Essential Readings in Light Metals: Electrode Technology for Aluminum Production.
Edited by Alan Tomsett and John Johnson.

From ***Light Metals 1982***, J.E. Andersen, Editor

A STUDY OF SOME ASPECTS OF THE INFLUENCE

OF CELL OPERATION ON CATHODE LIFE

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There are many identifiable causes that can contribute to the ultimate failure of an aluminium reduction cell. They can be broadly classified within the bounds of cell design, materials of construction, method of construction and preheating and lastly, cell operational history. This contribution correlates data obtained from a programme of failed cell autopsies with observations of cell design and operation in relation to the ultimate cause of failure. The following aspects were determined to be of particular importance in achieving a good pot life:

- A sidewall design which can maintain stable heat transfer conditions over the life expectancy of the cell.

- Heat-up and start-up procedures which preserve as near as possible the integrity of the lining materials.

- Operating parameters which minimise temperature disturbances or 'sickness' incidents during the life of the cell.

Case histories of individual failures or of specific cell populations invariably demonstrate the importance of one or more of the above aspects in achieving an improved cell life.

Introduction

Literature dealing with cathode failures has concentrated on the processes occurring within the lining. In recent years the industry has benefited through development of lining materials such as prebaked and graphitic carbon blocks and improved jointing pastes which aim to reduce the uptake of sodium and bath into the lining. This contribution differs in that it focuses on aspects of design and operation which contribute to premature failure of cells.

The observations reported have been made on 150 kA prebake anode cells installed at the NZAS smelter. The cell cathode lining consists of prebaked cathode blocks extending the full width of the cell with a steel collector bar rodded in with cast iron. Insulation consists of a bed of compacted alumina 24 cm thick under the cathodes. The sidewalls were monolithic rammed carbon. For most of the pots studied Silicon Carbide brick walls had been installed against steel shell at the back of the monolithic wall in zones vulnerable to erosion.

The cells were preheated resistively at full line current using a thin layer of sized petroleum coke between the cathode and anode blocks. In the course of this study two different anode sizes were used: 60 cm high and a smaller type 48 cm high with 7% smaller cross sectional area. The current carried by each anode assembly was measured periodically and reclamping performed to maintain even current distribution. Cathode surface temperatures were measured between the anodes and in the centre channel at the end of preheating. A preheat typically took 27 - 32 hours to reach 900°C when using 60 cm anodes and 20 - 24 hours to the same surface temperature with 48 cm anodes. A recent change in preheating practice has been to thermal preheating using diesel fueled burners to attain the same surface temperature as resistor starts in 45 - 50 hours.

The observations and conclusions presented have been derived from a continuing program of cell autopsies. Materials found in failed cells have been examined by X-ray diffraction and chemical analysis. In contrast to previous publications we have concentrated our attention on operating conditions and reported abnormalities in relation to the condition of the cell at failure.

Sidewall Studies

Studies of cell cathodes tend to concentrate on the floor section of cell cathodes despite a significant proportion of failures occurring through the sidewall (1). We have attempted to identify the main features of cell design and operation that predilect a cell to sidewall failure.

Preheating

The monolithic sidewall construction is characterised by being poorly baked at the end of the resistor preheat cycle. Baking continues for some days after "fluxing" with liquid "bath" (i.e. electrolyte) as evidenced by the fumes emitted from cracks and joints in the cell lining from pyrolysis of binder pitch. The maximum temperature observed on the external steel shell during this period is 250 - 300°C. It has been demonstrated by Jones and Hildebrandt (2) that carbon deposited by low temperature pyrolysis is more reactive as it has both a high surface area and a less graphitic structure. The quality of the bake-out achieved will therefore affect the integrity of the wall, its resistance to erosion, air oxidation and penetration by sodium and bath material, and the thermal characteristics of the cell itself.

Ledge Formation

The initial operation of a new cell followed traditional practices with higher than normal bath temperatures and bath ratio, followed by a reduction to standard operating conditions during the first month.

