Essential Readings in Light Metals: Electrode Technology for Aluminum Production.
Edited by Alan Tomsett and John Johnson.

INVESTIGATION OF THE QUALITY OF RECYCLED ANODE BUTTS

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ABSTRACT

Anode butts are recycled and used together with petroleum coke and pitch for the manufacture of anodes. The quality of these butts has a strong influence on the properties of the anodes.

For this reason butts of different origins were examined to ascertain what makes a good butt. It was ascertained that good butts are hard, have low sodium contents, a high ignition temperature in air and low reactivities in CO_2 and air. Butts of bad quality are soft and very reactive. The butt quality was defined by measuring the physical properties and the contaminations of the butts.

INTRODUCTION

In the electrolytic production of aluminium from alumina, carbon anodes are needed. Large anodes reach sizes of 1.65 * 1.0 * 0.65 m^3. They are in the reduction pot for 24 to 30 days, but cannot be fully consumed there. The mechanical suspension of the anode and the current supply make it necessary to remove the butt, which can be 15 to 30 % of the initial weight of the anode at the end of the pattern days. These anode butts are cleaned of any adhering particles of electrolyte - the latter consists of a mixture of cryolite, AlF_3 and other fluorides - and are then recycled for the production of new anodes. The dry aggregate in anode fabrication mainly consists of petroleum coke. 0 to 30 % anode butts in granulated form are added to the dry aggregate. Anodes made from 100 % anode butts in the dry aggregate have also been produced and successfully used in the potroom.

The properties of the petroleum coke essentially determine the quality of the anodes produced. Every anode producer endeavours, therefore, to use good and suitable petroleum cokes and subjects them to a quality control, in which the relevant physical and chemical properties are determined (1).

Because of the fact that the anode butts are re-used, their quality features are also of great importance. It was found that when poorly cleaned or soft anode butts are used, the anode quality suffers considerably.

The butt quality and its influence on the anode quality have been examined, therefore; this will be described in the following sequence:

- o behaviour of the anodes in the reduction pot
- o assessment of anode butts after anode changing
- o properties of butt granulates
  - crushed butts of good quality
  - crushed butts of poor quality
  - poorly cleaned butts
- o properties of test cylinders of good and poor butts
- o influence of good and poor butts on the quality of the anodes.

BEHAVIOUR OF THE ANODES IN THE REDUCTION POT

An anode is set with ambient temperature in the 930 - 980° C hot electrolyte. 25 to 50 % of the lower part of the anode is thus immersed in the liquid bath melt. Depending on the pot design, the part of the anode which is out of the bath is covered more or less with granulated electrolyte material and/or alumina. There are pots in which parts of the anode do not have any protective cover at all for many days.

The anode temperature rises by heat being conducted out of the electrolyte and by the current flow. The temperatures reach 350 - 600° C on the upper parts of the anodes after 1 - 3 days. Depending on the protective effect of the cover, airburn sets in at the upper part of the anode; this airburn represents non-electrolytic or excess carbon consumption.

With current flow, the electrolytic consumption begins on the immersed part of the anode; it amounts to 350 - 380 gC/kgAl and causes a loss in height at the lower part of the anode of 1.4 to 1.7 cm/day. Due to the electrolytic decomposition of the Al_2O_3 the oxygen, which is released, combines with the carbon of the anode to CO_2 and CO. CO_2 now attacks the anode; CO_2 burn develops, which also means non-electrolytic carbon consumption.

Non-electrolytic and electrolytic consumption together give the net consumption (2). It amounts to 390 - 450 gC/kgAl; the non-electrolytic consumption amounts to 10 - 30 % of the electrolytic consumption, therefore.

CO_2 and air oxygen normally attack the anode selectively (3). That means that the binder coke is attacked and consumed earlier and faster than the grains of the dry aggregate. They lose their mechanical bond with the anode and drop into the electrolyte as carbon granulate (carbon dust). In that way the electrolyte temperature can increase sharply so that above all the airburn and with it the carbon dust formation increase exponentially.

CO_2 mainly attacks the lower part of the anode, which is subsequently consumed by the electrolysis. The situation is a different one for the airburn. The airburn begins when the ignition temperature is reached and now has many days' time until the upper part of the anode has disappeared below the protective covering layer of electrolyte and alumina.

The airburn is now unfortunately not a reaction which only takes place on the surface of the anode. The air oxygen penetrates, due to gas permeability and open porosity, a few centimetres into the interior of the anode and reacts selectively there too, with the carbon. The result is that the anode structure is also mechanically weakened on the inside.

If this damaged part becomes electrolytically active at the end of the pattern days, the CO_2 attack continues its destructive effect. The anode butt which is taken out at the end is soft and only has a small butt cross-section.

If a lot of carbon dust is swimming on the electrolyte, then it represents, due to the combustion, an ideal and plentiful supply of CO_2. The upper part of the anode is then additionally considerably attacked by this in the last few pattern days. This can lead to small and soft butts, even when the quality of the anodes was good, until the carbon dust has been removed from the bath.

Soft butts are, therefore, not inevitably due to poor anode quality. If the electrolyte temperatures are high for other reasons, the airburn will increase considerably as a result and again lead to soft butts with small butt cross-sections.

ASSESSMENT OF ANODE BUTTS AFTER ANODE CHANGING

The assessment of the anode butts by the potroom personnel is done by measuring the average butt cross-section and the degree of softness.

