NEW TWO-STAGE CALCINATION TECHNOLOGY

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Abstract

Alcoa has been investigating and developing technologies for reducing energy consumption and GHG emissions in alumina refining. This paper reports the development of a novel two-stage calcination technology that has the potential to reduce plant energy consumption by up to ~ 1.1 GJ/t and potentially allows the recovery of an additional 0.4 t of condensate per t of SGA processed.

The two-stage calcination technology is a variation of the pressure calcination technology developed by Alcoa in the 1980s [1] and has a number of significant advantages over its predecessor. The paper discusses the results from pilot test work, flow sheet modelling and preliminary design.

1. Introduction

The Bayer calcination step converts the aluminium trihydroxide crystals from the precipitation building into the smelter grade alumina product (SGA). This dehydroxylation process is energy intensive. In earlier times, the calcination step was performed in rotary kilns, which typically required ~ 4.5 GJ/t to perform the conversion. Modern calcination technology, sometimes called stationary calciners, involves a general counter-current flow of the solid and the gas phases with intimate contacting of the particles and the hot gases, resulting in good heat transfer and heat recovery, typically requiring ~ 3 GJ/t to perform the conversion.

Alcoa's stationary calciners are thermally very efficient and there is limited scope to lower the energy intensity by further improving the heat recovery between the counter-current phases. However, significant heat, ~ 1.3 GJ/t, leaves the calciner through the flue stack in the form of latent heat associated with the water vapour.

In the 1980s, Alcoa patented a novel pressure calcination technology [1, 2] that has the potential to lower the effective energy required for the calcination step to <1.6 GJ/t. It lowers the net calcination energy by recovering some of the water vapour released during the calcination process as medium pressure steam (~8 bar) for use in the plant, i.e. reducing power house steam demand. In effect, it acts as both a calciner and a medium pressure boiler. The MP steam is recovered from the first stage of the calciner, where the hydrate is heated indirectly to a temperature up to 600°C by the hot furnace gases from the second stage of the calcination process that have been boosted by a pre-heater. A number of designs were considered for this first stage unit, called a decomposer. The design piloted was essentially a vertical shell and tube heat exchanger, with the hot gases on the shell-side and the particles flowing down the tube-side. Any free moisture and some of the chemically bound water are driven off as steam at a pressure of ~ 8Mpa. This steam is collected, cleaned and used in the process. One additional benefit is that less energy is required to dehydroxylate gibbsite at higher pressures, reducing the energy requirement further. The partially calcined solids from the 1st stage are then sent to a second stage to complete the conversion to SGA. Another energy efficient feature of the technology is that the second calcination stage can be operated at a lower temperature (~850°C) than conventional modern calciners, typically 950°C to 1100°C. Figure 1 shows a schematic of the pressure calcination process.

This pressure calcination technology was successfully piloted at Alcoa in the 1980's and 1990's, even reporting an increased SGA toughness benefit. However, the development was not taken further and commercialized. Key reasons for this outcome were that at that time it was not thought that there would be a sufficient market for new alumina calciners, the energy costs were relatively low and some engineering and technical risks remained. A subsequent review of the technology identified the following components as being critical to reducing the technical risk, capex and opex.

- The hydrate feed system needed to deliver to the pressurized 1st stage.
- The pressure blow-down system for delivering the partially calcined material from the 1st stage to the 2nd calcination stage.
- The shell-side heat transfer rates through the gas phase are limiting, leading to the requirement for large heat transfer surface areas.
- Shell side fouling management is a key operating consideration.
- Materials of construction for the first stage of the calciner.
- The current decomposer unit design comprises of very long tubes housed in a shell requiring design complications to make allowance for 100mm to 300mm of thermal expansion.

Figure 1. Schematic of the original pressure calcination process.

This, and other reviews, led to the identification of an alternative pressure calcination design involving direct heating by high pressure steam, rather than indirect heating in a decomposer vessel. This novel 2-stage calcination technology, and its development, is described below.

2. The New Two-Stage Calcination Flowsheet

The main difference between the new Two-Stage Calcination flowsheet and the earlier one described above is that the hydrate is directly contacted with high temperature and pressure steam in the first stage, i.e. the decomposer. The partially decomposed material produced in this stage is then also passed to a second stage, operating at atmospheric pressure, to complete the calcination to SGA.

