Role of Pitting in the Formation of Potholes in Carbon Cathodes - A Review

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Abstract

The formation of potholes on carbon cathodes is one of the main causes of pot failure in the aluminium industry. A single pothole deep enough to cause the molten metal pad to come in contact with the collector bar is enough to fail a pot. Based on current theories, the cathode wear mechanisms, industrial experiences in formation of potholes and their characteristics and the role of pitting in the formation of potholes, are discussed. Pitting, a highly localized form of cathode erosion that produces relatively small pits on the cathode surface is a phenomenon observed in potholes of the cathode block during autopsies of spent pot linings. The presence of pitting within these potholes shows that pitting plays an important role in their formation.

Keywords: Pitting of cathode carbon blocks; potholes in carbon blocks; cathode erosion; carbon cathode.

1.   Introduction

Cathode life is still one of the major challenges for the primary aluminium industry due to the major costs involved in replacing pot linings, loss in production and disposal of spent pot linings [1]. Reduced cathode service time has evolved in parallel to the demand for higher productivity, either through increased amperages in existing cathode technologies or introduction of modern high amperage cathodes. In addition to increasing amperage, changes towards more acidic compositions of the cryolite bath have also taken place [2]. Traditional amorphous/anthracite based carbon cathodes are less suitable for the emerging higher amperage regimes due to their higher electrical resistance and sodium swelling, and the industry has largely moved to graphitized blocks with lower electrical resistance, higher thermal conductivity and lower expansion due to sodium [1]. These changes have increased the productivity and energy efficiency of the aluminium industry [3], but faster cathode wear have become a major challenge due to reduced lifetime of the cells [1]. Autopsies of shut down cells have also demonstrated that the cathode wear is not even, but typically shows a so-called W or WW wear pattern [1]. Understanding the underlying mechanism(s) for these uneven wear is therefore of paramount importance in order to increase the lifetime of the cells.

The mechanisms for the cathode wear have been the subject of several studies in the past [1]. The mechanisms discussed in the literature will be reviewed in this paper. Moreover, industrial experiences have also shown that the cathode erosion is irregular and occurs through the formation of potholes on the carbon cathodes. In the worst cases, a single pothole is deep enough to reach the collector bars, which may fail a pot as the molten metal pad will dissolve the collector bar and potentially cause cell tap out [1]. The industrial experiences are

summarized in this review with attention to potholes and particularly pitting of the carbon cathode, which may act as precursors to the potholes.

2. Mechanisms for Cathode Wear

Cathode wear have previously been discussed in relation to several mechanisms involving pure mechanical erosion and mechanisms related to chemical and electrochemical reactions.

Physical or mechanical wear is today proposed to occur mainly through cavity cleaning in connection with metal tapping and anode change operations as well as alumina particles scratching the surface of the cathode blocks [1]. Tests by Toda and Wakasa [4] showed that graphitized blocks had lower abrasion resistance than their more amorphous and anthracitic counterparts. This may, to some extent, explain the observation of the graphitized cathode blocks being more eroded than the narrow joints (rammed joints) between them [5]. Erosion measurements performed in reduction cells by Wilkening and Reny [6], however, showed that graphite cathodes with superior mechanical abrasion resistance index displayed poorer wear resistance. This supports the conclusion that mechanical abrasion is not the key mechanism for cathode wear.

Cathode wear may also be chemical involving the formation and dissolution of aluminium carbide (Al_4C_3). This is because the reaction between aluminium and carbon as shown in reaction (1) is thermodynamically favourable (Gibbs energy of -147 kJ at 970 °C) at all temperatures of concern in electrolytic aluminium production [1].
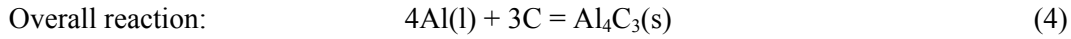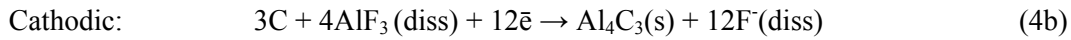
$$4Al(l) + 3C(s) \rightarrow Al_4C_3(s) \qquad (1)$$

