

PARAMETERS OF THE COKEMAKING PROCESS CONTROL ¹

Luiz Cláudio Costa²
Francisco Javier Ramirez-Fernandez³

Abstract

The process control of a coke plant depends on a lot of particular parameters. This study describes an experimental design in a pilot oven aiming at investigating the influence of the main control factors in a coke oven battery, relating these parameters to coke production and heat consumption, and using them for future process control automation. The result of the experiment showed statistical significance regarding factors such as: temperature and coal blend moisture, and regarding the interactions between temperature and coal blend moisture and between moisture and coal grain size, in relation to the heat consumption as well as to the temperature factor during the net coking time. These relations can be used to develop coking control at an industrial plant. In addition to the design of experiments in a pilot oven, an experiment was also carried out in an industrial battery oven whose methodology proved to be appropriate to an industrial design of experiments. With the experimental data, it was possible to write mathematical equations in order to estimate the heat consumption and net coking time of the process.

Key words: Automation; Process control; Experimental design; Coking process; Coke plant.

PARÂMETROS DE CONTROLE DO PROCESSO DE COQUEIFICAÇÃO

Resumo

O controle de processo de uma planta de fabricação de coque depende de muitas variáveis particulares de cada planta. A busca de modelos de controle próprios torna-se necessária. O presente trabalho apresenta um projeto de experimentos, em forno piloto, para investigar a influência dos principais parâmetros de controle de fabricação do coque quanto à produção e consumo de calor e para utilizá-los futuramente num modelo de automação do controle do processo dessa planta. O resultado do experimento apresentou significância estatística para os fatores temperatura e umidade da mistura enforada e para as interações entre umidade e temperatura e entre umidade e granulometria com relação ao consumo de calor e também o fator temperatura com relação ao tempo líquido de coqueificação. Além do projeto de experimentos em forno piloto, foi feito também um experimento em um forno industrial cuja metodologia mostrou-se adequada para um projeto em escala industrial. Com os dados dos experimentos obtiveram-se também equações matemáticas de previsão do consumo de calor e do tempo líquido de coqueificação.

Palavras-chave: Automação; Controle de processos; Projeto de experimentos; Processo de coqueificação; Coqueria.

¹ *Technical contribution to the 3rd International Meeting on Ironmaking, September 22 – 26, 2008, São Luís City – Maranhão State – Brazil*

² *Metallurgical Eng., MSc Electric Eng., Cosipa's Coke Plant Technical Staff*

³ *Professor at USP University – SP- Brazil,*

1 INTRODUCTION

A metallurgical industry consumes a large amount of energy for the steel production. All the efforts for the reduction of this energy result in cost and environmental impact reductions. The coke plant is one of the main responsible causes of energy consumption in metallurgy and also a fuel generator. The aim for a larger productivity of the plant, the quality improvement and the reduction of the fuel consumption generates energy reductions for the customer plants of the coke plant. Because of this feature, the coke production process control is of strategical importance to the metallurgical industry, either concerning cost reduction, or environmental control.⁽¹⁾ So that there is an optimization of the energy consumption by the coke plant, one must have deep knowledge of the heating control and of the cokemaking process.⁽²⁾ Besides this, an optimized control of the heating process of the ovens guarantees a larger useful life for the oven battery as a whole⁽³⁾. In this way, the knowledge of the variables influencing this process is essential for this optimization to be reached.

1.1 The Coking Process at the Coke Plant

The pyrolysis process of the coal for the coke production undergoes several stages that can be divided into three main phases. The first phase takes place during the heating of the coal up to 350°C. In this phase, the vaporization of the moisture and the beginning of the devolatilization occur. The second phase, called plastic phase, happens between 350°C and 500°C. The decomposition of the coal into tar and gases forms a molten paste that keeps enveloping the parts still solid, many of which being diluted by the tar already formed. The third phase happens above 500°C and lasts until the end of the process when the temperature reaches 1000°C. In this phase, the paste loses more volatile material and begins to harden and crunch, forming the semicoke and, finally, the coke.^(4.5) The coke oven has the shape of a parallelepiped whose dimensions vary from 12 to 15 meters in length, 4 to 8 meters in height and 0.35 to 0.60 meters in thickness. With this shape, the heat transfer occurs, preferentially, from the walls to the center of the coal charge. Figure 1 displays a graph of the temperature distribution in relation to the heating rate of the oven from the heating walls to the center, in several moments of the coking process, and also the phases described above. The coking process occurs dynamically inside the industrial oven. The pyrolysis reactions are endothermic at around 600°C and exothermic at temperatures above this.^(6.7) With these factors, the heat transfer takes place by conduction, convection and radiation.⁽⁸⁾ All this complexity leads to difficult analyses in mathematical models, and experiments are necessary in order to obtain data for the industrial process.

