ANODE REACTIVITY
INFLUENCE OF THE BAKING PROCESS

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Net carbon consumption is one of the parameters most frequently employed in characterizing anode performance in an aluminium reduction cell.

It is generally agreed that the crystal structure of the carbon is one of the decisive factors governing non-electrolytic consumption of the anode.

The organization of the crystal structure depends on the nature of the raw materials used, but even more on the degree of baking, which is in turn determined by a combination of time and temperature.

The twofold objective of the economic optimum and of quality expressed in terms of reactivity means achieving a standard of baking which is nearly as possible uniform over the total furnace charge.

Various approaches such as digital simulation, scale models and test rigs have generated technological improvements that successfully reduce the variability of the results of baking.

Together, these developments, in combination with high-performance process control, now add to the attractions of the horizontal-flue ring furnace as measured by consumption and uniformity of baking.

INTRODUCTION

Net carbon consumption, or simply "net carbon" is the figure generally employed to characterize anode performance in a reduction cell. It includes both electrochemical consumption and "excess" consumption of the anode carbon.

Electrochemical Consumption

This is a direct consequence of the electrolytic reduction of alumina to aluminium, which results in the formation of "primary" carbon dioxide. The overall electrolytic process for the reduction of alumina may be simply presented by :

$$Al_2O_3\ (diss) + 3/2\ C(s) \xrightarrow{960°C} 3/2\ CO_2(g) + 2\ Al(l)$$

It is possible that some primary carbon monoxide CO may also be generated, but at the current densities normally employed, the production of primary CO_2 predominates (1).

Excess Consumption

Carboxyreactivity. This refers to the tendency of the primary CO_2 to react with the anode carbon, according to the equation :

$$CO_2\ (g) + C\ (s) \rightleftharpoons 2\ CO\ (g)$$

This reaction goes completely to the right above 930°C.

Even though the anode surface in contact with the electrolyte is shielded against this reaction, CO_2 can nevertheless diffuse through, and react within the pore structure at the anode/bath interface (2).

Oxyreactivity. This relates to the surfaces exposed to the action of air during the working life of the anode in the reduction cell. The type of pot and method of operation can have a significant influence on oxyreactivity (3).

Dusting. This is the name given to the loss of carbon from the anode due to the selective oxidation of the binder coke. Generally, the failure of aggregate-binder bonds reflects "underbaking" of the anode, but it can also be due to a deficit of pitch.

Reducing all these contributions to consumption of carbon is one of Aluminium Pechiney's ongoing objectives, warranted by the potential for savings represented by improved net carbon values.

After first putting an overall figure on what is at stake financially, we shall discuss the influence of the degree and uniformity of baking on excess carbon consumption and then go on to present the action taken to improve baking performance and the results obtained by Aluminium Pechiney.

THE FINANCIAL STAKES : THE NET CARBON COST

For the purposes of our study, we developed a technical and economic model of the complete process of anode production. The model generates mass balances, thereby enabling the overall economics of production to be computed, including consumptions of all raw materials, i.e. coke, pitch, packing, rodding iron and refractories. More generally, it also takes due account of plant times on stream, maintenance costs and inventories.

A. Tomsett and J. Johnson (Eds.), *Essential Readings in Light Metals*

The model was applied to the case of a smelter comprising 240 pots of 300 kA and producing 190 000 metric tons of aluminium per year.

Net carbon values were varied from 390 to 420 kg per production ton of aluminium (kg/t Al) in steps of 10 kg, the reference value being set at 410 kg/t Al. Excess anode consumption due to oxidation of the anode tops was in every case deemed to be constant at an arbitrary value of 10 kg/t Al.

Results are shown in Table 1.

Net Carbon	kg/t Al	390	400	**410**	420
Gross Carbon	kg/t Al	517	543	**543**	572
No. of shifts		85	83	**81**	79
No. of shifts corrected		84	80	**80**	76
TOTAL annual saving	k$/t Al	-1076	-570	0	+570

Table 1 - Net carbon cost

A reduction in consumption of 10 kg/t Al holds out hope of savings of some $ 0,5 million per year.

