Testing a new 'STARprobe'

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In addition to the two main tasks an aluminium reduction cell controller has to perform, namely to keep both the dissolved alumina concentration in the bath and the anode cathode distance (ACD) under tight control [1], modern cell controllers are also in charge of keeping the bath ratio (or excess AlF_3) concentration under control.

This task has proven to be quite challenging despite the fact that, at first glance at least, it looks quite straightforward. Fluoride evolves out of the cell in the off-gas; a big fraction of that fluoride is captured by the fresh alumina in the scrubber and returns to the cell as part of the secondary alumina feed to it. The part that does not return to the cell must be compensated by direct AlF_3 feeding in order to maintain a constant bath ratio in the cell. The cell controller performs that task using feedback control algorithms based on regular measurements performed by cell operators.

Recently Alcoa has develop a revolutionary new technology to measure bath ratio in the potroom almost as quickly as you can measure bath temperature [2, 3]. Furthermore, in addition to the excess AlF_3 concentration, the new STARprobe also measure the bath temperature, the dissolved alumina concentration, and the cell superheat. That last information can be used as part of the cell control logic, as previously presented in [4] for example.

GeniSim's Dyna/Marc dynamic aluminium reduction cell simulator has been used to model and evaluate the efficiency of the traditional combined bath sample/XRD analysis and bath temperature measurement bath ratio control logic, and to compare it with a new control algorithm based on STARprobes excess AlF_3 concentration and superheat measurements.

Performing the AlF_3 mass balance

Using a 300 kA cell as an example, the fluoride mass balance can be performed as follows. Fluoride evolved out of the cell at a rate dictated by many factors, like the bath ratio and temperature and the state of the anode cover [5]. In the current example, the fluoride evolution rate is calculated to be 33.6 kg F/t Al with the cell conditions selected, namely 10% excess AlF_3, 970 °C, and a good anode cover. For a 300 kA cell producing 94.7 kg Al/hr, this represents the equivalent of 4.7 kg of AlF_3 that evolves out of the cell and hence must be replaced each hour.

Taking into consideration the neutralisation of some of the fluoride absorbed by the fresh alumina in the scrubber by the sodium already present in it, we can assume that the equivalent of 3.6 kg/hr of AlF_3 is fed back to the cell by the secondary alumina (on average or at the nominal 100% alumina feeding rate). This leaves 1.1 kg/hr of AlF_3 that must be directly fed using a point breaker feeder (PBF) under the supervision of the cell controller.

However, this hourly dose is only about 0.14% of the excess AlF_3 in the bath, since the cell contains close to eight tonnes of bath and hence about 800 kg of excess AlF_3. This means that if the direct AlF_3 feed were to be completely stopped for some reason, it would take about 72 hours for the excess AlF_3 concentration to drop by 1 to 9%. In view of this relatively slow response time of the cell, it should be quite easy to keep the excess AlF_3 concentration under tight control. But such control is clearly lacking in the great majority of smelters, so some other factors must be complicating things.

How daily operations influence the bath ratio: In the above mass balance calculation, about 75% of the AlF_3 is fed back to the cell as part of the alumina feeding. However, in