1.2 The Cosipa Coke Plant Process Control

The control of the coking process at Cosipa is established according to two main parameters: the battery average temperature and the visual observation of the ovens in order to determine the net coking time. The average temperature is obtained by the reading of the temperature of the combustion chamber base of the pilot oven. This reading is taken once in all the heating walls of each battery, and at intervals, through an infrared radiation pyrometer. The observation of the net coking time is made through the opening of the ascension pipe at the end of the coking time. The transparent white smoke indicates the end of the coking process. This observation is made in all of the ovens. Both the average temperature data and the net coking time

data are plotted in spreadsheets that generate control graphs which help correct the deviations. The control of the amount of heat injected into the batteries is done in agreement with the information provided by the graphs of temperature control and of net coking time.

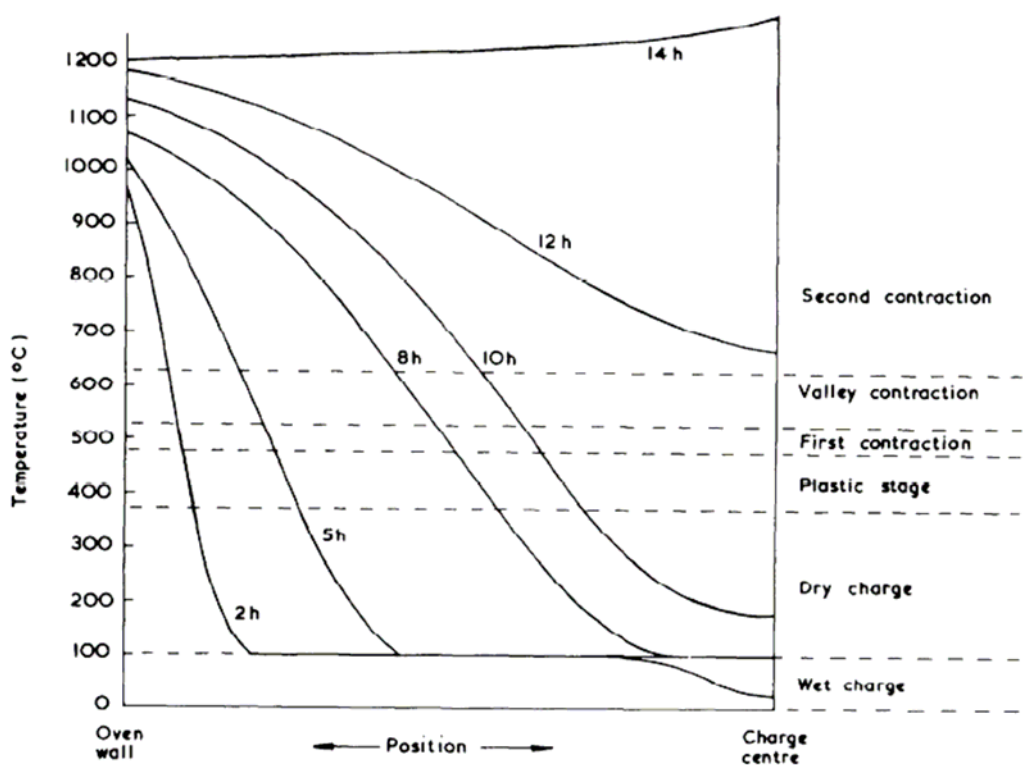


Figure 1 - Profiles of temperature of the mass of the coal charge and the coking stages

