Essential Readings in Light Metals: Alumina and Bauxite.
Edited by Don Donaldson and Benny E. Raahauge.

8. ALUMINA QUALITY

The papers in this section, and the recommended readings that follow, are a cross-section of the physical and chemical properties that are of common interest to alumina producers, customers in aluminum smelters and in downstream processing of metal products.

The definition of alumina quality has been ambiguous. Quality is sometimes more of a perception and something that is "in the eye of the beholder." Beyond this, consistency of the smelter grade alumina (SGA) delivered to the smelter is of prime importance. But it is not all SGA properties or measures of variability that can be easily defined on a Certificate of Analysis. Such matters are in the realm of the literature and the technical papers that have been, and will be, presented over the years, as we move forward.

The use of virgin SGA in dry-scrubbing was the primary driver for smelters to turn away from floury to sandy SGA with a specific surface area typically ranging from 60–80 m2/gram, and much lower Alpha content, resulting in a relatively higher rate of dissolution in the smelter electrolyte.

The particle size distribution and morphology of the hydrate particles is produced in precipitation, while the chemical impurities of the hydrate are largely determined by the Bayer process subject to the bauxite processed. The resulting particle size distribution of alumina correlates well with flow ability of the alumina; however this is less so when it comes to the complex issue of alumina dustiness.

The primary chemical impurities in SGA are Fe2O3, SiO2, Na2O, and CaO. Specification for the first two impurities is a result of metal customer requirements, while specification of the latter two impurities is a result of smelter process requirements caused by formation of surplus bath. Calcium and silica chemistry, as well as incorporation of Na2O into the hydrate particles during precipitation are covered elsewhere in this book and its recommended readings. The minor content of soluble soda is controlled by counter-current washing of the production hydrate with hot condensate on the horizontal pan filters.

Control of the Fe2O3 impurity level in SGA has not attracted the same level of published investigations as the other impurities mentioned above, but a few references can be found in the recommended readings in Part 2: Bayer Process. Minor contamination with sulfur, vanadium, iron and silica oxides of the SGA may take place during calcination, subject to the technology applied, fuel type used and durability of the refractory lining.

Given the above physical and chemical properties of the production hydrate, all other physical properties as well as the mineral phases of the SGA are determined by the calcination technology applied. This includes the particle size distribution of SGA, which to some extent, depending on alumina particle strength, is subject to a certain amount of particle breakdown, or attrition, taken place during calcination and subsequent downstream handling and transport en-route to the smelters.

In the smelter itself, further change in the chemical impurities and particle size distribution of SGA takes place during dry-scrubbing with SGA of the potroom off-gasses in the gas treatment centers.

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DEHYDRATION PRODUCTS OF GIBBSITE BY ROTALY KILN AND STATIONAL CALCINER

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Gibbsite was dehydrated in a fluid calciner with suspension preheaters (SPF).

Crystal forms of the dehydration products were determined and compared with those obtained by a conventional rotary kiln.

The former products were similar to those obtained by a suspension heater of lab scale whose heating velocity was of an order of 10^4 °C/S. The latter products were similar to those calcined in an electric furnace.

The surface area of products obtained by SPF is higher than that by the rotary kiln at a same α-Al_2O_3 content.

At a same surface area level, both products show the same reactivity with fluorine.

1. Introduction

Hydrated aluminas change to α-Al_2O_3 forming transition aluminas via various routes by the successive calcination.

Since Stumpf et al (1) reported the existence of several transition aluminas with different crystal structures, a variety of investigations have been reported with respect to their structures, the mechanisms and conditions of formation. Among the various hydrated aluminas, such as crystalline alumina monohydrates, crystalline alumina trihydrates and amorphous alumina hydrates, gibbsite obtained by the Bayer process is the most widely used alumina trihydrate.

Many reports have been presented on the dehydration process of gibbsite. Especially Brown et al (2) proposed two series of transition aluminas and studied the effect of the particle size of starting material and that of the calcination atmosphere on the dehydration products. In their studies heating velocity was relatively low, that is less than 100 °C/min.

