The quality of alumina produced by the hydrochloric acid process and potential for improvement

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Abstract

In the hydrochloric acid process, alumina is directed to calcination as aluminum chloride hexahydrate $AlCl_3 \times 6H_2O$ (ACH). During the calcination process it loses approximately 80 % of its mass. This leads to physical and morphological characteristics of the product considerably different compared to those of smelter grade alumina (SGA), namely: fraction - 45 μm is above 60 mass %, which is six times greater than SGA; bulk density is lower than 0.35 g/cm^3 (about three times lower compared to SGA); flow time of approximately 22 minutes (about seven times greater than SGA), etc. So, alumina produced by the hydrochloric acid process has low bulk density and relatively high attrition index. The external surface of the particles is rough, which increases friction between particles and the angle of repose up to 32° and above, as well as the increased flow time from standard funnel test. All of the above prevents the use of alumina produced by the hydrochloric acid process in a modern high technology reduction process and requires research into process development aimed at modification of the physical, chemical and mechanical properties of alumina produced by acid method.

Keywords: Hydrochloric acid process; alumina calcination; aluminum chloride hexahydrate; smelter grade alumina flow time and bulk density; angle of repose.

1. Introduction

Actual commercial realization of SGA production by hydrochloric acid process from non-bauxite ore has revealed some challenges associated with chemical composition and physical-mechanical properties of the produced alumina.

Modern aluminum smelters are designed for processing of sandy grade SGA with strictly regulated characteristics. For example, particle size distribution should be in a narrow range from plus 45 to minus 150 μm; particle shape should be close to isometric; particles should be resistant to attrition; special requirements to specific surface and absorption capacity to hydrogen fluoride, bulk density, angle of repose, flow time, etc., etc. All these properties of SGA are formed at earlier stages of the Bayer process, namely:

- In digestion for caustic- aluminate liquor generation with considerable Al_2O_3 supersaturation;
- In two stage precipitation with complex system of crystals and aggregates growth of specified form and size followed by classification of the produced aluminum hydroxide in several stages;
- In calcination in modern stationary calciners.

For alumina produced by the hydrochloric process, properties are formed at different process stages. After leaching of Al-silicates by HCl, alumina is transformed into liquor in form of $AlCl_3 \times aq$, next the product is precipitated (by crystallization) in form of aluminum chloride hexahydrate $AlCl_3 \times 6H_2O$ (further ACH). The process modes during ACH crystallization affect the shape and size of crystals.

During thermal decomposition of ACH in the following reaction:

$$2AlCl_3 \times 6H_2O \rightarrow Al_2O_3 + 6HCl\uparrow + 9H_2O\uparrow$$

it loses 80 % of mass which obviously impacts the properties of the produced Al_2O_3. This paper is dedicated to the study of the properties of aluminum oxide depending on process conditions.

2. Temperature and ACH thermal decomposition impact on phase analysis of produced alumina

With a calcination temperature of about 600 °C, near 20 % of the initial chloride from ACH remains in the calcination product in the form of aluminum oxychloride with general formula $Al_2(OH)_nCl_{6-n}$. The other 80 % is removed in the form of HCl gas and water vapor while in the solid phase, forming the mix of polymorph aluminium oxide varieties with admixture of oxychloride of variable composition. With the increase of calcination temperature the volume of chlorine reduces.

Thermal decomposition of $AlCl_3 \times 6H_2O$ to aluminum oxide is an endothermic process with theoretical heat $\Sigma\Delta H_{298°K}$ = 9.63 $MJ/kg_{alumina}$ which requires considerable amount of heat. As compared to conventional Al_2O_3 calcination from aluminum hydroxide ($Al(OH)_3$), heat consumption and the specific volume of exhaust gases is about 4 times higher.

For experiments with aluminum chloride calcination, a laboratory unit (Fig. 1) was assembled, including a tubular kiln (1), six carborundum heaters (2), control block (3), and reaction chamber (4). The control block is equipped with temperature indicator (5) and control elements for zero setting (6), and setting of the required temperature (7).