The research effort devoted to reductions in carbon consumption is therefore fully warranted by the size of the savings to be expected.

REACTIVITY - THE PART PLAYED BY BAKING

Measuring Reactivity

We currently possess a variety of means of characterizing anode quality in terms of reactivity.

Two different laboratory approaches are employed, depending on whether we wish to predict anode performance in the pot or determine the mechanisms governing the reactivity of the anode carbon. This is because no simple relationship exists between the reactivity of carbon to a stream of CO_2 and excess consumption in the reduction pot, where the reaction occurs under conditions which are entirely different and also vary with the type and method of operation of the pot (4, 5).

At Aluminium Pechiney, we have equiped ourselves with a dual means of characterization, consisting of:

i) A laboratory-scale electrolytic cell ideally suited to the investigation of excess consumption of anode carbon.

ii) An apparatus for measurement of the reactivity of carbon to a stream of CO_2 or oxygen, this being essential to any study of the parameters governing reactivity.

The reactivity measurement apparatus has enabled us to investigate the effects of raw materials and process parameters on reactivity, with special reference to the influence of :

i) Pitch content and the quality of mixing.

ii) The content and distribution of recycled material.

iii) The degree of baking and variability of results.

We shall confine ourselves in this paper to presenting some of the results of investigation of the relationship between degree of baking and reactivity.

The importance of baking temperature as a factor in excess consumption of anode carbon has already been clearly demonstrated. It is accepted that consumption can differ by as much as 15 % for a variation in baking temperature from 1 000 to 1 200°C (4, 6, 7). This being so, we have examined how reactivity varies with the degree of baking.

Effect of Degree of Baking (Laboratory Study)

This investigation was carried out in the laboratory on pressed blocks prepared from various types of coke and a standard grade pitch.

The effect of degree of baking was found to depend on the type of coke employed. In general, rates of oxidation in air and in CO_2, respectively, were both found to reduce as the real density of the baked sample increased. Additionally, only the samples exhibiting the highest real densities were found to yield any significant residues on oxidation.

These findings illustrate the phenomenon of underbaking, characterized by preferential attack on the binder coke, in an anode baked at below a certain critical treatment threshold. The result of such preferential attack is that the sample disintegrates on oxidation, foreshadowing a tendency to "dusting" in the pot.

In the case of a high-sulphur coke, the rate of oxidation was found to increase again above a certain heat treatment threshold, with no diminution in the quantity of residue. This is to be explained by loss of sulphur, creating fresh microporosity, with an attendant increase in specific surface and hence in rate of oxidation. In this case, however, the attack is on the filler coke. This is why no diminution in residue is observed.

When verifying the degree of baking, therefore, we have both to check that we have obtained the right texture of coke ex-pitch and at the same time check the effect on the filler coke.

Additionally, and whatever the raw materials employed, oxyreactivity and carboxyreactivity residues are considerably influenced by the degree of baking and reach their maxima when heat treatment is taken above a certain threshold, generally that yielding a baked real density equal to the filler coke real density plus 0,02 g/cm^3.

The dual objectives of the economic optimum and of quality, as determined by reactivity, call for a degree of baking sufficient to avoid excess consumption due to reactivity and dusting, together with the minimum possible variation in characteristics over the furnace charge as a whole.

Characterization and Monitoring of the Results of Baking

While temperature is still the parameter most commonly employed to control the anode baking process, it is far from sufficient for characterization of the degree and uniformity of baking throughout the furnace charge. This is because the degree of baking reflects the degree of order exhibited by the crystal structure, which in turn results from the combined action of temperature and the length of time for which energy is fed to the material.

