

INFLUENCE OF COKE REAL DENSITY ON ANODE REACTIVITY CONSEQUENCE ON ANODE BAKING

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Abstract

An increase in the real density of coke has been observed in recent years.

This increase, which is due to higher coke calcination temperatures, leads to an improvement in coke reactivity.

A study has been carried out using different cokes and baking temperatures.

The effects of the real density of coke on anode reactivity and the required anode baking temperature are discussed.

Introduction

In the last ten years, an upward trend in the real density of coke has been observed.

This increase, which is due to higher coke calcination temperatures, leads to an improvement in certain coke properties, in particular air and CO₂ reactivity.

However, since coke is not the only component of anodes, it is legitimate to query the influence this trend has on anode reactivity.

In this article, we shall endeavour to answer the following questions:

- Does the improvement in coke reactivity actually bring about an improvement in anode reactivity?
- What adaptations should be made to the anode production process in order to derive the full benefit of decreased coke reactivity ?
- In the final assessment, is it advisable to use coke with a high real density ?

Bibliographic survey : effect of the increase in the calcination level on coke and anode properties

Wide mention is made in the literature of the increase in real density (RD) which occurs when the coke calcination temperature is raised ([1], [2], [3], [4], [5], [6], [7]).

The same trend is observed for Lc (crystallite size), which is another characteristic which makes it possible to measure the rearrangement and alignment of the graphite planes that are produced when the calcination temperature is raised ([1], [2], [5], [6], [7], [8], [9]).

Granular electrical resistivity decreases when the calcination level is raised.

Real density, coke granular resistivity and Lc are therefore good indicators of the coke calcination level.

Much discussion is also devoted to the evolution of coke reactivity in relation to air and CO₂ as a function of the calcination level measured by real density or Lc ([2], [5], [6], [10], [11], [12], [13], [14]).

Coke reactivity (in relation to air or CO₂) decreases as the calcination level is raised. This is due to an increase in the size of the crystallites and hence a decrease in the more highly reactive carbon atoms on the edge in proportion to the carbon atoms in the crystal basal plane [15].

However, at a certain temperature, desulfurization occurs and the specific surface area and porosity of the coke increase ([16], [17], [18]). This phenomenon leads to a renewed increase in reactivity caused by an increase in the number of reactive sites ([10]). Desulfurization occurs at an even lower temperature and is even more substantial as the sulfur content of the green coke increases ([19]).

Whereas the effects of the level of calcination on coke properties have been widely examined, few studies mention the effect on anode properties and performance.

Among the positive effects mentioned, we note :

- a decrease in anode electrical resistivity and air reactivity when the calcination level is raised ([1]);
- a decrease in anode consumption in mini reduction cells when coke Lc increases [13].

The second point, however, appears to raise some controversy since [20] reports an increase in anode consumption when the coke calcination level is raised, at a constant anode baking level.

A negative point is also mentioned in [3] where it is stated that there is an increase in anodic over-voltage when the coke calcination level is raised.

Given the lack of information regarding the influence of the level of coke real density on anode reactivity, the study presented hereafter was conducted.

Experimental methodology

The study consisted of producing bench scale anodes with two different grades of coke, labeled H and L, which were used in pure form and in 70/30 and 30/70 % blends, and baked at different temperatures.

Properties of the cokes used

The properties of the two cokes are given in table I.

Table I : Properties of the two cokes used

		H	L
Real density		2.098	2.069
Lc	Å	23.1	23.3
Ash	%	0.07	0.23
Sulfur	%	1.14	2.69
Fe	ppm	80	570
Si	ppm	25	200
V	ppm	90	230
Ni	ppm	95	150
Na	ppm	30	50
Ca	ppm	40	75
Air reactivity (0,5°C/min)			
Ignition T	°C	567.9	535.6
R 525°C	%/min.	0.05	0.24
CO ₂ reactivity (1000°C)	%	8.4	5.3

Real density was measured by toluene pycnometry ; sulfur and impurity contents were measured by X-ray fluorescence; and air reactivity and CO₂ reactivity were measured according to R & D CARBON methods (RDC 142 and RDC 141 apparatus).

The L coke is a coke with a relatively low real density and relatively high sulfur, nickel and vanadium contents.