As with the earlier technology, the overall plant energy saving associated with this technology is realised through using the water released during the first calcination stage as plant steam. Cleaned and conditioned steam is returned to the plant's steam reticulation system at ~ 8 bar. A block flow diagram of the process is shown in Figure 2.
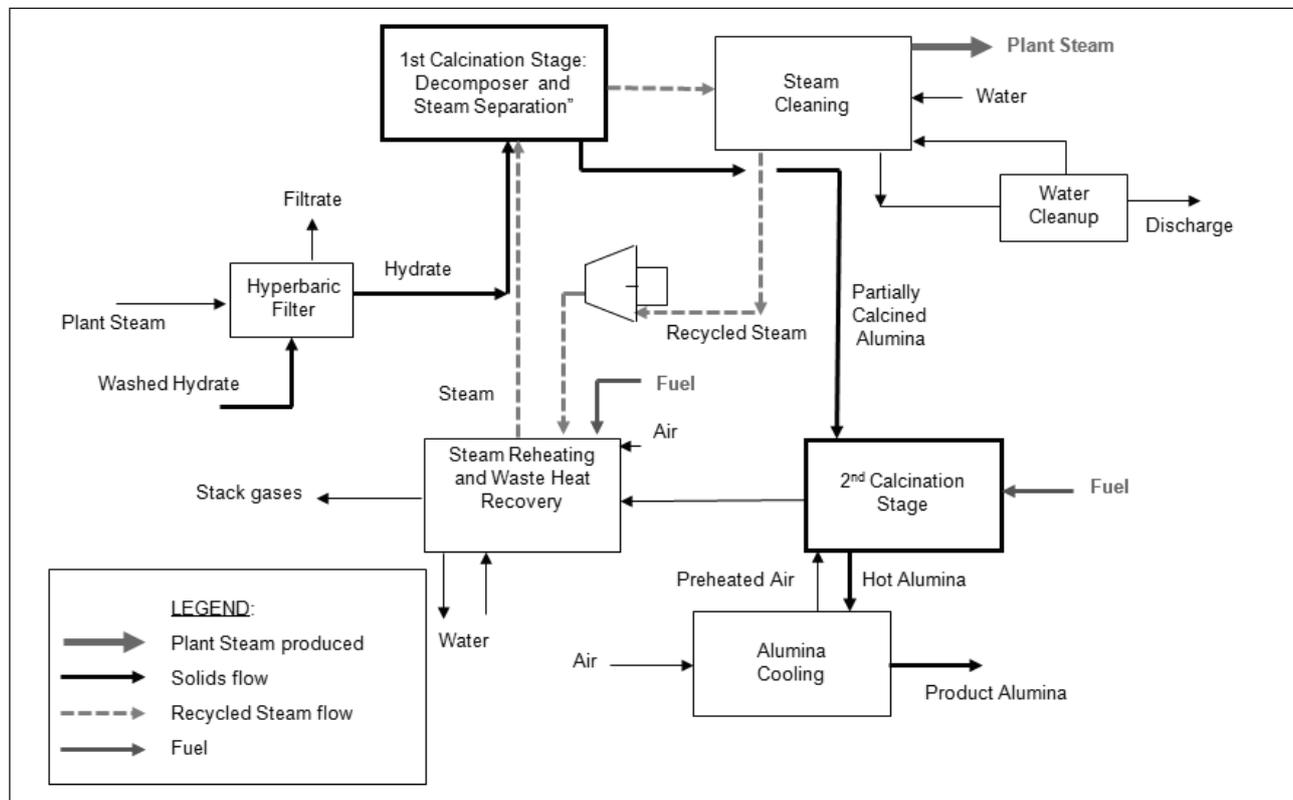
Figure 2. Block flow diagram illustrating the new 2-stage calcination technology.

The hydrate is delivered, under pressure, to the calciner via a screw feeder connected to a hyperbaric steam pressure filter. These filters typically comprise a disk filter within a pressure vessel and are available commercially. A commercial filter manufacturer was commissioned to conduct some hyperbaric filtration tests on Alcoa hydrate (see next section).

The feed hydrate is entrained by the superheated steam, at approx 480oC and > 6 bar, in a riser and transferred to the decomposer unit. The hydrate first dries and then dehydroxylates to produce a partially calcined alumina in the decomposer. The steam flow is increased by the addition of the water released by the partial calcination of the feed, i.e. comprising both moisture entering with the feed hydrate and some of the chemically bound water. Sufficient steam is added so that the target mixture temperature is reached, i.e. up to ~ 350oC.

