EXAMINATION OF DROP IN BATH ACIDITY DUE TO CHANGE-OVER OF ALUMINA QUALITIES IN THE SUNNDAL ALUMINIUM SMELTER, NORWAY

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Abstract

It is well known that alumina qualities with seemingly similar analysis results on the shipment Certificate of Analyses (CoA) may result in different smelter responses. The reasons are often complex and difficult to determine. During a few cases of change-over from alumina quality A to alumina quality B, significant drops in bath acidity have been observed at the Sunndal aluminium smelter. This could not be explained satisfactorily by the CoA or by changes in operating routines.

It was investigated if the reason could be from losses from the bath through additional HF formation and/or reduced HF capture in the dry scrubbers caused by alumina quality B. Primary and secondary alumina samples of both quality A and B were characterised. Potroom operating data and historical data from our alumina shipment and analyses database were also studied.

The results indicate that the drop in bath acidity could be related to certain alumina properties that are not given in the CoA. This includes i) total water content including gibbsite; ii) particle size distribution and the amount of total water in the different particle size fractions; and iii) pore size distribution.

In order to better predict smelter responses, and hence prevent similar operational disturbances in the future, implementation of additional alumina characterisation methods have been initiated.

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1. Introduction

In order to run an aluminium smelter at peak performance, instability in production should be avoided. An alumina source with little variation in quality parameters is important to maintain a stable production. As potline amperage has increased, a predictive alumina quality has become more and more important. Hydro Aluminium has historically sourced a large number of different alumina qualities. This has given additional challenges in predicting smelter responses to the new qualities. However, there are also cost advantages in flexibility if the smelters are able to adapt operation to different alumina qualities.

Fluorides are lost from the bath due to vaporization from the electrolyte (mainly $NaAlF_4$ (g)) and reaction of the dissolved AlF_3 with water forming gaseous HF. These reactions give a net removal of AlF_3 from the bath, even if dry-scrubbing causes most of the fluorides to be returned with secondary alumina. Other important losses are caused by impurities in alumina, such as Na_2O and CaO, which also react with bath AlF_3. The loss has to be compensated for by extra consumption of AlF_3 (Grjotheim and Kvande 1993), giving additional costs.

There is a strong correlation between bath acidity and bath temperature in the cells, where the bath temperature increases as the acidity decreases. A controlled bath acidity and temperature is important to ensure enough superheat for efficient alumina dissolution, but low enough to avoid a negative impact on current efficiency and melting of the side ledge. High bath acidity (AlF_3 content) will also reduce the metal solubility, which is important to prevent loss in current efficiency.

The Hydro smelter in Sunndal has received a number of different alumina qualities the last couple of years. Their preferred quality is here called quality "A". During 2009 and 2010 Sunndal received four shipments of another alumina quality, here called "B". Two of the B shipments caused unexpected drops in bath acidity that could not be explained by sodium levels or under reporting of these. The drops occurred simultaneously in all three sections of the potline. These sections have individual fume treatment plants and different operation teams. Hydro's other Norwegian smelters have from time to time experienced the same effects of quality B.

Quality B is known to contain higher fines content as well as higher amounts of residual hydroxyls than quality A. The difference in LOI between the two qualities is often larger than the CoA values indicate, however it does not explain why the smelter response to B is so strong and unpredictable. The reason for the drops may be linked to some characterisation parameters which are not given in the CoA. Some of the CoA parameters for the four change-overs at the Sunndal smelter are summarised in Table 1.

Table 1: CoA values of selected parameters for the five change-over from alumina A to B.

Change-over	1st 2009		2nd 2009		1st 2010		2nd 2010		2011
Alumina quality	A	B	A	B	A	B	A	B	A
Shipment ID	A09-N	B09-N	A09-D	B09-D	A10-D	B10-D	A10-N	B10-N	2011
LOI 300-1000 (%)	0.90	0.82	0.93	0.92	0.88	0.86	0.86	0.86	0.82
Alpha (%)	2.70	5	3.03	3	2.51	3	2.53	-	1.95
BET (m2/g)	76.1	73	76.0	74	78.5	72	76.7	68	76.9
+150 µm (%)	3.0	7	3.9	10	3.3	11	3.1	3	3.7
-45 µm (%)	6.2	9	7.1	11	6.9	9	7.9	9	7.3
-20 µm (%)	0.43	2.8	0.53	2.4	0.48	1.9	0.72	1.8	0.47
Smelter Response	No change		Bath acidity drop		Bath acidity drop		No change		-

Extended characterisation of alumina A and B samples has been carried out and operating data have been compared to investigate why drops in bath acidity occur for some change-overs from A to B, but not every time. The hypothesis is that alumina quality B must either form more HF or cause a higher loss of fluoride, and/or it will bring less fluoride back to the pot due to reduced scrubber efficiency. The inconsistency in the smelter responses makes it more difficult to find the determining parameters. This paper presents observations made and correlating trends in alumina quality and operation.

