

INFLUENCE OF INTERNAL CATHODE STRUCTURE ON BEHAVIOR DURING ELECTROLYSIS PART III: WEAR BEHAVIOR IN GRAPHITIC MATERIALS

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Keywords: Porosity, graphitic cathode, aluminium carbide formation, wear

Abstract

Graphitic cathode samples with varying granulometries were tested under a number of controlled laboratory electrolysis conditions to determine the effect of internal cathode structure and operating conditions on wear behavior and rates.

The graphitic samples produced were all relatively dense materials with low open porosities and in some cases a narrow pore size range which helped to reduce bath penetration into the cathode and thus reducing the ability for internal aluminium carbide formation to occur. However, though bath penetration was minimal, wear rates were still significant and it was thought that accelerated and preferential aluminium carbide (Al₄C₃) formation was occurring with the disordered carbon in the binder phase material. This wear behavior was accelerated with increasing current density and excess AlF₃ content indicating that the main wear process was electrochemical.

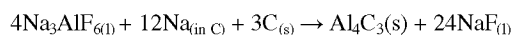
Introduction

Graphitic and graphitized cathode blocks have become more prevalent in modern aluminium smelters as they have proven to have superior thermal and electrical properties than previously used anthracite based cathode blocks. With lower electrical resistivity, smelters have been able to increase production through continual increases in cell current density; however this positive increase in production does have an associated negative in terms of cathode life. Accompanied by the shift from anthracitic cathodes to cathode blocks with higher degrees of graphitization cell life has dropped considerably in most smelters.

It has been widely accepted that the increase in wear rate and non-uniform wear corresponds to an increase in current density. This increase in current density is believed to be the driving force behind aluminium carbide formation which is one of the main degradation reactions occurring at the cathode. Al₄C₃ can form through a number of means, firstly through direct contact between molten aluminium and the carbon material [1].

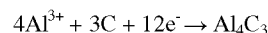


Though this reaction is thermodynamically favoured at electrolysis temperatures, the amount of aluminium carbide actually produced this way is well below that predicted by the reactions kinetics and thermodynamics. Therefore, other phenomena must be occurring to account for the actual degree of aluminium carbide formed [1]. The second proposed method for aluminium carbide formation is a chemical reaction between intercalated sodium, cryolite and carbon [2].



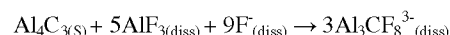
This reaction relies on significant amounts of intercalated sodium in order for it to be the dominant method for aluminium carbide formation. This is unlikely to be the case in highly graphitized cathode blocks where sodium intercalation is minimal within the bulk material [2].

Increasing wear rate with increasing current density suggests that an electrochemical reaction may be the dominant aluminium carbide forming mechanism.



This reaction relies on a supply of Al³⁺ ions which is formed through the anodic dissolution of molten aluminium at the metal/electrolyte interface. Increasing the current within the system will increase the driving force for the anodic dissolution of Al³⁺ and will increase the driving force for the transport of Al³⁺ ions to and into the cathode material, thus increasing the chance of aluminium carbide being produced [3,4].

The formation of aluminium carbide is not the sole mechanism that contributes to the cathode wear. The aluminium carbide formed will dissolve into the bath if exposed to it through the following suggested dissolution reaction [5].



The bath however has a limited solubility of aluminium carbide which when reached will cause the aluminium carbide layer on the cathode surface to grow. This phenomenon is also believed to occur within the pores of the cathode and can lead to internal stresses in the material leading to particle detachment and uneven wear [3,6].

This paper is an extension of previous papers presented at TMS 2005 [6-7]. Part one of the previous papers discussed comparisons in mechanical properties between graphitized and graphitic materials with similar granulometries. For each case a range of materials were prepared with each having varying degrees of porosity. Generally it was found that isotropic coke based graphitized material were more sensitive to changes in formulation than the graphite based graphitic material. This was shown with the large spread in open porosity between samples with varying composition and also in the large difference in the mechanical properties between high and low porosity samples. Greater sensitivity to formulation changes was attributed to the granulometry of the isotropic coke particles [7].

Isotropic coke material as its name suggests means the grains are similar in size and shape in all directions, therefore during extrusion there will be no preferred orientation for grain alignment and this could lead to inadequate packing of the aggregate material. Further restrictions to grain alignment and packing could also occur due to the hard nature of the isotropic grains. This would restrict the movement during extrusion and will lead to a less than ideal-packed product [7].

