

REACTIVITY AND ELECTROLYTIC CONSUMPTION OF ANODE CARBON  
WITH VARIOUS ADDITIVES

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Effect of  $\text{Na}_2\text{CO}_3$ ,  $\text{ZnS}$  and  $\text{Al}_2\text{O}_3$  additions on the reactivity and electrolytic consumption of anode carbon was investigated.  $\text{CO}_2$ -reactivity increased with increasing additions of  $\text{Na}_2\text{CO}_3$  confirming the catalytic effect of sodium.  $\text{ZnS}$ , when added alone, did not have any significant effect on the  $\text{CO}_2$ -reactivity. However, when it was added to samples already containing some  $\text{Na}_2\text{CO}_3$ , a considerable decrease in the reactivity was attained.  $\text{CO}_2$ -reactivity was not affected by additions of  $\text{Al}_2\text{O}_3$  (0-5 wt%). Air-reactivity, on the other hand, decreased with increasing additions of  $\text{Al}_2\text{O}_3$  whereas it showed a small increase with  $\text{Na}_2\text{CO}_3$  additions.  $\text{Al}_2\text{O}_3$ -containing anodes were also subjected to laboratory electrolysis tests. Carbon consumption was found to increase significantly and the excess consumption was purely due to increased extent of dusting. Contribution of carboxy reaction to carbon consumption remained unchanged with additions of  $\text{Al}_2\text{O}_3$ .

#### INTRODUCTION

The quality of anode carbon raw materials can affect the anode manufacturing process and also the performance of the anode during the electrolytic production of aluminium. Significant and continuous variations in the raw material properties have been experienced in recent years. Petroleum coke purity is one of the major properties which can be mentioned in this context. The trend had been towards higher sulphur content and increased amount of metallic impurities. Some of the impurities are known to influence the  $\text{CO}_2$ - and air-reactivity of the carbon anode and thus leading to higher anode consumption. A review article on the influence of impurities on anode reactivity has recently been published (1). It has been well established that V and Ni are catalytic to the airburn reaction while the same is true for Na and Fe in the case of carboxy reaction. However, it has often proved to be rather difficult to separate the effects of different elements due to the co-presence of other impurities. An example of this is the presence of sulfur where conflicting results have been reported (1).

Additives have also been used in order to improve anode performance and  $\text{AlF}_3$ ,  $\text{B}_2\text{O}_3$ ,  $\text{SiO}_2$  and

phosphorous-containing compounds have commonly been suggested as inhibitors (1) for the carbon oxidation reactions. However, there is only few published data on the effect of  $\text{Al}_2\text{O}_3$  additions on reactivity and consumption of anode carbon.  $\text{Al}_2\text{O}_3$  was found to catalyze the oxidation of graphite<sup>2</sup> in air in a fundamental study (2). Rhedey (3) reported a significant increase in consumption of Söderberg test electrodes containing  $\text{Al}_2\text{O}_3$  as additive without giving any detailed information. In recent years, composite anodes consisting carbon and  $\text{Al}_2\text{O}_3$  (20-85 wt%) have been suggested as an alternative to the conventional Hall-Heroult technology (4,5). Carbon consumption had not been the major scope of these works. However, in one of them (5) the authors claim a minimal airburn of such composite anodes due to extensively reduced fraction of carbon in the anode.

The aim of the present work was to study the reactivity of carbon anodes with additions of  $\text{Na}_2\text{CO}_3$ ,  $\text{ZnS}$  and  $\text{Al}_2\text{O}_3$ .  $\text{ZnS}$  was added as a sulphur source both alone and in combination with  $\text{Na}_2\text{CO}_3$ . Consumption of  $\text{Al}_2\text{O}_3$  containing anodes during electrolysis was also studied.

#### EXPERIMENTAL

##### Sample Preparation

The anode carbon materials used in this study were obtained from the Norwegian aluminium industry in the form of cores drilled either from full-scale prebaked anodes or from small-scale laboratory blocks compacted by vibration and baked at 1265°C. Cores drilled from the full-scale anodes were used to study the effect of  $\text{Na}_2\text{CO}_3$  and  $\text{ZnS}$ , while the laboratory anodes were specially produced to study the effect of  $\text{Al}_2\text{O}_3$ .