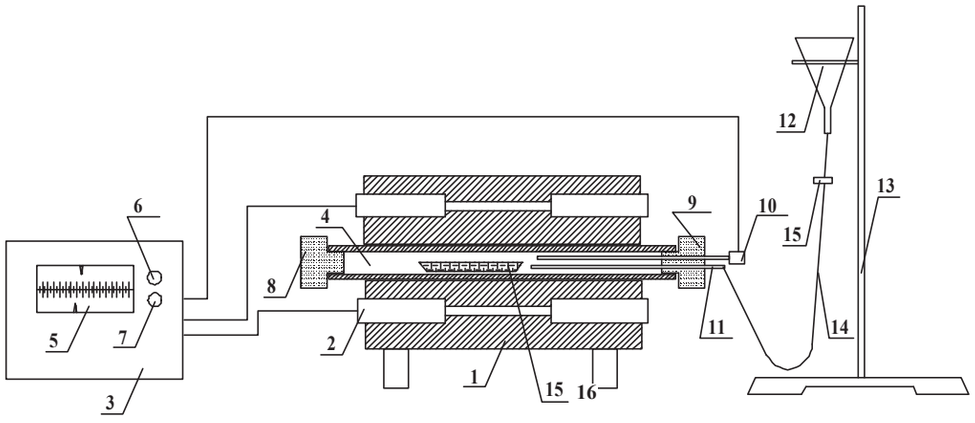


Figure 1. Laboratory tubular kiln for ACH calcination.

The reaction chamber is equipped with lids (8 and 9) made of lightweight fireclay. The lid (9) is equipped with thermocouple (10) and socket for steam or water supply (11). A water tank (12) is installed on a stand (13) and is connected by flexible hose (14) to a supply socket (11). The hose (14) is equipped with an adjustable clamp (15) to control liquid flow rate into the reaction zone. The calcination of product was conducted in a corundum boat (16) installed in reaction chamber (4).

While assessing the results, first of all, residual Cl content in the product was considered. This is because of the harmful influence of increased Cl content on dioxins formation during electrolysis process.

Experiments with variation of chlorine content in the samples calcined at temperatures 650, 850 and 1000 ºC and residence time 60 min with and without steam supply is presented in Fig 2. In these series of experiments the sample was heated to the specified temperature in the kiln.

As presented in Fig. 2, with a temperature increase to above 650 °C, a sharp reduction in chlorine content in the samples occurs. This fact was also noticed by other researchers [1, 2]. Further, as temperature goes up, the declorination process slows down. At very long residence times, the Cl can be removed completely [3, 4]. This effect was also revealed in industrial ACH calcination [5].

The rate of the process can be significantly increased if calcination is conducted in an atmosphere of steam, hydrogen or their mixture [6, 7], an effect that was also confirmed by our data [8]. Under steam conditions chlorine content is ~ 1.5 – 2.0 times lower compared to calcination without steam. It is only with the supply of steam to the calcination zone that the Cl^- content in the samples was below 0.01 mass %, considered to correspond to typical Bayer alumina quality according to [4]. Steam flowrate was 100-150 dm^3/kg Al_2O_3, which increases specific heat energy consumption, but assures alumina quality.

Removal of residual Cl in high temperature calcination of ACH without declorination aid gases leads to an increase of α– Al_2O_3 phase.

