

LOSS IN CATHODE LIFE RESULTING FROM THE SHUTDOWN AND RESTART OF POTLINES AT ALUMINUM SMELTERS

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Abstract

Cathode damage due to cooling resulting from the shutdown and restart of cells is commonly recognized in the primary aluminum industry. Cooling cells to ambient temperature results in the freezing of bath and metal in cells and causes irreversible and non-repairable damage to the carbon cathode lining. Cooling ultimately causes the formation of numerous cooling cracks on the surface of cathode blocks and in the seams between blocks. The cracks are caused because the strain setup by thermal gradients in the cooling cathode lining exceeds the strain capacity of the sodium saturated cathode. Carbon cathode behaves as an elastoplastic material under stress. Sodium intercalated between carbon layers changes the properties of carbon cathode blocks causing them to become less elastic and more brittle. The loss in potlife due to the shutdown of potlines can be substantially different at smelters depending on the specific circumstances.

Introduction

Power modulations have been conducted in aluminum smelters by; a) reducing the power in potlines or, b) total interruption of power for short intervals in potlines [5-7]. Repetitive cooling due to modulations may eventually result in the precipitation of hard corundum alumina under the metal pad that causes operational difficulties and decreases performance. However, little cathode damage has been reported as a result of the temporary cooling due to power modulation.

Longer power interruptions (>3 hours) due to rectifier failures or loss in power transmission cause extreme difficulty in pot operations. In some instances extended power outages result in first, freezing bath (~850°C) and later freezing aluminum metal (660°C) in cells, and the shutdown of all operating cells in the potline. It takes a great deal of hard work, experience, and pre-planning in order that smelters survive long power interruption in potrooms. Three different irregular power events are shown in Figure 1 for a potline of 175 kA prebake cells.

- 1) Extended periods of operations at reduced amperage (140 to 160 kA)

There is limited information in the literature regarding the loss in potlife due to shutdown and restarting cells resulting from power interruptions. Loss in potlife has been reported to vary widely from 100 to 400 days [1-4]. The cause for variation in the loss in potlife and number of premature failures at smelters has not been examined. While there are numerous studies and publications regarding the temperature gradients and resulting stresses that occur in cathodes during preheating and cell operations, very little is known about the phenomenon during rapid cooling of cathodes

Potline Power Reductions and Interruptions

Potlines may experience power reductions and power interruptions ranging from very short intervals to long extended periods of time as indicated in Table I due to specific events at smelters. Short term power reductions or interruptions from 10 to 30 minutes are commonly carried out at some smelters for power modulation in order to take advantage of reduced power costs or may be necessary to change out cathodes and make potline bus bar and rectifier repairs.

Table I. Consequences of Power Reduction and Interruptions in Potlines

Power Event	Duration	Cause	Result
Reduced power	<1 hour to several months	Power modulation, rectifier repairs	Cooling to ~940°C; anode effects, excessive muck, increased ledge and ridge
Short power Interruptions	1 to 2 hours	Power modulation, change cathodes, repairs, rectifier failure, power transmission	Cooling to ~900°C; anode effects, excessive muck and ledge, shutdown some cells
Long power interruption	>3 hours	Rectifier failure, power interruption	Cooling to 25°C; freezing and shutdown of all cells in potlines

- 2) Short (~1 hour) interruption of power
- 3) Long (>3-hour) interruption of power that resulted in the shutdown of all cells in the potline.

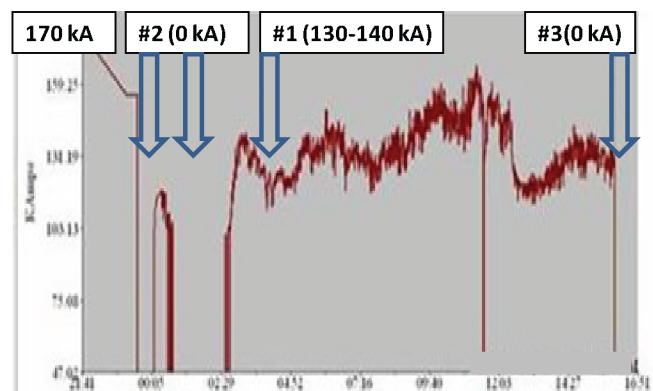


Figure 1. Changes in potline amperage during power reductions (#1) and power interruptions (#2&3) in a potline.