The formation and dissolution of aluminium carbide from the carbon block under the metal pad is enhanced by the presence of cryolite based melts [1]. Laboratory tests conducted by Novak et al. [7] showed the presence of an oxide film between the metallic aluminium and the carbon cathode. This oxide film prevents wetting of aluminium on carbon [8]. Thus for any direct carbide formation to occur, aluminium must diffuse through the oxide film to react with carbon [9]. The dynamics, however, change when cryolite melt is introduced to the system. The cryolite melt act as a wetting agent by dissolving the oxide film (thereby increasing the wettability of aluminium on carbon) and paving the way for carbide formation [8].

Absorbed sodium in carbon can also react with carbon and cryolite or alumina to form aluminium carbide within the pores of the carbon cathode as shown in Reactions 2 and 3 below [1]. High activity of sodium is necessary for any of these two reactions to be the dominant aluminium carbide forming reaction [10].

$$4Na_3AlF_6(l) + 12Na(in\ C) + 3C = Al_4C_3(s) + 24NaF(l) \qquad (2)$$

$$8Al_2O_3(s) + 12Na(in\ C) + 3C(s) = Al_4C_3(s) + 12NaAlO_2(s) \qquad (3)$$

Øye and Lossius [11] analysed different industrial cathode samples by drilling core samples covering the whole depth of the bottom linings at different locations. Aluminium carbide was observed as one of the phases within the cathode samples. They also observed that Al_4C_3 was both formed at the surface as well as inside the pores of the cathode.

The wear of carbon cathodes may also be electrochemical as shown in Reaction 4 below.

Anodic: $4Al + 12F^- \rightarrow 4AlF_3 \text{ (diss)} + 12e^-$ (4a)

Cathodic: $3C + 4AlF_3 \text{ (diss)} + 12\bar{e} \rightarrow Al_4C_3(s) + 12F^-\text{(diss)}$ (4b)

Overall reaction: $4Al(l) + 3C = Al_4C_3(s)$ (4)

It is proposed that Reaction 4 relies on a constant supply of Al^{3+} ions, which is formed by the anodic dissolution of molten aluminium at the metal/electrolyte interface (zone A). Increasing the current within the system will increase the driving force for the anodic dissolution of Al^{3+} and will increase the driving force for the transport of Al^{3+} ions to and into the cathode material (zone B), thus increasing the chance of aluminium carbide formation [2, 12]. Figure 2.2 is a sketch showing the interfaces and zones as explained by Rafiei et al. [2].

Figure 2.2. Sketch of the interfaces and zones at the carbon cathode from [2].