The steam to the decomposer unit is to be delivered at approximately medium pressure plant steam reticulation pressures, i.e. 6-8 bar. The steam temperature in this unit is restricted to below 480oC to avoid the need for expensive materials of construction; conventional boiler materials can be used. The target solids temperature in the decomposer, i.e. >350oC, is lower than the design temperature for the original indirectly-heated decomposer unit, which was targeting solids temperatures up to 600oC that in turn required gas-side temperature >800oC. However, given that about two-thirds of the hydrate's LOI can be removed at temperatures below 350oC this does not affect the design intent for this unit and significant dehydroxylation of the hydrate occurs.

A number of designs for the decomposer unit have been considered. Direct steam-particle contact means that the decomposer unit can be a fluidized bed or comprised of a combination of pneumatic transfer lines, gas cyclone separators and holding vessels. Compared to the shell and tube heat exchanger design for the original decomposer, these have the advantages of good heat transfer and fewer complications associated with thermal expansion. Two versions are shown in Figure 3.

The simple arrangement shown in Figure 3(a) comprises of a riser duct for mixing the hydrate and the superheated steam followed by a drop out vessel with steam filters to separate and clean the steam. Two risks with this design are the limited particle residence times available at a desired contact temperature and the steam filtration system is expensive and may prove to be difficult to operate optimally. The alternative design with solids and steam flowing counter-current, shown in Figure 3(b), has the benefits of good heat transfer and reaction conversion. Another feature of this design is that relatively low levels of fines are expected to report with the steam, which allows for cost effective and operationally effective technologies to be used for cleaning and conditioning the return steam.
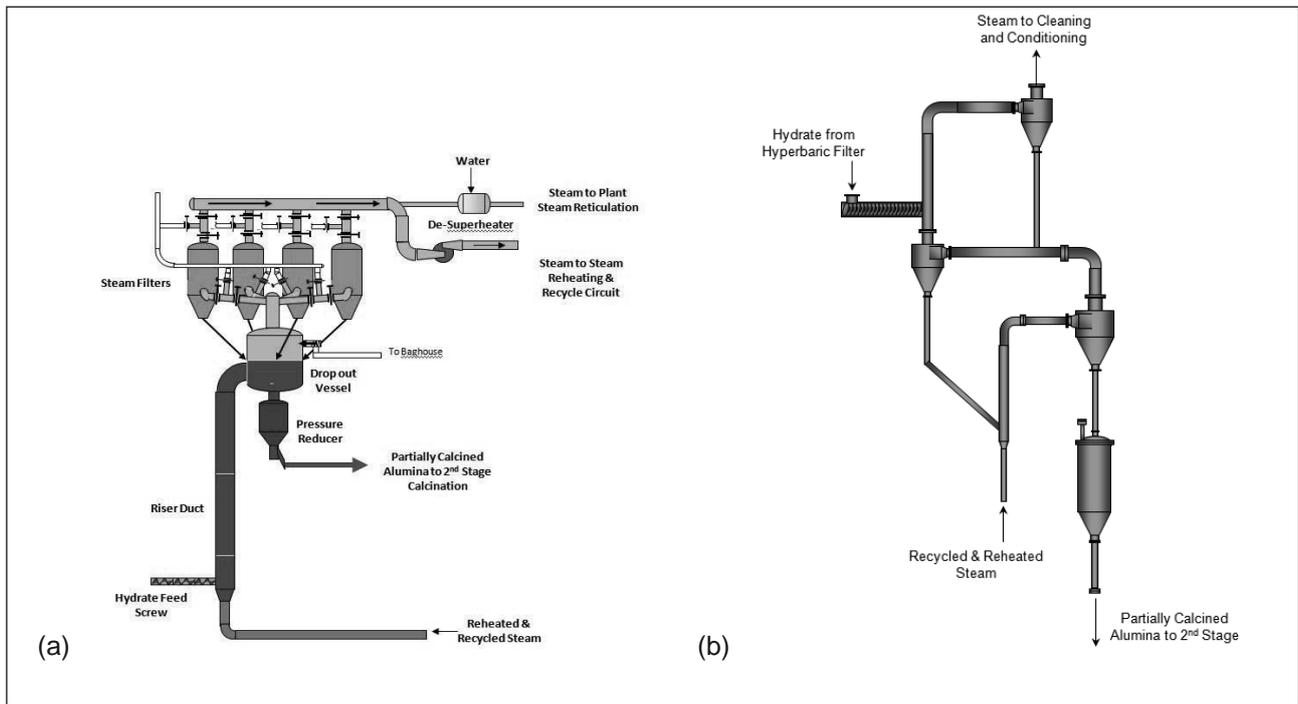
Figure 3. Two designs for the first calcination stage.