If power interruptions are anticipated specific steps can be taken to minimize problems and reduce the risk of freezing of bath in pots, for example, increased pot voltage and amperage prior to the event, and adjustments to the alumina feed control, bath and metal levels, bath chemistry and modification of work practices, e.g., anode setting and covering to reduce the risk of freezing of all the bath in pots.

Potline Cooling

Cooling occurs in potlines when the amperage is significantly reduced or power is interrupted. The power input to cells is reduced or stopped which reduces the internal cell heating in the anodes, bath and cathode. The cell continues to lose heat at the same rate from the cathode sidewall surface and the anode top surface resulting in a rapid decrease in bath temperature, at a rate of 15-20°C in six hours [5]. The heat losses out of the sides of cells may decrease during cooling due to the freezing of cryolite and formation of thicker side ledges. The average bath temperature for the prebake cells in the potlines shown in Figure 1 prior to the power interruption was 955°C. Cooling due to the power interruptions in the potline decreased the bath temperatures in all cells during cooling.

- The average bath in cells decreased to 920°C in cells during the first 24 hours period,
- 24 Hours after the power interruption bath temperatures were measured to be as low as 850°C in individual pots.

Large variations in bath temperatures in individual cells are due to differences in cell voltage, open areas in the pot crust, anode covering and multiple anode effects.

Large changes in cell operational parameters due to cell cooling were determined by Dupuis and coworkers [8] using thermal modeling and actual measurements. The measurements were taken during a 3-hour power shutdown event on a 240 kA cell preceded by 4 hours of preheating,

- The bath temperature decreased from 960°C to 920°C causing,
 - a. bath superheat decreased 15°C,
 - b. electrical resistance of the bath increased by 20%.
- The bath volume decreased in cells due to formation of frozen ledge causing,
 - a. bath level decreased from 18 to 12 cm,
 - b. AlF_3 in bath increased from 9% to 13%,
 - c. Al_2O_3 in bath increased temporarily by 1%.

Increased Muck and Sludge Formation due to Cooling

During cell cooling the sidewall ridge of mostly frozen cryolite grows farther under anodes. The solubility of alumina is significantly reduced at lower bath temperatures and the undissolved alumina sinks and forms muck deposits on the bottom of cells under the aluminum metal pad. The density of bath becomes heavier at lower bath temperatures and mixes with metal causing metal rolls in cells. These events cause severe cell instability, or high pot noise due to the irregular current flow in the metal which eventually requires higher pot voltage.

Cathode Cooling Cracks

Cooling aluminum cells from 960°C to ambient 25°C causes the formation of numerous cooling cracks on the surface of cathode blocks and in seams between blocks.

- The width of cooling cracks observed is 1.6 to 3 mm and they often extend the length of the cathode blocks, ~300 cm.
- The distance between cooling cracks varies widely, but they often are found to occur about two cathode blocks apart.



Figure 2. A cooling crack formed in the cathode block after an extended power interruption and cell shutdown.

The cathode crack shown in the Figure 2 was formed in the cathode block during cooling and not during cell operation as indicated by the absence of bath or a yellow film of aluminum carbide on the surfaces of the crack. Cooling cracks, without bath or aluminum carbide are observed in the cathode carbon lining in nearly all cathodes in which the metal pads are removed and the surface is cleaned for inspection.

Mechanism for the Formation of Cooling Cracks

Øye and Sørli reported that the shutdown of cells will always lead to cracks in the rigid carbon plane that creep and plastic deformations of the pot shell will aggravate the cooling-crack opening as the supporting pressure from the surrounding steel shell diminishes when cooling starts [9].

Fracture Behavior and Propagation of Cracks in Cathodes

The fracture behavior of carbon cathode has been described by D'Amours and coworkers as *elastoplastic* in a study of the thermo-electro-mechanical behavior of cells during preheating [10]. Carbon cathode blocks initially behave elastically with reversible deformation as stress is applied, but when stress increases the carbon material starts to behave in a plastic manner with irreversible deformation until fracture occurs. It is projected that carbon cathode also behaves in the same *elastoplastic* manner due to high stress induced by large temperature gradients when cells are rapidly cooled to ambient 25°C. In addition the carbon cathode is substantially weakened as it undergoes ductile-brittle transformation during cell operation. Intercalation of sodium into carbon causes micro-cracking during operation. Peripheral penetration of the cathode material by sodium can be considered as a short crack opening-up between the atomic carbon layers creating tension normal to the atomic layer structure at the base of the crack. If the tension rises to a sufficient degree the crack will be propagated catastrophically throughout the interlayer plane, breaking down the bonding of inter carbon atomic layers.