According to Keller et al. [12], when bath penetrates into a cathode block, it will have to equilibrate with the more negative potentials that exit in the carbon due to an ohmic voltage drop. This will cause electrochemical reactions similar to Reaction 4 to occur leading to the formation of aluminium carbide within the cathode block. According to the authors, these electrochemical reactions will proceed until a higher bath ratio and accordingly a more negative potential corresponding to the one in the cathode is reached [12]. Figure 2.3 illustrates an electrochemical wear model developed by Li et al. [13]. The model is based on the concept of a "carbon pump" proposed earlier by Solheim and Tschöpe [14]. Solheim and Tschöpe proposed that the aluminium carbide layer formed on the carbon cathode is porous and filled with electrolyte. The pores filled with electrolyte can be considered as a small electrolysis cell where porous aluminium carbide is formed at the bottom of the pores (cathode side of cell) whiles the aluminium carbide is oxidized at the top of the pore (anode side of cell). This forms a "pump" where carbon is transported from the carbon cathode [14]. Sodium ions (Na^+) are assumed to be the sole carrier of current within the cell.
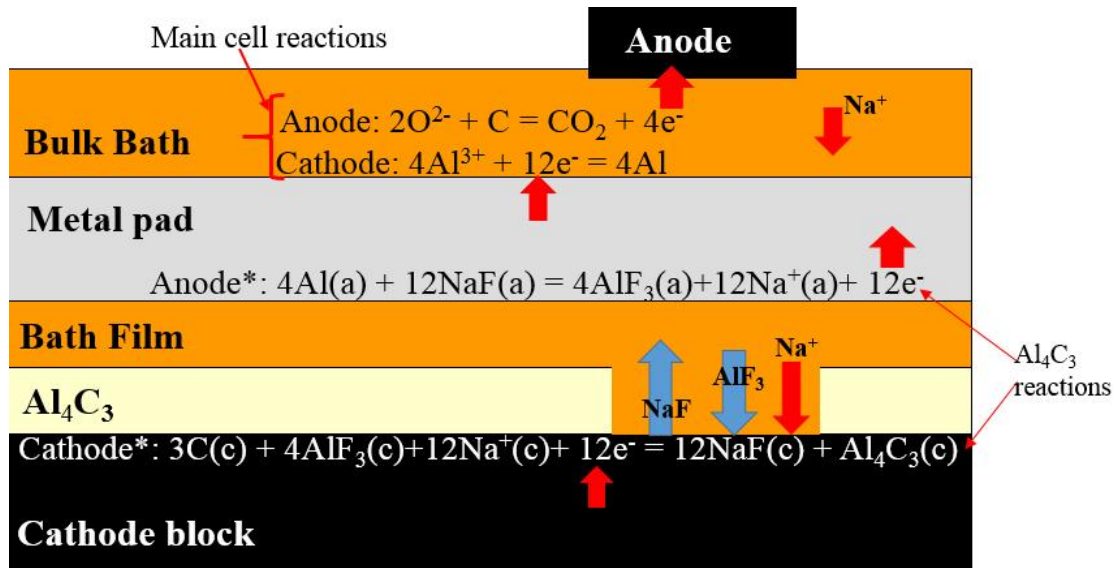
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Figure 2.3. Model for the electrochemical formation of aluminium carbide from [13].

Cathode wear tests by Novak et al. [7], Tschöpe et al. [15, 23], Skybakmoen et al. [16], Wilkening and Reny [17], Liao and Øye [18], Rafiei et al. [2], Patel et al. [19], Keller et al. [12] and others researchers have all shown that cathode erosion increases with increased current density. Their results show a clear correlation between cathode wear and current density.

Vasshaug et al. [20] investigated the effect of keeping the total amount of electrical charge passing through the cathode constant (by varying the electrolysis time) on cathode erosion. They observed that the carbon consumption decreased with increasing current density. This observation was attributed to increased activity of NaF (resulting from the high current density) at the cathode surface leading to increasing cryolite ratio and hence reduced carbide solubility. They also observed that at higher current densities there seemed to be weak correlation between carbon consumption and current density. The explanation given for this was that the wear is an electrochemical process that depends on the actual charge passed. By keeping the total amount of charge passed constant throughout the experiments, the carbon consumption would also be expected to remain the same. This is a further confirmation of the dominant role of electrochemical wear in the cathode wear mechanism.

Gudbrandsen, Ødegård and Sterten [21] demonstrated in a laboratory test that carbon can be cathodically dissolved into the cryolite melt according to Reaction 5. The test was carried out in a laboratory cell containing an alumina saturated melt with a cryolite ratio of 1.8 and temperature of 940 °C. The results from their test showed that the rate of cathodic dissolution increased with current density. They calculated the current efficiency to be 80 % at the limiting current density (0.09 Acm^{-2}). An additional increase in current density beyond this limit led to a reduced current efficiency for the carbon dissolution reaction [21].

