CO-PRODUCTION OF CHEMICAL GRADE AND METAL GRADE ALUMINIUM-HYDROXIDES

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ABSTRACT

Besides metal grade alumina, one of the main goals of existing alumina plants (especially old and small ones) is to produce added value, specialty alumina-based chemicals. Production of pure and white aluminium hydroxides requires special liquor purification and precipitation processes. The economic feasibility of manufacturing these specialty hydrates depends on the proper combination of metal and chemical grade hydrate precipitation process stages.

Pure and white aluminium hydroxide products have been developed by Aluterv-FKI Ltd. and Ajka Aluminium Ltd. to widen the products' list of Hungalu and improve the competitiveness of the Ajka Alumina Plant.

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1.0 INTRODUCTION

The recession in the aluminium industry makes it important that alumina factories improve alumina quality and reduce production costs. Smelters which remained in operation need low contaminated alumina feedstock. In general, medium and high purity alumina are required to satisfy the demand of non-metallurgical market.

Non-metallurgical alumina production has been increased rapidly in the last decade. Non-metallurgical calcined alumina is used in the industries of refractories, abrasives and ceramics while aluminium-hydroxide is used as feedstock for chemicals and as filler or flame retardant filler for plastics and rubber (Mátyási, Kaptay and Tóth 1983; Mordini and Cristol, 1983; Sato et al, 1987; Csige et al. 1990; Sleppy et al, 1991).

Due to the recession and high competition Hungalu lost a part of its alumina markets in Russia in the last few years, so it had to decrease the production level in alumina refineries and shut down two of its three smelters. Alumina production has been reduced by about 50% at the Ajka alumina plant and the aluminium smelter has been shut down as well.

In these circumstances, the alumina refineries of Hungalu in this situation will manufacture more and more specialty alumina based products which can be produced profitably at present, unlike traditional metallurgical grade alumina (Csillag, K lm n and Szalay 1989; Baksa et al, 1992).

The smaller, more flexible alumina plants in Europe, which could transform successfully their production range according to the market demand should be able to survive the recession period (Greenaway and Brandt, 1992).

Nevertheless, the larger works which produce mainly metallurgical grade alumina also could improve their profitability if they joined special production lines with the Bayer-cycle adequately (Chin, 1987 and 1989). There is more chance to achieve this connection in plants where the capacity has been reduced and consequently a large number of equipment is available to develop new (special and separated) systems for specialty products with a minimum investment.

Ajka Aluminium Ltd. has developed smaller production systems to produce specialities: dried and ground hydrates, synthetic zeolites, gallium metal (Baksa et al, 1992). Development activity aims to produce white, low-contaminated aluminium hydroxide products for direct use (e.g. as filler) or for further treatment. The latest development activity will be discussed in this paper (Aluterv-FKI Ltd. and Ajka Aluminium Ltd., 1991).

2.0 LABORATORY TESTS

Aluterv-FKI Ltd., the Engineering and Development Centre of Hungalu has developed a laboratory scale procedure to manufacture pure (low soda and 0.008-0.01% SiO_2 and Fe_2O_3 containing), white aluminium hydroxides. It was found that the Na_2O content of hydrate can be controlled by the precipitation rate which can be regulated by the caustic soda concentration and A/C ratio of the pregnant liquor, the temperature profile and seed charge.