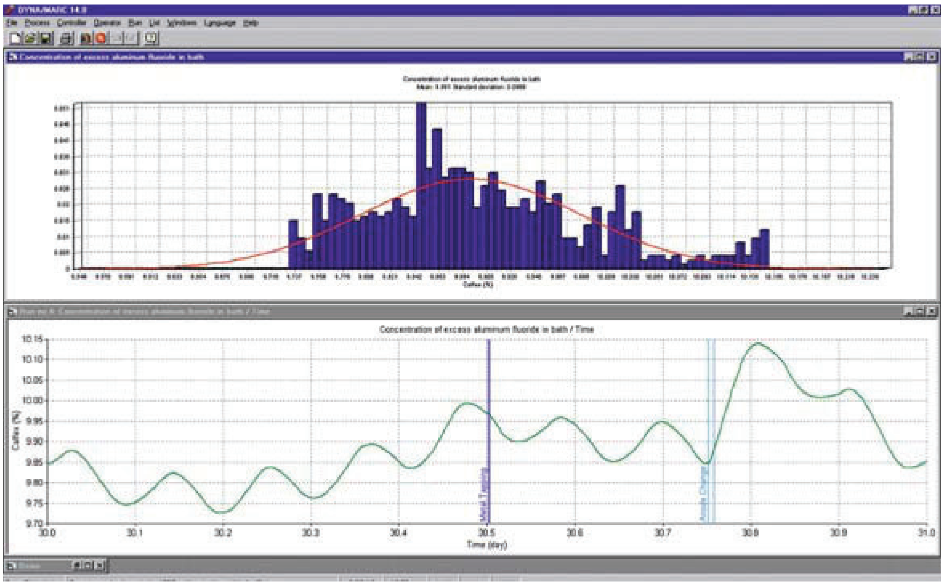

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Fig. 1: Daily excess AlF_3 concentration variation modelled without control and any mass imbalance as generated by Dyna/Marc cell simulator

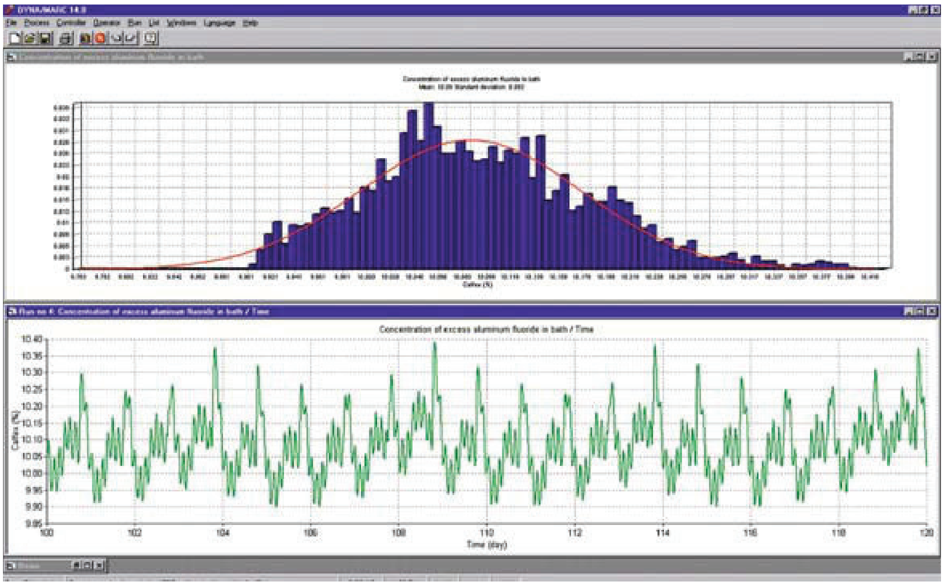

Fig. 2: 20 days excess AlF_3 concentration variation modelled without control and any mass imbalance

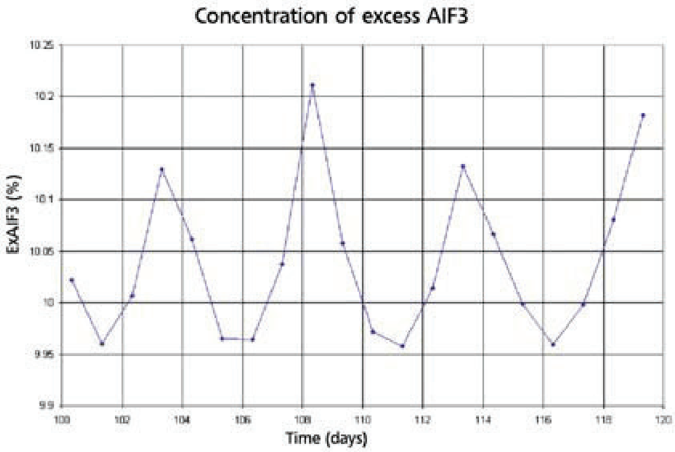

Fig. 3: Corresponding 20 days of excess AlF_3 concentration sampling results modelled assuming no bath sampling noise