The H coke, on the contrary, has a higher real density, is purer and has a low sulfur content. Its air reactivity is distinctly better than that of the L coke. However, its CO₂ reactivity is higher.

We also studied the evolution of the real density of the two cokes versus temperature by calcining the raw cokes at different levels (see figures 1, 2 and 3).

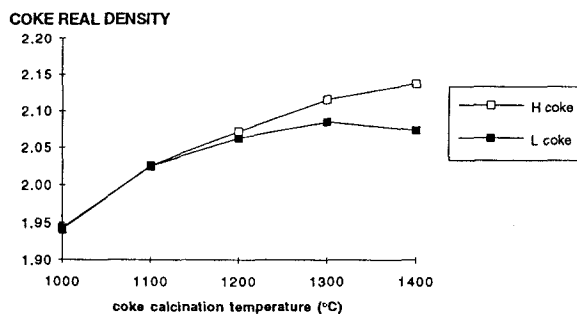


Figure 1 : Real density of cokes H and L as a function of calcination temperature.

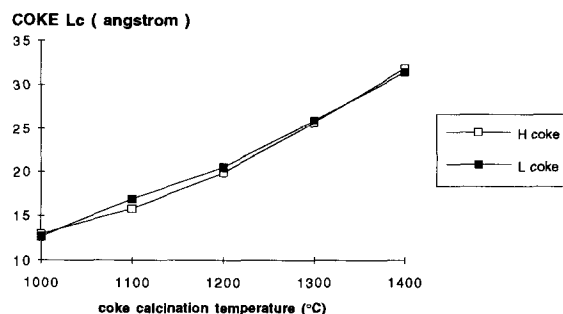


Figure 2 : Crystallite size of cokes H and L as a function of calcination temperature.

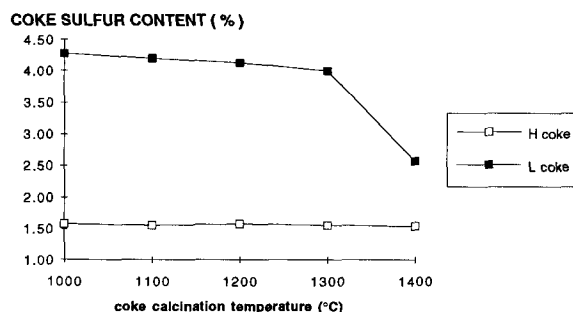


Figure 3 : Sulfur content of cokes H and L as a function of calcination temperature.

The real density of H coke evolves far more rapidly as a function of the calcination temperature than does that of the L coke. This explains the fact that, in spite of similar calcination temperatures (indicated by Lc), the real density of the H coke is distinctly greater than that of the L coke.

Desulfurization occurs at high temperature for coke L whose sulfur content is high.

Bench scale anode production

All the anodes were produced without the addition of any recycled materials and with the same grain size distribution.

The 70/30 and 30/70 blends were obtained by mixing the two cokes in the aforementioned proportions in each of the eight fractions used to reach the target grain size distribution.

The paste was prepared using a coal tar pitch with a Mettler softening point of 104°C and the proportion of pitch used was 18%. This percentage was high enough to ensure that the anodes would never be underpitched, whatever the coke blend. This point was verified a posteriori by permeability measurements.

After being mixed at 170°C, the paste was formed by a press at 450 bars into cylinders 90 mm in diameter and 180 mm high.

The bench scale anodes were then baked in a gas-fired furnace in which the gases were raised to their final temperature in 30 h, followed by a temperature holding period of 55 h.

Five series of anodes were baked at the following final anode temperatures : 920°C - 1000°C - 1080°C - 1160°C - 1260°C.

Four bench scale anodes were made for each coke or coke blend and each baking temperature. The values given hereafter will be the averages of the four results that were obtained.

Anode characterization

The anodes were characterized as follows:

- chemical analysis (S, V, Ni, Fe, Si, Na, Ca)
- geometrical density, permeability, thermal conductivity (RDC 143)
- real density in toluene
- air reactivity (RDC 151) and CO₂ reactivity (RDC 146).