$\text{Na}_2\text{CO}_3$  was introduced into the ready-machined samples<sup>2</sup> by dipping them into an aqueous solution of  $\text{Na}_2\text{CO}_3$  with varying concentrations for a predetermined length of time. After soaking, the samples were dried at 150°C for 15 h, cooled in a desiccator and weighed. This drying cycle was sufficient to get rid of all the water and the  $\text{Na}_2\text{CO}_3$  concentration was determined from the weight gain of the samples.

Addition of  $\text{ZnS}$  was not possible by the above mentioned impregnation technique since it is not soluble in water. In this series of reactivity

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testing the specimens were prepared from crushed and finely ground anode carbon with desired amounts of  $\text{Na}_2\text{CO}_3$  and  $\text{ZnS}$ . Approximately 4 g of mixtures with predetermined composition were pressed ( $\approx 850 \text{ kg cm}^{-2}$ ) into cylindrical tablets (15 mm diameter,  $\approx 15 \text{ mm}$  length) by using a commercial organic binder ("CMC", carboxy-methyl cellulose).

Laboratory blocks were produced from the same source of raw materials by adding  $\text{Al}_2\text{O}_3$  in desired amounts (0 - 5 wt%) during the mixing stage of the filler coke and pitch binder. All the processing parameters were kept constant in the production of these anodes. They were also characterized with respect to density, porosity, thermal conductivity and specific electrical resistivity.

Mercury porosimeter (Carlo Erba 1520) was used for the determination of cumulative pore volume and pore size distribution.

Specific electrical resistivity was measured according to the four pole method (6), by recording the voltage drop through the cylindrical specimen (20 mm diameter, 50 mm length) upon passage of 1A current.

Thermal conductivity was measured by employing a transient hot-strip method (7) where a thin (0.050 mm) tantalum foil was used as electrical conductor. The method is, in principle, based on the measurement of change in resistance of the conducting foil as a function of temperature by recording the voltage drop at a constant current of 5A. Logging of the experimental data and calculation of the thermal conductivity was carried out by a microcomputer (Apple IIe).

#### Reactivity and Consumption Testing

Reactivity testing of carbon materials was carried out in a conventional manner as already described by several authors (8,9,10). Cylindrical specimens were exposed to continuous flow of  $\text{CO}_2$  or air for 2-4 h at a constant temperature. Drilled-core specimens (20 mm diameter, 40 mm length) were directly suspended into the furnace from an electronic balance (BLH Electronics, LBP1) which allowed continuous recording of the specimen weight. Pressed tablets were suspended in buckets specially prepared from perforated platinum foil. Temperatures for the  $\text{CO}_2$ - and air-reactivity tests were  $948 \pm 3^\circ\text{C}$  and  $530 \pm 2^\circ\text{C}$ , respectively. Reactivities were expressed in terms of weight loss per exposed geometric surface area and time for the core samples. However, in the case of pressed tablets the data was expressed as percent weight loss per hour due to extensive destruction of the geometric shape during reactivity testing.

Consumption of anode carbon with  $\text{Al}_2\text{O}_3$  additions during electrolysis was studied by using an air tight laboratory furnace equipped with a gas absorption line for collecting the anode gas ( $\text{CO}_2 + \text{CO}$ ). Details of the electrolytic cell and the experimental procedure has already been reported previously (11). The anodes (42 mm diameter) were subjected to electrolysis for 3 h at a constant current of 13A. Electrolysis temperature was  $980 \pm 2^\circ\text{C}$  and cryolite containing 7 wt%  $\text{AlF}_3$  and 5 wt%  $\text{CaF}_2$  which was saturated with  $\text{Al}_2\text{O}_3$  was used as electrolyte. Experimental conditions were kept strictly the same in all runs.

The main advantage of the present electrolysis technique was the complete elimination of airburn of the anodes and the possibility of determining the anode consumption independently from the weight loss of the anode as well as from the total amount of carbon in the absorbed anode gas. Thus, the method provided a quantitative evaluation of the excess carbon consumption due to the two major mechanisms, namely carboxy reaction and dusting. The consumption data is usually expressed as a percentage over the theoretical value corresponding to 100%  $\text{CO}_2$  evolution at the anode.

