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REFLECTIONS ON THE CARBON CONSUMPTION OF PREBAKED ANODES

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Introduction

The main objective of this paper is to combine very practical aspects of anode consumption with more theoretical ones. Dealing first with two procedures used for the determination of the carbon consumption and the height of the spent anode, some ideas are then presented on how the carbon anode is consumed in the electrolytic cell and what kind of basic electrochemical mechanism is assumed at its bottom surface.

In modern reduction technology, bath material management plays an important role and has a great impact on anode consumption. This subject will also be looked at.

Determination of the net carbon consumption

Beautifully tabulated figures for the gross and net consumption of prebaked anodes are listed in the monthly report of every aluminium smelter. They are considered as prime performance symbols in the carbon area as well as in the potroom. Frequently, the consumption figures are accompanied by the reject rates of the main manufacturing stages in the anode plant. Such figures, if they are true, shed more light on the efficiency of anode production. It may be questioned, however, whether extremely low gross and net consumption levels really represent the most economical mode of operation.

Another critical question that may be raised concerns the determination of the net carbon consumption and, in particular, its comparability to other smelters.

A flow diagram, shown in Figure 1, shows the use of the carbon materials through the different steps of production and consumption. The reprocessing circuits of rejected products in the carbon plant have been deliberately omitted. The series of minor and major losses along the manufacturing path are indicated.

It has been seriously suggested by some experts to calculate the net carbon consumption from the carbon raw materials supplied to the smelter. It may be agreed that the total consumption of the incoming and processed carbon materials per ton of aluminium could be an excellent bench mark of production efficiency. In the practical application of such an idea, however, three problems arise. Firstly, the weight determinations of large petroleum coke cargos delivered by vessels do not seem to be accurate enough (accuracy 2 %). Secondly, it is rather difficult to quantify precisely the various carbon losses occurring in anode manufacture. Thirdly, the intervals between coke arrivals as well as between the dates of delivery and conversion to anodes are probably too long to allow reliable monthly computations to be made.

The simplest and most proven way of calculating the net anode consumption is to determine the difference between the quantity of new anodes sent to the potroom and the quantity of cleaned butts received from the potroom. The weight of a new anode block can either be obtained by means of a weighing machine installed in the roller conveyor before rodding or, after rodding, by a weighing device in the power-and-free system or overhead trolley conveyor (see lines V and VII in Fig. 1).

