RUSAL Alumochloride Technology – Efficient and Waste-Free Alumina Production from Non-Bauxite Resource

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Abstract

To reduce the costs for transportation of bauxites to alumina refineries and transportation of alumina to aluminium smelters RUSAL is currently developing an alternative technology for alumina production using abundant non-bauxite raw material from West Siberia. Upon successful completion of the laboratory experiments, the tests at the specialized demonstration mini-plant have been conducted. Consumption parameters and rates were determined for the following stages: acid digestion of kaolin, filtration and washing of silica residue, crystallization of aluminium chloride hexahydrate followed by calcination, rectification of hydrochloric acid. Respective chemical and physical processes were studied and the data required for technology industrial implementation were obtained. Research works are in progress to process the silica residue into valuable products thus bringing the technology closer to waste-free process.

Keywords: Non-bauxite ores, alumina, hydrochloric acid method, waste free production.

1. Introduction

At a new stage of development of aluminium industry, interest is growing in perspective sources of raw materials such as non-bauxite high-silica ores (e.g. kaolin clays) and coal fly ash. In fly ash processing the environmental problems are solved connected with their disposal. It is not expedient to process kaolin and ash from thermal power plants by conventional alkaline technologies due to high content of silica. However, they become rather attractive raw materials when acid processes are used [1] among which recently mostly developed are processes based on hydrochloric digestion of raw materials. In spite of higher capital expenditures as compared to widely known Bayer process, this method has noticeable advantages against other acid processes due to low silica solubility in hydrochloric acid; possibility of selective crystallization of aluminium hexahydrate (ACH) $AlCl_3 \cdot 6H_2O$ with removal of most of the detrimental impurities; and also simplicity of hydrochloric acid regeneration for the use in a closed cycle [2].

2. Modern Developments within Hydrochloric Method of Alumina Production

Previously a number of foreign companies repeatedly turned to hydrochloric processes of aluminium-bearing raw material processing. It is possible to distinguish investigations executed in1970 – 80 by Pechiney, Alcan, US Bureau of Mines (USBM), VEB Mansfeld Kombinat (GDR) as well as by Commonwealth Scientific and Industrial Research Organization, (CSIRO) Australia [3], that formed a basis for subsequent development of the process and equipment.

In 2004 Junggar Energy Resource Co., Ltd. opened a new period of activity in improvement of hydrochloric method in fly ash processing [4]. The process comprises preliminary beneficiation by magnetic separation to decrease iron content in raw material to < 1 %, hydrochloric leaching, sorption of impurities from aluminium chloride solution by ion-exchange resins, extraction of ACH residue and its calcination with subsequent recycling hydrochloric acid and hydrogen chloride from gas phase to the process [5]. On August 19, 2011 a 4,000 t/a pilot plant for alumina extraction by hydrochloric process from coal fly ash was successfully commissioned. The longest period of operation of the pilot plant was 5 months, which allowed to reach design capacity and, according to the company, gave an opportunity to select corrosion-resistant materials and to confirm the technology. A batch of 80 tons of produced alumina was tested at the cells of Yunnan Aluminium Co., Ltd. with satisfactory results on quality of metal. On the basis of the novel technology the company plans to construct an industrial complex including production of coal, electric power, alumina, primary aluminium and gallium, aluminium products, etc. The 1st stage of the complex will be commissioned before 2020 [6].

In 2007 Orbite Technologies Inc. (Canada) for the purpose of integrated processing kaolin argillite of Quebec yielding smelter grade alumina, reactive silica, pure iron oxide, rare and rare-earth elements (REs and REEs) , including scandium oxide and gallium developed a proprietary technology of acid processing. The process comprises a stage of hydrochloric leaching of raw material, separation of insoluble siliceous residue, selective extraction of aluminium chloride hexahydrate (ACH) by saturation solution with gaseous HCl, its cleaning and calcination to Al_2O_3. From the filtrate containing other soluble in hydrochloric acid metals, iron is extracted as hematite by means of low-temperature steam hydrolysis (PORI process), RE and REE are recovered by extraction methods, and the other non-hydrolysable impurities are removed at a pyrohydrolysis stage, at that HCl and water vapors obtained at different stages of the process are condensed and recycled to the production cycle [7]. Having originally set as the purpose construction of the 560 000 tpy "acidic" alumina refinery for SGA production, Orbite further focused on a small enterprise, 1000 – 5000 tpy, for production of high purity alumina (HPA, at least 99.999%). The product is meant for the production of leucosapphire monocrystals used for substrates of light-emitting diodes and special military optics. However, in developing the process, the company met serious technical difficulties in calcination of high-pure alumina. After modernization of ACH calcination unit, according to the press release of the company [8], is planned to begin a new stage of industrial tests.

