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IMPROVING ANODE COVER MATERIAL QUALITY AT NORDURAL – QUALITY TOOLS AND MEASURES

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Abstract

Anode cover material (ACM) composition and granulometry determines the properties of the anode cover. This paper describes the experience Nordural has had with a new ACM mixing station employing autogeneous milling and pressure vessel conveying of the material to the potrooms. The pros and cons of this system for delivering the required granulometry is discussed by showing the evolution of the ACM granulometry before and after the commissioning of the new mixing station. To evaluate the effect of the conveying system the granulometry of the material at the output of the mixing station is compared with the granulometry of the material on the anodes. The automated XRD/XRF method for bath analysis has also been used for evaluating the alumina- and chiolite composition of the ACM which can impact the bath mass balance and structural stability. Finally, heat flux data is shown as one measure of quality.

Introduction

The Nordural smelter was started in 1998 with an initial production capacity of 60,000 tpy in one potline. Subsequent expansions have increased the production capacity to 260,000 tpy from 520 cells. The line current is 189 kA in Line 1 and 193 kA in Line 2. Capacity creep plans forecast the line current to increase to 195 kA in Line 1 and 210 kA in Line 2 in four year.

The Nordural smelter has always had an emphasis on strict bath height management and the influence of ACM quality there on. The main considerations have been:

The relatively generous space around the anodes that needs to be covered, the greater the volume of ACM required between and on the anodes the greater the possible impact on bath height. [1-2]

The narrow window of bath height control 16-19cm is required to decrease Gross Carbon Consumption and butt thickness to the minimum.

The content of soda in Primary Alumina is on the high side making the smelter a bath producer.

As described elsewhere [4] the anode setting and anode covering practice have been optimized to help minimize Gross Carbon consumption to values of 515 kg/t Al in 2005. With good control of bath height combined with good quality anodes it is possible to achieve an average amount of carbon under the stub of less than 20 mm while still staying with specifications of metal quality.

With the startup of Line 2 in 2006 a separate ACM processing plant (Figure 1) was constructed. Prior to the expansion the plant was situated in the Rodding Room.

Figure 1. ACM mixing station at Nordural

The functional design of the ACM mixing station is to meet three criteria:

1) All bath rich materials from the pot rooms are to be recycled. Dust from the mixing station is also recycled.

2) Tapped bath can be recycled in a controlled way when needed otherwise it must be easily removed from the ACM cycle.
3) The composition and granulometry of the ACM must be consistent and able to meet the desired targets.

According to Taylor [5] the composition and granulometry determine the important ACM properties:

- Thermal conductivity of the bulk material
- The crusting behavior and the resistance against subsequent thermal weakening.
- Flow characteristics of the bulk material during anode covering.

The crusting behaviour, i.e. how the ACM binds together once on the anodes occurs by mainly two mechanisms since it is roughly a two phase structure [3,5]:

- By slow sintering of the alumina portion due to conversion of transition phases to alpha platelets which interlock.

- By consolidation and welding of granular bath particles at 500-700°C.

But at the same time various mechanisms work towards weakening the material:

- Fluoride vapors such as $5NaAlF_4$ can form the following phases:

$$5NaAlF_{4\,(g)} = Na_5Al_3F_{14(s)} + 2AlF_{3(s)} \qquad (1)$$

- The chiolite then transforms to cryolite and liquid at 734°C

$$Na_5Al_3F_{14(s)} = Na_3AlF_6 + \text{liquid} \qquad (2)$$

Depending on the amount of chiolite and the position of the isotherms a fair portion of the cover can weaken and fall in.

A higher thermal conductivity for the granular cover material is important in the crust formation mechanism because it allows rapid penetration of the 500 and 600 deg isotherms into the cover giving more rapid consolidation and strengthening of the crust. For this reason Shen [6] studied the relationship between thermal conductivity and granulometry of the cover material. The final packing density and voidage of the blended material is the key to its thermal conductivity.

The following figure from [7] shows that when two sizes of spherical particles are mixed at various size ratios, the theoretical voidage can be reduced from 0.4 to 0.2-0.3 in some size ratios at a coarse particle weight percentage of about 75%. In the case of a bath – alumina mix Taylor [5] equates the particle diameter ratios approximately to a 100 micron (alumina) finer fraction, with 500-2000 micron as the peak coarser fraction diameter range.