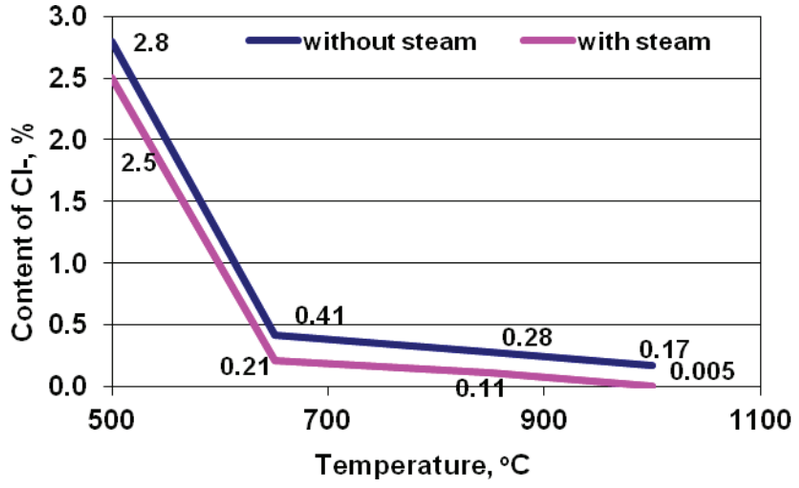


Figure 2. Variation of chlorine content in the samples versus calcination temperature with residence time 60 min.

Figure 3 shows calcination kinetics at a temperature of 1000 ºC versus residence times of 15, 30, 45 and 60 minutes with a gradual reduction of chlorine content in Al_2O_3 in three stages. At the first stage within the time interval 15 - 30 min, a sharp reduction in chlorine content from 0.12 to 0.064 mass % is observed. Within the time interval 30 - 45 min, we observe the induction period with practically invariable chlorine content in the calcined sample. With a further increase in the residence time to 45 - 60 min, the third stage of chlorine reduction in the sample occurs down to 0.018 mass %.

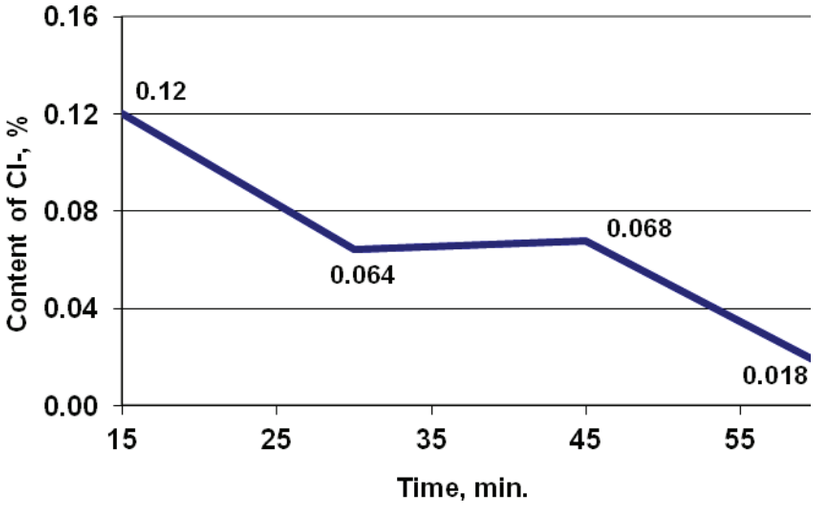


Figure 3. Chlorine content variation in samples versus residence time at calcination temperature 1000 °C.

Phase analysis of calcined samples after 60 min and at different temperatures, with and without steam supply in reaction zone, is presented in Table 1.

Table 1. The results of X-ray phase analysis of calcined samples.

T, °C	Steam	Phase	Intensity of basic lines, d/n, Å / imp./ sec.		
			α – Al_2O_3, 2.085 Å	**γ – Al_2O_3, 1.39**	**θ – Al_2O_3, 2.72 Å**
500	-	X-ray amorphous	-	-	-
	+	X-ray amorphous	-	-	-
650	-	x/a phase– basis, γ – Al_2O_3	-	215	-
	+	x/a phase– basis, γ – Al_2O_3	-	345	-
850	-	x/a phase– basis, γ – Al_2O_3, traces θ– Al_2O_3,	-	365	traces
	+	x/a phase– basis, γ – Al_2O_3, θ– Al_2O_3	-	360	165
1000	-	γ – Al_2O_3, θ– Al_2O_3, α– Al_2O_3	315 (~ 3 %)	370	230
	+	α– Al_2O_3 , γ – Al_2O_3, θ– Al_2O_3,	2065 (~ 22 %)	160	130

As evident from the presented data when the steam is not supplied at a temperature of 1000 ºC, the sample is mainly presented by γ, θ and α phases. With steam, the α is the main phase with minor θ phase and traces of γ-phase. The differences in phase analysis of the produced alumina are depicted in Figure 4.

