

IMPROVEMENTS BY THE NEW ALUSUISSE PROCESS
FOR PRODUCING COARSE ALUMINUM HYDRATE IN THE
BAYER PROCESS

Dr. Otto Tschamper
Swiss Aluminium Ltd.
P.O. Box 495
8034 Zürich
Switzerland

The liquor productivity in the American Bayer process with a maximum of about 55 grams Al_2O_3 per litre compares very unfavourably with that obtained in the European process of up to 80 grams Al_2O_3 per litre. By the new Alusuisse process a liquor productivity can be obtained nearing that of the European process, while obtaining a strong aluminum hydroxide of coarse particle size of about 5 % less than $45\mu\text{m}$. The process has been used for the conversion from floury to sandy of the Gove Alumina Plant with a nominal capacity of 1.0 million tons per year. The modified plant has been running since November 1979 at the increased nominal capacity of 1.1 million tons per year producing an aluminum hydrate of about 5 % less than $45\mu\text{m}$.

Introduction

Two processes for the manufacture of aluminium oxide by the Bayer process find large scale application today, namely that usual in European plants (European Bayer Process) and that practised in American plants (American Bayer Process). The product from the European Bayer plants is the fine and highly calcined floury alumina with a low surface area. In the American Bayer plants the coarse and low calcined sandy alumina with a high surface area is produced.

The Alusuisse alumina plant in Gove (Australia) was designed to produce floury alumina. When it became necessary to convert this plant from floury to sandy product, a modified improved decomposition process was developed. This improved process is applicable to both European and American Bayer plants.

Comparison of European Bayer Process Technology
with American Bayer Process Technology

1. European Bayer Process

The process usual in European plants employs a high Na_2O concentration, up to 150 g/l, for the decomposition. So that a good productivity may be obtained at this high liquor concentration, the decomposition is carried out using a sufficiently great amount of seed hydroxide, for example 200 - 250 g $\text{Al}(\text{OH})_3/\text{l}$ (and more) at a sufficiently low enough temperature, for example at 55°C or less. Productivities of up to 80 g of aluminium hydroxide per litre are thereby obtained at residence time of about 50 - 70 hours. However, the precipitated hydroxide in such plant is finer than that produced in American plants. As long as the fine hydroxide from these plants is calcined at high temperature, an oxide with little tendency towards dustiness is obtained. The introduction of the dry scrubbing of waste gases demands an oxide with a BET-surface area between 30 and 60 square metres per gram, which can only be obtained by a weak calcination of the aluminium hydroxide. However, a weak calcination of the fine aluminium hydroxide produced in European plants gives an oxide with a strong tendency to dustiness, which is not readily acceptable to the consumer.

2. American Bayer Process

The process practised in American plants is so designed to produce a coarse hydroxide, which, under the weak calcination usual in these plants, results in an oxide with little tendency to dustiness. In order to manufacture a coarse hydrate, a liquor concentration normally under 110 grams Na₂O caustic per litre is chosen in the American process. The starting temperature is high, for example 70° C, and the amount of seed material low, for example 50 - 120 grams Al(OH)₃ per litre. The residence time is mostly not above 30 hours. If too low a starting temperature for the decomposition is chosen, and the amount of seed hydroxide too high, then a fine product is obtained. The conditions in the American process for the production of the desired coarse product are in opposition to a good liquor productivity. The lower liquor productivity of this process is shown in that at best about 55 grams of aluminium oxide per litre of liquor is produced in opposition to a productivity of up to 80 grams per litre from the European process. Expressed in another way, under the American process, 18 - 20 cubic metres of liquor need to be decomposed to produce a tonne of aluminium oxide, compared to only about 13 cubic metres for the European process.

3. Conclusions

As already referred to above, a coarse aluminium hydroxide, as produced in American plants and not produced in European plants, is required for the production of a weakly calcined aluminium oxide with a BET surface area of 30 to 60 square metres per gram. European plants could very well adopt the American practice, however, the productivity of the European plants would fall about 30 - 40 percent, with a corresponding rise in heat consumption per tonne of aluminium oxide. It is therefore very desirable that the European plants have a process which allows the production of a coarse aluminium hydroxide, without however having to accept a reduction in capacity of the plant with a corresponding increase in the specific heat consumption of the manufactured product.

