THE REDUCTION IN ANODE AIRBURN WITH PROTECTIVE COVERS

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In recent years, the variability in raw materials has resulted in attention being focussed on the optimisation of formulation and pitch quality of anodes. The quality criteria used have been based on physical properties such as porosity, reactivity to air and carbon dioxide. However, an integral part in the overall performance of anodes relates to the protection afforded to them in operating cells, especially the quality of sprayed or powder cover. This paper focusses attention on how airburn is reduced with aluminium coatings or varying depths of alumina and crushed bath. The latter is finding increasing use in smelters which are attempting to reduce the thermal disturbances associated with anode changing, and therefore recycling a greater amount of crushed bath as anode cover.

The airburn reaction of various unprotected carbons at temperatures above 700°C, is controlled by mass transfer of air. When specimens are covered, the airburn reaction is mass transfer controlled (by the protective layer) at all temperatures. This diminishes the sensitivity reaction rate has on the quality of the anode. The rate of reduction in air burn rates diminishes as the depth of cover exceeds 25mm indicating the importance of having a uniform cover rather than a deep cover. While no difference is discernable for crushed bath of a similar particle size distribution when the anode surface temperatures are below 700°C, at higher temperatures sintering effects can change the net reactivity of anodes covered with crushed bath.

INTRODUCTION

The economic implications of the changed performance characteristics arising from both the variability in quality of raw materials and manufacturing procedure used to produce anode blocks is well known. The 10 to 20% wastage of anodes is seen by many in the industry as being partially avoidable and therefore it has been the focus of considerable research. Studies of plant anodes have shown that airburn usually accounts for more than half of the wastage. The other major source is carbon monoxide formation (predominantly by reaction of carbon dioxide in the pores above the electrode interface) but a little of the excess is accounted for by dusting and other factors. As demonstrated in Figure 1, the technology, cell efficiency and anode quality all play an important role in the overall consumption.
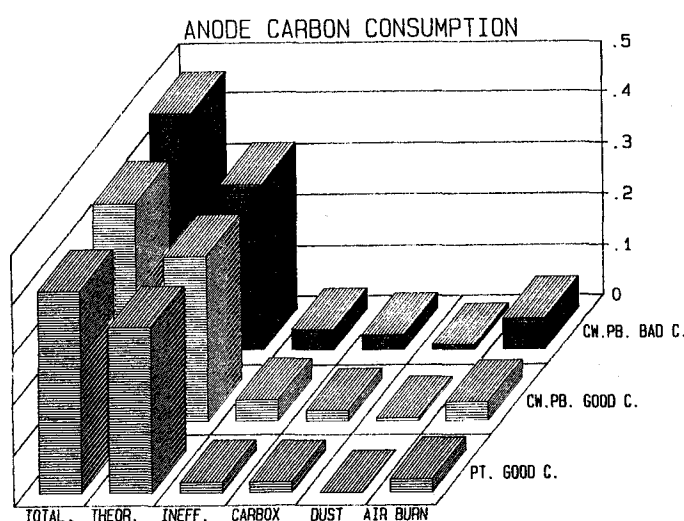

Figure 1 Depicting the different carbon consumptions as carbon quality and cell technology changes.

It is seen that of the excess consumption over the theoretical (theor.) the major contribution is from airburn. However reaction with carbon dioxide (carboxy) and dusting also can be important, especially in cells with poor quality anodes. The better performance of point fed cells (PT) over centre worked prebaked ones (CW.PB.) is due to both the high current efficiency and better airburn protection.

The difference in reactivities of both anode specimens and the raw materials can be demonstrated in the laboratory either by the reaction with carbon dioxide or reaction with air - typically the former is tested at about 950°C and the latter in the region 500-600°C. While the laboratory data often indicate consistent trends for manufacturing variables, invariably there is considerable scatter in results, and comparison between investigators is seldom good. The latter is due to differing designs and mass transfer conditions of techniques used.

Much of the recent anode research has focussed attention on formulation and manufacture of the anodes to give a minimum carbon consumption. For example publications by Fischer and co-workers (1-3) have shown that inherent reactivity of baked carbon anodes (and also the air permeability) are key

factors in assessing likely performance. The inherent reactivity test is performed with carbon dioxide, in the absence of protective cover on the specimen.