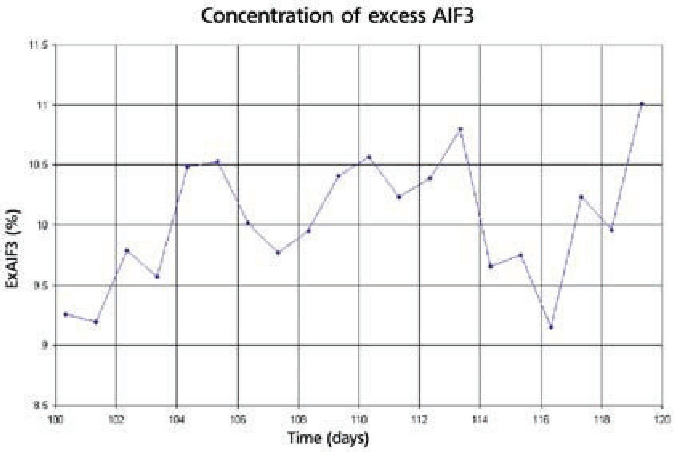

Fig. 4: Corresponding 20 days of excess AlF_3 concentration sampling results modelled assuming 0.5% standard deviation white sampling noise

modern continuous tracking control logic, the alumina is never fed constantly at the nominal 100% rate to the cell. As a result, the excess AlF_3 concentration swings up and down according to the alumina feeding cycle. The direct AlF_3 additions are also performed in discrete events, for example 2 kg every 110 minutes, in order to average 1.1 kg/hr. Those discrete additions also influence the short term variation of the excess AlF_3 concentration.

As well as the irregular AlF_3 addition, several thermal events also affect the AlF_3 evolution, such as the bath temperature, but more importantly the ledge thickness variation: as ledge is mostly pure cryolite, ledge formation concentrates the excess AlF_3 in the molten bath. Ledge formation occurs after anode change events, for example. Fig. 1 shows the calculated daily variation of the concentration of AlF_3 in the modeled bath in the absence of control additions and of any AlF_3 mass imbalance. The standard deviation on the average value is about 0.1%.

Sampling frequency and delayed XRD results: The next factor complicating things is the long delay in evaluating the bath chemistry through manual interventions. The traditional way of proceeding requires manual bath sampling, manual processing of the bath samples, at best semi-automatic analysis of the bath samples by a XRD instrument, and manual input of the results in a database accessible to cell controllers. Considering the cost of a XRD analysis, it is typical to take bath sample every second day and to get results at 8 to 24 hours after the actual bath sampling.

Fig. 2 shows the calculated variation of the AlF_3 for a period of 20 days, again in a model without control additions or any mass imbalance. Fig. 3 shows the results of the bath sampling performed once a day, always at the same time of the day. The delay between taking the sample and receiving the results of the analysis is clearly not an issue when the concentration is drifting very slowly. Yet any delay in the feedback response can cause instability, depending on the controller setup.

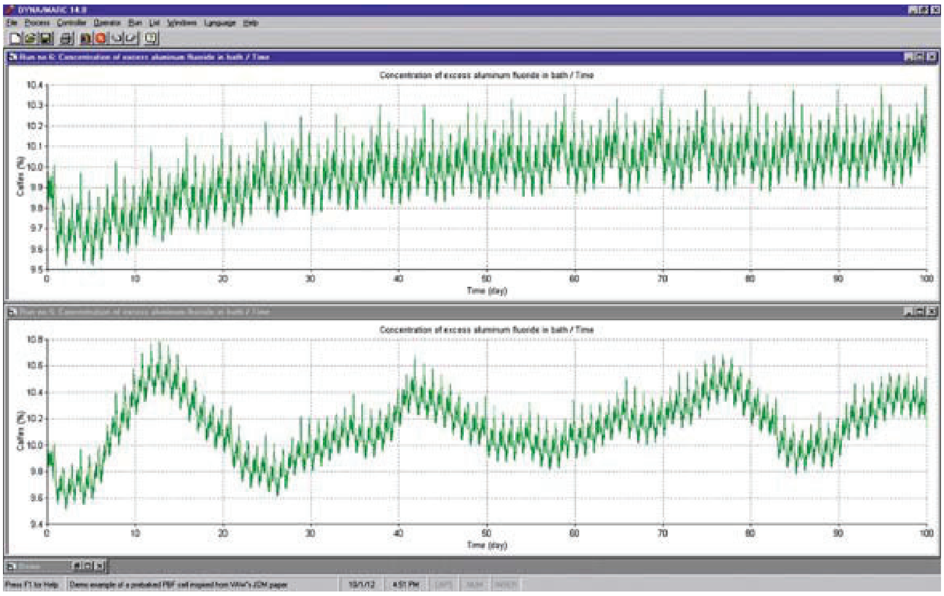

Fig. 5: Simulation of the process without perturbation; top without control, bottom with feedback control, 10% target concentration (XRD results, once per day, 1 day delay, 0.5 kg/hr% proportional band and -0.1 kg/hr°C proportional band)

