IMPACT OF COKE CALCINATION LEVEL AND ANODE BAKING TEMPERATURE ON ANODE PROPERTIES

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Abstract

The effect of the two factors mentioned in the title on anode properties was tested on a laboratory scale. The main results were as follows: Increasing anode baking temperature decreases anode O_2 and CO_2 reactivities across the tested range below present typical commercial calcination temperatures. An increase in coke calcination level has a negative effect on O_2 and CO_2 reactivity. Anode geometrical density increases as a function of coke calcination temperature, but this effect vanishes at high anode baking temperature. The anodes with the highest thermal shock resistance are those baked at high temperature and made with cokes calcined at low temperature. These results show that it would be useful to carry out further investigation of the use of cokes calcined at a lower level than those typically used in industry. Furthermore, results obtained on an industrial scale agree well with the trends found in the laboratory**.**

Introduction

All producers of prebaked anodes for aluminium electrolysis are continually seeking to improve anode quality in order to reduce aluminium production costs.

With this in mind, a study was carried out on bench anodes, with the aim of highlighting the effect of the two factors mentioned in the title of this paper.

Due to the usefulness of the results obtained, this study was followed up by experimentation on an industrial scale, which is still in progress.

This article presents the main results of experiments on both the bench and the industrial scales.

1. STATE OF THE ART

Anode quality may be characterized by three main properties:
- Reactivity, which determines the greater part of the excess carbon consumption per tonne of aluminium produced. The lower the reactivity, the lower this excess carbon consumption. For more than 50 years, it has been known that excess consumption arises mainly from:

  · either direct oxidation of the anode by oxygen : $C + O_2 \rightarrow CO_2$. This reaction mainly concerns the top of the anode, which may be in contact with the ambient air.

  · or oxidation of the anode by carbon dioxide gas, according to Boudouard's reaction: $C + CO_2 \Leftrightarrow 2\,CO$, which occurs in the pores of the anode or on the grains of carbon dust floating in the bath. These grains of carbon dust are themselves the result of preferential corrosion, according to the same reaction, of pitch coke, which is more reactive than the anode coke grains of the matrix.

- Density, which is the main factor determining the lifetime of anodes in the pots. The greater the density, the longer the lifetime. Increasing anode lifetime decreases the number of anode changes that are necessary.

- Thermal shock resistance, which determines whether or not cracking or fractures occur when anodes are placed in the pots, or during their cycles.

We have looked through the literature to find what has already been written concerning the effect of both baking temperature and coke calcination temperature on these three properties.

➢ **Effect of anode baking temperature on anode properties**

- All authors observe that anode reactivity decreases when anode baking temperature increases (9)(14)(16)(20)(18)(23). This is true as long as anode desulphurization does not occur on a large scale (23). Also, when baking temperature increases :

   · Certain authors show that carbon dust in the pots decreases (10)(13)(22)

   · Pot anode carbon consumption also decreases (1)(3)(4)(5)(8)(12)(16)(17)(19)(22).

- Anode density increases as baking temperature increases (14)(16) : this effect is particularly strong for anodes made with undercalcined cokes (16).

- Anode thermal shock resistance increases as baking temperature increases (14)(21)(23).

In conclusion, there is general agreement concerning the beneficial effect of an increase in anode baking temperature.

➢ **Effect of coke calcination temperature on anode properties**

The effect of coke calcination temperature has not been discussed in many publications. What has been written shows that :

- As far as anode reactivity is concerned, dust carboxy-reactivity increases with coke calcination temperature (15)(24) and reactivity in air decreases to reach an asymptotic line (16). In addition,

   · There do not appear to be any publications concerning the effect of coke calcination temperature on carbon dust formation.

   · Depending on which papers you read, pot consumption :

   either decreases as calcination temperature increases (7)(18).

   or remains independent of calcination temperature (16).

   or increases with calcination temperature (2)(11).

- As far as anode density is concerned, all possible situations are found :

   · It decreases as coke calcination temperature increases ; for very high calcination levels, real density (RD) >2.07 g/cm^3) (23).