The degree of softness can be objectively determined with a measuring device which has been developed and tested by the authors (Fig. 1). The measuring device is placed on the anode butt. Two pins are turned circularly and penetrate the butt until the hard core is reached (Fig. 2). The depth of penetration (mm, measured in semi-turns of the spindle) determines the degree of softness of the anode butts.

The quality assessment which can be carried out after removing the butts from the pots, can be classified according to Table 1 as follows:

	Butt Quality		
	Good	Medium	Poor (soft)
Butt cross-section (%)	> 90	85 - 90	< 85
Penetration depth (mm)	0 - 2	3 - 5	> 5

Table 1: Assessment of the quality of anode butts after their removal from the reduction pot

Figs. 3 and 4 show good or poor anode butts.

PHYSICAL AND CHEMICAL PROPERTIES OF ANODE BUTTS

Introduction

Anode butts are crushed and fractioned after cleaning. They then become a part of the dry aggregate for anode fabrication just like petroleum coke. The obvious procedure is therefore, to subject anode butts to the same measurements as the petroleum cokes. In addition test cylinders can be taken from the butts as from the anodes. A test scheme can then be applied to them as in the case of the prebaked anodes (1,4).

Basically and logically those anode butts are best, which do not differ or differ as little as possible from good cokes or good anodes.

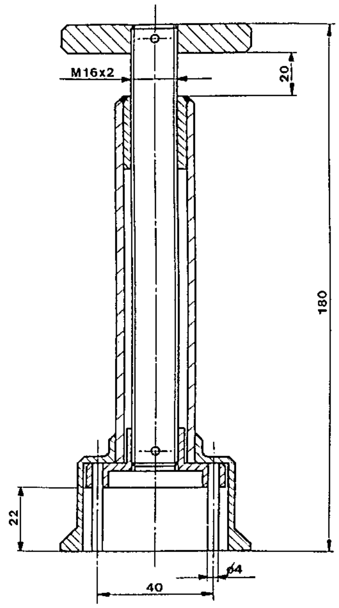
A certain increase in the contaminations cannot be avoided even if the butts are properly cleaned.

In the following these butt properties are examined for different qualities of butts. The qualitative selection of the butts took place according to the criteria of Table 1.

Examinations of Fractions of Crushed Butts of Good Quality:

For the following considerations it will suffice to look at the average properties of crushed and then screened butts. The analysis results on granulates of good, hard and poor, soft butts are shown. Both butt populations are summarized in Table 2. The following statements regarding the data relevant to burning can be made from this table:

- good butts are similar to coke.
- compared to coke, above all the two reactivities and the ignition temperature deteriorate in butts.
- Table 2 and the Tables 3 to 5 shown later contain analysis data. The typical data of similar materials are in a range around the data indicated.



(in millimetres)
Fig. 1: Measuring Device for Determining the Degree of Softness of Anode Butts