During the initial operation of new cells the temperature is above the maximum under which ledge formation occurs and direct contact between bath, metal, and sidewall carbon occurs. We have measured cell wall thickness as a function of time (over successive feeding cycles) and as a function of the age of the cells. Profiles are shown in Fig. 1. A permanent stable ledge is apparently not formed in the first six months of operation. The difference in dynamic and actual ledge thickness was determinated by monitoring the ledge profile under both normal conditions and under conditions where extra pot voltage had been applied. In the latter case once the ledge had completely melted stable conditions could be observed. In the aged cell (i.e. after 66 months) the stable ledge thickness was approximately 5 cm but this increased to 8 cm during the operating cycle. The frozen ledge in the younger cell (6 months) disappeared completely during each operating cycle - that is between break and feed.

Sidewall Reactions

Considerable sidewall erosion therefore occurs in the early life of the cell, until operating temperatures and sidewall heat losses allow formation of a permanent protective ledge. According to Grjotheim et al (3) the formation of Al_4C_3 proceeds in the presence of bath and metal provided the alumina concentration is below 4 wt%. These conditions exist for the early operating cycle of the cell and would be accelerated by the high metal solubility associated with the higher than normal bath ratio and temperature. Dewing (4) has demonstrated that aluminium carbide has a solubility in bath of 0.35 wt%. We have not noted the characteristic colouration of aluminium carbide in bath, although the concentration probably remains below 0.35% due to the dissolved aluminium carbide being oxidised at the anode by CO_2.

$$Al_4C_3 + 9CO_2 \rightarrow 2Al_2O_3 + 12CO \qquad [1]$$

If the carbide formation reaction proceeded on the more reactive carbon sites, a general erosion of the inner surface of the cathode could be expected during the early stages of a cell's life with maximum attack occurring on the sidewall carbon. Measurements of sidewalls confirm the rapid carbon erosion as would be expected by this mechanism. This is supported by the excessive carbon dusting observed in bath during the early life of the cell, the ash analysis of which corresponds to sidewall carbon material. We have clearly identified the presence of carbide in new pot bath by X-ray diffraction analysis.

Observations on Failure

Examination of cell sidewalls was often hindered by bath having flooded across the sidewall. However, where this did not occur there was a marked difference in the residual sidewall carbon between that against the outer steel shell and that on the inner working surface. Preferential oxidation of the binder carbon was prominent in areas where air penetration was possible (around cathode collector bars and under the sidewall deckplate) creating soft powdery carbon with characteristic ash colouration. Zones of

