

HYDRATE TOUGHNESS DEVELOPMENT AND APPLICATION: BREAKAGE INDEX

E.A.J.M. Boom^{*}, B Cloutt

South32 Worsley Alumina Pty Ltd, Collie WA

Corresponding author: Eric.Boom@South32.net

ABSTRACT

The minus 20 μ m (superfines) content in alumina feed is an important property for aluminium smelters as high superfines content causes lower energy efficiencies, and health and environmental issues at the smelters. Although superfines are generated in calcination the root cause lies within precipitation. The bridge between precipitation conditions and superfines content in shipped alumina is hydrate toughness. A routine hydrate toughness test method is not available and needs to be developed.

In calcination, cracks at grain boundaries and within primary crystals of product hydrate are formed at 400°C. These cracks, combined with mechanical forces in calciners result in particle breakdown and are impacting the superfines content in smelter grade alumina. During calcination gibbsite dehydrates but the particle shrinkage is slower than the change in solids density inducing tensile stresses and resulting in the formation of cracks and pores. This tensile stress should be simulated in the toughness test method to be developed.

A hydrate toughness test method based on confined compression is being developed. Confined compression simulates the random distribution of tensile forces well, as shown by both the same size profile in particle breakdown and the same morphology of breakdown products after calcination and compression. The confined compression test method can be applied to hydrate powders from all sections of precipitation. The test method encompasses a force of 4500N giving a compression pressure of 13MPa. The particle size distribution before and after breakage is measured. The extent of breakage, or toughness, is expressed as Breakage Index (BI).

The breakage index clearly indicates that agglomeration is the dominant factor in making a tough product hydrate. The trend of breakage index of agglomeration overflow matches very well with the trend, inclusive a 10-day lag, of the superfines content in shipped alumina.

1. INTRODUCTION

Production of aluminium metal involves two completely different processes requiring transport of the aluminium oxide powder (alumina). In handling and transporting the alumina a most important characteristic is the particle size distribution, especially the superfines (-20 μ m) fraction. High superfines content of the alumina is commonly manifested by dust formation, causing health and environmental issues, changes in bulk flow behaviour (segregation, reduced flow rate, Lindsay 2005) and causes reduced conversion efficiencies at the smelter.

The superfines in shipped alumina is mainly generated in calcination, although the root cause of superfine generation is within precipitation. Limited information is available on precipitation factors that affect the generation of superfines in shipped alumina.

Several papers are available on hydrate and alumina strength measured by the attrition index (AI). The work of Anjer and Marten (1982), Stählin et al. (1985) and Wind et al. (2010) highlighted the importance of the product hydrate structure. Sang (1987) and López and Quintero (1991) suggest strong final products are obtained when a high alumina supersaturation is maintained. The particle size distribution of the seed used for agglomeration has no impact on the hydrate strength as shown by Thomas and Armstrong (2002). Addition of calcium carbonate to agglomeration increases the strength of hydrate (Brown, 1990).

This report will give an overview of toughness tests used in various industries and propose the most applicable for hydrate powders.

2. EXPERIMENTAL

Selection of the develop toughness test will be based on:

- how well the test method applies the type of stress that is considered as the main source of particle breakdown in calcination (Werther and Reppenhagen, 2003),
- how well the morphology of the breakdown products of the test method compare to the morphology of calciner discharge

The experimental work includes measuring typical breakdown profiles in the calciners and identifying stresses on the particle from static calcination at various temperatures.

2.1 Breakdown in Calciner

Breakdown of particles in the calciner is studied by comparing particle size distribution (PSD) of calciner feed and discharge. Laser diffraction technique (Coulter LS13 320) giving a particle volume distribution is used for PSD measurement. Morphology of the particles are measured by scanning electron microscope (JEOL JSM 5610LV).