## RESULTS AND DISCUSSION

### Effect of $\text{Na}_2\text{CO}_3$

The results of the  $\text{CO}_2$ - and air-reactivity tests with  $\text{Na}_2\text{CO}_3$ -impregnated samples are given in Figure 1.  $\text{Na}_2\text{CO}_3$  seems to catalyze both reactions. However, while the catalytic effect of  $\text{Na}_2\text{CO}_3$  on the airburn reaction is rather small, it is almost seven times stronger in the case carboxy reaction. In Figure 2 the reactivity data is expressed as a function of total sodium concentration, by adding the amount of sodium which is originally present in the carbon sample to the corresponding amount introduced as  $\text{Na}_2\text{CO}_3$ . The same figure also includes the data reported by Houston and Øye (10) where anode samples were made from different raw materials with varying sodium content. This surprisingly good agreement can be taken as an indication for the extremely high sensitivity of carboxy reaction on the sodium content regardless of other metallic impurities.

The big difference in the catalytic effect of  $\text{Na}_2\text{CO}_3$  on  $\text{CO}_2$ - and air-reactivity is believed to be mainly due to the difference in the behaviour of  $\text{Na}_2\text{CO}_3$  at the temperatures involved for the two reactions. A number of alternative mechanisms have been proposed in the past to explain the catalytic behaviour of alkali metal carbonates on the carbon

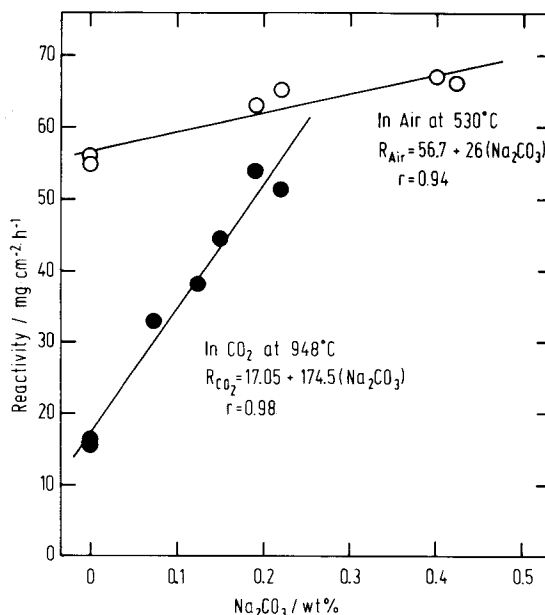


Figure 1. Effect of  $\text{Na}_2\text{CO}_3$  on the reactivity of anode carbon in air and  $\text{CO}_2$

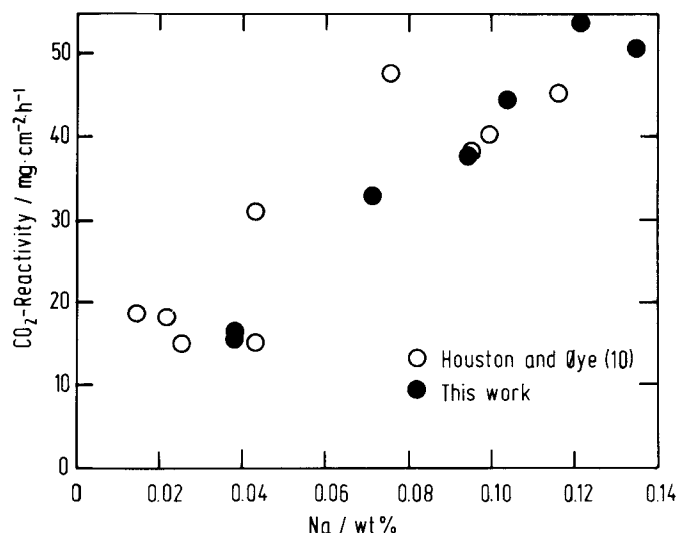
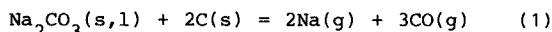
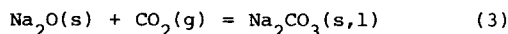
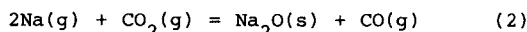