Fig. 2: Softness Test on Anode Butts

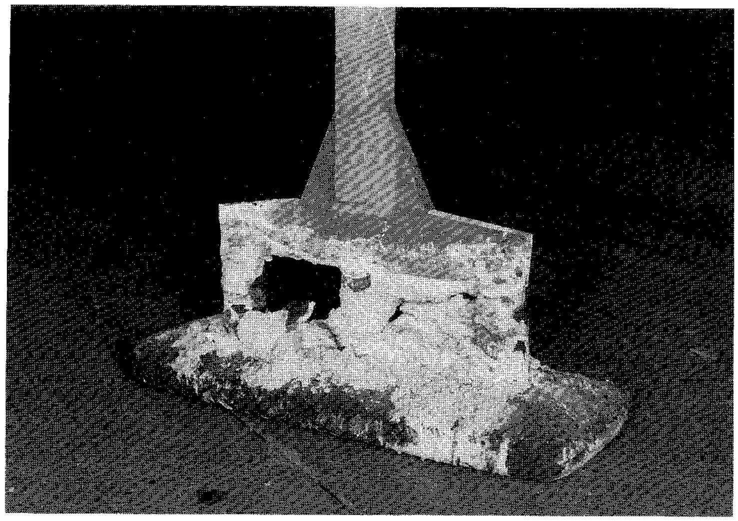


Fig. 3: Anode Butt of Good Quality

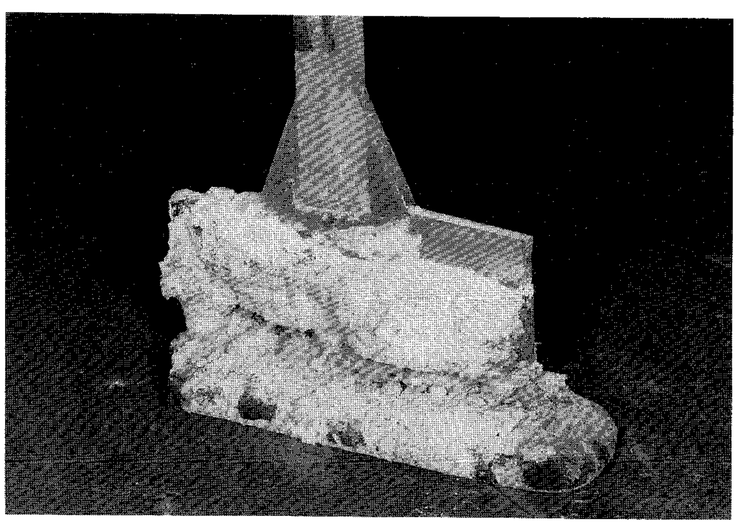


Fig. 4: Anode Butt of Poor Quality

Properties	Unit	Typical value for coke	Good butt quality	Bad butt quality
Reactivity, in CO_2, 1000 °C	%	5.0 - 10.0	18.0	27.5
Ignition temperature	°C	615.0 - 630.0	599.3	576.0
Reactivity in air, 600 °C	%/min	0.100 - 0.200	0.363	0.799
Crystallite size, Lc	Å	26.0 - 30.0	27.9	28.1
Density in xylene	kg/dm^3	2.050 - 2.090	2.072	2.083
Specific electr. resistance	μΩm	480 - 520	454	438
Total porosity	%	15.0 - 20.0	21.3	20.8
Elements S	%	1.00 - 3.00	1.32	1.30
V	ppm	80 - 300	90	94
Ni	pmm	80 - 160	111	111
Si	ppm	50 - 250	38	42
Fe	ppm	50 - 250	903	989
Al	ppm	50 - 250	121	351
Na	ppm	30 - 120	199	684
Ca	ppm	20 - 100	67	102
K	ppm	5 - 15	1	3
Mg	ppm	10 - 13	13	18
Cl	ppm	10 - 50	26	26

Table 2: Physical properties of crushed and granulated butts of good and bad quality

Examinations of Fractions of Crushed Butts of Poor Quality

If one takes large, cleaned butts, crushes, fractions and analyses them, then one gets results in accordance with Table 3. From them it can be seen that:

- o the fraction >4 mm is closest to typical coke data.
- o the reactivity in CO_2 is significantly poorer than that of coke.
- o the air reactivity is also significantly poorer than that of coke; it will get all the worse, the finer the fraction.
- o in the case of the fractions <4 mm values of up to 1 %/min. were found on other samples; these values are then as bad as found on poorly cleaned butts (see next chapter).
- o the ignition temperature is lower than that of coke and it drops further with declining grain diameters.
- o poor butts differ from good butts in the two reactivities and the ignition temperature through a marked further deterioration.
- o Fe content: drastic deterioration and increase in the finer fractions.
- o Al-, Ca-, Na- and F contents: these are electrolyte components although the butts were cleaned. Drastic increase with declining grain diameters.

Examinations of Fractions of Poorly Cleaned Butts

Butts arriving from reduction plants have a lot of fine material. It contains a high percentage of contaminations of electrolyte components. If the material <50 mm is screened out, fractioned and analysed, results in accordance with Table 4 for poorly cleaned butts are obtained. Compared to the typical coke data and to the values in Tables 2 and 3 (good and poor butts), the following can be ascertained:

- o CO_2, air reactivity and ignition temperature are reduced to very poor values. This is due to the catalytic effect of the contaminations. A use of this material for further anode production would badly affect the anode quality.
- o Also the porosity has increased; since here only the total porosity is shown, it will be left to a subsequent detailed analysis to show the reasons for this.

Examination of the Pore Distribution on Granulates of Good and Poor Butts

The results are shown in Fig. 5. From this it can be seen that:

- o In the case of soft butts a second, characteristic peak occurs in the pore distribution, which is not found in hard, good butts, good cokes and good anodes.
- o The cumulative specific surface considerably increases in the range of this second peak.

It is to be assumed that the second peak is caused by partial CO_2 burn and airburn and that in the range of the pores affected by these reactions, new, increased porosity has developed. This can make the mentioned reactions in the inside of the butt easier.

Examinations of Test Cylinders of Good and Bad Butts

These results are entered in Table 5. The following can be ascertained:

- o Here too again the values of good butts are close to those of good anodes.
- o The air permeability increases due to the creation of new porosity by CO_2 burn and airburn. This is particularly marked in the case of poor butt quality.
- o The compressive strength drops very considerably in the case of poor compared to good butts; in these cases the potroom personnel ascertains that the butts are soft.
- o The CO_2 reactivity residue deteriorates considerably in the case of poor butts.
- o The air reactivity residue drops drastically and reaches values which are normally encountered in poor anode quality.

Properties	Unit	Typical value for coke	Bad butts, crushed					
			> 4 mm	4-2 mm	2-1 mm	1-0,5 mm	0.5-0.25 mm	< 0.25 mm
Grain stability, 8 - 4 mm	%	75 - 85	90	70	56			
Reactivity, in CO_2, 1000 °C	%	5.0 - 10.0	29.0	25.8	28.9			
Ignition temperature	°C	615.0 - 630.0	597.8	594.4	588.8			
Reactivity in air, 600 °C	%/min	0.100 - 0.200	0.370	0.420	0.500			
Crystallite size, Lc	A	26.0 - 30.0	27.8	26.9	26.9	26	27.8	28.8
Density in xylene	kg/dm³	2.050 - 2.090	2.091	2.083	2.077			
Specific electr. resistance	μΩm	480 - 520	452	447	456			
Total porosity	%	15.0 - 20.0	19.7	18.3	17.6			
Elements S	%	1.00 - 3.00	1.43	1.39	1.47	1.46	1.47	1.45
V	ppm	80 - 300	108	109	120	114	112	109
Ni	pmm	80 - 160	110	109	111	114	116	108
Si	ppm	50 - 250	27	6	4	10	9	56
Fe	ppm	50 - 250	992	721	913	842	949	2133
Al	ppm	50 - 250	940	796	877	926	1460	3281
Na	ppm	30 - 120	1017	845	955	1189	2066	5025
Ca	ppm	20 - 100	100	78	80	103	169	365
K	ppm	5 - 15	4	3	3	4	5	14
Mg	ppm	10 - 13	16	15	11	18	22	43
Cl	ppm	10 - 50	33	31	31	35	34	44