So far, despite the daily events 'process noise', the sparse sampling frequency, and the delay in getting the sampling analysis results, should make it easy to stabilise the bath ratio. So there is no obvious explanation for why it is so difficult to control the bath ratio.

Bath sampling noise problem: But a new problem affecting bath ratio control has recently been identified: it is the bath sampling noise due to the bath composition being far from homogeneous [6]. The standard deviation of that bath sampling noise has been evaluated to be around 0.5%, which is five times greater than the process noise generated by daily events. That bath sampling noise, contrary to the daily events noise, is completely unpredictable. Fig. 4 shows the simulated results of bath sampling performed on the 20 days period presented in Fig. 2, but when 0.5% white noise is added to the noise-free results presented in Fig. 3. The fluctuations are about seven times greater.

Simulated process response using standard control without any process perturbation: Now, we want to test a typical control logic where both the delayed XRD analysis from bath samples and measured bath temperature are used to correct the direct AlF_3 feeding rate as it is commonly done in the industry these days. The proportional band was set to 0.5 kg/hr% for the 24 hours delayed bath XRD analysis results, and to -0.1 kg/hr°C for the bath temperature measurement. The bath sampling and the temperature measurement for the model are done simultaneously every 24 hours.

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A bath sampling noise having a standard deviation of 0.5% has been added to the XRD analysis results following observation recently reported [6]. For the temperature measurement, a bath sampling noise having a standard deviation of 2.5 °C has been added as reported in [6].

Fig. 5 presents the modeled results in the dynamic cell simulator for a period of 100 days. The top graph presents the results obtained without any control and in the absence of process perturbation. The initial bump is an indication that the steady state conditions used as initial transient conditions are not 100% representative of the long term pseudo steady state conditions.

The bottom graph presents the results obtained with feedback control active. Unfortunately, it is not as good as the results without control. This shows that the bath sampling noise, combined with the 24 delay in the bath sampling analysis result, is destabilising this feedback control loop.

Simulated process response using standard control with a significant process perturbation: In order to more seriously test the stability of the feedback control loop, we added a major perturbation to the simulation. On day 14, we simulated removal of about half of the cover material from the anodes. This increases the anode panel heat loss by about 30 kW from 230 to 260 kW. As we can see in Fig. 6, as a natural response, the cell must reduce its cathode heat loss by the same amount. It does this by reducing its superheat by about 1 °C and by increasing its ledge thickness by about 5 cm. This extra ledge formation concentrates the excess AlF_3 in the molten bath by about 2%, where it remains close to 12% if the direct AlF_3 additions remain unchanged.