Recently saving energy processes are very important in the Bayer process and suspension type calciners or fluidized bed type calciners with high thermal efficiency instead of a conventional rotary kiln have been developed. In these type calciners, heating velocity is very high and it achieves over 1000 °C/sec at near the dehydration temperature of gibbsite.

In this paper, the kinds and the properties of dehydration products obtained by the rapid heating process are described in relation to the slowly heated dehydration products. And the rates of various aluminas to α-phase transformation are also discussed.

2. Experimental

2.1 Raw material

Gibbsite was used for the starting material of the test. The mean diameter of the gibbsite was 55~90 μm. It contained 0.20 % of Na_2O, 0.02 % of SiO_2 and 0.01 % of Fe_2O_3.

2.2 Procedure

Four types of apparatus were used for the calcination of gibbsite. Two types (1), (2) were lab apparatus, and other two types (3), (4) were plant equipments.

(1) Electric furnace (lab apparatus)

10 g of gibbsite was heated at 5 °C/min to 300~1300 °C, and soaked for 2 hours.

(2) Rapid-heating apparatus (suspension heater, lab apparatus)

The apparatus was composed of a furnace, a gibbsite feeder, a heating zone (25 mm^{Φ} x 3000 mm^{L}), a cyclone for separation. The furnace was heated by LPG. The gas velocity in the heating zone was typically 6.9 Nm/sec. Gibbsite was supplied typically at the rate of 0.1 kg/Nm^3. The elevation rate of the temperature was estimated about 30000 °C/sec. The residence time of gibbsite in the heating zone was less than 0.2 sec.

(3) Rotary kiln (plant equipment)

A conventional rotary kiln was used. The inlet temperature was 200~300 °C, and the outlet temperature was 1300~1400 °C. The residence time of gibbsite was 2~3 h.

(4) Fluid calciner with suspension preheaters (SPF, plant equipment)

SPF (3) was used. The inlet temperature of the first preheater was typically 40 °C, and the outlet temperature of the lost preheater was 1100~1200 °C. The residence time of gibbsite was approximately 2~3 minutes, its exact measurement was not possible. The calcined gibbsite was sampled from the nozzles attached to the under part of the SPF cyclones.

3. Results and Discussions

3.1 Dehydration products by electric furnace

Dehydration products by an electric furnace were investigated in order to compare with results of rapid-heating apparatus. The properties of dehydration products are shown in Table I.

As Brown has already reported, the transformation route of gibbsite is as follows : (2)

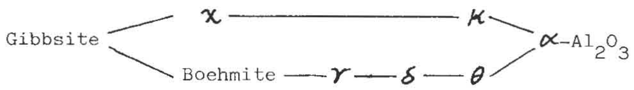


Table I. Dehydration product and surface area of calcined gibbsite in electric furnace

No.	Calcination temp. (°C)	Dehydration product (%)				Surface area (m^2/g)
		Gib.	Bo.	χ	γ	
E300	300	32	16	30	20	190
E400	400	0	15	50	35	180
E500	500	0	6	50	40	171
E600	600	0	0	50	50	151
E700	700	0	0	50	50	110
E800	800	0	0	50	50	95

Calcination time : 120 min

Gib. : gibbsite

Bo. : boehmite

χ : χ-Al_2O_3

γ : γ-Al_2O_3

3.2 Dehydration products by rapid-heating apparatus

The properties of dehydration products are shown in Table II. The pore volume distributions of them are shown in Fig. 1. These figures give the following results :

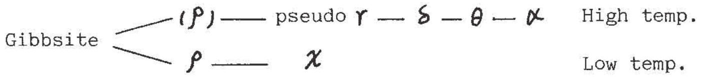
(1) The dehydration product contained only 5 % of boehmite (calcination temp., 385 °C).