The partially calcined alumina is then transferred to the second calcination stage, which is a gas suspension style calciner operating at atmospheric conditions; it comprises of a holding vessel, furnace, pre-heat burner and cooling section. The transfer system required to transport the partially calcined alumina, at ~330°C and ~ 8 bar, to the 2nd calcination stage at near atmospheric pressure is a new technical problem for alumina calcination but a common one in other bulk processing industries. Various technologies for doing this are available and have been investigated, including commercially available dense phase continuous pneumatic conveying technologies, lock hopper arrangements and pressure feeders for solid fuel particles.

Conventional alumina calciners producing commercial smelter grade alumina (SGA) operate at temperatures approaching 900 °C to 1100 °C. Test work has shown that the second calcination stage can be operated at lower temperatures, 750°C - 950°C, and still produce SGA of acceptable quality. The target temperature depends on the performance of the decomposer and the optimization of the energy trade-off between the fuel to the 2nd stage and the energy in the products of combustion (POC) used to help reheat the re-circulating steam.

The steam leaving the first stage needs to be cleaned. The options considered were: dry filtration using sintered stainless steel filters and wet scrubbing. A small pilot-scale trial with the dry filtration option (see next section) was found to be effective but capital intensive, also blockage and scale formation are potential operational risks. Its advantage is the opportunity to deliver cleaned steam at higher temperatures than the wet scrubber system. The current preferred option is wet scrubbing, envisaged as a venturi scrubber followed by a tray column. Wet scrubbing

increases the amount of steam and also desuperheats it. The water containing the collected solids is blown-down and then passed to a settler from where the overflow and the underflow streams can be re-introduced into appropriate parts of the process.

The steam recirculation flow is large, expected to be between 500 and 800 tph depending on the calciner size. The steam reheater required to raise the recycled steam temperature up to 480 °C is also large. Two examples of the steam recycle and reheating circuit configurations that have been considered are: (1) dedicated stand alone fuel fired steam heater and (2) an arrangement where the steam heater is a recuperator integrating the products of combustion from the 2nd calcination stage together with some boosting from a burner system, as shown in Figure 4. A preliminary design and sizing of the steam reheater, prepared by an engineering consultancy, showed that while the unit will be large it is commercially feasible. Various process configurations were evaluated, including arrangements that produced both medium pressure and high pressure steam.