Each of the reactivities (air and CO₂) is characterized by three variables:

- reactivity loss which measures the chemical reactivity of the anode
- reactivity dust which measures anode crumbling and hence the tendency to produce carbon dust (dusting)
- reactivity residue which is the quantity that remains, which has not been consumed either by dusting or by chemical reaction.

Results

Desulfurization

When the baking temperature and sulfur content of the base coke are increased, desulfurization occurs, as shown in figure 4. Desulfurization creates porosity (figure 5).

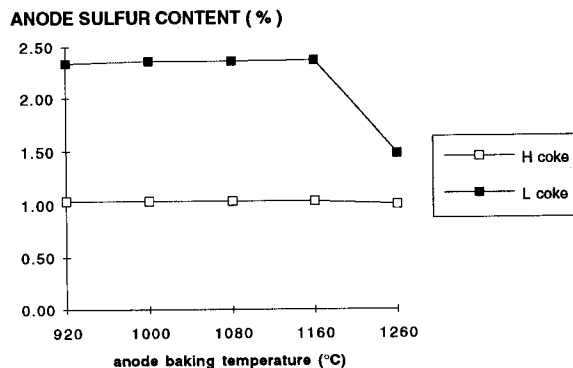


Figure 4 : Desulfurization of anodes with coke L occurring at high baking temperature.

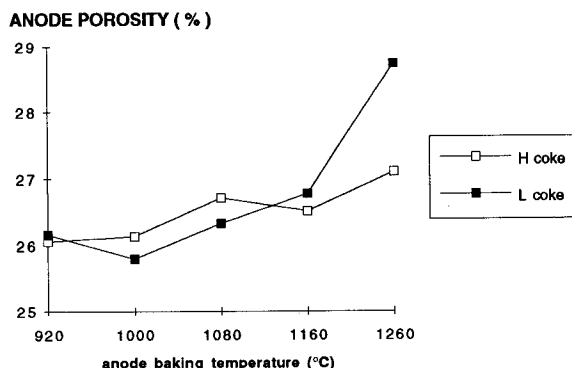


Figure 5 : Increase in porosity of anodes with coke L due to desulfurization.

Physical properties

- Geometrical density increases slightly as the level of baking rises and then decreases once desulfurization occurs (creation of porosity).
- Permeability is hardly affected by the level of baking. The levels reached are low and constant, which confirms that the percentage of pitch used was sufficient to ensure that none of the anodes would be underpitched.
- Thermal conductivity increases as the level of baking is raised. This increase accelerates with desulfurization.

Air reactivity

The H coke dust decreases substantially as the baking temperature rises and reaches zero at 1160°C (figure 6).

For the L coke, the zero point is reached at 1000°C and dust begins to increase from 1160°C.

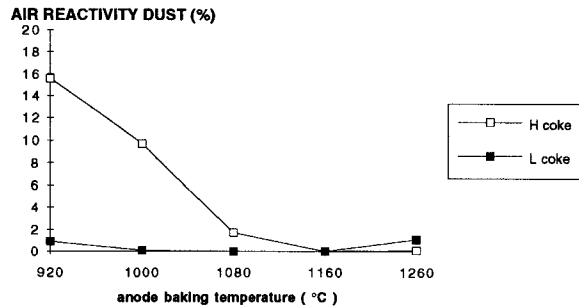


Figure 6 : Air reactivity dust as a function of anode baking temperature.

The H coke reactivity loss decreases continuously. L coke loss is more or less constant up to 1160°C and then rises quite significantly beyond that point (figure 7).

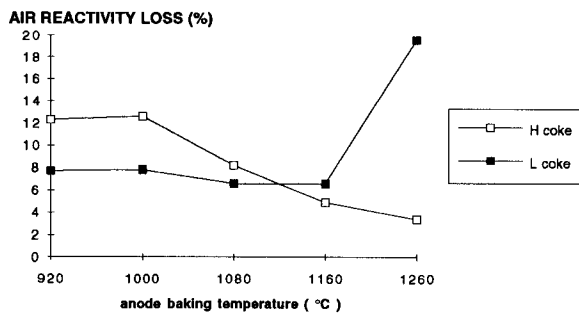


Figure 7 : Air reactivity loss as a function of anode baking temperature.