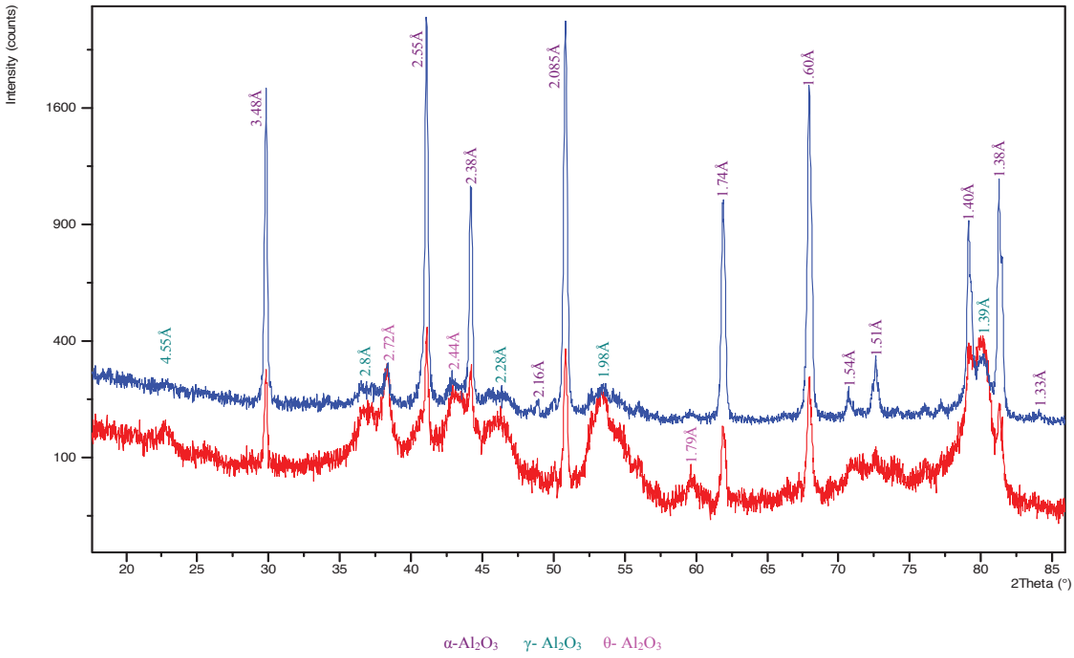


Figure 4. XRD analysis (top sample – calcined alumina after 60 min residence time, temperature -1000 °C with steam input into reaction zone; bottom sample: 60 min, 1000 °C, no steam).

As can be seen from the obtained data at a temperature of 1000 °C, it is possible to produce alumina with chlorine content not exceeding that of the conventional Bayer alumina and α Al_2O_3 at 3 - 5 mass%. Calcination of ACH in stationary kilns may result in a different alumina phase analysis.

Much serious concern is related to phosphorous content in alumina, which impairs the current efficiency of an electrolysis cell. Unfortunately under the available technology studies on the HCl process, practical technologies for its removal have never been developed. Therefore the content of P_2O_5 in the SGA produced by the hydrochloric acid route is directly proportional to its content in initial raw material [4, 9].

3. Physical properties of the produced alumina

The morphology traits of alumina produced by Bayer process and from ACH were investigated using an electron microscope (see Figures 5 and 6).