2.2 Static Calcination

The generation of tensile forces during phase transformation from gibbsite to alumina is studied under static conditions. When gibbsite is calcined the solids density at the different phase transformation is increased and as the particle doesn't shrink with the same rate, tensile forces are generated. In a platinum crucible a small quantity of product hydrate is placed in a pre-heated muffle furnace for 10 minutes. The selected temperatures are 400°C (formation of boehmite/chi alumina), 600°C (formation of mainly gamma alumina) and 1000°C (maximum calcination temperature).

The feed and calcined samples are characterised for PSD, morphology, loss on ignition (LOI), specific surface area (SSA) by nitrogen adsorption and toughness using the newly developed breakage method and attrition index determination (AS2879.10-2003).

3. RESULTS AND DISCUSSION

3.1 Fragments formed in Calciners

For the toughness test to be successful, it should simulate the process/transformations that occur during calcination. The first step is to identify the typical fragments that are formed in calcination by comparing the feed and

discharge. Exactly how and where fines are formed in calcination is not known due to a lack of sampling points in the field.

Fines generated during the transformation from gibbsite to alumina in a calciner can be divided into three groups (Figure 1 and 2):

- Breakage of plate type particles perpendicular to the crystallographic c-axis with a size between 30 and 50µm with a thickness of a few microns.
- Large fragments of an agglomerate with a size larger than 50µm. Smaller fragments of single crystals with a size between 5 and 10µm or a section of an agglomerate with a size between 5 and 20µm.
- Dust type material covering the whole particle and randomly distributed. Size is typically less than 1µm.

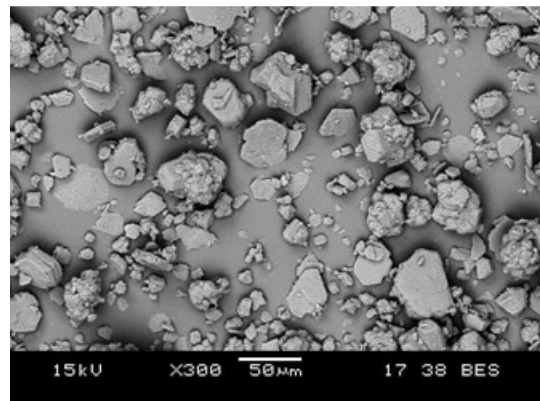


Figure 1. Collected dust showing large plates, fragments of mono crystals and fragments of agglomerates

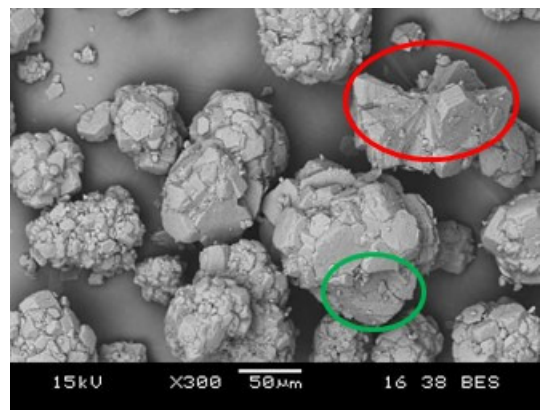


Figure 2. Large fragments of cleavage through the middle of a particle (red circle) and missing part of aggregate (green circle)

A typical difference in PSD of calciner feed minus discharge (Figure 3) shows:

- Particles with a size between 125 and 200 μm are fragmented.
- Large amounts of fragments with a size between 50 and 90 μm .
- Some fragments with a size between 25 and 30 μm .
- No significant amount of 'dust' particles.
- These observations of the particle size distribution are in-line with the observations of the SEM.

