

The Properties of Superfine ATH Precipitated by Carbonation

Andrey Panov¹, Alexander Senyuta², Alexander Damaskin³

1. Director of Technology and Engineering Directorate,

2. Leading Researcher,

3. Chief Researcher

RUSAL ETC LLC, Saint Petersburg, Russia

Corresponding author: andrey.panov@rusal.com

Abstract

Superfine precipitated alumina trihydrate (ATH) is a very promising and environmentally acceptable filler and flame retardant for plastic and rubber materials, for paper, cardboard, paints, and as a component in ceramics and polishing compounds. For these applications, the most important product qualities are a high thermal stability (dehydration temperature ≥ 200 °C), brightness (≥ 95 %), fine average particle size (0.8 - 2.0 μm), and the low alkali content (soluble $\text{Na}_2\text{O} \leq 0.2$ %). Total consumption in the world exceeds 800 000 tons a year at the average price of 1000 €/t, and an annual growth rate of 4.3 %. The properties of superfine precipitated alumina obtained by RUSAL's carbonation technology is analysed and compared in this paper to similar products obtained by conventional technology involving the Bayer process.

Keywords: Superfine precipitated hydrate, properties, carbonation process.

1. Introduction

Superfine precipitated alumina trihydrate is a very promising and environmentally acceptable filler and flame retardant for plastic and rubber materials, for paper, cardboard, paints, and as a component in ceramics and polishing compounds. For these applications, the most important product qualities are a high thermal stability (dehydration temperature ≥ 200 °C), brightness (≥ 95 %), fine average particle size 0.8 - 2.0 μm), and the low alkali content (soluble $\text{Na}_2\text{O} \leq 0.2$ %). Total world consumption of this product exceeds 800 000 tons a year at an annual growth rate of 4.3 % and at the average price of 1000 €/t. The properties of superfine precipitated alumina obtained by RUSAL's carbonation technology is analysed and compared in this paper to similar products obtained by conventional technology involving the Bayer process.

The conventional production of superfine precipitated ATH is a complicated technology. As a rule, it is based on the classical Bayer process and further processing by application of a special milled submicron seed, with powders practically consisting only of the gibbsite phase in monocrystalline form.

The main challenge is in achievement a high product whiteness as Bayer process liquors usually contain colored organics which result in a hydrate with a brownish color after precipitation.

Meanwhile, there is a technology for processing high-silica aluminium ores which allows the production of sodium aluminate solutions which do not contain organic substances. This is the Sinter process (Figure 1). Because of its relatively high energy consumption, it has been gradually superseded by the Bayer process. Today, Sinter technology is applied only at few alumina refineries globally.

The technology of superfine alumina trihydrate production utilizing the Sinter process has been studied and refined in RUSAL's Engineering and Technology Centre (ETC). The product has very high whiteness, thermal stability, and well controlled particle size distribution

according to the market specification and requirements. It practically contains mostly bayerite. It is proposed that the process deficiencies in the limestone Sinter for metallurgical alumina production, (high thermal energy and electrical power consumption), on the other hand, allows production of chemical grade ATH with a low production cost and of high quality.

So long as the Sinter process is at 1100 - 1300 °C, organic substances are completely destroyed, and solutions after sinter leaching are absolutely transparent and colorless. Consequently, there is no necessity for stages of repeated dissolution and precipitation of ATH, or oxidative liquor treatment (by ozone, perchlorates, etc.) for the purpose of removing humate organics for decolouration. Moreover, the requirement for ATH classification is eliminated. The product particle size is controlled by the carbonation rate, the duration of precipitation is reduced tenfold, and the final product washing efficiency is increased in comparison to gibbsite obtained in the Bayer cycle.

