alumina Suspensions as a way to Improve the Hall-Héroult Process. Part. 1. Evolution of Aluminum Electrolytic Process Technology. *SPU Journal. Engineering and Thechnology,* issue 1, pp. 135-154.

[3] Vetchinkina, T. N., *et al*. (2017). Processing of Mineral Raw Materials by Chlorine Method Using Acid Enrichment. Presented at *Proceedings of the Congress "Non-ferrous alloys and minerals", Krasnoyarsk, Russia*.

[4] Balmayev, B. G., *et al*. (2017). Test of Experimental Complex of Alumina Production by Acid Method from High-Silicon Aluminum Raw Material. Presented at *Proceedings of the Congress "Non-ferrous alloys and minerals", Krasnoyarsk, Russia*.

[5] Akhmedov, S. N., *et al*. (2002). State and Trends in the Technology of Aluminum Production in the World. *Non-ferrous Alloys,* issue 3, pp. 47–52.

[6] Borisoglebsky, Y. V., *et al*. (1999). *Aluminum Metallurgy: Tutorial.* Novosibirsk: Nauka.