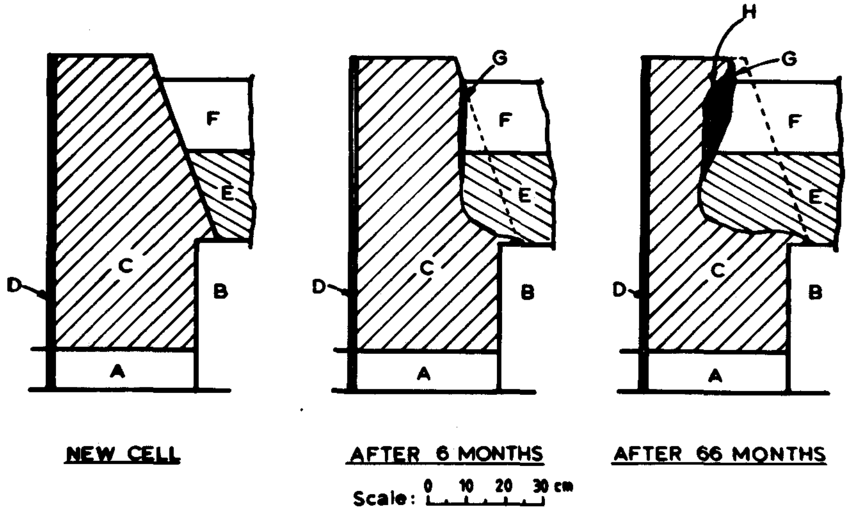

Figure 1 - Sidewall Erosion and Ledge Profiles

A. Collector Bar
B. Prebaked Cathode
C. Sidewall
D. Shell
E. Metal Pad
F. Bath
G. Transient Ledge
H. Stable Ledge

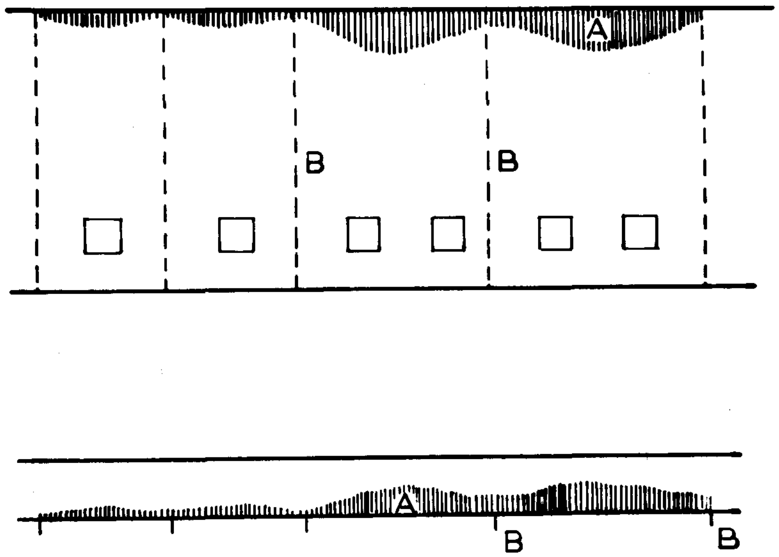

Figure 2 - Side and top views of sidewalls showing the location of unbaked (or oxidised) carbon relative to shell cradle support spacing.

A. Powdered Carbon
B. Cradle Centres

powdery carbon tended to be a distorted mirror image of the steel shell distortion, and became extreme in areas where the spacing of shell supporting cradles was increased (Fig. 2). Other areas of soft, powdery carbon but without ash colouration were noticed in 'colder' areas of the sidewall - the result of partial volatilisation of the binder pitch due to the slow, low temperature baking of the sidewall.

The final eroded shape of the inside of the sidewall at failure is seemingly controlled by a number of factors, the major factors being the:

- Overall thermal conductivity of the sidewall system (which is governed by the carbon quality of the sidewall and the degree of shell distortion.
- Metal velocities in the periphery of the cell (which are influenced by the metal depths and the magnetic fields).
- Thermal profiles attained during operation of the cell (these are controlled by the parameters of cell operation and cell design).

Based on a number of cells studied it was apparent that the wear profile and rate of erosion correlated best with the metal pad velocity. Cells with bus-bar configurations that led to higher velocities eroded the sidewalls faster. It should be emphasised that sidewall erosion can only occur when the cell temperature prevents the maintenance of a ledge. Thus erosion should follow predicted isothermal profiles (5) and this was observed in zones where the other effects are minimal.

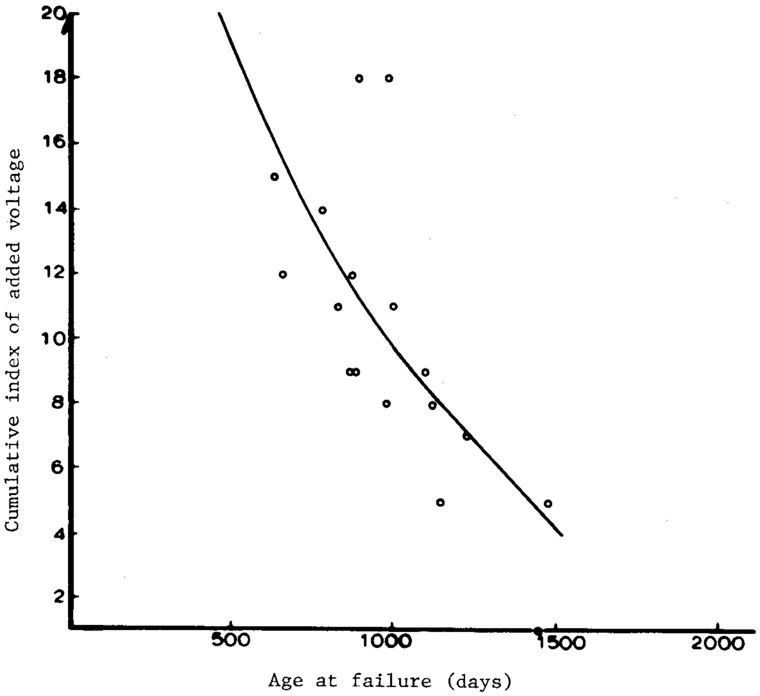

Figure 3 - Effect of cumulative additional cell voltage on sidewall life.