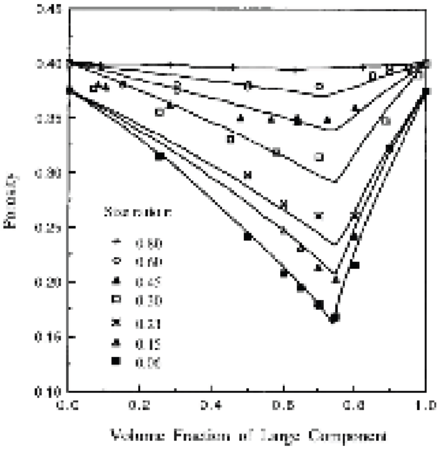


Figure 2. Porosity versus Volume Fraction of the large Component from [9].

The granulometry of the final blended material (bath and alumina) can only achieve high density if the bath material is coarse enough and then the added alumina enhances the density of the blend by decreasing the voidage.

ACM Processing Plant at Nordural

The layout of the plant is shown in Figure 3. The significant aspects are as follows:

- Autogeneous mill with automatic cleaning every 2-3 hours. The mill delivers -22 mm material.
- Material transported to the station is pure bath, anode cavity grab material (Grab) and recovered anode cover material (RACM) from anode butts. The type of material received is entered into the control system and conveyor belts move the material after milling to the appropriate silos. Dust from the stations dust treatment plant is also added to the mix.
- The mixed ACM material is sent from Pressure Vessels at the ACM station to six roof filling stations for Pot Tending Machines (PTM's). The distance is from 150-450 meters.

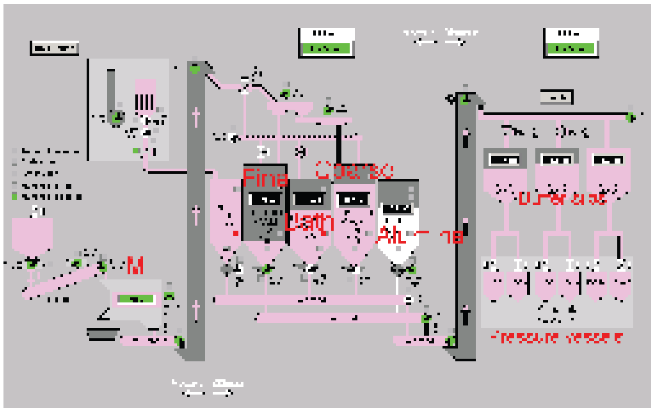


Figure 3. Functional diagram of the ACM mixing station. The material enters the station on the left, goes through the mill and into the appropriate silos. The material is mixed onto conveyor belts from the silos according to a recipe and moved to buffer silos above the pressure vessels.

<u>Material use and removal</u>

The ACM is mixed by recipe for each buffer silo so it is possible to have a slightly different recipe for each line. The recipe includes:

- Primary Alumina
- Fine RACM/Grab (-6 mm)
- Coarse RACM/Grab(6-22 mm)
- Filter dust from mixing station
- Pure bath with -22 mm grain size (Bath)

The use of primary alumina plus a steady input of pure tapped bath helps to keep the concentration of chiolite and AlF_3 in the ACM at a steady level.

The mill goes through a cleaning cycle every 2-3 hours during which tramp metal, carbon and uncrushable material can be removed. Figure 4 shows the typical material removed. Typical carbon content of the ACM is 0.8-1wt%C. The uncrushable material over 22mm has a very similar alumina content (35-40 wt%) as the fractions 1-22 mm which shows that the alumina addition also contributes to coarse particles.

Figure 4: Material removed from mill during cleaning.

Monitoring of granulometry and alumina content in the ACM is used to fine tune the recipe. An important constraint to the recipe is however to use material in the same ratio as it enters the ACM station to avoid accumulation or shortage of the individual components. For bath producing smelters the bath make must be removed so it does not accumulate as ACM.