Residue, which is added to the sum of dust + loss to make 100%, therefore varies inversely (figure 8). For the H coke, its continual rise is substantial. For the L coke, the rise is gradual up to 1160°C. Beyond that, residue drops sharply.

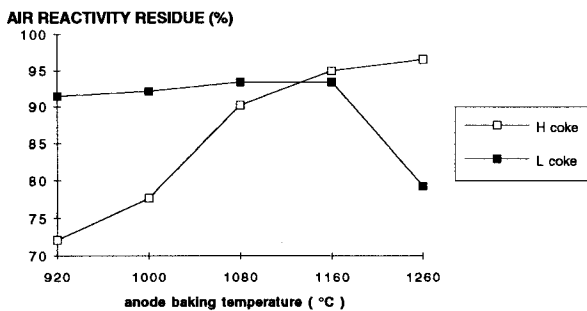


Figure 8 : Air reactivity residue as a function of anode baking temperature.

CO₂ reactivity

The observations are the same as those regarding air reactivity (figures 9 to 11).

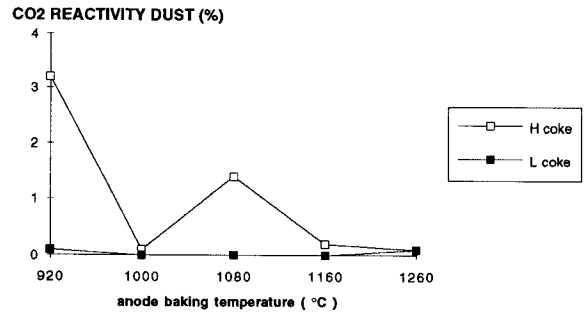


Figure 9 : CO₂ reactivity dust as a function of anode baking temperature.

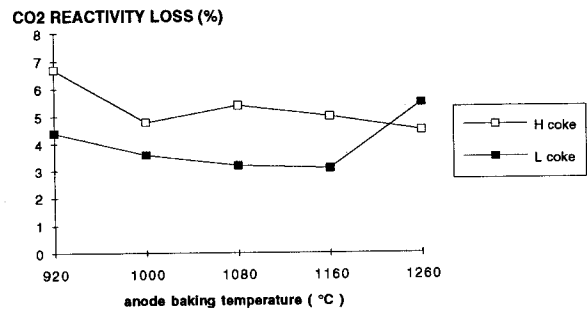


Figure 10 : CO₂ reactivity loss as a function of anode baking temperature.

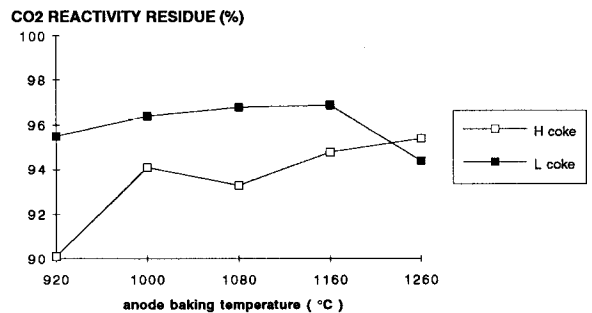


Figure 11 : CO₂ reactivity residue as a function of anode baking temperature.

Overall reactivity trends

At first glance, the curves shown in figures 6 to 11 appear very different for the two cokes. This is due to the fact that the properties are plotted as a function of the baking temperature.

However, it was shown previously that the two cokes show very different behaviours with respect to temperature.

To resolve this point, the same properties were plotted not only as a function of the baking temperature, but as a function of the difference $RD_{anode} - RD_{coke}$ (figures 12 to 17) where RD_{coke} is the RD of the base coke given in table I.

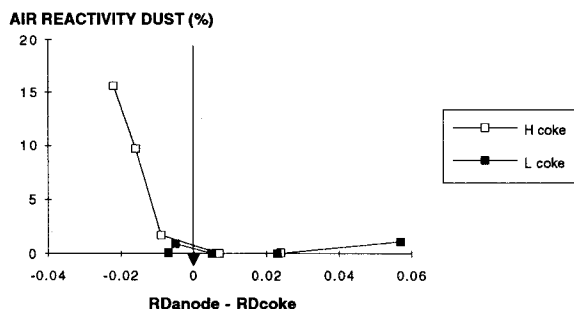


Figure 12 : Air reactivity dust as a function of $RD_{anode} - RD_{coke}$.