Because cell design should maintain the protective frozen sidewall ledge, erosion should only be associated with abnormal cell operations - particularly those that result in extra heat generation. The effect of such an abnormal operation on sidewall life is demonstrated in Fig. 3 where reported occurrences of additional cell voltage are correlated with cell life at sidewall failure.

In older cells it was found that the zone of erosion moved lower suggesting a movement in the isotherm as the bottom insulation degraded. In these cells the lower sections of the carbon material showed the presence of sodium. The swelling effects of this material (6,7) would cause further degradation of the structure.

Cathode Studies

Preheating of Cathode Linings

The primary aim of preheating is to raise the cathodes to the operating temperature without producing abnormal thermal gradients across the working face of the cathodes and down through the thickness of the lining. The effects of non-uniform heating of cathodes (8) leads to the blocks cracking and ultimately reducing the service life. Similarly, the temperature distribution across the working face of the cathodes is important since fracturing of the cathodes may arise from the thermal shock incurred on fluxing with molten bath. A typical resistor start preheat is shown in Fig. 4. This cell had thermo-couples implanted under cathode blocks during construction, thus enabling better estimation of vertical temperature distributions as is shown in Fig. 5.

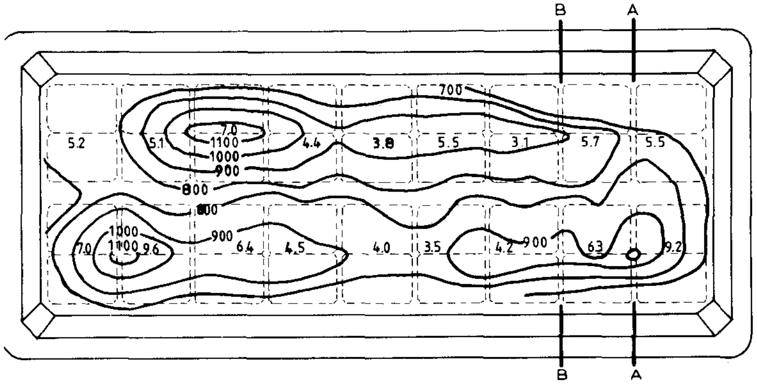

Figure 4 - Surface isotherms after 26 hrs resistive preheat of a cell, showing percentage of total current loading drawn by each anode.

Despite reclamping, uniformity in current is seldom attained. It is seen that a general correlation exists between current loadings and the final temperatures attained. From studies on a large number of resistor start preheats the following general conclusions may be drawn:

- The heating rate under the anodes is approximately twice that for the centre channel.
- The thermal gradients across the working face of a cathode are 300°C/m while the maximum gradients observed can be as high as 1100°C/m. Vertical temperature gradients are not as severe since heat cannot be easily lost from the bulk of the cathode.
- Maximum heating rates are achieved with the smaller (48 cm) anodes, these also achieve a much higher final temperature. This is probably due to the smaller heat capacity of the anodes and the reduced surface area available for the heat dissipation.
- Air burning around the edges of the lower face of an anode during preheat can lead to a disparity between observed current distributions and the final temperatures achieved. The reduced contact area further increased the rate of air burning by an increase in the current density and consequentially the heating rate.
- Temperatures up to 1500°C can occur in localised zones due to high current loadings induced by irregularities in the anode surface and variations in the thickness of the resistor bed.

By comparison, thermal preheating using diesel-fired burners has been shown to provide a less severe heat-up rate and improved temperature distribution (Fig. 6 and 7). Although the use of this technique is too recent for us to estimate its impact on cell life, an autopsy of a healthy cell examined after cut-out revealed none of the surface cathode cracking typical of the resistive preheat method.