There are further opportunities to reduce overall energy by recovering waste heat from the flue gas and the alumina coolers. Given the low moisture content of the flue gas, a baghouse rather than an ESP is required.
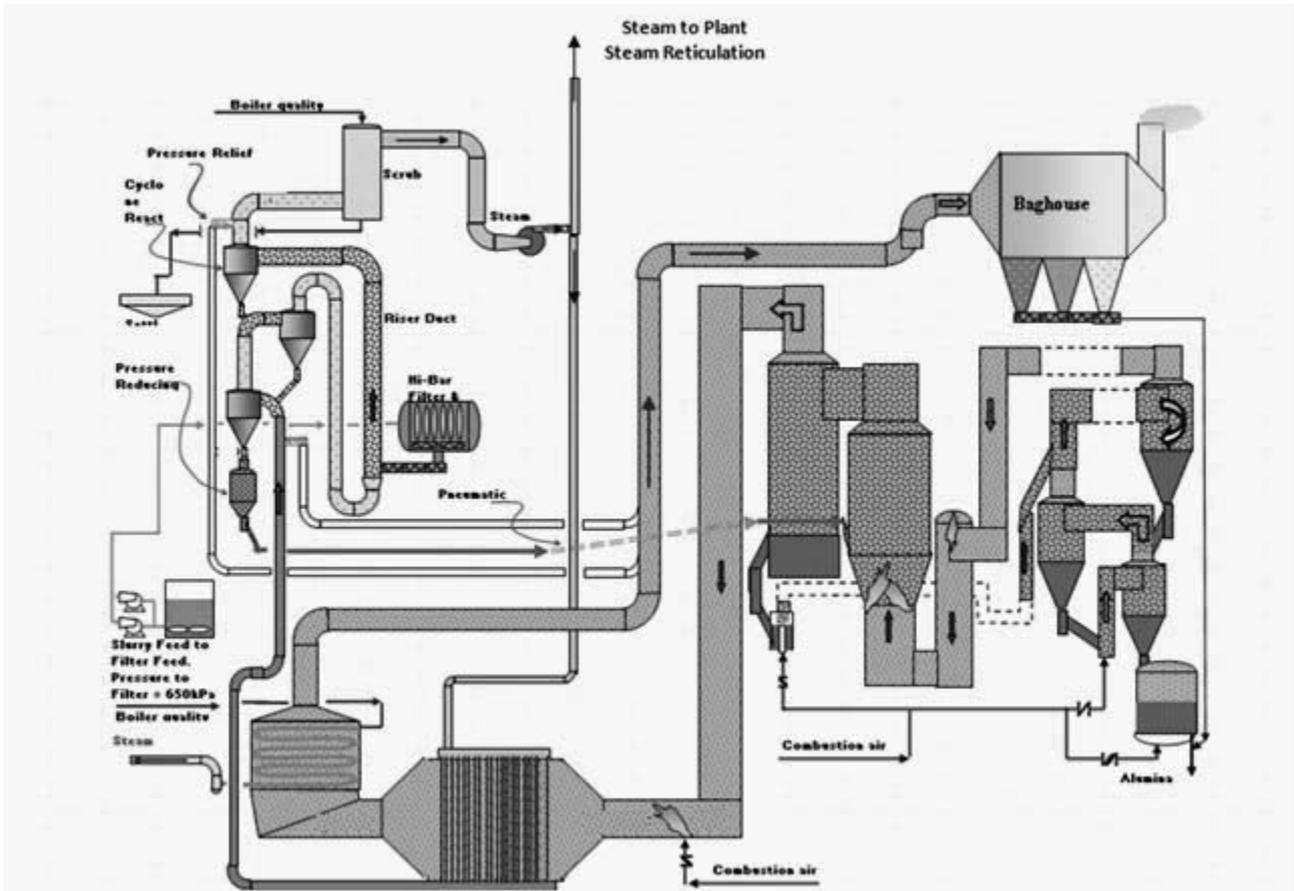
Figure 4. Schematic of one of the preferred versions of the 2-stage calcination process, integration of 2nd stage POC with steam reheating.
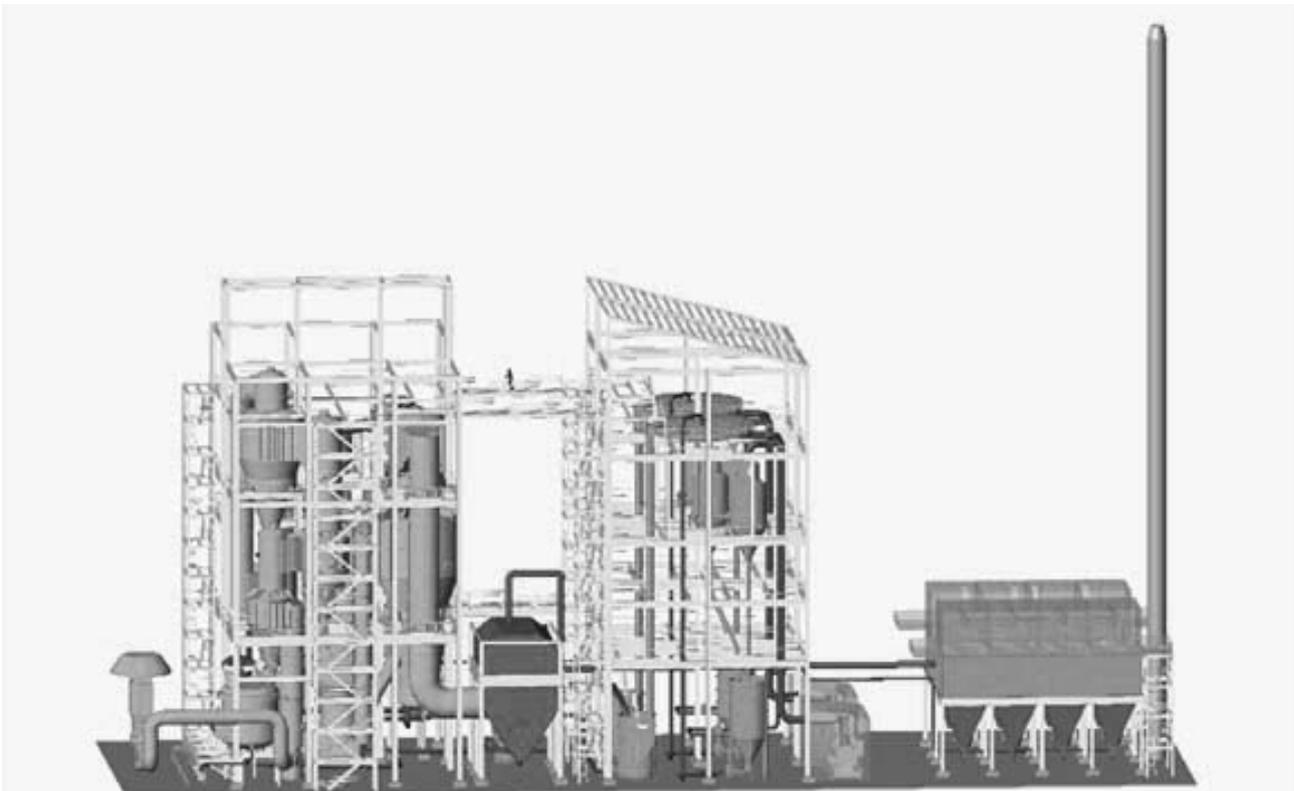