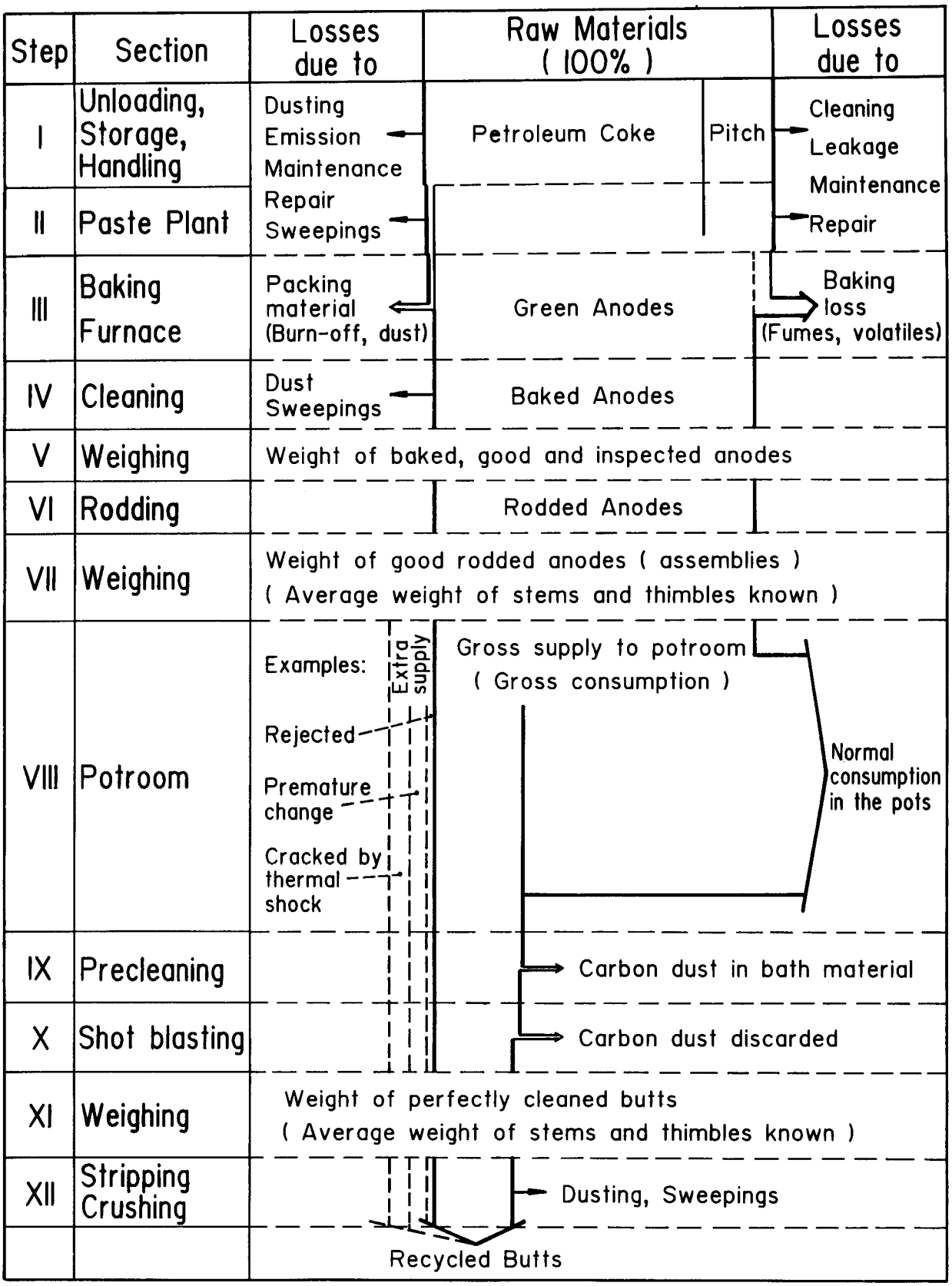

Fig. 1: Flow sheet of carbon materials in an aluminium smelter
(without intermediate reject streams in the anode plant)

The spent anodes returned from the potroom are usually weighed by a balance in the trolley rail after having undergone intensive cleaning in a shot blaster. The weighing of the butts may also take place later following stripping and crushing or tumbling.

It is common practice to discard and dispose of the dirty dust and fines from the butt cleaning units. How to treat the amount of removed dust in the calculation of the net carbon consumption is a controversial issue. Some potroom people say that this carbon material is not consumed in the electrolytic reduction process and therefore claim that the net carbon consumption should be reduced by the amount of dust. The effect of dust on the net consumption figure may be 0.5 % or more. In our company, the opinion is that all dust losses from the butts are part of the net consumption and should be charged to the potroom division.

Calculation of the butt height

When designing new or retrofitted electrolytic cells, it is very helpful to have a formula at hand for the calculation of the final height of the butts. The progressive decrease in anode height can easily be computed using the formula:

$$\Delta h = f \times \frac{CD}{AD} \qquad (1)$$

where

Δh_C = Decrease in anode height in cm/h.
f = Specific carbon consumption in gC/Ah.
CD = Anodic current density in A/cm².
AD = Apparent density of the anode in g/cm³.

It can be seen from equation (1) that the decrease in anode height is directly proportional to the anodic current density and inversely proportional to the apparent density of the anode.

Theoretically, factor f refers to the real electrochemical consumption of carbon material in the electrolytic reduction process. Therefore, factor f depends essentially on the primary composition of the anode gas, i.e. on its CO_2/CO-ratio. There is, however, a quite practical route to obtain a numerical value for factor f. It can be derived from operational data, where the excess carbon losses due to burn-off and dusting, as well as the actual current efficiency, are included:

$$f = \frac{CC_n \times CE}{2.980} \qquad (2)$$

CC_n represents the net or specific carbon consumption in gC/gAl. CE denotes the current efficiency, and 2.980 is the electrochemical equivalent expressed here in Ah/g Al. Hence, the value of f is as follows:

$$f = \frac{gC/gAl \times CE}{Ah/g\ Al} = \frac{gC}{Ah} = \frac{\text{grams carbon}}{\text{ampere} \cdot \text{hour}} \qquad (3)$$

In deducing equation (1), it was tacitly assumed that the original cross-section of the anode remains constant. It is a matter of fact that the cross-section of the anode shrinks with advanced usage, and that the edges of the spent anode are rounded. This, therefore, involves making a correction to the calculated height when using equation (1), and means a transformation of the butt shape into a rectangular prism. The sketch in Figure 2 illustrates the dimensional changes and the geometrical notation. According to Figure 2, the following denotation is used for the calculation:

h_0 = Original height of the anode block
h_C = Calculated decrease in anode height
h_C = Δh_C x residence time of the anode in the pot in hours
h_B = $h_0 - h_C$ = Height of the spent anode as a rectangular body
S_0 = Original cross-section of the anode
S_B = Rectangular cross-section of the spent anode
h^*_B = Corrected height of the spent anode in the form of a rectangular prism

