OXIDATION OF “BLACKHEART“ DURING THE FIRING OF CERAMIC PIECES

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1. INTRODUCTION

Clay minerals normally used in the formulation of ceramic mixtures for paving and tiling usually contain some organic material as an impurity [1-4]. In this country red clays with a ferric oxide content of between 5 to 8% are generally used. During the firing of ceramic pieces which contain organic material in their composition, a dark nucleus may appear in its interior; this is known as “blackheart” (Figure 1) [5-6].

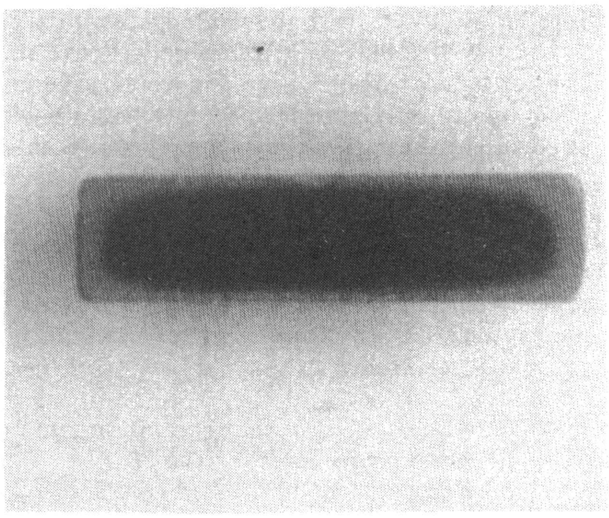

Figure 1. Black nucleus in the interior of a ceramic piece known as “Blackheart”.

This problem can arise during the firing of single fired ceramic pieces for paving and tiling [7-13]:

a) When excessively short firing cycles are used (for both products).

b) In the manufacture of large format paving pieces, where it is necessary to increase the thickness and compactness of the piece in order to give it sufficient mechanical resistance.

c) In the production of tiling pieces which will be decorated by serigraphy, since polyalcohols that are usually used for this can be absorbed by the support, noticeably increasing its organic material content.

The presence of "blackheart" is normally considered as a production defect which must be avoided. Some of the consequences of its presence are:

a) Decrease in the mechanical resistance of the material in the case of vitreous products (tubes of vitreous tiles), although deformation does not appear [14-15].

b) Apparition of red colouring in plastered covered partitions.

c) Swelling of pieces.

d) Pyroplastic deformations [19]

e) Deterioration of technical and aesthetic characteristics of ceramic glazes [12] [20-22].

f) Alteration of shading in support and/or glaze [4][10][23- 25]

The formation of "blackheart" is considered to be beneficial in very few cases, either because it increases the degree of vitrification (9) or because it increases mechanical resistance or resistance to freezing [5].

Almost all studies carried out agree that blackheart is due to the formation of carbon through the thermic decomposition of the organic material initially contained in ceramic mixtures, at temperatures between 300-500º C [7][11][13][26-30]. Only five of them [7][11][31-33] suggest that iron in a reduced oxidation state, take part in the formation of this dark nucleus.

In some recently published work [31-33] we have confirmed that the components responsible for the darkening of the ceramic piece, when blackheart is formed, are coke and reduced iron oxides (FeO and/or Fe3O4). The first is formed by the carbonization or pyrolysis of organic material (catalysed by the clay itself), and the second due to the reduction of Fe2O3 (in a few cases structural Fe(III) is reduced too) by the coke formed and by the possible carbon monoxide resulting from the bad oxidation of carbon.