Large Thermal Gradients Due to Cooling

Rapid cooling of cathodes due to power interruption generates an uneven temperature distribution in the cathode lining which results in a thermally induced mechanical stress sufficient to cause cracking. Due to the rapid cooling in shutdown cells it is suspected that the temperature gradients due to cooling could be greater than those experienced during preheating. It has been determined that when a system of parallel equidistant cooling cracks propagates due to cooling of hot materials, the cracks reach a certain critical depth at which the growth of every other crack is arrested. The intermediate cracks open about twice as wide and advance further as cooling penetrates deeper [11-12].

Once a cathode has developed cracks, gaps, etc. there is no known method to repair the damage. When aluminum cells are restarted it is anticipated that the majority of the cooling cracks in cathode blocks close-up. Crack propagation is favored by large grain size, lower temperature, and higher stress. Thus as the temperature increases when pots are restarted a higher stress is required for cracks to propagate. Cracks weaken the carbon lining as some cracks fill with molten aluminum and/or bath, and some cracks continue to expand and link-up. The result is weakened blocks, leakage and eventual early failure. The long wide cracks contribute to the irregular distribution of electrical current in the cathode blocks.

Thermal Expansion of Cathode Blocks

Cathode carbon blocks expand when heated and shrink when cooled in an elastic manner. However when the stress becomes too high cathode blocks permanently deform in a plastic manner. Cathode blocks have a higher thermal expansion coefficient in the *direction perpendicular to the direction of extrusion*, (width of the cathode blocks), typically from 2.6 to 3.6 $\mu\text{m}/(\text{K}\cdot\text{m})$. The thermal expansion coefficient in the *same direction of extrusion* (length of cathode blocks) is 2.4 to 2.9 $\mu\text{m}/(\text{K}\cdot\text{m})$. There is a small trend for higher thermal expansion coefficient for higher graphite content in cathode blocks. The value for thermal expansion coefficient for cathode blocks increases 0.00175 per degree increase in temperature. The coefficient of thermal expansion for cathode block containing 30% graphite increases from 2.7 to 4.0 $\mu\text{m}/(\text{K}\cdot\text{m})$ in the direction perpendicular to extrusion with the increase in cathode block temperature from 200 to 1000°C as reported by Sun et.al. is shown in Table II [13].

Temperature	Parallel to direction of extrusion $\mu\text{m}/(\text{K}\cdot\text{m})$	Perpendicular to direction of extrusion $\mu\text{m}/(\text{K}\cdot\text{m})$
200°C	1.8	2.7
600°C	2.5	3.4
1000°C	3.2	4.0

Table II. Thermal expansion of carbon cathode materials versus temperature.

Thermal Expansion and Shrinkage of Cathode Carbon Lining

The length of the cathode carbon lining increases 0.4% when cells are heated from 25 to 960°C as shown in Table III. If the carbon lining behaves in an elastic reversible manner then the carbon would shrink by the same amount when cooled to ambient.

- The total thermal expansion/shrinkage in the direction perpendicular to extrusion, (across the width of all the cathode blocks and the width of all the seams), in the cathode carbon lining is from 2.7 to 6.9 cm, depending on the length of cells.
- The total thermal expansion/shrinkage in the extrusion direction, (the length of cathode blocks), is significantly less due to the lower expansion coefficient and less distance. For example the thermal expansion for a 300 cm long cathode block is less than 1.0 cm, as measured from side-to-side of the cathode lining in cells.

Potline Current kA	Total Cell Length cm	Total Thermal Expansion & Shrinkage cm	Increase %
100	700	2.7	0.4
175	790	3.0	0.4
200	850	3.3	0.4
300	1415	4.4	0.4
500	1800	6.9	0.4

Table III. Total linear thermal expansion and shrinkage across the length of the potlining in cells at startup and cooling.

Expansion of Cathode Blocks Due to Sodium During Cell Operation

Cathode swelling or expansion due to the ingress of sodium has been found to cause a much larger deformation and stress in the cathode carbon block than thermal expansion. Brilliot indicated that sodium metal penetrates and diffuses into the cathode lining with the formation of C60Na and C68Na intercalation compounds between the graphite layers causing swelling and disruption normal to the crystal planes. [14].