Table 3: Physical properties of butt fractions, crushed butts of bad quality

Properties	Unit	Typical value for coke	Insufficiently cleaned butts					
			> 4 mm	4-2 mm	2-1 mm	1-0,5 mm	0.5-0.25 mm	< 0.25 mm
Grain stability, 8 - 4 mm	%	75 - 85	88	72	55			
Reactivity, in CO_2, 1000 °C	%	5.0 - 10.0	52	49.6	50.8			
Ignition temperature	°C	615.0 - 630.0	574.6	575.1	562.2			
Reactivity in air, 600 °C	%/min	0.100 - 0.200	0.75	0.75	1.12			
Crystallite size, Lc	Å	26.0 - 30.0	27.8	28.8	26.9	27.8	26.9	28.8
Density in xylene	kg/dm^3	2.050 - 2.090	2.099	2.110	2.089			
Specific electr. resistance	μΩm	480 - 520	493	492	522			
Total porosity	%	15.0 - 20.0	14.4	22.1	20.9			
Elements S	%	1.00 - 3.00	1.39	1.47	1.44	1.40	1.38	1.24
V	ppm	80 - 300	111	119	116	109	106	97
Ni	pmm	80 - 160	90	92	96	98	107	102
Si	ppm	50 - 250	49	4	66	116	196	306
Fe	ppm	50 - 250	483	1077	744	759	905	1623
Al	ppm	50 - 250	8760	5363	4636	4875	7026	13911
Na	ppm	30 - 120	11775	7136	6805	6969	10154	20654
Ca	ppm	20 - 100	795	472	478	506	706	1330
K	ppm	5 - 15	26	14	18	18	23	36
Mg	ppm	10 - 13	72	46	45	44	57	114
Cl	ppm	10 - 50	40	33	35	36	36	40

Table 4: Physical properties of butt fractions, insufficiently cleaned butts

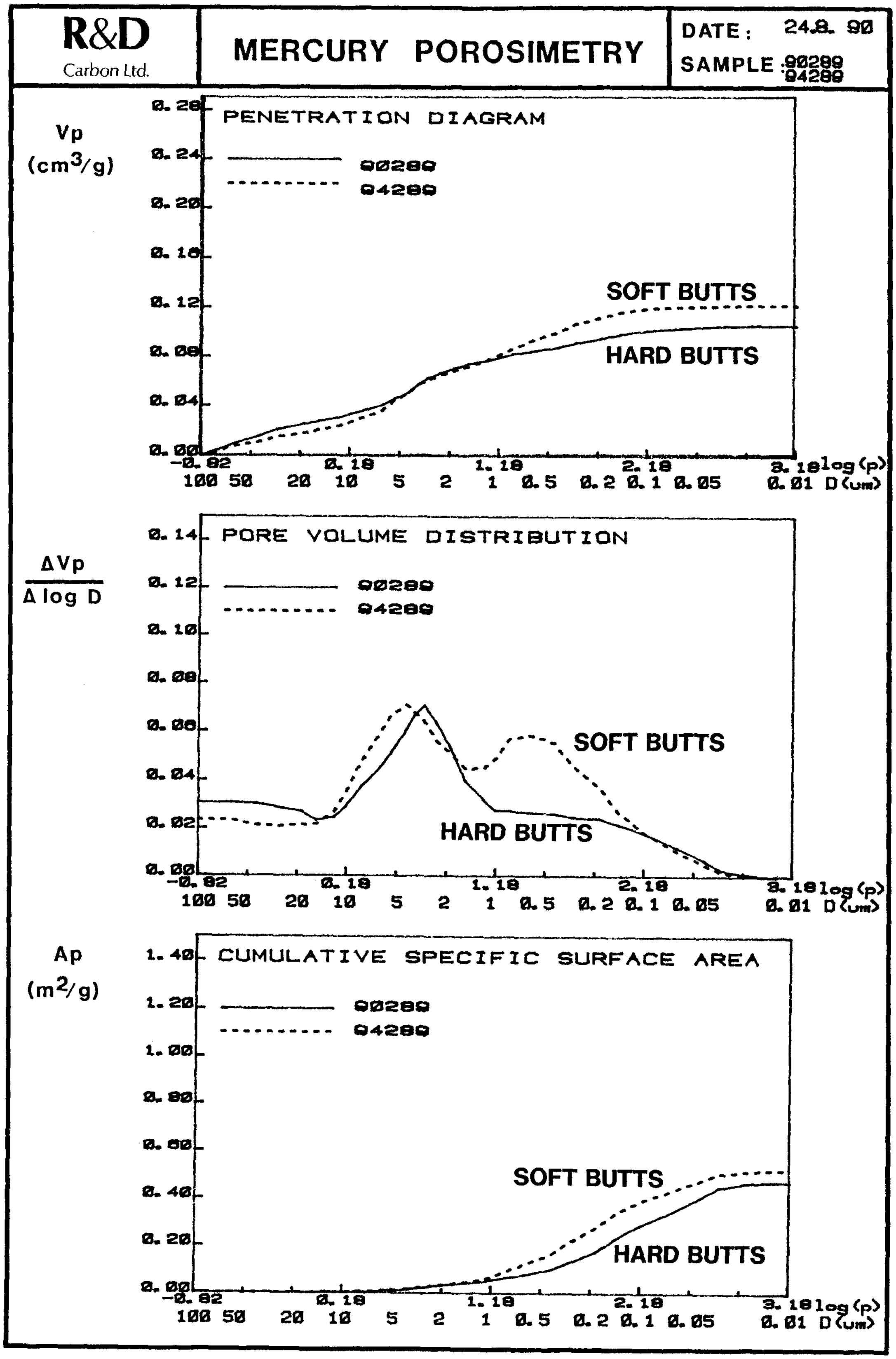


Fig. 5: Pore distribution of granulates
of good (hard) and poor (soft) anode butts