   · Other authors consider that it is independent of calcination temperature, but in this case the cokes involved are those with medium RD (2.04 to 2.085 g/cm^3) (16)(24).

   · It increases with calcination temperature : the cokes used in this case have very widespread RD values (1.935 to 2.07 g/cm^3) (15).

   In light of these apparently contradictory results, it would seem that the effect of coke calcination temperature on anode density varies according to coke calcination level. In this case, anode density will come to a maximum as a function of coke calcination temperature at a coke RD around 2.05 to 2.08 g/cm^3.

- As far as anode thermal shock resistance is concerned, no positive or negative trend has been shown within the scope of the calcination level under study (25).

   In conclusion, in contrast to the effect of anode baking temperature, the effect of coke calcination levels on anode properties needs to be studied further.

2. BENCH EXPERIMENTS

2.1 Experiment Contents

The experiments were carried out using a green coke from the USA. They involved the following steps:

- Calcination of this coke was carried out in the baking furnace used for baking bench anodes

- After calcination, the different cokes were screened and ground

- The bench anodes were all pressed under the same conditions, but with formulations having greater or lesser ultrafine and pitch contents

- After forming, the anodes were baked at different baking levels by means of a 40-hour end-of-baking stage.

Given the different formulae being tested, these experiments involved studying the effect of the following 4 factors on anode properties:

- Coke calcination temperature, between 680 and 1080°C

- Final anode baking temperature, between 700 and 1100°C

- Ultrafines content (grains smaller than 0.003mm) in the dry formula, between 5 and 35%

- Pitch content, between 12 and 18%

In the interests of brevity and clarity for this paper we will only present results concerning the effect of the first two factors mentioned above.

The anode properties characterized in this study were:

- Reactivity : to oxygen and carbon dioxide gas,

- Density,

- Thermal shock resistance.

2.2 Experimental Conditions

- The experiments involved preparing 16 bench anodes according to the conditions required by a "Hybrid" type statistical experimental design. Table 1 shows the conditions of each of the 16 experiments.

Looking at this table, it can be seen that 5 different anode baking temperatures and 4 different coke calcination temperatures were tested.

Table I : Experiment Design Conditions

	Pitch (P) %	UF (UF) %	Anode baking temperature (Abt) °C	Coke calcination temperature (Cct) °C
1	13.2	11.1	781	941
2	16.8	11.1	781	941
3	13.2	28.9	781	941
4	16.8	28.9	781	941
5	13.2	11.1	1 019	941
6	16.8	11.1	1 019	941
7	13.2	28.9	1 019	941
8	16.8	28.9	1 019	941
9	12	20	900	752
10	18	20	900	752
11	15	5	900	752
12	15	35	900	752
13	15	20	700	752
14	15	20	1 100	752
15	15	20	900	1 080
16	15	20	900	680

- The advantages of using such an experimental design are as follows:

  · It becomes possible to model each of the desired responses (reactivity, density, thermal shock resistance) in the form of a mathematical model as presented below

Response=
Cte+a*P+b*UF+c*Abt+d*Cct+
e*P*UF+f*P*Abt+g*P*Cct+h*UF*Abt+i*UF*Cct+j*Abt*Cct+
k*P²+l*UF²+mAbt²+nCct²   where a, b, c, d, e, f,
 g, h, i, j, k, l, m, n are constants

  · the effects of each of the 4 factors (P, UF, Abt, Cct) can be separated and the significance of each factor determined,

  · the presence of any significant double interactions (P*UF, P*Abt,…..) can be detected

  · the presence of any significant squared effects (P², UF², Abt²,Cct²) can be detected

  · the number of experiments can be minimized

The 16 points in this design are chosen to ensure that there is no correlation between the 4 factors, double interactions and squared effects as shown by the correlation matrix in table 2 :