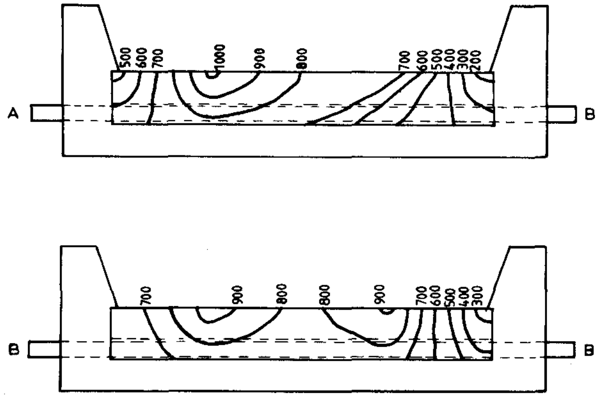

Figure 5 - Estimated vertical temperature distribution of cell section, resistive preheat.

Cathode Reactions During Cell Life

Sodium Absorption: The uptake of sodium in a new cell can be explained by the tendency for sodium to be absorbed or intercalate by direct reaction with the cathode carbon. The extent to which this occurs can be reduced by making the carbon cathode more graphitic (7). Following metal transfer into the cell direct sodium deposition mechanisms are inhibited, although sodium penetration into the lining continues as is evidenced by the swelling and distortion of the cathodes. In an attempt to explain this we have measured the sodium content of the metal pad as a function of cell age, these results are summarised in Table 1. Because the expected equilibrium sodium content is related to the bath ratio and temperature (9,10) results are presented as the difference between equilibrium and observed sodium contents. From

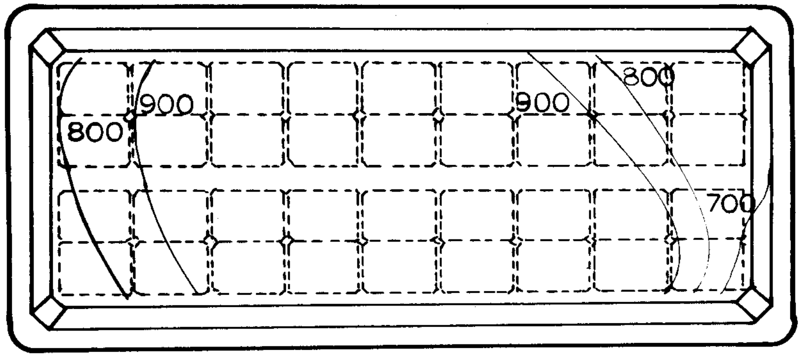

Figure 6 - Typical surface isotherm at Fluxing, thermally preheated cell.

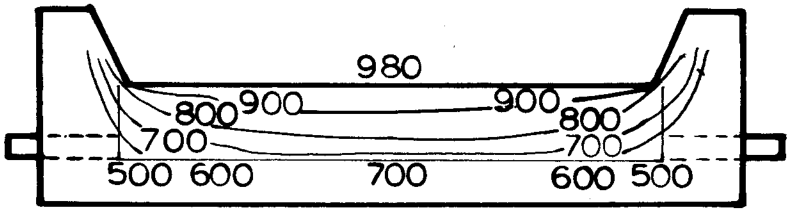

Figure 7 - Typical sub-cathodic isotherms at Fluxing, thermally preheated cell.

studies of cathode polarisation (11) and the cathode reaction mechanism one would expect the sodium content of the cathode metal to exceed equilibrium values unless sodium is being removed by, for example, the penetration of sodium into the cathode lining. The results obtained show that a deficit is higher during the first few days of cell operation indicating that sodium is absorbed more readily in the early life of a cell. In all cases studied the migration of sodium was found to occur preferentially through poorer grade carbon.

