

## 5. PRECIPITATION, CLASSIFICATION, AND SEED FILTRATION

The precipitation (crystallization) of aluminum trihydroxide, gibbsite, from the supersaturated (with respect to alumina) aluminate liquor plays a key role in the technical and economic performance of the Bayer alumina refinery. **Supersaturation is achieved during alumina extraction from bauxite at elevated temperatures which is followed by separation of impurities from the liquor by decantation settling and polishing filtration.**

In industrial practice, the performance of the precipitation operation is evaluated with respect to following criteria:

- Liquor productivity or alumina yield per unit volume of feed liquor.
- Alumina quality: particle size distribution, strength against size degradation, impurity content—particularly Na<sub>2</sub>O which is incorporated within the particle and cannot be removed by washing.

Papers in the TMS *Light Metals* publications over the years cover the precipitation operation extensively and include 130 papers. The topics discussed can be grouped under the following categories:

- Crystallization mechanisms involved (growth, agglomeration, nucleation and breakage) in the precipitation process and their kinetics
- System design and engineering including tank design, agitation systems, hydrodynamics
- Mathematical modeling and process optimization
- Incorporation of impurities, particularly Na<sub>2</sub>O
- Particle morphology and its relation to strength
- The effects of organic matter dissolved in liquor derived both from bauxite and additives used as process aids
- **Hydrate classification and filtration systems used for separating seed and a product suitable for calcination to alumina**

**Papers selected for the present publication represent some of the defining work on the different aspects of the precipitation operation.**

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## PRECIPITATION TECHNOLOGY

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The precipitation of alumina trihydrate crystals from supersaturated sodium aluminate solution is unique to the Bayer process. After remaining basically unchanged for 96 years, a combination of economic and environmental factors have necessitated major changes in the processes and equipment used to produce these crystals.

Increased energy costs have caused operators of the "American" Bayer process to increase yields, while producing coarse, sandy alumina. At the same time, the use of dry gas scrubbers at reduction works has caused operators of the "European" process to produce coarse, sandy alumina, while maintaining high yields.

The more rigorous conditions of stationary calciners have promoted the development of process improvements to increase alumina particle strength to reduce product dustiness.

This paper reviews technology developed to meet these changing requirements.

Introduction

Most of the world alumina has been produced by the Bayer Process since the original Bayer patents expired in 1911 (3). Although there was one basic process, it was practiced two different ways through the 1950's (13). These were developed because of differences in bauxite composition, energy costs and reduction cell design. The "European" process produced fine, highly calcined, flourey alumina at high digestion temperatures and caustic concentrations with precipitation yields in excess of 60 gpl. The "American" process produced coarse, sandy, moderately calcined alumina at low digestion temperatures and caustic concentrations with precipitation yields of about 45 gpl.

In the 1950's and 1960's the discovery of mixed trihydrate and monohydrate bauxites in the Carribean, Africa and Australia resulted in the development of American technology utilizing higher digestion temperatures. These bauxites had little impact on the European process design (4). During this period, both European and American precipitation technology remained virtually unchanged.

As has been reported in the literature, increased energy costs, environmental concerns over aluminum smelter operations, new reduction pot designs, the use of stationary calciners, and new pneumatic unloading and conveying equipment now require revising process conditions in the two Bayer processes to make them more similar (2,7,8).

Perhaps all alumina plants will eventually produce strong, coarse, sandy alumina with a high surface area using a process which combines the high yield of the European process with the controlled particle size and moderate calcination conditions of the American process.

Historical Perspective

A brief description of the history of the Bayer process may help to understand the dramatic changes in the process in recent years (3,15).

The Bayer process was originally developed in Europe to process monohydrate ores. These bauxites required stringent digestion conditions with caustic concentrations up to 450 gpl expressed as  $\text{Na}_2\text{CO}_3$  and a temperature of around 170°C with digestion times of two to four hours. After digestion, the red mud was separated from the pregnant liquor, and diluted to about 200 gpl  $\text{Na}_2\text{CO}_3$ . The pregnant liquor was then cooled to about 60°C and stirred in precipitators with previously precipitated alumina trihydrate seed for three to five days. The alumina yield from this process was 60-70 gpl. The main caustic source for this process was caustic soda.