$$h^*_B = (h_0 - h_C) \cdot \frac{(1 + S_0 - S_B)}{S_0} \qquad (4)$$

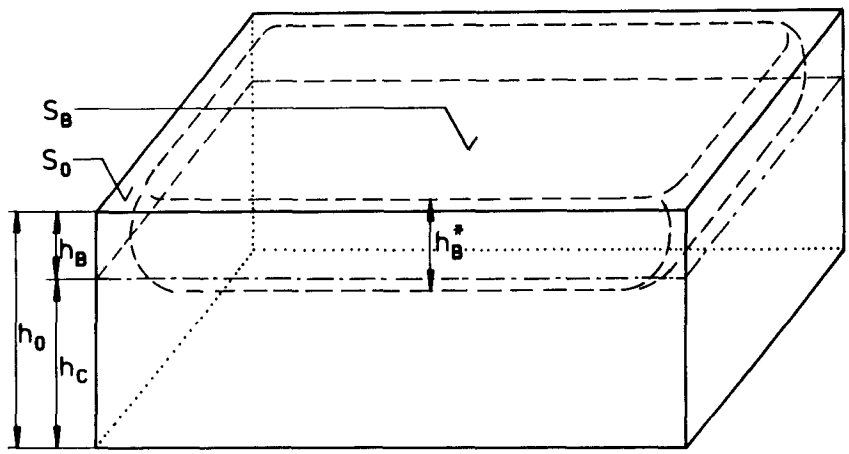

Fig. 2: Definition of the dimensions for calculating the final height of the spent anode

In order to calculate the corrected height h^*_B of the spent anode or butt, it is necessary to determine the cross-section of the butt in the form of a rectangular block. Well-shaped butts from optimal pot operation are reduced to approximately 85 % of the original cross-section of the new anode.

An example may demonstrate the usefulness of equation (1).

The following data are assumed:

Anodic current density CD = 0.78 A/cm²
Apparent density AD = 1.57 g/cm³
Ratio $\frac{CD}{AD}$ = 0.497 $\frac{A \cdot cm}{g}$
Net anode consumption CC_n = 0.41 gC/g Al
Current efficiency CE = 0.95
Factor $f = \frac{0.41 \times 0.95}{2.980}$ = 0.1307 gC/Ah

Specific decrease in anode height
Δh_C = 0.0649 cm/h = 1.56 cm/day
Residence time of the anode in the pot
= 80 shifts = 640 h
Decrease in anode height during the cycle time, h_C
= 41.5 cm
Original height of the anode h_0 = 60 cm
Height of the butt h_B = 18.5 cm
Corrected height of the butt h^*_B = 18.5 x 1.15
= 21.2 cm

The calculated height h^*_B of the spent anode is in good agreement with the actual measured height.

In conjunction with the anodic current density and the apparent density of the anode, the preceding values for f may be applied to estimate the final height of the spent anode. In a process of optimisation, either the cycle time of the anode or its apparent density may be adjusted.

Approximate correlations between the net or specific anode consumption, the current efficiency and factor f in equation (1) could be inferred from data collected during actual potroom operation. It has to be borne in mind that the following figures do not represent universal relationships. They have to be regarded as orienting examples.

Specific or net anode consumption gC/g Al	Current efficiency	Factor f gC/Ah
0.43	0.925	0.1335
0.42	0.935	0.1318
0.41	0.945	0.1300
0.40	0.955	0.1282