On the other hand, it is very desirable to lift the productivity of American plants to the level of European plants while maintaining the coarse product quality. Such an improvement in the American plants would mean an increase in capacity, accompanied by a reduction in the specific heat consumption per tonne of manufactured aluminium oxide.

Development of the Improved Precipitation Process

1. Introduction

In principle precipitation of aluminium hydrate out of

seeded supersaturated aluminate liquors, as obtained in the Bayer process, is a combination of agglomeration, crystal growth, nucleation and crystal breakage.

The American process with the aim to produce coarse hydrate makes effective use of the agglomeration and growth mechanism which both are favoured at high initial precipitation temperature and relatively low seed surface per litre of pregnant liquor.

In the European process at relatively low initial precipitation temperature and high seed surface, practically no agglomeration occurs. Precipitation proceeds in this case mainly as growth and as a controlled limited nucleation.

The mechanism of the improved process is a modified combination of American with European Bayer process technology. The first phase of the process, the agglomeration phase of fine seed is similar to the American process practice but with a liquor concentration used in European practice, followed by the second phase, the growth phase which is similar to the European practice and which is initiated by addition of more (coarse) seed and cooling.

2. Agglomeration Phase

We have first investigated the practical limits wherein agglomeration occurs using plant liquors and plant seed hydrate. Many hundreds of laboratory scale tests were conducted, supported by pilot plant scale tests in 200 m³ tanks and plant tests in 3,000 m³ tanks. Caustic concentration, supersaturation, temperature and seed surface were varied. It was found very early in this investigation that under the applied practical limits agglomeration was nearly complete after a residence time of 6 hours and therefore the time was set at 6 hours. The comparison of the various tests was done by calculation of the degree of agglomeration in percent, which we defined as follow:

$$\frac{I - A}{I} \times 100$$

I = Fraction of seed (in percent) less than 45 micrometres in size

A = Fraction of agglomeration product (in percent) less than 45 micrometres in size

To bring the test conditions on a common basis we introduced the quotient

" supersaturation of the liquor to be decomposed in grams Al₂O₃ per litre of the liquor to the surface area of the seed material used in square metres per litre of liquor. "

A plot of the degree of agglomeration versus the quotient supersaturation to seed surface area in $\frac{g/l Al_2O_3}{m^2/l}$ is shown in figure 1. All test results obtained within the temperature range of 66 - 77° C and within the liquor concentration from 70 to 150 grams Na₂O caustic per litre were used in this graph. As can be seen from the graph figure 1, the quotient supersaturation to seed surface area determines the degree of agglomeration in the temperature and concentration range considered. Agglomeration under the high caustic liquor concentration used in the European process was found to be possible.

The investigations in the laboratory and in the plant have shown that the necessary degree of agglomeration may be attained without effort when the amount of fine seed in the first stage of decomposition is so fixed that the relationship of the supersaturation of the aluminate liquor to be decomposed (grams per litre Al₂O₃) to the surface area of this fine seed (square metres per litre) is between 7 and 25 grams per square metre, preferably between 7 and 16 grams per square metre.

