INFLUENCE OF ANODE BAKING TEMPERATURE AND CURRENT

DENSITY UPON CARBON SLOUGHING

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Experiments were conducted using industrial anodes to determine the influence of baking temperature and operating current density upon carbon sloughing.

The anodes were baked between temperatures of 942 and 1095°C and operated at current densities between 0.6 and 1.8 amp/cm².

Our results indicate that anode baking temperature is much more influential than operating current density upon the amount of slough carbon (dirt) originating from an anode. Poorly baked anodes (~ 950°C) tend to slough more carbon into the electrolyte than well baked (~ 1100°C) anodes. No uniform trend for sloughing was observed at current densities of 0.6, 0.8, 1.0 and 1.3 amp/cm².

Our results support the evidence published in the literature that electrolytically generated CO_2 is forced up through the interior of the anode and reacts most probably with the binder coke according to the Boudouard Reaction (C + CO_2 → 2CO). However, this work shows that the Boudouard Reaction is not the mechanism responsible for the majority of slough carbon generation. The majority of the carbon sloughed from anodes originates from the sides of the anodes, below bath level, operating at very low current densities.

Introduction

Carbon sloughing (i.e., dusting) from an anode takes place as shown in Figure 1 and is generally accepted to be due to differences in the reactivities of the carbon aggregate and the binder(1-8). The binder fraction of a baked anode has a higher reactivity and is consumed during electrolysis (either chemically or electro-chemically) at a more rapid rate than the aggregate. This preferential consumption leaves surface aggregate particles with few, or no, binder bridges attaching them to the bulk carbon phase. Mechanical agitation such as bath turbulence can then detach these particles from the anode.

Prior work in this area has shown that a portion of the CO_2 produced electrochemically is forced up through the working face of an anode, primarily due to the hydrostatic pressure

generated by the electrolyte(4, 9-13). This CO_2 will react with the carbon inside the anode forming CO. It has been suggested that sloughing is entirely due to this CO_2 penetration and subsequent reaction with interior carbon(9,14). If this model is correct, the working face of an anode should be somewhat roughened and more friable than the bulk carbon phase.

Other works in the literature have also shown that carbon consumption, a portion of which is sloughing, increases significantly with decreasing baking temperature(1,2,15,16) and decreasing current density(2,17).

The present work is the second in a series of two papers which evaluates the proposed CO_2 penetration model as the precursor to sloughing and determines the relative importance of certain operational variables, including baking temperature and current density, upon the sloughing process.

The first of these two papers(13) dealt with the mechanism of sloughing and the influence of baking temperature and anode effects. In this first paper we found that an anode effect has a relatively small influence upon sloughing, but that anode baking temperature, that is finishing temperature, has a very significant influence. The lower the baking temperature, the greater the amount of slough carbon. Additionally, we found that the majority of the slough carbon comes off the sides of the anode. Very little carbon is sloughed from the electrolytic face.

However, this work was conducted at a current density of 1.3 amp/cm², a rather high operating value for that which is typical throughout the world today. At lower current densities (0.6 → 1.0 amp/cm²), it would not be unrealistic to assume that the sloughing mechanism might change. As the current density is decreased, the potential for sloughing from the working face might increase. The more reactive carbon sites (the binder) on the electrolytic face could be preferentially attacked to an even greater degree causing the binder to be burned away more rapidly than at the higher current densities and the sloughing potential to increase from this location. Additionally, the CO_2 penetration into the anode could possibly increase at lower current densities, increasing the influence of this proposed sloughing mechanism.
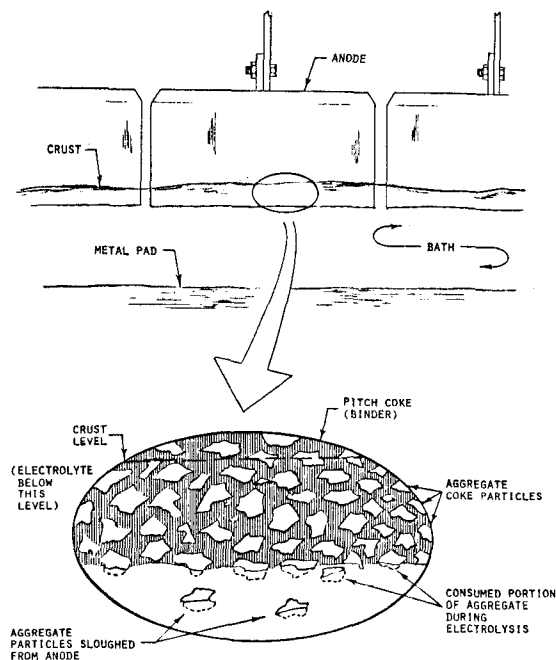
The anodes were electrolyzed in one of three cells showing comparable bath chemistry and temperature at current densities of 0.6, 0.8, 1.0 and 1.3 amp/cm². A typical anode weighing 263 lb before electrolysis had the following dimensions: 21" L x 15" W x 17" H.