Graphitic material on the other hand proved to have a much higher tolerance to granulometry and formulation changes. Graphitic material produced much denser material with more consistent mechanical properties. This was attributed to the alignment of the anisotropic graphite grains during extrusion. During extrusion graphite grains will preferentially align their major axis with the direction of extrusion. This coupled with the soft, self lubricating characteristics of the graphite grains allowed greater aggregate movement and alignment to take place and create a denser final product [7].

In terms of mechanical properties the following conclusions were made for isotropic coke samples versus graphite samples.

- Graphitized isotropic coke materials tended to form products with higher porosity and less grain orientation than the graphitic samples under the same extrusion conditions and formulation.
- Graphitic material had superior density, flexural and compressive strength than isotropic coke samples with the same grain size formulations. This was found to be due to the superior packing arrangements found in the graphitic material.
- Isotropic coke based samples had lower electrical resistivity than graphitic samples. This was expected due the difference in processing of the two types of samples. Isotropic coke samples were fully graphitized while graphitic samples were baked to 1100°C thus giving the graphitized material higher structural order and thus lower resistivity.
- Cut direction had a significant effect on the properties in graphitic material, indicating definite grain orientation and alignment. The same phenomenon was practically not found with the isotropic coke samples.

Experimental

Experimental work was based around the design of a 2nd order factorial matrix, which defined the compositions of the cathode samples and the operating parameters that would be used during the laboratory electrolysis experiments. The objective of this investigation was to investigate the effect of porosity and pore size distribution in graphitized and graphitic material during electrolysis, therefore the matrix was used to define the compositions needed to achieve a range of porosities and pore size distributions. Table 1 shows the variables which were investigated in this work.

Table 1: Key variables assessed

Variable	Variance 1	Variance 2
Filler type	Isotropic coke	Graphite
Granulometry	Coarse	Fine
Flour content	Low	High
Cut direction	Parallel	Perpendicular
Bath acidity	5% excess AlF ₃	10% excess AlF ₃
Current density	0.6 A/cm ²	1 A/cm ²

From this matrix four core formulations for both isotropic coke and graphitic material were formulated. These formulations defined the granulometry of the samples.

Table 2: Core formulations for sample production

ICL	Isotropic coke, Coarse granulometry, low porosity
ICH	Isotropic coke, Coarse granulometry, high porosity
IFL	Isotropic coke, Fine granulometry, low porosity
IFH	Isotropic coke, Fine granulometry, high porosity
GCL	Graphite, Coarse granulometry, low porosity
GCH	Graphite, Coarse granulometry, high porosity
GFL	Graphite, Fine granulometry, low porosity
GFH	Graphite, Fine granulometry, high porosity

All samples were extruded and initially baked to 800°C to allow carbonization of the binder pitch to occur. Isotropic coke based samples were then graphitized at 2700°C to increase structural order within the material (will be referred to as graphitized isotropic coke material). Anisotropic graphite based material was re-baked to 1100 °C. Re-baking the graphitic material at 1100 °C left the binder phase in a relatively disordered state compared to the graphitized material (will be referred to as graphitic material). An in-depth account of the processing and mechanical properties of the produced samples can be found in previous work [7].

All samples were tested in an inverted cell configuration as shown in figure 1.

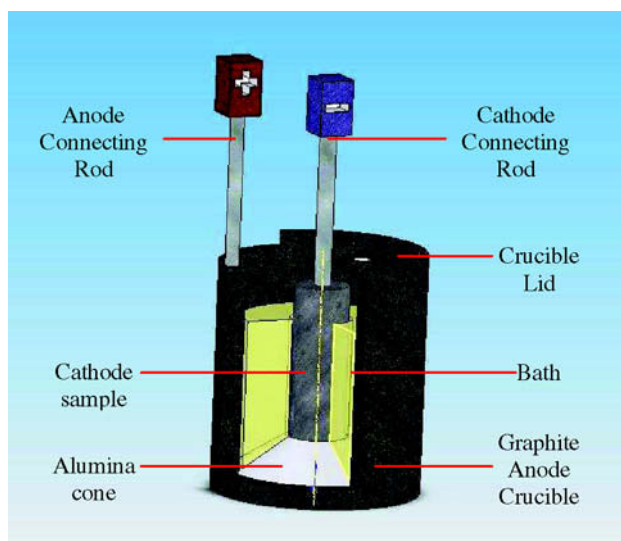


Figure 1: Schematic showing the laboratory electrolysis configuration

Samples, 30mm diameter x 110mm length were subjected to 96 hour electrolysis trials; this length of time produced measurable wear and allowed enough time for wear phenomena such as aluminium carbide formation and dissolution to take place and be observed.