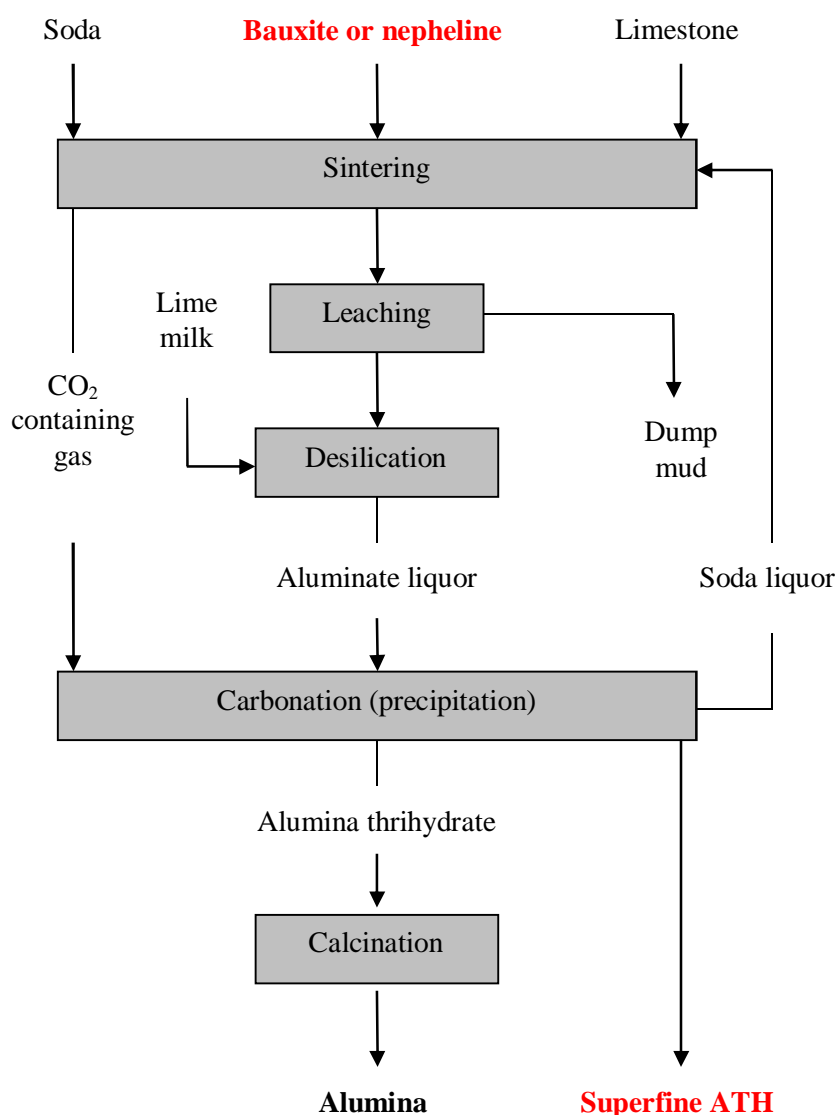


Figure 1. Flowsheet of Sinter alumina refinery.

However, as the requirements for quality of superfine alumina thrihydrate for use as flame retardants are strict, the comparison between the properties of precipitated bayerite and gibbsite products, which are well-known in the world market, is very interesting.

2. Size and Form of Product Particles

The RUSAL product sample was prepared especially for the further comparison with a market-typical flame retardant. The particle size distributions of both samples, measured by laser diffraction using two devices (Micro Sizer 201 and Cilas 1180), are similar, as can be seen in Figures 2 and 3. The data from the Micro Sizer 201 are presented in differential distribution and the identity of the samples are clear. However, the mineral phases of the particles of each powder are distinctly different.

Unlike gibbsite, it is known that bayerite is crystallized in a hexagonal form. The bayerite powder is characterized not by platelet, but prismatic single crystals. The micrographs obtained with scanning electron microscope (SEM) of bayerite and gibbsite particles are shown in Figure 4. It is necessary to note the small amount of aggregated bayerite crystals, which is evidence of a high rate precipitation process. For fillers and flame retardants, the absence of aggregates in a powder is a positive property.