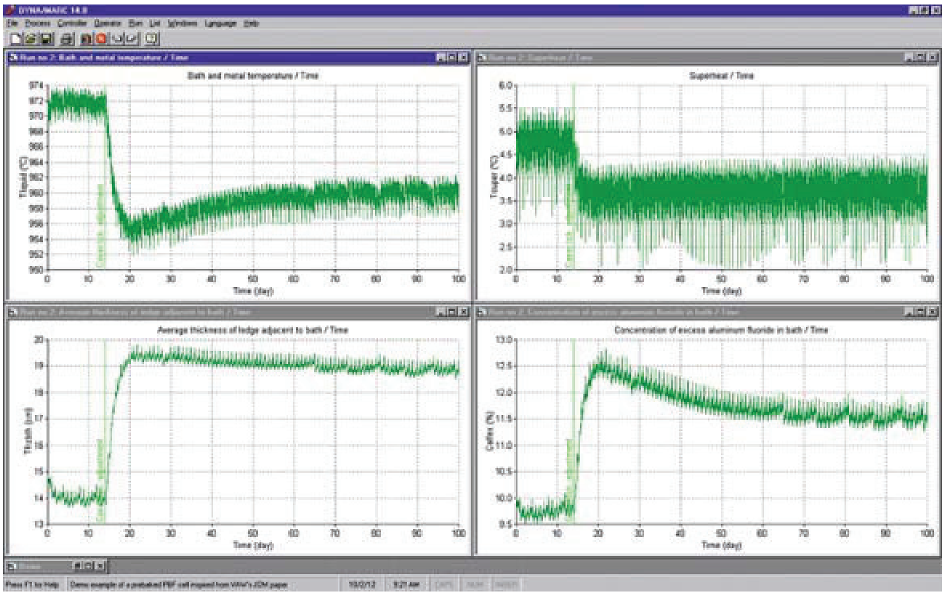

Fig. 6: Simulation of 100 days natural response (no control) to a significant reduction of the anode cover material thickness resulting in an increase of the anode panel heat loss by 30 kW

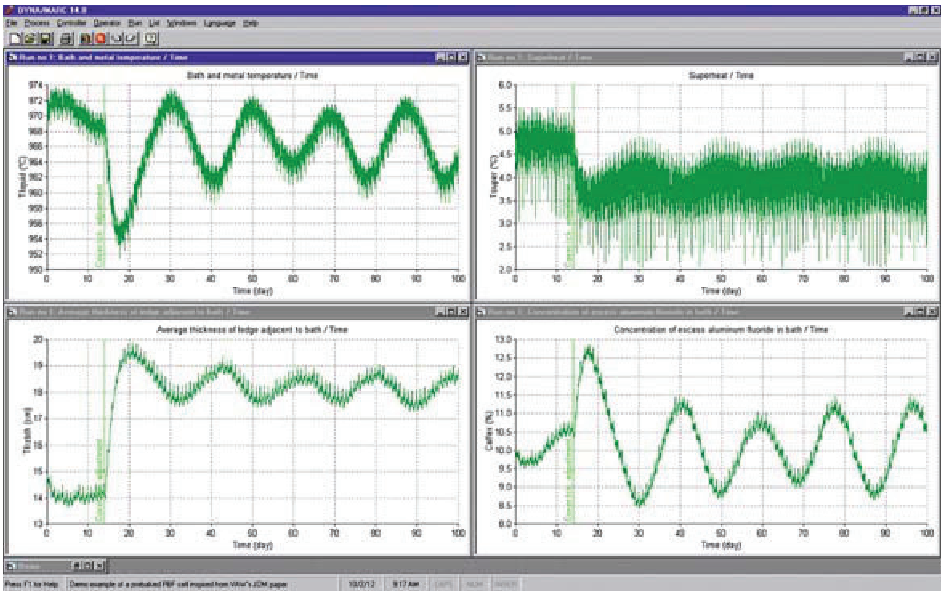

Fig. 7: Simulation of the process with a significant perturbation; feedback control, 10% target concentration (XRD results, once per day, 1 day delay, 0.5 kg/hr% proportional band and -0.1 kg/hr°C proportional band)

This is clearly a case where some feedback control is required. Fig. 7 presents the model results obtained using the standard control described above. After the change of superheat, the 970 °C temperature target is no longer compatible with the 10% excess AlF_3 target. Combined with the 1 day offset between the AlF_3 feedback and the temperature feedback, this generates a cyclic response characteristic of somewhat unstable feedback control. This type of oscillation with a wave length of about 20 days and an amplitude of about 2.5% is very often seen in real smelters. Those undesired oscillations occur despite careful selection of the values of the proportional constants in an unsuccessful attempt to avoid feedback loop instabilities.

The new STARprobe

The STARprobe is a portable device that takes real-time measurements of bath properties in electrolysis cells, such as **S**uperheat, **T**emperature, **A**lumina concentration and bath **R**atio or acidity (STAR). This synchronicity of measurements is a most important step forward in improving the control and efficiency of electrolysis cells. It unites the conventional processes of temperature measurement and bath sampling analysis into one online measurement. This simplifies and greatly shortens the process and time delay from measurement/sampling to pot control decision. The pot control decision can therefore be based on the real-time cell conditions rather than on conditions from few hours ago, or even from as long as 24 hours ago.