Each anode, after being set in a cell, reached its specified current density after 8-10 hours of operation. Current passing through the anode stem was measured using an inductively-coupled Halmar digital, clamp-on ammeter. Readings were taken every 30 minutes. Current density adjustments were made, when necessary, by changing the AC distance of the anode using a manual anode jack. Standard procedure was to make a change when necessary and then wait at least one-half hour before making another change.

At the end of three days operation, each of the anodes was removed from its cell. Stem clamps were not loosened until the overhead crane was attached to the anodes and a slight upward tension applied. The anodes were pulled from the cell the moment the stem clamp was loosened to avoid bath penetration into the anode. In order to avoid air burning, each anode was then placed, as soon as it was removed from the bath, in a closed steel box and the box flushed with argon until the anode had cooled to less than 200°C as measured by a thermocouple placed underneath it. No oxygen could penetrate the box due to the positive pressure of argon. The box assembly is shown in Figure 2.

Figure 1. Carbon Sloughing.

The present work was conducted to answer these questions, that is, to further elucidate the mechanism of sloughing, determine the influence of operating current density and to confirm the major influence of finishing temperature.

Experimental Details

The baking procedure used to obtain the experimental anodes will not be repeated here but is detailed in Reference 13. The finishing temperatures of the anodes along with their proposed operating current densities (calculated based upon the geometric surface area of the bottom of the anode) are listed below in Table I.

Table I. Anode Parameters

Block Number	Finishing Temperature, °C	Operating Current Density, amp/cm²
1	1092	0.6
2	1095	0.8
3	1095	1.0
4	1092	1.3
5	1033	0.8
6	1027	1.3
7	956	0.6
8	962	0.8
9	953	1.0
10	942	1.3

Blocks baked to near one of three temperatures (950, 1030 and 1100°C) were selected for study in the experiments.
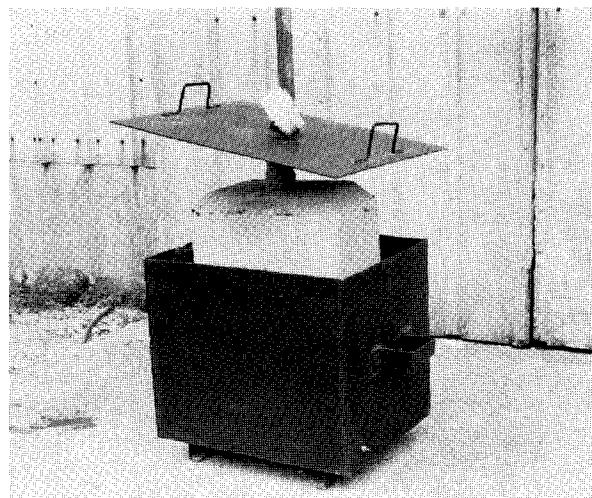

Figure 2. Anode Quenching Box.

After cooling to ambient temperature, each anode was cored as shown in Figure 3, the core extracted from the anode, machined to 2 inch O.D. and sliced into sections approximately 1 cm thick. Surface area was determined for the individual sections using a Quantachrome Monosorb surface area analyzer.