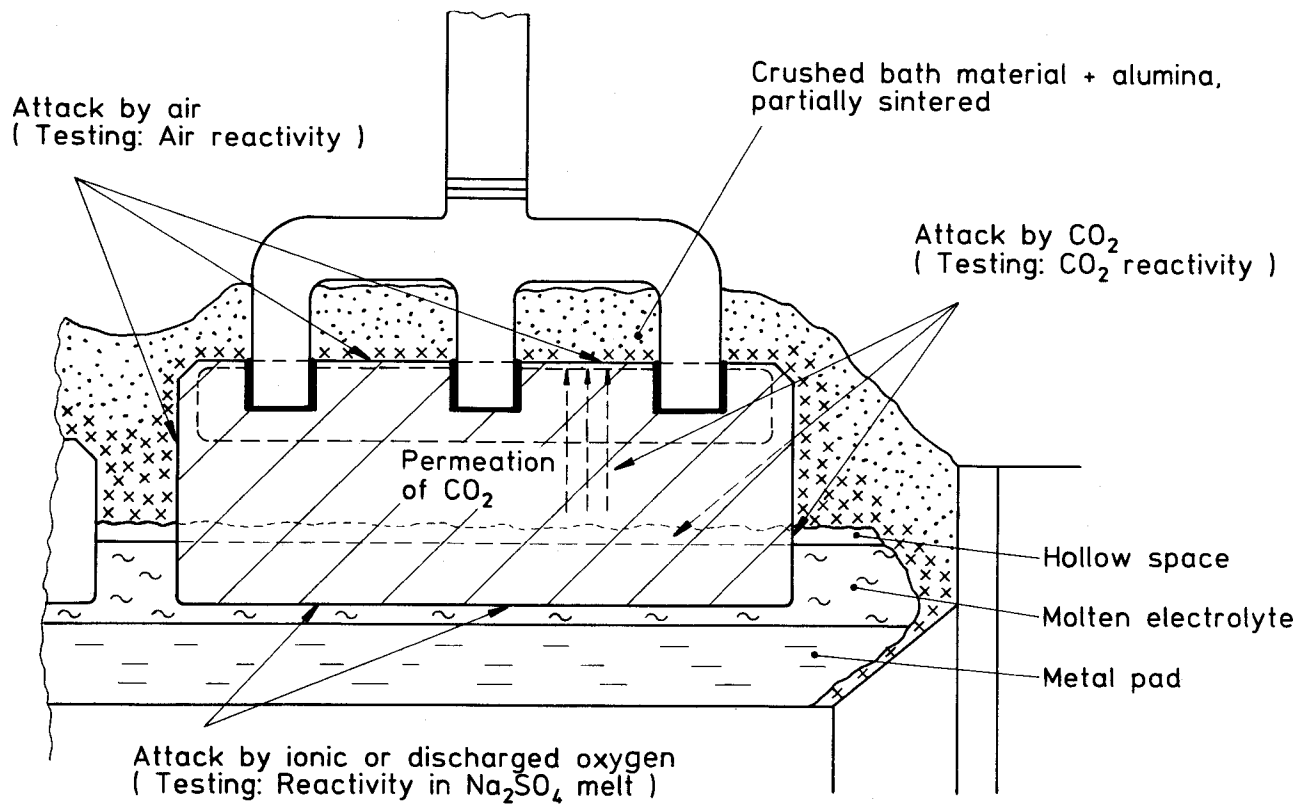

Fig. 3: Carbon consumption in an aluminium reduction cell

Process of carbon consumption

Three different oxidation processes can be identified or distinguished by which the carbon anode is consumed. The schematic drawing in Figure 3 shows the places around the anode block where these three types of oxidising reactions occur.

As is already well-known, pure oxygen is liberated at the bottom of the anode by the electrolytic decomposition of alumina. The electrochemical reaction between the oxygen and the anode carbon accounts for about 80 - 85 % of the total carbon consumption.

Most of the gasified carbon material is converted to carbon dioxide. This is also an oxidant for the carbon anode at the prevailing temperatures but with a much weaker intensity. The primary, CO_2-rich anode gas forms myriads of bubbles which travel through the electrolyte to the periphery of the anode and subsequently emerge at the bath surface. Above the electrolytic bath and below the arch of the crust, the CO_2 comes into contact with a few-centimetre wide zone of the anode side faces. A small portion of the primary anode gas is forced by the existing overpressure into the open pore channels of the carbon anode and may permeate it, preferably in a vertical direction. The extent of anode gas penetration through the anode depends on the permeability of the anode as well as on the permeability of the crust layer on top of the anode. CO_2 is reduced to CO along the path of the gas across the anode.

The proportion of carbon loss which exceeds the electrochemical consumption up to the net carbon consumption is commonly called "excess carbon consumption". The latter normally lies in the range of 15 - 20 % of the net carbon consumption, and it has always been an ambitious target of the aluminium smelters to bring this carbon loss down to below 15 %. It is difficult to differentiate exactly between what percentage of excess carbon is lost due to air oxidation and what quantity is consumed by burn-off with CO_2. We believe that under modern operating conditions at least two thirds of excess carbon consumption has to be attributed to air burn.

Each of the three aforementioned areas of anode oxidation is associated with the formation of carbon dust. The attack of the oxidising reactants is usually selective and disintegrating. Generally, much carbon dust appears if the matrix or bond structure is highly reactive and more sensitive to oxidation than the coarse filler material.

Whilst the oxidation of anode carbon by air or CO_2 is significantly catalysed by various metals (V, Na, Ca, for example), the electrochemical reaction between the ionic or discharged oxygen with the carbon anode on the bottom surface is only negligibly affected by catalysts. In such cases, the sort of carbon material and its heat treatment are of great importance. We have found that the performance of this essential part of the anode can best be correlated with the results of the sodium sulfate test, in particular to the degree of adverse dust formation. The specific behaviour of the carbon anode against air and CO_2 attack should be determined by testing methods that feature a close transferable similarity between the testing and the operating conditions.