Australian company Altech Chemical also developed the acidic technology of processing high purity Al_2O_3. As initial raw material, Altech Chemical considered kaolin clays of high purity from Meckering deposits in Western Australia, which after ore pretreatment are sent to hydrochloric leaching. Residue is neutralized and sold to local consumers such as brickworks and/or cement plants, and alumochloride solution is directed to crystallization, the obtained aluminium chloride hexahydrate is recrystallized for cleaning from impurities and calcinated at 1200 ℃ [9]. In September, 2015 Altech signed an exclusive distribution agreement in the Japanese market with Mitsubishi Corp, and in November of 2016 a 20 years lease agreement for the proposed construction site of HPA plant in Johor, Malaysia (Tanjung Langsat Industrial Complex, Johor, Malaysia). The planned enterprise capacity - 4,500 tpy 4N - high pure alumina (HPA). Altech Chemical is going to start the plant during 2020 – 21 [10].

Norwegian company Nordic Mining ASA and Institute for Energy Technology also took the tack of hydrochloric technology developing jointly a process of alumina production from the anorthosite ores with integrated use of carbon dioxide comprising crushing and leaching of aluminous materials in concentrated HCl; separation of unreacted material from chloride solution; ACH crystallization and calcinating in 2 – 3 stages to alumina with regeneration of the emitted hydrogen chloride. The technology comprises an ecological component, since mother liquor containing after ACH extraction large amount of chlorides, mainly, calcium, undergoes solvent extraction with tertiary amines, and then unseparated mix is bubbled by furnace gases with CO_2 absorption and formation of carbonate residue and recycled hydrochloric solution. Thus, there is "disposal" of greenhouse gas formed at combustion of fuel for the process. The remained solution of complex ammonium chloride salt is thermally or chemically processed for amines recovery [11]. Currently this original technology appears to us far from commercial implementation, first of all, due to inevitably high consumption of expensive organic reagents.

In recent years in connection with expected rapid increase in requirement in high purity alumina nanopowders for separators of new efficient lithium-ion batteries [12] information periodically appears on plans from various companies in Canada, Australia and other countries to start production of these hi-tech materials. As a rule, a general list of process stages is given, as raw materials kaolin or anorthosite are mentioned, and publications are of one-off character [13 – 15]. However, it confirms a new round of interest in hydrochloric processes.

3. RUSAL Alumochloride Technology

To reduce the costs for transportation of bauxites to alumina refineries and transportation of alumina to aluminium smelters RUSAL is currently developing an efficient alternative technology for alumina production using kaolin clays of domestic deposits. The process is based on a complex acid-alkaline technology called by the authors 'alumochloride technology' (Figure 1) [16].