CORRELATION MATRIX

	Cct	Abt	UF	P	Cct*Abt	Cct*UF	Cct*P	Abt*UF	Abt*P	UF*P	Cct²	Abt²	UF²	P²
Cct	1													
Abt	0	1												
UF	0	0	1											
P	0	0	0	1										
Cct*Abt	0	0	0	0	1									
Cct*UF	0	0	0	0	0	1								
Cct*P	0	0	0	0	0	0	1							
Abt*UF	0	0	0	0	0	0	0	1						
Abt*P	0	0	0	0	0	0	0	0	1					
UF*P	0	0	0	0	0	0	0	0	0	1				
Cct²	0	0	0	0	0	0	0	0	0	0	1			
Abt²	0	0	0	0	0	0	0	0	0	0	-0,35	1		
UF²	0	0	0	0	0	0	0	0	0	0	-0,35	-0,30	1	
P²	0	0	0	0	0	0	0	0	0	0	-0,35	-0,30	-0,30	1

Significant correlation (95%): r>0,50
1 means : perfect correlation
0 means : no correlation at al■

Table II : Correlation Matrix

- In order to get a better view of what the absence of correlation means, 2 examples are presented in Figures 1 and 2:
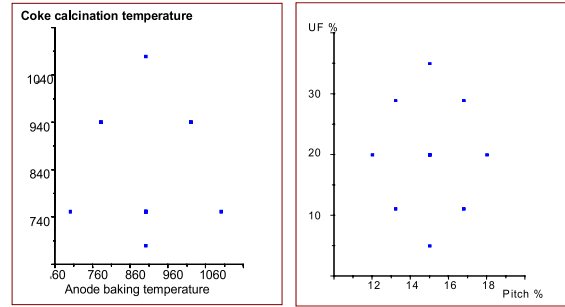
Figures 1-2 :   2 examples of correlation absence

2.3   Experimental results

2.3.1   Coke Characteristics According to Calcination Temperature

As expected, the RD value of the coke increases as calcination temperature increases

Crystallite size, characterized by Lc, also increases with calcination temperature. There is an excellent correlation between RD and Lc.

It should be noted that the coke calcination temperature tested in the laboratory is below the usual calcination for industrial cokes. In fact, the coke that was the most highly calcined in the laboratory (1080°C) had an RD of 2.06 g/cm^3 while industrial cokes have values around 2.07 g/m^3.

Table III : Coke Characteristics as a Function of Coke Calcination Temperature

	Coke Calcination temperature (°C)	RD fines g/cm^3	Lc (Å)
Laboratory calcined coke	680	1.800	15.3
	750	1.830	15.4
	940	1.947	16.6
	1080	2.062	24
Industrially calcined coke	1250-1400	2.069	25.3

2.3.2   Anode Reactivity

2.3.2.1   Anode Carboxy-reactivity

- Figure 3 shows the evolution of CO_2 Loss as a function of anode baking temperature. The fact that a strong correlation is observed, no matter what the pitch and UF content and no matter what the coke calcination temperature, shows that the baking temperature is indeed the predominating factor of the 4, with respect to CO_2 Loss. On its own, it explains the majority (84%) of the observed variations in CO_2 Loss. Figure 4 shows the model calculated by the computer. According to this model, CO_2 Loss decreases as final anode baking temperature increases, but with the following additional information:

· The higher the coke calcination temperature, the lower the slope of curve.

· At a high final anode baking temperature, CO_2 Loss tends to be less for anodes made with undercalcined coke.
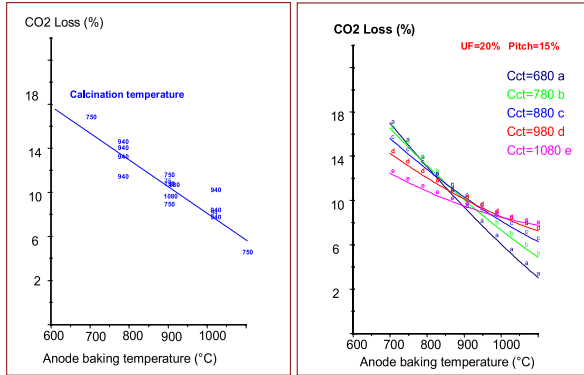
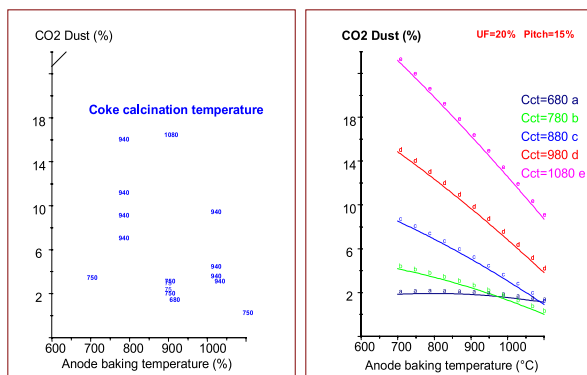Figures 3-4 : CO_2 Loss as a function of anode baking temperature

