IMPROVING THE BAYER PROCESS BY POWER ULTRASOUND INDUCED CRYSTALLIZATION (SONOCRYSTALLIZATION) OF KEY IMPURITIES

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Abstract

The Bayer process, used worldwide to produce alumina from bauxite, is a precursor to aluminium and many other high value products but productivity can be hampered by dissolved organic impurities in the process liquor. Sonocrystallization technology [utilizing large-scale power ultrasonic devices to aid crystallization] has been shown to have significant beneficial effects on the removal of the key impurity sodium oxalate from the caustic process stream by crystallization. Favourable results have been seen in laboratory experiments, pilot trials carried out over a 6-month period and more recently in full-scale trials. Overall benefits include increased alumina productivity, reduced sodium hydroxide consumption, caustic liquor disposal, operating cost and energy consumption with concomitant reduced environmental burden.

1 Introduction

Sonocrystallization is the application of power ultrasound (20–100 kHz) to promote and control industrial crystallization processes. Whilst the first applications of sonocrystallization date from 1927 (Richards 1927), the past ten years has seen important progress in this area. Indeed, with the emergence of C^3 proprietary large-scale equipment, industrial scale sonocrystallization has become a reality in a variety of chemical processing areas including pharmaceuticals, fine chemicals, minerals, foodstuffs and agrochemicals. More specifically, by using these large-scale devices, sonocrystallization has been shown to have significant beneficial effects on the removal of the key impurity sodium oxalate from the caustic process stream in the Bayer process; the process used worldwide for obtaining smelter and chemical grade alumina from bauxite ore.

2 The Bayer Process and its Inherent Problems

The Bayer process involves treatment of bauxite with hot sodium hydroxide solution at up to 255°C so the alumina dissolves to form sodium aluminate leaving other minerals in the ore in the form of red mud. The saturated sodium aluminate solution is cooled, and seeded with aluminium trihydroxide crystals. The alumina in solution precipitates as the trihydroxide, and can then be calcined at 1050°C to form pure alumina. The remaining solution, which may be referred to as Bayer liquor, can be recycled to treat fresh ore. As the spent caustic liquor is re-circulated, sodium oxalate can build up in the liquor over time leading to (i) reduced precipitation rates (ii) co-precipitation with alumina leading to either re-work or disposal of substandard product (iii) small particle size and possibly brittle particles. Cost effective removal of sodium oxalate, in order to increase productivity of an existing facility, is highly attractive given the growth in demand for alumina related products. Inefficient impurity removal, often linked to the presence of other organic contaminants, limits the concentration of caustic that can be used in the facility. Using a higher caustic concentration is extremely beneficial as it allows more bauxite to be processed per unit volume of caustic liquor re-circulated in the plant, and hence more alumina can be produced from the existing facility.

Whilst it is known that precipitation of sodium oxalate in supersaturated solutions can be triggered by adding recycled seed crystals of the same to act as initiator (Yamada 1975), in practice it is found that the surfaces of the crystals become poisoned by other organic materials present in the liquor, and become inactive as crystal growth initiators. The C^3 sonocrystallization technology works by significantly increasing the frequency of primary nucleation events in the waste liquor stream and by a process that might best be described as 'acoustic washing' of the crystals and so enhancing both secondary nucleation and crystal growth. Importantly, the issue of other organic contaminants inhibiting impurity crystal growth can be reduced significantly.

3 Sonocrystallization

Power ultrasound is proven to have significant effects on crystallization and particle size distribution of organic molecules (McCausland 2002, 2003; Dennehy 2003; Kim 2003) as well having broader application in other areas of chemical and biochemical reactions and processing. The most important effect of ultrasound on crystallization is the induction of nucleation and the principal benefits derive from an ability to manipulate this phenomenon.