This integrated real-time measurement system consists of four major components:

- Reusable probe tip
- Portable stand to fit various pot configurations
- Electronics for data acquisition and analysis, and wireless communications for data transfer
- Tablet PC with programs to perform all necessary tasks during measurements.

Considering the great advantages of the STARprobe, Alcoa has decided to share the technology with the rest of the aluminium industry starting from 2012. In this regard, Alcoa has just appointed STAS, a well recognised leader in the aluminium industry, to commercialise the new STARprobe analysing system.

Simulated process response of STARprobe to a significant process perturbation: Exactly the same major perturbation was used to test the efficiency of the feedback control loop using STARprobe measurements. The same day measurement frequency is used and the same 0.5 kg/hr% proportional constant for the AlF_3 feedback loop. Obviously in this case however, the measurement results are available without delay. In addition, the measured superheat was also used to activate a separate feedback loop which adjusts the target cell resistance based on the offset between the target and the measured superheat.

The measured superheat is also affected by a very significant bath sampling noise. That bath sampling noise was estimated to have a standard deviation of about 2 °C in [6], so we added a 2 °C standard deviation white sampling noise to the simulation.

The obtained results are shown in Fig. 8. In this case the response to the perturbation is slower than in the previous case, because there is no longer a correction based on the temperature offset, and because a ±1 °C deadband was imposed on the superheat target in order to inhibit wrong responses to the noise in the superheat measurements. Yet after a 25 days transient response to the perturbation, the excess AlF_3 concentration goes back to its target value and remains on target without oscillations after that.

Fig. 9 shows the evolution of the target cell resistance. After a delay of 6 days, a 0.01 µΩ correction to the target cell resistance was applied each day for 15 days giving a total 0.15 µΩ correction. This 0.15 µΩ 'permanent' correction ensures that the superheat remains within the 3.5 to 5.5 °C range, despite the fact that the anode panel now dissipates an extra 30 kW of heat loss.

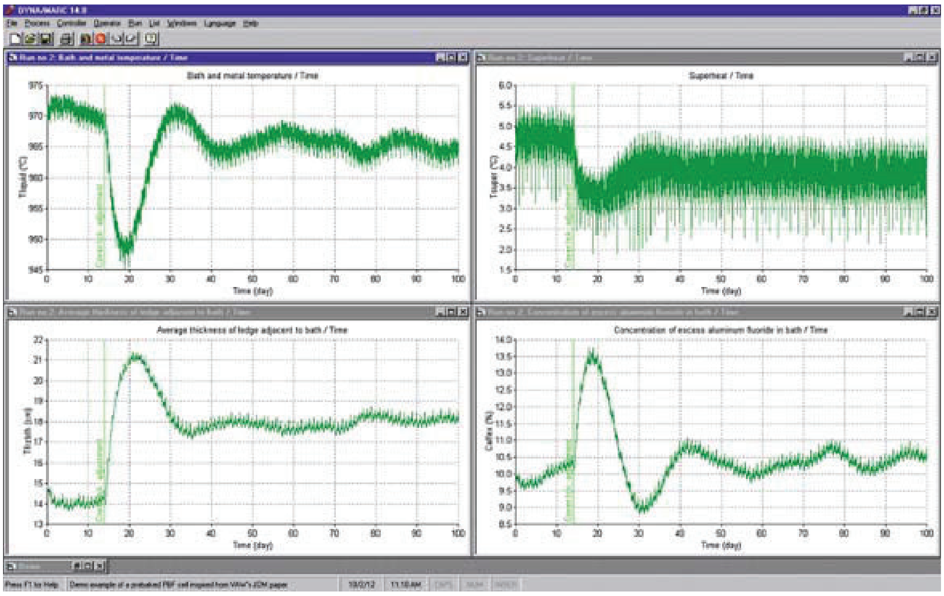

Fig. 8: Simulation of the process with a significant perturbation; feedback control, 10% target concentration (STARprobe measurements once per day, 0.5 kg/hr% proportional band and daily 0.1 µΩ target resistance correction due to superheat offset from target)