- Figures 5 and 6 show the evolution of CO_2 Dust values according to anode baking temperature.

As can be seen in Figure 5, there is no correlation . This means that anode baking temperature is not a predominating factor with respect to one or more of the 3 others.

In Figure 6, the model explains what happens :

· When the anodes are made of coke calcined at low temperature, CO_2 Dust remains constant no matter what the anode baking temperature.

· In contrast, when the anodes are made of coke calcined at high temperature, CO_2 Dust decreases considerably as the final anode baking temperature increases.

The CO_2 Dust of anodes made of coke calcined at high temperature is always higher than that of anodes made of lower temperature calcined coke.

Figures 5-6: CO_2 Dust as a function of anode baking temperature

- As for the residue, which is equal to (100-Dust–Loss), it is logical to find in Figure 7 that it increases with baking temperature. There is quite a strong correlation, which highlights the importance of the effect of anode baking temperature on this residue. This result agrees with what is found in the literature.

Figure 8 confirms the correlation, and shows that the best results (strongest residues), are obtained with anodes made of undercalcined coke.
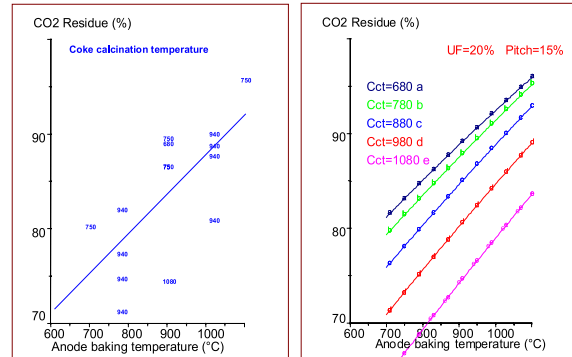

Figures 7-8: CO_2 Residue as a function of anode baking temperature

- One way of clearly highlighting the effect of coke calcination temperature is to look at the figures showing CO_2 Loss and CO_2 Dust for the anodes as a function of coke calcination temperature.

These 4 figures show clearly that:

· there is no correlation between CO_2 Loss and coke calcination temperature (see Figure 9)

· there is a strong correlation (confidence >95%) between CO_2 Dust and coke calcination temperature (see Figure 11) . The lower the coke calcination temperature, the lower the Dust value. The calcination temperature alone accounts for 62% of the variations in CO_2 Dust values.
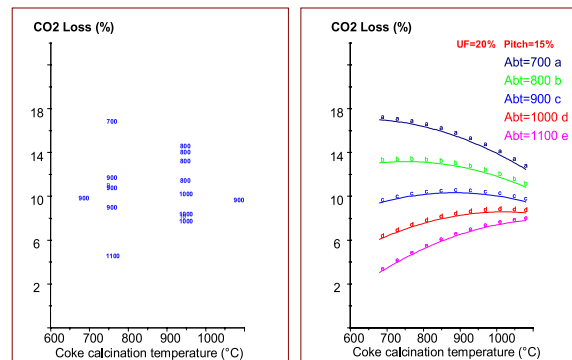
Figures 9-10 : CO_2 Loss as a function of coke calcination temperature
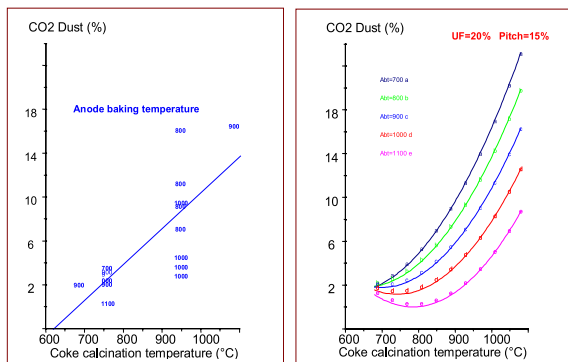
Figures 11-12 : CO_2 Dust as a function of coke calcination temperature