Figure 5. A general arrangement drawing for the full scale 2 stage calciner.

3. Laboratory and Pilot-Scale Testing

The following technical hurdles were identified at the outset of the project:

1. Can SGA of acceptable quality be produced?
2. The direct steam contact decomposer unit is novel; need to identify the design and process conditions to produce commercially sufficient quantities of steam and a partially calcined alumina of the suitable characteristics.
3. Minimize the steam recycle flow.
4. A technically and economically feasible method for cleaning the large steam flow.
5. The condensate condition?
6. Transfer of the partially calcined alumina from the pressurized 1st calcination stage to the atmospheric 2nd calcination stage.
7. Feeding the hydrate from atmospheric conditions to the pressurized 1st calcination stage.
8. Integration with a site's steam-power balance.

The value of the steam produced by the 2-stage calcination technology is strongly impacted by the site's steam-power balance and commercial energy arrangements, and is specific for that site. Discussion of this is beyond the scope of this paper but these considerations were included in the techno-economic analyses on the various case studies investigated.

Bokela Gmbh were commissioned to conduct hyperbaric filtration tests on their bench scale steam pressure filtration unit. Their test results were used to scale-up for a full-scale disk filter hyperbaric filtration system; these showed that <20 m^2 filter area would be required for a 153 tph hydrate throughput. They reported that for throughputs of ~ 5 t m^{-2} h^{-1}, moisture levels between 5% and 10% could easily be achieved; the actual moisture content depends on the steam temperature and the steam consumption rate. To reach a hydrate cake moisture content of ~ 9%, which was deemed the correct level to ensure a reliable cake discharge by steam blow back, >0.036 t steam per t hydrate would be required.

A number of technologies for transferring solids from high pressure to atmospheric pressure were identified. Alcan Alesa Engineering (Birrus International) were commissioned to assess the feasibility of using commercially available dense phase continuous pneumatic conveying for such a duty; it was deemed to be feasible.

Two small-scale pilot plants were commissioned. One was built at CSIRO's Clayton pilot plant facility in Melbourne (see Figure 5a). The focus of the CSIRO trial was to establish if SGA of acceptable quality could be produced in a two stage calcination process with direct steam in the 1st stage. This unit was also used to investigate the transformations occurring during the calcination stages. The second pilot plant was built at Control & Thermal Engineering's pilot plant facility in Perth. It was focussed on the decomposer stage and allowed for a wider set of conditions to be tested.
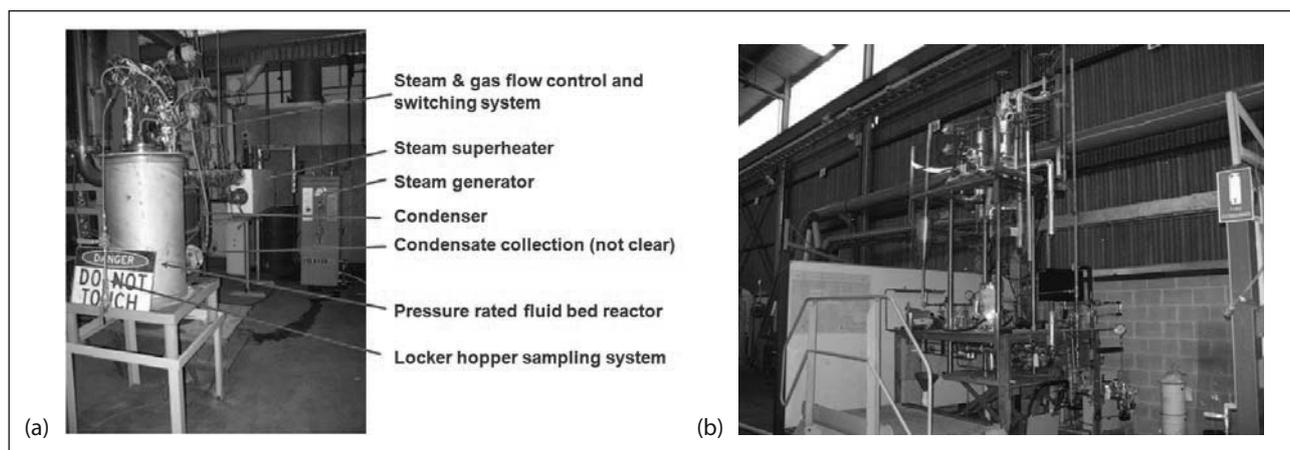