Additionally, surface roughness was determined along the bottom and side of each anode according to the method explained in the previous
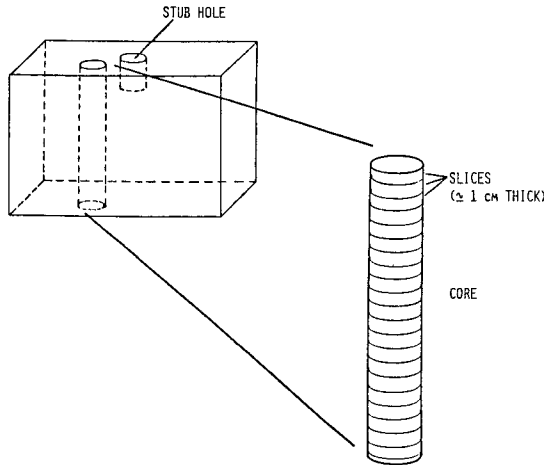
Figure 3. Anode Sample Preparation.

paper(13). This method involves multiple measure-
ments of the distance between an aluminum plate
lying on the carbon surface and the carbon surface
itself. Standard deviation of the measurements
for each carbon surface is then calculated to
indicate how much variation there is between the
mean and the individual measurements. The
standard deviation should directly correlate to
roughness which in turn should give a relative
indication of the sloughing tendency.

Results and Discussion

Surface area and surface roughness
measurements were made on the anodes listed in
Table I. Additionally, measurements were made on
two anodes used as controls which were not
electrolyzed. The finishing temperatures of these
anodes are listed below in Table II.

Table II. Finishing Temperature of Control Anodes

Anode Number	Finishing Temperature, °C
11	1078
12	973

Surface area and roughness measurements of these
control carbons give baseline values against which
data from the experimental anodes were compared.

In our prior work(13), we showed that CO_2 had
penetrated the working face of our experimental
anodes and reacted with interior anode carbon by
measuring the physical properties of the anode
(apparent density, porosity, permeability and
surface area) as a function of the distance above
the working face. The properties of the anodes
were determined by examining sections of anode
cores as shown in Figure 3. Relative degree of
penetration of CO_2 was then determined by looking
at profiles of these properties as a function of
distance above the anode's working face.   In this

work we found that surface area was by far the
most sensitive indicator for CO_2 penetration;
therefore, all work reported on here dealing with
the relative degree of CO_2 penetration and,
therefore, sloughing if the CO_2 model is correct,
will be gauged by surface area measurements.

Surface area data from all anodes listed in
Tables I and II as a function of distance above
the working face are given in Table III, and shown
graphically in Figure 4. The non-electrolyzed
control blocks show nearly constant surface area
within the same block. The surface area of the
low temperature control block is slightly higher
than that of the higher temperature control block,
as would be expected(9). The sharp increase in
surface area of the low temperature block near the
face is most probably due to air burning during
baking, since this was a top layer block in the
baking pit.

Concerning Figure 4, the graphs for each
temperature range show anodes operating at
selected current densities between 0.6 and 1.3
amp/cm². In each temperature range we see that
the surface area and, therefore, the degree of CO_2
penetration and reaction in the anode does not
depend on current density. The shape and position
of the curves at each current density are
basically the same. The major factor influencing
the surface area is the anode's finishing
temperature. The lower the finishing temperature,
the greater the surface area and the greater the
amount of interior anode carbon consumed. A
proposed explanation for the increase in surface
area near the electrolytic face of the anodes,
especially the low temperature ones, is that the
CO_2 is reacting to open porosity which is normally
closed to surface area measurement. This proposed
explanation is confirmed in Figure 5 which shows
the porosity distribution for one of the low
temperature anodes, Anode 8, and the control anode
baked to approximately the same temperature, Anode
12. The sample for which the porosity
distribution was determined for Anode 8 was
located approximately 2 cm above the working face.
In this figure dV/dR is plotted against R where V
is the pore volume intruded and R is pore radius.
The CO_2 has reacted to open additional porosity
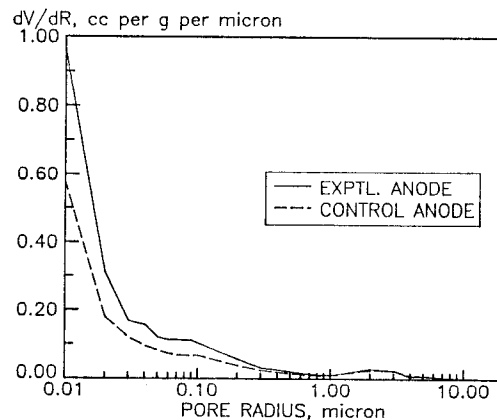for pores with radii $\leq$ 0.3 μ.