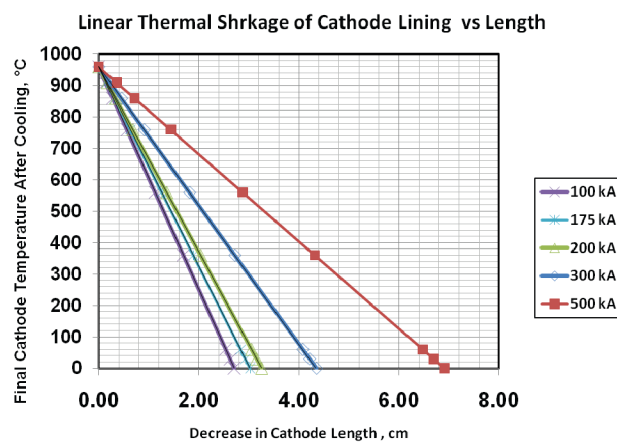


Figure 3. Linear thermal shrinkage for the total length of the cathode lining of 100, 175, 200, 300 and 500 kA cells.

Modeling by Sun et.al, demonstrates that sodium expansion gradient and thermal excursion are two main reasons for cathode carbon block heaving and that creates a void under the blocks [12]. The stress in the cathode carbon caused by both sodium expansion and thermal expansion can exceed the mechanical strength of the cathode carbon block causing cracking. If stresses due to cathode swelling become too high, heaving cracks occur near the pot centerline, lengthwise of cells, rather than at the ends of cathode blocks.

Cooling the Cathode Lining to 25°C Results in Cathode Cracks

Cooling cracks form in cathodes as a consequence of the mechanical stresses resulting from the large temperature gradients cathode carbon lining during rapid cooling to ambient temperature. During cell operation the cathode blocks and seams become saturated (>3%) with sodium that intercalates into the carbon lattice. This causes swelling and changes the properties of the carbon lining which makes the material less ductile and more brittle.

- Rapid cooling of cathodes to ambient due to power interruption generates an uneven temperature distribution in the cathode lining which results in a thermally induced mechanical stress sufficient to cause cracking.
- The cathode blocks are significantly weakened by micro-cracking caused by the diffusion of sodium into the carbon lattice.
- Sodium intercalated inside the carbon cathode causes additional mechanical stresses during the shrinkage of the cathode lining.
- Consequently cracks form on the surface of the cathode during cooling to relieve the high mechanical stresses that develop due to the unequal temperature distribution in the cathode.

Graphitized Cathode Blocks Reduces the Number of Cooling Cracks

Despite having a higher thermal expansion, it is expected that cells with graphitized cathode blocks will have significantly fewer cooling cracks in the cathode lining when the cells are shut down.

- A significantly lower diffusion of sodium into cathode blocks reduces the permanent plastic deformation under stress, thus reducing the total shrinkage of the graphitized blocks (0.5%); the carbon material remains more elastic during reversible shrinkage; and stresses are reduced due to the lower amount of intercalated sodium during shrinkage of blocks.
- Also, a significantly higher thermal conductivity of the cathode lining reduces the temperature gradients during cooling and thus lowers the mechanical stresses.

This hypothesis has been confirmed thus far in a small number of observations of potlines that were shutdown and restarted.

Cooling the Cathode Lining to 850°C Does not Cause Cathode Cracks

Potline power interruptions of short durations, less than 2-3 hours, cool cells from 960°C to 850°C. Thereby they do not result in

sufficient shrinkage or thermal gradients in the cathode lining to cause high stress which is required to form cooling cracks, thus not generating a major impact on the cathode of life.

- The calculated linear thermal expansion, as well as shrinkage, is less than 1 cm across the width of all cathode blocks and all seams (length of the cell).
- The bath temperature will eventually return to normal when the cell heat balance is re-established. However repetitive cooling could eventually cause freeze isotherm cracks to occur in cathode blocks due to actual freezing of bath components within the cathodes. These cracks are characterized by a shape that closely follows the contour of to 850-900°C temperature isotherms within blocks [9].