(2) The dehydration product did not contain boehmite or γ-Al_2O_3. It was composed of about 80 % of χ-Al_2O_3 and 20 % of ρ-Al_2O_3. (calcination temp., 520~705 °C)

(3) The dehydration product was composed of pseudo γ-Al_2O_3 alone. (calcination temp., 1100 °C)

In the case of rapid heating above 520 °C, gibbsite did not transform to boehmite, because of lack of hydrothermal conditions during heating. It is known that the transformation to boehmite occurs under hydrothermal conditions in gibbsite particel (4) (5), and gibbsite transforms to ρ-Al_2O_3 under vacuum heating conditions (6) (7).

The above experimental results suggest the following transformation route of gibbsite.



Dehydration products by the rapid heating have high surface area, such as 300 m^2/g, compared with dehydration products in an electric furnace. This high surface area is due to the large micro-pore volume (radius < 20 Å) shown as in Fig. 1.

3.3 Dehydration products by rotary kiln

Next, we investigated the properties of calcined gibbsite sampled from different places of the rotary kiln, in order to clarify the transformation route in a plant equipment. The results are shown in Table III.

The samples at the inlet of the kiln (for example RK-1 and RK-2) contained 35~40 wt % of α-Al_2O_3. These high contents of α-Al_2O_3 were caused by mixing of α-Al_2O_3 powders which were accompanied by combution gas and recycled.

Table II. Dehydration product and surface area of rapid-heated gibbsite in suspension heater

No.	Calcination temp. (°C)			Dehydration product (%)						Surface area (m^2/g)
	T_1	T_2	T_3	Gib.	Bo.	χ	ρ	γ		
R385	500	415	385	83	5	5	0	0		23
R440	600	480	440	7	0	60	30	0		206
R520	700	565	520	0	0	80	20	0		270
R600	800	645	600	0	0	80	20	0		302
R675	900	725	675	0	0	80	20	0		312
R705	950	755	705	0	0	80	20	0		277
						P-γ	δ	θ	α	
R1100	1360		1100	0	0	120	0	0	0	144
R1300	1580		1300	0	0	15	15	12	40	

P-γ: pseudo γ-Al_2O_3

Flow velocity ≈ 7 Nm/sec

Residence time : 0.12~0.19 sec ($T_3 \leq 705$)

0.04~0.05 sec ($T_3 \geq 1100$)

Table III. Dehydration product of calcined gibbsite in rotary kiln

No.	Temperature °C	Gib.	Bo.	χ	γ+δ	θ	κ	α
		%						
RK1	600	1	7	20	30	0	0	37
RK2	720	0	4	20	50	0	0	38
RK3	850	0	0	20	60	0	0	36
RK4	970	0	0	10	70	2	1	49
RK5	1100	0	0	tr.	20	11	4	49
RK6	1200	0	0	tr.	tr.	5	1	76
RK7	1300	0	0	0	0	0	0	100

Gib. : gibbsite tr. : trace
Bo. : boehmite

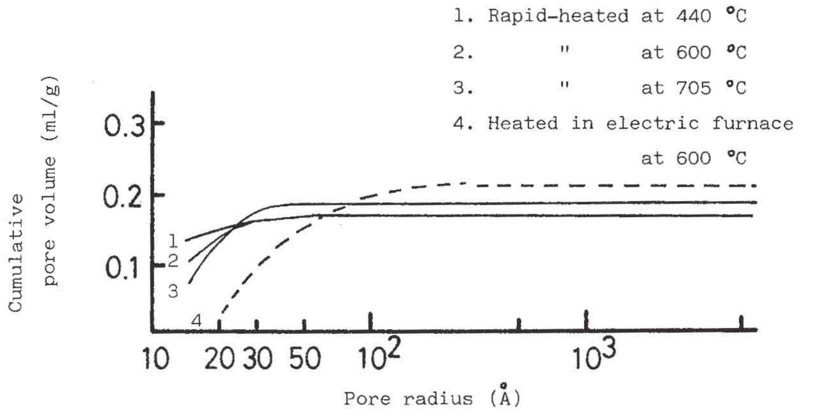


Fig. 1 Pore size distribution of dehydration products.