$$C(s) + 3AlF_3(l) + 4Na^+ + 4e^- = Na_3Al_3CF_8(l) + NaF(l) \qquad (5)$$

The rate determining reaction for carbide formation is its dissolution in the cryolite bath [1]. Dissolution of the formed carbide layer will expose a fresh cathode surface for further carbide formation to maintain a stationary thickness [1]. The solubility of aluminium carbide in the metal pad is less than 0.01 wt% at reduction cell temperatures [8]. This is far lower than its

solubility in the cryolite melt, which was found to reach a maximum of 2.5 wt% at cryolite ratio and temperature of 1.8 and 1020 °C, respectively, by Ødegård et al. [22]. Wilkening and Reny [17] observed that cathode wear increased with increased acidity (AlF_3) of the cryolite melt. Aluminium carbide dissolved in the electrolyte is assumed to be oxidised by the anode gas (CO_2) or deposited as carbon on the anode [1].

As the dissolution of carbide in the metal is known to be low compared to the solubility in the cryolite melt, it is proposed that the presence of a bath film at the carbon-metal pad interface is very important in the erosion of carbon cathodes [1]. The continuous presence of cryolite at the carbon-metal interface is enhanced by the convective patterns set up by the magnetic field within the metal pad [20]. K. Tschöpe et al. [23] observed that by increasing the speed of rotation of a cathode sample with slots, the wear rate increased. This was attributed to mass transport of carbide to the electrolyte bath above the aluminium pad. Figure 2.4 is a sketch illustrating the cathode wear mechanism described here.
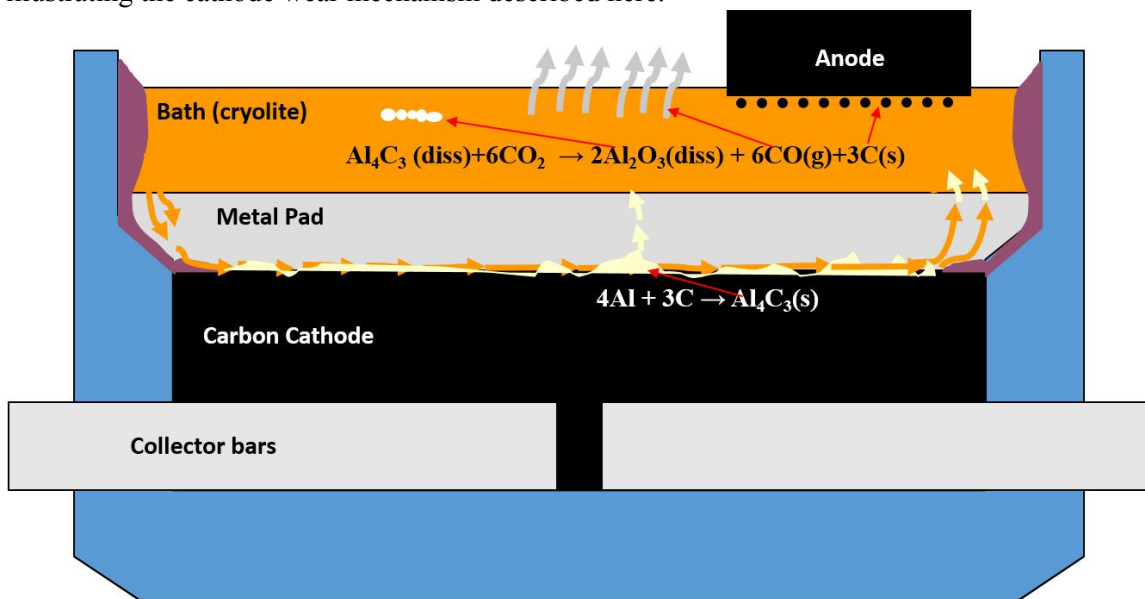

Figure 2.4. A sketch illustrating the cathode wear mechanism.