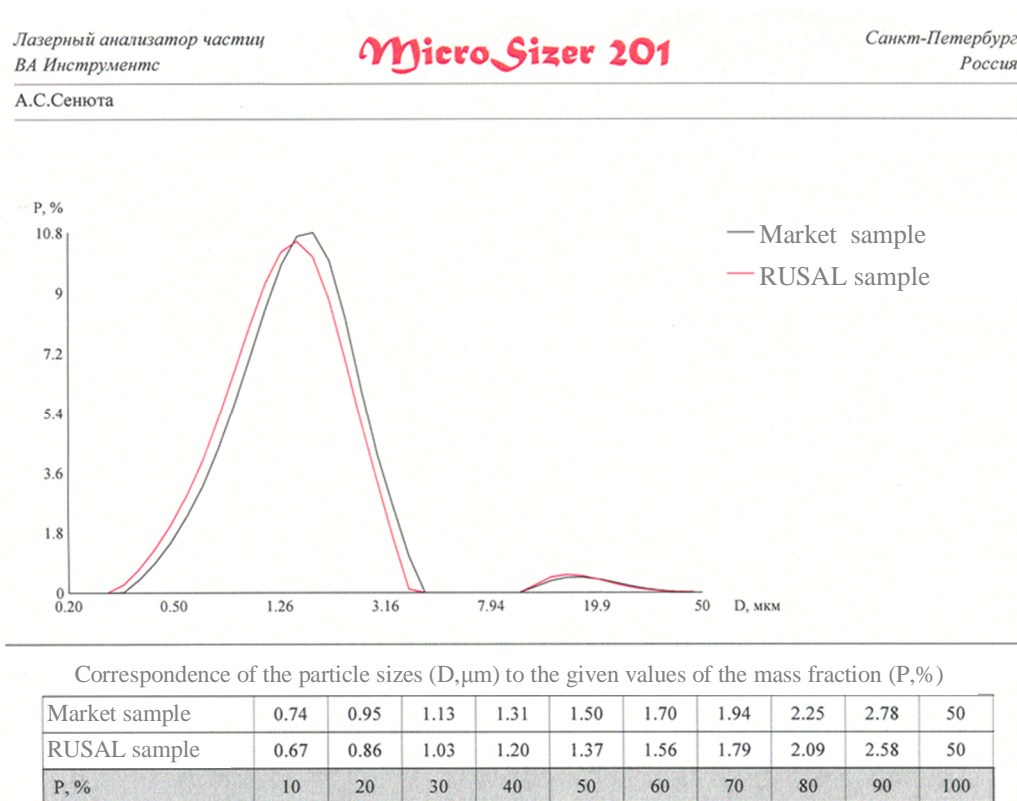
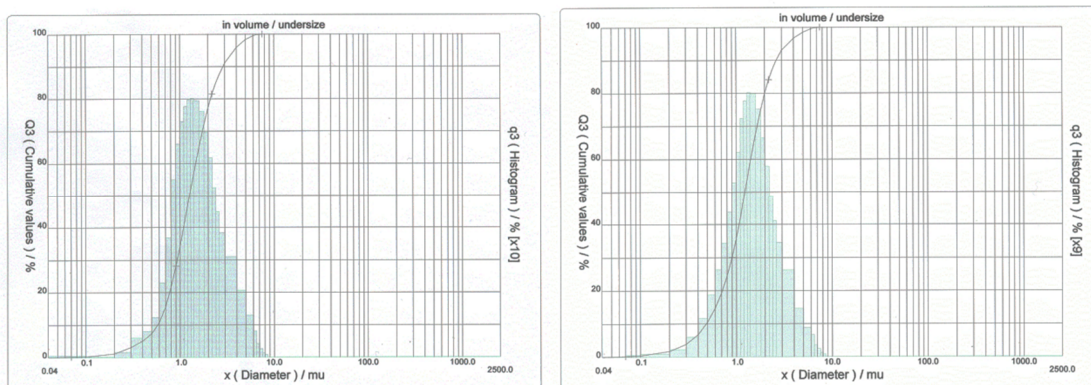
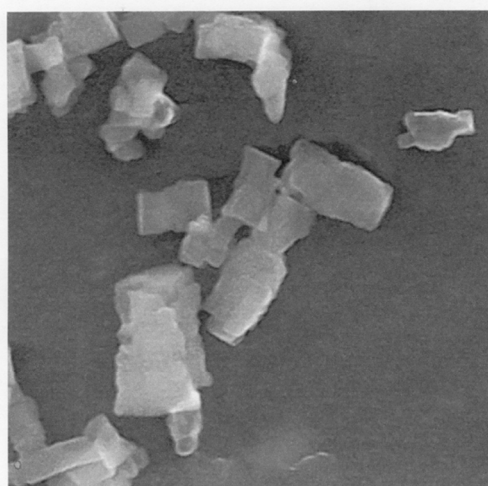
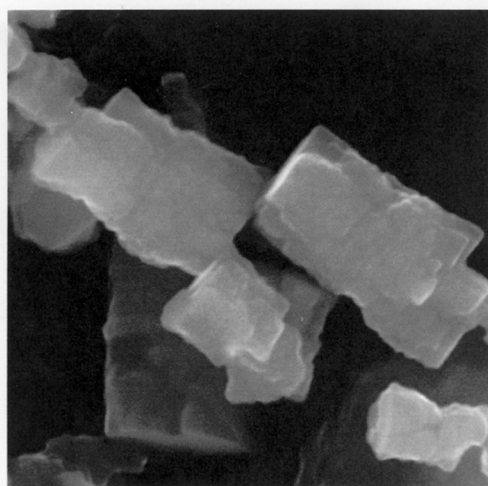