When there is a delay in the operational cycle, there are rules to calculate the amount of heat to be removed from the thermal flow according to the delay time. However, when there is a variation of the coal moisture or after this variation has affected the battery average temperature or the net coking time, some actions concerning the heating should be taken by an operator. In all of these actions, the knowledge of the amount of heat to be removed depends on the operator's experience, who always acts with a margin of safety to avoid very high temperatures or the increase of the net coking time. With an appropriate automation system, the control of the coking process can be tuned to a point that guarantees the most stable quality of the coke, and at the same time, the reduction of the heat consumption or the increase in productivity. The ACC system by NSC,⁽⁹⁾ the CETCO system by Danielli Corus⁽¹⁰⁾ or other variants of these systems^(3,11,12) are systems of process automation more applied to the coking control in Asian and European coke plants and are also beginning to be used in Brazil. To implement one of these systems, it is necessary to correlate the variables of the control of the average temperature of the battery heating walls and the control of the net coking time with the heating flow coming from the combustible gases, taking into account the characteristics, the operational rhythm and the coal blend charged. The objective of this study is to choose and analyze the variables that can help the automatic coking process control, through statistical analysis, in a design of experiments, in pilot coke ovens. The present study assumes that there is a constant stay time that guarantees the quality of the coke in blast furnaces and deals with the variation of the net coking time through the manipulation of the variables of the process.

2 THE EXPERIMENTAL DESIGN

The analysis of the parameters of an industrial process requires in-depth knowledge of this process and capacity of carrying out representative experiments of the system under study as a whole, including their boundary conditions. The methodology of the design of experiments meets these requirements. This methodology is still more appropriate when the experiment is performed in a pilot scale, due to a larger control of the involved variables. However, the experiments conducted in a pilot scale account for a loss of representativeness for the industrial process. To compare the industrial process with a pilot scale process, some comparison parameters should be set, which was made through an experiment in an industrial scale. Montgomery⁽¹³⁾ mentions that a statistical design of experiments refers to a process of planning of an experiment so that appropriate data, which can be analyzed by statistical methods, should be collected properly, generating valid and objective conclusions. The three basic principles of a project of experiments are: randomness, repetition or replication and blocking or grouping. The planning of the project of experiments follows a well-structured guide in such a way to obtain effective data to the studies in question, commonly called delineation. The pilot oven, now used to test coal at Cosipa, measures: 465mm, in average width, 1,260mm, in length and 1,025mm, in height, being 825mm useful height. The oven was prepared for the execution of the experiments, receiving preventive maintenance to avoid problems throughout the processes. The oven was controlled by a PLC, which controls the temperature of the heating walls and monitors, besides this temperature, the charged coal temperature, through thermocouples put into the charge through the oven door. Three thermocouples were used inside the charge: one in the center of the oven, another at a distance of 112 mm from the oven wall, and the third one placed against the oven wall. A supervisory system allows to obtain some set point data on the heating controls and to visualize, through graphs, the behavior of the temperatures of the heating walls and the charged coal, besides generating a database. Taking into account the reasons described in item 1.2, the problem intended to solve is the analysis of the factors that influence the coking process, more precisely, the amount of heat consumption and the net coking time. In this way, two variables of the experimental project are obtained. It is necessary now to identify which the most significant factors are, and in which levels they significantly influence these variables. The temperature of the oven wall is the factor that helps meet all requirements of the choice of the variables, as well as the moisture and the grain size. The bulk density is more adequate than the grain size to measure the porosity, but it is difficult to achieve repeatability in the pilot oven. The coal blend factors, such as thermal conductivity, heat of reaction and internal porosity were discarded in view of measurement difficulty, and just the moisture was used as a factor in the experiments. Coke fissures are formed due to several factors of the coal blend and of the coking process, resulting in low repeatability and measurement difficulty. In order not to have any coal blend factor variations, except for the moisture, the same blend for all experiments was programmed. Chosen the factors, moisture, wall temperature and grain size, it is now necessary to determine the type of project of experiments, its levels and the range of each level. As it is important to know not only the influence of the factors, but also of their interactions, a complete factorial design is the most applicable one for this study. A complete factorial design with three factors, using two levels and a repetition, will create 16 projects of experiments to be carried out. The level range of each factor was determined in agreement with the one that most represents the industrial process and is more appropriate to the execution of the