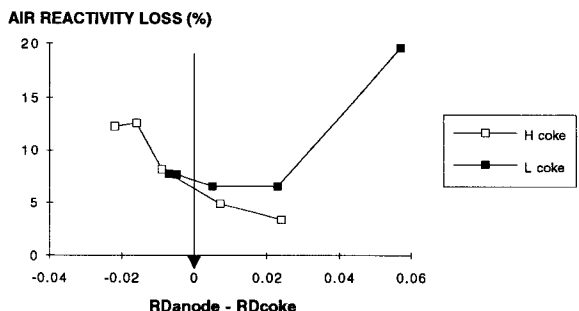


Figure 13 : Air reactivity loss as a function of $RD_{anode} - RD_{coke}$.

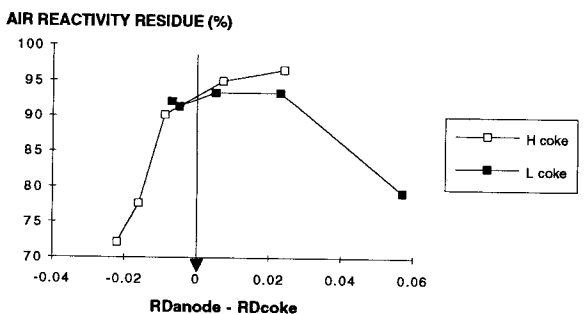


Figure 14 : Air reactivity residue as a function of $RD_{anode} - RD_{coke}$.

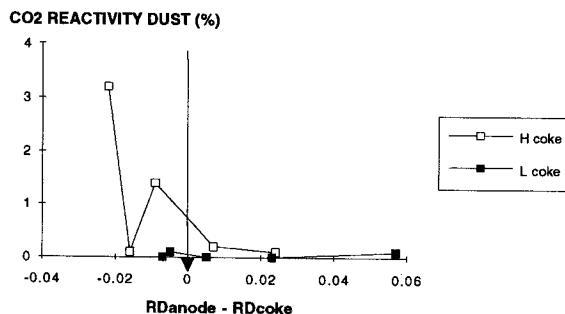


Figure 15 : CO_2 reactivity dust as a function of $RD_{anode} - RD_{coke}$.

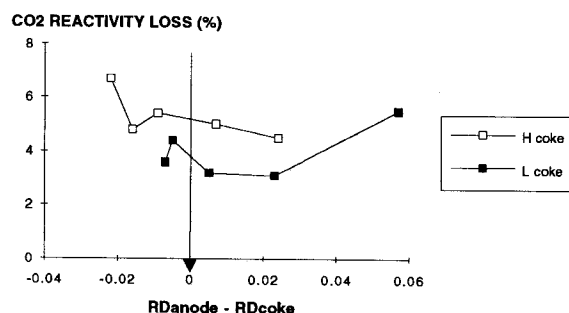


Figure 16 : CO_2 reactivity loss as a function of $RD_{anode} - RD_{coke}$.

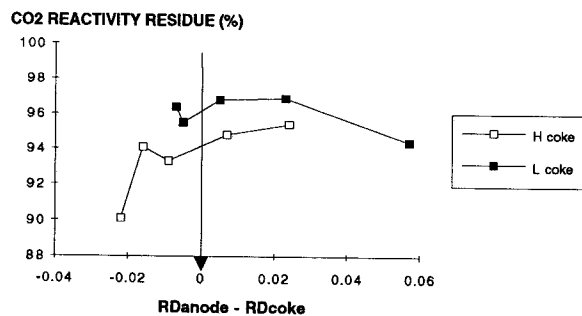


Figure 17 : CO_2 reactivity residue as a function of $RD_{anode} - RD_{coke}$.

When the $RD_{anode} - RD_{coke}$ quantity becomes nil, it signifies that the anode was baked at a temperature such that the binder coke reached the same level of real density as that of the base coke.

The negative values signify that the level of real density of the binder coke was less than that of the base coke.

The positive values correspond to an RD_{anode} greater than the RD_{coke} . A quick calculation shows that this is not possible with the evolution of the binder coke RD alone. The base coke RD therefore also evolves during anode baking when the level of anode real density exceeds the initial real density of the base coke.