Table 1. Observed Sodium Deficits in Cathode Metal

Cell Age (Days)	Average Deficit (ppm)	Range	No. Samples
0 - 10	130	80 - 150	13
10 - 50	110	90 - 130	12
50 - 100	90	70 - 110	14
100 - 500	80	50 - 100	20
500 - 1000	90	70 - 100	15
1000 - 1500	90	50 - 130	21
1500 - 2000	90	70 - 120	16

Bath Penetration: The absorption of bath occurs preferentially through cracks in the cathode lining, through the more porous carbon in cathode joints (slots) and through sidewall seams at the cathode block ends. The quantity of bath present in the cathodes appeared to be correlated with the extent of damage incurred at start-up.

Bath-Sodium Reactions: The dominant feature of the materials underneath cathodes in failed cells was the extent to which bath had been reacted with sodium. The pattern of reactions was consistent over a large number of cells and these reactions seem to be a dominant factor in the ageing of cells. The primary reactions was the production of aluminium carbide on the underside of the cathodes by:

$$4Na_3AlF_6 + 12Na + 3C \rightarrow 12NaF + Al_4C_3 \qquad [2]$$

Immediately under the Al_4C_3 layer a layer of nearly pure NaF crystals of columnar form was observed. The Al_4C_3 layer appeared to act as a diffusion barrier to carbon. Further reactions with sodium occurred by:

$$Na_3AlF_6 + 3Na \rightarrow 6NaF + Al \qquad [3]$$

when there was sufficient bath present. For cells with a limited amount of bath present below the cathodes the reactions did not appear to proceed past [2] producing a bed of NaF crystals 2 cm thick. For cells found with a thick (4 - 6 cm) bed of NaF crystals, aluminium was always associated with the crystals as small intercrystal flakes and layers between the Al_4C_3 and NaF. Considerable attack on the underside of the collector bars had occurred in these cells with up to half of the bar thickness either transformed to alloy or replaced by a heterogeneous mixture of Al_4C_3, NaF, ferro-aluminium alloy and bath constituents.

Consequences of Cathode Reactions

Reactions of the type discussed can lead to a number of effects which are deleterious to the cathode carbon and also to the ease of cell operation. The slow formation of NaF crystals under the cathodes exerts sufficient pressure to result in a general heaving of the cathodes.

Although minor cracks were usually filled with carbide which precluded further bath penetration, wider cracks contained crystallised fluoride which probably caused widening and extension of the cracks by the same mechanisms as those occurring under the cathodes. The aluminium formed underneath the cathode by bath reaction with sodium attacks the underside of the collector bars and can also be injected back in to the metal pad reducing metal purity. Severe iron contamination of the cathode metal often follows high temperature episodes, suggesting a temporary melting of the bath in the pores of the cathode lining.

The cathode ageing processes described create increasing operating difficulties during the life of the cell, with respect to heave and disturbed metal pad behaviour, impaired cathodic current distributions and progressive degradation of the subcathodic insulation. As a result, the ageing cell requires increasing power input to maintain thermal balance, and operates at lowered efficiencies due to disturbed current distribution and irregular anode - cathode separation. Ultimate failure of the cell is generally caused by cathode degradation to the extent that a direct short circuit can occur between one or more of the steel collector bars and the pot metal pad. The resistance heating so generated rapidly results in dissolution of the bar and catastrophic leakage of the cell.

Conclusion

It has been our intent in this contribution to create a conceptual basis on which the causes of cell failure and the processes leading to failure may be understood.

The examination of failed cells has elucidated a number of effects which appear to be common to the ageing processes of all cells. By correlating these effects with cell design and operational history, improvements in construction and operating procedures can be highlighted to improve the life expectancy of future cells. For example, sidewall failure can be controlled by:

- Ensuring complete bake-out of the monolithic carbon at start-up.
- Providing effective air sealing and shell support.
- Choosing construction materials and operating parameters which provide for maintenance of protective ledge and stable heat balance throughout the life of the cell.

Similarly premature cathode failure can be controlled by:

- Use of a preheating procedure which avoids thermal stressing.
- Minimisation of bath penetration into the lining by correct design, reconstruction procedures and selection of materials. It has been shown that subcathodic reactions, primarily between absorbed sodium and bath, play a dominant role in the degradation of the cathodes and can lead to difficult and

inefficient cell operation.

- Avoiding high temperature and 'sickness' incidents which can accelerate the rate of bath penetration and degradation of subcathodic insulation.

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