In the late 1880's bauxite was discovered in the United States in both Georgia and Arkansas. This bauxite contained the more easily solubilized trihydrate alumina. When the American Bayer process was started in 1903, soda ash was used as the source of the caustic soda. This limited the caustic concentration to that which gave efficient lime utilization in the causticizing reaction. Because of these two factors, the American digestion conditions were much less rigorous. The caustic concentration was only about 150-170 gpl  $\text{Na}_2\text{CO}_3$  at digestion temperatures around 140°C and holding times of less than one hour. The precipitation conditions were also less rigorous. The caustic concentration in precipitation was 130-140 gpl  $\text{Na}_2\text{CO}_3$  at temperatures of 65-71°C. Alumina

trihydrate seed was added and the mixture stirred for about 45 hours. The American process gave an alumina yield of 40-45 gpl.

Reduction Alumina Specifications

Although it is possible to produce "floury" alumina in either process, Europeans generally produce "floury" alumina and Americans "sandy" alumina.

Table I Comparison of Sandy and Floury Alumina

Type	Angle of Repose°	LOI, %	Surface Area BET, M <sup>2</sup> /gm	-44 Micron %
Sandy	30	1.0	65	5-10
Floury	45	0.5	10 or less	50-60

As can be seen, the physical properties of the two aluminas are considerably different. Environmental pressures to reduce fluoride emissions into the atmosphere and water used for wet scrubbing brought about the development of dry scrubbers using high surface area alumina to absorb the fluorides. This "enriched" alumina was then fed to the reduction cells. The alumina used in the scrubbers had to have a high surface area and strength to withstand the additional handling in these systems. Floury alumina does not meet these new requirements. In addition, the scrubbers also recover additional impurities which are also recycled to the pots. Thus, to maintain previous metal purity, the impurities in the alumina must also be minimized.

These changing alumina specifications resulted in the need for European process plants to convert from floury to sandy alumina. At the same time, the American producers were producing alumina suitable for scrubbing, but were doing it in a process which was not energy efficient. This set the stage for the development of the high yield, sandy alumina process now in practice or development by many alumina manufacturers.

Particle Size Control and Yield

Prior to 1911, when the Bayer patent expired, American producers used CO<sub>2</sub> to precipitate the alumina from solution(3). The use of seed is a simpler process and allows the particle size of the product to be controlled.

Several crystallization mechanisms have been identified as taking place in seeded precipitation (7,9,14). These are:

1. Agglomeration of fine particles
2. Growth on existing particles
3. Nucleation of new particles
4. Attrition and breakage of existing particles

Producing a strong, coarse particle at high yields requires that these mechanisms be balanced by controlling the process conditions and/or the design of the equipment.

The productivity of the liquor in an alumina plant is calculated from the change in alumina concentration (gpl) across precipitation. In process control terms, the yield from the precipitation process can be maximized by increasing holding time, the seed charge, caustic concentration and initial A/C and decreasing the pump-off temperature. These are the conditions of the European process which, unmodified, produces fine alumina. Producing a coarse, strong particle becomes the controlling objective in the development of a high yield, sandy alumina process.

The crystallization mechanisms which increase the coarseness of the particle size distribution of a precipitated product are agglomeration and growth. Uncontrolled nucleation and attrition will produce a finer product. Since all of these mechanisms are taking place at the same time, the chosen process must maximize agglomeration and growth and control nucleation and attrition. Operators of the American process have made coarse alumina by controlling seed charge and precipitation temperature at caustic concentrations of 180-195 gpl Na<sub>2</sub>CO<sub>3</sub>.

The problem becomes one of using American process conditions to produce large particles and European conditions to increase yield. Two approaches to solve this problem have been reported in the literature and patents (7,16,17).

High Yield Coarse Alumina Processes

A search of the patent literature finds six patents or applications which specifically claim the production of coarse, sandy alumina at yields of 60-90 gpl. A seventh patent does not claim high yield but the process could achieve this.

Five patents separate the process into agglomeration and yield steps. These processes use agglomeration conditions to produce large particles and differ only in the configuration in which strengthening, growth and seed balance are achieved.