Following electrolysis, samples were cleaned of excess bath and the volume loss measured through mercury displacement and dimensional analysis techniques.

Wear rates were then analyzed to determine which of the variables outlined in Table 1 were important contributors to wear. Analysis of the effects of variables on wear rates were conducted using a second order factorial analysis method which allowed individual effects and combinations of effects evaluated.

Results and Discussion

The results reported in this paper mainly concentrate on the wear phenomenon observed during laboratory electrolysis trials of graphitic cathode materials with varying granulometries and open porosities. Samples were tested under constant current density which was either 0.6 or 1 A/cm² with bath compositions of 5% or 10% excess AlF₃ content. Configuration of experimental conditions and samples were determined by the experimental matrix outlined earlier.

In part II of this series of papers it was found that the graphitized isotropic coke materials showed distinct wear behavior as open porosity was increased [6]. As porosity was increased it was found that the uniformity of the wear declined. With greater open porosity, a higher degree of bath penetration took place and led to a greater degree of internal degradation reactions occurring such as aluminium carbide formation. Internal aluminium carbide formation, dissolution and growth coupled with the already weak internal structure of the cathode due to high porosity lead to the phenomenon of particle detachment. This was the cause of the pitting and uneven topography on the high porosity graphitized cathode material [6].

With the graphitic material however, much denser materials were formed even with formulations designed to generate high porosity samples. This increased density coupled with the processing steps used to produce the graphitic cathodes gave rise to quite different wear patterns and behavior than what was observed with the graphitized isotropic coke. Figure 2 shows the open porosity and pore size distributions achieved for graphitic samples.

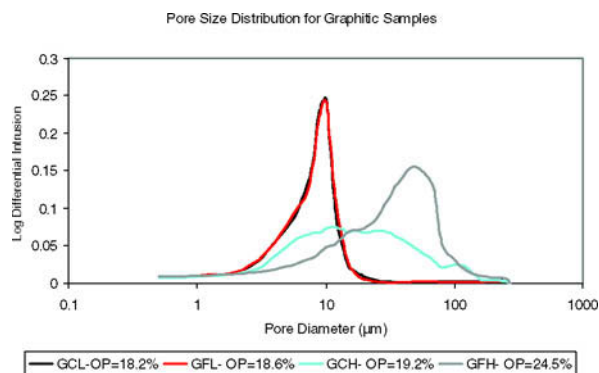


Figure 2: Pore size distribution of graphitic samples

The main contrasting difference between the graphitized and graphitic material tested was that all graphitic materials showed uniform wear behavior with very little evidence of pitting and particle detachment. This was generally expected as previous testing of graphitized material lead to the conclusion that the denser a material is the more uniform the wear profile will be. Figure 3 shows the typical wear pattern of low and high porosity graphitic material.