Again, determinations of real density, or mean crystallite size (Lc), the results of which are representative of the combined effects of time and temperature, also have their disadvantages. While the determination of real density to toluene is a very sensitive method of characterizing the degree of heat treatment, it may give spurious results where certain substances are present as impurities in recycled anode carbon. As for the determination of Lc, this requires apparatus designed for very accurate measurements and which, in many cases, cannot be set aside solely for this use in each and every plant.

However this may be, these determinations share one major disadvantage : the results in both cases depend on the type of coke employed, thus ruling out any systematic comparison between different baking plants.

For the purposes of this study, therefore, we employed the method of indirect temperature measurement ; this is now in widespread use and consists of correlating the real density of a control sample of green coke subjected to a given heat treatment with a value of temperature read from a calibration curve of density versus "equivalent temperature" (Teq) (8, 9).

The relationship between coke real density and equivalent temperature depends on time and temperature and hence, as we shall see, on the calibration procedure.

Calcination of Green Coke (Calibration Curve). The green coke calcination study was carried out in the laboratory for temperatures ranging from 950°C to 1 270°C and times at treatment temperature ranging from 3 to 48 hours.

Temperature build-up times were varied from 3 to 140 hours.

Effect of Treatment Temperature :
Figure 1 plots real density of the control coke versus treatment temperature, temperature build-up time and time at treatment temperature both being constant at 3 hours each.

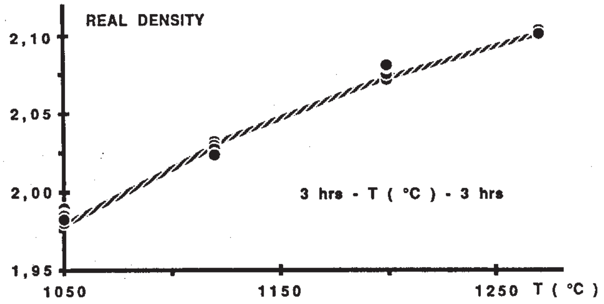


Figure 1 - Treatment temperature versus real density.

Effect of Time at Temperature :
Figure 2 plots real density of the coke versus time at a treatment temperature of 1 050°C, again for a 3-hour build-up time.

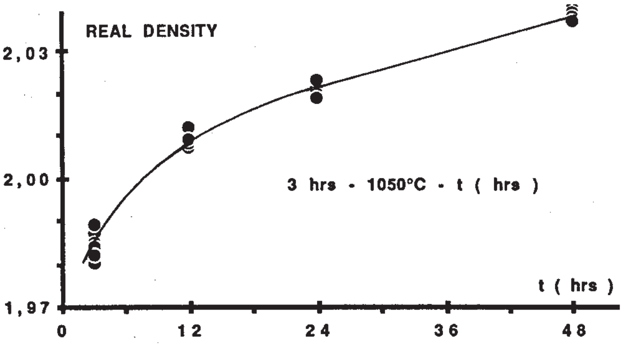


Figure 2 - Time at temperature versus real density.

Variance analysis of the results of 165 measurements revealed that real density (RD) was significantly influenced by the combined action of treatment temperature and time at temperature.

Regression analysis based on the same data enabled a satisfactory correlation between these parameters to be established in the form:

$$RD = \exp\left[10^{-4}\left(68141 + 13.2t - 0.167t^2 + 11.79T - 0.004T^2 - 0.0217t.T\right)\right]$$

$$3\text{ hrs} < t < 48\text{ hrs}$$
$$950°C < T < 1\,270°C$$

The rate of build-up of temperature was not found to have any effect over the range investigated.

Construction of a Calibration Curve :
The "3-hour build-up/3 hours at temperature" cycle was chosen to study the variation with equivalent temperature of real density and Lc, respectively. The two plots obtained are shown in Figure 3.