The question therefore arises as to whether protective covers used in industrial practice have any effect on the reactivity, and especially its sensitivity to formulation and raw materials. Standard industrial practice incorporates methods to reduce airburn by covering surfaces which would otherwise be hot and exposed directly to air. Historically the most common covering material has been powdered alumina but more recently, an increasing emphasis is being placed on minimising thermal disturbances during the anode changing process. Consequently crushed bath must be recycled back to the cell and it is sometimes used. This crushed recycled bath is high in alumina but contains similar fluorides to the bulk electrolyte. In cell designs which utilise tall anodes it is impractical to cover the hot sides of an anode initially. Then sometimes spray coating the surfaces with aluminium is also practiced.

The objective of the present study has been to quantify the role protective covers have in reducing airburn, and also to determine whether they have any impact on the importance of formulation and reactivity.

EXPERIMENTAL

All specimens studied were either cores taken from plant anodes where the manufacture and baking conditions were accurately known or, alternatively, produced from pilot plant specimens. In the latter case preparation was carried out using size fractions similar to those recommended by Fischer and co-workers(1-3) and the manufacturing and baking conditions were precisely known. A thermogravimetric technique was used to measure the rate at which the specimen was oxidised, but the experimental arrangement differed from those of other publications.

The major change in technique was to only study the reaction of the upper surface of the specimen (thus drawing a direct analogy with the upper surface of plant anodes) and having a specimen of sufficient size to give general representation of the heterogeneous surface. The specimen was inserted in a closely fitted recrystallised alumina crucible so that reactions on the sides were prevented. Also the carbon could be covered with varying depths of protective cover. The reactive surface area studied was 14cm^2. In order to prevent depletion of oxygen a high flow rate of the pre-heated air was used at all times.

The investigation was performed in the temperature range 450-800°C and the duration of reaction at any temperature was sufficient to ensure steady state conditions were achieved. The typical duration of an experiment was 20 hours.

For studies of anode specimens covered with a spray coating of aluminium, the samples were not inserted in an alumina crucible, but were suspended from a similar balance.
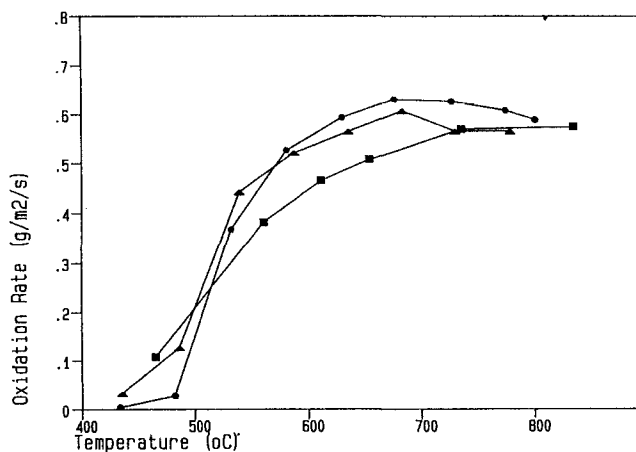

Figure 2 The variation in unprotected airburn rate with temperature for a selection of anode carbons.

AIRBURN RESULTS

Unprotected Airburn

Figure 2 presents typical oxidation rate data for three of the many specimens studied - each of them having a different formulation but common baking conditions. The curves demonstrate airburn characteristics similar to those expected from studies of Rhedey and co-workers (4). From an ignition temperature of about 400-450°C we have a strong dependence on temperature until about 700°C and thereafter mass transfer dominates. It should be noted that in these studies the build up of an ash layer plus the differential reactivity accentuates the transformation between reaction and mass transfer control causing a decided flattening of the temperature dependence. The results also demonstrate that manufacture plays an important role on unprotected airburn.

At 550°C, the oxidation rate for the specimens studied varies between 0.3 and 0.5g.m^{-2}.s^{-1}, this large range demonstrating the typical dependence on carbon quality and formulation.
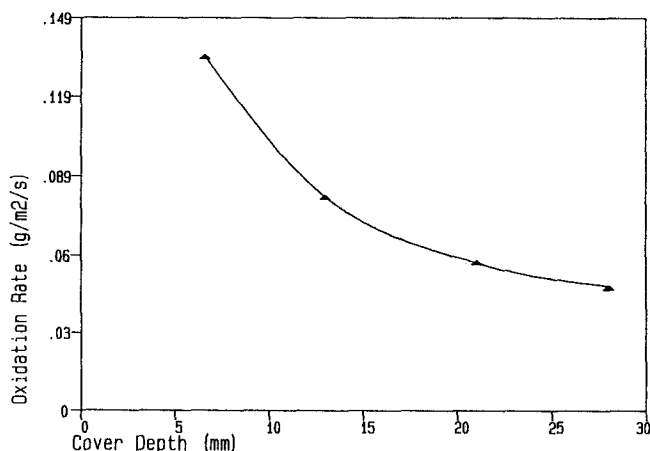

Figure 3 The reduction in airburn rate at 550°C as the depth of alumina cover is increased.