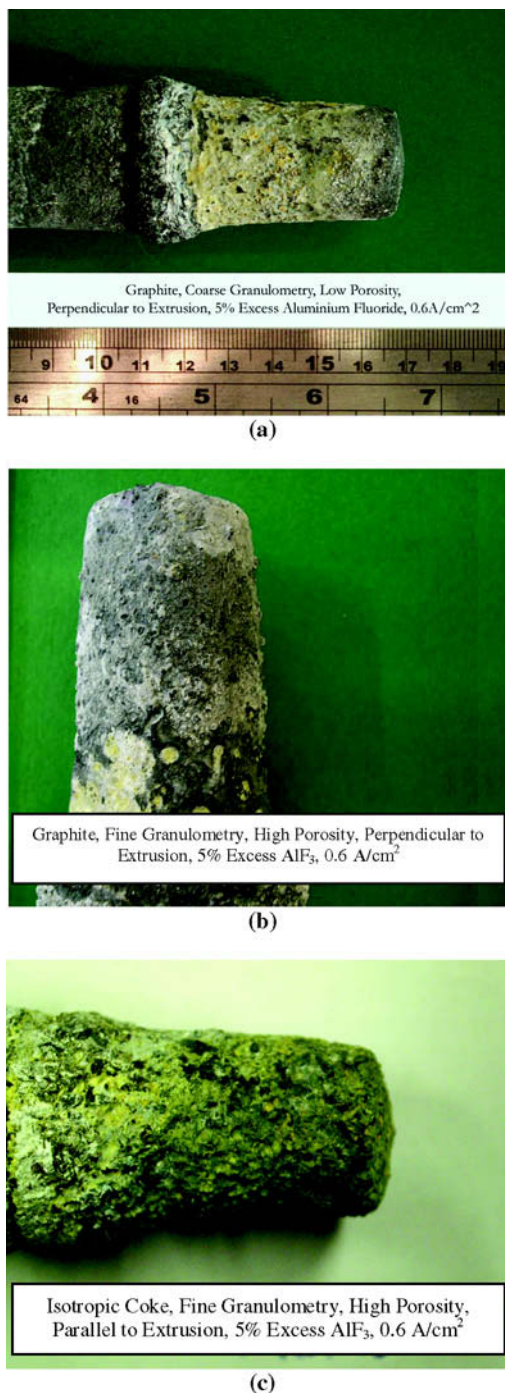


Figure 3: Typical wear pattern of (a) low porosity graphitic material (b) high porosity graphitic material (c) high porosity graphitized sample for comparison

Though Figure 3a-b show even wear along the electrolyzed length (in terms of no great evidence of pitting or particle detachment as shown in figure 3c), there was however a strong indication of preferential wear occurring at the graphitic cathode surface (fig 3a-b). In many cases a grainy, coarse appearance was found on the cathode surface. This is believed to be due to the preferential aluminium carbide formation and dissolution of the disordered carbons in the binder phase material [3]. Figure 4 shows a close up of a worn graphitic cathode sample.



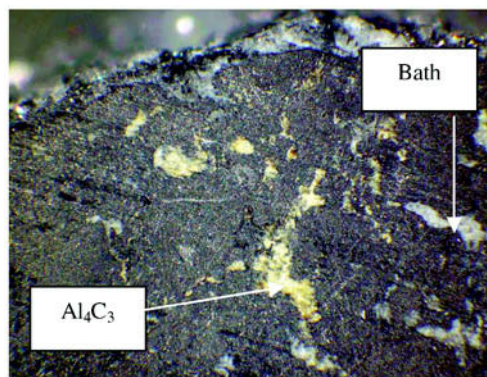
Figure 4: Course, grainy topography of electrolyzed graphitic cathode material

The graphitic cathode material used in these trials had only been heat treated to 1100°C which while still allowing carbonization to occur will only allow low levels of structural re-alignment to occur, thus leaving the binder phase in a relatively disordered state compared to the highly ordered graphite filler material. Thus as mentioned during electrolysis this binder phase will facilitate aluminium carbide formation and dissolution preferentially over the graphite filler leading to the binder phase having a higher wear rate. Therefore resulting in the course grainy appearance of the cathode material as the graphite filler has worn but not to the same extent as the binder phase.

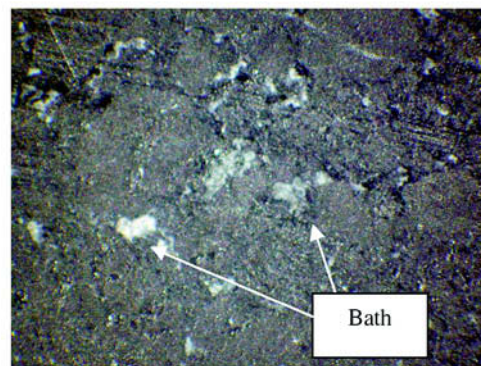
Bath Penetration and Internal Aluminium Carbide Formation

In theory the preferential degradation of the binder phase over the filler material could lead to possible pitting and particle detachment due to bath penetration and internal aluminium carbide formation. However, as mentioned no definitive evidence of particle detachment was found in any of the graphitic cathode material.