- A way of summarizing the preceding information is to look at the diagram in Figure 13. This diagram shows the following :

    · On the ordinate, the sum (Dust + Loss) that characterizes the overall reactivity of the anode, i.e., its likelihood to react according to Boudouard's reaction,

    · On the abscissa, the (Dust/Loss) ratio, known as the "soot factor" (6). This characterizes the extent of the difference in reactivity between the pitch coke and the coke grains of the matrix.

In this diagram, it can be seen that:

    · An increase in baking temperature mainly tends to decrease overall anode reactivity but has little effect on the extent of reactivity heterogeneity.

    · An increase in coke calcination temperature affects both properties, giving an increase in the overall reactivity and an increase in reactivity heterogeneity.

Quantitatively speaking, coke calcination temperature accounts for 33% and 84%, respectively, of the variations in (Dust+Loss) and (Dust/Loss). Baking temperature accounts for 49% and 5%, respectively, of the variations in (Dust+Loss) and (Dust/Loss). As a result, if we admit that carbon dust in the pots is linked to reactivity heterogeneity and thus to the (Dust/Loss) ratio, it is easy to understand why a decrease in coke calcination temperature is a much more efficient remedy than an increase in anode baking temperature.

2.3.2.2   Anode Oxygen Reactivity

As far as oxygen reactivity is concerned, the situation is slightly different:

- An increase in baking temperature acts on both properties, but mainly when the coke is highly calcined. It only affects (Dust + Loss) when the coke is undercalcined and the (Dust/Loss) ratio remains close to 0.

- An increase in coke calcination temperature mainly increases reactivity heterogeneity (Dust/Loss) and variations in (Dust/Loss) increase with a decrease in baking temperature.
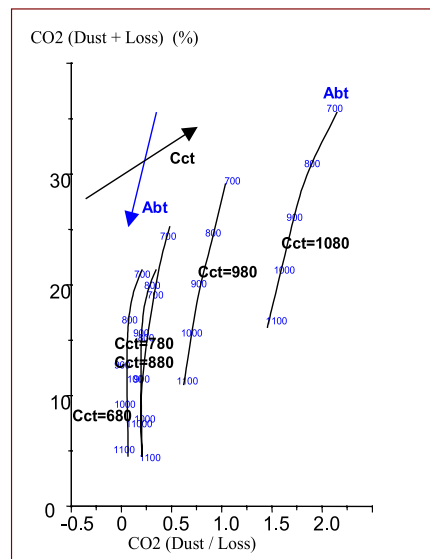

Figure 13 : Anode carboxy-reactivity diagram

As with carboxy-reactivity, anodes become better as baking temperature rises and coke calcination temperature falls.
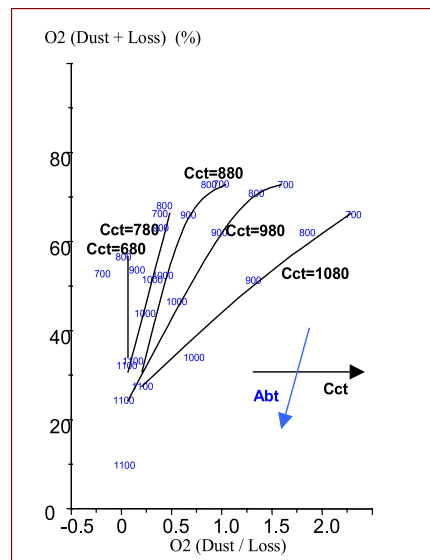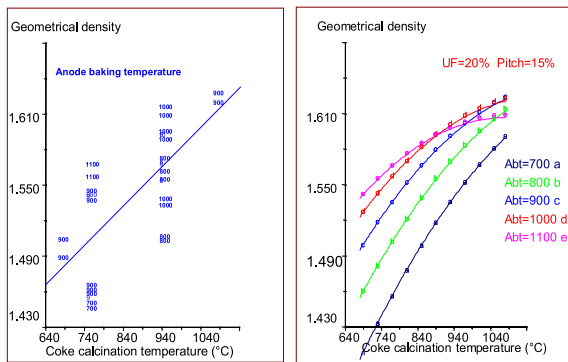