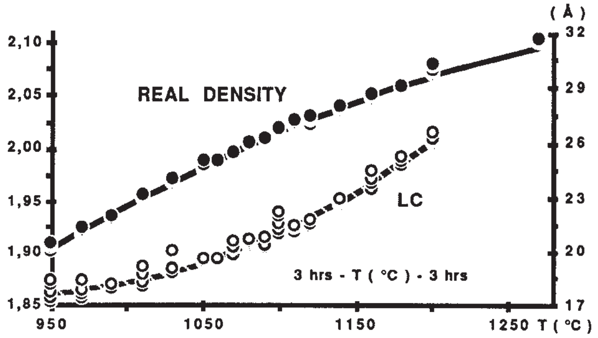


Figure 3 - Calibration curve : Real density/Lc versus equivalent temperature.

The method of characterization which takes account both of maximum treatment temperature and length of treatment, while being unaffected by the grades of raw materials employed, thus proved to be perfectly suited to the kind of study under discussion.

UNIFORMITY OF DEGREE OF BAKING OBTAINED ON THE PLANT

In addition to the assessment of the minimum heat treatment requirement, the uniformity of the final results of baking, in terms of all the anode blocks in a furnace pit, is a particularly important aspect of the baking process.

The greater the range of variation in results, the higher the mean and maximum baking temperatures required, assuming the same cycle, to maintain a minimum temperature above the critical threshold. This, in turn, has implications as regards furnace fuel consumption and damage to refractories which can be serious if the temperature differentials are substantial.

Experimental

Samples of the control coke were placed in a rodding hole of each anode loaded into a pit. On completion of baking, each of the anodes, previously marked for identification, was cored in proximity to the sample holder.

Results

Correlation Between Degree of Baking and Reactivity. By means of parallel investigations of degree of baking and anode reactivity, we were able, under conditions entirely representative of industrial production, to confirm the existence of a straightforward correlation between degree of heat treatment and oxyreactivity and carboxyreactivity residues.

This statistically-designed study was conducted on a hundred or so data points and several different sets of baking process conditions. The confidence level attained was very satisfactory.

Figure 4 is an example of variations in carboxyreactivity residue with equivalent temperature.

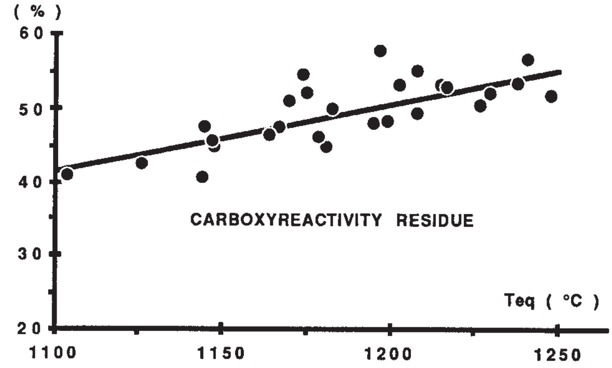


Figure 4 - Carboxyreactivity residue versus equivalent temperature.

This correlation highlights the influence of baking on reactivity residues, which foreshadow the susceptibility of the anode to dusting.

Distribution of Equivalent Temperature Within a Pit. The results of this study can be expressed in either of two ways :

Distribution of equivalent temperature within a pit (40 data points) :
This mode of representation emphasizes the differences between minimum and maximum degrees of baking, thus enabling the degree of uniformity of baking within a pit to be assessed.
Figure 5 is an example of a typical plot obtained for a furnace dating from 1978.

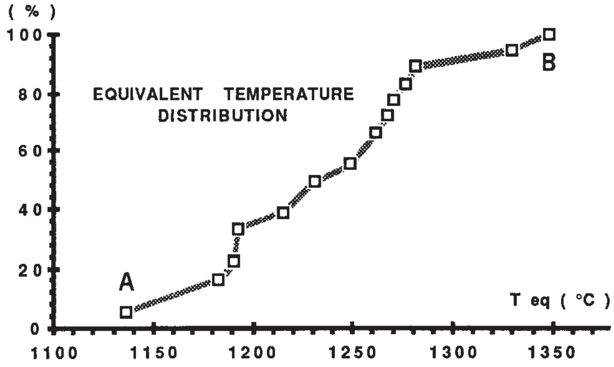


Figure 5 - Equivalent temperature distribution (Old furnace).