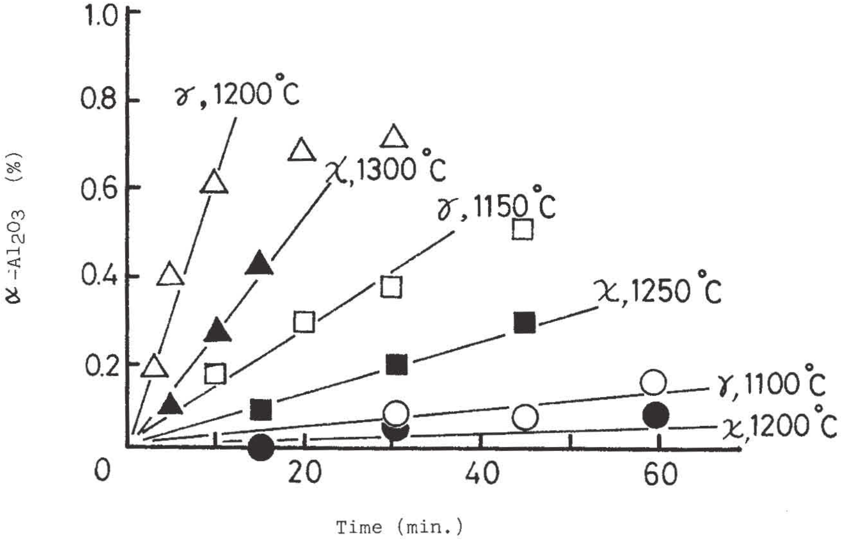
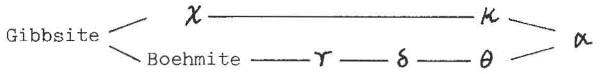


Fig. 2 Rate of α-Al_2O_3 phase transformation of χ, γ-Al_2O_3 in electric furnace.

Observed boehmite content of sample RK-1 in Table III was 7 %, but corrected content obtained after subtraction of α-Al_2O_3 was 10~20 %. This value was the same as for the dehydration product in the electric furnace.

These experimental results indicate the following transformation route of gibbsite as Brown proposed (2).



3.4 Dehydration products by SPF

The properties of dehydration products by SPF are shown in Table IV. The samples analysed were sieved and fine α-Al_2O_3 powder (under 44 μm) was removed.

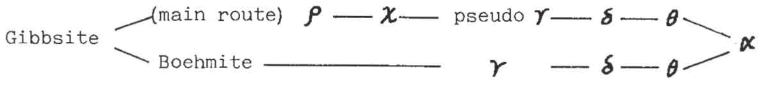
The results were as follows :

(1) Boehmite content was less than 3 %.

(2) κ-Al_2O_3 was not observe, even though χ-Al_2O_3 was present.

(3) The sample of SPF 2 rehydrated easily in water at 100 °C. This fact demonstrated the presence of ρ-Al_2O_3.

From these experimental results, it is concluded that the transformation route in SPF is identified as that in rapid-heating apparatus.



3.5 Rates of rapid-heated dehydrates and the transition aluminas to α-Al_2O_3 phase transformation

The rates of χ , γ-Al_2O_3, R600 and R1100 to α-Al_2O_3 phase transformation were measured in the electric furnace, as well as that of gibbsite in the suspension heater. Experimental results are shown in Fig.2.

α-Al_2O_3 phase transformation of these aluminas obeys zero-order kinetics ($\frac{dx}{dt}$=k) at the initial stage of the reaction, but deviates in the final stage (α-Al_2O_3 content X > 0.6) as reported by Yanagida (8).

Table IV. Dehydration product of calcined gibbsite in SPF

	Temperature °C	Gib.	Bo.	ρ	χ	$\gamma+\delta$	θ	κ	α
		%							
SPF1 (1st cyclon)	170	100	0	0	0	0	0	0	1
SPF2 (2nd ")	380	0	3	20	tr.	20	0	0	2
SPF3 (3rd ")	1100	0	0		tr.	60	7	0	15
SPF4 (Fluid bed)	1100	0	0		tr.	70	11	0	19

Before measurement, fine powder (under 44 μm) were removed by sieving.