Figure 14 : Anode oxygen reactivity diagram

2.3.3   Anode Density

Anode density increases considerably as coke calcination temperature increases. (see Figure 15).
According to the model presented in Figure 16, the lower the final anode baking temperature, the greater the slope of the curve.

Figures 15-16: Anode geometrical density as a function of coke calcination temperature

For final baking temperatures that are close to 1100°C, as is the case in industry, density is practically constant when the coke calcination temperature remains limited to the range of 900-1100°C.

It is therefore possible to use moderately calcined cokes without a significant change in anode density, provided a high baking temperature is used.

2.3.4   Thermal Shock Resistance

Anode thermal shock resistance can easily be characterized by the use of a diagram showing resistance to crack initiation on the X axis and resistance to the spread of long cracks on the Y axis (Figure 17) The way in which these two resistance values are obtained is described in detail in the referenced publication (25).
The greater the resistance to the initiation of cracks and the greater the resistance to the spread of long cracks, the better the behavior of the anode in the pot, in terms of thermal shock.
An anode that is very resistant to the thermal shocks is represented by a point that is far from the origin.
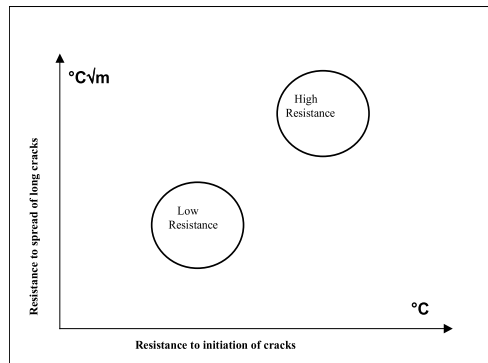

Figure 17 : Thermal shock resistance diagram

Figures 18 and 19 show the results. These 2 Figures are the same, with the exception of the numbers at the locations of the points, which, in Figure 18, indicate coke calcination temperature and, in Figure 19, indicate final baking temperature.

- According to Figure 18, it would appear that the majority of anodes that are most resistant to thermal shocks (which are in the ellipse) are made of undercalcined cokes.

- According to Figure 19, the majority of anodes that are most resistant to thermal shocks are those baked at a high final baking temperature.
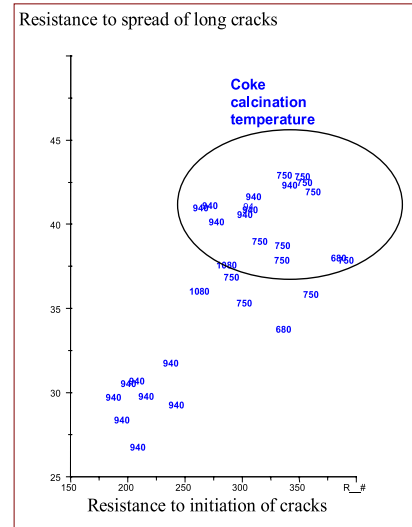

Figure 18 : Influence of coke calcination temperature on anode shock resistance
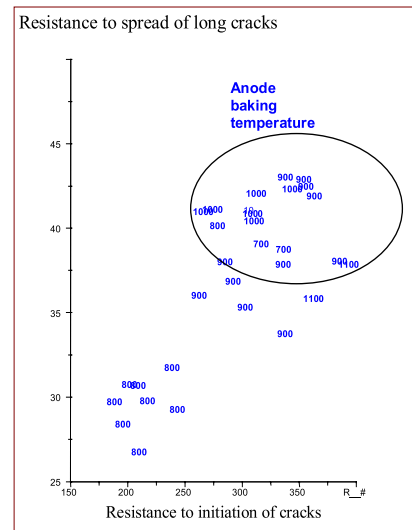

Figure 19 : Influence of anode baking temperature on anode thermal shock resistance

Following these 2 observations, it may be deduced that to obtain anodes that are resistant to thermal shocks, it is a good idea to bake the anodes at high temperature and to use undercalcined cokes.