experiments. In relation to the grain size, its range was determined by the collection of crushed and uncrushed materials, resulting in a average range of 6% lower than 3.36 mm. Due to the experience learned from the operation with the pilot oven, the possible minimum temperature of the wall was set at 900°C, and taking the industrial process into consideration, the highest temperature was set at 1,000°C. The coal blend moisture was set as being equal to the lowest monthly average during the industrial process in the years 2005 and 2006, and to the highest monthly average in the same period. The limitations of the experiments to study the parameters of the process should be compensated by the strictness in their execution and, in this case, it is necessary to take care of each stage of the experimental design for the process to succeed. As always, unexpected factors may occur; however, at all times it is important to deal with them with reservations and look for new ways of avoiding problems. To facilitate the conduction of the experiments and to maintain a good representativeness of the industrial process, a blend of four types of materials was chosen, which corresponded, approximately, to the average quality of the coking blend usually used in industrial processes. Each material was proportionally collected according to the coal blend as shown in Table 1.

Table 1 – The coal blend of the experimental design.

Material	Participation (%)	Ash (%)	Volatile Matter (%)	Uncrushed (kg)	Crushed (kg)
AV	15.0	6.29	31.68	540	540
MV1	35.0	8.48	21.84	1260	1260
MV2	30.0	7.59	25.89	1080	1080
CP	20.0	0.58	11.82	720	720

3 THE RESULTS OF THE DESIGN OF EXPERIMENTS

After the end of the experiments, the data were gathered for statistical analyses. The obtained values of energy consumption were the measured values of the heating electrical resistances of the pilot oven. All the heat losses of the system that integrated the oven were included in these values. The net coking time was defined as the time measured between the insertion of the coal blend into the pilot oven and the moment in which the temperature of the oven center thermocouple reached a difference of approximately 5°C, in relation to the average temperature of the central heating area thermocouples of the oven walls. Having defined this, the net coking time is a little longer than the time of the final moment of the plastic layer inside the oven. Nevertheless, it can be measured more precisely, which is very important when comparing the several experiments. Figure 2 shows a graph of the profile of the average temperatures of the thermocouples inside the charge. Each curve represents the average of a group of experiments, utilizing the same moisture and temperature in each point of the charge.