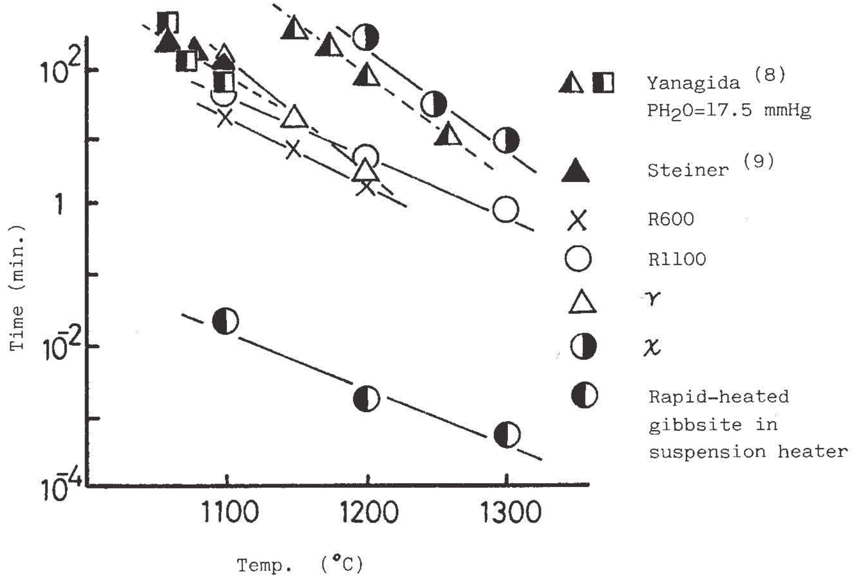


Fig.3 Relationship between time and temperature for formation of 20 % α-Al_2O_3 from various aluminas

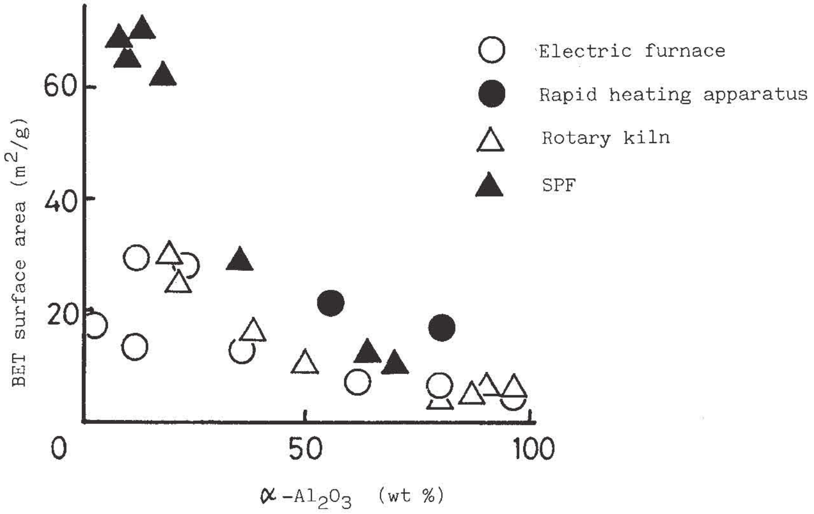


Fig. 4 BET surface area vs. α-Al_2O_3 content.