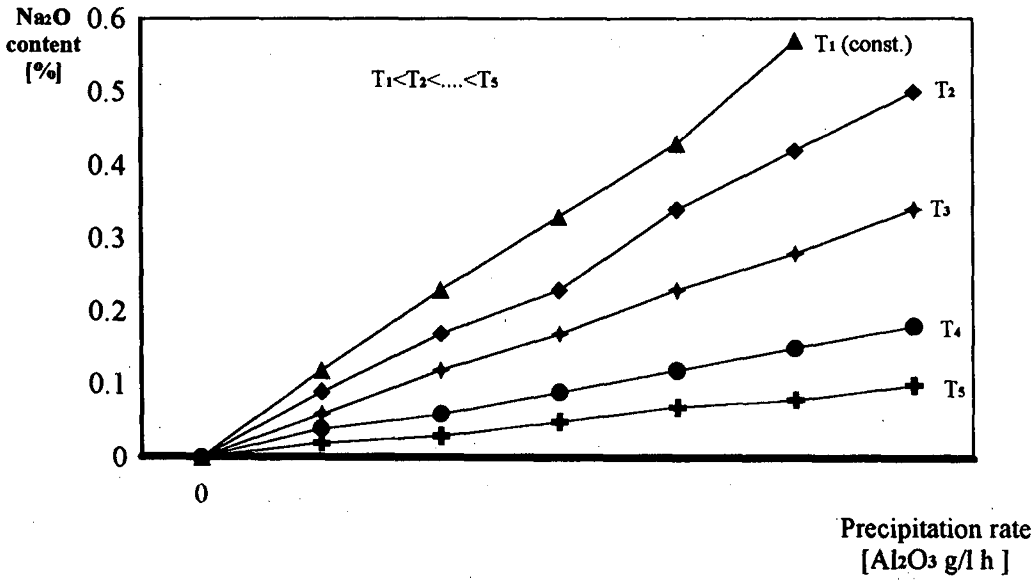

Figure 1

Effect of the precipitation rate on Na_2O content of aluminium hydroxide

Figure 1 shows the effect of precipitation rate on the Na_2O content of product hydrate at different temperatures. It can be seen that a low level of Na_2O content can be reached at low precipitation rate and relatively high temperature. Other impurities from the pregnant liquor (Fe_2O_3, SiO_2, colouring organic compounds) can be reduced significantly during a pre-crystallization process followed by a separation and/or by means of a special control filtration process.

3.0 PILOT PLANT TESTS

Pilot plant tests were carried out at Ajka Alumina Refinery in order to confirm laboratory results. The process flow diagram of the pilot plant system is represented in Figure 2.

The first test-series have been performed by means of pre-crystallization and adjusting the A/C ratio of the green liquor. A significant part of the impurities of the green liquor could be removed by the filtration of hydrate precipitated in the pre-crystallization stage ("scalping precipitation"). Then isotherm crystallization was carried out using the pre-cleaned green liquor and product hydrate of the alumina plant as seed in a batch process.