Two patents claim the production of coarse particles by growth alone and have no separate agglomeration step. These processes use classification techniques to produce a coarse product.

These seven patents are examples of the current published thinking on designing processes to produce coarse strong alumina at high yields. A comparison of the conditions and equipment follows.

Agglomeration

Agglomeration is the quickest way to produce large particles. In this step, small particles collide and are cemented together to produce a larger particle. Particle numbers in the precipitator will dramatically decrease and the particle size distribution of the product will show a coarser grain distribution than the seed in 2-8 hours. Generalized conditions which favor agglomeration regardless of the caustic concentration are low to medium charges of fine seed, high initial A/C, seed surfaces free from sodium oxalate and fill temperatures high enough to prevent uncontrolled nucleation. Laboratory investigations reported by

Tschamper (16) combined these variables to show that the degree of agglomeration is related to the ratio of the supersaturation of the aluminate solution and the surface area of the fine seed provided (9,14).

Large particles which are produced by agglomeration are loosely cemented and not densely packed. Therefore, they can be easily broken mechanically in agitating and pumping systems and by the thermal shock of calcination systems. Because of this, agglomerated particles require further processing to produce a strong product (12).

Agglomeration Conditions

In those patents which use agglomeration to produce large particles, the important process variables are the initial alumina supersaturation, the fill temperature and the seed charge.

The following Table shows the applicable ranges of conditions.

Table II Agglomeration Conditions

	<u>Initial A/C</u>	<u>Temperature °C</u>	<u>Seed Charge</u>
ALCOA Chemie (24)	0.650 - 0.700	65 - 80	15 - 70 gpl
Kaiser (20)	0.575 - 0.700	75 - 85	70 - 140 gpl
Sumitomo (21,22)	0.534 +	65 - 80	30 - 150 gpl
Swiss Aluminium (9)	-	46 - 77	7 - 25 gms Al <sub>2</sub> O <sub>3</sub> * M <sup>2</sup> seed
<u>Range</u>	<u>0.534 - 0.700</u>	<u>46 - 85</u>	<u>15 - 150 gpl</u>

\* Al<sub>2</sub>O<sub>3</sub> Supersaturation (gm/L)/M<sup>2</sup> seed surface

These conditions are applicable for caustic concentrations of 150 - 300 gpl Na<sub>2</sub>CO<sub>3</sub>. This range covers both the American and European process conditions. Thus, the production of large particles by agglomeration is independent of caustic concentration if the fill temperature, seed charge and supersaturation are controlled within a fairly narrow range of conditions.

The holding time required to agglomerate particles is from 2 - 8 hours. Most of the particle size increase takes place in the first six hours (19).

Sumitomo controls their process by the solution A/C rather than holding time and converts from agglomeration to growth conditions when the A/C reaches 0.400 - 0.480.

Growth

Growth is the mechanism by which particles are enlarged by the addition of newly precipitated alumina trihydrate to the original crystal. Conditions which favor growth and strengthening at all caustic concentrations are similar to those which favor agglomeration. That is moderate seed charges, high initial supersaturation and relatively high temperature.

Large particles produced predominantly by growth are dense and five to seven times less friable than those produced by agglomeration (1).

Growth Conditions

Differentiating those conditions which produce growth and which produce high yields is not clearly defined in most of the patents. Kaiser Aluminum claims a three step process in which the second step is the production of strong, cemented, coarse particles by recirculating the coarse friable particles from the agglomeration step for an additional precipitation step at the same liquor and temperature conditions of the agglomeration section.

The remainder of the two step patents either recycle previously processed seed as a second seed charge or use solids retention precipitators to increase the seed charge on line. A comparison of conditions is shown in Table III.

Table III Growth Conditions

	<u>Initial A/C</u>	<u>Temperature °C</u>	<u>Seed Charge gpl</u>
ALCOA Chemie (24)	0.490	70	300 - 900*
Aluminium Pechiney (25)	0.590 - 0.620	50 - 75	700 - 2000
Kaiser Aluminum (20)	0.575 - 0.700	75 - 85	120 - 300
Norsk Hydro (18)	0.600 - 0.650	60 - 75	500 - 600*
Sumitomo (21,22)	0.400 - 0.480	45 - 65	400 - 1500*
Swiss Aluminium (19)	-	40 (Final)	130 - 400

\* solids retention precipitators

As can be seen, a wide range of conditions is specified but generally the temperatures are lower and the seed charge significantly higher than in the agglomeration section.