The most common erosion pattern observed in the more modern high-amperage prebaked anode cells is the so called W or WW wear pattern characterized by highest erosion towards the ends of the cathode block and least erosion towards the centre cavity [1]. Measurements by Tabereaux et al. [5] showed that the maximum erosions were located under the anodes near the ends of the cathode blocks and that the wear was deeper under some anodes than others. They however found almost no erosions in the centre of the cell. Dreyfus and Joncourt [24] explained the mechanism behind the W or WW wear pattern formation as being the result of the heterogeneity in the current density distribution along the cathode blocks. According to them, for a given geometry of cathode block and collector bar, the current density distribution along the cathode block will be influenced by the electrical conductivity of the block and bar. The higher the electrical conductivity of the block (as in graphitized blocks), the higher will the current density peak at the ends of the block (higher level of heterogeneity) leading to more erosions at the ends and less at the centre (W or WW). The less graphitized blocks on the other hand because of their relatively low electrical conductivity (or higher resistivity) will attain a certain level of uniformity in the current density distribution and thus uniform wear when compared to their graphitized counterparts. Thus, the level of W or WW wear pattern will be higher for graphitized blocks than the less graphitized ones [1]. Actions such as introducing variable electrical resistivity along the length of the cathode block, modifying electrical

resistance over the collector bar-to-block joint and placing copper inserts inside the collector bars are believed to help even out the current distribution at the carbon-aluminium interface and thus reduce the occurrence of W or WW wear patterns [1].

2.1.   Pothole formation

Dell et al. [25], Siew et al. [26] as well as Sørlie and Øye [1] have over the years discussed pothole formation extensively. Pothole formation is a cathode wear mechanism characterised by a rapid localized erosion of the carbon lining [1]. The cavity created may sometimes have the approximate appearance of an inverted cone but can also have shapes that are more irregular. At failure the pothole will always extend from the surface down to a collector bar leading to tapout through the bar if no drastic action is immediately taken [1].

In their paper on the fundamentals of potholes formation, Siew et al. [26], described potholes as eroded holes in the carbon cathode that are roughly hemispherical in the base and can range in size from golf balls to basketballs. They went on to propose that potholes generally have steep sides that form angles of 70 - 90° with the cathode surface and have an aspect ratio of equal or slightly greater than one as shown in Figure 2.5.
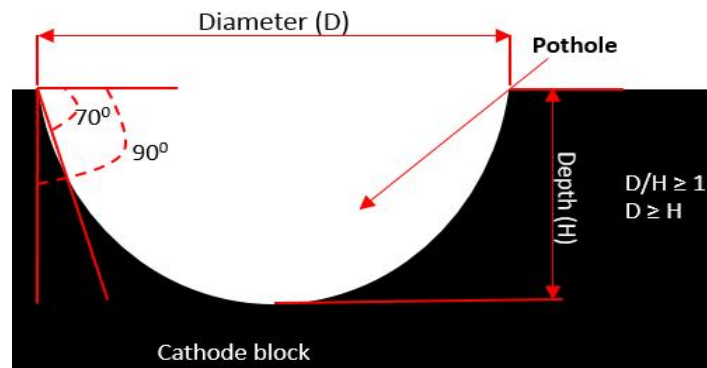

Figure 2.5. Schematic diagram of a pothole. Redrawn from [26]

Dell et al. [25] proposed as early as 1967 that potholes formed as a result of the swirling of metal also referred to as whirlpools. The whirlpool effects were believed to have formed by the combined effects of metal pad flowing across the cracks, current flowing down the hole and the longitudinal components of the magnetic flux. The origin of the metal swirling theory according to Siew et al. [26] came from Waddington [27]. Waddington reported that it is possible for the aluminium carbide formed in the metal veins (areas of carbon that were penetrated by molten metal) to be removed by the circulation of aluminium metal formed through the effects of current and magnetic fields. He assumed the removal of carbide by the circulating metal will ensure the metal veins are kept open and gradually enlarged [27].

