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A COMPARATIVE EXAMINATION ON AGEING OF CATHODES: AMORPHOUS VERSUS GRAPHITIC TYPE

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A B S T R A C T

In two potlines, shut down because of economical reasons, the possibility existed, to take core samples from the used cathode carbon material.

One line was equipped with standard amorphous blocks and the other with graphitic blocks.

The very wide ranging lifetime of the cells and the two clearly different types of cathodic blocks were of interest for a comparative analysis. In the first step of examination, erosion, melt penetration and change in electrical resistance were investigated.

I N T R O D U C T I O N

The examination of spent cathode carbon lining material from Hall-Héroult cells is a useful tool for understanding and explaining peculiarities in the operating behavior of a pot. The general disadvantage of this procedure is the fact that the results are available only after shutdown and therefore can only be utilized for the next pot generation. Data which are available during operation, like pot voltage, bottom voltage drop, temperatures, bath ratio etc., are used for controlling a cell.

However, these values are normally relative and have to be compared with known standard data for interpretation. To understand entirely what happens in a carbon cathode during electrolysis, it is necessary to go back to the post mortem analysis or laboratory tests. A lot of autopsies of used carbon material have been carried out with very interesting and valuable results (1, 2). One problem with these studies was that they were mostly carried out on failed cells; that means, there was no statistically valid background, in terms of pot age and the reason for the failure.

In this study an opportunity to overcome such uncertainties was available: a whole potline was shut down because of economical reasons, not technical ones. With this, it was possible to study used cathode carbon ranging in lifetime from 81 to more that 2000 days.

E X P E R I M E N T A L

1 Construction of the cell

The cell was an open pot with prebaked anodes, designed in the early sixties with sidebreak and to operate at a current intensity of 90 kA. In the eighties, the operation was changed to a hooded point feed pot with 100 kA current intensity.

Figure 1 shows a cross section through the pot,

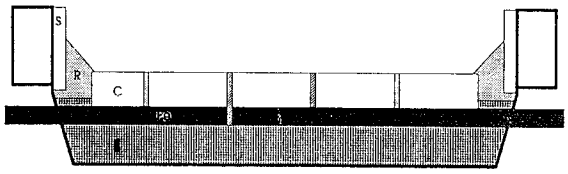

FIGURE 1: CROSS SECTION OF THE CELL

which was built with short amorphous cathode blocks (C), split collector bars (Fe), amorphous sidewall blocks (S), and a standard thermal insulation (I). The joints between the cathode blocks and sidewall blocks / cathode blocks were sealed with cold ramming paste (R) with an application temperature of 20°C.

2 Baking and start up

The cathodes, together with the anodes, were preheated with gas to a temperature of about 400°C. Then a layer of 4-5 cm of liquid aluminium was poured onto the cathode. As soon as all the metal was

frozen, the space between the anodes and the sidewall was filled with crushed bath or cryolite and soda ash. The pots were started with liquid bath with a ratio of about 1.35 (ca. 4 % AlF_3 excess) and kept on this level for 1 week. During the following 3 weeks, the ratio was gradually lowered to 1.15 (ca. 11 % AlF_3 excess) and the bath temperature stabilized between 950 and 960°C.

After 1 month of operation, the seals between the collector bar (Fe) and the steel shell were visually checked and replaced or repaired if necessary.

3 Sampling of shutdown cathodes

From each cathode, 3 samples were drilled (see figure 2): In the wing of the cathode block (1), together with a joint (2) and on top of the collector bar (3).

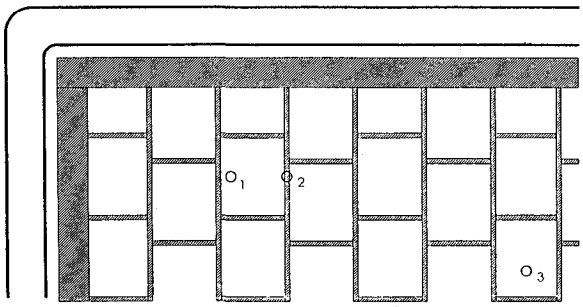

FIGURE 2: POSITION OF THE SAMPLES

The samples were drilled dry and immediately sealed in plastic bags filled with dried nitrogen.

4 Sample preparation

For determination of the laboratory data, the core samples were prepared in the following way. Firstly, residues of adhering bath (hot face) and insulating bricks (cold face) were removed by hand, after which the length of the cores was measured. Then, small slices were sawed from both ends of the cores. In this way, cylindrical samples with right-angled ends were prepared for measurement of the specific electrical resistance. The cut off ends were used for determining the ash-content of the hot and the cold face of the sample. All of these preparations and measurements were carried out under atmospheric conditions but without using water.

5 Graphite samples

The graphitic core samples were taken from another potline. Overall, the type of these cells and the way of operating them were similair to that from where the amorphous samples were taken. Size and amperage of the pots were about 10 % lower, but specific numbers, like cathode current density etc. were nearly the same. The method of drilling, conserving and preparing the samples was carried out in the same manner as with the amorphous samples.

RESULTS FROM AMORPHOUS BLOCKS

The results are shown in the following graphs.

Figure 3 exhibits the decrease in height of the cathode blocks with time. After a period of about two hundred days with high erosion, a time of appeasement occurs, lasting for three years. Thereafter, erosion rises again and scatter increases.

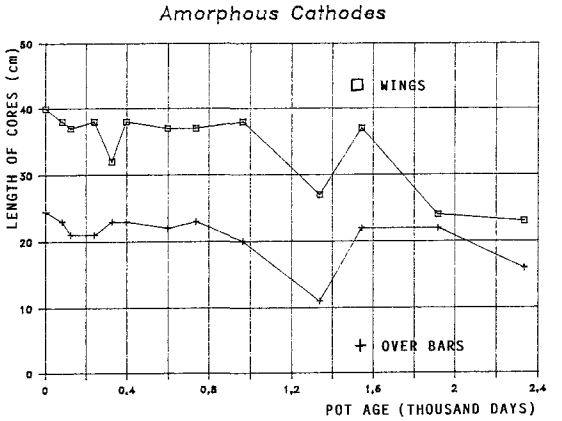

FIGURE 3: CATHODE THICKNESS

The core samples were taken over the wings and over the bars. Therefore the corrosion lines should result parallel to each other. If this is not the case local erosion is indicated. It is clearly visible that this effect increases with time.

Figure 4 shows the ash content of the cores, taken from the cathode wings. Ashes means, in this connection, the sum of the cathode ashes, i.e. mineral material from anthracite, bath infiltration and reaction products. The two lines in the graph correspond to the ash content on the hot and the cold face of the core. Besides the high variation in the ash values of the individual core samples, a certain saturation is again evident after 200 days of operation. A statistically valid difference between top and bottom ash content does not exist. However there does seem to be a detectable tendency that in the early stage of operation, the hot face and later the cold face shows a higher ash content.

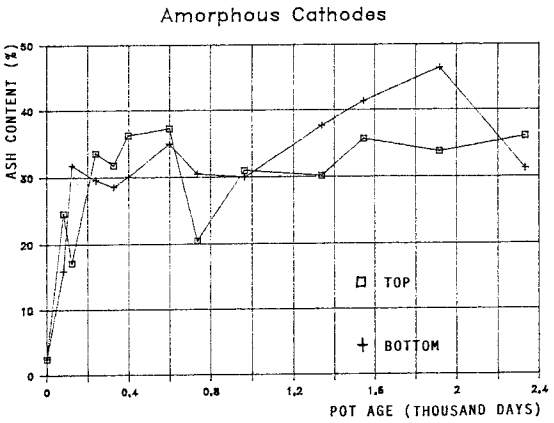

FIGURE 4: ASH CONTENT (WINGS)

Figure 5 shows the amount of infiltrations from cores drilled over the collector bar. The tendency to increase and stabilize is similar to that of the wing samples, but the scatter of the cold end of the cores, located directly over the collector bar, is much smaller. This leads to the conclusion that the wide scattering of the ash data is due to adhering parts of bath or insulation bricks on the ends of the cores.

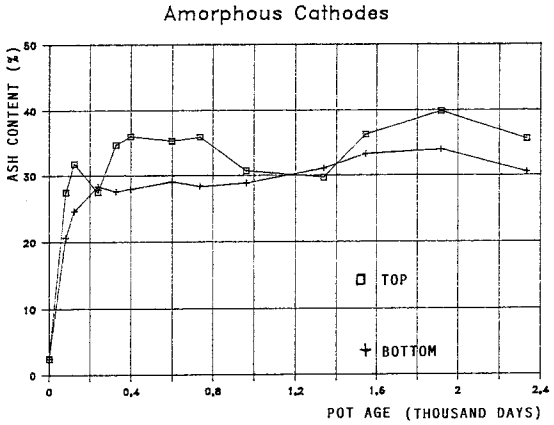

FIGURE 5: ASH CONTENT (OVER BARS)

In Figure 6 the change of the specific electrical resistance is shown. The increase in conductivity based on catalytic graphitization via sodium intercalation can be clearly seen. After a minimum of about 1200 days the resistance increases again and stabilizes at a level of 25 Ω µm.
This is an advantageous development, although it is well known that the cathode voltage drop normally increases with cathode life. One reason for this behavior is the worsening of collector bar to cathode contact by deposition of different insulating salts (3). A second

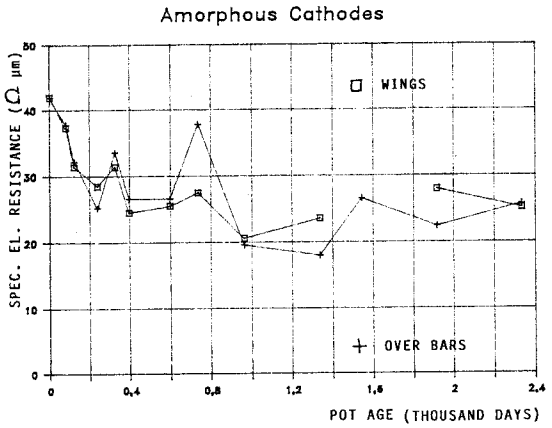

FIGURE 6: SPEC. ELECTRICAL RESISTANCE

cause is the beginning of destruction of the cathode. This second reason is often underestimated, because the cathode is still operating. The fact, that one core (the only one) broke during drilling (of the 1543 day cores) indicates the beginning of weakening, caused by infiltration and temperature variations.

As a provisional result it can be stated that:

a) Bath infiltration stabilizes at 200 days.
b) Erosion continues more or less uniformly with time.
c) Catalytic graphitization is a slow process, that is finished after three years of operation.

RESULTS FROM GRAPHITIC BLOCKS

For the graphitic core samples, much fewer cells were available. Therefore the tendency rather than individual data is presented.

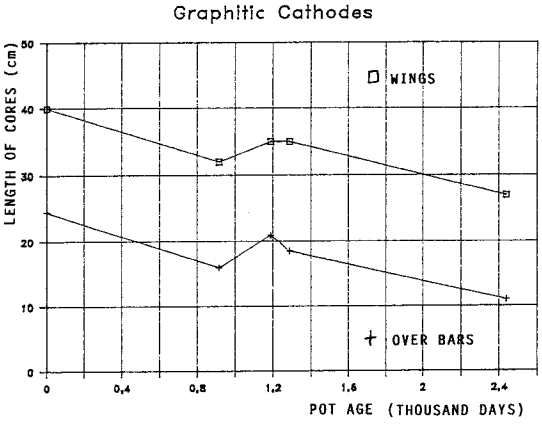

FIGURE 7: CATHODE THICKNESS

Figure 7 shows the erosion of the blocks with time. The parallel decrease of the wing cores and the bar cores demonstrates a very homogeneous erosion.

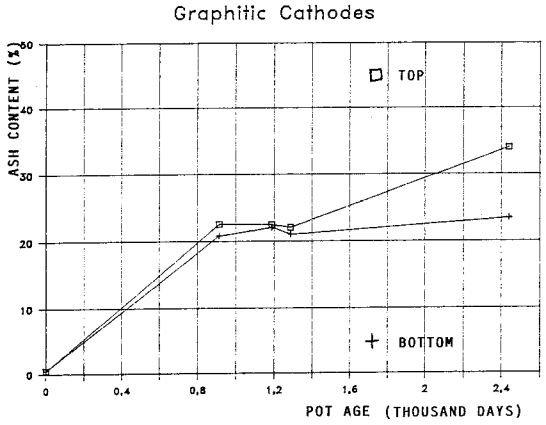

FIGURE 8: ASH CONTENT (WINGS)

In figure 8 the ash content of the wing cores is shown. Aside from one measuring point the distribution of the hot face / cold face infiltration is very uniform.

The same can be demonstrated on the bar cores, as shown in figure 9.

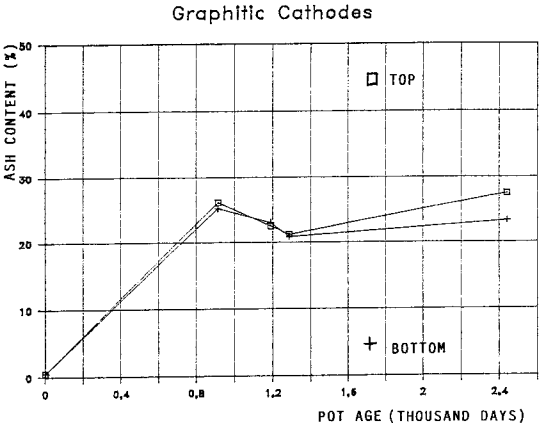

FIGURE 9: ASH CONTENT (OVER BARS)

The specific electrical resistance of the graphitic samples is shown in figure 10. Again, besides one wing core with a (relatively) high resistance (and a high infiltration, see figure 8), a very uniform distribution of resistance values is visible. The slow decrease in resistance with time can be explained by the fact that graphitic cathodes consist mainly of graphite. Therefore a catalytic graphitization can take place only to a limited extent, as depicted in figure 10.

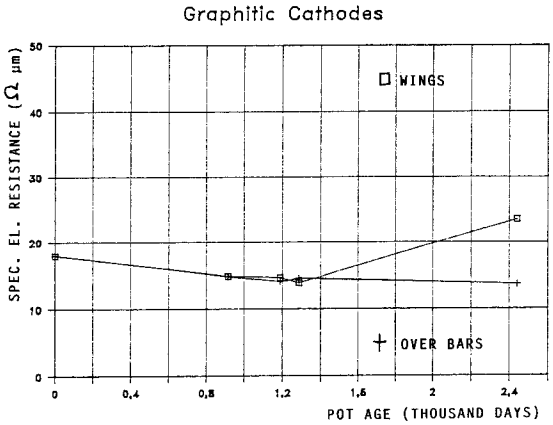

FIGURE 10: SPEC. ELECTRICAL RESISTANCE

D I S C U S S I O N

The discussion about the results relates mainly to the differences in long term behavior of the two different types of cathodes: anthracitic versus graphitic. The general changes in characteristics of cathode blocks with time in operation are well known: erosion from the hot face as a result of mechanical abrasion in combination with Al_4C_3-formation. For both cases higher velocity of the metal pad from poor magnetic compensation is disadvantageous with regards to chemical erosion because of destruction of the protective layers and disturbances to the equilibrium concentrations. Comparing figures 3 and 7 it can be seen that erosion behavior of anthracitic and graphitic cathode material is comparable. At first this result seems surprising, but a look at the wear mechanisms explains the findings:

Chemical erosion over aluminium carbide formation is not influenced by the type of the cathode (4). The mechanical abrasion is difficult to measure in the laboratory under realistic conditions. It can be assumed, that mechanical erosion is related approximately to compressive strength. In these data the anthracitic and graphitic cathode carbon is very similar, therefore comparable behavior can be expected.

A comparison of bath infiltration with the two different types of cathodes (see figures 4/5 and 8/9) shows clearly the dissimilar behavior. Whilst the ash content of the graphitic blocks stabilizes at a level between 20 and 30%, the infiltration of anthracitic blocks reaches 30 to 40%. This is disadvantageous, because the coefficient of thermal expansion increases with bath infiltration, if it solidifies. Therefore

resistance of pot lining against temperature fluctuations decreases with increasing bath infiltration. The higher initial ash content of the anthracitic blocks can be neglected in this context.

Specific electrical resistance is one of the major characteristics of cathode carbon material. The variation with time of the two different types of cathode carbon can be explained as follows: The amorphous blocks, based on gas calcined anthracite, undergo a process of catalytic graphitization via sodium intercalation, yielding a lower electrical resistance. This reaction is accompanied by a volumetric increase (5, 6, 7), which can partly be suppressed by applying mechanical pressure (8). During this period of time the cathode is not stable (9). The sodium swelling of carbon leads to a tighter lining but risks cracking, especially in the first months of operation, when the effect is the strongest.

The same reaction takes place in a graphitic cathode carbon, but in a much smoother way and to a lesser extent. In a graphitic cathode, only the amorphous binder coke can be catalytically graphitised; the so-called filler is already graphite. Therefore the change in characteristics is much less pronounced. This is of fundamental advantage for bigger cells, where the absolute figures for chemical (and thermal) expansion play an important role.

CONCLUSIONS

- The decrease in cathode thickness is a more or less uniform process over the life time of the cell.
- Erosion of amorphous and graphitic blocks is comparable.
- Melt penetration in amorphous blocks is a fast process, being finished after 200 days of pot operation.
- Melt penetration in graphitic blocks is lower than in amorphous blocks.
- The effect of catalytic graphitization can be clearly demonstrated on intact core samples. The resistivity of amorphous carbon drops from 42 Ω µm initially to 25 Ω µm.
- The effect of catalytic graphitization is much less pronounced with graphitic cathodes. The resistivity is lower than with amorphous blocks over the whole potlife.

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