Nucleation

Nucleation is a special condition characterized by the spontaneous generation of crystals and the consequent rapid increase of sub-sieve particles (9). Controlled nucleation is required to produce the new seed particles necessary to maintain the precipitation reaction. Uncontrolled

nucleation and insufficient agglomeration are the main causes of seed balance problems in the American process. Seed charge and temperature are important variables in controlling both agglomeration and nucleation.

Solid sodium oxalate can also contaminate seed stocks and cause nucleation. Sodium oxalate is a product of the reaction of organic compounds found in bauxite with sodium hydroxide in the Digestion section of the Bayer process. Oxalate as such is not an operating condition but a factor which affects the choice of operating conditions of fill temperature and seed charge. Solid oxalate not only acts as a promoter of nucleation but also co-precipitates with alumina trihydrate to produce a loosely agglomerated particle which does not have the strength of agglomerates formed without oxalate (12). For these reasons, oxalate is removed either by washing seed or by liquor purification techniques. Depending upon the bauxite used, either or both of these operations may be required to implement a high caustic, high yield process.

#### Yield

As stated earlier, high yield is achieved by high caustic concentration, high seed charge, low pump-off temperatures and long holding times. All of the patents reviewed claim yields of 50 - 90 gpl with no more than 10% -44 micron particles in the product.

Most of the patents achieve high yield in their growth section. The Kaiser patent and the ALCOA Chemie application contain a separate yield section (24,19). In the Kaiser patent, the slurry from the agglomeration and the growth sections is classified to produce a coarse underflow and an overflow which contains the fines and most of the liquor. This overflow stream is cooled to 57°C, charged with additional seed and held for 6-24 hours. ALCOA Chemie does not classify but cools their entire slurry stream to 55°C and holds it in solids retention precipitators for 15 hours.

#### Alumina Strength

The advent of stationary calciners and dry scrubbing systems increased the breakdown of alumina particles. The strength of alumina is a major concern of smelter personnel. A.M. Archer has defined strong attrition resistant alumina as one of four alumina quality requirements (2).

The factors which produce strong alumina are not well understood, but they are related to the structure of the alumina particle and the inclusion of sodium oxalate in the alumina crystal (12). We know that alumina trihydrate strength is inversely related to the amount of agglomeration of fine particles achieved in the precipitation cycle. These agglomerated particles can be strengthened in as little as four hours by processing the agglomerates at conditions in which growth is the dominant precipitation mechanism (1). Raahauge has reported studies of the effect of particle structure on breakdown in the calciner and ultimate alumina strength (12). These studies show that crystals produced by growth are less likely to breakdown during calcination but once through the kiln, the alumina is more friable than that produced by agglomeration. These are contradictory results for the process designers wishing to produce strong, sandy alumina at high yields.

Agglomerates are strengthened by filling in the voids in the crystal structure and depositing additional alumina on the surface of the particle. Conditions which produce the strongest particle in the shortest period of time are high supersaturation and moderate seed charge (1). These are the conditions found in the Kaiser Growth section (20).

Particles can also be strengthened by repeated recycling in the process as a second seed charge. Sumitomo claims strengthening by adding 0.05 - 2 gpl of -10 micron particles to their agglomeration step (21). This fills in the voids and strengthens the resultant particle. They also claim strengthening in their solids retention precipitators. These precipitators reportedly allow growth but also abrade the rough edges from the agglomerates. This reduces breakdown in the kiln.

#### Conclusions

1. Changing alumina specifications caused by economic and environmental factors have initiated significant research into the production of sandy alumina under high yield conditions.
2. This research has produced fundamental changes in the way in which we design and operate the precipitation section of the Bayer plant.
3. Two approaches to the production of coarse sandy alumina are reported in the literature. The first uses agglomeration conditions to produce large particles and growth conditions to strengthen particles and increase yield. The second uses growth conditions to produce yield and classification to produce the required particle size.
4. A comparison of the published conditions for agglomeration and growth shows many similarities. Additional work is necessary to define process conditions and the mechanisms which produce strong hydrate and alumina.