Application of ultrasound to a liquid induces the phenomenon of cavitation in the process fluid (Figure 1). This effect creates bubbles during successive cycles of compression and rarefaction to a point of transient bubble collapse, perhaps after only 2 acoustic cycles. In essence the ultrasonic pressure wave finds discontinuities (existing bubbles/surface) in the liquid medium and upon rarefaction, a negative pressure is exerted which results in the formation of a cavity. Upon compression, the bubble collapse produces regions of extreme excitation, temperature and pressure (often in the region of 5000 K and 2000 atm), as well as concomitant release of shockwaves. There are a number of reasons why transient cavitation enhances crystallization: (i) the passage of shockwaves through the super-saturated solution leads to nucleation, (ii) rapid local cooling rates close to the collapsing bubble favours nucleation and growth, (iii) pressure change leads to different crystallization temperature and (iv) overcoming excitation barriers associated with nucleation. The intensity of cavitation depends on factors such as frequency, power, temperature and viscosity.

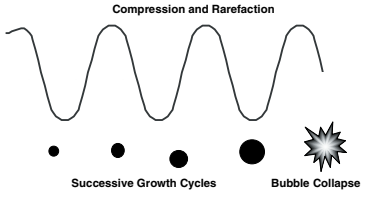

Figure 1: The effects of acoustic cavitation upon a liquid medium

4 C^3 Crystallization technology

Whilst ultrasonic probes are suitable for laboratory scale studies they are very prone to erosion at the probe tip due to cavitational damage over time, which can sometimes lead to loss of acoustic effects (see Figure 3). Key to the Bayer liquor pilot studies was the use of a C^3 patented modular 5 L flow cell (Perkins 2000), (Figure 2) which circumvents these problems. This vessel can be operated in batch

mode or, for larger scale work, in continuous mode whereby a number of units can be combined in a modular fashion for 'scale-out' and increased residence time. The ultrasound is supplied by a multiplicity of transducers attached to the nominal 150 mm diameter stainless steel duct. The ten attached transducers are arranged in a regular array. Each one comprises a 50 W piezoelectric transducer, resonating at 20 kHz, attached to a conically flared aluminium block, which in turn is attached to the wall of the flow-cell. The flared aluminium block has a key role in distributing the acoustic energy over a larger surface area at reduced amplitude. The power intensity is thus around 1.6 W/cm^2, and is such that cavitation does not occur at the surface of the inner wall. In the 5 L flow-cell the power density is of the order of 5–50 W/L and power can be applied continuously or pulsed. Since the electrical to acoustic power conversion is greater than 80%, the actual plant power consumption for the ultrasonic devices will be negligible compared to other plant power usage.

The key attributes are as follows:

- Cylindrical pipe section with no transducers being in contact with process fluid
- Pipe section can be varied in length and diameter
- Can be operated in batch mode or, for larger scale work, in continuous mode
- Multiple units can be combined in a modular fashion for "scale out" and increased residence time
- A plurality of low electrical and acoustic power (~3 Wcm^{-2}) transducers produces 25–150 WL^{-1}, but ideally 40–80 WL^{-1}
- Power can be applied continuously or pulsed

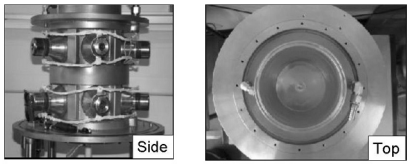

Figure 2: C^3 Proprietary Ultrasonic Flow Cell (Perkins 2000)

5 Sonocrystallization and the Bayer Process

Aughinish Alumina in Ireland currently use a side stream deep evaporation approach where a percentage of the recirculating spent liquor flow is sent through an evaporation train and then a flash cooling train to effectively halve the liquor flow and double the oxalate concentration and supersaturation. The concentrated liquor is then sent for filtration to remove precipitated solids, the filtrate being reintroduced into the recirculating liquor line. As identified in the section above (*The Bayer Process and its Inherent Problems*), there is a significant need to increase the amount of solids (particularly oxalate) crystallized / precipitated at this stage.

In collaboration with C^3 Technology an extensive series of laboratory trials ensued involving both commercially available ultrasonic test probes and a 5 L C^3 flow-cell described above but operated in batch mode. For the probe-based trials a 20 kHz probe, as shown in Figure 3 (left), was immersed in a 1 L jacketed vessel suitably equilibrated with respect to temperature.