With this new presentation, an overall trend appears, showing a variation in reactivity characteristics according to the level of baking.

This trend can be generalized to include all the cokes.

Each of the curves comprises three zones:

Zone 1 corresponds to $RD_{\text{anode}} - RD_{\text{coke}} < 0$

Zone 3 corresponds to the high values of $RD_{\text{anode}} - RD_{\text{coke}}$ (beyond 0.02 to 0.03 approximately).

Zone 2 corresponds to the intermediary zone.

From this point forward, we will no longer distinguish between air reactivity and CO_2 reactivity since the overall trend is the same.

In zone 1, reactivity dust evolves considerably: it drops as the level of binder coke real density increases and nears the level of the base coke. Hence there is a decrease in the differential reactivity between binder coke and base coke. When $RD_{\text{anode}} = RD_{\text{coke}}$, differential reactivity is nil and so is reactivity dust. Zone 1 therefore corresponds to underbaking of the anode with the risk of carbon dust in the reduction cell. This risk increases as the quantity of $RD_{\text{anode}} - RD_{\text{coke}}$ becomes negative. A decrease in reactivity loss when RD_{anode} increases, is also observed, due to the decrease in the intrinsic reactivity of the binder coke. The combined evolutions of reactivity dust and loss, to a lesser extent, create a sharp increase in residue as the baking level rises in zone 1.

In zone 2, reactivity dust is nil. There is no more differential reactivity between binder coke and base coke. Reactivity loss decreases due to the increase in the level of binder coke and base coke real density and hence in their intrinsic reactivity. H coke anode loss evolves more rapidly than that of the L coke anodes due to the higher evolution of the H coke real density versus temperature. Residue therefore increases in zone 2. This zone corresponds to adequate baking.

In zone 3, there is desulfurization. Reactivity loss increases sharply and dust increases to a lesser extent. The result is a sharp drop in residue. Zone 3 corresponds to overbaking.

This concept, when conveyed as a function of baking temperature, gives the curve shown in figure 18, where the three zones can be visualized.

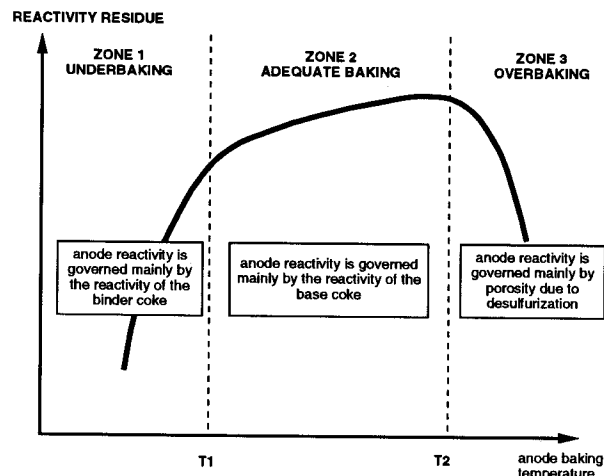


Figure 18 : Overall evolution of reactivity residue as a function of anode baking temperature.

The baking temperatures which delimit these zones are:

T1 : function of the base coke real density.

T2 : function of the tendency towards desulfurization and hence, as an initial approximation, of the sulfur content of the base coke.

The curves in figures 6 to 11 become easier to interpret:

- only the part of the curve which corresponds to zones 1 and 2 is visible for the H coke (baking at a higher temperature would have been necessary in order to see zone 3)
- only the part of the curve which corresponds to zones 2 and 3 is visible for the L coke (baking at a lower temperature would have been necessary in order to see zone 1).

There is a shift in temperature between the curves of the two cokes.

Baking temperature T1, beyond which there is no more underbaking, is much higher for the H coke than for the L coke, which is explained by the difference in the real density level of the two cokes. The binder coke must reach a higher real density level in the H coke anodes. It is therefore necessary for the H coke anodes to be baked at a higher temperature.

Optimal anode reactivity

As it has been seen, the dust and loss minima and the residue maximum are reached at the borderline between zones 2 and 3.

Table II gives the minimal loss values reached at this level of baking for both cokes and both reactivities.