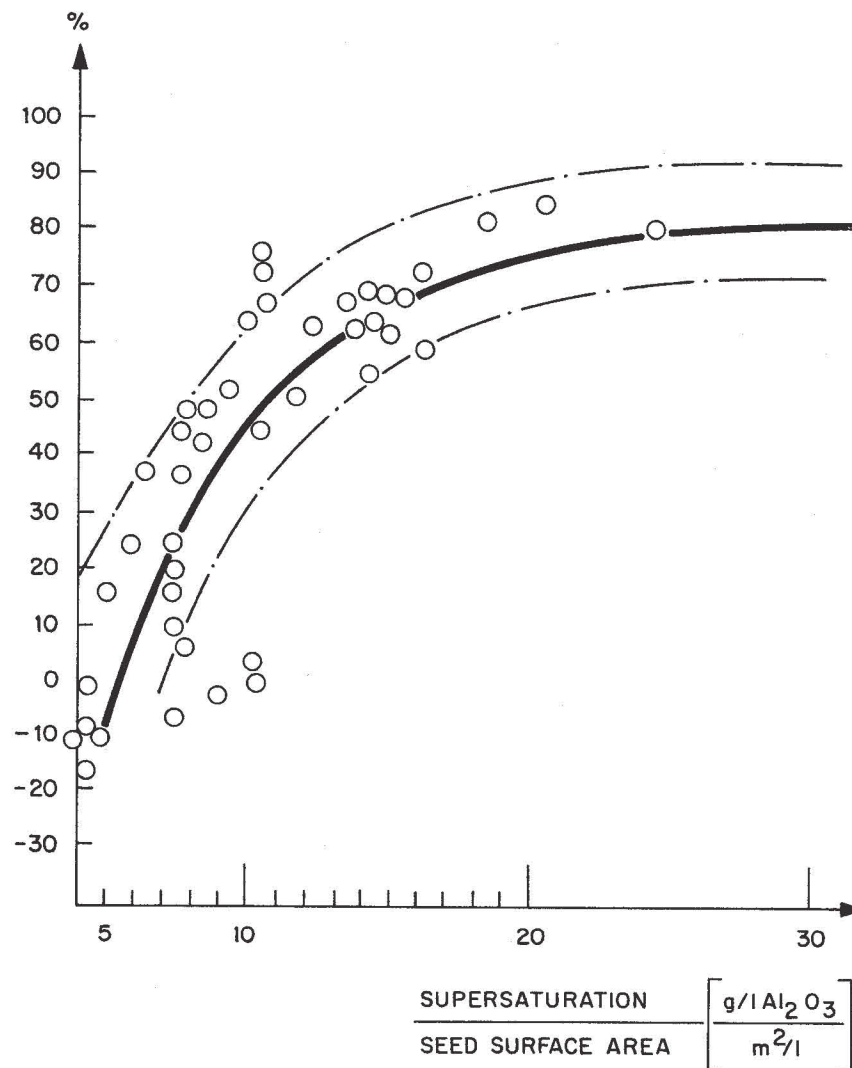
It is advantageous if the duration of the first processing step is chosen to be as short as possible, although long enough so that the necessary coarsening is achieved. This leaves as long as possible a residence time for the second stage of decomposition.

In Figure 2 it is shown, as already mentioned, that after 6 hours of residence time agglomeration is nearly complete. The degree of agglomeration is plotted versus the residence time for a series of agglomeration tests with different seed surface areas, while temperature, aluminate liquor concentration and degree of supersaturation were practically the same. It may be derived from this presentation that after only 2 to 3 hours approximately 50 % of the total degree of agglomeration is attained.

The conclusions drawn from these investigations were that

- good agglomeration can be achieved within the temperature range of about 66 - 77° with caustic liquor concentration used in the European process of up to 150 g Na₂O caustic per litre by selecting the right ratio of supersaturation to seed surface.
- agglomeration within technically feasible conditions, is nearly complete after a residence time of 6 hours.

DEGREE OF AGGLOMERATION



3. Growth Phase

The agglomeration reaction is practically finished after 6 hours under the applied conditions. Then the growth phase begins which has a very low productivity under the agglomeration conditions. We investigated therefore whether the European Bayer conditions could be used for the growth phase without generation of fines by nucleation. We recall the European Bayer process conditions, namely high amount of seed hydroxide up to 400 g per litre and low enough temperature, down to 55° C or less at residence time of 50 - 70 hours.

It has been found that over a very wide range these conditions can be applied without generation of fines. Critical process conditions are too low an amount of seed or excessive cooling in one step.

By using up to 400 g per litre of seed (coarse and fine seed together) in the growth phase 15 - 20° C of cooling is possible in one step without generation of fines. This is applicable with molar ratios or A/C ratios normally obtained in the liquor after 6 hours agglomeration, with pregnant liquors as produced in Bayer plants.