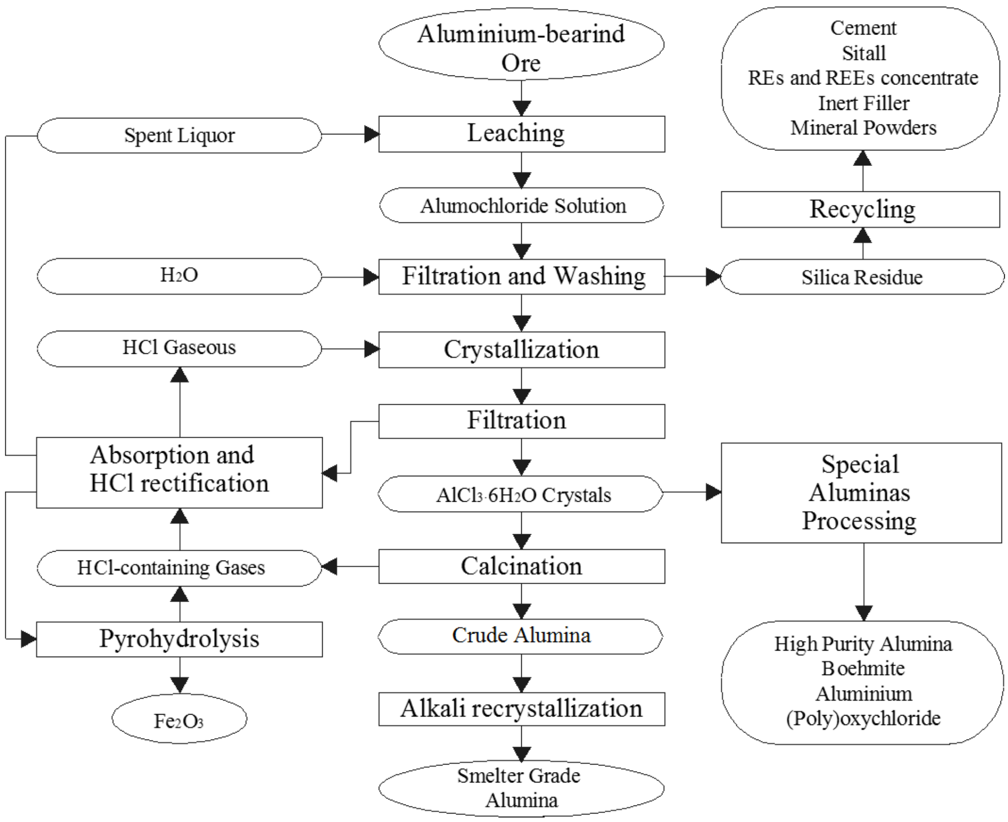

Figure 1. Basic flow sheet of RUSAL Alumochloride technology.

The technology consists of hydrochloric processing of raw materials, with separation of silica residue, crystallization of aluminium chloride hexahydrate from clarified chloride solution with its subsequent calcination to an intermediate aluminium oxide product that due to considerable content of iron and other impurities (with the exception of silicon) is considered crude alumina.

Further follows leaching of an intermediate aluminium oxide product by recycled alkaline solution, decomposition of the resulting aluminate solution, water washing and subsequent calcination of extracted aluminium hydroxide, evaporation of mother liquor after decomposition and wash water of aluminium hydroxide with formation of the recycled alkaline solution returned to leaching of an intermediate aluminium oxide product.

The advantage of this scheme is the fact that for leaching mostly spent liquor is used and only part of it is directed to impurity removal by pyrohydrolysis method. Large and complicated stages of evaporating and salt rectification are missing, the pyrohydrolysis stage is reduced as far as it is not related to crude alumina production, and is meant for impurities removal only, in that case energy consumption is also reduced. Crude alumina contains minimal quantity of impurities, including chlorides, though for its quality it is not suitable for smelting [17].

For obtaining smelter grade alumina of proper quality an additional processing stage in alkali cycle is required. Firstly, crude alumina has remarkably low bulk density and huge amount of ≤ 45 µm fraction ratio, which is related to specifics of ACH thermal decomposition. Secondly, it does not satisfy the quality standards for smelter grade alumina due to the quantity of impurities such as iron, alkaline metals and earths.

The specifics of alkali recrystallization of crude alumina by Bayer method (unlike natural bauxites processing) is not significant due to very small amount of mud production the water consumption for its washing. The water balance of alumina production process can be closed without full mother liquor evaporation stage considering that input of fresh water for aluminium hydrate washing is approximately equal to the output water removed with product hydrate. Furthermore, heat recovery is possible on the autoclave leaching stage by using slurry-slurry heat exchangers. During the evaporation stage alkaline metal chlorides are removed. By moving from acidic cycle to alkali cycle all impurities, limited by quality standards, are separated with the mud, moreover titanium, REs and REEs are accumulating in the alkali residue. The alumina produced is of sandy type. Simplifying processes in acidic and alkali cycles together leads to significant saving in energy sources.

After half-year large-scale technological tests in 2017 [18] the results from earlier experiments were confirmed, high rates of extraction were achieved, material balance of the process was detailed and engineering of the pilot plant is started (Figure 2). Comparison of basic characteristics of the process is shown in Table 1.

Table 1. Comparison of characteristics of the process, obtained during exploitation of mini-plant and laboratory tests.