The extreme data points (A, B) on this plot represent regions of the charge in the pit that are under and over-baked, respectively. They correspond to an equivalent temperature difference of some 200°C.

Temperature differences of this magnitude can arise variously from :

i) The condition of the flue wall.

ii) Malfunction of a burner.

iii) Faulty regulation.

iv) Indifferent operation of the furnace.

vi) Air inleakage.

We shall now see how these various problems can be identified by means of the alternative method of presentation ; this is based on the construction of diagrams of constant equivalent temperature.

Constant equivalent temperature diagrams :

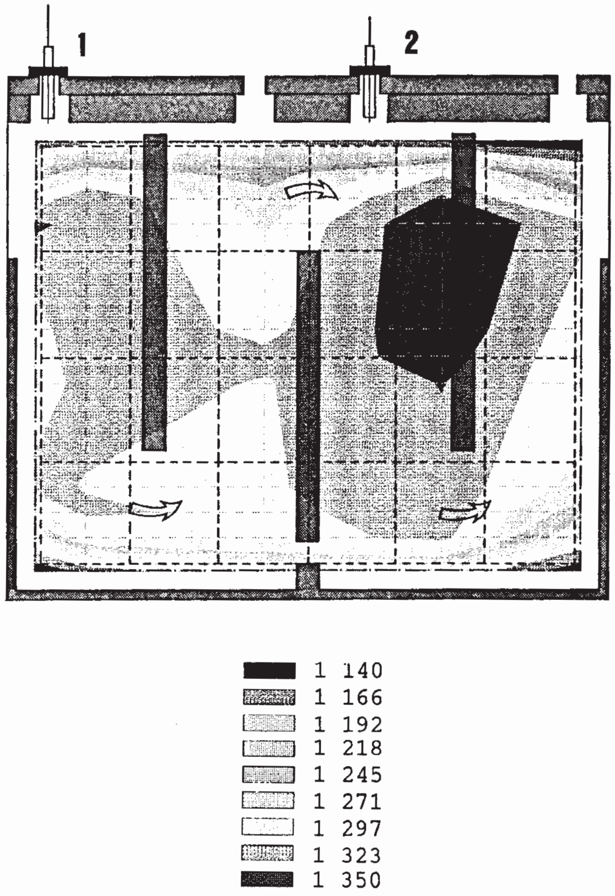


Figure 6 - Constant equivalent temperature
Superimposed :
- the anodes to be baked (dotted lines)
- the internal path taken by the flow of gas.

The example depicted in Figure 6, chosen for the purposes of discussion is based on measurements carried out on a ten years old, gas-fired, Aluminium Pechiney furnace operating on the cocurrent principle.

An examination of the isotherms enables us to make out the presence of burners at positions 1 and 2 and prompts a number of comments.

A high equivalent temperature, corresponding to overbaking, was recorded opposite burner 2. This indicates a hot and highly localized flame throughout the period of operation of the burner.

Also evident are the interactions between the gas flow through the flue wall and the flame, which is flattened against the baffle.

Next, we note a disproportionate difference between the energy inputs from burners 1 and 2, which may be as a result of faulty burner settings, or to a problem of regulation, or to a substantial intake of air at shaft one.

Also detectable are certain clues to the intake of cold air at the upper corners of the pit.

Finally, the poor gas circulation at the lower corners and bottom of the flue wall, and the heat losses, are both clearly revealed by this analysis.

By means of this diagnosis, we were able to identify the fundamental improvements needed in order, at one time, to minimize differences in baking, reduce specific consumption and limit premature damage to refractories.