Cross-sections of high and low porosity graphitic material provided a number of explanations to why pitting caused by particle detachment was not a major contributor to wear in the tested graphitic material. Figure 5a-c shows various cross-sections of low and high porosity graphitic cathode material.



(a)



(b)

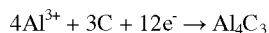


(c)

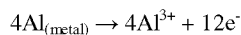
Figure 5: Cross sections of electrolyzed graphitic cathode material. (a) Fine granulometry, high porosity, edge of sample (b) Fine granulometry, high porosity, center of sample (c) coarse granulometry, low porosity, edge of sample

Figure 5a shows the edge of a cross sectioned graphite, fine granulometry, high porosity sample after 96 hours of electrolysis. The key point of interest is the presence of a yellow compound within the pores of the cathode. This yellow compound was established to be aluminium carbide and could be found mainly situated close to the sample/bath interface of the cathode material. Figure 5b shows a section from the center of the same sample where yellow aluminium carbide is not present. Here a greater degree of white areas were found which indicates bath penetration without carbide formation.

It is thought that the internal aluminium carbide formation is mainly situated close to the bath/cathode interface as in this region there will be a higher concentration of available Al^{3+} ions which are needed for the electrochemical formation of aluminium carbide.



Al^{3+} ions are generated by the anodic dissolution of the aluminium metal when it comes in contact with the bath through the following mechanism. [3,4]



This dissolution reaction allows sustained current flow through the penetrated bath in the cathode which will be further enhanced with increasing potential gradient in the system. Thus, leading to the theory that increasing current density will lead to increased aluminium carbide formation due to a larger potential gradient in the system which will increase the driving force for Al^{3+} and Al_4C_3 formation. This theory has been confirmed by previous trials with graphitized cathode materials and also by recent work carried out by Wilkening et al [8].

Though in high porosity graphite samples there is evidence of internal aluminium carbide formation there was still no evidence of particle detachment which was apparent in high porosity graphitized isotropic coke samples [6]. This is due to the greater structural integrity of the graphite samples due to the low open porosities and high densities. The GFH sample shown in figure 5a has an open porosity of 24.5% which will allow bath to penetrate into the material but due to grain alignment and high packing efficiencies of the aggregate material the internal strength of the material will be high enough to resist particle detachment. Figure 2 shows the pore size distributions of the various graphitic materials.

Low porosity graphite samples however showed little to no penetration of bath into the cathode. This lack of bath penetration can be seen in Figure 5c where there are no large white or yellow regions indicating the presence of bath and aluminium carbide. This is due to the superior density of the low porosity samples and the small range of pore sizes present in the material. As can be seen from figure 2, GCL and GFL samples had very low open porosities of approximately 18% and the pores were generally less than 20µm in diameter. With the apparent lack of bath penetration in the low porosity samples it does suggest that there is possibly a critical pore diameter that will start facilitating bath penetration and subsequent internal reactions.

With the absence of wear phenomena such as particle detachment and pitting it can be said that for graphitic samples the dominant wear mechanism was not internal aluminium carbide formation and degradation but surface aluminium carbide formation and dissolution. On most samples there was clear evidence of aluminium carbide on the cathode surface as shown by the yellow colouring on the cathode surface in Figure 3a.

Wear Rate Analysis

As mentioned earlier, a 2nd order factorial matrix was used to define the testing regime in this investigation. The matrix allowed

the analysis of the effects and interactions of five variables that were considered to be important to cathode wear. These were:

1. Bath chemistry
2. Granulometry
3. Porosity (Flour content)
4. Cut direction
5. Current Density

Note: Table 1 defines the variance for each variable used in the 2nd order factorial design.

The evaluation of the matrix results showed some indifferent results which were due to the fact that the matrix formulations used to produce the cathode samples produced samples with similar densities, open porosities and properties. This meant that during electrolysis different materials under similar operating conditions exhibited quite similar wear behavior and wear rates. Therefore making it difficult to determine the effects and interactions of porosity and granulometry on the wear behavior.

This was not the case for the graphitized isotropic coke material where different formulations gave rise to distinct properties and wear behavior which allowed effects and interactions to be clearly seen [6].

Though it was difficult to establish the clear effect of porosity and granulometry on the wear behavior the effect of operating parameters such as current density and bath chemistry could be seen.