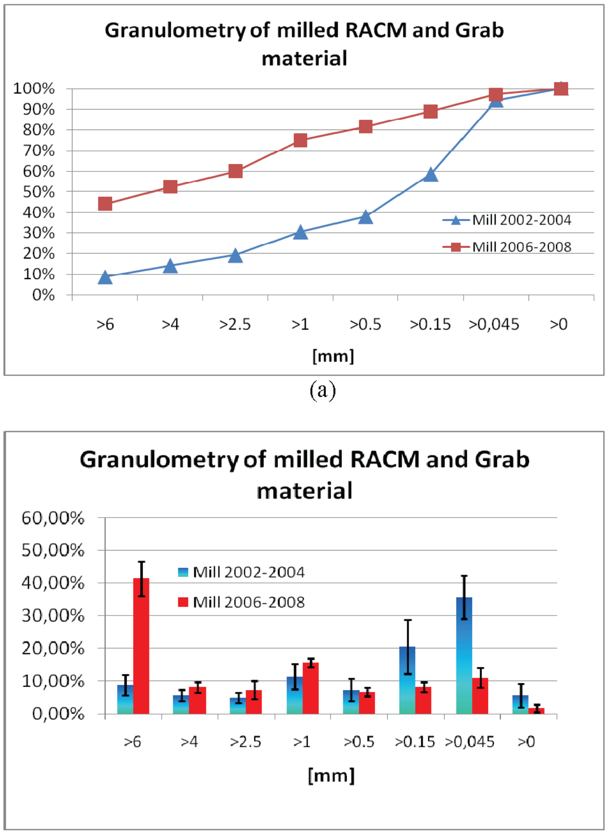
Composition and granulometry

The recipe is tuned to use as little alumina as possible or about 20-25wt% added alumina. The target total alumina content is however 52-55 wt% total alumina content which historically has given the most stable bath height. If the fraction of coarse alumina rich particles increases the addition of primary alumina is decreased to keep the total target composition.

ACM granulometry

Mill material granulometry

Figure 5 shows the evolution in grain size of the milled RACM and grabbed material before and after the new ACM plant became operational. The great improvement in coarseness is due to the frequent cleaning of the mill plus a greater diameter of holes in the autogeneous mill (from 15 to 22 mm).



(a)

(b)

Figure 5. Granulometry of material coming out of the mill before and after the new mixing station. (a) Accumulated grain size distribution (b) Grain size distribution

ACM material granulometry

Figure 6 shows the granulometry of the mixed ACM after adding roughly 20wt% alumina. This shows the granulometry of the ACM before it is conveyed by pipe to the potroom filling stations.

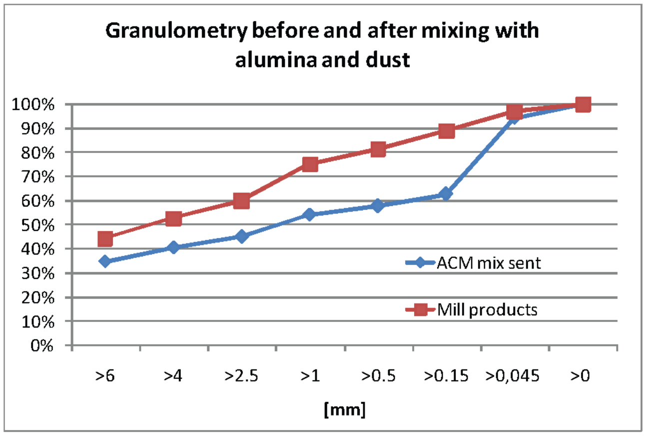
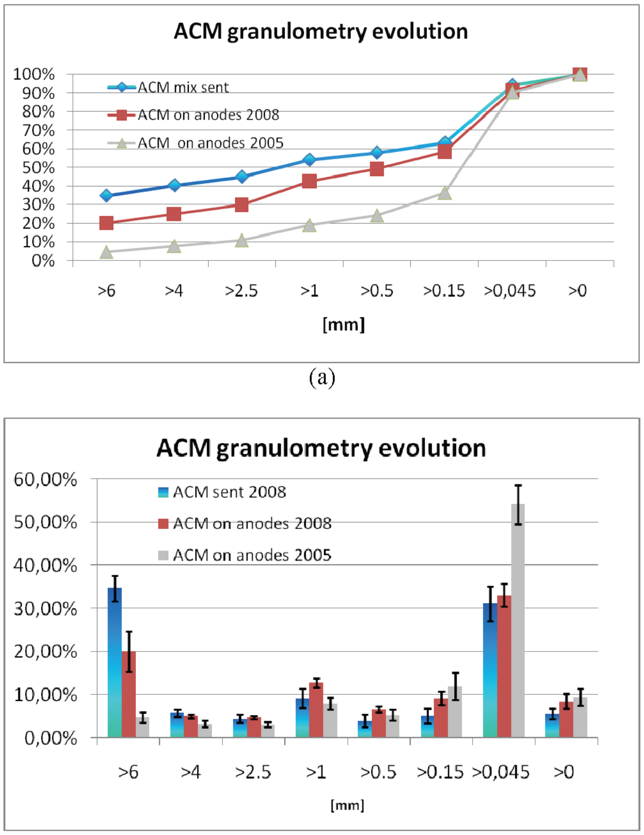


Figure 6. Granulometry of the ACM mix compared with the milled bath products.