2. Alumina Characterisation and Analyses

Various analyses have been carried out on quality A alumina and alumina samples from quality B shipments giving different smelter responses.

2.1 Different types of water content: Gibbsite, residual H$_2$O and the ability to form HF

Normally, LOI (300-1000°C) is the reported value for the water content in alumina. This is a measure of the content of strongly chemisorbed water and structural hydroxyls incorporated in the transition alumina phases. The MOI, also called LOI (Room Temperature-300°C), measures mainly the surface adsorbed or physisorbed moisture, which is claimed to flash off rapidly in contact with the pot bath. It is also reported to contribute less than LOI (300-1000°C) to the HF formation (Hyland et al. 1997, Hyland et al. 2004).

Some structural water from gibbsite in alumina is included in the MOI value. If measureable amounts of gibbsite are present, the reported LOI value will underestimate the actual potential for the alumina to generate HF, as even a few percent of gibbsite would add significantly to the total HF formation (Perander et al. 2009). Because of this, it has previously been suggested to measure LOI from 250-1100°C (Metson et al. 2005, Perander et al. 2011). In which particle size fractions the gibbsite is present may influence the amount of gibbsite that actually reaches the bath and may form HF. It is possible that gibbsite in fines may flash off in volcano effects where as gibbsite in coarse particles may reach the bath.

X-ray diffractometry was performed on a PanAlytical X'pert Pro instrument to quantitatively determine the gibbsite content. The Rietveld refinement of the diffractograms was not included. Primary alumina bulk samples as well as the -45 µm and +150 µm fractions were analysed separately.

Thermo Gravimetric Analysis (TGA) was performed on a Netzsch QMS403C instrument. 20–30 mg of each alumina sample was heated with a constant heating rate of 10°C min^{-1} from ambient temperature to 1000°C. Bulk samples as well as the -45 µm and +150 µm fractions were analysed separately for primary alumina. Losses of mass for the selected temperature intervals RT-160°C, 160-350°C and 350-1000°C were calculated.

A laboratory setup (described in detail in Sommerseth et al. 2012) was used to compare the HF formation potential of various alumina samples of different quality and size fractions. The principle of the method is to add alumina samples to a cryolitic melt in a gas tight furnace kept under a constant nitrogen flow rate, during which the HF concentration in the off gas is measured as a function of time by a tuneable diode laser (NEO LaserGas II). The HF concentration typically increases rapidly upon addition and then declines back to baseline. The amount of HF generated from each alumina addition is found by using Riemann sums to calculate the area under these peaks in the HF concentration curve. In the current work, to avoid any influence of moisture, all samples were kept at 160°C for at least two hours before the addition to the cryolite melt. Bulk samples as well as the -45 µm and +150 µm fractions were analysed. Modified MOI/LOI measurements for loss of mass above 160°C were used to relate HF gas formed to water content in alumina samples.

2.2 HF adsorption capacity - Pore Size Distribution and Pore Volume

The Pore Size Distribution may give valuable information when evaluating the surface properties of an alumina quality. Lower calcined particles with smaller pores have a large surface area; however it is questionable whether these small pores are accessible to HF during the retention time in the fume treatment. The narrow pores may also become blocked when HF reacts to form oxy-fluorides. This further limits access to internal porosity, thus reducing the capacity and rate of HF adsorption (Perander et al. 2009, Perander et al. 2011).

Most alumina qualities fall under the desired range for BET of 60-80 m²/g. However, two qualities with similar BET values may have a very different pore size distribution. The BET method may thus have limitations in describing the surface area available for reaction with the HF gas and hence could be insufficient in predicting the dry scrubber performance.

The BJH method (Barret et al. 1951) was used on a TriStar instrument to evaluate the pore size distribution and pore volume of primary alumina bulk samples. The samples were initially degassed under a nitrogen purge at 150°C.