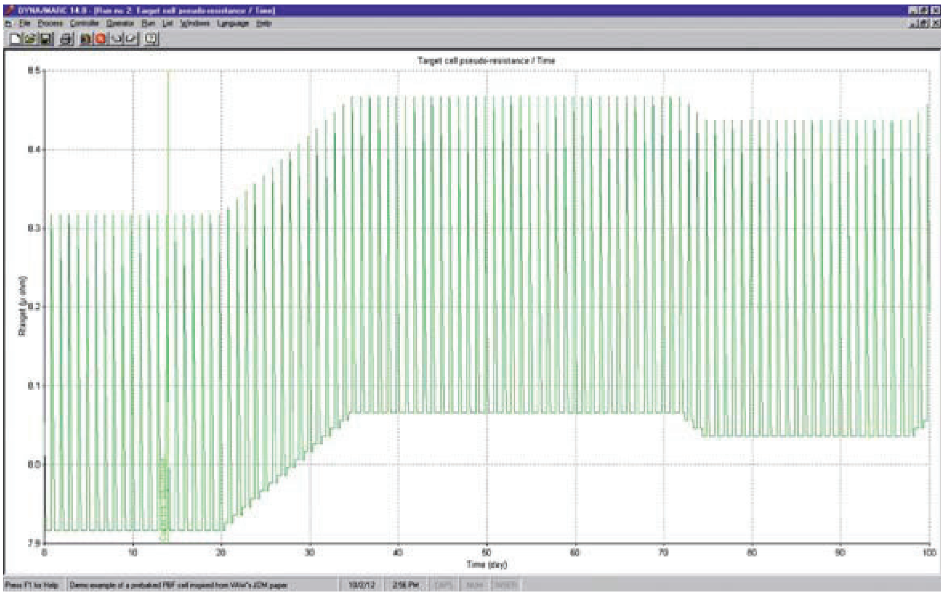

Fig. 9: Evolution of the cell target resistance (there is a 0.4 µΩ change of target resistance each day during the anode change event)

Conclusions

This study demonstrates the value of using a dynamic cell simulator to optimise existing cell controller algorithms and to test new ones without putting real cells at risk. The Dyna/Marc cell simulator used in this study is available to the whole aluminium industry through GeniSim Inc. Version 14 supports adding the simulated bath sampling noise at the level seen in the AlF_3 measurements. The model can also use STARprobe measurements instead of bath samples/XRD analysis to perform bath ratio control.

The revolutionary new STARprobe measurement tool makes possible a new control logic scheme based on independent control of the excess AlF_3 and of the cell superheat. Modelling proves this to be superior to the standard single feedback control loop, which uses two target variables (namely the excess AlF_3 and the operating temperature) to control a single control action, namely the direct AlF_3 additions.

The STARprobe developed by Alcoa [2, 3] is now available to the whole aluminium industry through STAS (http://www.stas.com/en/starprobetm.html).

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Dr. Marc Dupuis is a consultant specialised in the applications of mathematical modelling for the aluminium industry since 1994, the year when he founded his own consulting company GeniSim Inc. (www.genisim.com). Before that, he graduated with a Ph.D. in chemical engineering from Laval University in Quebec City in 1984, and then worked ten years as a research engineer for Alcan International. His main research interests are the development of mathematical models of the Hall-Héroult cell, dealing with the thermo-electric, thermo-mechanic, electro-magnetic and hydrodynamic aspects of the problem. He was also involved in the design of experimental high amperage cells, and in the retrofit of many existing cell technologies.

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Carbothermic reduction – An alternative aluminium production process

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About twenty years ago the present author co-authored a paper [1] with the title *Carbothermal production of aluminium – technically possible, but today economically impossible?* Since then significant resources have been spent on the study of this process and much experimental work has been done. So, it is time to ask again if such a carbothermic process for production of aluminium really is still economically impossible. The present paper reviews the published literature of the last two decades to try to evaluate the current status of carbothermic aluminium production.