Due to the fact that, in the majority of cases, the formation of blackheart during firing of paving and tiling pieces is considered as a defect, it is necessary to avoid its formation or to eliminate it during the firing cycle, before it can create problems that will affect the quality of the finished product.
Amongst the actions recommended for eliminating blackheart or for avoiding its formation the following can be stressed:

a) Avoiding the use of raw materials (clays) that contain organic material and/or inorganic compounds of Fe(II) in elevated proportions [1] [34-35].

b) The use of additives that release water vapour during firing, so that this will react with the carbon, between 700 and 800º C, to give hydrogen and carbon oxides [8].

c) The use of compositions and additives that give the piece a sufficiently high permeability during the preheating phase of the firing cycle to oxidise the blackheart (if it has formed) before this phase finishes [6-7][11-12][27][36].

d) Optimization of temperature profile of oven [7].

e) Injection of oxygen into the preheating zone of the oven [4-5][7][9-10][37-39].

Given that the information in the bibliography for correctly carrying out actions c), d), and e), described above, was totally empirical [29][40-43], it was considered useful to have available a kinetic model. This would include the majority of operation variables and would allow these to be related to the time necessary to oxidise the blackheart formed in ceramic pieces, with gaseous oxygen present, during the preheating period of the firing cycle at temperatures up to 900º C on account of the release of gases that occurs as a consequence of this oxidation, it is suitable, for various reasons, [4][6] [15-18][20-22] that the operation takes place at temperatures below this.

2. PROPOSED KINETIC MODEL

The oxidation of the "heart" or black nucleus formed in ceramic pieces during firing, using air or oxygen, is a non-catalytic heterogeneous gas-solid reaction, that can be represented as [33]:

[Inert] + C (s) + $O2(g)$ = Inert (s) + $CO2$ (g) (1)

In this reaction we assume that the oxygen from the oxidising gas (an O2-N2 mixture) reacts only with the carbon present in the initial solid, which contains a high proportion of clayey compounds that are inert for oxidation reactions. This hypothesis is based on the proven fact that all reactive compounds present in blackheart caused in ceramic pieces made from clays containing Fe2O3 and organic material can be traced back to the carbon initially present in the unfired piece, regardless of the percentage of ferric oxide that the piece contains [33].

Observing the manner in which blackheart is formed during the period of oxidation with air, a complete parallel is seen with the changes that are produced in a solid that reacts according to the kinetic model called "unreacted core model" which is applicable to a large number of non-catalytic gas-solid reactions [44-48] (figure 2). This kinetic model is based on the assumption that the initial solid is not very porous, while the external layer or crust of the inert product that is formed after oxidation is sufficiently porous to allow the displacement of the reacting O2 and of the CO2 formed [reaction(1)] by the former's diffusion (molecular and/or Knudsen), accepting that, at any instant, the chemical reaction is developed on a clearly defined surface that delimits the non-reactive core. This surface is displaced as the reaction advances from the solid surface towards its interior (progressively decreasing the size of the non- reactive core and increasing the thickness of the outer porous layer).

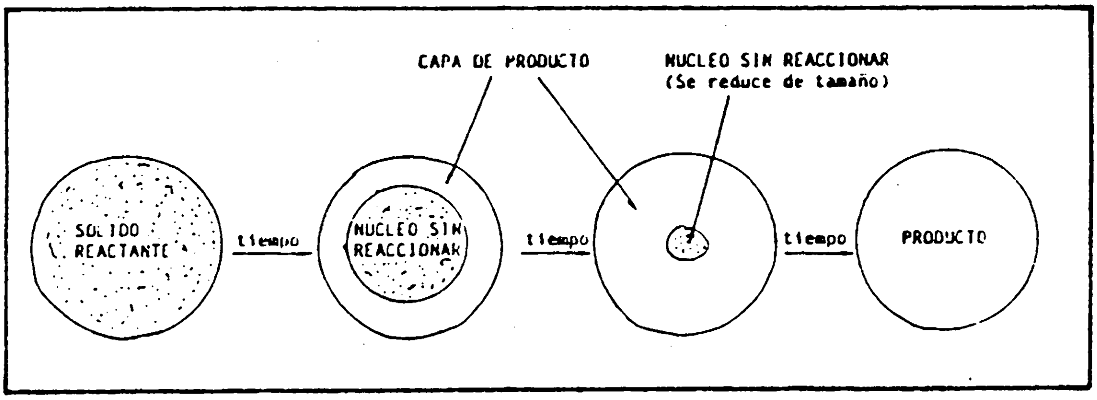

Fig. 2

In accordance with this kinetic model, if it is assumed that the solid is a lamina with parallel sides of a very small thickness compared to the other two dimensions and that, given the low porosity of the exterior crust of the oxidised product, the overall process is controlled by the diffusion of O2 across the porous structure of this crust, the following mathematical expression is obtained [33]:

$$X^2 + A + \frac{8.C^{\circ}_{O2}.Def}{P.t\ c.L^2} \qquad (2)$$

when the kinetics of the chemical reaction stage is considered of prime importance with respect to the oxygen, which is often. In this equation X is the degree of conversion, given by the equation:

$$X = 1 - \lambda / L \qquad (3)$$

l= Thickness of the blackheart at any given instant (m).

L = thickness of the sample or ceramic piece.

C°_{O2} = concentration of oxygen in the inside of the gas Kmol/m3).

Def = effective diffusivity of O2 across the porous solid in the presence of CO2 (m2/min).

t = oxidation time (min).

Pc = AtKg of C present in blackheart per m3 of solid.

A = constant whose value depends on oxidation time necessary for the diffusion of oxygen across the product crust stage to begin to control the process.

If the proposed model is suitable for representing the kinetics of the process, it must correspond to the experimental results obtained.

3. MATERIALS AND PROCEDURE

All the samples used in the experiment were prepared from a standard mixture that contained 50% white clay HVA/R (WBB) and 50% sodium feldspar (Extra Pyrenees Feldspar) to which active carbon and Fe2O3 were added in different proportions, for analysis. The resulting group was homogenized in water, dried and pulverized, it was subsequently wetted to make samples by unidirectional dry pressing; the samples were 40mm in diameter and 10mm thick. Table 1 gives details of the quantities of Fe2O3 and C (in weight) added to 100g of standard mixture in each one of the compositions used.

The equipment that was used (Figure 3) for the kinetic study of the oxidation of "blackheart" was a controlled atmosphere tubular oven, electronically heated The samples to be treated in each reaction cycle were placed in the oven which was fed with a O2- N2 mixture of constant composition, precisely controlled for each experiment. The volume of the gases is measured with measuring orifices and differential manometers.

TABLE 1 Quantities of Fe_2O_3 and C (by weight) added to 100g of standard mixture.

Composition N.º	Fe_2O_3 (g)	C (g)
1	2	0.50
2	-	0.20
3	-	0.25
4	-	0.30
5	-	0.35
6	-	0.40
7	-	0.45
8	-	0.50
9	5	0.30
10	8	0.30
11	11	0.30
12	14	0.30