Figure 5. Anode Porosity Distribution.

Table III. Surface Area of Experimental Anodes

Anode Number

Anode 1		Anode 2		Anode 3		Anode 4		Anode 5		Anode 6	
Distance, cm	Surface Area, m²/g	Distance, cm	Surface Area, m²/g	Distance, cm	Surface Area, m²/g	Distance, cm	Surface Area, m²/g	Distance, cm	Surface Area, m²/g	Distance, cm	Surface Area, m²/g
0.59	0.93	0.52	1.09	0.66	0.98	0.52	1.03	0.71	2.06	0.85	1.56
1.78	0.89	1.69	1.06	1.81	0.97	1.69	1.01	1.91	3.03	2.02	1.93
2.98	0.94	2.88	1.17	2.96	0.94	2.89	1.00	3.08	2.75	3.21	1.84
4.19	0.85	4.08	1.09	4.14	0.92	4.09	0.99	4.28	2.18	4.38	1.61
5.41	0.85	5.27	0.96	5.30	0.93	5.28	0.93	5.43	1.53	5.57	1.44
6.60	0.79	6.42	0.90	6.45	0.90	6.46	0.91	6.58	1.07	6.75	1.32
7.82	0.74	7.59	0.80	7.60	0.83	7.65	0.83	7.73	1.04	7.91	1.02
9.03	0.71	8.77	0.72	8.74	0.87	8.84	0.84	8.89	0.79	9.29	1.06
10.24	0.71	11.30	0.64	9.82	0.84	10.03	0.83	10.06	0.76	10.25	1.03
11.44	0.67	12.49	0.65	12.10	0.77	11.22	0.83	11.24	0.70	11.41	1.00
13.85	0.65	14.81	0.67	14.44	0.63	13.56	0.87	13.56	0.73	13.75	0.98
16.24	0.62	17.17	0.66	16.79	0.67	15.90	0.74	15.89	0.69	16.08	0.97
18.64	0.64	19.55	0.66	19.14	0.65	18.32	0.66	18.24	0.74	18.41	0.82