Measurements of the total fluoride content in secondary alumina samples were carried out at the Sunndal smelter using Sintalyzer, a well established method for determination of fluoride by direct potentiometry (Metrohm Information Issue). Samples from B10-D and the following quality A shipment were analysed. The analyses were included to find out if less fluoride was brought back to the pots with quality B.

3. Results and Discussion

The operating data for the four quality B shipments in 2009 and 2010 were studied and compared. The first 2009 shipment did not lead to any changes in bath chemistry, whereas the second led to a significant drop in bath acidity from approximately 10.7% excess AlF_3 to approximately 8.5% in a time period of 11 days. The first shipment of alumina quality B in 2010 also led to a drop in excess AlF_3 from 10.6 % to 8.8 % within three days, where as the second 2010 B shipment did not lead to any significant changes in bath chemistry.

Figure 1a presents the bath acidity data for the second 2009 B shipment. Bath acidity data for the first 2010 shipment are shown in Figure 1b below.
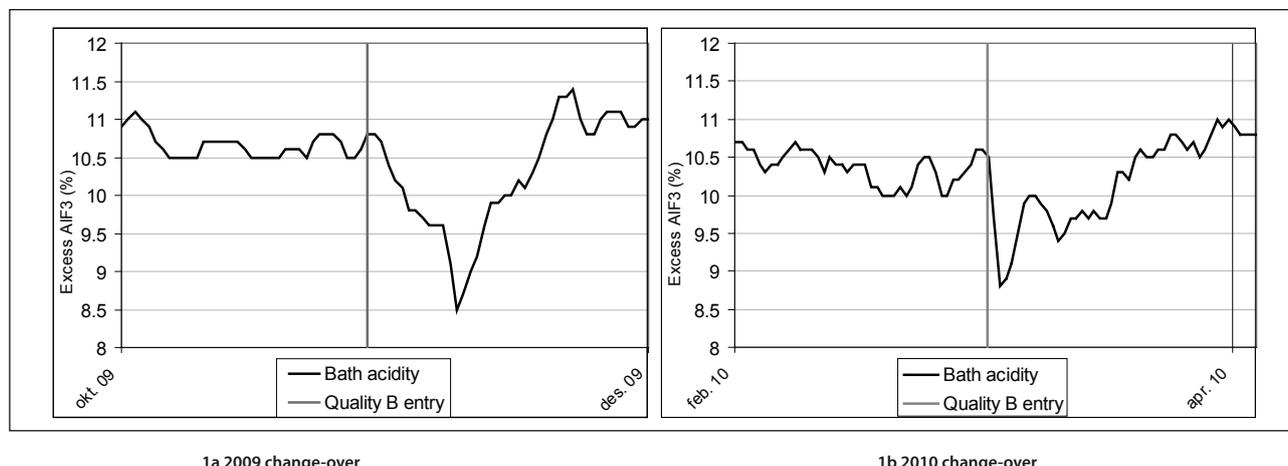
1a 2009 change-over

1b 2010 change-over

Figure 1: Bath acidity data from Sunndal smelter line 4 for the two quality change-overs that caused bath acidity drops.

Repeated analyses of Na and Ca content in the shipment samples showed no significant deviations from the CoA. It is therefore unlikely that the observed drop in bath acidity is caused by higher sodium levels than expected. Both the CaO and the Na_2O levels in alumina are accounted for in the fluoride feeding regulation system.

Several operating data were studied, and no other parameters that could have caused the drops were identified. This includes changes in fluoride feeding, anode deviations and alumina dissolution.

### 3.1 Total water content and HF formation potential

Gibbsite was determined by XRD of the samples and fractions listed in Table 3 below. The gibbsite content is higher in quality B than in quality A, both in the bulk and fines fraction. It is surprising to see that there is also a significant amount of gibbsite in the coarse fraction of quality B.

Table 3: Results of XRD determination of gibbsite content in shipment samples

Alumina quality and sample	A 10-D	B 10-D	B 10-N
smelter response		drop	no drop
Gibbsite bulk (%)	< 0.1	0.9	1.7
Gibbsite -45µm (%)	< 0.1	5.6	8.1
Gibbsite +150µm (%)			4.7

The TGA results presented in Figure 2 clearly show the differences between quality A (2011) and B 09-D. Where quality A does not have any detectable gibbsite content, quality B shows significant gibbsite contents in the bulk as well as the -45µm and +150µm fractions. This gibbsite content is apparent from the significant drop in mass around 220-310°C as seen in Figure 2b. A similar mass loss is not found for alumina A. A bulk sample from a quality B shipment that did not cause a drop in bath acidity (B10-N) was also analysed; the results showed no significant deviations from figure 2b.