Properties	Unit	Typical value for anodes	Good butt quality	Bad butt quality
Apparent density	kg/dm^3	1.52 - 1.60	1.555	1.541
Specific electr. resistance	$\mu\Omega m$	55 - 70	56	62
Flexural strength	$10^5 N/m^2$	80 - 130	114	
Compressive strength	$10^5 N/m^2$	150 - 400	313	262
Young's modulus	$10^8 N/m^2$	20 - 40	38	29
Thermal conductivity	W/mK	3.00 - 4.50	3.44	3.44
Air permeability	nPm	0.6 - 2.5	2.32	4.51
CO_2 reactivity, residue	%	80 - 95	91.9	83.9
dust	%	5 - 10	2.5	7.9
loss	%	6 - 12	5.6	8.2
Air reactivity, residue	%	75 - 95	82.4	62.6
dust	%	2 - 12	5.2	16.3
loss	%	5 - 15	12.5	21.1
Elements Na	ppm	60 - 600	188	348
Ca	ppm	> 100	61	66

Table 5: Properties of butts of good and bad quality

INFLUENCE OF GOOD AND POOR BUTTS ON THE ANODE QUALITY

Introduction

Now that figures have been established for good and poor anode butts defining the two populations and allowing a clear distinction between them, the influence of the quality of the butts on the anode quality should be ascertained.

For this purpose bench scale anodes were produced where the following butt additions were made:

- o no butt addition
- o baking scrap representative of extremely good and clean butts
- o soft butts of bad quality
- o poorly cleaned butts for ascertaining the sodium sensitivity of different cokes (5).

Production of Bench Scale Anodes

The dust fractions of the cokes were produced with a collision mill (20 kg/h). A standard recipe for bench scale anodes adding 20 % anode butts was chosen.

The bench scale anodes were baked in special laboratory bake furnaces. Here the time-thermal treatment was different from baking in anode production. For that reason the level of the air reactivity values is lower than could be expected with the same recipes in anode production. The differences between the individual populations are significant, however.

Four cokes were chosen, the burning properties of which are compiled in Table 6:

Coke	CO_2 Reactivity (%)	Air Reactivity (%/min.)	Ignition Temperature ^oC
I	3.4	0.16	619.8
II	6.8	0.10	631.0
III	8.2	0.07	642.3
IV	8.3	0.06	646.7

Table 6: Burning Properties of the Cokes for the Bench Scale Tests

The cokes have from I to IV deteriorating CO_2 and improving air reactivities. The ignition temperatures correspond to the air reactivities. Deteriorating air reactivities are correlated with a decrease in the ignition temperature. Cokes with oppositely directed reactivities were chosen for reasons of the logic of permutation. This opposition is not absolutely necessary; there are cokes with all possible combinations of the two reactivities.

Falling values in both reactivity tests and rising ignition temperature mean fewer loss-sensitive cokes with favourable effects on the anode quality and vice versa.

The anode quality reacts to a high degree to a deterioration in the air reactivity of the butts.

The most important properties of the three butt qualities used are listed in Table 7:

Kind of butt	CO_2 reactivity (%)	Air reactivity (% / min.)	Ign. temp. (^oC)	Na Content (ppm)
Baking scrap	19.2	0.304	605.0	510
Soft	28.3	0.407	595.2	1137
Poorly cleaned	51.0	0.805	571.6	10384

Table 7: Properties of the butt qualities for the Bench Scale Tests

Results

The results of the tests can be seen in Figs. 6 to 9. The following can be ascertained therefrom:

- o The addition of soft butts (elevated porosity) does not influence the CO_2 reactivity residue of the anodes.
- o In the case of cokes I and III the air reactivities deteriorate due to the addition of soft butts. Cokes II and IV hardly react. Here very different sensitivities of the cokes appear. The causes of these different sensitivities cannot, however, be recognized from the coke properties measured to date.
- o The addition of poorly cleaned butts negatively affects all reactivities, the CO_2 reactivities reacting more strongly but differently for the four cokes. Here too the differing sensitivites of the cokes can be recognized.
- o Since different cokes can have different sensitivities to soft or poorly cleaned butts at both reactivities, material blending tests are necessary in any event for new raw materials in order to be able to make a decision about the influence of the butt addition.
- o The permeability is reduced by the addition of good butts. This decreases CO_2 burn and airburn of the anodes.

It can be recognized that the addition of good butts is to be given preference over anodes without butts. But even if the butt quality is not ideal, an admixture of butts should be carried out in most cases. Decisive is the still tolerable deterioration in the anode quality, which in turn depends on the anode conditions in practice. The fact that otherwise all the butts would have to be rejected and that a considerable financial loss would occur as a result also speaks for this solution.