The rate constant (α-Al_2O_3 content/min) in the range of less than 0.6 is shown in Eq.(1) ~ Eq.(4) as a function of the reaction temperature, T (°K).

$$\chi\text{-}Al_2O_3 : K=10^{18.43} \exp(-143.7 \times 10^3/RT) \qquad (1)$$

$$\gamma\text{-}Al_2O_3 : K=10^{16.63} \exp(-120.0 \times 10^3/RT) \qquad (2)$$

$$R600 : K=10^{11.50} \exp(-84.3 \times 10^3\ RT) \qquad (3)$$

$$R1100 : K=10^{12.84} \exp(-92.3 \times 10^3\ RT) \qquad (4)$$

Activation energies to α-Al_2O_3 transformation are calculated to be 143.7, 120.0, 84.3 and 92.3 Kcal/mol for χ , γ-Al_2O_3, R600 and R1100, respectively. The dehydration products by rapid heating have lower activation energies than χ or γ-Al_2O_3. These lower activation energies can be due to the highly defective crystal structure of the starting material.

Usuallly alumina with ca. 20 wt % crystalization are used for aluminum smelting. Fig. 3 shows the relationship between the reaction time to attain X=0.2 (α-Al_2O_3 20 %) and the reaction temperature.

The rate of gibbsite to α-Al_2O_3 phase transformation in the suspension heaters is 10^4 as high as that of R600, which most easily transformes to α-phase in the electric furnace among other transition aluminas. This is caused mainly from the steam produced by fuel combution and from highly deformed crystal structure formed by instataneous dehydration.

The crystalization temperature of χ-Al_2O_3 at X=0.2 is 100~200 °C higher than that of R600 or R1100, but that of γ-Al_2O_3 is approximately the same temperature for R600 or R1100.

Table V. Properties of calcined gibbsite

Apparatus	α-Al_2O_3 %	Surface area m^2/g	Density g/cm^3	Reactivity with F F-g/100g-Al_2O_3	Angle of repose	Dehydration product % χ	$\gamma+\delta$	$p\text{-}\gamma+\delta$	κ	θ	α
Electric furnace	12	30	3.55	2.3	36	tr.	20	0	30	15	10
	23	28	3.57	2.1	37	tr.	20	0	17	11	23
Rapid-heating apparatus	0	144	3.54	10		0	0	120	0	0	0
	40					0	0	15	0	12	40
Rotary kiln	3	73	3.45	6.0	32	20	50	0	1	8	3
	21	26	3.63	2.1	34	tr.	tr.	0	7	24	21
SPF	10	65	3.54	5.1	36	tr.	0	70	0	4	10
	18	62	3.60	4.5	35	tr.	0	70	0	10	18
	42	25	3.74	1.9	37	0	0	20	tr.	32	42

Before measurement, fine powder (under 44 μm) were removed by sieving.

Raw material gibbsite : 90 μm (average particle size)

3.6 Properties of α-Al2O3 obtained by rapid-heating

As described above, the transition alumina obtained from gibbsite heated rapidly differs from that heated slowly in the electric furnace in its crystal structure. Hereafter, the relationship between surface area and α-Al_2O_3 content and reactivity with fluorine gas are shown.

(1) BET surface area

Fig. 4 shows the relationship between the surface area and α-Al_2O_3 content for aluminas obtained by four different calcination apparatus, which are the electric furnace, rapid-heating apparatus, rotary kiln and SPF.

Fig. 4 indicates that rapid heated alumina calcined in SPF gives higher surface area at a same α-Al_2O_3 content as compared with those calcined in the electric furnace or in the rotary kiln. Because the rapid-heated product contains such transition aluminas as χ, ρ or pseudo γ-Al_2O_3 which have much higher surface areas than that of κ or θ -Al_2O_3 which are contained in the rotary kiln product.

(2) Reactivity with fluorine gas

In aluminum smelting, it is desired for alumina to adsorb fluorine containing gas. The results shown in Table V indicates that the reactivity of alumina obtained by rapid heating with fluorine is approximately twice as high as that of alumina obtained by the calcination in the rotary kiln at the α-Al_2O_3 content of 20 %. At a same BET level, all aluminas show the same reactivity with fluorine.

4. Conclusion

A different thermal decomposition process of gibbsite in SPF was found compared with the process in a conventional rotary kiln.

The surface area of alumina obtained by SPF is higher than that by the rotary kiln at a same α-Al_2O_3 content.

At a same surface area level, both aluminas shown the same reactivity with fluorine.

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