Figure 7 shows a comparison between the ACM sent to the pot rooms and the actual grain size as sampled on the anodes after covering. Included is also the actual grain size as sampled on average in 2005. It is clear that the coarseness of the material sent from the station degrades during the conveying which is then the price payed for the convenience in transporting the material. The ACM on the anodes is however markedly coarser in 2008 compared with 2005 when it was also transported by pressure vessel conveying.



(a)

(b)

Figure 7. Actual granulometry of ACM on anodes in 2008 compared with the ACM sent from the mixing station. Actual granulometry of ACM on anodes in 2005 in comparison. (a) Accumulated grain size distribution. (b) Grain size distribution

ACM composition

Analysis methods:

The methods used at Nordural for following ACM composition are as follows:

- Leco oxygen/carbon analysis
- Bath analysis method by XRD/XRF

The Leco method for analyzing oxygen and carbon gives results regardless of how the elements are bound but the drawback is the small quantity of material used or only about 1 g of sample. The Leco oxygen method can however be used calibrate the bath analysis method by XRD/XRF by assuming that all the oxygen is bound to alumina. The bath ratio analysis method for ACM is uses the assumption that the quantity of bath in the mix is diluted simply by the alumina fraction. This method is quick and automated and thus suitable for analyzing many samples.

Figure 8 shows the calibration of alumina measurements in alumina-bath mixtures using the dilution of CaF_2 as the measure. This measure must be used instead of the combined CaF_2 / chiolite content used for bath samples since ACM can accumulated chiolite over time. The actual alumina concentration is verified by Leco measurement. The CaF_2 concentration in the bath is quite stable, in 2005 – 2008 the value is 6.1-6.2 wt% and follows the CaO content of the alumina.

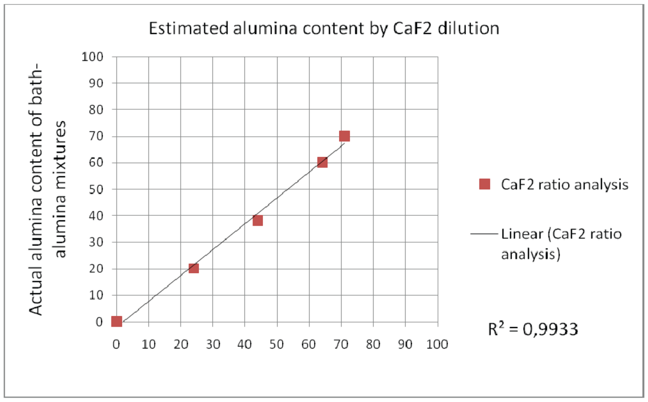


Figure 8. Alumina content of known bath-alumina mixtures measured by CaF_2 dilution using the bath analysis XRD/XRF method.

Monitoring of ACM composition:

Figure 9 shows the amount of chiolite in ACM in 2005 as measured by XRD/XRF method. The concentration of chiolite in the bath portion of the ACM is of course higher than in the bath alumina mix but the important thing is the stability of the chiolite content during most of the year. It was only in late 2005 that there was a problem with stability which was due to problems with alumina mixing.

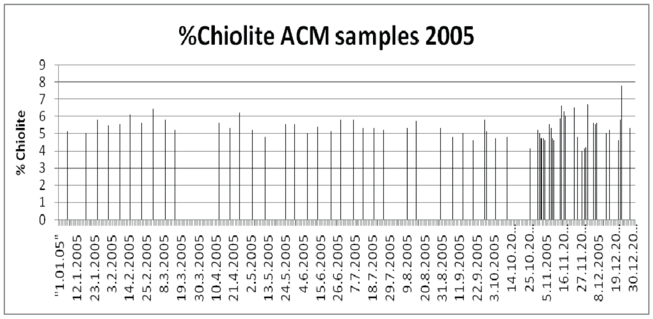


Figure 9. Chiolite content in ACM samples.