3. DISCUSSION

The results obtained :

- Confirm results that are already well-known particularly with respect to final baking temperature, which has a beneficial effect on anode reactivity as well as on anode thermal shock resistance

- Present new ideas with respect to the effect of coke calcination temperature on both reactivity and anode thermal shock resistance. In fact, in the minds of many experts, the trends that have been shown here are the opposite of what was expected. However, it is relatively easy to find explanations for these results:

  · The more undercalcined the coke is, the better the coke-pitch contact. The mechanical characteristics of the anode improve as the coke calcination level decreases. This correlation becomes more accentuated as baking temperature rises (see figure 20) .

  · After baking, coke-pitch contact comprises the weak point of the anode in terms of both mechanical characteristics and reactivity. When it is improved, this in turn explains the improvement in reactivity and in thermal shock resistance of the anodes.

  · It might be expected that if a green coke is used instead of a calcined coke, the contact would be even better, as pitch and the grain are products that are chemically very close to one another and they would finish by combining to form a large grain of green coke instead of a grain coated with pitch. This is what was published 15 years ago (11).
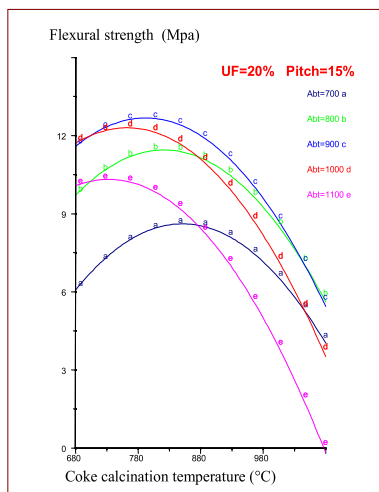

Figure 20 : Anode flexural strength as a function of coke calcination temperature

4. INDUSTRIAL EXPERIMENTATION

The first industrial tests were undertaken in a plant where there had been a continuous carbon dust crisis, making it necessary for the personnel to skim the electrolytic pots systematically to prevent a deterioration in performance.

Analysis of the carbon dust problem led to the following actions :

- Firstly, an unsuccessful attempt at modifying certain process parameters, in particular:

  · Modifying the anode pitch content and

  · Increasing anode baking temperature

- Secondly, replacement of coke A with another coke B. This measure was successful

- Thirdly, contact with the supplier of coke A, requesting a reduction in the coke calcination level.

The use of a lower temperature calcined coke A led to the following observations:

- The carbon dust crisis had been reduced which means that the difference in the reactivity of the pitch coke and the anode coke grains of the matrix had been reduced, as predicted by the decrease in the Dust/Loss ratio of the anodes with the decrease in coke calcination temperature.

- Anode density was not changed by the use of the less calcined coke, which confirms results obtained on the bench scale.

- The anode breakage rate is still 0 in this plant, which used to be prone to breakage problems. There is therefore no noticeable increase in the sensitivity of anodes to thermal shocks, which agrees well with results obtained on the bench scale.

These encouraging preliminary results should lead to testing of a greater decrease in coke calcination level.

5. CONCLUSIONS

To sum up the results obtained on the bench scale, it should be remembered that in the area being explored:

- An increase in final baking temperature is beneficial for the 3 anode properties under study : reactivity, density and thermal shock resistance.

- An increase in coke calcination temperature is unfavorable to anode reactivity and thermal shock resistance. On the other hand, it is favorable to anode density, although it has little effect at high baking temperature.

The results obtained up to now on the industrial scale are encouraging and appear to confirm the laboratory results on all points.
In conclusion, it is necessary to continue industrial experimentation with undercalcined cokes, in order to determine the optimum coke calcination level, as it appears relevant that this should now be re-examined.

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