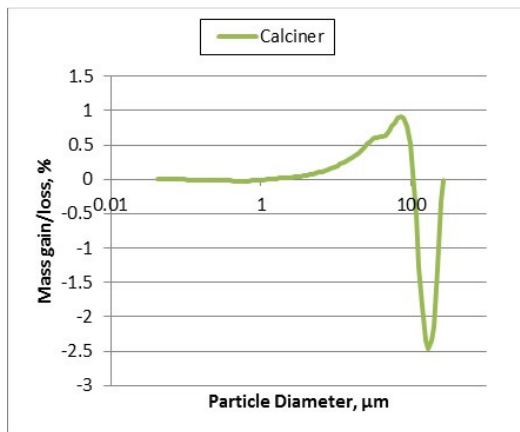


Figure 3. Change in particle size distribution across calcination

For the toughness test to be relevant the different morphologies and similar impact on PSD should appear in the breakage product of the test method.

3.2 Morphology change without mechanical force

Static calcination tests with product hydrate were performed to investigate: 1) the morphology change at the various transformation temperatures to assist in selecting the most appropriate toughness test method, 2) change in PSD without applying mechanical forces to the particles.

The static test for product hydrate in muffle furnace shows:

- Cracks at the grain boundaries of primary crystals appear at 400°C (Figure 4). The number of cracks is increasing with higher calcination temperature and widen significantly at 1000°C. At 1000°C large cracks from top to bottom of the particle are observed (Figure 6a).
- At 1000°C cracks appear within the primary crystals with a size between 30 to 50 μm (Figure 7). The cracks are along the twinning axis (Sweegers,

2001) and randomly distributed over the surface (Figure 6b).

- No pores are observed at 400°C, due to the resolution of the scanning electron microscope. The specific surface area (SSA, Table 3) at 400°C of 268 m^2/g indicates the presence of meso-pores (Wefers and Misra 1987). At 600°C first pores can be observed in large primary crystals (size between 30 and 50 μm , Figure 5b) perpendicular to the c-axis. The SSA at this temperature is dropped to 212 m^2/g . At 1000°C pores in large primary crystal become wider and pores in small primary crystals can be observed (see Figure 7a and 7b). At the same time the specific surface area sharply decreases to 88 m^2/g , indicating that the alumina is sintering
- At 1000°C plate type material perpendicular the c-axis was dislodged from large primary crystals (see Figure 7a).

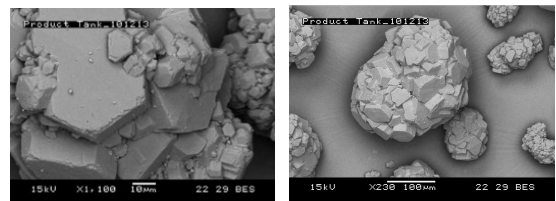


Figure 4a and 4b. Product hydrate showing agglomerates with small and large primary crystals

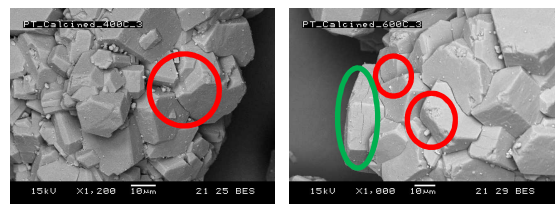


Figure 5a and 5b. Product hydrate statically calcined at 400°C (left) and 600°C (right)

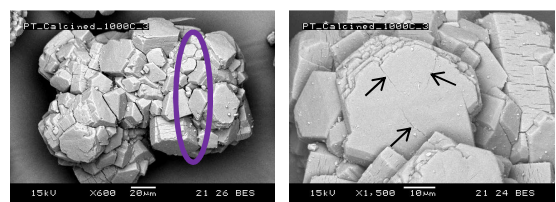


Figure 6a and 6b. Product hydrate statically calcined at 1000°C showing large crack through the particle (left) and cracks within large primary crystals along twinning axis (right)

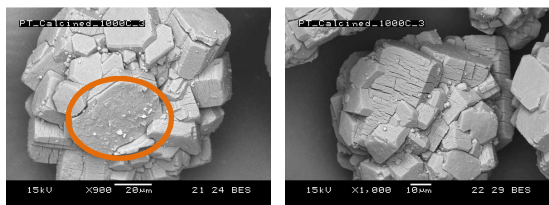


Figure 7a and 7b. Product hydrate statically calcined at 1000°C showing dislodgment of a plate perpendicular to the c-axis (orange circle) and large pores in large primary crystals

