BATH IMPREGNATION OF CARBON ANODES

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Abstract

A rapid bath impregnation in anode butts set in contact with the cathodic metal has been observed. The sodium content of the butts is raised by 0.2 % per minute of contact. Slower rates of impregnation have been measured in cases of pot current interruptions.

The impact of the impregnated butts on the anode reactivity is so dramatic that sorting of these butts is absolutely needed. Critical electrolysis conditions which may lead to impregnation are reviewed and the mechanism of impregnation is examined.

Introduction

The interdependence between the physical and chemical properties of anode butts and the quality of prebaked anodes has already been reported in a previous paper [1]. Butt recycling can possibly contaminate the anodes with sodium. The catalytic impact sodium has on the anode air and CO_2 reactivity depends on the raw material's sensitivity [2] and the process conditions [3] (i.e. butt preparation and anode baking degree).

The use of soft butts (due to poor anode burning behaviour) and dirty butts (poor cleaning) deleteriously influences the burning behaviour of the anodes and creates increasingly softer butts, due to the vicious circle. An extreme amount of carbon foam also accumulates in the pot which disturbs the entire electrolysis process.

It was also recognized by other authors [4, 5] that the addition of hard (unattacked) and cleaned butts improves the anode performance. Currently the average concentration of sodium in crushed butts lies in the range of 0.05 to 0.15 %.

This improvement is due to better butt cleaning techniques such as modern staged cleaning using shot blast and automatic single stage using the impact of falling balls [6].

It is well-known that pieces of broken butts, coming from a burn-off or thermal shock, which stay in the bath several days are highly contaminated by bath. For this reason such pieces of butts are normally not recycled in the green mill as there is no way to reduce the sodium content to an acceptable level even with water-blasting techniques [7]. It has also been observed that perfectly cleaned butts, showing no white spots of bath, could contain up to 3 % sodium [1] due to a massive bath impregnation. The recycling of one single impregnated butt contributes to the sodium contamination of anodes as much as 30 normal butts. Therefore, knowledge of the reasons for this anode bath impregnation is of utmost importance to avoid critical electrolysis conditions leading to this phenomenon.

In this study two impregnation scenarios have been examined :

- Cathodic contact of the anode without current
- Interruption of the pot current

Pot trials

Pot characteristics

The tests were run on a "trial pot line" with 80kA pots equipped with 24 anodes of 1100 x 520 x 520 mm^3 dimensions. The following pot conditions and features were observed :

Bath temperature	:	950 – 965 °C
AlF_3 excess	:	9 %
Bath Ratio	:	1.15
Bath Height	:	25 cm
Butt Height	:	18 cm
Interpolar Distance	:	6 cm
Anode Consumption	:	1.1 cm/day
Cycle Days	:	30

Cathodic contact of butts without current

During the normal scheduled removal of the butts (Figure 1), the rods were disconnected so that the electrical contact with the anode beam was suppressed. The anode butt was lowered by 8 cm in order to place the bottom of the butts in contact with the metal (Figure 2). The following periods of contact were tested :

0, 1, 2, 4, 8 and 16 minutes

For each period, two butts were collected for further analysis.

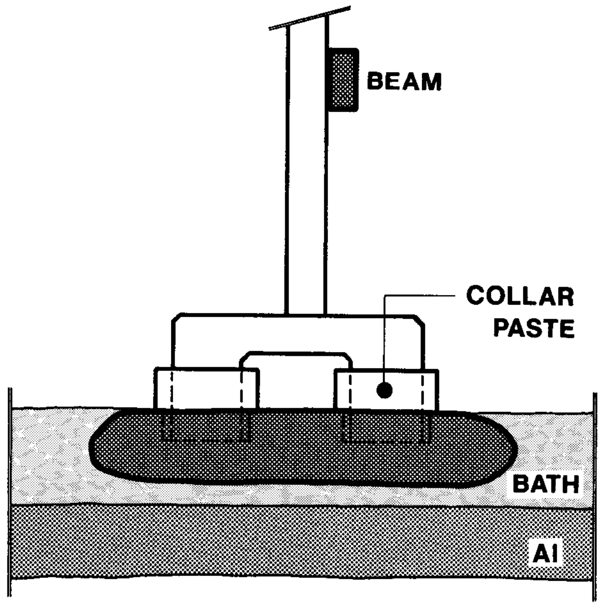

Figure 1 Normal situation of a 30 day old anode. The stubs are protected with collar paste

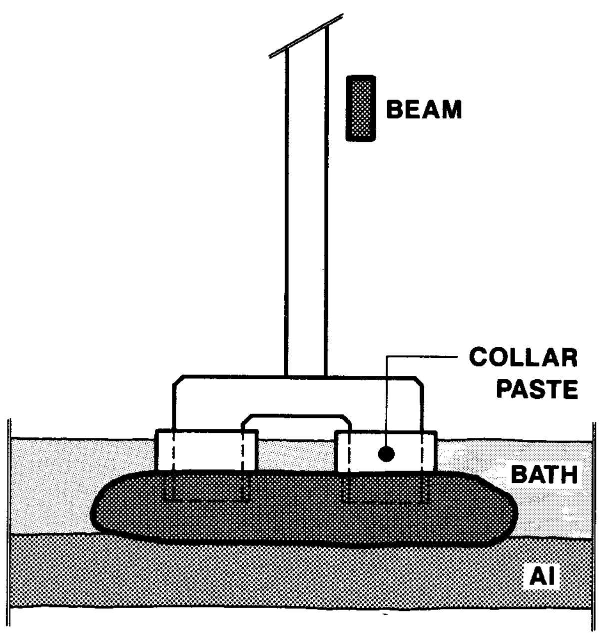

Figure 2 30 day old butts in contact with the cathodic Al–metal pad (2cm immersion depth)

Current interruption

During the final week of production, prior to the shutdown of the "trial pot line", half of the pots (12/24) were taken out of service at a rate of two per day. The remaining twelve pots were taken out of service all at once on the last day of production. Immediately after the current shutdown the anodes were lifted out of the electrolyte.

Four anodes at a time were collected from this final half of the pot line, being 10, 20 and 30 day old respectively. This gave twelve anode butts which were then tested.

Due to the gradual shutdown sequence the second half of the pot line had 6 current interruptions averaging 20 minutes each. Therefore the anodes which were sampled experienced a total of 2 hours of current interruption.

Butt testing

The butts were drilled in order to collect 10 cores of 50 mm diameter and a length corresponding to the butt height. As shown in Figure 3 the cores were drilled half–way from the stub hole to the long side of the butts.

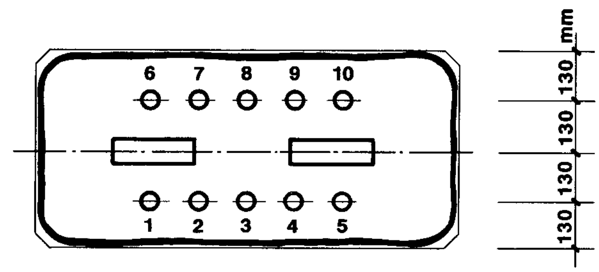

Figure 3 Drilling schedule of the butts showing the position of the 10 cores

The even numbered cores were cut in 20 mm slices for the measurement of the impurities by XRF and the odd numbered cores were cut in 50 mm cylinders for the measurement of the compressive strength and further characterization as shown in Figure 4.

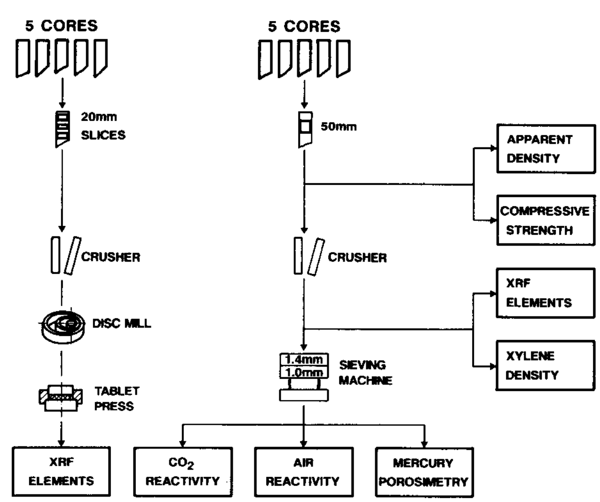

Figure 4 Test schedule on the butt cores

Results

Butts with cathodic connections

The impregnation of bath as a function of the contact time with the cathodic metal can be followed by measuring the sodium concentrations, as shown in Figure 5.

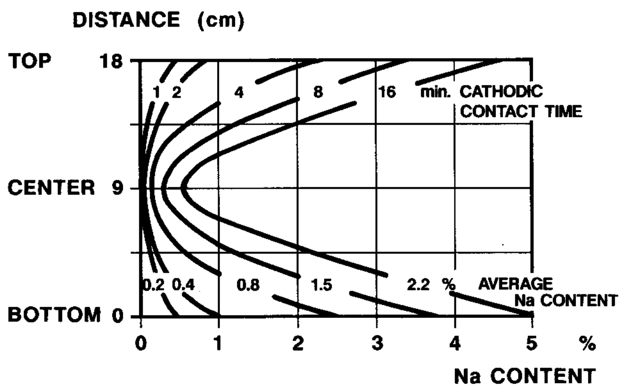

Figure 5 Concentration profile of sodium in butts connected with the cathodic metal

After only 4 minutes of contact with the metal the average sodium concentration was almost 1 %. As shown in Figure 6 the impregnation of the butt centre zone was not as rapid as the top and bottom. Although the average sodium concentration of the butts was above 2 % after 16 minutes the centre zone was not saturated. As can also be seen in Figure 6 the concentration of sodium at the bottom was slightly higher even though the butts were partially submerged (2 cm) in the metal while the tops were completely surrounded with cryolite. The initial bulk impregnation rate of sodium was 0.2 % per minute and the maximum bulk concentration appears to be just below 5 %.

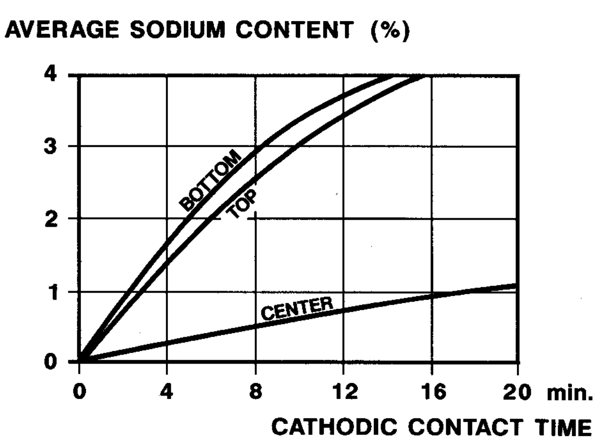

Figure 6 Sodium content at the bottom and top sides as well as in the centre of butts which were connected with the cathodic metal

Current interruption

The extent of impregnation on butts used in pots having experienced several current interruptions was much lower than for butts which came into contact with the cathodic metal.

No impregnation at all was noticed on the anodes which were 10 day old and only half of the anodes being 20 day old were slightly impregnated. However all the anodes being 30 day old were significantly impregnated with sodium. As shown in Figure 7 no impregnation at the top of the butts occurred but the bottom corresponded to the sodium concentration found after 4 minutes of cathodic contact.

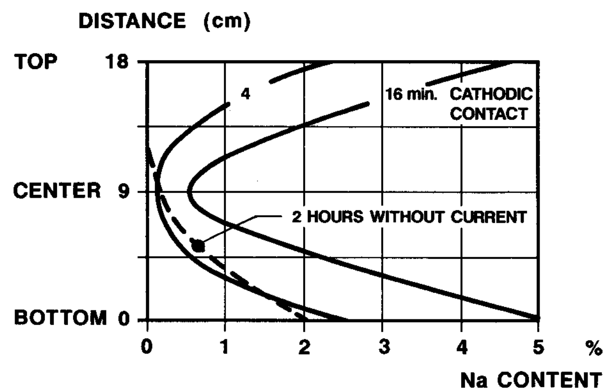

Figure 7 Sodium profile in 30 day old anode butts with 2 hours pot current interruptions compared to butts with 4 and 16 minutes cathodic connection

The average sodium concentration of the 30 day old anode butts was approximately 0.5 %.

Impact of impregnation

Butt properties

The impregnation by bath components significantly increases the apparent density and compressive strength of the anodes as shown in Table I.

PROPERTIES	UNIT	0 min.	16 min.
Apparent Density	kg/dm^3	1.59	1.69
Compressive Strength	MPa	25	38
Na	%	0.02	2.2
Al	%	0.01	1.1
F	%	0.01	3.0

Table I Butt core properties with 16 minutes cathodic contact compared to the butts without cathodic contact (0 minute)

The impact of the sodium contamination on the reactivity to oxidant gases is dramatic as shown in Figure 8.

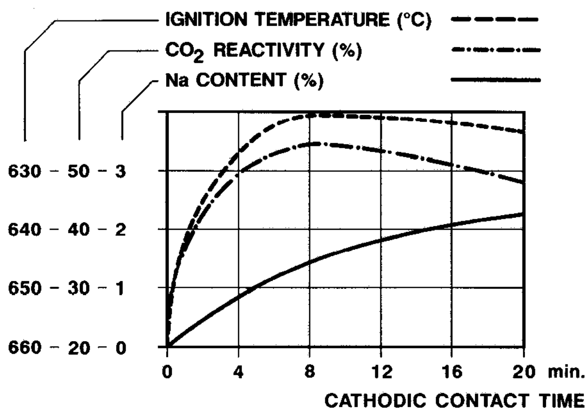

Figure 8 Crushed butt quality as a function of the cathodic contact time

The ignition temperature in air (10°C/min heat-up rate) decreases rapidly from 0 to 4 minutes contact time. The CO_2 reactivity also follows the same trend. For long contact time the reactivity decreases slightly as the ash protects the carbon surface from combustion during the test.

Impact on the anode behaviour

The butts with different cathodic contact times were crushed and their impact on the anode air and CO_2 reactivity were tested with a low sulphur petroleum coke according to a bench scale procedure described in [8].

Two typical green mill situations were tested :

1. butt and coke circuits completely separated
2. butt undersize feeding the ball mill

To assess the impact of fine butt removal, recipes 3 and 4 were prepared with the fractions below 0.5 mm and 1 mm, respectively, removed. The percentage of each butt fractions are summarized in Table II.

RECIPE	Total Butts	8 - 1 mm	1 - 0.5 mm	0.5 - 0.1 mm	Ball mill feed
1	20 %	14.0 %	3.0 %	3.0 %	-
2	20 %	11.2 %	2.4 %	2.4 %	4 %
3	17 %	14.0 %	3.0 %	-	-
4	14 %	14.0 %	-	-	-

Table II Bench scale recipes : butts addition characteristics

The impact of the bath impregnation of butts on the air and CO_2 reactivity of anodes is dramatic. As shown in Figure 9 most of the deterioration of the air reactivity residue occurred when recycled butts were cathodically connected for only 2 minutes. When part of the butts were fed to the ball mill (recipe 2) the CO_2 reactivity level was even worse, as shown in Figure 10 while the impact on the air reactivity was not so significant.

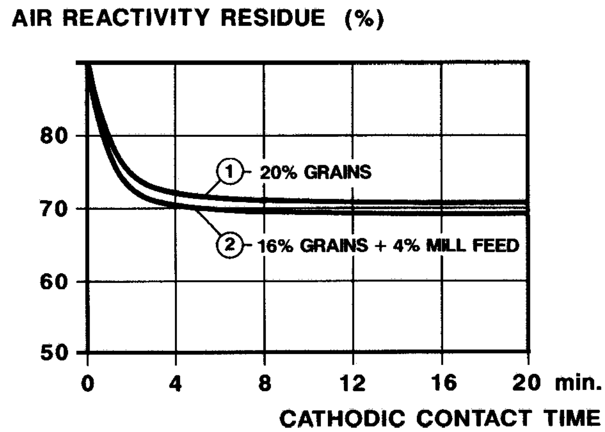

Figure 9 Anode air reactivity residue as a function of the cathodic contact time of the butts

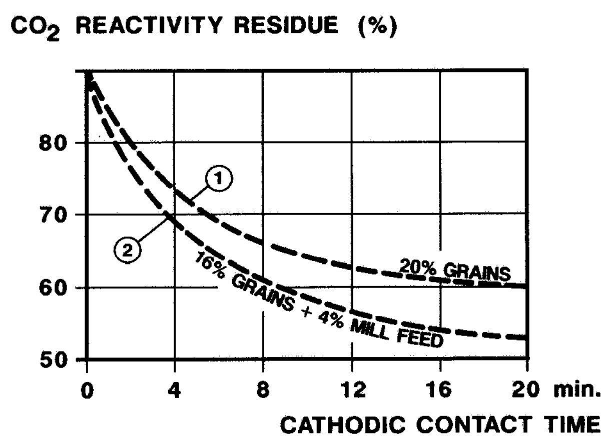

Figure 10 Anode CO_2 reactivity residue as a function of the cathodic contact time of the butts

The removal of the finer butts (recipe 3 and 4) improves the CO_2 and air reactivity as shown in Figures 11 and 12 but the negative impact of the butt impregnation remains unacceptable.

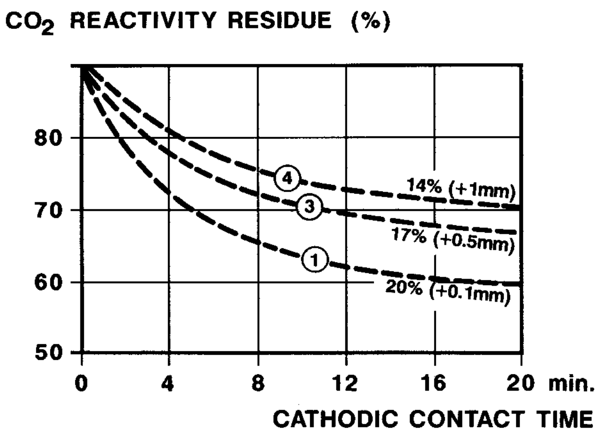

Figure 11 CO_2 reactivity of anodes as a function of the cathodic contact time of the butts comparing different grain size of the crushed butts

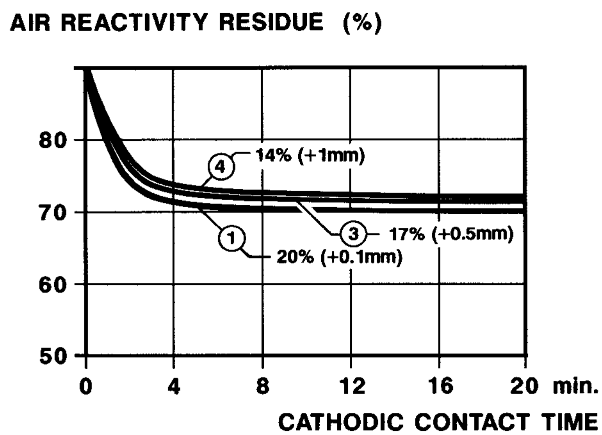

Figure 12 Air reactivity of anodes as a function of the cathodic contact time of the butts comparing different grain size of the crushed butts

Discussions

Impregnation mechanism

The rate of impregnation of a porous body depends on the liquid-solid contact angle. For amorphous carbon like anodes the wetting of the electrolyte bath is rather poor when no electrical potential is applied (no electrolysis). All wetting angle values reported in the literature, [9, 10, 11, 12] for typical bath temperature and composition, are well above 90° (180° = no wetting and 0° = complete wetting). This explains the very slow impregnation rate observed in the laboratory on carbon floating in a crucible of cryolite melt. As shown in Figure 13 the contact angle on positively charged carbon is slightly lower than for conditions without electrolysis.

Nevertheless the penetration of bath in the anodes under normal electrolysis conditions (~ 2 Volts) is negligible. This is partially due to the anode consumption rate (1 - 2 cm/day) being the same order of magnitude as the rate of impregnation.

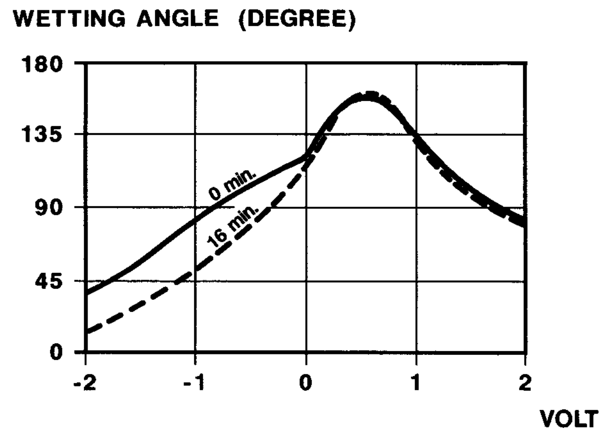

Figure 13 Wetting angle of cryolite on graphite as a function of the potential referred to a graphite reference electrode. Redrawn from [13 and 14]

On the contrary when the electrode is charged negatively the wetting of bath becomes quite efficient and even increases with the electrolysis time. This is a sign that as the electrolysis proceeds, the chemical composition at the carbon-bath interface changes.

It is believed that the sodium formed at the negatively charged anode (during cathodic contact) quickly diffuses into the carbon due to the rapid Na-C intercalation. Consequently, due to this intercalation, NaF is formed by reacting with cryolite at the carbon-bath interface which enhances the penetration of bath into the carbon anode [15,16]. This explains why the impregnation of bath was so rapid when the carbon anodes came in contact with the negatively charged metal. The sodium concentration at the top of the butts was also slightly lower than at the bottom which was in contact with the metal. This suggests that the hydrostatic pressure of the bath is a driving force.

In the case of current interruption reverse electrolysis can occur (i.e. the pot can become a battery) if oxygen is available at the anodes, which is obviously not the case.

Therefore the impregnation mechanism of bath in this case is not well understood and the reasons why only the oldest anodes were impregnated is not explained. The sodium data found in this case suggests that the capillarity forces are not very efficient as the impregnation level was not higher than the bath level on the anodes. This can be explained by the fact that capillarity forces are inversely proportional to the pore size and, as seen in Figure 14, the bath does not wet nor penetrate the micropores.

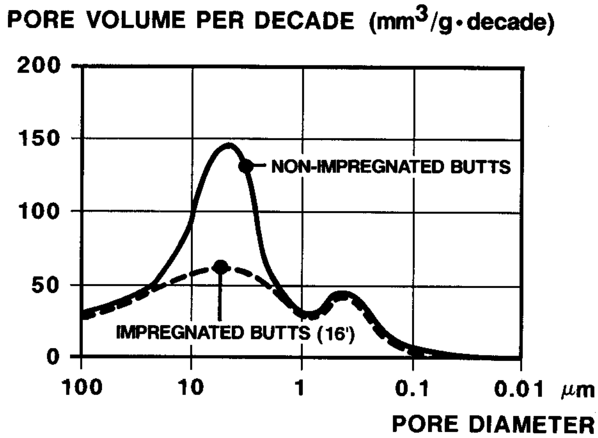

Figure 14 Pore volume distribution of crushed butts materials (1 – 1.4 mm) showing the limit of penetration of bath (~ 2 μm pore size)

Due to this limited penetration the maximum bath content in impregnated butts lies around 15 % by weight even though the anode total porosity is 25 %.

Impregnation of the carbon anodes may occur when the following problems are encountered [17].

- Too small interpolar distance (pinch effect)
- Carbon lumps in bath under the anode
- Broken stem (burn–off)
- Grounded or spiked anodes
- Cell current interruption

Extreme care should be taken when the anode effects are quenched with anodic table movements (pumping [18] or tilting [19]) especially when the number of anode effects per day is higher than usual.

Pushing the anodes down to the metal during the anode change operation must be avoided. Carefull breaking of the crust allows to avoid this bad practice.

The dramatic impact of the impregnated butts on the anode reactivity is enhanced due to the fact that NaF penetrates preferentially into the anode body as suggested by Grjotheim et. al. [14] and confirmed by the data in Table 1. Indeed the relative Na content (35 %) is much higher than in the original acidic bath (bath ratio 1.2) where the Na content was 25 % relative. The basicity of the bath on one hand and the uniform distribution of the crushed butts grains throughout the anode body on the other, explain the extreme catalytic activity observed with the use of impregnated butts.

It should be emphasized that for two baked anodes with the same average sodium content the reactivity of the anode simply contaminated by pieces of crushed bath (mm size inclusions) due to poor cleaning is much better than the addition of impregnated butts.

It is interesting to observe that in case of a severe impregnation problem any improvements made by the electrolysis side or by the green mill in better butt management, will in this case first improve the CO_2 reactivity of anodes and later the air reactivity (see Figure 9). This fits well with observation made of full size anodes prepared with the same raw materials where positive trends were first observed on the CO_2 reactivity residue.

Conclusions

This study has shown that the dramatic impact of bath impregnated butts can not be sufficiently compensated by butt processing modifications. It has been demonstrated that contact of the butts with the liquid aluminum rapidly leads to an unacceptable sodium contamination of the anode. Interruption of the cell current represents a potential risk of impregnation too and more work is needed to quantify completely the impregnation phenomenon under these conditions.

If the impregnation ability is a function of the anode life time, as suggested by this preliminary study, the optimization of the cycle days discussed in [20], can largely be affected by this parameter.

Clearly the sorting of impregnated butts appears to be as important as an efficient butt cleaning. However direct remedies to avoid butt impregnation in the reduction cells are recommended as a first action.

Acknowledgements

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