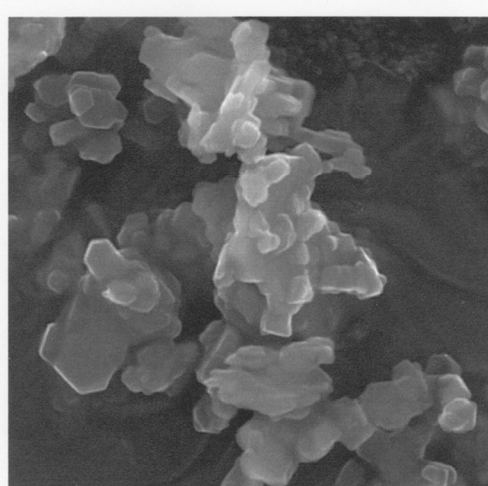
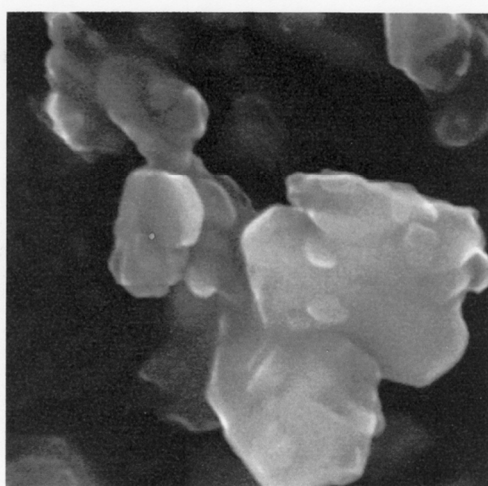
Figure 2. Particle size distribution measured by Micro Sizer 201.



a *b*
Figure 3. Particle size distribution measured by Cilas 1180.
a – market sample (gibbsite),
b – RUSAL sample (bayerite)



a – RUSAL sample (bayerite)



b - market sample (gibbsite)
Figure 4. SEM Micrographs of ATH powders.

3. Thermogravimetry

The temperature where bayerite begins to dehydrate is higher than gibbsite. This is a very important factor for the stirring and extrusion of resilient melted plastic compounds (Figure 5).