Now for a description of the various ways and means developed and employed by Aluminium Pechiney to improve baking quality and the operation of its baking plants.

FACTORS UNDERLYING HETEROGENEITY
DEVELOPMENT OF SPECIFIC AIDS TO INVESTIGATION

Burner Testing Unit

The predominant influence of the burner is to be explained mainly by the strong release of thermal energy localized in the vicinity of the flame ; which is also deflected by the gas flow.

This led us to imagine a means of testing a burner under its actual conditions of use in a baking plant.

General Description of the Testing Unit. The testing unit consists of a full-size hollow wall constructed of ceramic fibre and comprising two shafts to enable burners to be tested under conditions of co- and countercurrent operation. The wall is fitted with 46 S type thermocouples connected to a data processor.

Downstream of this arrangement, a preheating burner and heat accumulator serve to preheat the combustion air to as much as 900°C.

The system is fully equipped with conventional means of measurement.

Sketch of Testing Unit.

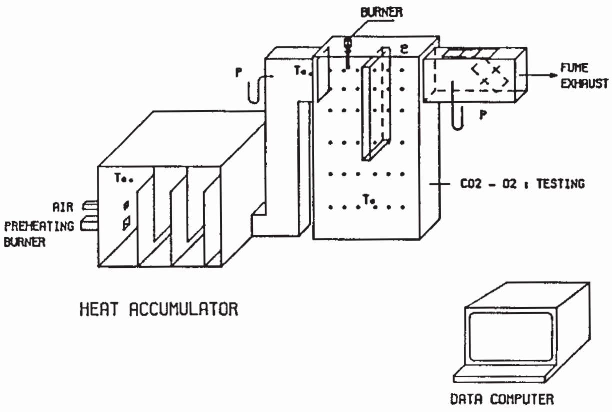
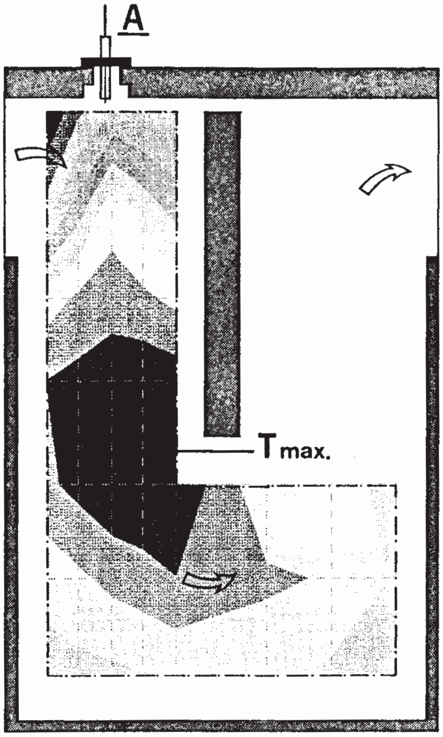


Figure 7 - Burner testing unit.

Experimental. Generally speaking, the testing unit is applied to determine isotherm variations and distribution patterns in response to changes in type of burner and burner settings. It can therefore be used to evaluate the heating ability of a burner. Interactions between the flame and gas flows under various operating conditions can also be depicted.

To illustrate the type of results we can now obtain, Figure 8 offers some comparative data on two commercially available burners, A and B.