The quantified TGA results of mass loss within the temperature intervals RT-160°C, 160-350°C, 350-1000°C as well as total loss of mass is presented in table 4.
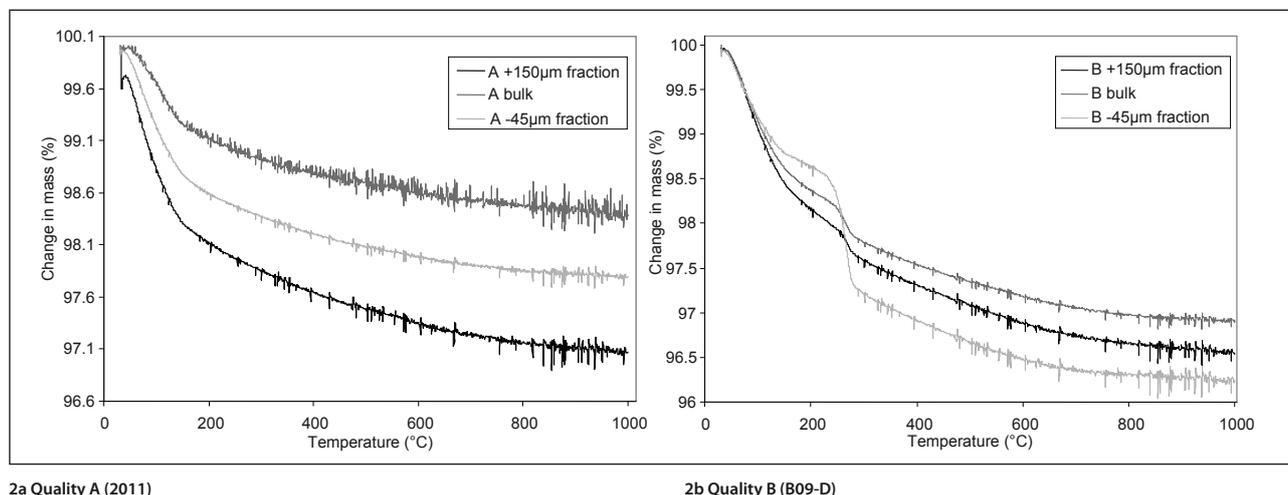
2a Quality A (2011)

2b Quality B (B09-D)

Figure 2: TGA Results for alumina quality A (2a) and B (2b) for bulk, -45µm and +150µm fractions.

Table 4: Quantified TGA results within selected temperature intervals

Primary alumina sample	Mass loss (%) RT-160°C	Mass loss (%) 160-350°C	Mass loss (%) 350-1000°C	Mass loss (%) RT-1000°C
A 2011 bulk	0.80	0.29	0.53	1.62
A 2011 +150 µm	1.74	0.52	0.67	2.93
A 2011 -45 µm	1.27	0.45	0.49	2.20
B 09-D bulk	1.44	0.90	0.74	3.09
B 09-D +150 µm	1.62	0.94	0.89	3.45
B 09-D -45 µm	1.24	1.70	0.82	3.76
B 10-N bulk	1.29	1.04	0.73	3.05

The results of the TGA and XRD measurements clearly show that quality B samples contain more gibbsite as well as total water than the quality A samples. This is valid for bulk and separate size fractions. However, none of the analyses of total water content show any significant differences between the quality B shipments.

The higher levels of gibbsite and residual hydroxyls in quality B suggest that quality B has a higher HF formation potential than quality A. As expected, the laboratory HF measurements presented in Figure 3 below confirm this. The results show a linear relationship between total water content of an alumina sample and the amount of HF gas formed. A lab-calcined sample (heated to 1000°C) of quality A is included in Figure 3 for comparison.

The difference in HF formation between the bulk, fines and coarse fractions is small for alumina A. For B 09-D, however, the difference is significant. This is in agreement with the XRD, TGA and LOI measurements, where especially the fines of alumina B contain significantly more gibbsite than the bulk.