Figure 2. CO<sub>2</sub>-reactivity of anode carbon as a function of sodium content.

oxidation reactions. Excluding the electrochemical mechanism, the rest usually involve thermal dissociation of Na<sub>2</sub>CO<sub>3</sub> in one way or another (12,13). For the carboxy reaction due to relatively high temperatures formation of free alkali metal according to the following reaction seems to be the most feasible possibility.

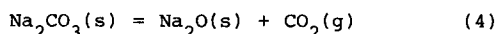


The equilibrium constant for the above reaction is around  $\approx 4 \times 10^{-7}$  at 927°C which may give rise to significant pressures of sodium metal vapor depending upon the pressure of CO. Alkali metal vapor formation was actually observed during the catalytic oxidation of graphite by CO<sub>2</sub> at temperatures around 1000°C (12). Since sodium vapor is highly reactive its formation may complete the catalytic cycle with the following two reactions

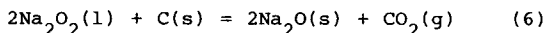
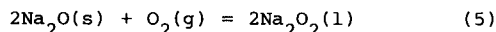


both being thermodynamically favourable at the temperature under consideration.

In the case of airburn reaction, due to lower temperatures of interest (<600°C) sodium metal vapor pressure according to reaction (1) will be almost insignificant since the equilibrium constant is only  $\approx 4 \times 10^{-24}$  at 527°C. Thermal dissociation of Na<sub>2</sub>CO<sub>3</sub> according to reaction (4) can occur only to a very small extent at this temperature.



However, as suggested by McKee and Chatterji (12) enhanced dissociation of the carbonate in the presence of carbon and oxygen as a result of the following sequence of reactions



might be the explanation of experimentally observed weak catalytic effect.

Combined Effect of Na<sub>2</sub>CO<sub>3</sub> and ZnS

The effect of ZnS additions on the CO<sub>2</sub>-reactivity of anode carbon with and without Na<sub>2</sub>CO<sub>3</sub> is shown in Figure 3. As can be seen from the figure addition of 0.40 wt% ZnS alone does not cause any significant change in the CO<sub>2</sub>-reactivity. While the reactivity loss of undiluted anode carbon is  $\approx 10\%/h$ , it is  $\approx 11\%/h$  for the sample containing 0.40 wt% ZnS. This difference is within the limits of experimental uncertainty. This almost unchanged reactivity is consistent with the previous literature (1,13) where zinc and zinc oxide are reported to be inactive for carboxy reaction and there is no sound thermodynamic reason for ZnS to behave differently. Addition of 0.45 wt% Na<sub>2</sub>CO<sub>3</sub>, as expected, increases the reactivity loss from  $\approx 10\%/h$  to  $\approx 25\%/h$  in the absence of ZnS. It is hardly possible to compare these values with those obtained by impregnated samples, since the sample geometry and morphology is highly different.

The interesting feature of ZnS appears when it is added to anode carbon which contains Na<sub>2</sub>CO<sub>3</sub>. The points presented in Figure 3 are the average values of at least two parallel runs at each composition. The amount of Na<sub>2</sub>CO<sub>3</sub> was kept constant at a level of 0.45 wt% while the ZnS content was increased from 0 to 0.47 wt%. There is a clear tendency towards lower reactivity with increasing additions of ZnS. Reactivity loss is reduced from  $\approx 25\%/h$  down to  $\approx 18\%/h$  as a result of 0.47 wt% ZnS addition. In other words, the catalytic effect of Na<sub>2</sub>CO<sub>3</sub> is reduced with increasing ratio of S/Na in the sample. The reason for such a behaviour is probably the existence of an additional chemical equilibrium in the presence of ZnS which can be expressed as:

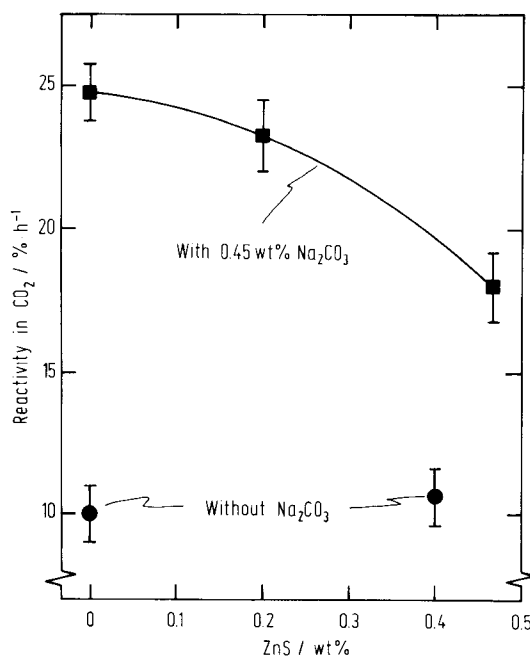
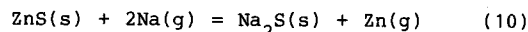
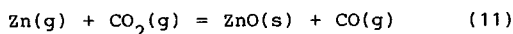


Figure 3. Effect of ZnS on the CO<sub>2</sub>-reactivity of anode carbon without Na<sub>2</sub>CO<sub>3</sub> (●) and with 0.45 wt% Na<sub>2</sub>CO<sub>3</sub> (■).

Sodium vapor pressure is again generated according to reaction (1) due to dissociation of  $\text{Na}_2\text{CO}_3$ . However, at the second step of catalytic cycle, reaction (2) has to compete with reaction (10). Purely from thermodynamic point of view reaction (10) with  $\Delta G^\circ = -136.8 \text{ kJ}$  is clearly more favourable compared to reaction (2) ( $\Delta G^\circ = -67.8 \text{ kJ}$ ) at  $927^\circ\text{C}$ . It is therefore reasonable to expect, at least, part of sodium vapor to be converted to  $\text{Na}_2\text{S}$  and thus leading to reduction in the amount of free sodium vapor available for the catalytic cycle. Zinc vapor generated as a result of reaction (10) would normally be expected to oxidize to  $\text{ZnO}$  according to following equilibrium.



As stated above  $\text{ZnO}$  is inactive to carboxy reaction and  $\text{Na}_2\text{S}$  being a highly stable compound is very unlikely to be active in catalyzing the carboxy reaction. Therefore, reaction (10) is believed to be an obstacle for the observed catalytic effect of  $\text{Na}_2\text{CO}_3$  and leads to reduced reactivity.

Further support to this suggested mechanism was obtained from X-ray diffraction analysis of the samples after reactivity testing. Reactivity residue from two samples containing both  $\text{Na}_2\text{CO}_3$  and  $\text{ZnS}$  was burned off in air at  $500^\circ\text{C}$  and the remaining ash was analyzed by X-ray diffraction. This diffraction pattern was compared with that of an ash obtained from anode carbon without any additives. The additional peaks appearing in the former pattern indicated the presence of both  $\text{ZnO}$  and  $\text{Na}_2\text{S}$  supporting the occurrence of reactions (10) and (11) during reactivity testing.

Under the light of above discussion, one may speculate a similar kind of interaction between sodium and sulphur in commercial anode compositions. Petroleum coke with high sulphur content may as well have a positive influence on the  $\text{CO}_2$ -reactivity by reducing the catalytic power of sodium impurity. This may be the reason for the broad disagreement in the previous literature with respect to the effect of sulphur on  $\text{CO}_2$ -reactivity. There are, in fact, some indications that samples with higher sulphur content are less reactive even if they may contain more sodium compared to a sample with low sulphur and low sodium content (10).

Effect of  $\text{Al}_2\text{O}_3$

Effect of  $\text{Al}_2\text{O}_3$  additions on the physical properties of the anode carbon is summarized in Table I.