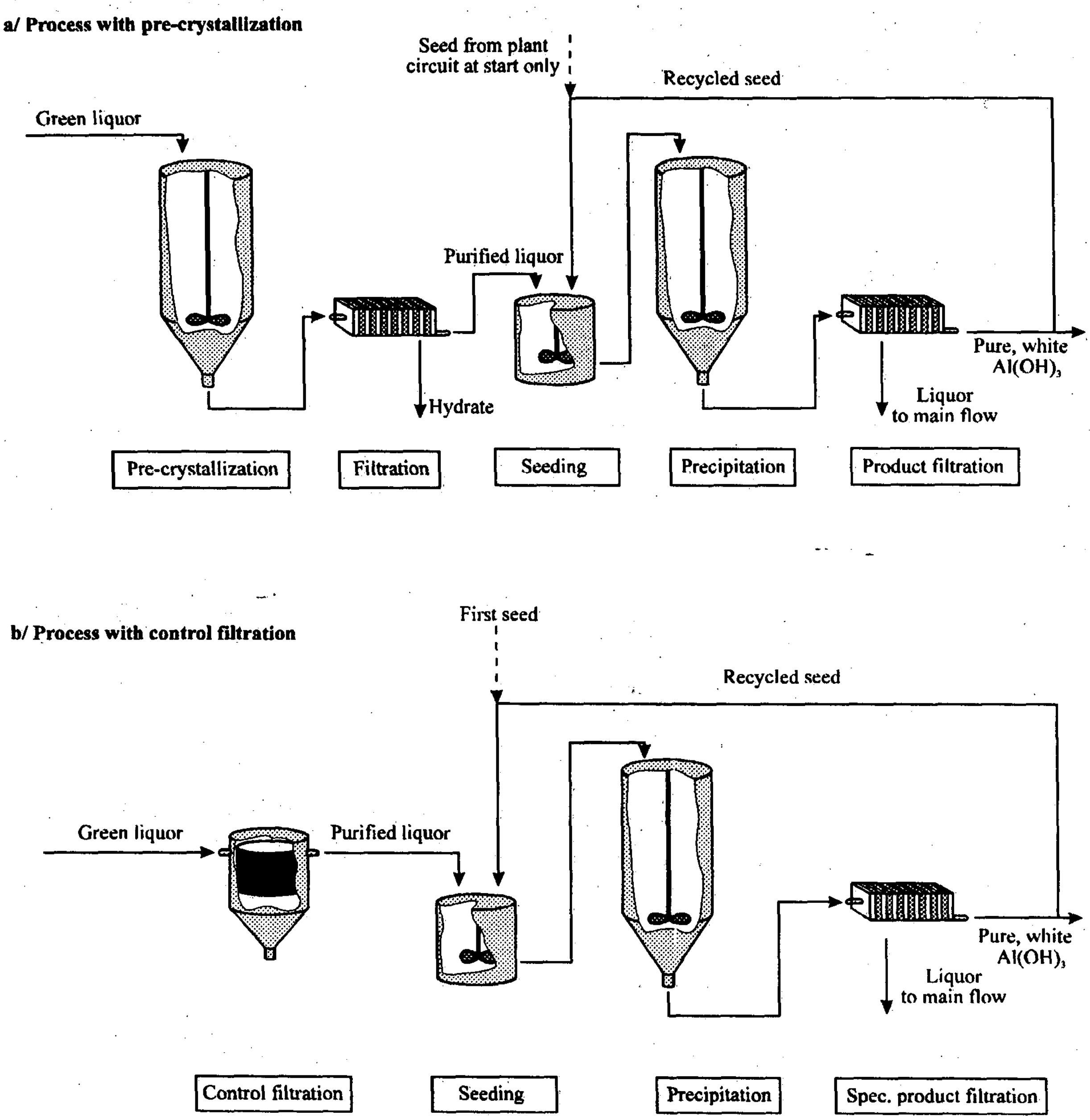

Figure 2
Batch pilot system for precipitation

The whole procedure has been repeated for a number of cycles using product hydrate of the former cycle as seed. Characteristics of hydrate products/seeds obtained in each cycle are summarized in Table 1. The gradual improvement of the whiteness and purity of the hydrate products has been confirmed.

The precipitation efficiency at isotherm crystallization is relatively low, therefore further tests were carried out under controlled cooling, which raised the efficiency.

Table 1
Characteristics of $Al(OH)_3$ obtained by isotherm precipitation in pilot plant
(after pre-crystallization)

Sample	Chemical composition					Whiteness	Medium particle size
	$Al(OH)_3$ (%)	tNa_2O (%)	sNa_2O (%)	Fe_2O_3 (%)	SiO_2 (%)	(%)	(d50) (μm)
Seed	99.84	0.12	0.005	0.016	0.010	64	52
Cycle 1	99.86	0.10	0.006	0.016	0.010	69	50
Cycle 2	99.87	0.09	0.006	0.015	0.010	73	43
Cycle 3	99.88	0.08	0.006	0.012	0.010	75	41
Cycle 4	99.89	0.077	0.005	0.011	0.010	77	39
Cycle 5	99.89	0.073	0.005	0.009	0.009	80	37
Cycle 6	99.90	0.07	0.005	0.008	0.008	82	36

Component measured	**Instrument used:**
Fe_2O_3 and SiO_2	ARL 72000 (XRF)
Total Na_2O	Flame emission spectrometry
Whiteness	MOMCOLOR 100 ($BaSO_4$ as reference material)
d50	FRITSCH sedimentograph

tNa_2O = total Na_2O
sNa_2O = water soluble Na_2O

The second precipitation test series were carried out in green liquor which was purified by careful (and specially modified) control filtration instead of pre-crystallization. These tests were also carried out over several cycles. Properties of hydrate crystallized in the last cycle are shown in Table 2. The precipitation efficiency was almost the same as the first series under similar conditions.

Table 2
Characteristics of $Al(OH)_3$ precipitated in pilot plant
(after control filtration of the green liquor)

Chemical composition					Whiteness	Medium particle size (d50)
$Al(OH)_3$ (%)	tNa_2O (%)	sNa_2O (%)	Fe_2O_3 (%)	SiO_2 (%)	(%)	(μm)
99.9	0.06	0.005	0.009	0.009	85	42

4.0 PLANT RESULTS

Based on the laboratory and pilot plant tests two variants have been developed for industrial scale manufacturing according to market demand, namely a continuous and a batchwise process.