Figure 5. (a) The CSIRO pilot-scale test unit; (b) CTE pilot-scale test unit.

The CSIRO unit comprised of a pressure rated (25 bar) fluid bed (Incoloy 600 & 253MA) fitted to a stainless steel gas filter and with a solids sampling system. The piping to the fluid bed's distributor was configured such that either heated air or superheated steam could be used as the fluidizing medium. The steam was sent to a condenser and collected for analysis. The unit was operated semi-continuously in a manner simulating the two stages of calcination: starting with a 800 g batch of hydrate, there was an initial short period using superheated steam to fluidize the bed under pressure, following by a 2nd heating cycle using furnace heated air to raise the bed up to 950 °C. The steam temperature and pressure was varied to explore the impact of conditions in the decomposer on the product quality. Solid samples were taken at various times, e.g. just after the steam cycle, and analysed for: LOI, specific surface area (SSA), pore size distribution, alumina phase composition, internal structural changes and attrition index.

The test work showed that alumina produced in a two stage calcination, i.e. a steam stage followed by an air heating stage, has indistinguishable properties of alumina (i.e. phase composition, LOI and SSA) to alumina produced in the pilot unit by air heating only. As shown in Figure 6, the SSA, LOI, pore size changes and the extent of calcination relationship appears unchanged by the intermediate steam treatment, i.e. the "air heating only" data points are positioned on the same curve as the steam-air data. Hence, it is expected that SGA of acceptable quality can be produced by 2-stage calcination.
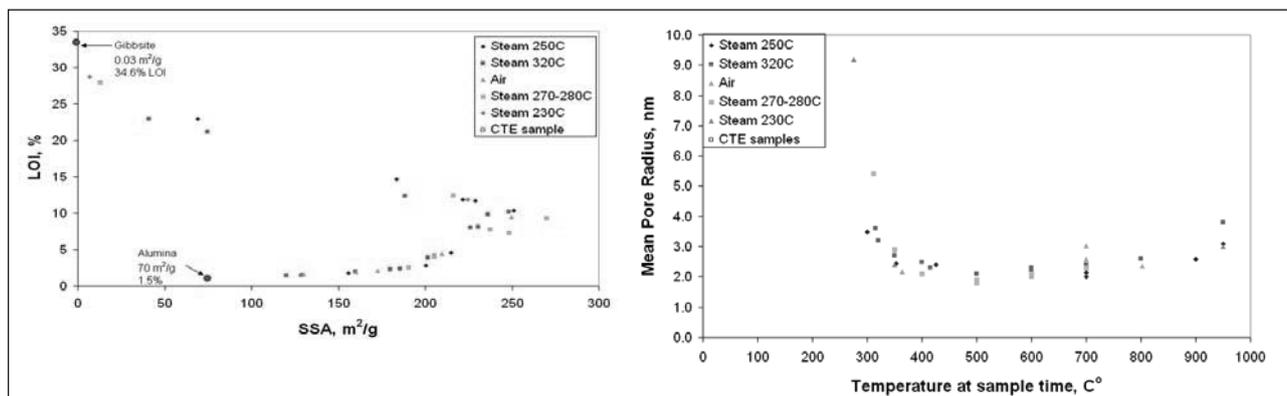
Figure 6. The LOI, SSA and pore size relationships for both 2-stage calcined and "air only" calcined aluminous particles.