It may be worthwhile to seek for a clearer understanding of the electrochemical process by which the carbon anode is consumed. A simplified model is outlined in Figure 4. In essence, it represents our point of view on the mechanism. To be very precise, one should define the following four types or stages of anode gas with different compositions in CO_2 and CO.

"Primary" anode gas is formed right at the anode and originates from the reaction of the nascent oxygen with the anode carbon. Evolving in an adsorbed gas film on the carbon anode, primary anode gas accumulates and separates itself from the thin gas layer in the form of bubbles, then moves through the electrolyte underneath the anode and is eventually released from the electrolyte as "secondary" anode gas. The primary anode gas reacts with cathodic species in the course of its passage through the electrolyte whereby its CO_2 content is reduced to CO (see Fig. 4). Strictly speaking, the electrochemical process ends with the emission of the secondary anode gas. Before, however, the secondary anode gas leaves the electrolytic region through openings in the cover of crust, its still high CO_2 content may react further with the anode carbon, either internally along the pores or on the bare side faces, as well as with abundant carbon dust. By means of such a reaction, the secondary anode gas is changed to a "tertiary" anode gas with a slightly higher CO content. Since the difference in the CO_2/CO composition between the secondary and tertiary anode gases is marginal, they are often taken as being equal, but to prevent any confusion, it is proposed to differentiate between these two. The tertiary anode gas mixes with the carbonic oxides generated by air-burn and, in addition, its CO-content may be partially combusted to CO_2. When considering the combined, overall composition of the final anode gas with respect to the oxidised electrode carbon (carbon fluorides can be neglected), one may even define a "quaternary" anode gas.

In our opinion, the electrolysis of alumina proceeds with a definite oxygen partial pressure at the carbon anode. That oxygen pressure determines the theoretical back e.m.f. (electro-motoric force) of the cell, i.e. the sum of the alumina decomposition and the anodic depolarisation voltages (see Figure 5). In the case of a thermodynamic equilibrium occurring at the carbon anode, a gas composition corresponding to the so-called "Boudouard equilibrium" should be observed (see Figure 6). Referring to the graph in Figure 6, it would mean an anode gas consisting of approximately 99 vol.-% CO und 1 vol-% CO_2, an oxygen partial pressure as low as 10^{-18} bar and a theoretical decomposition voltage of 1,06 V at 977 ° C. For kinetic reasons, i.e. because of slow reaction rates, the O_2 partial pressure is shifted to higher values. It mainly happens with increasing current density and decreasing carbon reactivity. With regard to prebaked anodes under normal electrolysis conditions, an oxygen partial pressure in the range of 10^{-10} to 10^{-8} bar is reached which is related to a decomposition voltage of 1.6 to 1.7 V and a primary anode gas of almost pure CO_2 (>99.5 vol.-%). The shifting from the state of equilibrium to the dynamic state of practical operation results in a remarkable reduction in carbon consumption to nearly 50 %, but this gain has to be paid for by a higher decomposition voltage of around 0.65 Volt or additional electrical energy of around 2.1 kWh/kg Al. If the oxygen pressure is raised further, for instance up to