Table I. Some Physical Properties of the Anode Blocks Containing  $\text{Al}_2\text{O}_3$  as additive

$\text{Al}_2\text{O}_3$ content (wt%)	Apparent Density ( $\text{g cm}^{-3}$ )	Cumulative Pore Volume ( $\text{cm}^3 \text{g}^{-1}$ )	Total Poro-sity (%)	Electrical Resistivity ( $\mu\Omega\text{m}$ )	Thermal Conductivity ( $\text{Wm}^{-1} \text{K}^{-1}$ )
0	1.53	0.156	23.6	$62.2 \pm 1.4$	$3.99 \pm 0.03$
1	1.50	-	-	$66.4 \pm 1.1$	-
2	1.52	0.157	23.9	-	$3.94 \pm 0.04$
3	1.51	-	-	$60.3 \pm 2.0$	-
5	1.55	0.153	23.7	$65.8 \pm 0.6$	$3.80 \pm 0.04$

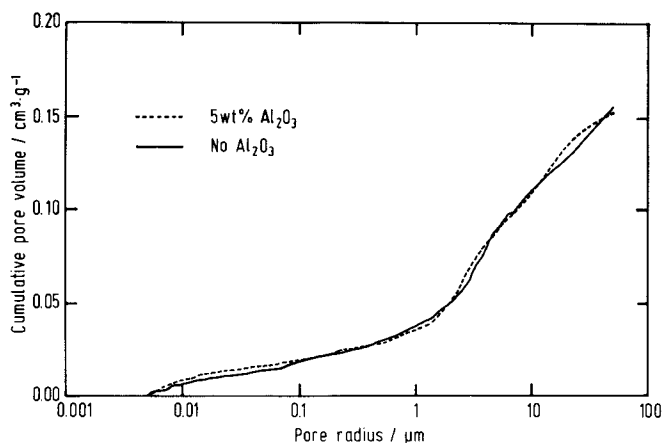


Figure 4. Typical pore spectra of the anode samples with 0 and 5 wt%  $\text{Al}_2\text{O}_3$ .

Apparent density and porosity of the anodes were not affected by additions of  $\text{Al}_2\text{O}_3$ . Pore size distribution was also almost the same for anodes with varying  $\text{Al}_2\text{O}_3$  concentration. This is demonstrated in Figure 4 where the pore size distribution for two samples, one without  $\text{Al}_2\text{O}_3$  and the other with 5 wt%  $\text{Al}_2\text{O}_3$ , are given. There was no correlation between the specific electrical resistivity and  $\text{Al}_2\text{O}_3$  concentration. All the measured values were, however, within the range specified for industrial prebaked anodes. Thermal conductivity, on the other hand, seemed to decrease almost proportionally with increasing additions of  $\text{Al}_2\text{O}_3$ .

The results of the reactivity tests of the anode carbon samples containing up to 5 wt%  $\text{Al}_2\text{O}_3$  are presented in Figure 5. While the air-reactivity decreases linearly with increasing  $\text{Al}_2\text{O}_3$ -content,

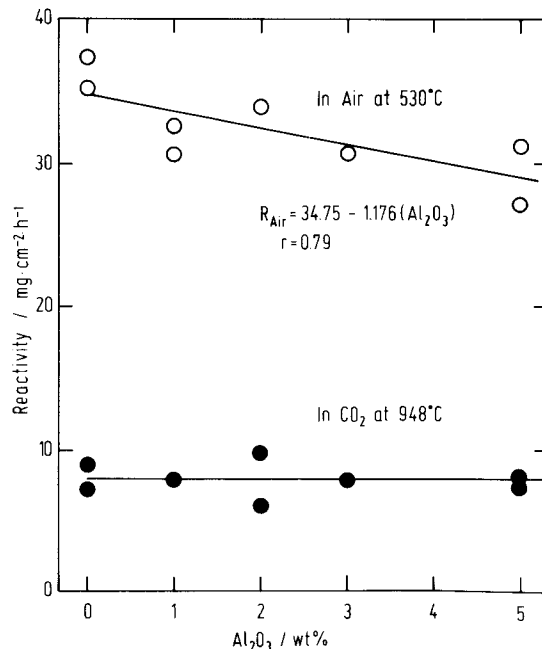


Figure 5. Effect of  $\text{Al}_2\text{O}_3$  on the reactivity of anode carbon in air and  $\text{CO}_2$ .