The results in (Sommerseth et al. 2012) indicated that in this laboratory setup, all types of moisture contribute to HF formation. This includes physisorbed and chemisorbed moisture, as well as structural hydroxyls. The water vapour does not have the possibility to rapidly escape the reaction zone with the off gases as it does in a smelter, where there is a fairly strong drought of air passing through the hood. Rapidly evaporating water will therefore also contribute to the HF formation in the lab cell. The situation in a smelter is different, where water in fines including gibbsite may flash off during feeding and contribute less to HF formation. However, this may not be the case for gibbsite in the coarse particles. The laboratory test does not give any answers to whether water in different phases contributes differently to the HF formation, or if water in different size fractions has a different probability to react to form HF. A study involving variation of the residence time of the water vapour in the laboratory set-up is planned.
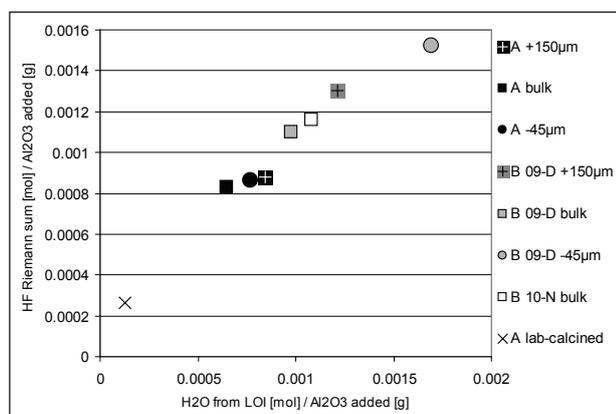

Figure 3: HF formation potential for primary alumina samples A (2011) and B 09-D bulk, -45µm and +150µm and B 10-N bulk, all preheated to 160°C for two hours to remove any physisorbed moisture. A lab-calcined sample is included for reference.

3.2 Pore Size Distribution and HF adsorption capacity

A pore size distribution analysis was carried out on one quality A sample (2011) and two quality B samples, B09-D and B10-N. The results presented in Figure 4 below shows no significant difference between the two quality B samples. This means that the pore size distribution alone cannot explain the difference in smelter behaviour between the two shipments.

However, there is a significant difference between quality A and quality B. Quality A has a pore size distribution centred close to the desired range (6-8 nm), whereas quality B shows presence of some material with a lower degree of calcination (peak around <2.5 nm) and some over-calcined material (>10 nm) (Perander et al. 2011). This may indicate that quality B has less adsorption capacity than quality A.
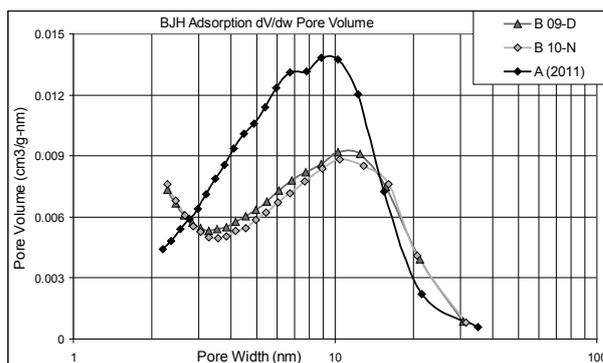

Figure 4: Pore Size Distribution of Quality A (2011) and Quality B (B09-D and B10-N).

The results of the total fluoride analyses on Sintalyzer are presented in Figure 5. The quality B shipment analysed (B10-D) resulted in a drop in bath acidity. The quality B samples (from day 2) contain less fluoride than the quality A samples (from day 31-32). The samples from day 8-9 are an unknown mixture of quality B and a third quality not included in this study.

Based on these few samples it may seem that less fluoride was brought back to the pots with the secondary alumina for this B shipment. The difference in fluoride content may be an indication that quality B has a lower adsorption capacity than quality A, however there are numerous other possible explanations for this observation so no conclusion can be drawn.
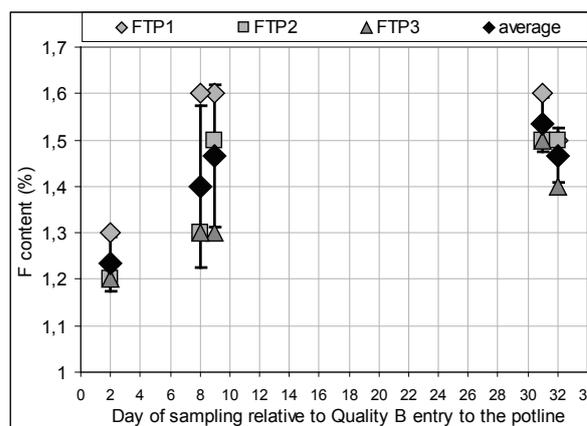
5a Secondary alumina bulk samples
Figure 5: Concentration of total fluoride content in secondary alumina samples. Samples from day 2 are quality B and samples from day 31-32 are quality A. The samples from day 8-9 are a mixture between quality B and a third quality.