Anode Number

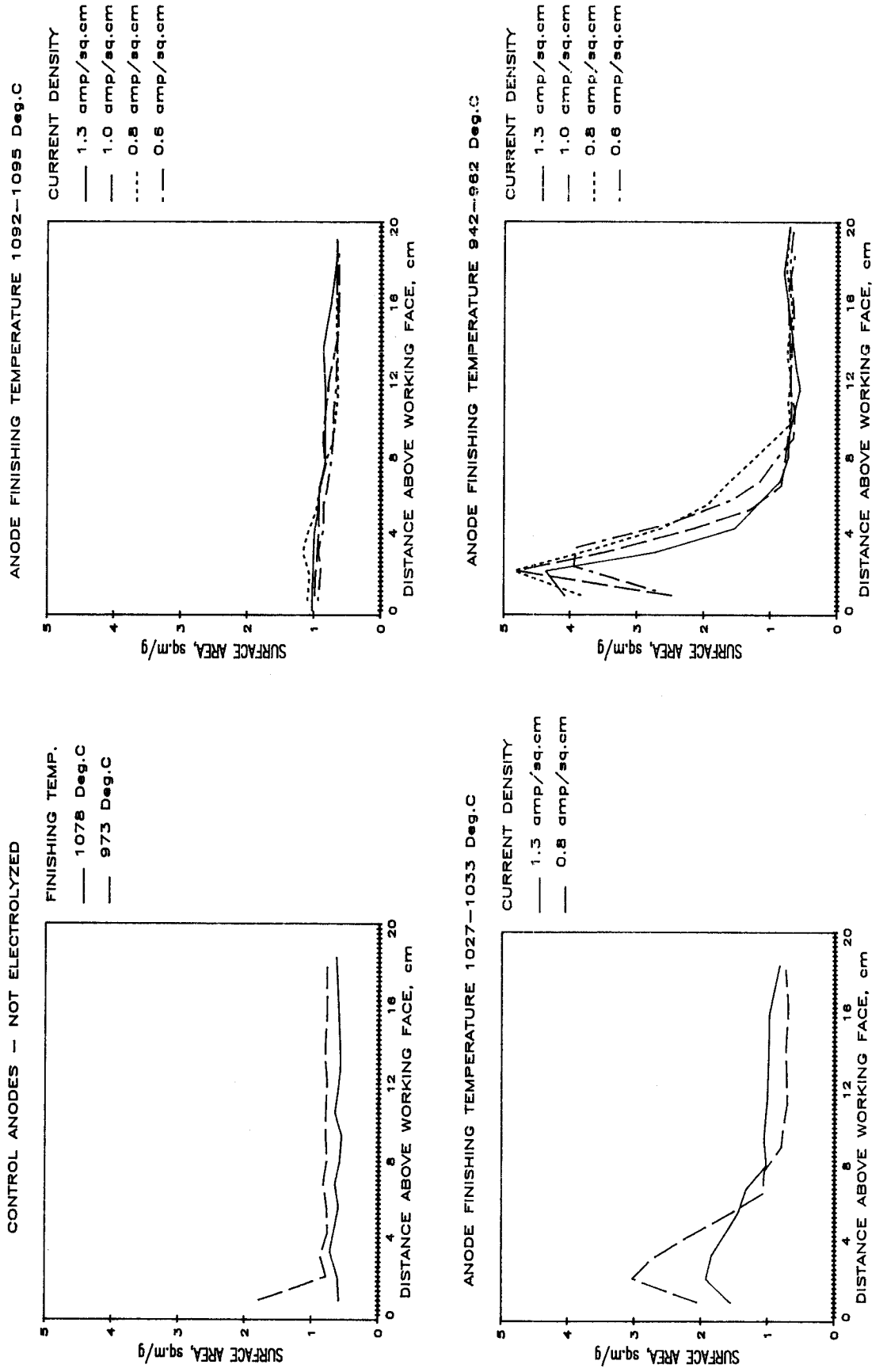| Anode 7		Anode 8		Anode 9		Anode 10		Anode 11		Anode 12	
Distance, cm	Surface Area, m²/g	Distance, cm	Surface Area, m²/g	Distance, cm	Surface Area, m²/g	Distance, cm	Surface Area, m²/g	Distance, cm	Surface Area, m²/g	Distance, cm	Surface Area, m²/g
1.01	2.72	0.85	3.84	0.79	2.48	0.78	4.09	0.80	0.60	0.70	1.78
2.18	3.95	2.00	4.84	1.94	4.79	1.93	4.37	1.96	0.62	1.93	0.78
3.34	3.90	3.17	3.56	3.08	3.46	3.08	2.72	3.19	0.73	3.12	0.87
4.48	2.52	4.34	2.62	4.22	2.14	4.26	1.53	5.57	0.60	4.33	0.76
5.64	1.57	5.52	1.94	5.37	1.30	6.87	0.85	6.79	0.66	5.52	0.78
6.79	1.15	6.68	1.60	6.52	0.83	8.04	0.73	7.99	0.58	6.73	0.83
7.93	0.89	9.68	0.70	10.35	0.68	9.19	0.71	9.18	0.55	7.94	0.77
9.08	0.65	10.85	0.74	11.52	0.70	10.38	0.63	10.38	0.66	9.14	0.80
10.23	0.63	12.01	0.69	13.91	0.72	11.55	0.56	11.57	0.61	11.92	0.77
11.39	0.71	13.17	0.76	16.25	0.75	12.71	0.63	12.74	0.57	13.13	0.81
15.34	0.65	15.46	0.67	18.55	0.64	15.05	0.71	15.10	0.60	15.54	0.77
17.65	0.72	17.73	0.77			17.42	0.81	18.42	0.65	17.92	0.78
19.91	0.65	20.01	0.71			19.90	0.71				

Figure 4.   Surface Area vs. Distance Above Working Face.