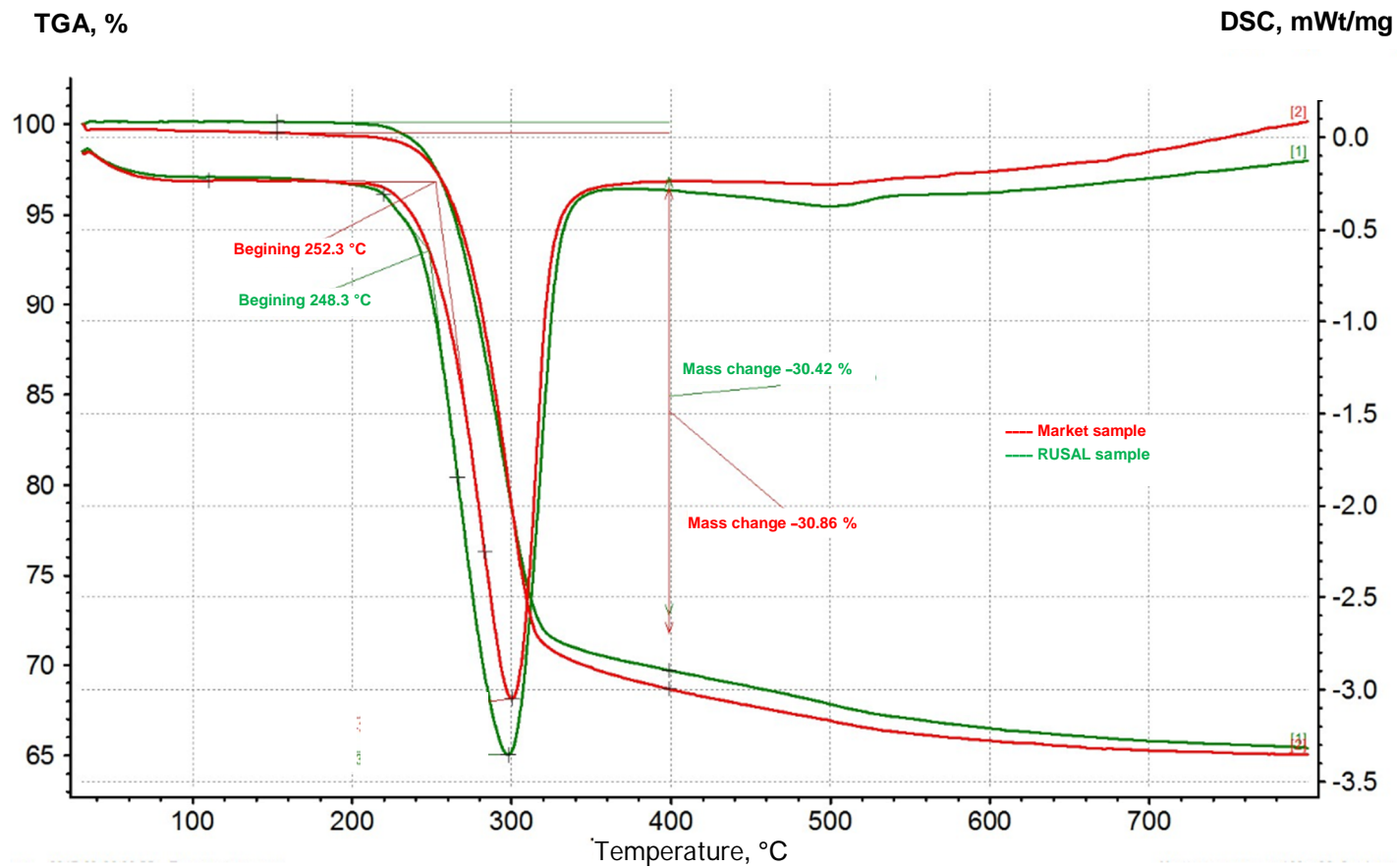


Figure 5. Results of thermogravimetric analysis.

Table 1. Main properties important for fillers and flame retardants.

Property	Market product	RUSAL product
Al(OH) ₃ content, %	99.6	99.6
Moisture (105 °C), %	0.2	0.2
Loss on ignition (1200 °C), %	34.5	34.5
Na ₂ O (soluble) content, %	0.08	0.08
Solubility in water (20 °C, pH 7), g/l	0.0015	0.0015
Refractive index	1.58	1.58
Electrical conductivity (10 % in H ₂ O), μS/cm	70	60
Whiteness, %	95	98
Specific Surface Area (BET), m ² /g	3.8	3.6
Density, g/cm ²	2.42	2.53
Particle size contribution (CILAS), μm		
d ₁₀	0.74	0.67
d ₅₀	1.50	1.37
d ₉₀	2.78	2.58
Viscosity (30 % suspension in water, 20°C), cp	18500	19000

Small differences between the properties of both samples except density and specific surface area can be explained by the higher d₅₀ of the market product.

Density as a basic physical property measured by the crystal optic method is an effect of crystal lattice parameters. But the specific surface area as well as viscosity probably depends on the differing form of gibbsite and bayerite particles.

Table 2. Test results for PVC plastic compound filled with uncoated superfine gibbsite and bayerite*.

Property	Market product	RUSAL product
Density, g/cm ³	1.516	1.525
Hardness, Shor D	53	51
Rupture strength, MPa	15.6	14.3
Specific elongation at rupture, %	170	170
Melt flow index, g/10 min (150 °C, 21.6 kg)	4.6	4.07
Oxygen index, %	39.0	37.5

* RUSAL sample

4. Conclusions

Superfine precipitated bayerite is a very competitive filler and flame retardant and opens potential new products and markets for alumina refineries using the Sinter process.