Indicator	Unit	Miniplant	Laboratory
Acid leaching			
Extraction of alumina	%	94.5	95.1
Si-residue filtration and washing			
Moisture of Si-residue	%	55.0	56.1
Filtration rate	$kg/m^2 \cdot h$	100.0	102.5
Optimal number of washing steps	times	4	n/d
ACH crystallization			
Concentration of HCl in solution	%	31	31.8

Indicator	Unit	Miniplant	Laboratory
Achieved extraction of $AlCl_3$	%	92	92
Residual concentration of $AlCl_3$	%	2.5	1.8
ACH calcination			
Residual Cl-content in alumina	%	1,5	2,5
Phase	%	γ-Al_2O_3	γ-Al_2O_3

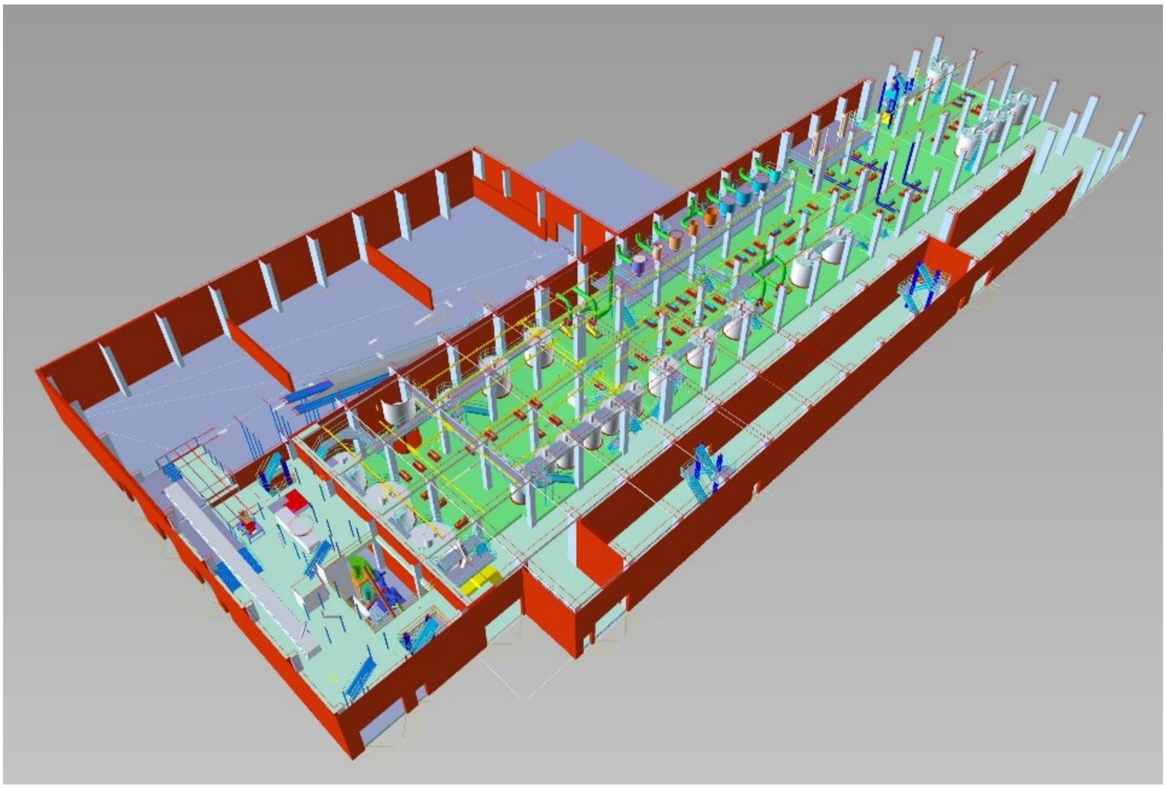

Figure 2. 3D-plan of experimental plant for kaolin processing by alumochloride technology.

Stationary model of the process with detailed calculation of all staged was developed, based on the results of mini-plant operation (Figure 3). As the result of calculations material balance of technological process for water and chlorine was closed, energy and major resources consumption was summarized. The developed model allowed performing sensitivity analysis of the process to changes in basic technological parameters.