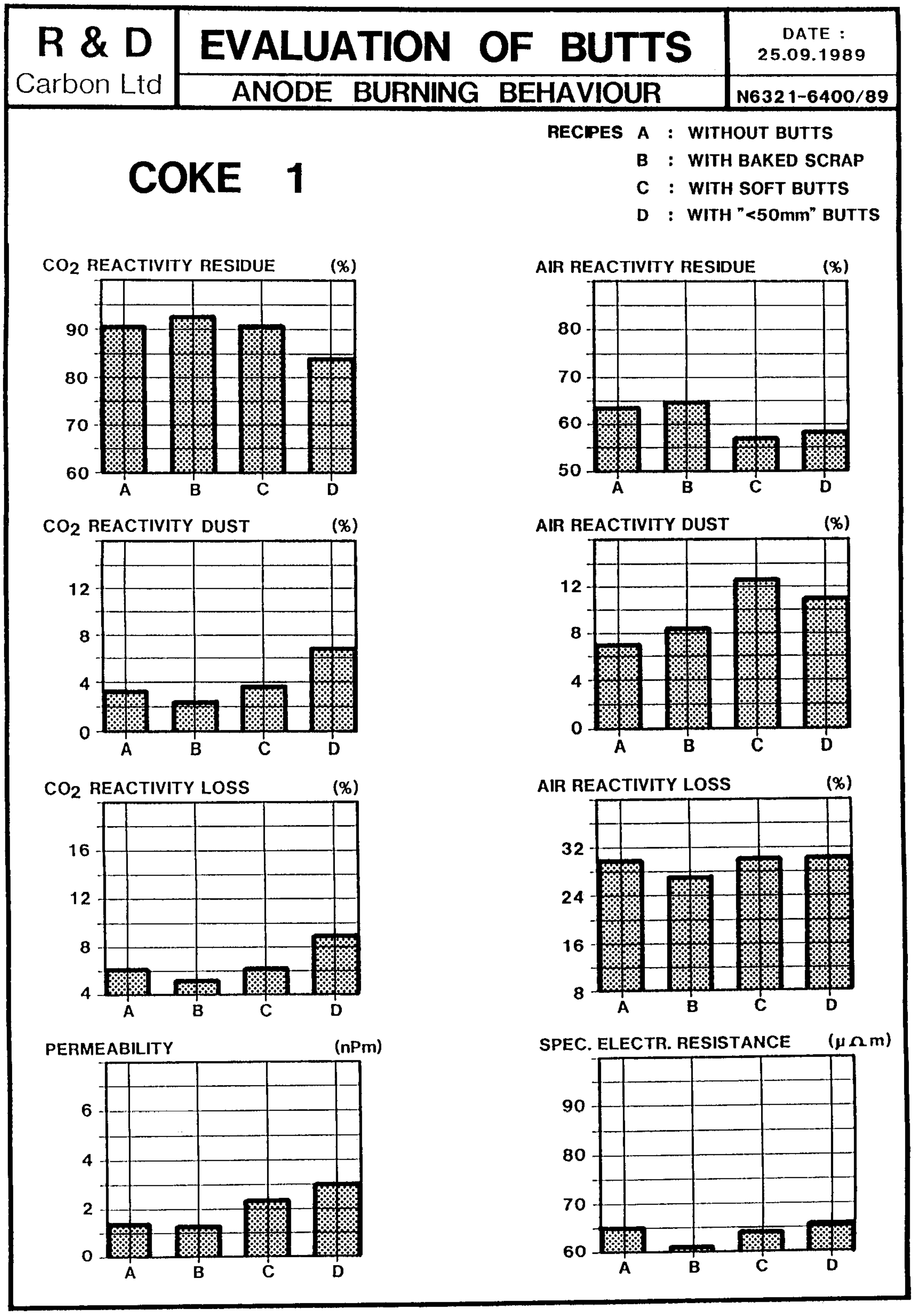


Fig. 6: Coke I, Influence of the quality of the butts on the anode quality

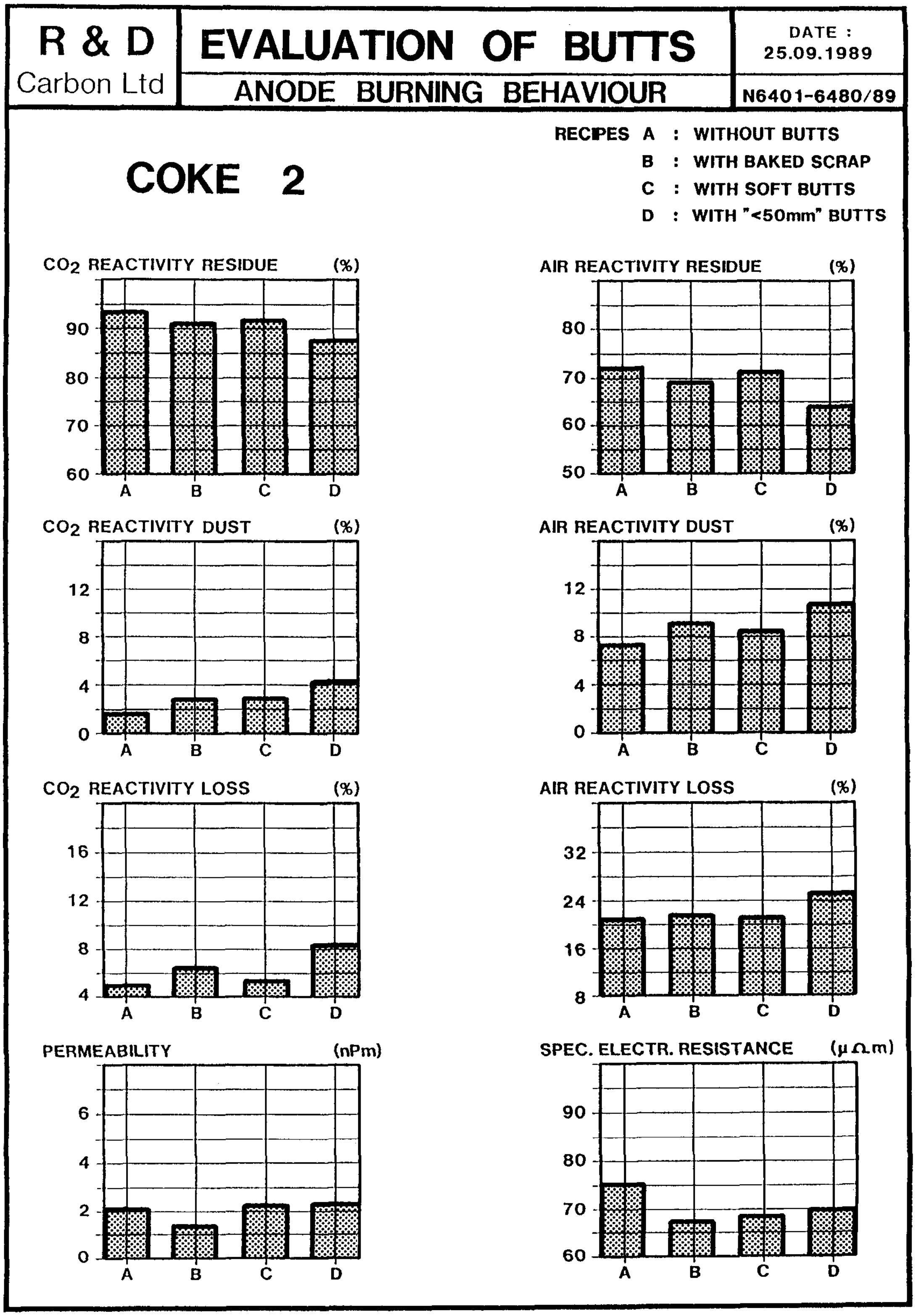


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Fig. 7: Coke II, Influence of the quality of the butts on the anode quality