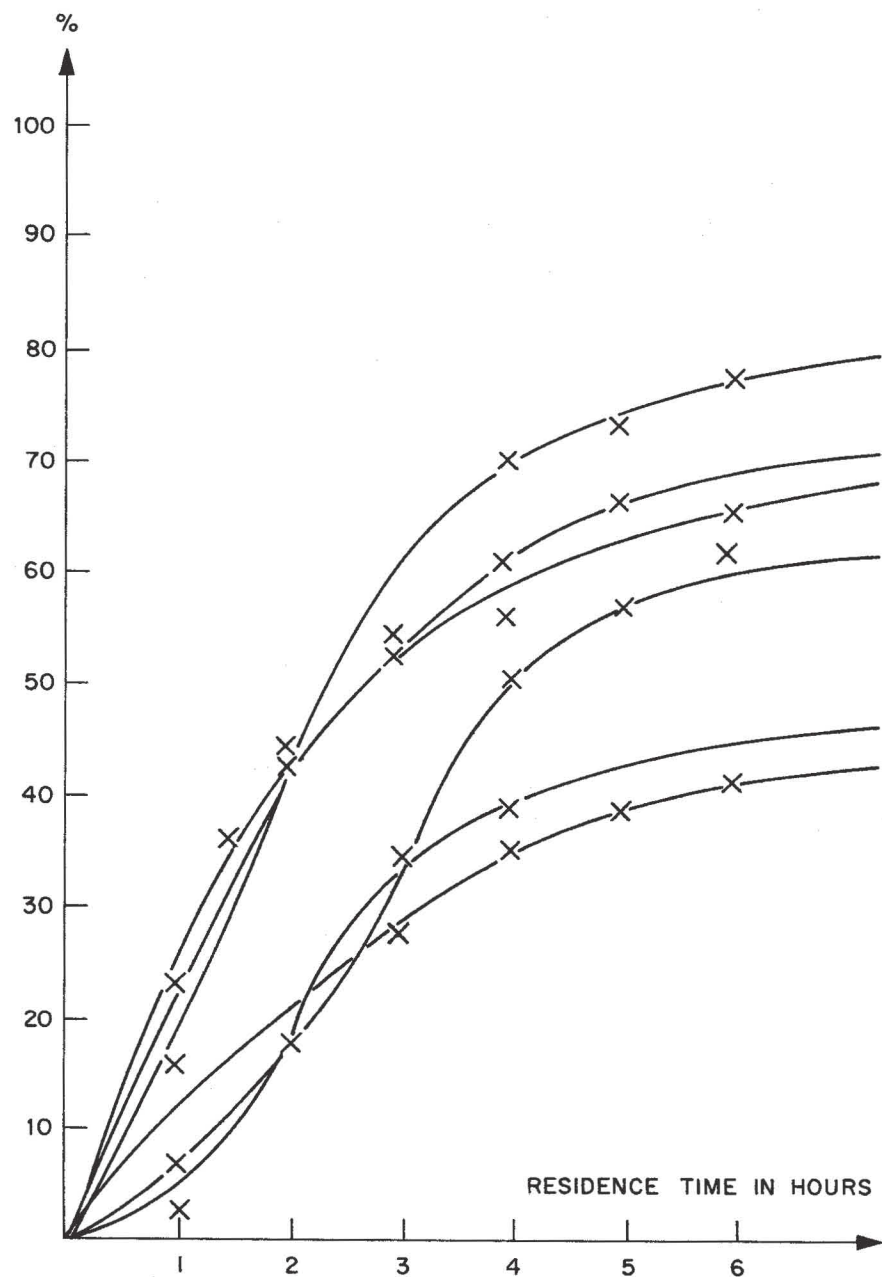
Table 1 gives test conditions for test results as listed in Table 2.

Table 1

Test run	Na ₂ O g/l	Al ₂ O ₃ g/l	Aggl. Temp. ° C	Cooling		Residence time		Supersaturation seed surface area g/l Al ₂ O ₃ m ² /l
				steps	° C	Aggl. hours	growth hours	
1	120.2	142.3	71	2	2x7.5	6	39	12.1
2	124.6	146.4	71	2	2x7.5	6	39	12.1
3	120.3	142.4	71	1	1x15	6	39	12.1
4	111.7	130.5	71	1	1x15	6	39	11.4
5	130.6	163.2	70	3	3x7.5	6	64	7.3
6	136.8	174.5	70	3	3x7.5	6	94	7.7

DEGREE OF AGGLOMERATION

FIG. 2



The test results in Table 2 show the yield and the grain size of the product. Primary seed is the seed used in the agglomeration phase, secondary seed is used in the growth phase.