Figure 3: Laboratory based ultrasonic equipment
(Left: 20kHz probe, Top right: ultrasonic generator,
Bottom right: the damage to probes following 30h non-continuous ultrasound applied when immersed in water at 20°C)

The initial results showed that ultrasound greatly increased the rate of crystal formation of sodium salts. In all experiments where crystal yield was measured, the application of ultrasound significantly increased the yield of recovered sodium salts, particularly sodium oxalate Increasing the recovery of sodium salts at this stage in the process was key to being able to run a higher concentration of caustic through the plant. This in turn would allow more bauxite to be dissolved at the front end of the process. Those early results indicated that there was potential to significantly increase the plant throughput by introducing sonocrystallization into the current plant arrangement.

6 Pilot studies

An extensive six-month pilot plant trial followed: It was recognised that the plant needed to remain operational at all times with minimisation to both cost and disruption caused by this work. Thus, a C^3 5 L ultrasonic treatment loop was plumbed into a diverted secondary flow-line from the main plant immediately after the last crystallizer (Figures 4, 5). The diverted flow of approximately 3.3% of the main plant flow was treated with ultrasound prior to transfer to a 2 m^3 hold-up tank. The insonation of the supersaturated liquor at this point would stimulate both nucleation and growth of crystalline forms of the identified impurities in the hold up tanks for subsequent removal by the belt filter.

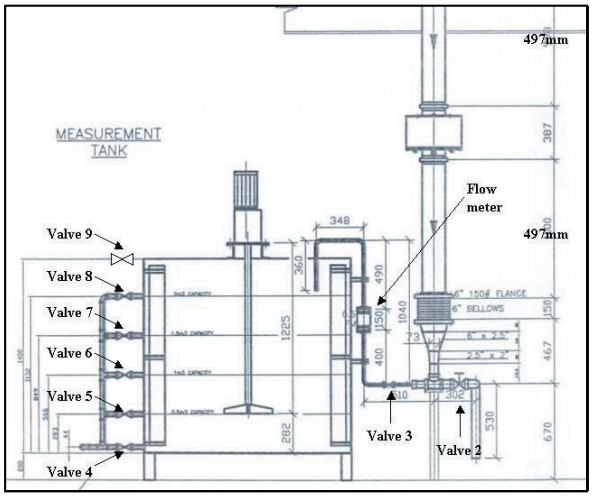

Figure 4: Process drawing for the C^3 Flow-cell linked to the temperature controlled 2m^3 stirred tank

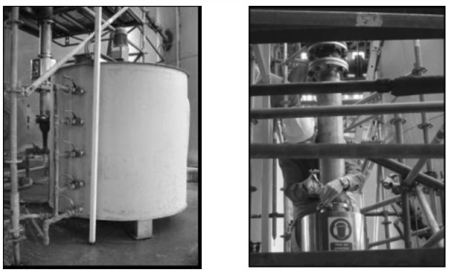

Figure 5: Left: 2m^3 temperature controlled stirred tank;
Right: Installation of the C^3 5L ultrasonic flow-cell

Following concentration of the Bayer liquor, typically the total oxalate solution concentration is around 5.5 g/L. Under normal operating conditions some crystallization does indeed take place in the last crystallizer leading to a solution concentration of around 3.8 g/L upon discharge into hold-up tanks. When non-ultrasound based nucleation and crystallization was carried out using the equipment set-up described above, the solution oxalate concentration was reduced to around 2.5 g/L. This was achieved when the stirred tank was at steady state 55°C (a $\triangle$T of 15°C between input stream and tank). However when the ultrasonic test cell was switched on and operated

constantly, the solution oxalate concentration was reduced to 1.4 g/L at steady state. It was postulated that such a reduction would allow more straightforward recycling of the caustic liquor back into the front end of the process with marked economic benefits. In addition higher concentrations of sodium hydroxide could be tolerated, allowing for a significant front-end input of bauxite.

7 Full-scale design and implementation

Following the success of the pilot trials the design and manufacture of full-scale equipment was initiated: When flow-rates and residence times were considered alongside engineering issues, a 6 m section of insonated pipe with the same cross-sectional diameter of the 5 L flow-cell was deemed suitable for full-scale implementation. The fundamental design of the 5 L flow-cell and supporting patent [Perkins 2000] was crucial in developing more advanced flow-cells. Scaling out the 5 L flow-cell design in one dimension facilitated the design and manufacture of the 1m flow-cell as shown in Figure 6.