During calcination product hydrate (PH) starts to dehydrate above 150°C and forms ultimately alpha alumina at 1000°C. During this transformation the solids density changes significantly and the gibbsite particle shrinks. Whittington et al. (2003) measured the shrinkage along the 'c-axis' of gibbsite is twice the shrinkage along the 'a and b axis'. The maximum average shrinkage, based on density, depends on the calcination temperature and varies between 7 % at 400°C to 15% at 1000°C (see Table 1). The actual shrinkage, based on particle size analysis, is between 7.4% at 400°C and 8.9% at 1000°C. The difference between maximum and actual shrinkage can occur by forming cracks and pores.

Table 1. Specific surface area and shrinkage of product hydrate calcined at 400°, 600° and 1000°C

T, °C	SSA, m ² /g	SD, g/mL	Max shrinkage, %	Act. shrinkage, %	AI, %
PH	0.26	2.42	-	-	11.5
400	265	3.0	7	7.4	5.8
600	212	3.2	9	8.1	6.5
1000	88.1	3.6	15	8.9	6.6
Shipped	80	3.6			6

Cracks within primary crystals are only observed in the large crystals (30 – 50µm) as extreme tensile stress is formed due to shrinkage over a large distance. Randomly distributed cracks are most likely formed along crystal defects and disorder (impurity inclusions or converging crystal faces).

Furthermore, the particle size analysis of the static calcined product hydrate show no fragmentation or formation of small particles (Figure 8). This indicates that mechanical forces are required to cause fragmentation and chipping. In refinery calciners mechanical forces are generated from high velocity impacts.

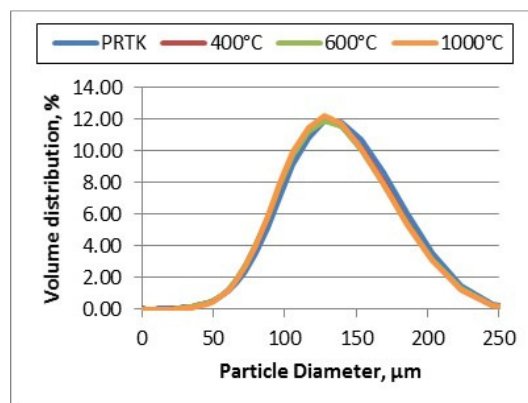


Figure 8. Particle size distribution of static calcined product hydrate

The static calcination test at 400°C shows cracks are formed at the grain boundaries of primary crystals, and SSA shows pores are formed as well. The cracks and pores are most likely formed due to the rapid loss of mass (dehydration) combined with its inability to change the particle size with the same rate (Wefers and Misra, 1987). This inability to change particle size results in a build-up of tensile stress between particles in the aggregate and within the particle. This stress is released at the weakest points, which could be at grain boundaries or at defects within the particle.

Both cracks at the grain boundary as well as pores can impact the toughness of the particles and when exposed to mechanical force cause fragmentation. As crack and pore formation already occurs at 400°C, any alumina toughness test should be independent of the calcination temperature. Frequently, toughness is measured with the alumina industry standard method AS2879.10-2003 - attrition index. The attrition index (AI) is independent of the calcination temperature (Table 1), confirming that cracks at the grain boundary and pores are the major factors impacting the toughness of calcined gibbsite. Furthermore, the attrition index at 400°C is the same as the attrition index of the alumina from the calciners, confirming as well that the weakening of the aggregate starts at 400°C.