CO<sub>2</sub>-reactivity does not seem to be affected at all by Al<sub>2</sub>O<sub>3</sub> additions. This different behaviour in air and CO<sub>2</sub> is believed to be due to the difference in the temperature at which those reactions were studied rather than due to the change in oxidizing gas. It is well known that at low temperatures chemical reaction at the active carbon sites is the rate controlling step. It is, therefore, reasonable that reduced fraction of carbon sites with increasing Al<sub>2</sub>O<sub>3</sub> additions would decrease the rate of airburn reaction. At higher temperatures, however, mass transport of reactant gas from the exterior surface to active sites within the porous solid and of products to the outer surface become more likely to be the dominating rate limiting step. Variation in the pore characteristics would then be a more important factor than the concentration of active carbon sites. It has already been suggested that pore volume distribution within a specific range (0.25-7.5 μm radii) is of importance to the CO<sub>2</sub>-reactivity (14,15). This explains the observed constancy of the CO<sub>2</sub>-reactivity since the pore size distribution was not affected with Al<sub>2</sub>O<sub>3</sub> addition as shown in Figure 4.

From technological point of view reduced air reactivity is highly beneficial since excess carbon consumption will be less for the industrial anodes. Another aspect of Al<sub>2</sub>O<sub>3</sub> additions is its effect on the thermal conductivity of the carbon anode. As shown in Table I, thermal conductivity decreases with increasing Al<sub>2</sub>O<sub>3</sub> content which will lead to a lower anode-top temperature in industrial cells. According to Fischer and Perruchoud (16) a 0.1 Wm<sup>-1</sup>K<sup>-1</sup> decrease in the thermal conductivity leads to a 2.75°C lower temperature at the top of the anode. It, therefore seems possible to attain ≈2-5°C lower anode-top temperature depending upon Al<sub>2</sub>O<sub>3</sub> content. Even such small decreases in the temperature at the top of the anode would lead to considerable additional saving in carbon consumption due to airburn since air-reactivity is strongly dependent on temperature. This combined effect makes Al<sub>2</sub>O<sub>3</sub> an attractive additive for industrial anodes.

The dependence of anode consumption on the Al<sub>2</sub>O<sub>3</sub> content during laboratory electrolysis is given in Figure 6. Theoretical carbon consumption corresponding to 100% CO<sub>2</sub> evolution for 39 Ah of electrolysis is indicated on the figure. It can be seen that the anode is consumed at a faster rate with increasing Al<sub>2</sub>O<sub>3</sub> concentration. However, part of that weight loss is caused by the dissolution of Al<sub>2</sub>O<sub>3</sub> into the electrolyte from the anode. Correction of the anode weight loss for the corresponding amount of Al<sub>2</sub>O<sub>3</sub> dissolution from the anode, then gives the net consumption of carbon which also increases with increasing Al<sub>2</sub>O<sub>3</sub> additions. Increased extent of dusting is the major cause of this behaviour since gas absorption data does not show any significant increase. The same data is presented in terms of excess carbon consumption in Figure 7. Carboxy reaction does not cause any increase in the excess carbon consumption and this is in agreement with the results of CO<sub>2</sub>-reactivity tests. However, excess consumption due to dusting increases significantly leading to a higher total carbon consumption. The dependence of total carbon consumption (excluding airburn) on the Al<sub>2</sub>O<sub>3</sub> content can satisfactorily be expressed with 1.90%/wt% Al<sub>2</sub>O<sub>3</sub> as shown in Figure 7. These results indicate that Al<sub>2</sub>O<sub>3</sub> is mainly distributed over the binder phase. Dissolution of Al<sub>2</sub>O<sub>3</sub> from the binder phase during