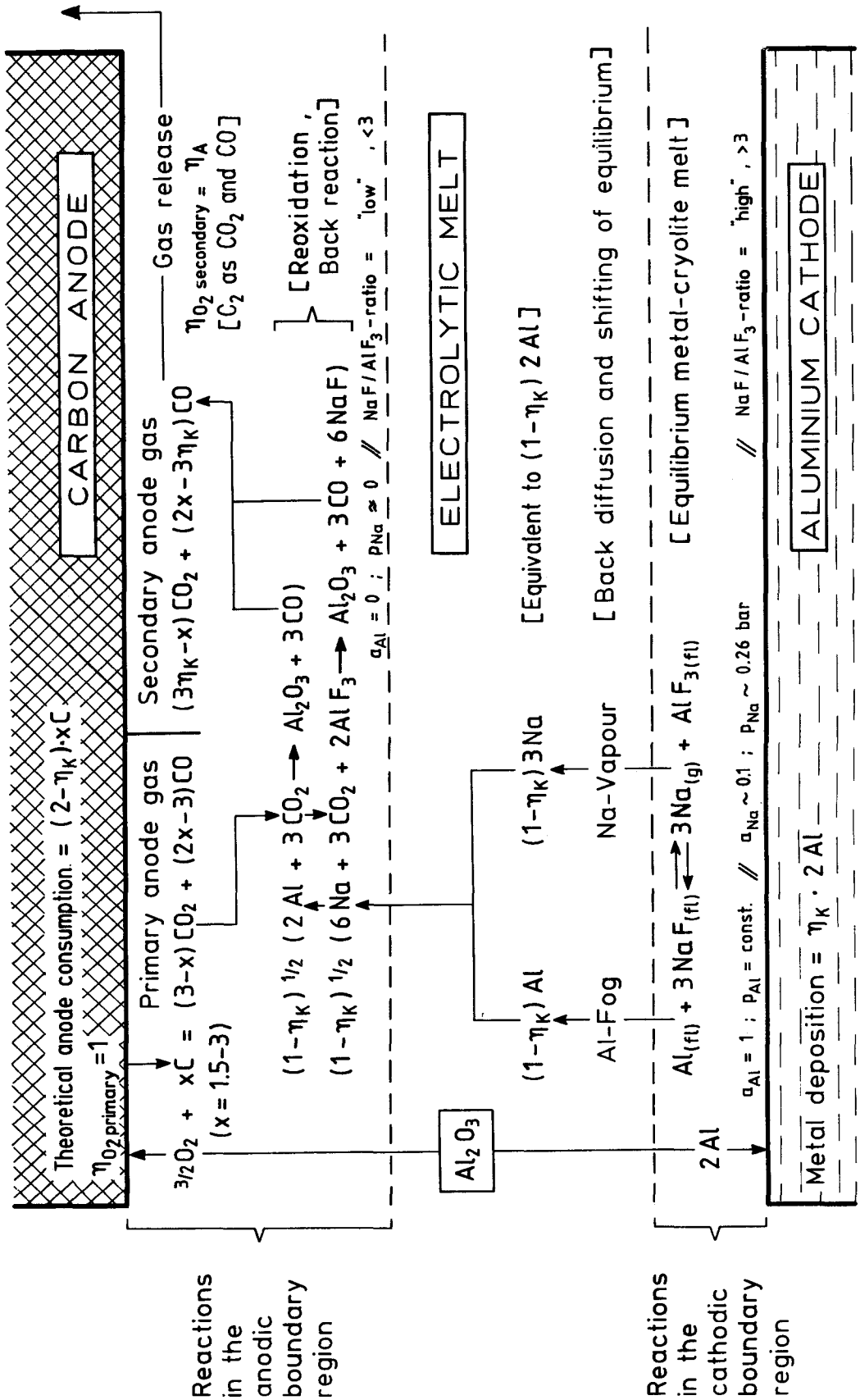

Fig. 4: Model to explain carbon consumption and current efficiency

10^{-2} bar, the primary gasification product will remain CO_2. This phenomenon gave rise to the hypothesis that CO_2 is the primary anode gas. When using the more reactive Söderberg anodes, the primary anode gas will contain substantial amounts of CO. It has also been proved that higher CO concentrations in the primary anode gas are obtained in superheated reduction cells and at fairly low current densities.

As pointed out above, a relationship can be established between the CO_2 content of the primary and the secondary anode gas if the current efficiency and a factor for the anode reactivity are taken into account. The correlation is given by the formula:

$$\varphi CO_2 = \eta\,(1 + C) - 100,$$

where φCO_2 is the volumetric CO_2 concentration of the secondary anode gas in percent, η the % current efficiency and C a specific constant for the type of anode. C is about 0.95 - 1 for prebaked anodes and 0.7 - 0.9 for Söderberg anodes under normal operating conditions.

The electrochemical anode consumption depends on the CO_2/CO composition of the secondary anode gas as shown by the diagram in Figure 7.