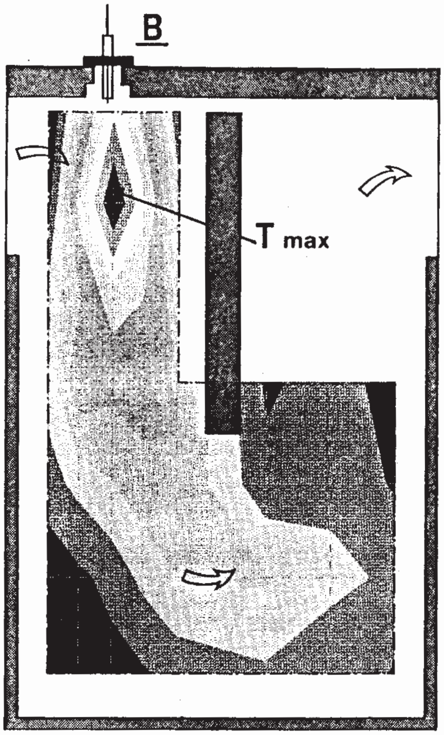


Figure 8 - Comparison of two different types of burners. Isotherms recorded after 300 seconds' operation.

These are the isotherms recorded with burners A and B after 300 seconds' operation, all other things being equal.

As seen in Figure 8, the hot points for burners A and B are not located at the same place. The maximum temperatures attained are, however, identical.

By integrating gas temperature over time, we can assess the power of each of the burners. A detailed analysis reveals that burner A is 1.7 times as powerful as burner B at exactly the same settings.

At the same rate of fuel consumption, this difference in heating power is reflected in a temperature differential of 200°C after 300 seconds'.

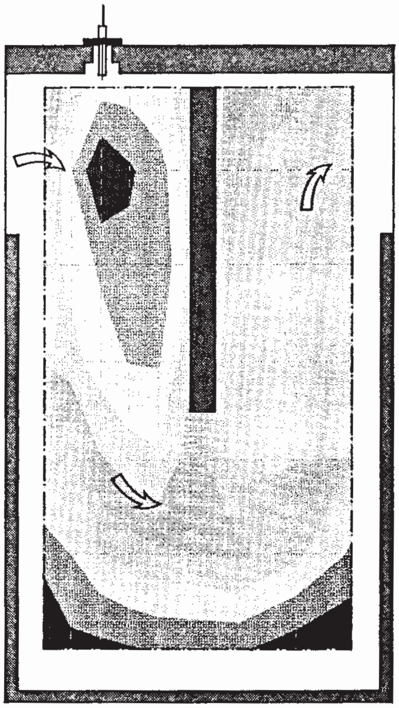
If the settings of burner B are adjusted to obtain a heating curve similar to that for burner A, then B will use twice as much fuel, with maximum temperatures of 1 030 and 1 405°C, respectively, for A and B. This represents particularly uneconomic use of burner B.

This sort of test can therefore be used to characterize the burner and optimise the flame to meet the desired criteria. It highlights the importance of the burner and its operation in terms of the existence of hot spots.

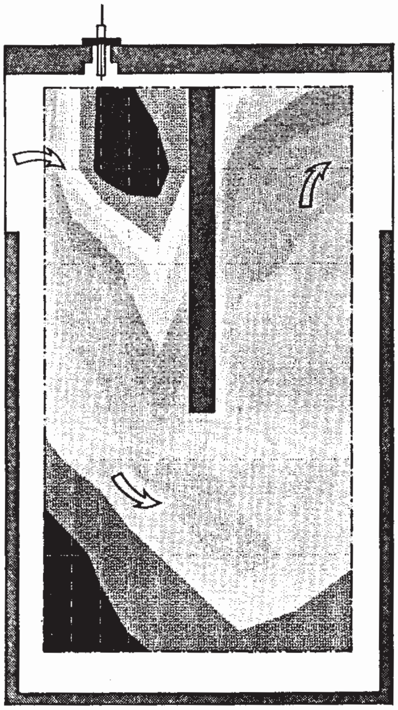
Similarly, the testing unit can be employed to assess the effects on the isotherm distribution profile of increasing the flow of air of combustion. The effects of increasing airflow by a factor of 2.5 are illustrated in Figure 9 by the isotherms recorded after 350 seconds' operation of a type B burner.

The deflection of the flame as airflow increases, is clearly illustrated by this figure. The flame is forced upwards and towards the baffle. This can be explained by the combined effects of flow velocity and the existence of a bypass at the top of the baffle.