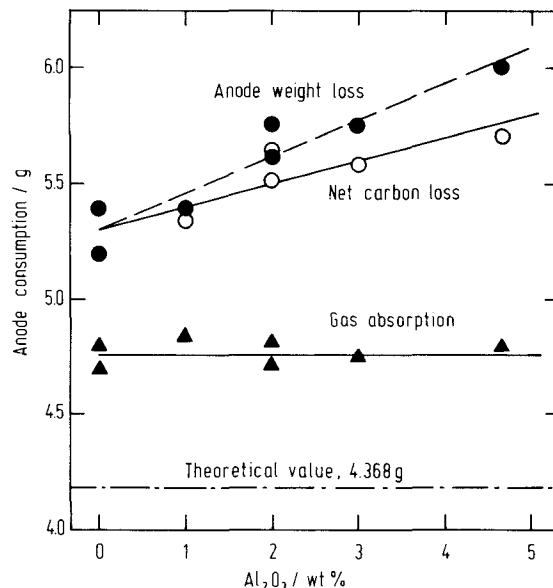


Figure 6. Effect of Al<sub>2</sub>O<sub>3</sub> on the consumption of anode after electrolysis at 980°C and 13A for 3h. Net carbon loss is obtained by correction of the anode weight loss data for the amount of Al<sub>2</sub>O<sub>3</sub> dissolving from the anode.

electrolysis combined with the already faster attack of the binder due to selective oxidation, makes dislodging of coke particles from the anode surface even easier. Therefore Al<sub>2</sub>O<sub>3</sub> additions, on contrary to its beneficial effect on airburn, seem to be detrimental with respect to dusting.

Several other important aspects need to be mentioned in an overall evaluation of Al<sub>2</sub>O<sub>3</sub> as an

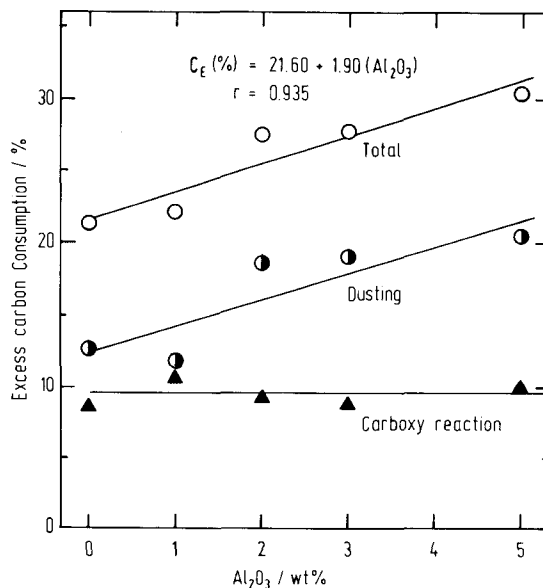


Figure 7. Dependence of excess carbon consumption on the Al<sub>2</sub>O<sub>3</sub> content of the anode.

additive to industrial anodes. For the first of all, the samples used in this work were prepared under the same conditions with same pitch level and coke granulometry. One may speculate a somewhat better performance of these anodes with some minor adjustments in anode formulation and processing. However, the present data is not sufficient to make any concluding remarks on this possibility. Secondly, temperature effect resulting from continuous dissolution of  $Al_2O_3$  from the anode surface has to be taken into consideration. A somewhat lower electrolyte temperature in the vicinity of the anode surface is likely to be attained in industrial cells, due to endothermic heat of dissolution. Such an effect can not be detected in temperature controlled laboratory furnaces but can lead to reduced  $CO_2$ -reactivity and this may partly compensate for the increased dusting loss. Finally, possible variations in electrical resistivity of anode carbon has to be taken into consideration. According to the present results  $Al_2O_3$  additions up to 5 wt% does not seem to have a pronounced effect on this property.

#### CONCLUSIONS

- $Na_2CO_3$  acts as a very strong catalyst for carboxy reaction while its effect is moderate on the airburn reaction.
- ZnS is inactive for carboxy reaction, however, it has an ability to reduce catalytic power of sodium significantly when present together with  $Na_2CO_3$ .
- $Al_2O_3$  does not affect the reactivity in  $CO_2$  but it decreases the reactivity in air.
- $Al_2O_3$ -containing anodes with a fixed pitch content and identical coke granulometry give rise to higher dusting loss during electrolysis.

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