Table II : Minimal anode reactivity versus intrinsic coke reactivity.

Anode reactivity	Minimum loss (%)	Air reactivity		CO ₂ reactivity	
		H coke	L coke	H coke	L coke
Intrinsic coke reactivity	R 525°C (%/min.)	0.05	0.24		
	R CO ₂ (%)			8.4	5.3

These values of anode reactivity are fully consistent with the intrinsic reactivity values measured on the cokes themselves : the lower minimal loss corresponds to the lower intrinsic coke reactivity.

The differences in reactivity between the two cokes were predictable due to their respective nickel and vanadium (air reactivity catalysts) contents, on the one hand, and their sulfur (CO₂ reactivity inhibitor) content, on the other hand.

Coke blends

Bench scale anodes were also made with two coke blends.

70% H + 30% L
30% H + 70% L

The anodes were produced and characterized in exactly the same manner as the anodes composed of pure cokes.

All the trends mentioned previously are also visible with the anodes made with the coke blends. We will only discuss air reactivity dust and air reactivity residue here (figures 19 and 20).

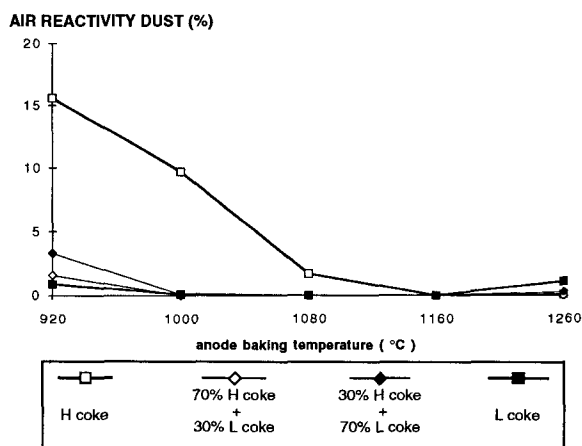


Figure 19 : Air reactivity dust versus anode baking temperature for the pure cokes and the blends.

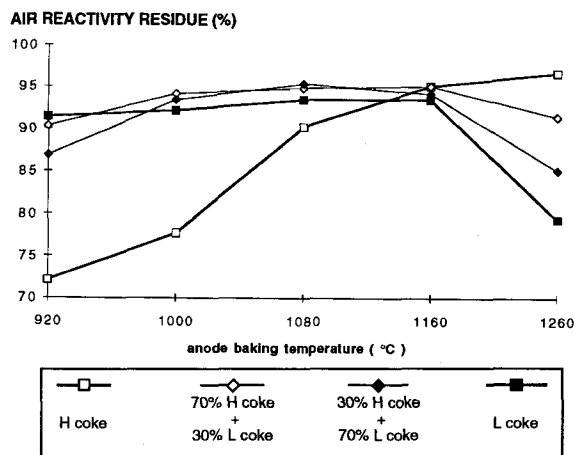


Figure 20 : Air reactivity residue versus anode baking temperature for the pure cokes and the blends.

At low baking temperatures, the coke blend anodes show similar behaviour to that of the L coke anodes: dust is low and residue is high.

The high temperature desulfurization phenomenon is found again, but the intensity depends on the quantity of L coke in the blend.

These observations are directly transposable to CO₂ reactivity.

The effect of blending L and H cokes can be interpreted as follows : adding a coke with a low real density level to a high real density coke makes it possible to reach zero differential reactivity between the binder coke and a part of the base coke at a lower temperature. The oxidation chemical reaction is dispersed and no longer concentrated on the binder coke.

This makes it possible to substantially reduce dust and, as a result, the risk of carbon dust in the reduction cell.

Estimated effects on carbon consumption

A formula has been published ([21]) that can be used to predict reduction cell carbon consumption (NC, kg/t Al) as a function of certain cell and anode properties.

$$NC = C + \frac{334}{CE} + 1.2 (BT - 960) - 1.7 CRR + 9.3 AP + 8 TC - 1.5 ARR$$

where:

- C is the reduction cell factor (kg/t Al)
- CE current efficiency (%)
- BT bath temperature (°C)
- CRR CO₂ reactivity residue (%)
- AP air permeability (nPerm)
- TC thermal conductivity (W/mK)
- ARR air reactivity residue (%).