Table IV. Anode Surface Roughness

| Block Number | Block Finishing Temperature, °C | Operating Current Density, amp/cm² | Surface Roughness, mm | | | |
| | | | Anode Side | | Working Face | |
			Average	Std. Dev.	Average	Std. Dev.
1	1092	0.6	1.38	0.75	1.20	0.72
2	1095	0.8	0.90	0.31	0.20	0.11
3	1095	1.0	0.82	0.38	0.20	0.11
4	1092	1.3	0.72	0.41	0.52	0.31
5	1033	0.8	3.41	1.26	0.49	0.20
6	1027	1.3	3.38	1.19	0.42	0.16
7	956	0.6	4.75	2.47	0.49	0.21
8	962	0.8	1.98	1.70	0.56	0.25
9	953	1.0	4.49	1.35	0.69	0.45
10	942	1.3	4.89	2.04	0.40	0.29
11	1078	Not Electrolyzed	0.69	0.25	0.61	0.17
12	973	Not Electrolyzed	0.86	0.39	0.32	0.16

Therefore, the degree of CO_2 penetration and reaction is not affected by current density in the range 0.6-1.3 amp/cm², but is greatly affected by anode finishing temperature. We have already shown(13) that the CO_2 does not initiate sloughing from the electrolytic face of an anode at a current density of 1.3 amp/cm²; but is this also true at lower current densities? To measure this influence we must determine the degree of roughness of the anode face at each of the lower current densities. It must be remembered that sloughing is simply the process of loosening of aggregate by the selective burning of binder bridges. As the binder is selectively burned away, the surface of the carbon becomes rougher. In order for appreciable amounts of carbon to be sloughed from the electrolytic face, this face will have to be roughened compared with its original state prior to electrolysis.

Surface roughness data for each anode as measured by the method discussed in the prior section are listed in Table IV and shown graphically in Figures 6 and 7. The measurements for anode sides were all made on the left "long" side of each anode facing the anode as it would be sitting in the cell. The portion of the side measured was that which was below bath level for the three-day duration of the experiment. Therefore, air burning should not influence the results. Values plotted in the figures are standard deviations for-the measurements taken on each surface.

Figure 6 shows the roughness measurements for the control and high, mid and low temperature blocks as a function of operating current density. One can see that with only two exceptions (0.6 and 1.3 amp/cm² high temperature anodes), the sides are much rougher than the working face. The data reinforce visual observations of the anodes. The working face of each anode was hard and smooth. No carbon could be removed from this surface by rubbing one's finger across it. With the exception of the high temperature anodes, the sides of the anodes were much rougher than the working face and

aggregate particles could easily be removed from these surfaces. This roughness on the sides was not generated by air burning. The portion of each anode side under consideration was below bath level for the entire three-day duration of each experiment. These data indicate that the majority of the carbon sloughed from prebaked anodes is coming from the side of the anode, not the working face. These findings are in agreement with the prior work and contradict the theory that slough carbon originates from the working face due to CO_2 penetration.

For anodes baked in the same temperature range and operated at current densities between 0.8 and 1.3 amp/cm², the normal range used in the aluminum industry, no uniform variation in roughness of the sides (i.e., sloughing) occurs. Therefore, there should be no large difference in the amount of dirt generated by a cell operating in the current density range 0.8-1.3 amp/cm². However, the two anodes which were operated at 0.6 amp/cm² did show a slight increase in roughness on the sides when compared with the higher current density anodes. This may indicate that at current densities even lower than that commonly used in the aluminum industry today (0.6 amp/cm²), an increase in dirt formation may be seen.

In Figure 7 the roughness data are plotted for anodes operated at the same current density but baked to differing temperatures. The roughness of the sides at both 0.8 and 1.3 amp/cm² increases as the finishing temperature decreases. These data confirm the prior findings that as finishing temperature decreases, sloughing increases.