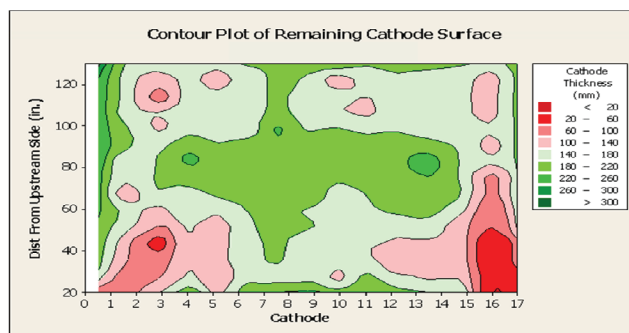


Figure 4. Contour Plot of the cathode surface of a P69 cell.

Minimum Carbon Height Above Steel Collector Bar

Cathode erosion was reported by Tabereaux and coworkers to occur at a rate of 1 to 2 cm/year for cells with amorphous cathode blocks and increases to 2 to 4 cm/yr for cells with graphitized cathode blocks [15]. The predominant surface erosion profile in well magnetically compensated cells is the so called "W" shape pattern where the cathode blocks are eroded deeper near the ends where the cathodic current density is highest and the lowest cathode erosion is in the center of the cell.

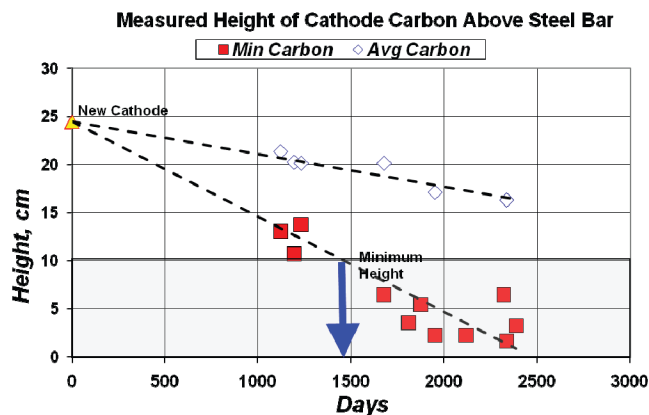


Figure 5. Measured height of cathode carbon above the steel collector bar of 175 kA cells versus pot age.

However the areas of deepest cathode surface erosion in end-riser P69 cells is typically near the down-stream corners as shown in Figure 4 for a cell that was 2334 days. One of the criteria that should be considered for restarting cells is the minimum height of carbon remaining above the steel collector bar. For example at one smelter the minimum height of carbon above the steel for restarting P-69 cells was determined to be 10 cm which corresponds to 1500 days as shown in Figure 5.

Another difficult decision is whether to restart older cells with very marginal sidewalls or to rebuild the cathode using a new steel potshell, or replace the entire sidewall and endwalls of the existing potshell prior to cell startup. It is difficult to get a good bond between carbon or silicon carbide sidewall blocks to the steel sidewall of the pot shell once the steel sidewalls are highly

distorted. Thus the steel cathode shell has a limited service life and should be replaced after several cycles. Another concern is evaluating the depth of potholes in the cathode lining to determine whether the cell should be restarted or rebuild the cell lining. One pothole is all that is necessary to cause the failure of a cell if the hole is deep enough for the molten aluminum to come in contact with the collector bar. Most of the potholes are at the edge of ridge toe with the fatal potholes most frequently found at the 2nd and 3rd cathodes from both ends in P-51 and P-69 end riser prebake cells [15]. Deep potholes with only ~2.5 cm carbon remaining above the steel bar were found in the majority of the P69 prebake cells inspected above 2000 days including some pot holes that had cooling cracks running through them.

Prebake Smelters	Potline Current kA	Loss in Pot Life, days	Premature Cell Failures After Startup	Restart Method	Comments
A,B,C,D	70, 70, 180, 180	176, 203, 915, 238	NA	Preheat & Cold	383 days average loss in potlife for only the 1 st to 2 nd startup for 4 smelters and 290 days average for all startups for all smelters
E	95	NA	2.5%	Preheat & Cold	160 cells restarted; 2.5% premature failures is for well prepared controlled shutdown & restart; if not, then 10% premature failures
F	95	250	<1%	Preheat	172 cells restarted x 6 potlines; controlled shutdown; higher number of premature failures if pots get too hot after restart
G	80	100	2 to 5%	Preheat	144 cells restarted; controlled shutdown
H	145	NA	30%	Preheat	200 cells restarted; controlled shutdown; most cells were greater than 2000 days
I	160	200	NA	Preheat	NA
J	180	NA	0%	Preheat	140 cells restarted; controlled shutdown; no cell was older than 1500 days
K, L, M	170, 190, 175	200, 200 to 300, 300	9 to 17%, 10%, 10 to 25%	Preheat & Cold	158, 209, 214 cells restarted; <u>uncontrolled shutdown</u> ; High number of premature failures occurred due to uncontrolled shutdown and high pot age.
N, O	225, 230	200, 400	2 to 5%, NA	Cold	240, 180 cells restarted; <u>uncontrolled shutdown</u>
P	240	200	12%	Preheat	164 cells restarted; <u>uncontrolled shutdown</u> ; high number of premature failures when sidewall are not replaced and/or pots get too hot after restart