Figure 10 shows the results of the alumina analysis in the ACM by XRD/XRF in 2005 with the Leco method calibration checks shown in Table I. As in Figure 10 there is an instability in the total alumina content late in the year.

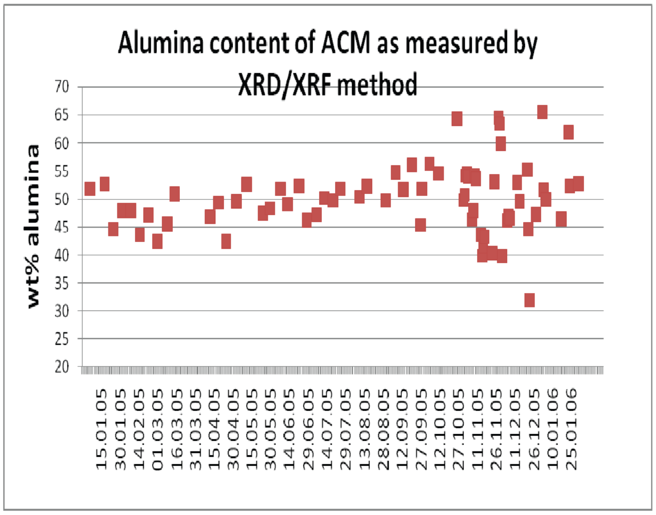


Figure 10. Total alumina concentration in ACM in 2005.

Table I. Calibration of alumina measurements in ACM

Date	Wt % alumina by Leco measurement	Wt% alumina by XRD/XRF measurement
1.02.05	48+/-2	48+/-3
19.07.05	48+/-2	50+/-3
4.11.05	50+/-2	54+/-2
7.11.05	46+/-2	46+/-4

Bath tapping and bath transfer between pots at Nordural has historically been empirically linked with the alumina addition to the ACM although other factors influence also such as:

- Line current fluctutations.
- Bath superheat.
- The quantity of ACM used during anode setting, redressing of anodes and the time delay between anode setting and covering.
- Bath tapping to match bath make of the pots

Figure 11 shows the correlation between the 21 day average alumina content of the ACM versus the bath height for the following day for a 19 month period from 2007-2008 as measured by CaF_2 dilution of the ACM. The hypothesis is that the average ACM composition of the last 3 weeks can influence the bath height but not day to day variations.

One possible objection to this correlation is that if the bath height and bath tapping is at a high level it could be argued that the bath is being added to the ACM and diluting it. The bath make at Nordural has for the past 17 months been about 5-6 tonnes per day. Daily bath tapping data is available and the data in Figure 12 is filtered to include only 21 day periods during which the running average of bath tapping is 10 tonnes or less.

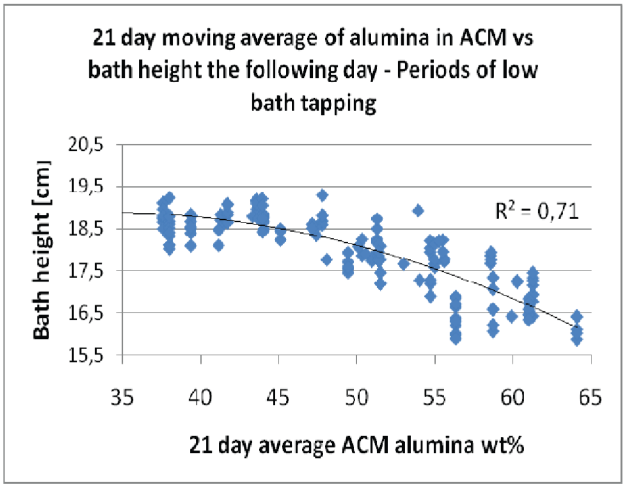


Figure 11. 21 day average of alumina in ACM versus bath height the following day only during periods of low bath tapping

ACM heat flux

In two measurement campaigns in 2007 and 2008 the average heat flux on the surface of the cover was in the range of 4-5 kW/m^2. The surface temperature was in the range of 200-270°C.

The heat flux probe was positioned on the cover surface at the midpoint between two anode stems and was measured for four cells at four evenly distributed positions in each cell.

Figure 12. Typical crust and loose cover cross section from an uncleaned butt. The total thickness is typically 6-12 cm. The standard for dressing is 12 cm

The density of the crust is typically 2.3-2.5 g/cm^3

An attempt was made to measure the thermal conductivity of the crust at the oldest anode. After measuring the total heat flux the loose cover was brushed away and in the progress its thickness was determined. The heat flux was then measured again on top of the hard crust. After that the crust was carefully broken so that a cross section could be measured at the positon of the measured heat flux. Table II shows the outcome of 5 measurements where the thermal conductivity of the combined loose cover and crust is calculated by Fouriers law. The individual thermal resistance of the loose cover was calculated to be 0.85 W/m K using the heat flux measurements from the crust and the combined loose cover and crust.

Table II. Heat flux, thickness and calculated thermal conductivity of the combined loose cover and crust.

Crust thickness, [cm]	Loose cover thickness, [cm]	Total thickness [cm]	Heat flux [kW/m^2]	T surface [°C]	Combined thermal conductivity [W/m K]
5	1	6	9.6	290	0.9
4	1.5	5.5	11.5	312	1.0
5.5	2.5	8	9.4	271	1.3
8	7.5	15.5	5.2	206	1.4
6	6	12	5.8	250	1.2

The average thermal conductivity of the loose cover and crust is (1.1+/-0.2) W/m K. The thermal conductivity of the crust was measured at 1.2-1.3 W/ m K which is comparable the value of 1.4 W/m K quoted by Richards [2] for a crust of that density (2.3).

Discussion of results

Taylor [5] reports a granulometry of milled bath products at the Boyne smelter achieving a high blend density with alumina (void fraction approaching 0.30). Figure 13 shows a comparison of the material coming from the mill at Nordural with the data from Boyne.

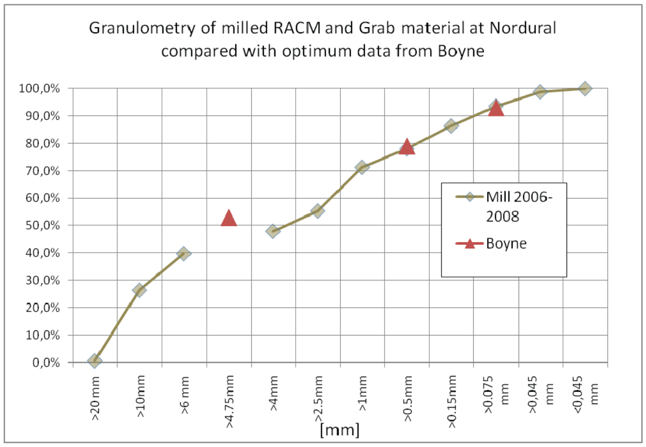


Figure 13. Granulometry of milled bath products at Nordural compared with data from Taylor [5].

The coarse fraction of the Boyne material appears to be slightly greater. This bath portion is then mixed with 20wt% alumina and is reported to have a thermal conductivity of about 1.6 W/m K [5].

The Nordural mixed ACM is therefore not quite as coarse before conveying. The material after conveying as it arrives on the anodes is yet finer and its thermal conductivity decreases because the coarseness of the material is not adequate to support the 20-25wt% alumina addition. Also the increased fraction of fines makes it more difficult to control the amount needed for dressing making it more likely that material will drop into the bath.

The average heat flux of about 4-5 kW/m^2 and the high flux at the oldest anodes supports that the cover is thinning and melting from below due to the lack of thermal conductivity. This results in a crust with a total thickness of 6-12 cm and a composition dependence of ACM on the bath height as shown in Figure 14.

Conclusions

ACM quality at Nordural has improved greatly in the past 3 years mainly through the following steps:

a) Mixing in with the recycled RACM and Grab pure bath and primary alumina to avoid thermal weakening.
b) Making the milled bath product coarser by design changes in the mill plus improved cleaning practices.
c) Measuring granulometry, chiolite and alumina content on a constant basis to ensure that the mixing is according to recipe.

The challenge in the coming years with the plans to increase line current is to offset the effect of the conveying which makes the material finer. Heat flux measurements and measuring the thickness of the crust support the lowering of the thermal conductivity due to the degradation of the granulometry. The correlation between alumina content of the ACM and bath height confirms that too much material is melting below the crust. Alumina additions will continue to be important for thermal conductivity and bath height management but the conveyed ACM must be coarse enough to ensure a successful mix.

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