In order to explain why the majority of all sloughing takes place from the sides of anodes, we have to consider the operating current density along the sides and on the electrolytic face. The electrolytic face of the anode operates at a high enough current density such that electrolysis is mass transport controlled. The carbon fractions of the anode, both binder and aggregate, are
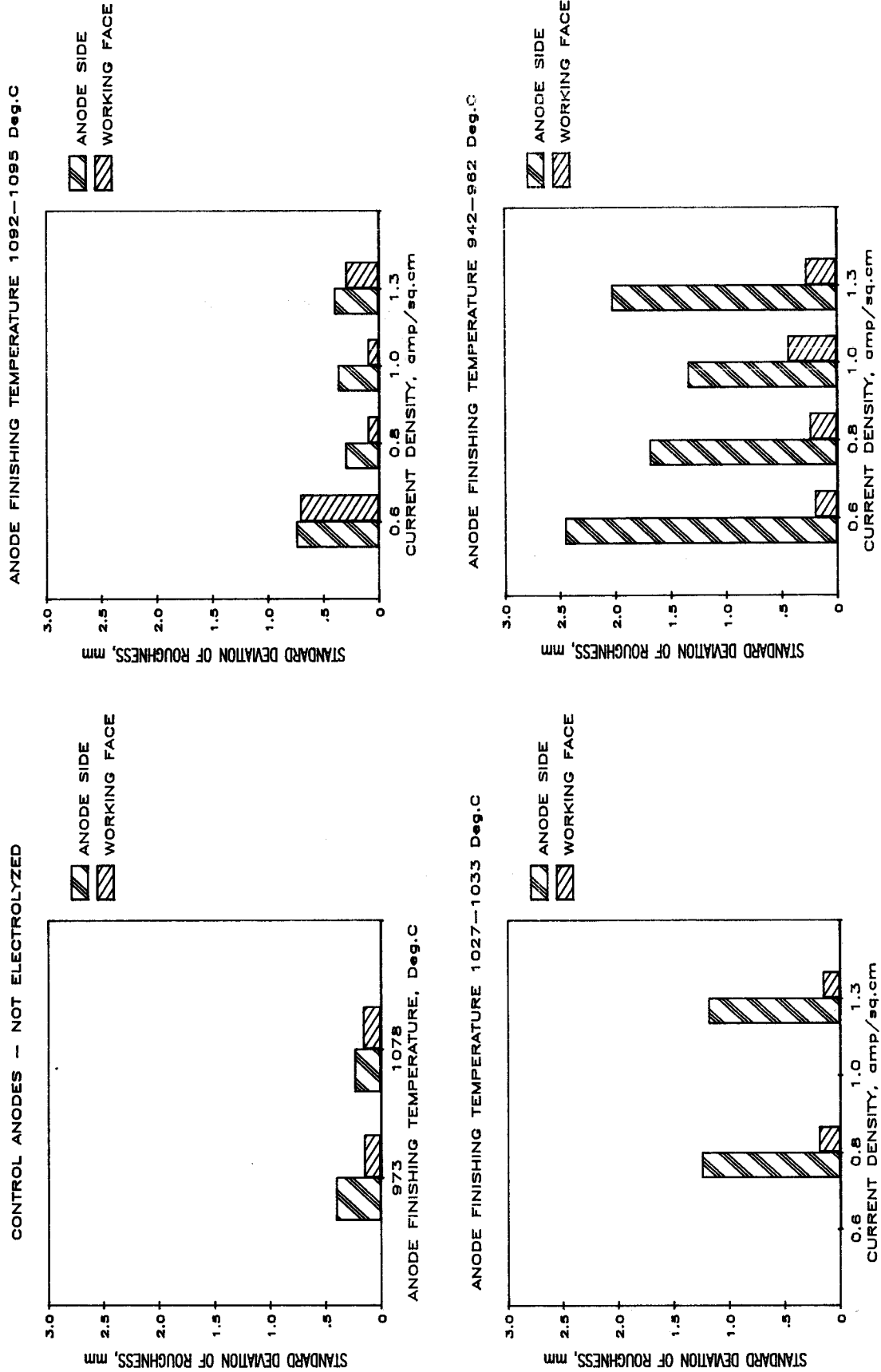
Figure 6. Anode Surface Roughness vs. Current Density.