FIG. 3

Table 2

Test run	FINE PORTION LESS THAN 45 MICROMETERS							
	YIELD	SEED MATERIAL					PRODUCT	
		PRIMARY		SECONDARY			seed plus precipitated material	
	Al ₂ O ₃ g/l	%	Al(OH) ₃ g/l	%	Al(OH) ₃ g/l	Al(OH) ₃ g/l	%	Al(OH) ₃ g/l
1	71.1	60.8	30.4	16.4	25.6	56.0	14.9	46.9
2	72.3	60.8	30.4	24.9	38.8	69.2	20.1	63.6
3	+72.1	+54.2	+27.1	+23.5	+36.7	+63.8	+18.9	+59.8
4	67.8	60.8	30.4	24.9	38.8	69.2	19.5	60.4
5	83.0	38.6	48.2	14.1	14.8	63.0	18.6	66.3
6	91.7	38.3	48.2	14.1	14.8	63.0	16.5	61.0

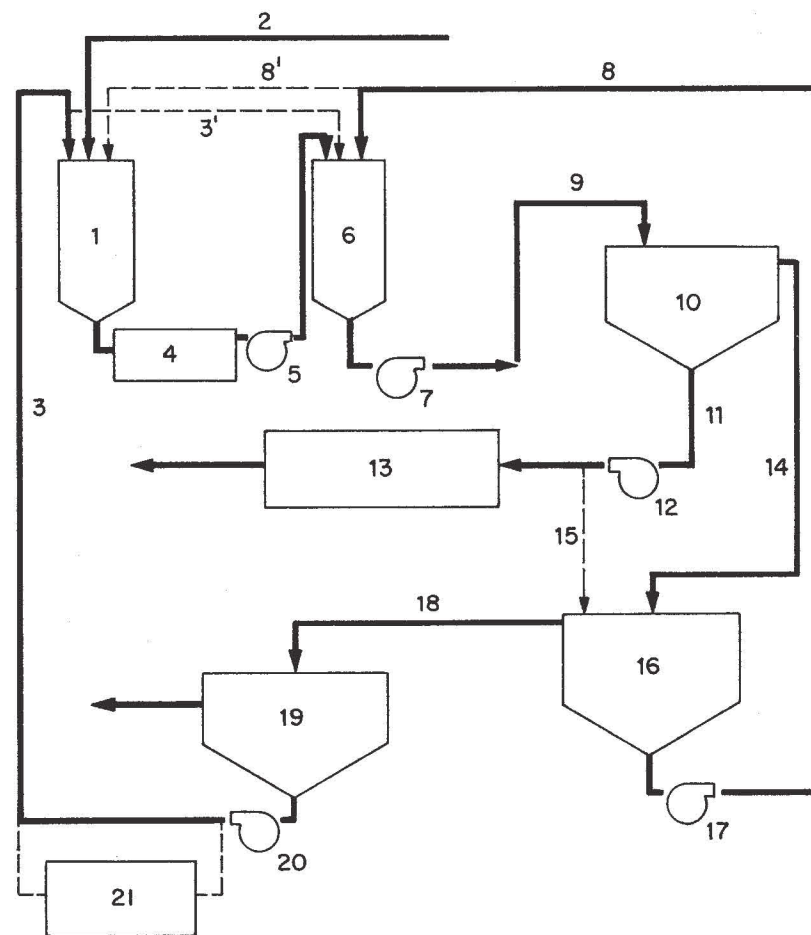
+ FRACTION LESS THAN 40 MICROMETRES

It may be derived from the table that, after return of primary and secondary seed hydroxides of the same amount and similar constitution as used, a product hydroxide with a very low fine portion can be produced, for example 3 to 5 weight percent less than 45 micrometres. The yield (productivity) is the precipitated aluminium hydroxide per litre of pregnant liquor used, expressed as aluminium oxide (Al₂O₃).

Description of the Improved Precipitation Process

As is schematically shown in fig. 3, decomposer tank 1 is supplied by pipeline 2 with sodium aluminate liquor supersaturated with aluminium oxide. Measured amounts of a fine seed suspension are delivered through pipeline 3 into decomposer tank 1. The temperature, amount of seed and the molar ratio are so adjusted to the characteristics of the seed material and the plant conditions that the desired degree of agglomeration of the fine seed material occurs in decomposer tank 1. The equilibrium of the fine seed inventory may be maintained if necessary through the addition of a certain amount of coarse seed through pipeline 8-8'.

This agglomeration proceeds relatively rapidly in a temperature range of 66 to 77 degrees Celsius. It is well advanced after a reaction time of two hours and practically complete after six hours. The suspension can now be cooled by about 15 - 20° C with a



device 4 and then delivered by pump 5 into decomposer tank 6 where the decomposition proceeds to completion. In this decomposer 6 the suspension from decomposer 1 is seeded with sufficient coarse seed material from secondary thickener 16 (up to 400 g per litre), so that the decomposition proceeds anew, with a larger seed surface area and a newly raised supersaturation obtained by cooling. Cooling can also result from contact with the surroundings through the uninsulated walls of the decomposer tank or tanks. If necessary small excess quantities of fine seed material can be added from tertiary thickener 19 through pipeline 3-3'. This second process stage permits the seed hydrate to grow further. Due to the relatively high amount of secondary seed, the secondary nucleation effect is held within bounds. The residence time in the second phase can last from 40 - 80 hours depending on conditions and finishing ratios to be achieved.

The suspension is then pumped by pump 7 through pipeline 9 into primary thickener 10. The thickened underflow consists of product hydroxide which is pumped through pipeline 11 by pump 12 into filtration plant 13. The resulting hydroxide filter cake is sent to calcination (not shown).

The overflow of the primary thickener 10 is sent through pipeline 14 into the secondary thickener 16. The thickened underflow of the secondary thickener 16 consists of coarse seed hydroxide which is pumped by pump 17 through pipeline 8 into decomposer tank 6. The overflow of the secondary thickener is sent through pipeline 18 into the tertiary thickener 19. The thickened underflow of the tertiary thickener 19 contains the fine seed material which is pumped by pump 20 through pipeline 3 into decomposer tank 1, to be agglomerated. The overflow of the tertiary thickener 19 consists of clarified, decomposed aluminate liquor which is directed back for a new digestion operation. Plant 21 permits a washing of fine seed material, if required, in order to reduce the content of organic substances, particularly sodium oxalate.

Pipeline 15 serves for return of production hydrate in the case that an increase in the production hydrate inventory should be shown to be necessary.

Under continuous operations, the process is carried out in more than one decomposer connected in series in the place of one single decomposer 1, and after the cooling device 4, further carried out in more than one decomposer connected in series in the place of one single decomposer 6.

European plants are not normally provided with classification devices for the separation of the product, secondary and tertiary hydroxides.

On the conversion of European plants to the improved process, appropriate classification devices are necessary, which however need not necessarily be gravity classifiers as in the American process, but may be any suitable known classification devices.

American plants are already equipped with the necessary classification devices. Figure 3 features such an arrangement. The conversion of American plants to the improved process consists of the introduction of the agglomeration phase and the second seeding stage as well as a possible increase of the caustic liquor concentration and the introduction of cooling following the agglomeration steps.

The decomposer suspension withdrawn from the last decomposer 6 could possibly exhibit too high a solids content which renders the classification in the primary thickener more difficult or even makes it impossible. By dilution of this suspension, for example with the clear overflow liquor from tertiary thickener 19, the solids content may be adjusted, if necessary.

Application of the Improved Precipitation Process to the Gove Alumina Plant

The Gove alumina plant has been built to operate with the European Bayer process technology with a nominal capacity of 1 million tons per year of flourey alumina. The world-wide introduction of the dry gas scrubbing process made a conversion of the plant to sandy alumina necessary. For this conversion the described improved process has been used.

1. Major new equipment for the process modification
 - a) Installation of a hydrate classification system, yielding product hydrate, coarse and fine seed hydrate.
 - b) Installation of an oxalate removal system for the fine seed hydrate.
 - c) Installation of the new seeding system allowing fine seed seeding in the agglomeration phase and coarse seed seeding in the growth phase
2. Operation results with the modified plant
 - a) Capacity:
The plant has been running since November 1979 with the improved precipitation process. A 10 - 15 % increase in capacity over that with flourey production before has been obtained.
 - b) Quality of coarse hydrate:
The chemical composition of the hydrate was not altered by the modification.
The typical hydrate size distribution which is achieved can be kept in narrow limits:

minus 62/μ	17 - 23 %
minus 44/μ	4 - 7 %
minus 22/μ	< 1 %

c) Typical grain size distribution of calcined alumina:
During calcination in rotary kilns an increase of the minus 45/u fraction by 1 - 1.5 % occurs due to the breakage of the hydrate. This is a low value. It indicates that a strong cemented hydrate particle is produced by this process.

Alumina size distribution:

minus 150/u	100 %
minus 105/u	87 - 94 %
minus 90/u	71 - 86 %
minus 63/u	24 - 29 %
minus 45/u	5 - 8 %