The key issues relating to this system are as follows:

- This flow cell is manufactured from 316 stainless steel with a hard chrome internal surface for added corrosion resistance.
- Each flow-cell section houses 40 bonded transducers that can operate at 50 W maximum power.
- The full modular skid mounted unit operates at 14.4k W unit maximum power.
- In normal use each transducer is operating between 10 and 30 W.
- Total electrical power consumption is of the order of 7k W.
- Six of these 1 m cells are joined together in a modular fashion as shown in Figure 7. Figure 7B shows the actual 6 m skid-mounted unit as installed at Aughinish Alumina.

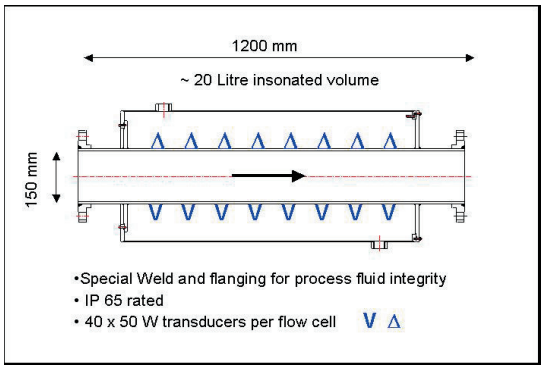

Figure 6: C³ 1 m section shown with bonded transducers

The actual plant equipment, as shown in Figure 7B, became operational in April 2005. Results of the commissioning trials will be reported at a later date.

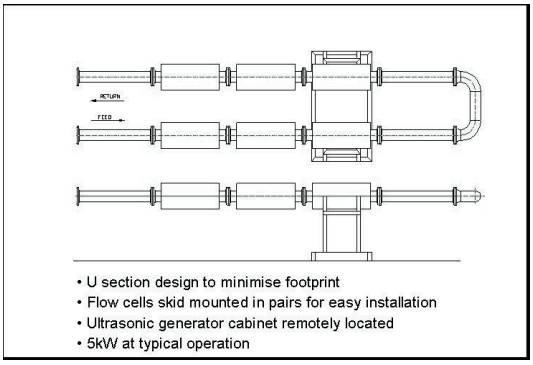

Figure 7 : Left: Schematic of full scale system; Right (7B): Actual plant installed equipment

8 Conclusions

The use of C³ Technology for the removal of impurities in the Bayer liquor has been demonstrated at laboratory, pilot and now full-scale.

This extensive effort carried out over 2.5 years has shown:

- A significant reduction in oxalate concentration, which is the major factor allowing the overall caustic increase of the Bayer liquor
- Enhanced impurity crystal formation and subsequent removal
- Significant reduction in the key issue of other organic contaminants inhibiting impurity crystal growth and formation
- Robustness of C³ Technology in real time plant conditions

Full-scale production benefits are expected to include:

- Increased alumina production capacity
- Increased liquor productivity
- Improvement in crystal morphology
- Reduced raw material wastage
- Reduced energy losses
- Reduced equipment scaling
- Reduced plant running costs

References

Dennehy, RD (2003) 'Particle Engineering Using Power Ultrasound', Proc. 4th Sci. Update Int. Symp.: 'Aspects of Polymorphism and Crystallization – Chemical Development Issues', Chester, UK.

Dennehy, RD (2003) *Org. Pro. Res. Dev.* vol. 7, p. 1002.

Kim, S, Wei, C & Kiang, S (2003) *Org. Pro. Res. Dev.* vol, 7, p. 997.

McCausland, LJ 2002, World patent WO 02/089942; (2003) World patent WO 03/101578.

Perkins, J (2000) World patent WO 00/35579, US patent 5658534.

Richards, WT & Loomis, AI (1927) *J. Am. Chem. Soc.* vol. 49, p. 3086.

Yamada, K, Hashimoto, T & Nakano, K (1975) US patent 3899571.