3.3 Particle Size Distribution

Hydro's database of shipment certificate values have been used to compare specific parameters for shipments to Sunndal smelter. When comparing the data for the two shipments that caused a drop in bath acidity with the rest of the shipments to Sunndal dating from 1991, no significant differences were found for BET, LOI, LBD, alpha and fines. When it comes to the coarse fraction, however, the two shipments stand out, see Figure 6. Both of these shipments contain a much higher proportion of coarse particles than average. This is especially interesting considering that the coarse fraction of quality B seems to contain a significant amount of gibbsite. However, quality B shipments with a low or more typical level of coarse particles have also caused drops in bath acidity at other Hydro smelters; hence coarse particles alone do not explain the smelter responses.
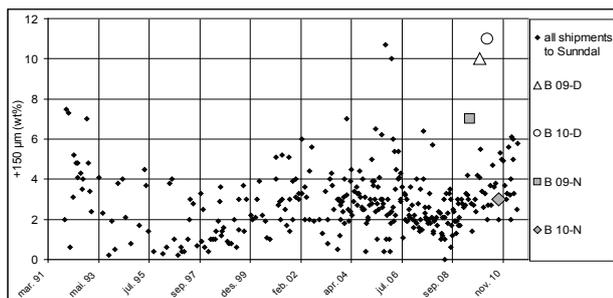

Figure 6: Coarse particles in all shipments to Sunndal (CoA values) and for quality B shipments. The quality B shipments that caused the bath acidity drops are marked with white symbols.

3.4 Other possible explanations

Quality B is known to contain a somewhat higher amount of phosphorus than quality A. This will lead to lower current efficiency and possibly to increased bath temperature, which may contribute to the observed drops. However, for the 2009 shipment, the bath acidity drop occurred prior to the temperature increase, indicating that bath acidity change is the initiating step. The smelter responses to higher phosphorus content in alumina is being investigated separately and is not included in the scope for this paper.

The dissolution rate of alumina depends on its physiochemical properties such as PSD, density, specific surface area, alpha content and LOI, in addition to mechanical stirring and superheat. Sufficient alumina solubility is important to avoid sludge formation, which disturbs the magneto hydrodynamic stability if formed on the bottom ledge. In that case a loss of current efficiency will be experienced.

Alumina with higher LOI is shown to dissolve faster than alumina with low LOI (Yang et al. 2011). Hence quality B should have good dissolution properties. However, quality B has a higher amount of both fines and coarse particles A. Both fines and coarse particles are reported to cause sludge formation due to slow dissolution (Lindsay, 2005).

4. Conclusions

For 2 out of 4 shipments of alumina quality B, significant drops in bath acidity and increased bath temperature were observed after introduction to the pot rooms.

Gibbsite is not accounted for by the traditional LOI (300-1000) measurement, and could lead to underestimation of the actual hydroxyl levels in the alumina fed to the pots. The analyses showed significantly higher amounts of gibbsite in quality B than in quality A, especially in the -45 μm and +150 μm fractions. No significant differences in gibbsite content were found between the different quality B samples. The quality B shipments that caused drops in bath acidity had a very broad PSD (high in fines and coarse particles), which in combination with high gibbsite content in these fractions gives higher HF formation potential for these shipments than expected based on the CoA LOI values.

The laboratory HF formation tests showed a correlation between the amounts of water lost above 160°C and HF formation. No significant differences in HF formation between the different quality B samples were found, but increased HF formation may have contributed to the observed drops in bath acidity.

Quality B has a different pore size distribution than quality A, and possibly less available surface area and hence lower adsorption capacity. No differences in pore size distribution were identified between quality B shipments. Because the drops do not occur for every quality B shipment, there must be additional reasons or more parameters coinciding at necessary levels for the drops to occur.

The findings support previous research stating that gibbsite plays an important role in bath chemistry and potroom operation. As a result of the study, implementation of the additional characterisation methods has been initiated to better follow up shipments in the Hydro portfolio.

5. Acknowledgements

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