(*Private communications)

Table IV. Loss in potlife and premature cell failures due to the shutdown and restart of potlines due to power interruptions.*

Loss in Potlife

The average loss in pot life due to shutdown and restart of individual potlines is 279 days for the 16 potlines at smelters shown in Table IV. However the loss in pot life typically varies from 100 to 400 days depending on the specific circumstances that exist at each smelter. Some of the major factors that impact loss in pot life are pot age distribution, cathode sidewall and bottom block materials, pot operational conditions prior to shutdown, cell restart methods and potline startup amperage.

A low loss in pot life (100 to 200 days) and low number of premature failures (0-2%) are obtained in potlines that have a low to normal age distribution of cells, controlled shutdown, slow restart practices and control of pot temperatures after the restart.

An average loss in pot life (200 to 300 days) and normal number of premature failures (2.5 to 5%) are obtained in potlines that have

a normal age distribution, controlled shutdown, improved restart practices and good control of pot temperatures after the restart.

A high loss in pot life (300 to 400 days) and high number of premature failures, (>5%) is obtained with potlines that have one or more of the following: high pot age distribution long extended cooling periods prior to shutdown, uncontrolled shutdown, and rapid restart practices with marginal control of pot temperatures after restart.

Experience has shown that the majority of premature cathode failures occur shortly after pots are restarted. The number of premature failures ranges from 0 to >20% depending on the specific circumstances that exist in each potline. The two major factors that impact the number of premature pot failures are, a) high pot age distribution, and b) cell overheating during restart.

Number of Premature Pot Failures

High Pot Age Distribution

More premature cell failures occur when the average age distribution of restart pots is high, e.g., >2000 days. The older cells have deep erosion of the cathode blocks with less than 10 cm of carbon above the steel collector bars, multiple cooling cracks in cathode blocks and seams, deep potholes and minimal sidewall thickness. The risk of premature pot failures after restart is very high in older cells having poor cathode lining conditions.

Cell Overheating During Restart

Operating cells at reduced amperage and/or multiple power interruptions prior to a final potline shutdown often causes hard alumina muck deposits to form on the cathode surface and the lower side ridge to extend farther under anodes. Due to magnetic forces these cells become unstable with higher metal waves which require cells to be operated at higher voltages. Consequently the additional voltage causes the bath temperature to increase and in some instances the cells become over-heated which melts the protective sidewall ledge. Instability often results in bath mixing with the metal and the mixture may freeze when the cell is stopped. During restart these cells have a tendency to become highly unstable due to extremely poor current distribution. These cells may operate at elevated bath temperatures, >1000°C for hours to several days. These high bath temperatures increase the risk of cathode failure due to a tap-out of the cell sidewall. It may be necessary to operate the potline at a lower than normal amperage or alternatively use shunts to by-pass some of the current to cells in order to provide a wider ac-distance to reduce instability, thus achieving a more stable cell operation.

Conclusions

The rapid cooling of cells to 25°C due to power interruptions results in irreversible and non-repairable damage to cathodes as a result of large thermal gradient which produces mechanical stresses in the cathode lining. The stresses eventually exceed the strength of the weakened *elastoplastic* cathode lining resulting in numerous long cooling cracks. In addition the cathode lining is weakened due to the diffusion and intercalation of sodium into the carbon cathode materials during cell operation. The cooling cracks weaken the carbon blocks and become a basis for failure in the future and thus result in a shortened potlife. The loss in potlife due to shutdown and restart of potlines varies from 100 to 400 days depending on the pot age distribution, cathode sidewall and bottom block materials, pot operational conditions prior to shutdown and cell restart methods. The number of premature failures after startup varies from 0 to 30% depending on the number of cells having a high pot age and overheating of cells during restart.

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