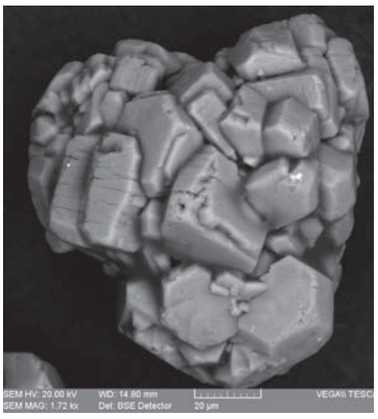
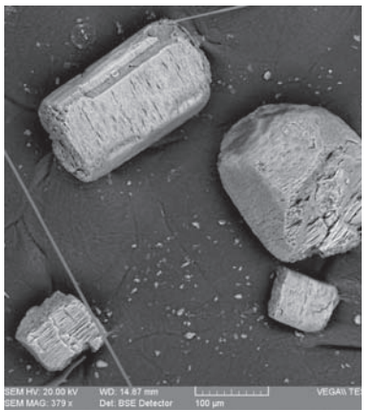


Figure 5. Bayer sandy alumina.



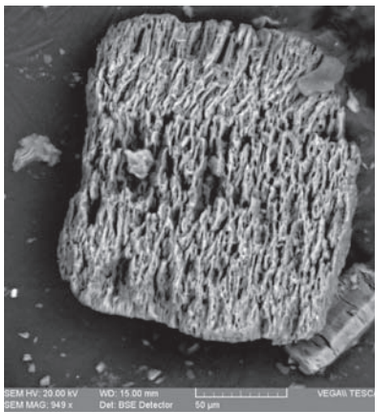


Figure 6. Alumina from ACH, temperature 1000 °C, static bed.

Conventional Bayer aluminas are mainly present as particle aggregates of micron size and the form of the aggregates is close to spherical, which determines its rheological properties (Figure 4). High specific surface area of SGA -70 - 80 m^2/g is caused by a large number of nano-dimensional pores not visible with the applied microscope scanning resolution.

Depending on crystallization and calcination conditions, the morphology of alumina particles produced from ACH may vary considerably. From ACH crystals we produced alumina samples of mesoporous structure from prismatic to rounded shape (Figure 5). The process of selection of crystallization and calcination regimes is in progress now and offers hope to improve the parameters of bulk density, angle of repose and flow time from the standard funnel test.

Due to the limited capabilities of lab equipment in the autoclave section, it was not possible to produce a representative sample of alumina with sufficient mass to conduct the analysis of its physical and mechanical properties. Therefore the attrition of alumina produced by the acid process was studied not by the generally accepted Alcoa method, but by an indirect method. Attrition was assessed through the impact of ultrasonic processing of powder/water suspension with simultaneous determination of its particle size. The experiments were conducted using a CILAS laser particle sizer equipped with an ultrasonic dispersion bath. The particle strength was low. For standard SGA, the breakage of particles stops after 60 seconds processing in the bath. The studied alumina continued to disperse even after 10 min processing; it is well demonstrated for the -45 μm fraction (Figure 7).

The adsorption capacity with regard to hydrogen fluoride of alumina produced from ACH was measured by a static method in the laboratory of the Ecological department RUSAL ETC in St. Petersburg. The obtained value (15 mg/g) is inferior compared to sandy alumina, but better than that of the floury alumina (– 45 μm fraction above 30%) produced by refineries in Russia.

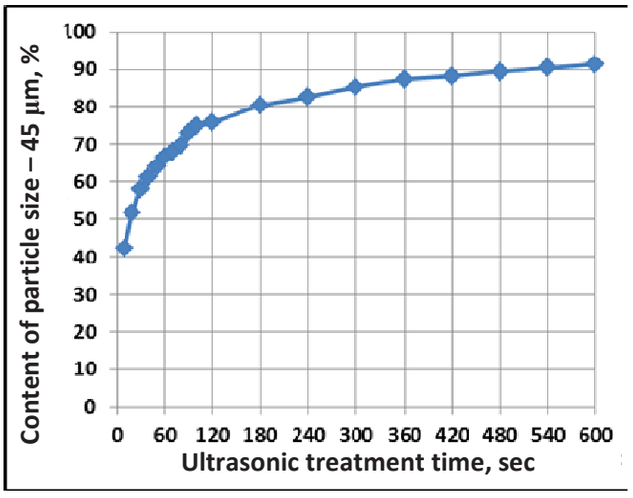


Figure 7. Impact of ACH alumina ultrasonic treatment time on the mass content of minus 45 µm fraction.