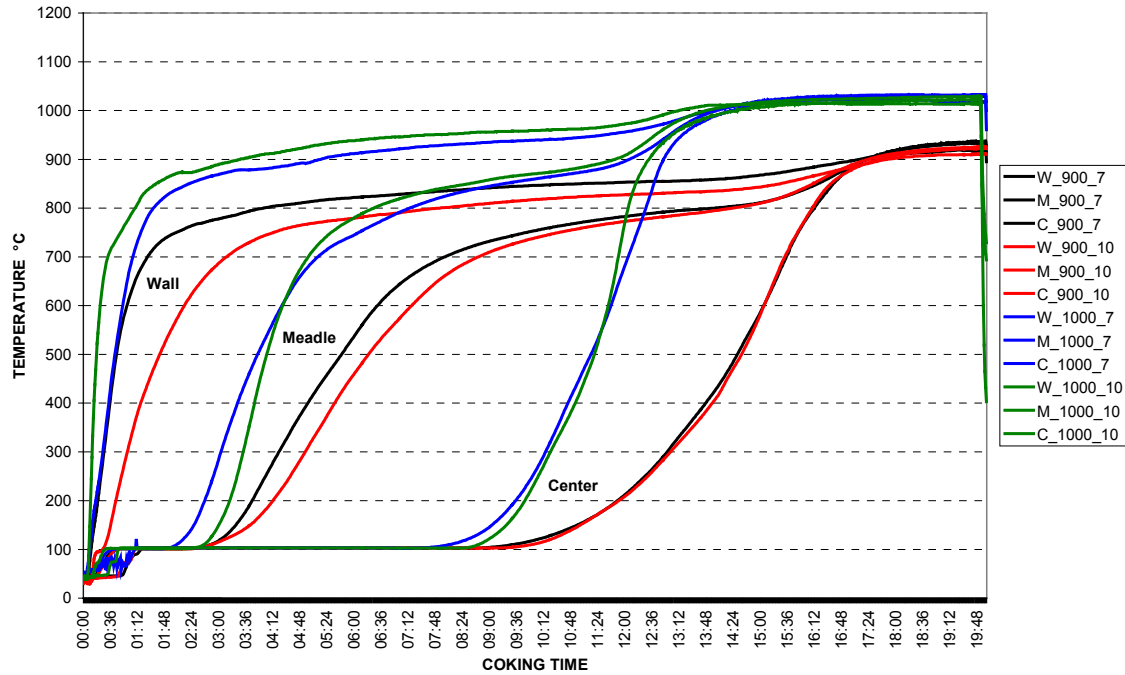


Figure 2 - Temperature average profile for all experiments.

3.2 The Experiment Results in the Pilot Oven

The data on the factors and the heat consumption and the net coking time results were inserted in the software Statistica, which made possible the analysis of the results and of the residues for each response variable. Table 2 presents the results of the analysis of variance (ANOVA) for the Heat Consumption. The value of the F factor of the Fisher-Snedecor distribution, in comparison with its distribution curve, showed that the temperature and moisture factors significantly affected the heat consumption. Also, statistical significance is verified in the interactions between moisture and grain size and between moisture and temperature.

Table 2 – ANOVA results for the Heat Consumption effect.

Factors and Interactions	SS	G of freedom	SM	F F _{0.05;1; 9} = 5.12	p
TEMPERATURE	1654.5949	1	1654.595	50.1498	0.0001
MOISTURE	1433.3728	1	1433.373	43.4447	0.0001
GRAIN SIZE	55.5936	1	55.5936	1.6850	0.2265
TEMPERxMOISTUR	494.1696	1	494.1696	14.9780	0.0038
TEMPERxSIZE	96.2058	1	96.2058	2.9159	0.1219
MOISTURExSIZE	330.4483	1	330.4483	10.0157	0.0115
Error	296.9375	9	32.9931		
Total SS	4361.3224	15			

After learning the significant factors of the heat consumption, these factors along with the results obtained could be used to generate a mathematical equation of these relations, through multiple regression. Equation 1 was obtained through the multiple regression of the three factors and their double interactions, and equation 2 was obtained through the multiple regression of the Temperature and Moisture factors and only its double interaction.

$$H = 1441.6 - 0.64735.T - 5.3278.M - 23.193.G - 0.068948.T.M + 0.014261.T.G + 1.0823.M.G \quad (1)$$

$$H = -307.1087 + 0.46438.T + 82.1864.M - 0.079352.T.M \quad (2)$$

where H is the heat consumption in kWh, T is the temperature of the pilot oven walls in °C, M is the moisture of the coal blend put into the oven in %, and G is the coal blend grain size < 3.36 mm.

Table 3 shows the results of the variance analysis for the Net Coking Time response variable. The values of the F factor of the Fisher-Snedecor distribution showed statistical significance just concerning the temperature factor. All the other factors and interactions, according to this test, did not have statistically significant influence on the net coking time variable in the pilot oven.

Table 3 – ANOVA for the Net Coking Time response variable

Factors and Interactions	SS	G of freedom	SM	F F _{0.05; 1; 9} =5.12	p
TEMPERATURE	0.06337	1	0.06337	405.99253	0.00000
MOISTURE	0.00006	1	0.00006	0.40860	0.53861
GRAIN SIZE	0.00000	1	0.00000	0.00000	1.00000
TEMPERxMOISTUR	0.00022	1	0.00022	1.42817	0.26260
TEMPERxSIZE	0.00014	1	0.00014	0.89289	0.36937
MOISTURExSIZE	0.00017	1	0.00017	1.11535	0.31845
Error	0.00140	9	0.00016		
Total SS	0.06538	15			

Equation 3 was obtained through the multiple regression of all factors and interactions, and equation 4 was obtained through linear regression, with the same data, but just considering the temperature factor.

$$Ct = 97.63 - 0.06751.T - 0.90056.M - 0.87089.G - 0.00112.T.M + 0.000655.T.G + 0.027794.M.G \quad (3)$$

$$Ct = 44.66 - 0.0303.T \quad (4)$$

where Ct is the net coking time, T is the pilot oven wall temperature in °C, M is the coal blend moisture in % , and G is the coal blend grain size < 3.36 mm. Here also, the two equations will be used as a basis for industrial experiments. The procedures and execution of the experiments met the expectations.