The tensile stress that is formed between crystallites in the aggregate and within particles, creates a force that is released by formation of cracks and pores. The strength and direction of the tensile force depends on the internal structure of the product hydrate aggregate and size of the primary crystals. South32 Worsley Alumina (SWAPL) product hydrate is characterised by aggregates consisting of primary crystals with a size between 10 and 50µm, which are randomly

orientated (Figure 9). The new test method for toughness needs to simulate this randomly orientated force.

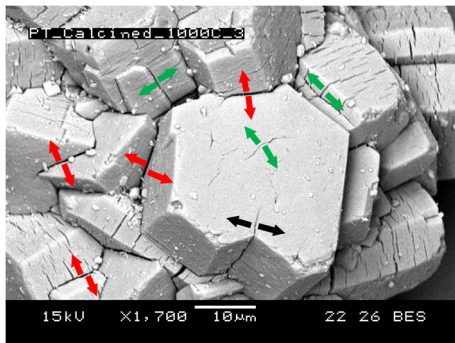


Figure 9. Cracks at the grain boundary, cracks within primary crystal and pores generated by static calcination at 1000°C

3.3 Selection of Toughness Test

The main purpose of measuring toughness is to use the outcome of the measurement to develop a control strategy to improve product quality of calcined alumina. The predictability of the control strategy is increased when the toughness test method simulates the breakage conditions.

Selection criteria for the toughness test method are:

- Nature of breakage. The change in PSD and morphology of a typical calciner discharge shows that fragmentation is the main breakage mechanism.
- The uniform force applied on the particles. The direction of tensile force generated during calcination depends on the hydrate structure and is in case of SWAPL hydrate randomly distributed. Unknown is the strength of the tensile force.
- The analysis time, which includes sample preparation, breakage, analysis and reporting, should be short.
- Applicable to hydrate powder to avoid additional preparation time.
- Applicable to a wide range of low and high toughness hydrate samples.

Potentially applicable toughness tests are;

- a) single particle crushing,
- b) confined compression,
- c) single particle impact,
- d) attrition performance.

Tests of breakage of single particles between two compression surfaces have been used for many years to assess grindability. While testing of single particles mainly leads to breakage and fragmentation due to crack propagation, there is a small contribution from wear or abrasion. By nature this test requires particles of at least a few millimetres in diameter and hence limits the applicability of hydrate powders.

Confined compression test methods can be divided in two types: test methods with high rates and low rates of application of force. In high rate compression tests a fast moving object impacts a bed of particles placed in a cylinder. In the slow rate compression test the sample is placed in a cylinder with a close-fitting piston and force is slowly loaded. Both high and slow rate methods are typically applied to material with a size between 1 and 10 mm. The high rate method is not directly suitable to hydrate powder, however the slow rate can be with modification of die and punch geometry applied to hydrate powder. In the slow rate confined compression test, the force applied by the punch in a powder bed is transmitted at the contact points of the particles resulting in a homogenous force distribution in all directions (Mahmoodi, 2012).

The single particle impact test for fine powders was developed by Boerefijn et al. (2000), which allows study of the effect of impact breakage at controlled force/energy. The sample is fed particle by particle into the air eductor and is accelerated to the required velocity before impact. The sapphire impact plate is perpendicular to the air eductor. The particle impact index is calculated from particle size distribution before and after treatment. Audet and Clegg (2008), developed an impact apparatus similar to Boerefijn for measuring alumina powders. The force that is created during impact will have a contribution along and perpendicular to the grain boundary. The impact force increases with particle velocity and mass.

For the attrition test the sample is placed in a vertical tube and fluidised using a high velocity air jet through a single 400µm orifice. Fluidising hydrate and alumina particles results in fragments as well as dust particles from abrasion. The highest mechanical force is generated when the orifice to particle size is larger than 10 (Boerefijn et al., 2000). In this case the fluidised bed has an air cone accelerating particles to a very high velocity and leading to particle - particle collision. The force dependence on the orifice to particle diameter ratio has the consequence that the

toughness depends on the starting PSD and the force is not constant during the measurement. The analysis time per sample is approximately one hour. The precision of attrition index for alumina samples is 1.2 absolute, which is approximately 10% relative.