Figure 9 clearly depicts the potentially undesirable effects on isotherm distribution in a heating shaft of an unnecessarily high flow of air of combustion. More will be said about this aspect of the process when discussing process control.



Q = 1



Q = 2.5

Figure 9 - Effect on isotherm distribution of increasing airflow.

<u>Flow Modelling</u>

The identification of the problems connected with the pattern of gas flow through the flue wall, which are fully reproduced in the experimental procedure we have described, led us to design and build a means of investigating the effects of the various modifications we wanted to make to the external and internal geometry of the flue wall. This is based on an adjustable, 1/4 scale, mock-up of three consecutive flue walls connected in series. Pressure, flow and velocity are all measured in the central flue wall.

Simple experiments can be carried out to determine values of pressure drop coefficients under steady-state conditions. These values can then be entered into the digital models employed to evaluate flowrates in a furnace for the purposes of diagnosis or optimisation of the design (10).

The physical mock-up can also be used to modify the internal geometry of the wall and check the effects on the flow profile. It is employed in conjunction with a mathematical model simulating thermal and mechanical distortion of the flue wall.

With this model, the geometrical displacements and the stresses affecting a slab of area equivalent to that of a flue wall free to move in the plane of the wall and subjected to thermal and mechanical loads equivalent to those accompanying an actual thermal cycle can be determined.

Process Control

The differences in operation between upstream and downstream burners, together with the considerable influence of gas flowrates on heat exchanger efficiencies and burner performance as reflected in isotherm distribution and stress loadings of refractories, compelled us to develop and perfect computer-control of the operation of our furnaces. There were three objectives :

i) Reduce specific energy consumption.

ii) Increase the working life of refractories.

iii) And, needless to say, minimise the range of variation of the results of baking.

This new version of process control continues to rely on monitoring and adjustment, by opacimetry, of flowrates per line of flue walls (11).

In its most sophisticated version, baking furnace operation is controlled by an improved algorithm based on mathematical modelling of interlocking process parameters.

The model can anticipate the reactions of the process and hence determine the most effective system of control. The hydraulic and thermal balance of the furnace is constantly maintained along each line of flue walls.

PERFORMANCE DATA

The improvements made possible by the purpose-designed developments tools described, have considerably reduced the heterogeneity of final results in the anode baking process. Redefined burner specifications, optimisation of flow in the flue wall and a high-performance process control system, have all contributed to narrowing temperature differentials in the latest generation of horizontal-flue ring furnaces to less than 80°C.

Figure 10 represents a typical plot obtained on one of these furnaces.

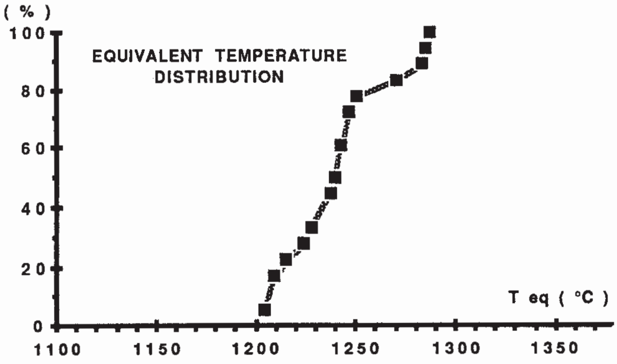


Figure 10 - Equivalent temperature distribution (New furnace).

CONCLUSION

We have examined the impact of underbaking on anode reactivity.

The dual objective of the economic optimum and of quality expressed in terms of reactivity calls for the definition of an optimum degree of baking and the achievement of minimum variation in characteristics over the whole of the furnace charge.

The ways and means developed specifically to meet these objectives and the investigations undertaken have already afforded a significant improvement in baking quality.

Although uniformity of baking was the principal objective of the work reported, additional benefits have been achieved with the specific consumption and the lifetime of refractories.

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