3.3 Discussion of the Results of the Design of Experiments

According to Merrick,⁽³⁾ the coal blend density, the wall temperature and the coal blend moisture have great influence on the heat transfer and, consequently, on the heat consumption. The grain size factor was expected to have significance for the heat consumption. One of the causes of this unexpected result is the fragility of the grain size, as an indicative of the coal blend density. Nevertheless, this is the only industrial control parameter for density. These experiments should develop ways or devices to minimize the effects of the variability of the density. According to the data obtained by Lia⁽¹⁴⁾ in his mathematical model, the net coking time also depends on the coal blend moisture as well as on the mass porosity, and the values obtained by his equation were

12% lower, on average, than the measured values in the pilot oven experiments. The porosity value was based on an equation used by Lia, starting from the bulk density. The reason for this difference is the fact that the pilot oven is capable of maintaining the wall temperature constant, maintaining, in this way, the coking front speed and, consequently, the net coking time, spending more or less energy according to the charge moisture. In the industrial process, the heat flow is constant during the coking process and, in this case, a variation of the moisture can affect the net coking time. As regards the heat consumption, the Lia equation presents, on average, values 26% lower than equations 1 and 2. However, in this case, the difference remains in the losses, mainly, due to the generated gases, and from the oven surface to the atmosphere, since the measured value in the experiments was the total heat consumed by the electrical resistances of the pilot oven. Loison; Foch and Boyer⁽⁸⁾, in their coke oven thermal balance, presented a value of 23.1% of losses due to the surface and the generated gases.

3.4 The Industrial Oven Experiment

An experiment with a coal charge in an industrial oven at Cosipa Battery 5 was conducted with the objective of studying the correlations between experiments carried out in a pilot oven and experiments carried out in an industrial plant. Six holes were made in the oven door in two different heights from the threshold: one at 1.5 m, and the other at 4 m. In each height, the holes were aligned so that the first was close to a heating wall, the second, close to the other heating wall, and the third hole, in the oven center. After the charging of the oven, thermocouples were introduced into these holes at a distance, inside the coal charge, of 2.5m in relation to the oven doorframe. In this oven, a thermocouple was also installed in the curve of the ascension pipe in order to measure the temperature of the generated gases as well as to determine the time when this temperature reached its maximum peak at the final third of the coking process. The data on these temperatures were collected and plotted in a graph as shown in Figure 3. One of the thermocouples had problems and the temperature measurement was not obtained at this moment. Since the difficulty in introducing the thermocouples into the coal charge was considerable, it was not known if each thermocouple was placed in their desired position, that is, one in the oven center and the other two, close to the walls. Figure 3 is a graph that displays the tendency of the temperatures of the coal charge and of the generated gases. The temperature of the generated gases reached its maximum peak at 634°C in 11 hours and 56 minutes. The temperatures of the charge measured by the inferior thermocouples began to show the same elevation rate 3 hours and 32 minutes after the temperature of the generated gases reached its maximum peak. The temperatures measured by the superior thermocouples also began to show the same elevation rate by the time of the inferior thermocouples. The measured temperatures of the generated gases in the ascension pipe behaved as predicted. The elevation of the temperature reaching a maximum peak and later on, falling until the moment of the discharging is described by Sadaki; Tanaka and Naganuma⁽⁹⁾. The measurement of the temperatures of the thermocouples inserted in the oven door had the purpose of repeating the same pilot oven measurement and of determining the net coking time. But the uncertainty of the correct position of the thermocouples in the coal charge hindered the same determination of the net coking time. In this case, the determination of the net coking time could be obtained when the temperatures measured by the three inferior thermocouples and by the two superior ones began to rise at the same speed, as shown by the stippled line of

Figure 3. The difference between the temperatures of the inferior thermocouples in relation to the superior ones is due to the temperature gradient of the heating walls, which falls according to the height. This manner of determining the net coking time in an industrial oven test is also described by Choi et al.⁽¹⁵⁾. This test shows that it is possible to conduct experiments in an industrial scale in order to determine the Δt ; in other words, the time interval between the moment of the maximum temperature of the generated gases and the net coking time. In the test, the value of Δt was 3 hours and 32 minutes, and the value of the net coking time, 15 hours and 28 minutes, which corresponds to the sum of the time of the maximum temperature of the generated gases with Δt , as shown in Figure 3.