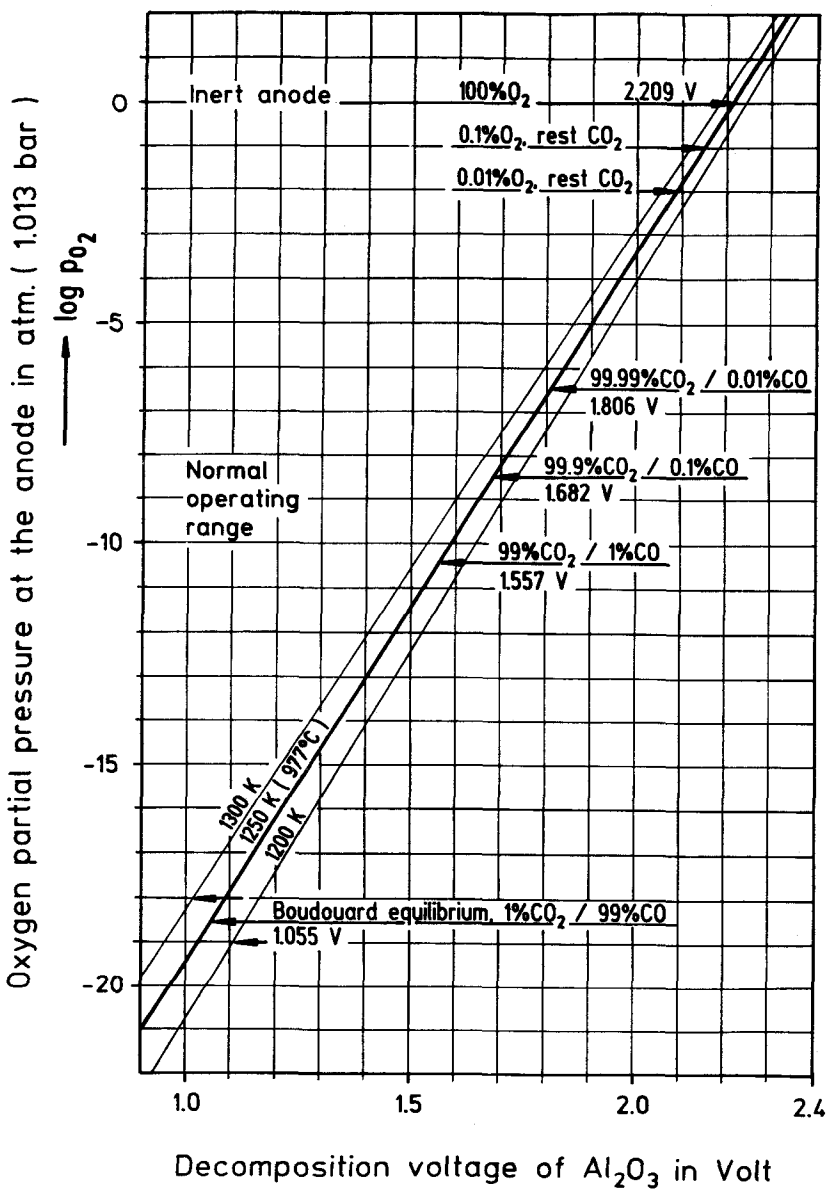

Fig. 5:

The composition of the primary anode gas in relation to the oxygen partial pressure at the carbon anode and the theoretical decomposition voltage of Al_2O_3.