Sørlie and Øye [1] proposed that potholes were formed as a result of weaknesses in the pot lining such as cracks or gaps formed from the effect of ramming paste shrinkage, low density areas or foreign bodies present in the cathode lining. At these weak areas, the molten aluminium metal is able to penetrate into the cathode resulting in a local increase in current density. This increased current density creates a local magneto hydrodynamic (MHD) disturbance in the metal pad. This in turn leads to a rapid exchange of the bath film under the metal pad and an increased dissolution rate of aluminium carbide. The rapid formation and dissolution of aluminium carbide leads to a very rapid wear of the carbon lining at the particular location.

Industrial observations from autopsies show that pothole formation occurs at locations with very high current densities such as the ends of the cathode blocks as well as locations with weaknesses in the pot linings such as cracks, gaps, narrow joints, veins etc. [1, 25, 26]. Figure 2.6 shows a picture of a pothole observed during an autopsy, the pothole was filled with aluminium metal. The presence of aluminium in such a pothole is likely to speed up the formation process, as the current density will be higher at this location. According to Sørlie and Øye [1], the concentration of current density along metal-filled surface cracks in the cathode may generate pothole-like cavities that erodes to veritable ditches across the carbon pane, sometimes several meters long [1]. Autopsied cathodes examined by Sørlie and Øye [1] may suggest that some cracks or veins of aluminium in the carbon may be wholly or partially converted into aluminium carbide, while in other veins the metal appears to have smoothed and enlarged the crack [1].
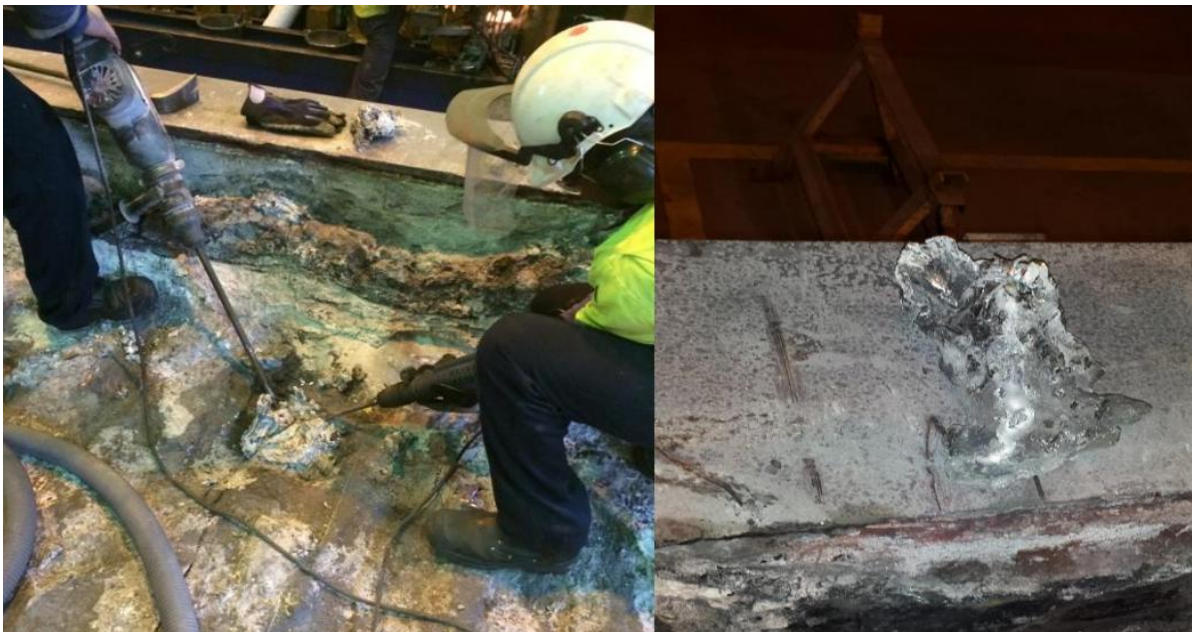

Figure 2.6. A pothole filled with aluminium metal (the metal removed is shown on the right).