The preferred toughness test method is confined compression. This test method meets 3 of the 5 selection criteria: uniform force applied to all particles, short analysis time and applicable to hydrate powder. Breakage nature and applicability to wide range of toughness, are unknown. These criteria will be measured after tailoring confined compression to hydrate powder.

3.4 Confined compression

The toughness can be based on the change in particle size distribution measured by laser diffraction. The required sample size is approximately 1 gram. This defines that the die volume should be to approximately 1 mL (Figure 10). The compression force of 4500N is applied with tensile and compression force testing apparatus (Mecmesin 5-XT), giving a pressure of 13.0MPa. The impact of this confined compression on morphology and particle size distribution is tested with calciner feed (product hydrate).

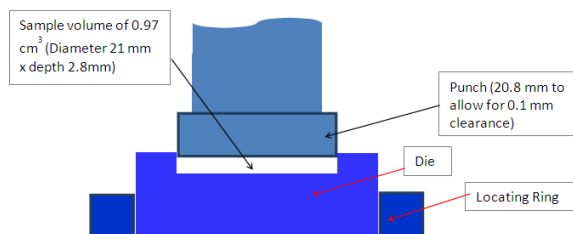


Figure 10. Punch and die made of hardened steel

The confined compression test should simulate the breakage of particles in the calciners. Key indicators are morphology of fragments and the particle size distribution. Figures 11a and 11b show scanning electron microscope images of product hydrate after confined compression at 4500N. The observations are:

- Fragments of primary crystals with a size between 10µm and 30µm and fragments up to 100µm is a result from aggregate cleavage
- Few plates with a size between 10µm and 30µm.
- Small, mostly single crystal particles with a size less than 2µm.

The morphology change due to confined compression is very similar to morphology of calciner discharge.

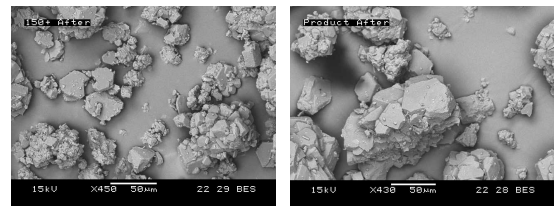


Figure 11a and 11b. Product hydrate after confined compression at 4500N

The profile of the change in particle size distribution after confined compression is the same as the profile for product hydrate after calcination, which indicates that the same type of breakage occurs in calcination and in confined compression (Figure 12).

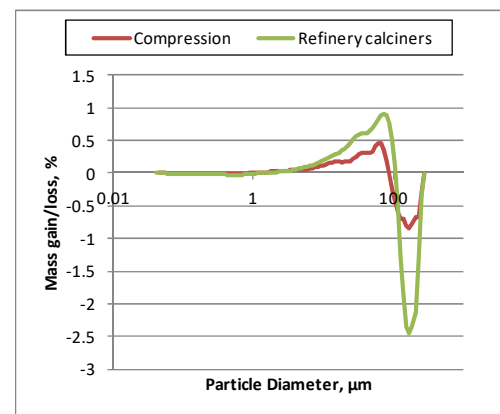


Figure 12. Product hydrate change in particle size distribution after confined compression at 4500N

Based on the morphology and change in particle size distribution it can be concluded that confined compression is a representative simulation of particle breakage in calcination.

3.5 Procedure Confined Compression

Confined compression can be applied to a wide range of hydrate samples from precipitation. Suitable test conditions of confined compression are:

- Punch displacement rate is 20mm/min.
- Compression force is 4500N, giving a pressure of 13.0MPa on the sample in the punch.
- Breakage Index (BI) is based on change in minus 45µm before and after compression divided by the plus 45µm fraction before.

$$BI (\%) = \frac{(\text{minus } 45\mu\text{m}_{\text{after}} - \text{minus } 45\mu\text{m}_{\text{before}})}{\text{plus } 45\mu\text{m}_{\text{before}}}$$

- Particle size distribution is measured with a laser diffraction based instrument.
- Total analysis time for one sample is 15 minutes and for ten samples is 75 minutes.
- Standard deviation at a compression force of 4500N for agglomerate overflow and product hydrate is 0.25% or relative standard deviation is less than 5%.