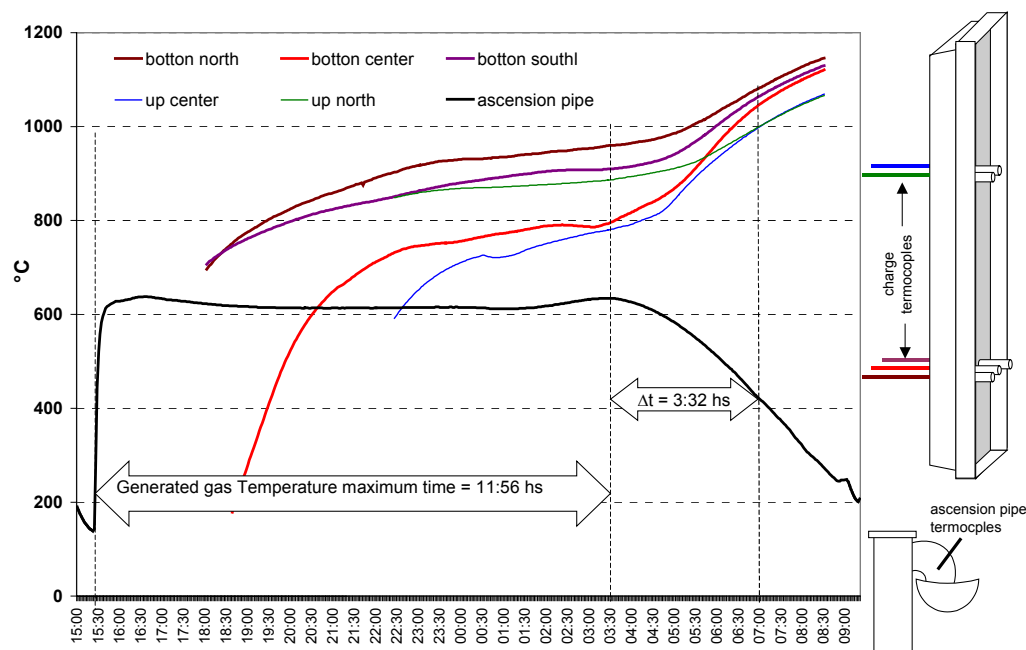


Figure 3 – Temperatures measured at Cosipa battery 5 number 72 coke oven.

The test in the industrial oven, in spite of its execution difficulties, presented good results, comparing with the tests in the pilot oven. The intention of using the door as a point of introduction of the thermocouples into the charge aimed at obtaining a higher precision when reaching the charge center. Because there was the need to measure the temperature in places far from the door, since the wall temperature in the first two combustion flues is much lower than the average, longer thermocouple wells were used. When introducing these wells into the charge, what had been expected did not happen. In spite of this, it was possible to visualize the convergence of the temperature curves of the thermocouples introduced into the charge, starting from a certain time, and then, to set a control point. This convergence was also observed in all of the experiments of the pilot oven and by Choi et al.⁽¹⁵⁾ as well. Sadaki; Tanaka and Naganuma⁽⁹⁾ described the use of visual observation to determine Δt , in order to set the net coking time. This method is very imprecise because it depends on the ability of the operator as well as on the environmental brightness, although it is simple and can be easily repeated. The experiments with thermocouples in the charge are more difficult to perform, but they can produce higher precision results, mainly when analyzing the factors of the design of experiments in the pilot oven.

The objective of learning the parameters of the Cosipa battery coking process is to automate the heating control of the ovens. Through the equations obtained from the

experiments in the pilot oven and through the design of the experiment in the industrial oven, it will be possible to get closest-to-reality parameters of the process in an industrial scale. Through the data obtained from the pilot oven experiments, it is possible to project an automatic control, and by using the equation of the heat consumption, to obtain the temperature control of the heating walls. And through the net coking time equation, it is possible to acquire the desired value of this temperature in order to set each coking time.