SEM images of the 2-stage calcined and the "air only" calcined particles did not show any obvious differences. However, attrition index tests suggest a correlation between the steam stage temperature and the attrition index of the product, see Figure 7. The data suggests that higher temperatures in the decomposer will lead to tougher product SGA. The Alcoa Technical Centre's investigation into the original 2-stage calcination process also reported [1] a tougher product.
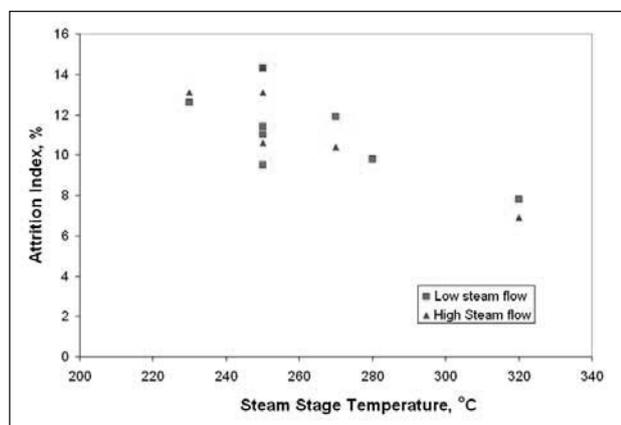
Figure 7. Attrition index measurements on alumina produced in the CSIRO pilot-scale unit after two-stages of calcination (i.e. steam stage followed by heated air stage).

Condensate analyses were not conclusive; the differences in the VOCs measured between the 2-stage calcination tests and the "air only" calcination test were within measurement uncertainty.

The results of the testing program were also used to build a detailed model of the 2-stage calcination process in ASPEN Plus, which was used for techno-economic analyses exploring different scenarios and sensitivity. The key outcomes of the laboratory, small-scale pilot studies and the engineering studies are illustrated in Table 1.

Table 1   Process Risk Assessment.

Risk Item	Impact	Likelihood of Issue	Risk Rating	Mitigation Opportunity Identified	Revised Risk Rating
Alumina Quality	Critical	Very unlikely	Medium	Yes	Very Low & Potential up-side
Large Steam Flow	Moderate	Likely	High	Yes	Low
Steam Purity	Critical	Likely	High	Yes	Low
Hydrate Feed System	Major	Unlikely	Medium	Yes	Very Low
Pressure Blow Down from 1st Stage	Major	Possible	High	Yes	Low
Design of Novel 1st Stage	Major	Unlikely	Medium	Yes	Low
Cleaning Stack Gas with Low Water Content	Moderate	Likely	High	Yes	Zero
Condensate Condition	Major	Likely	High	Yes	Low
Boehmite & Other Scale Buildup	Major	Likely	High	Partial	High

4. Current Status

the project ran from 2006 to 2008; there were a number of internal technical reviews, significant involvement of a number of engineering companies, equipment suppliers and research providers. Two small-scale pilot units were built, a detailed ASPEN plus model was constructed, the design was brought to FEL level 2 completion and the project passed two stage gates. It was concluded that he remaining issues (see Table 1) can only be resolved from trials on an appropriate scale continuously operated unit. The recommendation of the last stage gate meeting was to build a 1 tph pilot plant to resolve the remaining issues and to provide full scale design data; this was endorsed.
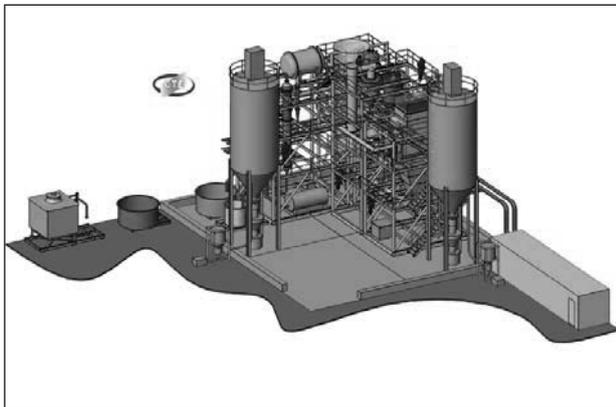
Figure 8. General arrangement drawing for the 2-stage calcination 1 tph pilot plant.

The design for the pilot plant was completed. The design package included:

*   detailed equipment specifications and sizings,
*   complete PFD and P&IDs
*   GA drawings (e.g. Figure 8)
*   cost estimate with ± 30% accuracy

The pilot plant design package was completed in January 2009, however, because of the 2008-2010 Global Financial crisis, the project was stopped and no further work done.

5. Acknowledgements

References

[1] S.W. Sucech and C. Misra, "Alcoa Pressure Calcination process for Alumina", TMS Light metals, 1987, 119-124.

[2] US patent 5141734, "Steam Producing Process", C. Misra and S.W. Sucech, Aug., 1992.