Reduction with Alumina

Figure 3 illustrates the marked reduction in oxidation rate that is achieved by covering the carbon specimen with alumina. An eight-fold reduction in rate is achieved by covering the specimen with 25mm of alumina and thereafter the benefits of increasing the depth are much less. In a practical cell the surface temperature will change as the depth of cover is altered. While this study cannot incorporate this relationship between temperature and insulating effects it will obviously influence the resulting reaction rate.

Use of Crushed Bath

The crushed bath used had an alumina content of less than 20%. In the temperature region 400-600°, no discernable difference was observed in carbon oxidation rate when alumina or crushed bath were used. The effect of a fixed depth (15mm) of crushed bath on the oxidation of the three different carbon qualities used earlier (Figure 2) is illustrated in Figure 4. This diagram also illustrates that the range of reactivities is reduced considerably for various carbon qualities. A change in behaviour is apparent in the temperature region 650-800°C. This aspect has been investigated by separate studies of the behaviour of crushed bath as discussed below.
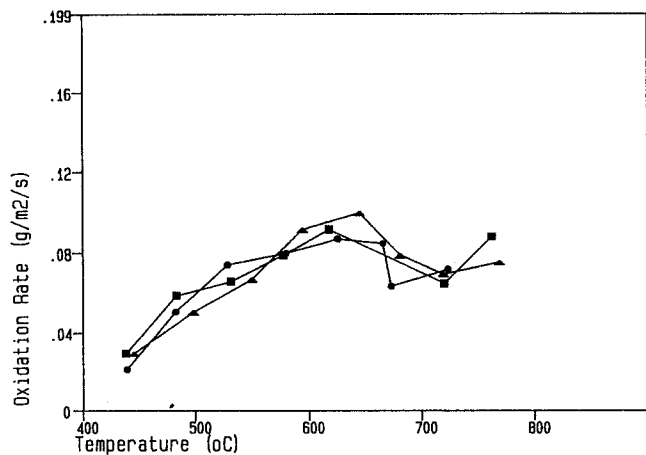
Figure 4 Effect of a fixed depth of crushed bath on the oxidation rate with temperature for selected anode carbons.

Effect of Heat Treating Crushed Bath

Samples of crushed bath were heat treated for various temperatures to 850°C. These samples had a higher alumina content than other crushed baths studied. The heat treated specimens were then impregnated with an epoxy resin and, sectioned and examined by image analysis. This procedure was performed in order to ascertain whether any sintering effects occurred, and also how these changes can affect the access of air.

Table I. Changes in Crushed Bath with Heat-Treating

Temp. (°C)	Time (days)	Part. Size (μm)	Pore Width (μm)
750	0	100	51
"	1	88	31
"	5	133	72
"	8	120	76
850	0	84	38
"	1	110	19
"	3	115	26
"	5	120	31

No change could be observed for specimens heat treated to temperatures below 650°C, irrespective of the time the specimens remain as a powder, as supported by the data presented in Table 1. However specimens heated at both 750 and 850°C showed some signs of sintering with time. The first effect is the average particle size increasing but also the average width of the pore channel in a packed powder increased. At both 750°C and 850°C, initially there is a decrease in pore width, but with time subsequent sintering occurs which opens up the channels, thus aiding the penetration of air.

Protection with Aluminium Coating

The technique used to spray coat aluminium can give a product of extremely variable quality. Typically the density of the coating is much less than theoretical, and the thickness varies considerably. Seldom is it totally impervious although certain zones will block air effectively. Thicker coatings when heated above the melting point of aluminium can flow a limited amount thus potentially sealing some of the pores.

Despite the widespread use of aluminium spray coating the published literature has little information on its effectiveness, although in the situations where it is used, cell operation would be impractical without it. Similarly there is no quantitative information on the fate of the aluminium - that is whether it melts into the cell or totally oxidises.