For smelters which use a given type of reduction cell and which adjust anode pitch content according to coke porosity, it may be considered that the CE and BT factors on the one hand, and AP, on the other, are constant. The formula therefore becomes :

$$NC = C' - 1.7 CRR + 8 TC - 1.5 ARR$$

The factor $- 1.7 \text{ CRR} + 8 \text{ TC} - 1.5 \text{ ARR}$ gives the coke and baking temperature effects on the quality of the anodes.

Figure 21 shows the evolution in carbon consumption as a function of baking temperature for the two pure cokes and the coke blends. (679 kg/t Al has been used as the constant C').

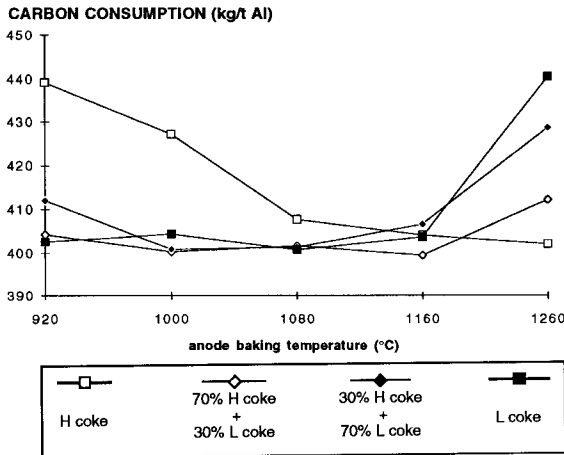


Figure 21 : The theoretical net carbon consumption as a function of anode baking temperature for the pure cokes and the blends.

Pure cokes

For the H coke, the decrease in carbon consumption is due to the increase in air reactivity and CO₂ reactivity residue.

For the L coke, the rise is due to the combined effects of desulfurization and increased thermal conductivity.

The absolute carbon consumption levels are similar for both cokes. However, in order to reach comparable levels, the H coke anodes must be baked at a much higher temperature (+ 100°C to + 200°C in this study).

Coke blends

As for the blends, for a given baking temperature, adding L coke to the H coke makes it possible to sharply decrease carbon consumption at standard anode baking temperatures.

At high temperatures (1260°C), however, carbon consumption rises due to the desulfurization of the L coke.

Another way of interpreting this figure is to state that adding L coke to the H coke makes it possible to substantially lower the anode baking temperature and still obtain a carbon consumption level that is the same as or even better than that obtained with pure H coke.

Conclusion

The curves showing the evolution of air or CO₂ reactivity residue as a function of anode baking temperature are divided into three distinct zones:

- At low baking temperatures, there is a differential reactivity between the binder coke and the base coke: the anode is consumed by the chemical reaction of the binder coke and by the formation of carbon dust.
- At high baking temperatures, the base coke is desulfurized. The ensuing increase in the active anode area creates a very sharp rise in anode consumption by chemical reaction.
- In the intermediary temperature zone, anode reactivity depends on the level of real density and the catalytic impurity contents.

The baking temperatures which delimit the three zones are linked to the following:

- the first one to the base coke real density level,
- the second one to the tendency of the coke towards desulfurization and hence, as an initial approximation, to its sulfur content.

It is necessary to bake the anodes at a minimum temperature such that the real density of the binder coke is equal to that of the base coke in order to obtain minimum binder coke/base coke differential reactivity. The use of coke with a higher real density therefore requires anode baking at higher temperatures.

The upward trend in real densities which has been observed for several years does lead to a decrease in coke reactivity, but, in order for this decrease to be accompanied by a decrease in anode reactivity, the anodes must be baked at a higher temperature, to avoid creating carbon dust.

It would therefore be better to revert to calcination levels which produce real coke densities that are around 2.07. Anode producers will then be free to adjust the anode baking temperature so as to optimize anode reactivity, without the risk of underbaking, and hence carbon dust.

Furthermore, adding a coke with a low level of real density to a coke with a high level of real density makes it possible, in comparison with anodes composed solely of coke with a high level of real density :

- to significantly reduce anode reactivity and especially dusting at a constant baking temperature,
- or to obtain the same reactivity at a distinctly lower baking temperature.

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