#### References

1. J.L. Anjier and D.F.G. Marten, "Particle Strength of Bayer Hydrate", Light Metals, 1982, The Metallurgical Society of AIME, pp. 199-209.
2. A.M. Archer, "Considerations in the Selection of Alumina for Smelter Operation", Journal of Metals, September, 1983, pp. 43-46.
3. C.C. Carr, An American Enterprise, Rinehart and Company, New York, 1952.
4. W.H. Cundiff, "In Aluminum Production the First Stage is Alumina"; "Aluminum, Light Metals King", Industrial and Engineering Chemistry, Volume 47 Nos. 9, 10, September, October, 1955, pp. 1672-1680, pp. 2066-2072.
5. R.C. Fritschy and G.P. Brown, "NABALCO Experiences with the New Alusuisse Process for Producing Sandy Alumina at Gove", Light Metals, 1983, pp. 111-121.
6. L.K. Hudson, "Recent Changes in the Bayer Process", Extractive Metallurgy of Aluminum, Volume 1, Alumina, Proceedings of AIME Symposium, New York, 1962, pp. 59-69.

7. E.A. Kirke, "Recent Trends in Bayer Precipitation Practice", Chemical Engineering in Australia, Volume Che7, No. 1, March, 1982, pp. 35-39.
8. S. Minai, et al, "Sandy Alumina Conversion", Light Metals, 1978, The Metallurgy Society of AIME, pp. 95-110.
9. C. Misra and E.T. White, "Kinetics of Crystallization of Aluminum Trihydroxide from Seeded Caustic Aluminate Solutions", AIME Alumina Symposium, Washington, D.C., 1969.
10. F. Orban, et al, "Advances in Bayer Process Design", Journal of the Geological Society of Jamaica, Proceedings of Bauxite Symposium, No. IV, June 1980.
11. T.G. Pearson, Chemical Background of the Aluminium Industry, Royal Institute of Chemistry, No. 3, Cambridge, 1955.
12. B.E. Raahauge, et al, Energy Saving Production with Gas Suspension Calciner, F.L. Smidth, 1982.
13. C. Sato and A. Furukawa, "Comparative Evaluation of the Economics of Flourey Type and Sandy Type Bayer Alumina", ICSOBA Proceedings, Volume III, October, 1969, pp. 15-24.
14. J. Scott, "Effect of Seed and Temperature on the Particle Size of Bayer Hydrate", Extractive Metallurgy of Aluminum, Volume 1, Alumina, Proceedings of AIME Symposium, New York, 1962, pp. 202-218.
15. R.S. Sherwin, "Extractive Metallurgy of Aluminum", Journal of Metals, Transactions AIME, Volume 188, April, 1950, pp. 661-667.
16. O. Tschamper, "Improvements by the New Alusuisse Process for Producing Coarse Aluminum Hydrate in the Bayer Process", Light Metals, 1981, The Metallurgical Society of AIME, pp. 103-115.
17. K. Yamada and M. Yoshihara, "Crystallization of Aluminum Trihydroxide from Sodium Aluminate Solution", Light Metals, 1978, pp. 19-38.

Patents and Patent Application

18. U.S. Patent 4,049,773, September 20, 1977, G. Mejdell and S. Kjolberg, assigned to Norsk Hydro A.S.
19. U.S. Patent 4,234,559, November 18, 1980, D. Tschamper, assigned to Swiss Aluminium, Ltd.
20. U.S. Patent 4,305,913, December 15, 1981, J.L. Anjier, assigned to Kaiser Aluminum and Chemical Corp.
21. U.S. Patent 4,311,486, January 19, 1982, Yamada, et al, assigned to Sumitomo Aluminium Smelting.
22. U.S. Patent 4,364,919, December 21, 1982, Yamada, et al, assigned to Sumitomo Aluminium Smelting.
23. U.K. Patent Application 2,123,806, July 7, 1983, A.B. Cristol and J. Mordini, assigned to Aluminium Pechiney.
24. Europaische Patentanmeldung 0 102,403, March 14, 1984, A. Tielens, et al, assigned to ALCOA Chemie GmbH.