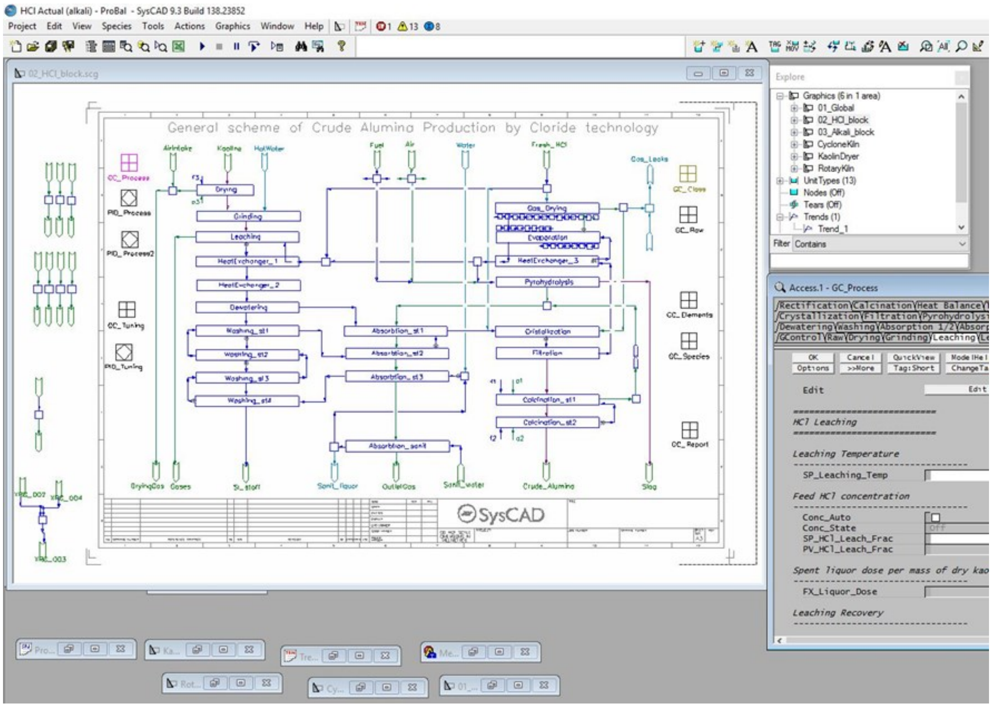

Figure 3. Model for material balance calculation, developed in SysCAD software.

As a result, in the economic environment of South Siberia region such complex technology shows high calculated profitability even without by-products and products with high added-value products. Comparison of major consumption factors between alumochloride technology and nepheline process is shown in the Table 2. The 30 % reduction in energy consumption can be achieved with alumochloride technology, also lower ore consumption per 1 ton of product, large amounts of additional raw materials (i.e. limestone) are not required, and remarkably lower (2.7 times) residue production than within nepheline process. In the meantime calculated prime cost of product, obtained by complex acidic-alkali processing of kaolin, is less than USD 200 / t.

Table 2. Major consumption factors - comparison with nepheline process.

Indicator	Unit, per t Al_2O_3	Alumochloride Technology	Nepheline process
Raw material	t	3.6	4.6
HCl acid (100% basis)	t	0.1	-
Limestone	t	-	6.3
Residue	t	2.5	6.7
Energy costs, incl.	GJ	38	53
- fuel for technology	tonnes fuel eq.	0.888	1.505
- heat (steam)	Gcal	2.053	1.267
- electricity	MW·h	0.900	1.108

4. Minimizing Quantity of Generated Waste and Searching Ways of its Processing

Rising complexity from raw kaolin usage is still on the agenda due to its significance in terms of economics and also ecology. Despite of the fact that at the moment the alumochloride technology is at stage of pilot plant engineering, project team develops perspective methods of waste processing since further resizing to a large-scale production inevitably leads to a key problem that

is disposal and utilization of wastes. Disregarding of this problem can lead to risks of disablement of significant fertile soil areas and loss of potentially valuable raw material for different manufacturing sectors that can impact on economic effectiveness of company. Developing method of processing wastes allows to solve potential ecological problems, enlarge raw materials source for new products and as a result improve profitability and returns for alumochloride technology. Since the raw material for processing alumina by alumochloride method can contain up to 60 wt % of SiO_2, which turns almost fully into residue on the stage of leaching, the main waste of the technology that considers disposing is silica-residue. Generally while processing beneficiated kaolin Si-residue can yield approximately 2 ton per ton of alumina.
Silica-residue basically contains silica and small amount of insoluble in hydrochloric acid minerals, its liquid phase is wash water with insufficient amounts of soluble chlorides. At an average the residue contains (wt %) (Table 3):

Table 3. Residue composition.

SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	LOI
85.3	4.9	0.3	0.9	0.15	0.15	6.0

Natural characteristics of silica-residue that define ways of its processing are:

- Chemical resistance to concentrated hydrochloric acid;
- Thermal stability in wide range of temperatures;
- Swelling at pH near 5 – 7;
- Relatively high surface area.

Regarding high moisture content (about 50 %) and difficulties due to drying, transportation of residue for long distances is impractical, so processing should be performed on site. Simple processing methods with higher residue consumption per weight of product are preferable.

One of the obvious areas of utilization is silicate concrete production, for silica-residue in chemical and phase composition meets the requirements for mortar sand [19]. Same as belite mud silica-residue can be used for dry mix mortar production as hydraulic binding agent or raw component [20]. For example, it is known that SiO_2-containing residue obtained from nepheline concentrate surpass all other known natural and synthetic materials by its hydraulic activity [2]. Experiments showed that silica-residue additives promote process of hydration of silicate cement compound (alite) and hydrosilicate formation. However it should be taken in account that introducing in cements more than 10 wt. % of silica-residue is unacceptable, because in that case water requirement of adhesive drastically rises and leads to degradation of main construction characteristics of materials. Also setting time of cement changes, especially with the increase of alumina content.

Thus for construction materials the most rational usage of Si-residue is in the form of hydraulic binding agent for white and coloured cement, because natural materials, used for this sake, are rare and scarce. Also chemical composition and fractional make-up of the residue allows to use it in place of quartz sand or fly ash in autoclaved aerated concrete blocks production.

Residue after acidic leaching is made up from inert, acid resistant and high-melting solids that allows to apply it in production of construction materials for special usage, i.e.:

- Refractory lining for steel structure, which is stable in corrosive environment and can expand while heated.

- Acid resistant construction materials inert to inorganic acid, as well as hydrochloric acid. Producing of such materials on site also provides a possibility to solve problems with replacing and maintenance of lining for alumochloride technology equipment.
- Thermally and chemically resistant adhesives, based on silica-residue and other fillers.
- Fillers for rubber or pulp and papermaking industry.

5. Conclusions

Starting from XXI century processing of alternative and industry-related highly siliceous alumina-bearing material, as well as processing by hydrochloric methods, starts to attract a lot of attention all over again. For the moment not less than three projects in China, Canada and Malaysia aimed for smelter grade alumina or HPA (4N – 5N) hydrochloric processing are at the stage of development and construction of a plant.

RUSAL developed its own alumoclhoride technology that allows to produce smelter grade alumina with high cost-performance ratio from kaolin clays. For the moment laboratory and mini-plant tests are finished. Basic indicators of the leaching process are confirmed in large-scale tests:

- 94.5 % extraction ratio of alumina at digestion is achieved.
- Basic indicators of the filtration and washing stages are confirmed in large-scale tests, especially cake moisture 55 - 56 % and filtration rate 90 – 100 $kg/m^2 \cdot h$.
- Basic indicators of the ACH crystallization stage are confirmed in large-scale tests and improved for the rate of crystallization process. 92 % of aluminium extraction from solution was achieved. Approximate rate of crystallization was three times faster than in laboratory tests.
- Basic indicators of the ACH calcination stage are confirmed in large-scale tests. Crude alumina with chlorine content ≤ 2.5 % was obtained. The obtained results showed good agreement between laboratory and large-scale tests and some parameters were improved.

Material and heat balance of alumochloride process were calculated. Based on balances the flowsheet of the process was specified, equipment was defined and CAPEX/ OPEX calculations of future alumina plant were made.

Scaling up of the technology to pilot plant stage has started and industrial pilot plant design process also started.

Economic efficiency of the process can be improved by processing the wastes for silicate construction materials, acid resistant and refractory lining, REs and REEs concentrating and making other value added products.

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