Table 3: Relative impact of variable interactions on wear

Variable effect/ Interaction	Effect
Bath	4.55*
Granulometry	-1.09
Porosity	4.76*
Cut Direction	3.32
Current Density	8.25*
Granulometry, Current Density	1.20
Cut Direction, Current Density	1.41
Bath, Granulometry, Current Density	1.97
Bath, Cut Direction, Current Density	2.31

(* indicates key variables found)

Table 3 shows some of the 1st, 2nd and 3rd order interactions found during this investigation. The variable effect/interaction column lists the specific effects and interactions being looked at and the effect column shows the relative increase/decrease on cathode wear that changing the variables from their variance 1 state to their variance 2 state, whilst all other variables are kept constant at the variance 1 state.

The key effects in Table 3 are those highlighted. These seem to have the greatest effect on the cathode wear. Variable 1 and 5 are bath chemistry and current density respectively. The results show that changing the current density from 0.6A/cm² to 1.0A/cm² would increase the wear rate by 8.25cm/year. This is a considerable increase and does support the theory that cathode wear in graphitic cathodes is current density driven with

increasing current density increasing the rate of electrolytic aluminium carbide formation.

Increasing the excess AlF_3 content (variable 1) in the bath does have an adverse effect on the wear rate as shown in Table 3. This is due to the aluminium carbide solubility in the bath increasing with increasing AlF_3 content, thus allowing more carbon material to be removed from the cathode and into the bath as dissolved aluminium carbide. However, in industrial applications the effect of AlF_3 may not be as pronounced as these results suggest. This is because as in industrial cells the molten aluminium pad on the cathode surface will protect the cathode from large amounts of bath contact, thus hindering the aluminium carbide dissolution reaction.

Though it is difficult to compare wear rates generated through the use of a factorial experimental design due to the uniformity in the samples produced; approximate comparisons between operating conditions can be made. Table 4 shows some of the conditions and wear rates found in this investigation. This table clearly shows the effect of current density and bath chemistry on the wear rate of the cathode samples.

Table 4: Wear rate comparison between GCL samples

Sample	Bath Chemistry (excess AlF_3)	Current Density A/cm^2	Extrapolated Wear Rate $cm/year$
GCL Perpen	5	0.6	19.45
GCL Parallel	5	1	24.56
GCL Parallel	10	1	35.9

In summary the results from the graphitic samples showed that denser materials produced uniform wear over the electrolyzed area, with little evidence of pitting or particle detachment. However, though the samples were dense it was found that wear rates were still quite high (when comparing them to the graphitized cathodes) especially at high current densities and high excess AlF_3 content. This was probably due to the ease of the aluminium carbide formation reaction with the relatively disordered binder phase material in the graphitic cathode.

Conclusions

Graphitic Material

- Graphitic material produced dense, low porosity cathode samples even with varying grain formulations. This indicates that graphite is quite tolerant to changes in grain formulation when producing extruded cathode samples.
- Due to the superior internal structure of the cathode material, very little evidence of cathode degradation by pitting and particle detachment was found.
- Low porosity graphitic cathode samples were found to have little to no evidence of bath penetration. These results could indicate that there is a critical pore size at which bath penetration will occur.
- Though dense samples were produced the wear rates observed were still significant. High wear rates were attributed to the preferential aluminium carbide

formation with disordered carbons in the non-graphitized binder phase.

- Due to the relative similarity in the various cathode properties between samples, it was difficult to conclude on the effect of porosity and granulometry on wear rate. However results showed a strong dependence of wear rate on current density and bath chemistry. This supports the theory that the main cause of wear is the electrochemical formation of aluminium carbide.

Comparisons between Graphitized and Graphitic Cathodes

The following conclusions are made based on the results reported in part II and III of this series of papers.

- Graphite filler material was less sensitive to formulation changes than isotropic coke material. Therefore accurate formulations will be needed to produce isotropic coke based samples with the same density as the graphitic based material.
- However, based on wear rate analysis on both graphitic and graphitized samples it was found that the wear rates were high for the dense graphitic material. Thus, indicating that density is not the only performance determining parameter.
- The results from this investigation suggest the best material regarding electrochemical behavior would be a combination of both these materials; a dense graphitized cathode material.

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