One of the draw-backs of the attrition index is the dependence of the breakage mechanism on the particle size distribution, which reduces the possibility of comparing samples with a significant different particle size distribution. The dependence on the particle size distribution of the confined compression test is evaluated by removing the minus 45 μ m material before breakage and compare this with the original material. The results are presented in Table 2 and show the breakage index is independent of the minus 45 μ m fraction in the feed.

Table 2. Breakage Index to measure impact of minus 45 μ m fraction of samples as is and minus 45 μ m removed

Sample id.	Before, %	After, %	BI, %
1-as is	12.3	26.4	16.1
1-removed	3.4	18.3	15.4
2-as is	20.4	37.3	21.2
2-removed	5.3	26.5	22.4
3-as is	11.0	26.4	17.3
3-removed	3.5	19.3	16.4
4-as is	6.8	23.5	17.9
4-removed	3.2	19.8	17.1

3.6 Application of Breakage Index

Since 2012 hydrate samples from various points in precipitation were measured bi-weekly. The BI of the various types of samples were trended with the superfines content in smelter grade alumina (SGA). Figure 13 shows how the superfines in SGA with a 10 day time lag correlates with the BI of the agglomeration overflow streams. The good match of the trend suggests the toughness of the hydrate particles formed in agglomeration is a key factor in generating superfine particles in calcination. There are other factors influencing superfines in SGA, such as oxalate and precipitation conditions in intermediates and finals, however, these factors are either minor compared to agglomeration conditions or constant over the evaluated period. The most likely reason for the strong influence of

agglomeration determines the underlying structure of the product hydrate particle. Note, the contribution to the hydrate particle of intermediate and final precipitators is further cementing of the agglomerated particle. Thus, using the BI measurement SWAPL is able to better control the superfines in SGA through improved agglomeration and predict 10 days in advance the superfines content of shipped alumina.

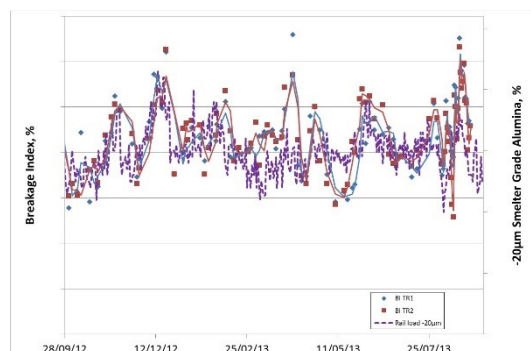


Figure 13. Trend of Breakage Index and superfines content in smelter grade alumina

4. CONCLUSION

A hydrate toughness test method is developed. Confined compression simulates the random distribution of tensile forces well, as shown by both the same profile in particle breakdown and the same morphology of breakdown products after calcination and compression. Confined compression test method can be applied to hydrate powders from all sections of precipitation. The test method encompasses a force of 4500N giving a compression pressure of 13MPa. The particle size distribution before and after breakage is measured and the extent of breakage or toughness is expressed as BI (Breakage Index). The BI is calculated from the change in minus 45 μ m fraction compared to plus 45 μ m fraction before breakage. The analysis time is very short; analysis of 10 samples takes less than 75 minutes and has a high precision; relative standard deviation is less than 10%.

The breakage index clearly indicates that agglomeration is the dominant factor in making a tough alumina. The trend of breakage index of agglomeration overflow matches very well with the trend, inclusive a 10 day lag, of superfines of shipped alumina.

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