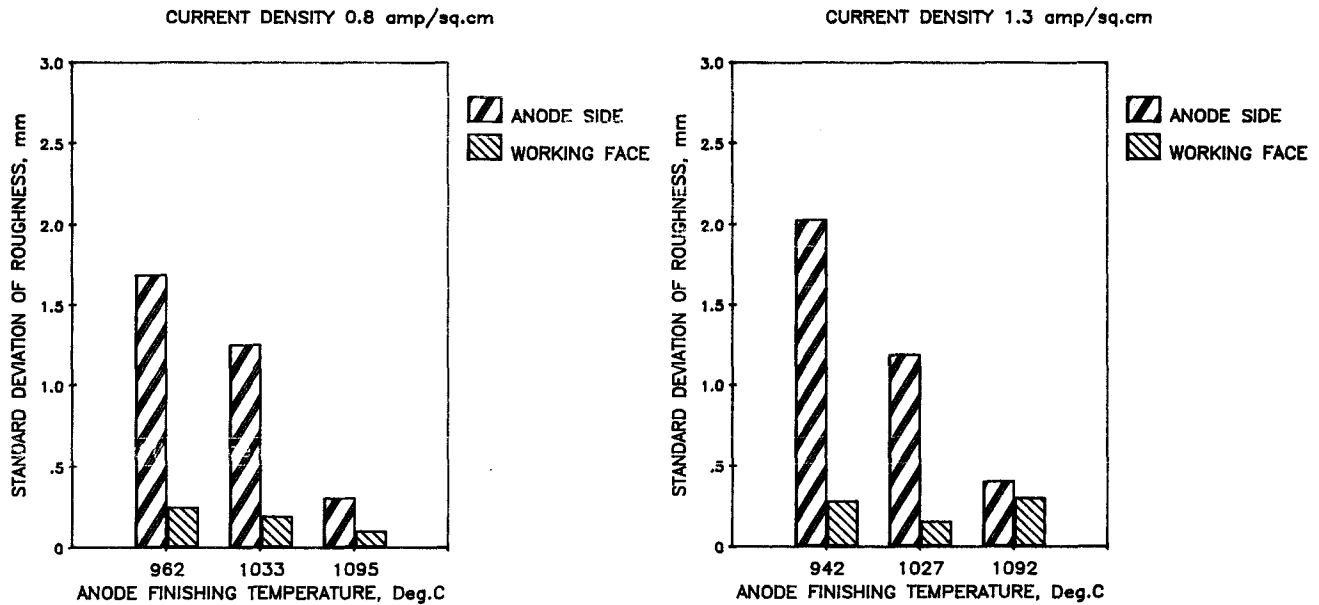CURRENT DENSITY 0.8 amp/sq.cm   CURRENT DENSITY 1.3 amp/sq.cm

Figure 7. Anode Surface Roughness vs. Finishing Temperature.

consumed at a nearly equal rate and few protrusions (i.e., rough spots) form. On the side of the anode the current density is much lower. Measurements based on volume of carbon consumed from the sides during our experiments indicate the current density to be less than 0.1 amp/cm^2. Here the electrolysis reaction must be chemically controlled. The more reactive carbon sites, the binder, are consumed at a more rapid rate than the aggregate causing the surface roughness observed. Additionally, at a current density this low, CO should be the predominate gas generated during electrolysis,(8,18) consuming carbon from the side at twice the rate of the primary electrolysis reaction.

In summary, the following conclusions can be drawn:

1. The majority of the carbon sloughed from an anode originates from the sides rather than the working face due to the greatly reduced current density of operation on the sides.

2. Operating current densities between 0.8 and 1.3 amp/cm^2 should show no difference in the amount of slough carbon generated. The data indicate that a current density of 0.6 amp/cm^2 could cause carbon sloughing to slightly increase.

3. Anode finishing temperature is very influential with respect to the amount of carbon sloughed into the bath. Anodes baked to $\leq$ 950°C will slough much more carbon into the bath than anodes baked to $\geq$ 1100°C.

Recommendations for minimizing the amount of carbon sloughing include:

1. Uniformly baking all anodes to at least 1100°C.

2. Minimizing the amount of anode side surface area exposed to the bath. This would involve using the minimum amount of bath allowable in the cell to solubilize enough alumina to get from one break cycle to the next without an anode effect.

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