4.1 Process with pre-crystallization (continuous)

The "pre-crystallization process" for liquor purification can be realized when a continuous special precipitation line is connected with the main Bayer precipitation row to produce special hydrate in large quantity. Pregnant liquor for the special precipitation will be supplied from the first stage (after 6-10 hours) of the Bayer precipitation row (after filtration of the limited, requested amount of the hydrate slurry). The A/C ratio of the green liquor in the special precipitation line can be adjusted by adding Bayer green liquor obtained after proper control filtration. The spent liquor of the special line will be recirculated to the appropriate stage of the main Bayer precipitation row ensuring the same precipitation yield for this process liquor.

4.2 Process with special modified control filtration (batchwise)

The batch process is preferred when only smaller quantity of specialty hydrate is required. A careful control filtration with dosage of selected synthetic polymers is applied for liquor purification as the first stage of the process. A few hundred tons of white and pure aluminium hydroxide were manufactured in two batch crystallization tanks of 2000 m^3 volume each separated from the main Bayer precipitation row using the specially purified green liquor. The flow-sheet of the system is shown in Figure 3. Characteristics of special hydrate are summarized in Table 3.

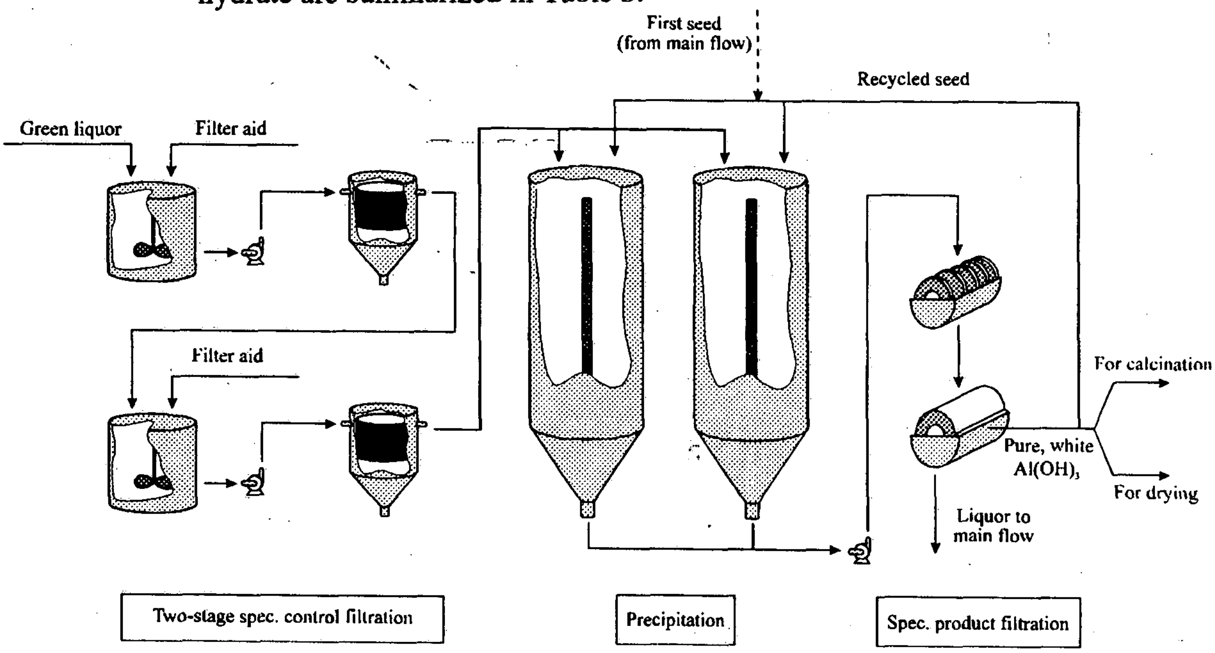

Figure 3
Batch plant system

Regular plant hydrate was used as seed at the start of operation and special products were recirculated during 3 cycles. After product filtration the spent liquor was fed back to the Bayer precipitation line. This batch system is connected with Bayer circuit according to the technological demand and in this way it can be operated economically. The capacity of the batch system is about 4000 t/y and can be increased using additional precipitator tanks for special precipitation.