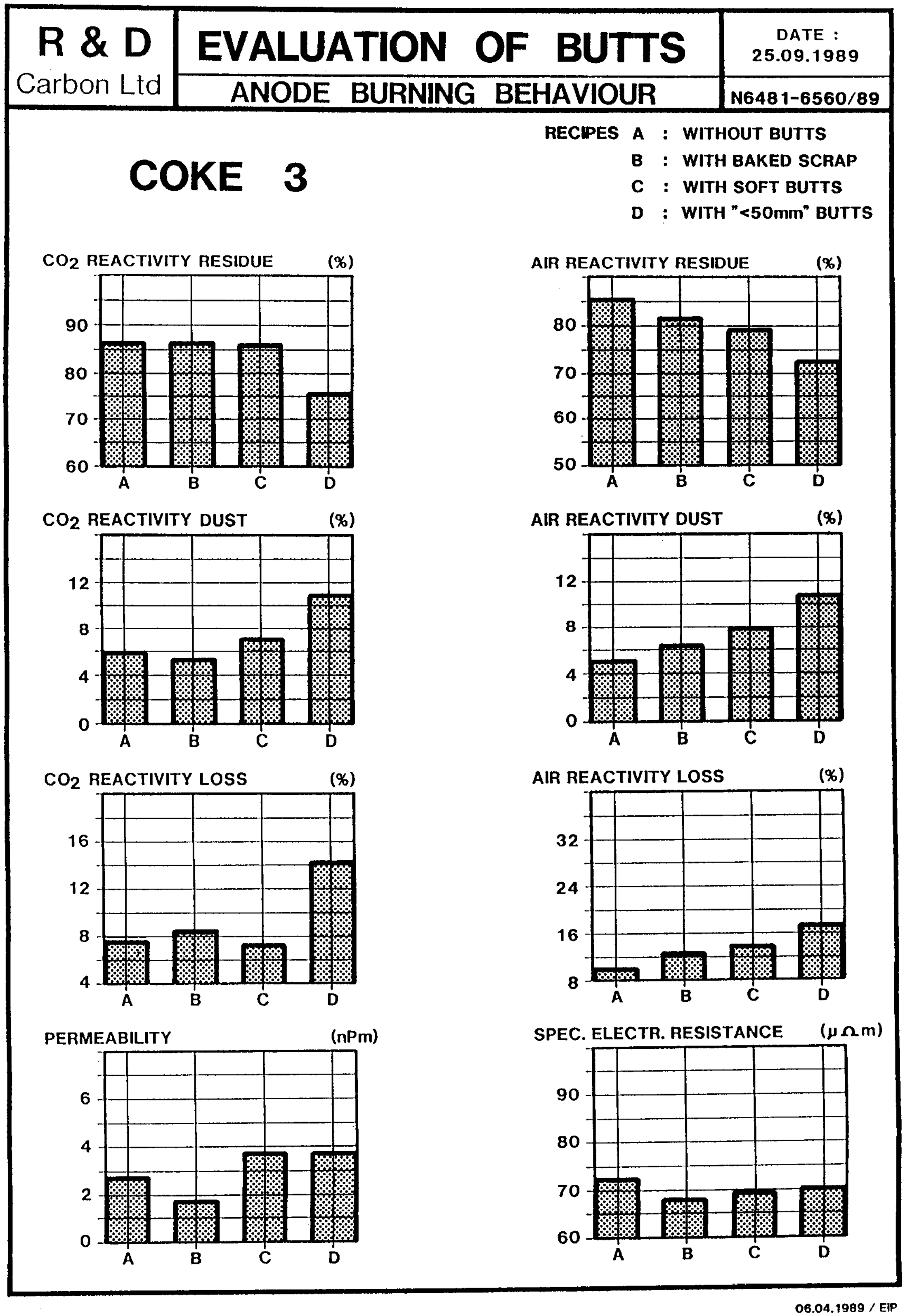

Fig. 8: Coke III, influence of the quality of the butts on the anode quality

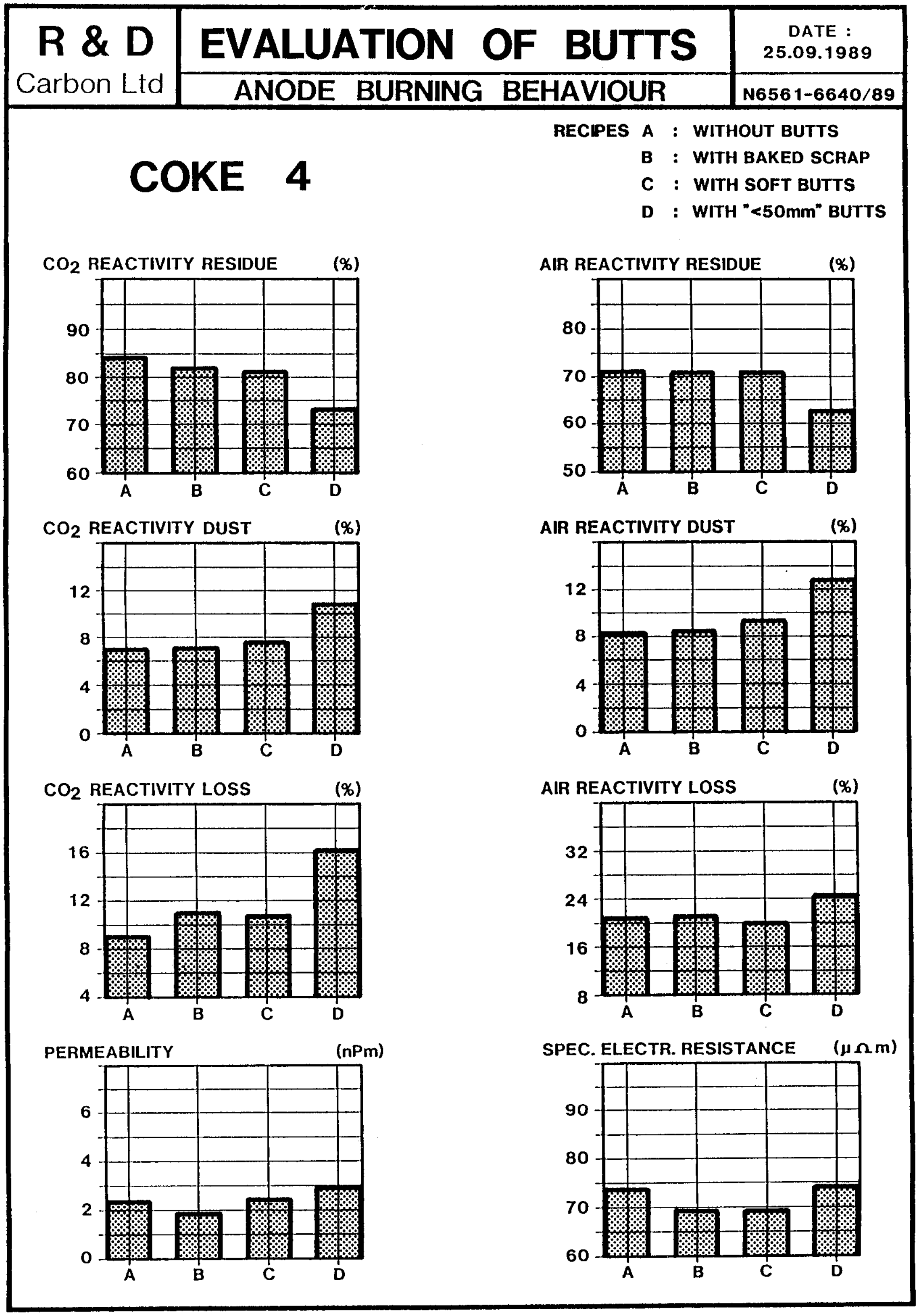

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Fig. 9: Coke IV, influence of the quality of the butts on the anode quality

RESUME

Anode butts are re-used for anode production. With that their properties determine the anode quality to the same degree as the cokes and pitches used. It is described how good and poor butts can arise in the potroom. Poor butts are soft and have a small butt cross-section or are badly contaminated with electrolyte components.

The physical and chemical properties of good and poor butts were determined on butt granulates and on test cylinders which were taken from the butts. The different butt qualities mentioned can then be defined in figures and clearly distinguished.

Good butts are similar to coke. Poor butts are very reactive to CO_2 and air and have low ignition temperatures.

It was proven on bench scale anodes that poor butts negatively influence the anode quality. But not all cokes are equally sensitive to poor butt quality.

The anode quality is improved by the addition of good butts compared to butt-free anodes. A decision whether or not to add non-ideal butts is determined by the tolerable deterioration of the anode quality.

The results presented allow a further improvement of the anode quality by control of the butt properties.

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