2.2   Pitting

Pitting is a terminology used mainly under the subject of corrosion where it represents a highly localized form of corrosion that produces sharply defined cavities [28]. Its usage in connection with cathode erosion is therefore reasonable since the cathode erosion is mainly a chemical or electrochemical corrosion of the carbon cathode involving the formation and dissolution of aluminium carbide [1]. Pitting is observed on the carbon cathode surface at locations with the highest current densities [5]. Figures 2.7 is a picture showing pitting on a cathode surface.

Figure 2.7. Pitting on the carbon cathode surface.

Rafiei et al. [2] proposed pitting to be caused by particle detachment occurring mainly because of carbide formation within the pores of the carbon cathode leading to weaknesses in the surface structure and making physical erosion easier. Rafiei et al. employed X-ray spectroscopy, electron microscopy and optical image techniques to analyse cathodic polarized degraded samples obtained from industrial cells and inverted laboratory electrolysis experiments showing extensive pitting. They observed that aluminium carbide is formed by an electrochemical reaction within the pores and cracks of the cathode carbon specimen and it is associated with electrolyte penetration. They also observed that electrochemical carbide formation is more favoured in amorphous carbons than in graphitized materials and the amount of carbide formed increases with increased disorder of the carbon [2]. It is proposed that the electrochemical formation of aluminium carbide in disordered carbon is more favoured due to high thermodynamic activity [1]. This suggests a high level of carbide formation within the binder matrix than the aggregate graphite or anthracite [1] leading to its easy destruction and rendering the surface structures weakened. Weakening of the surface structures may lead to physical erosion resulting in particle detachment [1]. Patel et al. [19] investigated four carbon core samples and observed that porosity was what differentiated the samples in terms of the outcome of their tests. The highly porous samples showed signs of pitting on the surface. They attributed the pitting or rough nature of the wear to particle detachment resulting from enhanced carbide formation within the pores of the more porous samples.

2.3   Role of Pitting in Pothole Formation

Pitting, as discussed above can be assumed to be a result of particle detachment due to carbide formation within pores of the carbon material leading to weaknesses [2] or pure electrochemical corrosion of the carbon cathode block due to high current densities [5]. The potholes created along the ends of the cathode blocks is assumed to occur because of extensive wear (due to high current densities at these locations). These potholes tend to show signs of extensive pitting as shown in Figure 2.7. The presence of extensive pitting within these potholes suggests that pitting plays a central role in their formation. Based on industrial experience and available literature [5] it can be assumed that once the pitting reaction is initiated (either through particle detachment or through pure electrochemical corrosion), the initial pits that are created act as spots for increased local current densities. The turbulence created at these locations (due to whirlpool effect on metal pad [25]) leads to more carbide formation and dissolution as it ensures continuous supply of bath to the particular location [1]. It can be further assumed that this process speeds up (due to increased current density) as the distance to the collector bars is reduced due to wear of the carbon cathode. The process continues until a potential pothole is

eventually formed. Upon the formation of a pothole, contact with the collector bar(s) may be reached and a tapout may be encountered if no drastic measures are taken. It is a common industrial practice to fill these potholes with recrystallized alumina once contact is made with the collector bar(s) [1] to stop or delay tapout. The strap to the affected collector bar(s) may also be cut to reduce the temperature and current density at the pothole area and allow bath to freeze around the recrystallized alumina and seal the pothole [1].

3.   Conclusion

Cathode wear as discussed in this paper is a combination of mechanical, chemical and electrochemical wear mechanisms. None of these mechanisms can alone explain all of the cathode wear patterns observed in industry and laboratory tests. However, laboratory tests as well as industrial autopsies show that electrochemical induced wear is probably the most dominant mechanism. The current trend of reduction in cathode life as amperage is increased is better explained by the electrochemical wear mechanisms.

4.   Acknowledgement

5.   Reference

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