Cores of anodes carbon were cut to size and spray coated, using a similar procedure to that practiced commercially. The mass of coating was measured to assess the coat quality. We have assessed the quality of the coatings by the mass of aluminium sprayed per unit surface area (g cm^{-2}). The higher the mass, generally the thicker the coating, although the presence of pores makes this only a generalisation. The coated specimens were then suspended from the thermo balance, heated to the desired temperature, and then reacted with a stream of air. The rates of oxidation were compared with the steady state airburn rates for the same quality of carbon at the same temperature. Results presented in Table II illustrate the reductions in oxidation rates achieved. It should be noted that this reduction is expressed solely in terms of weight reduction assuming none of the aluminium is oxidised.

Table II. The Reduction in Airburn Rate
With Varying Qualities of Aluminium Coatings

Temp (^{o}C)	Coating Quality (g.cm^{-2})	Percent Reduction In Rate
577	0.112	33%
599	0.115	41%
598	0.135	61%
697	0.102	53%
700	0.076	36%

It is seen from this, that, the thicker the coating the greater reduction in airburn. Visual examinations of the specimens showed preferential airburn occurred in zones near defects in the coating. This is illustrated by specimens in Figure 5. The sections of the heavily airburnt anode that showed no airburn corresponded to the zones of the spray coating (right hand side) that were completely impervious. Conversely severe airburn is observed when the coating is very porous.
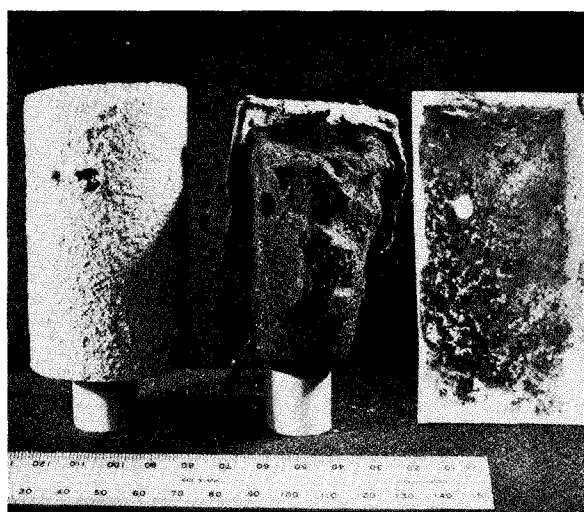

    (a)   (b)   **(c)**

Figure 5 Effect of porosity in aluminium spray coatings on airburn : (a) specimen after limited airburn at 600°C; (b) specimen airburnt at 700°C for 10 hrs (half coating removed); (c) the removed coating of specimen (b).

When the temperature exceeds the melting point of aluminium, some of the aluminium flows towards the bottom of the coating but very little falls off completely. The central photograph shows the dripping aluminium. Perhaps, surprisingly, the flow of molten aluminium does not tend to seal the pores-rather it tends to expand them through deformation as seen in the right hand specimen. Undoubtedly the coating of oxide prevents the sealing of pores and defects.

Chemical analyses have been performed on some samples of the oxidised spray coating. The amount oxidising is surprisingly small in view of the high surface area of the coating. For extended testing times the effect of the protection was found to redubecause of channelling that occurs once a void is created between the carbon and the aluminium spray coating.

GENERAL DISCUSSION

While the extent of airburn in unprotected anodes is extremely sensitive to carbon quality, the situation changes considerably with protection by powdered material. It is effective to use an increased depth of cover to reduce the differences that otherwise could arise from carbon quality difference. (However, this could have an impact on surface temperature, and could be important if the surface temperature is in the region between 450 and 700°C.) The difference in oxidation rates for unprotected carbons (Figure 2) as opposed to protected carbons makes it obvious that emphasis must be given to covering material effectively at all times. This includes avoiding cracks since, as found with the aluminium spray coating, once draughting channels can be formed oxidation rates approach those of unprotected airburn.

While spray coating is effective in reducing airburn, it is unlikely that a high proportion of that metal will find its way back into the cell; the molten aluminium is held within the oxide matrix by surface tension. Thus when spray coating is applied, it should only be applied to the surfaces that cannot be covered with oxide, but it should be a coherent pore-free coverage.

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