Table 3
Characteristics of $Al(OH)_3$ precipitated in plant test

Chemical composition				Whiteness	Medium particle size (d50)
$Al(OH)_3$ (%)	tNa_2O (%)	Fe_2O_3 (%)	SiO_2 (%)	(%)	(μm)
99.9	0.08	0.008	0.008	90	40

5.0 SPECIAL PROPERTIES AND USES OF THE PRODUCTS

As a result of the development, basically two types of aluminium-hydroxides can be produced, white hydrate and pure-white hydrate, depending on use of special liquor purification and controlled crystallization. Special characteristics and application opportunities of the two groups of hydrates are demonstrated in Table 4. Figure 4 shows some possibilities for manufacture of special white and pure-white hydrates and aluminas.

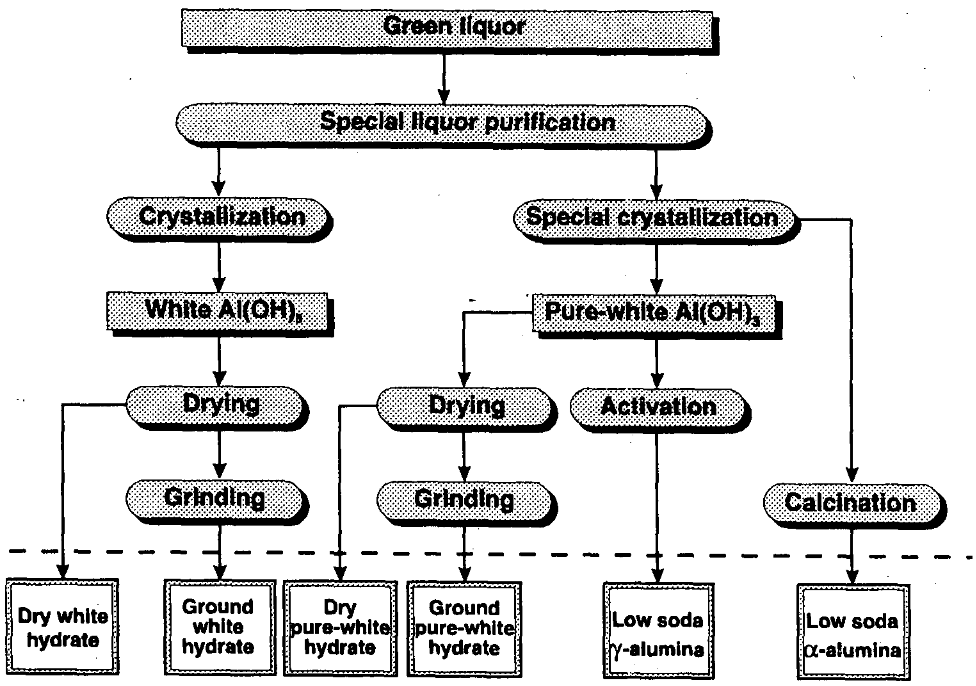

Figure 4
Alternatives for manufacturing pure and white products

6.0 CONCLUSIONS

Special alumina based products can be produced economically in a proper combination of special systems and the metal grade alumina manufacturing process.

After successful laboratory and pilot plant tests, pure and white aluminium hydroxides were manufactured in a separate precipitation system which was connected to the main cycle of Ajka Alumina Plant. The chemical grade hydrate products (Total Na_2O can be varied according to requirement in the range of 0.05-0.15%, Fe_2O_3 and SiO_2 maintained below 0.01% and whiteness above 90%). The chemical grade hydrate products can be used directly or after surface treatment as aluminium hydroxides and after calcination as aluminas in different industries.

Table 4
Characteristics and uses of special hydrates

	White hydrate	Pure-white hydrate (Low soda)
Chemical composition		
tNa_2O, (%)	0.15-0.35	0.05-0.15
sNa_2O, (%)	0.005	0.005
Fe_2O_3, (%)	0.006-0.01	0.006-0.01
SiO_2, (%)	0.008-0.01	0.008-0.01
$Al(OH)_3$, (%)	99.6-99.7	99.8-99.9
Whiteness, (%)	>90	>90
Medium particle size (d50), (µm)	40-50	40-70
Spec. surface area (BET), m^2/g	0.1-0.2	0.1-0.2
Morphology (SEM)	Agglomerates of smaller crystals	Larger monocrystals
	Filler for • toothpaste • paper Flame retardant filler for • white and coloured plastics	(Flame retardant) filler for • synthetic marble and onyx • soft polyurethane foams • plastic electric parts (low conductivity filler) Base for • activated alumina (catalyst carrier) • calcined alumina (ceramics)

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