4 CONCLUSIONS

The statistical analyses showed that the results obtained through the methodology of the project of experiments using a complete factorial design are impressive enough to be used as the basis for a mathematical model of control of the Cosipa battery heating process. It was possible to verify the influence of the factors: wall temperature, charge moisture and charge grain size for the heat consumption and for the net coking time.

The experiment carried out in the Cosipa battery 5 oven in order to identify the net coking time proved to be useful to check the data obtained from the pilot oven experiment, making it possible to correlate the net coking time with the maximum temperature of the generated gases. The determination of the value Δt for the control of the net coking time in an industrial scale is essential, and using more representative and sensitive measurements during the process will make its control much more effective. The determination of the net coking time is necessary to make comparisons with the tests carried out in the pilot oven and also to control the coking process in the future.

5 REFERENCES

- 1 LARSSON, M.; WANG, C.; DAHL, J. Development of a method for analyzing energy, environmental and economic efficiency for an integrated steel plant. **Applied Thermal Engineering**, n. 26, p. 1353-1361, 2006.
- 2 STONE, P. M. et al. Model based control of a coke battery. In: IRONMAKING CONFERENCE, 56., Chicago, 1997. **Proceedings**. Chicago: AIME Iron & Steel Society, p. 131-138.
- 3 MITRA, S. et al. Mathematical Model based Coking Control System. In: ANNUAL MEETING, 39., Seattle, 2004. Seattle: IEEE / IAS, 2004. p.183-187.
- 4 JÜNTGEN, H. Review of the kinetics of pyrolysis and hydrolyrolysis in relation to the chemical constitution of coal. **Fuel**, v. 63, n.6, p.731-737, 1984
- 5 KOCH, A. et al. A physicochemical study of carbonization phases: part I. Tars migration and coking pressure. **Fuel Processing Technology**, n.45, p.135-153, 1995.
- 6 MERRICK, D. Mathematical models of the thermal decomposition of coal. **Fuel**, v. 62, p. 534-561, 1983.
- 7 OSINSKI E. J. ; BARR P. V. ; BRIMACOMBE J. K. Mathematical model for tall coke oven battery: I - development of thermal model for heat transfer within oven charge. **Ironmaking & Steelmaking** , v.20, n.5, p.350-361, 1993.
- 8 LOISON, R.; FOCH, P.; BOYER, A. Coke: quality and production. 2. ed. London: Butterworths, 1989.

- 9 SADAKI, J.; TANAKA, K.; NAGANUMA, Y. Automatic coking control system. In: IEEE CONFERENCE ON CONTROL APPLICATIONS, 2., Vancouver, 1993. **Proceedings**. Vancouver: IEEE, 1993. v. 2, p.531-538.
- 10 VANDER, T.; Van BALLEGOOIE, A.L.; VOS, R.A. Automatic heating input control system batteries. In: IRONMAKING CONFERENCE, 49., Detroit, 1990. **Proceedings**. Detroit: AIME Iron & Steel Society, 1990. p.127-133.
- 11 MALINA, V.P. Process control at the Sidmar Coking Plant. **Coke and Chemistry**, n. 9-10, p. 44-47, 1993.
- 12 HOLLE, P.; VERFAILLE, J.; MUNNIX, R.; BORLEE, J. Heating and process control at the Sidmar coking plant. In: INTERNATIONAL COKEMAKING CONGRESS, 2., London, 1992. **Proceedings**. London: Institute of Materials, 1992. v.2, p.294-310,
- 13 MONTGOMERY, D. C. **Design and analysis of experiments**. 6.ed. Hoboken, NJ., John Wiley & Sons, 2005.
- 14 LIA, L. R. B. Modelo matemático unidimensional do processo de coqueificação. 1987. 173p. Dissertação (Mestrado) – Departamento de Ciências dos Materiais e Metalurgia, Pontifícia Universidade Católica do Rio de Janeiro, Rio de Janeiro, 1987.
- 15 CHOI, K. I. et al. A mathematical model for the estimation of flue temperature in a coke oven. In: IRONMAKING CONFERENCE, 56., Chicago, 1997. **Proceedings**. Chicago: AIME Iron & Steel Society, 1997. p.107-113.