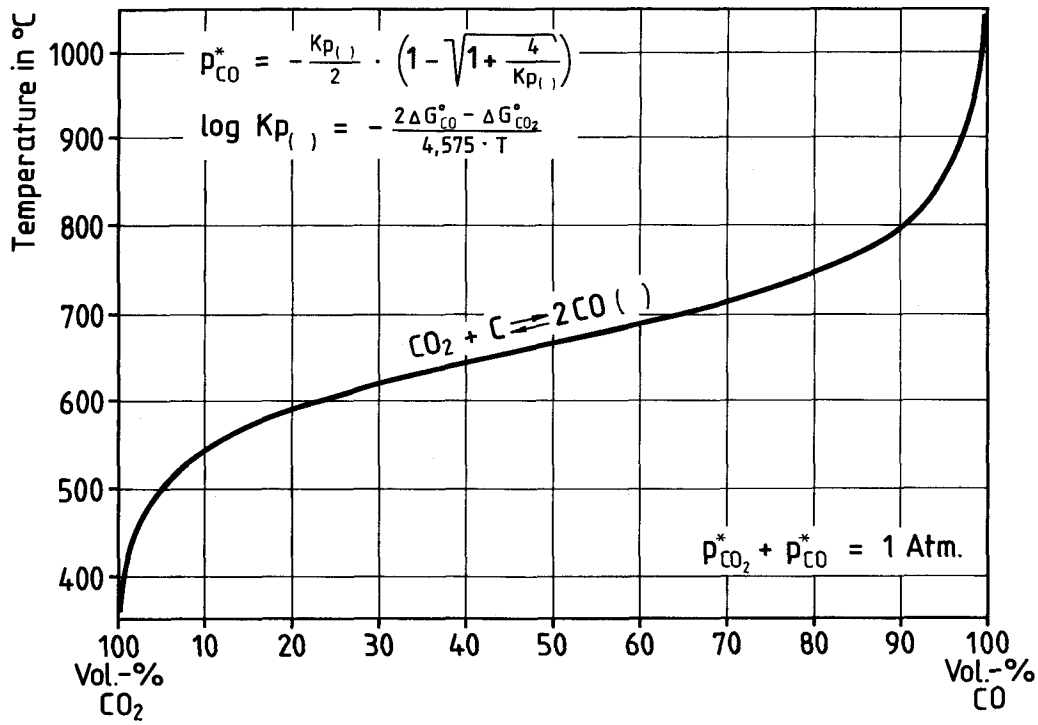

Fig. 6: The Boudouard equilibrium as a function of temperature

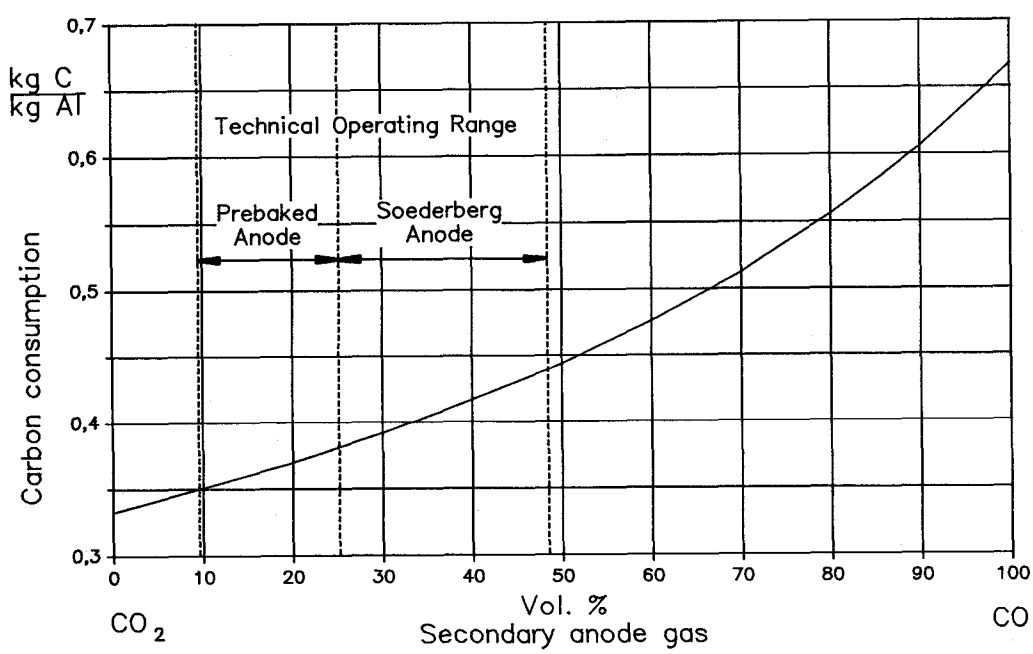

Fig. 7: Specific carbon consumption in dependence of the CO_2-CO composition of the secondary anode gas

Measures to reduce net carbon consumption

The best anodes made of high-quality raw materials and baked to optimum temperatures cannot be expected to resist air attack at glowing temperatures for periods over 3 to 4 weeks. Burn-off in air will escalate to catastrophic proportions. Consequently, it is logical to protect that part of the anode which is above the bath level as well as possible. The most effective protection consists of an appropriate coverage with comminuted bath material. Our measurements of permeability on a spectrum of differently-sized bath materials, alumina and mixtures of both have clearly shown that packings of alumina are more pervious than those of bath material. Moreover, bath material tends to give a faster sintering, especially with the aid of evaporating and penetrating constituents from the liquid electrolyte. With a progressively longer residence time, the cover of bath material with additional alumina settled on the top will become denser and less permeable to air diffusion. To utilise the big advantages of bath material coverage, a carefully elaborated bath material management has to be provided.

Many potlines of earlier generations still exist which are equipped with centre-break bars. In pots of such a design it is often an unsurmountable problem to cover the anode edges and head faces along the centre line properly. To avoid excessive air burn in this region, the only feasible solution up to now has been to coat the anodes with a dense layer of sprayed aluminium. Spraying of aluminium is quite an expensive counter-measure against air burn. It may thus partly justify a retrofitting of the potline to point feeders.

Another item which may be discussed here are anodes with a roof-shaped top or comparatively broad slopes at the upper edges of the anode block. Sloped faces of this kind are supposed to be intermittently flooded by the electrolyte at the end of the anode life time in the pot and to expose an enlarged anode surface to CO_2 attack. These surfaces are also believed to generate more carbon dust.

There is no doubt that net carbon consumption is influenced by the anode quality. This subject has been treated before in many other publications, and it would take far too long to consider it more extensively here.

Conclusions

The phenomena of carbon oxidation which lead to the total anode consumption are not as complicated as they seem at first glance.

The electrochemical oxidation process which occurs on the submerged bottom face of the carbon anode is explained by a theory developed earlier. This theoretical approach is believed to fit in with the overall picture of alumina electrolysis. The performance of the immersed part of the anode correlates with the sodium sulfate test.

The part of the anode which protrudes above the electrolytic melt is exposed to CO_2 and air oxidation and causes excess carbon consumption. The sensitivity of the anode to burn-off in air or CO_2 is usually examined by similar testing methods. One of the best measures to diminish carbon losses due to air burn is an optimal coverage of the anodes with prepared bath material. In this context, much attention has to be devoted to the treatment and handling of bath material.

A formula was presented to calculate the progress of anode consumption and the final height of the spent anode.

It was briefly discussed in which way the net carbon consumption is determined, and argued that discarded butt material in the form of fines and dust should be included in the net consumption.