Flow time, angle of repose and bulk density were assessed for alumina preliminary screened on a 0.85 mm sieve as presented in Table 2.

Table 2. Characteristics of alumina produced from ACH.

Parameter	Result	Note
Flow time 100 g, min.	21.9	At the end of the experiment the material is blocked in the funnel
Angle of repose, °	36.4	
Bulk density, g/cm^3	0.34	

From the data given in Table 2, it is evident that all the parameters of alumina produced by the acid process are inferior to Bayer SGA.

Table 3 summarizes chemical parameters of alumina produced from ACH as compared to UC RUSAL standard and GOST for SGA valid in the Russian Federation.

Table 3. Quality parameters of SGA.

Parameter	UC RUSAL standard	ACH alumina	GOST RF	
			G-00	G-0
Aluminium oxide (Al_2O_3), %, not less	98.5			
Silicon oxide (SiO_2), %, not more	0.01	0.031	0.02	0,03
Iron oxide (Fe_2O_3), %, not more	0.01	0.021	0.03	0.05
Sodium oxide (Na_2O), %, not more	0.1-0.2	0.099	0.4 (sum Na_2O, K_2O in terms of Na_2O)	0.5 (sum Na_2O, K_2O in terms of Na_2O)
Potassium oxide (K_2O), %, not more	0.01	0.020		
Phosphorus oxide (P_2O_5), %, not more	0.0005	0.012	0.002	0.002

Parameter	UC RUSAL standard	ACH alumina	GOST RF	
			G-00	G-0
Zinc oxide (ZnO), %, not more	0.005	0.0003	0.01	0.02
Titanium oxide (TiO_2), %, not more	0.001	0.0025	0.01 (sum TiO_2, V_2O_5, Cr_2O_3, MnO)	0.02 (sum TiO_2, V_2O_5, Cr_2O_3, MnO)
Chromium oxide (Cr_2O_3), %, not more	0.001	0.0003		
Vanadium oxide (V_2O_5), %, not more	0.001	0.0008		
Manganese oxide (MnO_2), %, not more	0.001	0.0002		
Magnesium oxide (MgO), %, not more	0.005	0.0020		
Calcium oxide (CaO), %, not more	0.05	0.0028		
Gallium oxide (Ga_2O_3), %, not more	0.005	-		
Chlorine content (Cl^-), %, not more	0.005	0.005		
Alpha alumina (α - Al_2O_3), %	2 - 5	traces		
Particle size distribution:				
- fraction -20 μm, %, not more	3.0	31.0		
- fraction -45 μm, %, not more	10.0	66.85		
- fraction +125 μm, %, not more	5.0	0.0		
Specific surface area (SSA), m^2/g	70 - 80	58.9		
LOI, %, not more	1.0	0.48	1.2	1.2
Moisture, %, not more	0.5	1.3	0.5	0.5
Attrition index, not more	10	25-33		
Bulk density, g/cm^3	0.95-1.00	0.34-0.7		
Angle of repose, °	28-32	36.4		
Flow time of 100 g sample from funnel with opening 2.4 mm and cone-generating angle and vertical 9°54' (Alcoa test), min, not more	3	21.9		
Adsorption capacity to HF, mg/g, at least	20	15		

From the data given in Table 3 we should note a favorable combination of LOI parameters (below 0.5%) and alpha phase (traces) that is practically unachievable for conventional alumina.

4. Conclusions

Alumina produced by the hydrochloric acid process having very limited amount of major impurities, can have high content of problematic P and Cl impurities. Its physical properties differ from those of conventional SGA, which prevents direct application of this product in a modern reduction process.

This problem can be solved in two different ways:

- Adjustment of alumina properties to modern smelter requirements. There are some ways to solve this problem, patents are pending in the Patent Office of Russia;

- Development of a new generation of cells suited for unique properties of this alumina.

Each approach is of interest.

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