The standard industrial aluminium electrolysis process (Hall-Héroult) has several weaknesses, as we know: very high capital investment, a complex anode change operation, high energy consumption, pollution of the environment and emissions of greenhouse gases. That is why the search for alternative methods for production of aluminium will probably never stop. In 2000 Alcoa announced that it had started to develop a process based on carbothermic reduction of alumina. Since then little published information has emerged about the progress of Alcoa's work. This is quite understandable in view of the importance which a successful result would have. So let us here first take a look at the present status of carbothermic aluminium production.

Carbothermic production of aluminium – its history

The idea of carbothermic reduction of alumina to aluminium is indeed an old dream. Aluminium-copper alloys with about 15% Al were produced industrially already in 1886 [2], the same year as the present industrial electrolysis process was invented. In the 1920s Al-Si alloys with 40-60% Al were produced in Germany, and about 10,000 tonnes of these alloys were produced annually in the period up to 1945.

The first attempt to produce *pure* aluminium by carbothermic reduction of alumina was performed around 1955. Pechiney worked on the process from 1955 to 1967, but terminated the programme for technical reasons. Reynolds worked on an electric arc furnace to produce aluminium from 1971 to 1984. Alcan acquired information from Pechiney and continued their research, but stopped in the early 1980s. Alcoa tried to develop the process to produce Al-Si alloys from 1977 to 1982.

However, in 1998 Alcoa started the carbothermic production project again, together with Elkem R&D in Norway. They changed their focus from an open arc furnace (with high generation of volatile aluminium-containing gases) to a submerged arc process. Elkem already had a long experience with modern silicon furnace technology, and so came up with the idea for a new type of high-temperature electric reduction reactor tailor-made for carbothermic production of aluminium. Alcoa had a good understanding of the fundamental chemistry and a long experience with carbothermic production of aluminium from the work in the 1960s until the 1980s. Together Alcoa and Elkem then agreed to try this again.

Carbothermic aluminium production: the three main steps in the process

As the name says, the purpose of the carbothermic method is to use carbon and heat to reduce alumina to aluminium, according to the overall reaction:

$Al_2O_{3(s)} + 3\ C_{(s)} + \text{heat} = 2\ Al_{(l)} + 3\ CO_{(g)}$

The reaction proceeds close to and above 2000 °C, and it produces CO as the primary gas. The gaseous by-product is therefore different from that of the Hall-Héroult process, which produces CO_2.

The carbothermic process can be divided into three steps, as shown in the flow chart:

- Production of a slag, which contains a molten mixture of alumina and aluminium carbide
- Production of a molten aluminium-carbon-(carbide)-alloy
- Production of pure aluminium (refining) from the aluminium-carbon-(carbide)-containing alloy.

The two most difficult steps here are steps 2 and 3; the production of the molten aluminium alloy and the subsequent refining of this alloy. In addition the process needs a gas scrubber to collect the aluminium-containing gases that evaporate from the furnace at these high temperatures. This is an engineering challenge. The main reactions are:

Overall carbothermic reduction:

$Al_2O_{3\ (l)} + 3\ C_{\ (s)} = 2\ Al_{\ (l)} + 3\ CO_{\ (g)}$ $\quad E^{\circ}_{\text{theoretical}} = 7.9$ kWh/kg Al

Stage 1 (T > 1 900 °C):

$2\ Al_2O_{3\ (s)} + 9\ C_{\ (s)} \Rightarrow (Al_4C_3 + Al_2O_3)_{\ (slag)} + 6\ CO_{\ (g)}$

Stage 2 (T > 2 000 °C):

$(Al_4C_3 + Al_2O_3)_{\ (slag)} \Rightarrow (6\ Al$ as metal alloy with $Al_4C_3) + 3\ CO_{\ (g)}$

The latter two chemical equations are not stoichiometrically correct here, because both the slag and metal phases will have varying compositions. The molten aluminium phase will always contain some dissolved carbon, and therefore it can be considered chemically as an Al-C alloy. There are two molten phases here and they will not mix. The molten alloy has the lower density and will float on top of the molten slag phase.

The carbothermic reduction process produces poisonous CO, which has to be captured. If the CO were later burnt as fuel it would produce CO_2. To avoid releasing this greenhouse gas this should then either be used as a chemical or captured and stored (CCS).

Information published after year 2000

Here is a list of expected potential gains from carbothermic aluminium production, as published by Alcoa in 2000 [3]: