

HYDRATE STRENGTH — AGGLOMERATION, GROWTH AND OXALATE IMPACTS

Thomas D. and Armstrong L.

Research and Development Group, Queensland Alumina Limited (QAL), Gladstone, Australia

Abstract

Hydrate strength is important to final alumina quality for smelters and to resist attrition during Bayer precipitation and calcination. Refiners rely largely on conditions during precipitation to achieve required particle strength. This paper outlines results of laboratory precipitation test work to explore the importance of growth and agglomeration conditions on hydrate particle strength.

The particle bonds formed during agglomeration were found to be quite weak, with attrition testing of the agglomerates producing particles with a similar particle size to the seed material fed to agglomeration.

Particle growth at sufficiently high supersaturation rapidly strengthens these agglomerates, particularly if about 12 μm of particle growth at a supersaturation above about 1.4 (A/A*) can be achieved between the end of agglomeration and product removal.

The presence of solid phase oxalate (SPO) during growth led to significantly more rapid hydrate strengthening. However, generation of fine particles also increases. The supersaturation reduction required to offset this nullifies or perhaps even reverses the strengthening effect.

1. Introduction

Control of hydrate strength in the Bayer process is important for process control and product quality. A recent review (Ilievski and Whittington, 2000) of the available literature summarises investigative work over many years but also highlights the inconsistencies and lack of knowledge in certain areas.

From a review of the literature and discussions with industry precipitation technologists, the following general findings consistently emerged:

- Conflicting opinions exist for the influence of agglomeration conditions on the strength of newly formed agglomerates.
- Newly formed agglomerates (ie without a subsequent growth step) are generally quite weak.
- Growth after agglomeration, particularly at "high" supersaturation, leads to significant strengthening.
- This strengthening can be achieved in a single growth cycle, although further strengthening can still result from additional growth cycles.
- Growth at "low" supersaturation can lead to significant weakening.
- The effect of the presence of solid-phase oxalate (SPO) on particle strength is not well understood.

In consideration of the above points, together with QAL product quality requirement, a laboratory test program was developed to test and quantify the following hypotheses:

- High supersaturation during growth will improve hydrate strength.
- This strengthening needs to be traded off against fines generation due to nucleation at high supersaturation, since increased fines generation leads to both increased classification load and, after agglomeration, an increased number of weak agglomerates that need strengthening.
- The presence of solid-phase sodium oxalate during growth leads to weaker product
- A high agglomeration index leads to high hydrate attrition index
- A broad particle size distribution feeding agglomeration leads to stronger agglomerates
- Differences in agglomerate strength are nullified by subsequent growth.

2. A Note on Hydrate Attrition Index and Product Quality

This study focuses on factors influencing hydrate attrition index. However, the true underlying issue is product quality, and specifically handling and dust generation during transportation and smelting. At this time, laboratory methods for assessing alumina handling and dust generation issues are scant. The Attrition Index (AI) method remains the industry standard, despite recognition that it is not a good predictor of either handling or dustiness issues.

Production of hydrate with low AI does not guarantee low alumina AI after calcination. Nor does production of low AI alumina guarantee good product quality for the smelters. Thus there is a fairly long string to the bow linking the present work to product quality. Nevertheless, production of hydrate with a reasonably low AI may be said to be a prerequisite to good refinery operation. Weak hydrate is likely to lead to breakage somewhere in the process, whether it be during precipitation, or in the pre-calcination stages of the calciner, or even during or after calcination.

Thus while the present work does not address the bigger picture, it at least hopes to provide another small step along the way.

3. Experimental

Two main sets of precipitation tests were carried out. The first examined the effect of growth conditions on strengthening of a "standard" agglomerated seed. The second examined the effect of agglomeration conditions.

The growth tests were carried out as follows:

- Starting liquor with the desired caustic concentration and A/C ratio was prepared. Two A/C ratios (0.600 and 0.500) were selected.
- To the start liquor was added 31 m^2/L of seed charge*, prepared from a single batch of plant agglomeration product. The seed was "spiked" with

* Note that the seed charge area was as measured by Malvern Mastersizer, and equated to about 250 g/L seed charge at 13% $-45\mu\text{m}$. Subsequent seed size analysis by Elzone revealed that the true surface area was about half that estimated by Mastersizer, ie about 15 m^2/L .

washed and/or unwashed tertiary seed to give the desired SPO level.

- The prepared slurries were allowed to precipitate in a standard bottle roller water bath. A programmed temperature profile was used to maintain constant supersaturation ratio, and precipitation was interrupted once the A/C ratio had dropped by 0.100.
- The resultant solids were collected by membrane filtration, then charged at 31 m²/L to a fresh batch of starting liquor and the cycle repeated.
- In all, 5 repeat cycles of growth were carried out for each experiment. In this way, a significant total amount of growth was achieved while maintaining relatively constant supersaturation.

Arguably, this result could have been better achieved by using a constant composition reactor with continuous liquor feed, although this carries with it some additional complications.

The agglomeration tests were carried out by agglomerating fine seed in bottle roller tests under a range of conditions. The resulting agglomerates were tested for strength, then also subjected to a series of standard growth cycles before subsequent testing.

The hydrate solids from all runs were tested for hydrate strength. This was measured in all cases on Forsythe-Hertwig equipment (Forsythe and Hertwig, 1949) modified to a two stage attrition-elutriation apparatus. (Matocha et al, 1987) An amended procedure was developed to use smaller quantities of hydrate or alumina (20g rather than 50g) and to give similar results to the standard method yet at acceptable precision. Attrition Index (AI) was calculated from Mastersizer sizing results. Any mass loss during the attrition test was accounted as <45µm material.

4. Impact of Growth Conditions on Hydrate Strength

The starting seed for these tests was plant agglomeration product. This had a high hydrate attrition index, and tests were carried out to observe its strengthening during growth. The range of experimental conditions covered were:

- (1) Starting A/C (0.500, 0.600)
- (2) Saturation Ratio ($A/A^* = 1.3, 1.4, 1.5, 1.6$)

- (3) Seed oxalate level (0.0, 0.2% as Na₂CO₃ / hydrate)

Each growth cycle represents about 15 cm³ of hydrate precipitated over 15 m² of surface area. Assuming roughly spherical particles and size-independent growth, this is equivalent to about 1 mm of growth, ie 2 microns increase in particle diameter per cycle.

Impact of Supersaturation and Number of Growth Cycles: Hydrate growth was shown to improve the attrition index at all supersaturation levels, as shown in **Figure 1** (which is for growth at high A/C in the absence of solid-phase oxalate). Strengthening is most pronounced on the first growth cycle, but appears to continue for several cycles. The same trend was observed when SPO was present, and also at lower A/C levels. Growth at higher supersaturation consistently showed better strengthening than growth at low supersaturation. This is consistent with the work of Sang (1987).

Impact of A/C and Oxalate: The hydrate strength achieved at the end of the five growth cycles is shown in **Figure 2**.

This figure shows that, in all cases, the hydrate attrition index is lower when solid-phase oxalate was present during growth. The data also indicates that increasing supersaturation during growth leads to a lower attrition index.

For a given supersaturation ratio, the same amount of growth at lower A/C (and temperature) gives stronger hydrate product.

Alternative Expressions for Supersaturation:

Figure 2 showed that precipitation at constant supersaturation ratio does not always lead to the same degree of hydrate strengthening. This suggests perhaps that supersaturation *ratio* is not the best way of expressing supersaturation when considering hydrate strength. Several alternative supersaturation expressions were tested to see if they gave less divergent predictions. These included:

- “Absolute” supersaturation ($A-A^*$)
- “King” supersaturation ($(A-A^*)/(\text{free caustic})$)
- Specific Precipitation Rate
- Soda Incorporation Rate

Of these, only the “absolute” supersaturation appeared to collapse the four curves from **Figure 2** to just 2 curves. This is illustrated in **Figure 3**.

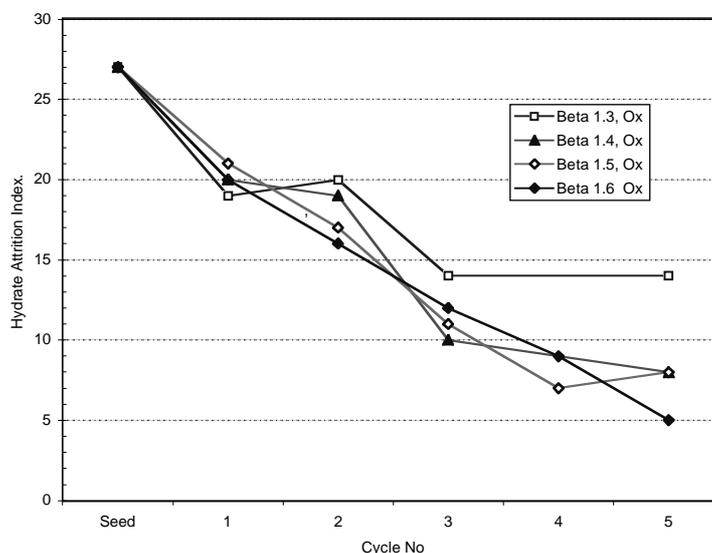


Figure 1 — Hydrate Attrition Index versus Growth Cycles — High A/C with SPO Present

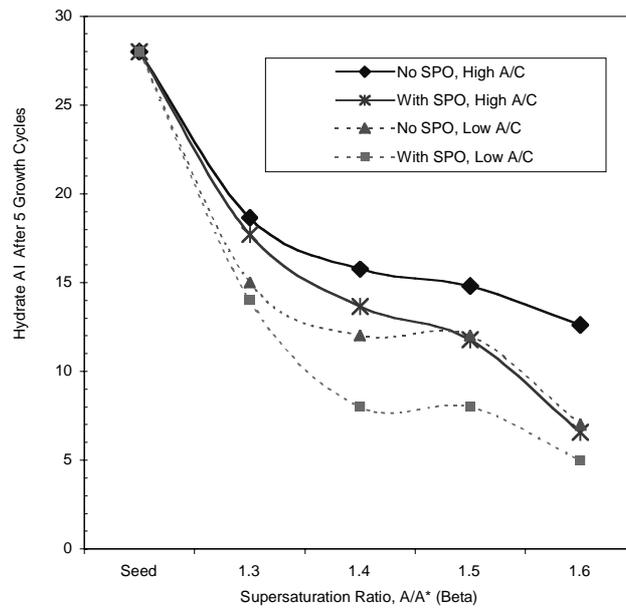


Figure 2 — Attrition Index for Product Hydrates After Five Cycles of Growth

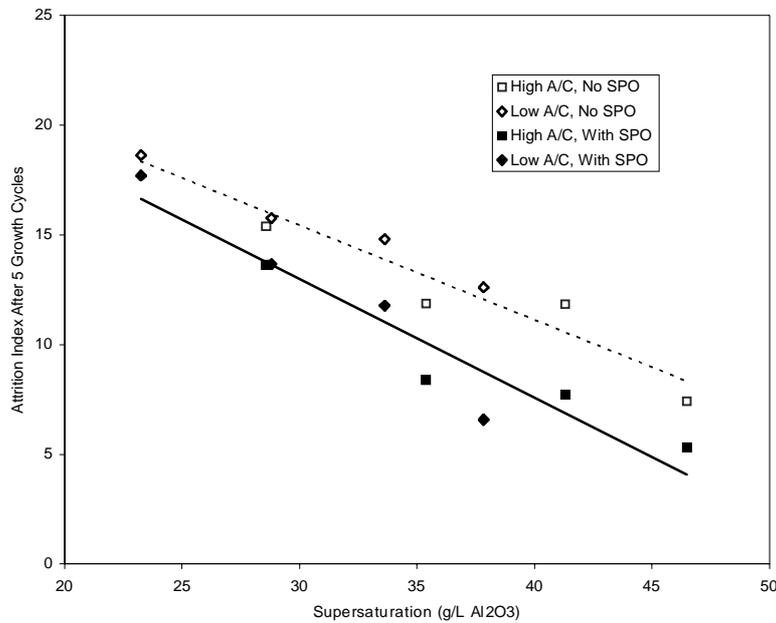


Figure 3 — Attrition Index versus Absolute Supersaturation

Particle Size Interference on Attrition Index: The Attrition Index test attempts to measure intrinsic particle strength. However, the test is significantly affected by particle size distribution (PSD). Large particles (eg +150 μm) can generate high-energy collisions in the apparatus and therefore increase the attrition index. Particles just above the attrition index “cut-off” size (eg 45 to 55 μm) require relatively little attrition in order to report to the sub-45 micron fraction.

The PSD’s varied significantly between the different growth runs. It is possible therefore that the trends seen in **Figure 2** are partly due to PSD effects. To suppress these effects, the attrition index measurements were repeated on a pre-screened 45 to 75 μm size fraction. The results are shown in Table 1. A similar trend is apparent for both the screened and unscreened samples.

Table 1 — AI of hydrate products and their 45–75μm fraction (with SPO, Cycle 5)

A/A*	Whole hydrate product		AI of 45–75μm Fraction	
	%+45μm in	AI	%+45μm in	AI
1.3	85.3	18	92.9	24
1.4	81.1	14	93.2	15
1.5	79.5	12	93.1	14
1.6	72.2	7	92.5	12

5. Impact Growth Conditions on Fines Generation

The favourable impact of supersaturation on strength, seen above, needs to be offset against the impact of supersaturation on nucleation. Higher supersaturation will tend

to increase nucleation rate, which will increase the demands on both classification performance and fines destruction.

A thorough investigation of fines generation is outside the scope of this paper, and only some indicative results are presented.

Typical sizing trends during the five cycles of growth, as measured on the Mastersizer, are shown in **Figure 4**. This particular case was for growth at “low” A/C in the presence of solid-phase oxalate.

There is a clear fining trend as supersaturation increases, particularly for the highest level ($A/A^*=1.6$). All samples fined significantly during the first growth cycle, probably due in part to attrition of the relatively fragile agglomerates. After this, the percentage of $-20\mu\text{m}$ material decreases for all but the highest supersaturation. However, taking into account the hydrate mass increase via yield, the mass of $-20\mu\text{m}$ is actually increasing in all cases.

Similar trends were observed in the other growth runs, although the fines generation rate was significantly lower when solid-phase oxalate was not present. Selected sites on oxalate are known (Reyhani et al, 1999) to promote single gibbsite nuclei or agglomeration of nuclei to finally envelop the whole crystal — under certain conditions the oxalate surface seems even more proficient at secondary nucleation than the gibbsite surface. Gibbsite nuclei on solid phase oxalate have been observed at $<1\mu\text{m}$ size and even at conditions of low oxalate supersaturation.

6. Impact of Solid-Phase Oxalate on Strength

The effect of solid phase oxalate on product strength is not well clarified or understood in the literature (Ilievski and Whittington, 2000). Occluded oxalate is believed to increase alumina attrition and dustiness during calcination and in subsequent handling operations, caused by particle weakening or fracture from thermal breakdown of the sodium oxalate (at 250°C) within the hydrate particle.

The impact of solid-phase oxalate appears to be favourable on final hydrate AI, as was seen in **Figure 3**. These trends are not caused by differences in oxalate occluded within the hydrate particles. Analysis of final hydrate product from pairs of runs at the same supersaturation show no difference in occluded oxalate ($\pm 0.0015\%$) whether solid phase oxalate was originally present or not.

This impact on hydrate AI by solid phase oxalate may seem at first to go against expectations from the literature, but there are two over-riding comments that are worth making:

- the above trend in this work is for hydrate strength, not of alumina
- the increased tendency for fine hydrate generation, when solid-phase oxalate is present, will tend to limit the supersaturation level that can be sustained in an oxalate co-precipitation circuit.

With regard to the second point, the question is whether the same attrition index can be achieved without an increase in fines generation rate. **Figure 5** shows the fines generated in achieving a given attrition index over five cycle. While the data are limited and noisy, it appears that:

- Moderate attrition index (12–18) can be achieved with reasonable little difference in fines generation, regardless of SPO presence.
- Achieving a low attrition index (5–8), when solid-phase oxalate is present, may lead to excessive fines generation relative to an oxalate-free case.

7. Impact of Agglomeration Conditions

Impact of agglomeration conditions on the agglomerate strength is not clearly established in the literature, although several studies have investigated effect of seed charge and sizing and other conditions. (Ilievski & Whittington, 2000). The current work does not set out to develop a definitive understanding, but rather to explore a few aspects of agglomerate strength relevant to QAL in the context of possible process modifications.

Influence of Agglomeration Index on Agglomerate Strength: One common theme in literature and discussions, regarding agglomeration and attrition index, is that high agglomeration index leads to high attrition index (eg Anjier and Marten, 1982). We were interested in exploring the mechanism for this. One possible explanation is that conditions conducive to high agglomeration index lead to weak interparticle (or inter-crystallite) bonds within agglomerates. An alternative explanation is that *all* interparticle bonds formed during agglomeration are weak, and that agglomeration at high agglomeration index simply generates more of them.

These alternatives were explored by conducting three experiments. In the first, fine seed was agglomerated in a single pass under “severe” agglomeration conditions (agglomeration index 65%[§]). In the second, the same seed was subjected to two passes under “moderate”

§ Agglomeration index defined by the industry standard: $(\text{wt}\% -45\mu\text{m in seed} - \text{wt}\% -45\mu\text{m in product}) * 100 / (\text{wt}\% -45\mu\text{m in seed})$

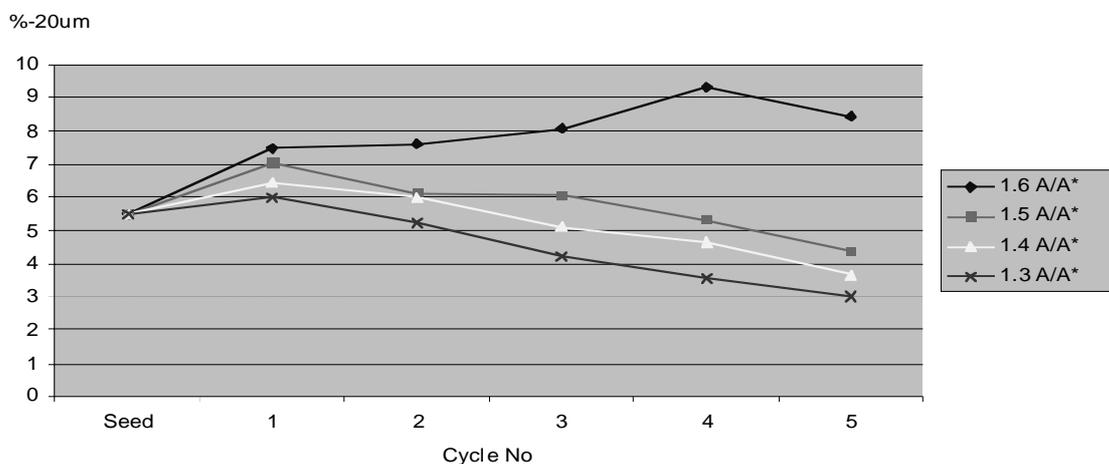


Figure 4 — Trends in %-20um for Growth at Low A/C with SPO Present

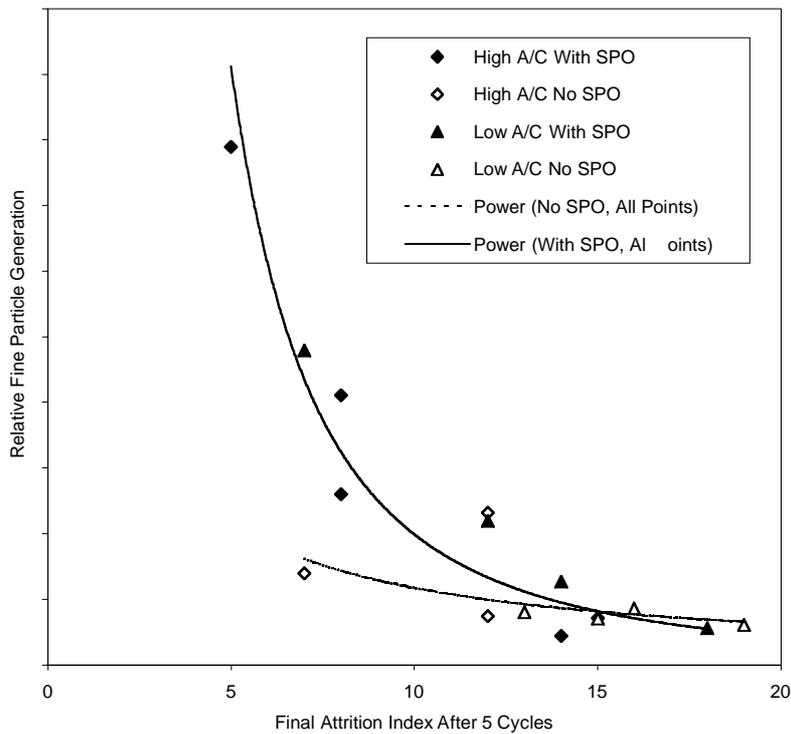


Figure 5 — Fines Generation versus Attrition Index Achieved

agglomeration conditions (agglomeration index 40% per pass, giving an overall agglomeration index of 65%). In the third, the seed was subjected to three passes of agglomeration under “mild” conditions (target agglomeration index 29% per pass, giving overall agglomeration index of 65%). Since all three experiments destroy the same amount of -45µm material by agglomeration, any differences in agglomeration index may be interpreted as being due to the strength of the inter-particle bonds formed. The results are presented in Table 2.

The hydrate attrition index results suggest that “moderate” agglomeration conditions may lead to stronger particle-particle bonds than either “severe” or “mild” conditions (AI of 34 compared to 41 and 38). However, after just one growth cycle at A/A*=1.4, this effect appears to have been totally masked (AI’s of 23, 25 and 25). A very similar effect was seen for growth at higher supersaturation (A/A*=1.5).

Effect of Seed PSD on Agglomerate Strength:

Another theme uncovered in discussions, was that a broad PSD in the seed to agglomeration leads to stronger agglomerates. Testing this hypothesis, without introducing confounding effects from seed strength, product PSD or agglomeration conditions, is difficult.

The test devised used a mixture comprising 70% fine seed and 30% coarse seed. In one test, the fine seed was

agglomerated and then added to the coarse seed. In the other test, the fine seed was added to the coarse seed and then agglomerated. Care was taken to try to produce the same %-45µm in the final product in both cases. The results are presented in Table 3.

The results in Table 3 do not show any significant direct benefit from charging a broader-PSD seed to agglomeration.

Effect of Temperature: A single result suggests agglomeration at higher temperature (85 vs 75°C) tends to produce weaker agglomerates than agglomeration at low temperature (see Table 4)

The “Fragile Agglomerate” Model: In the course of this work, a large number of agglomeration tests were carried out, producing agglomerates with a wide range of attrition indices. It was observed that the particle size distribution after attrition of these agglomerates, was generally quite close to that of the seed fed to agglomeration. This suggests a simple “Fragile Agglomerate” model, whereby the agglomerates are so weak that they disintegrate back to the starting seed size. Mathematically this is equivalent to:

$$AI = 100 * (1 - (Seed_{+45}) / ((Seed_{+45}) + (I_{Agg}) * (Seed_{-45}) / 100)), \text{ where } I_{Agg} \text{ is the Agglomeration Index.}$$

Table 2 — Agglomerate strength from different agglomeration conditions

Run	Number of Agglom. Cycles	Agglom. Conditions	Target Agglom Index per Cycle	Actual Net Agglom Index (Target 65%)	Hydrate Attrition Index of agglomerate	Hydrate Attrition Index after One Growth Cycle	Hydrate Attrition Index after Three Growth Cycles
1	1	Severe	65%	65%	41	23	12
2	2	Moderate	40%	64%	34	25	12
3	3	Mild	29%	53%	38	25	14

Table 3 — Agglomerate strength Seed PSD Effects

Conditions	Product %+45um	Hydrate Attrition Index of agglomerate	Hydrate Attrition Index After One Growth Cycle	Hydrate Attrition Index After Three Growth Cycles
Fine seed agglomerated to coarse seed size, blend with coarse seed	80.3	22	15	13
Fine & coarse seed blend agglomerated to coarse seed size	81.8	23	18	10

Table 4 — Agglomeration Temperature Effect

Agglomeration Temperature	Agglomeration Index	Hydrate Attrition Index of agglomerate	Hydrate Attrition Index After One Growth Cycle	Hydrate Attrition Index After Three Growth Cycles
75°C	65%	41	23	12
85°C	67%	44	27	14

Figure 6 shows that the measured attrition index is generally within 10% of this simple model. Statistically, the model explains 75% of the variance in observed attrition index. The graph includes data using fine seed, coarse seed and blended seeds. The majority of the data points used plant liquor, although one data point (the white diamond) used a synthetic liquor in which sodium chloride replaced the organic soda. All of the seeds were free of solid-phase oxalate. Also included in the graph are some reported data (Anjier and Marten, 1982) in plant liquors. These authors also reported data for agglomeration in synthetic liquor, which showed significantly lower attrition index relative to this model. It is possible that this is related to the low sodium ion content of the synthetic liquor used.

Influence of Agglomerate Strength on Product Hydrate Strength: To what extent does product hydrate strength depend on agglomerate strength, and to what extent on growth strengthening? Agglomerates with a range of attrition indices were strengthened over 3 cycles of growth, at 1.4 and 1.5 supersaturation ratio. On this occasion runs were conducted across a “full row” profile

(0.600 to 0.400 A/C) at constant supersaturation ratio, again achieved by varying temperature and time. Each cycle represents about 4 mm of diameter growth.

Figure 7 shows how the attrition index improved for the eight different starting agglomerates, for growth at $A/A^*=1.4$. After about 12 mm of diameter growth (3 cycles), the trend has flattened out, implying that there is little or no “memory” of the underlying agglomerate strength. After 4 microns of growth (1 cycle), the attrition index is generally half way between the agglomerate strength and the ultimate strength, implying equal contributions from agglomeration and growth. Similar trends were observed for growth at $A/A^*=1.5$.

Thus in a precipitation circuit, growth conditions will be the main factor influencing product hydrate strength, provided that more than about 8µm (preferable 12µm) of diameter growth occurs between agglomerate formation and product removal. Conversely, if less than about 4µm of diameter growth occurs after agglomeration, the strength of the particles formed in agglomeration will be the dominant factor.

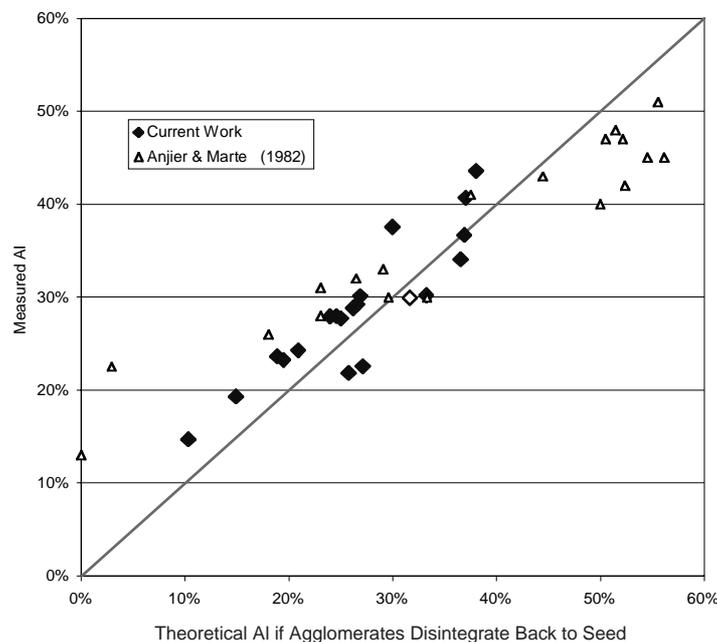


Figure 6 — Attrition Index of Agglomerates Compared to “Fragile Agglomerate” Model

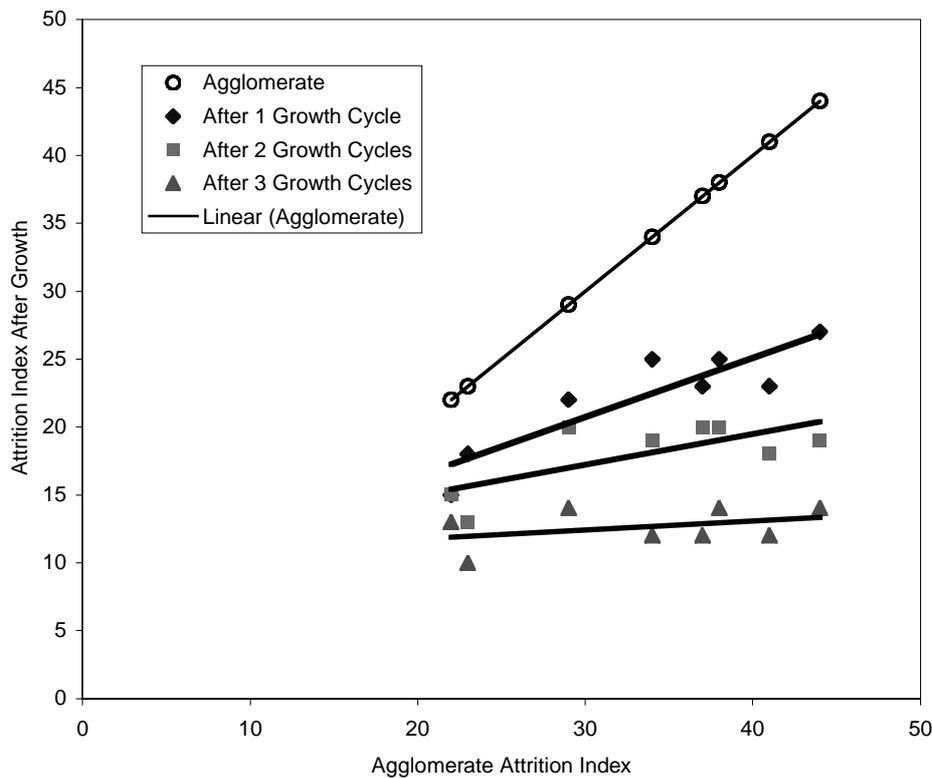


Figure 7 — Hydrate Agglomerate Strengthening During Growth Cycles

8. Plant Hydrate AI — Regression Model

The laboratory tests outlined above were augmented by a survey of hydrate samples from 14 different hydrate samples from 10 different plants. The attrition index of each sample was measured, and stepwise multiple linear regression was used to determine the best fit for AI as a function of process conditions. Terms included in the model were:

- Relative supersaturation ratio ($A/A^* - 1$) in last growth tank (“Last Ssat”)
- Relative supersaturation ratio ($A/A^* - 1$) in first growth tank (“G1 Ssat”)
- Oxalate co-precipitation (assigned 0 for none, 1 for plants with significant oxalate coprecipitation, 0.2 for plants with a “low level” of solid phase oxalate in precipitation)
- Agglomerator $-45\mu\text{m}$ destroyed (tonnes per tonne of production)
- Hydrate $(45-74\mu\text{m}) / (+45\mu\text{m})$ — this relates to the situation where samples with a high percentage of material just above 45 microns are susceptible to high attrition index because relatively little attrition is required for them to report to -45 micron fraction.
- Agglomeration Index (“I_{ag}”)

The best fit for [Hydrate AI] with this data is:

$$[\text{Hydrate AI}] = -3.7 - 4.20 * [\text{G1 Ssat}] + 48.5 * [\text{Hydrate}(45-75)/(+45)] + 12.3 * [\text{Agglom} -45 \text{ destroyed t/t}]$$

This gives a reasonable fit (adjusted $R^2 = 0.93$) across the range of data. The regression results imply that measured hydrate strength can be improved by increasing growth supersaturation, changing PSD to decrease the 45–75 micron fraction, and reducing the mass amount of agglomeration taking place.

9. Conclusions

- Agglomeration in the Bayer process tends to produce weak hydrate agglomerates, regardless of agglomeration conditions.
- These agglomerates, when exposed to the modified Forsythe-Hertwig attrition apparatus, tend to break down to give a particle size distribution close to that of the seed fed to agglomeration — we have termed this the “Fragile Agglomerate Model”.
- Changes in agglomeration conditions (seed size, agglomeration index, temperature) generate only relatively small deviations from this simple “Fragile Agglomerate Model”.
- Therefore, in the absence of any agglomerate strengthening mechanisms, the mass of weak hydrate particles produced in a Bayer plant will be directly proportional to the mass of fine particles “destroyed” by agglomeration.
- Thus the mass of weak hydrate particles produced in a Bayer plant is strongly linked to the rate of fine particle generation (unless there is significant fines destruction by a process other than agglomeration).
- Hydrate agglomerates strengthen rapidly during hydrate growth. After about 12 microns of diameter growth, there is little or no “memory” of the agglomerate strength. Even after just 4 microns of diameter growth, about half of the agglomerate strength impact has been wiped out.
- The relative supersaturation (A/A^*) during growth has a strong impact on hydrate strength in the range A/A^* between 1.3 and 1.6, with higher supersaturation leading to lower attrition index.
- However, because higher supersaturation also leads to increased fine particle generation, this will

- generally tend to lead to an increased rate of weak agglomerate formation (see point (e) above)
- (i) There is therefore an optimum growth supersaturation level for hydrate strength. Below this level, growth produces weak hydrate. Above this level, excessive agglomeration demand will produce a large amount of weak material, which subsequent growth will struggle to offset.
 - (j) The presence of solid-phase oxalate during growth leads to stronger hydrate. However, it also leads to increased generation of fine particles, which will tend to cancel out this effect via point (e) above.
 - (k) Regression analysis of 14 refinery hydrate samples as a function of process conditions, confirms that (a) high supersaturation during growth tends to

reduce hydrate AI, and (b) high destruction rate of fines in agglomeration tends to increase hydrate AI. In addition, a strong effect of particle size distribution was observed, whereby hydrate with a high percentage of 45–75 μ m material reports a high attrition index. This is probably related to breakage function rather than particle strength.

Acknowledgements

The valuable contribution of QAL R&D staff are gratefully acknowledged: Amanda Taylor, Tony Leong, Vicki Mitchell, Rebecca Hilla, as is the assistance of Comalco Research and Technical Services with some of the agglomeration runs.

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