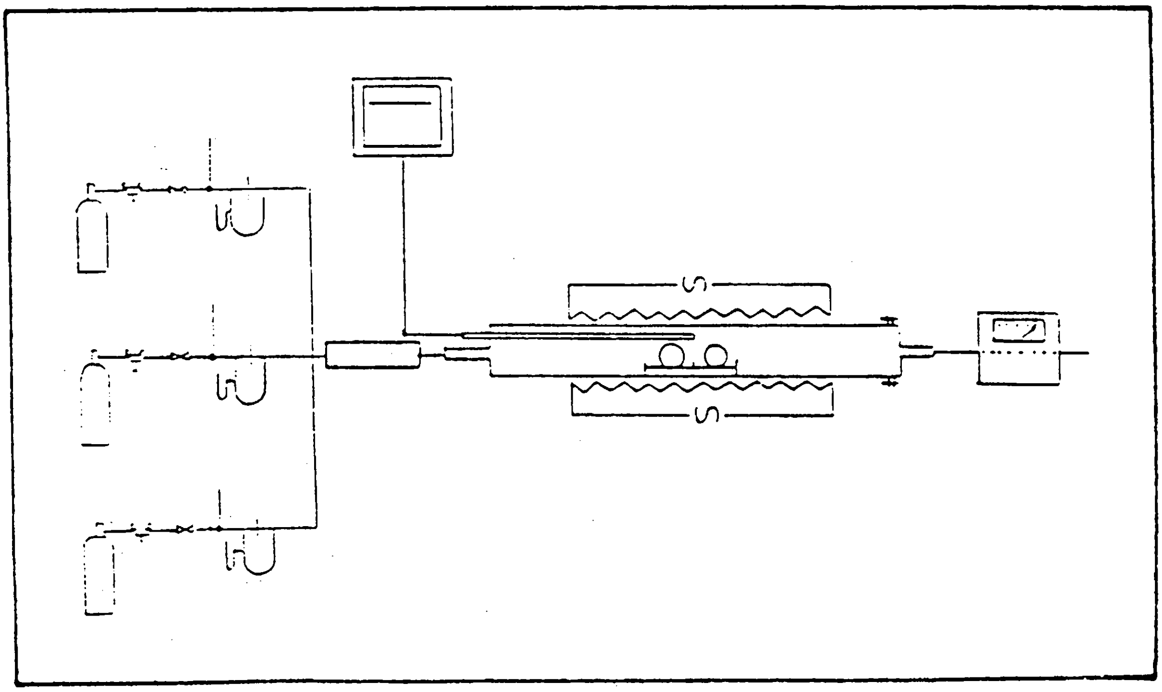

Figure 3. Diagram of basic equipment used.

Each experiment was performed in the following manner:

a) Preheating of the samples up to the pre-established reaction temperature, in a N_2 atmosphere, for 20 minutes, to provoke blackheart in the pieces.

b) Reaction period at constant temperature, in controlled composition atmosphere, and for different times for each experiment.

c) When the reaction period is finished, the samples are immediately removed from the reactor and rapidly cooled, in an inert atmosphere, until ambient temperature is reached.

The samples submitted to the reaction cycle above are diametrically sectioned and the nonoxidised layer (l) is measured with a graduated magnifying glass, whilst the total thickness (L) is measured using a callipers (Figure 4).

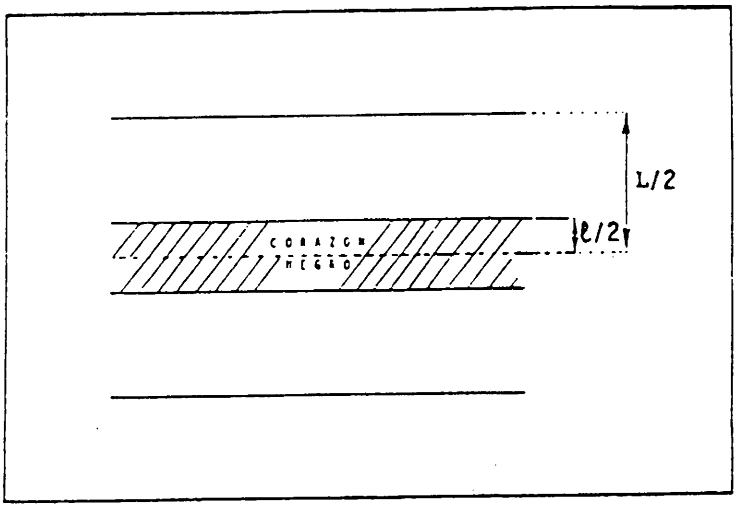

Figure 4. Diagram of diametric section of a sample.

The minimum velocity of gas across the reactor was measured in previous experiments, so that the stages of material transfer across the gaseous phase were not the slowest and thus controllers of the overall speed of the process in the interval of operation conditions studied. It was found that the value for this minimum velocity was 0.0117 m3/s.M2. Consequently, all experiments in this study were carried out with the velocity of the oxidising gas within the reactor 65% higher than this minimum.

4. RESULTS AND DISCUSSION

To study the influence of the concentration of oxygen in the gas phase, the reaction temperature, the thickness of the piece and the content of carbon and ferric oxide on the speed of oxidation of blackheart, 23 sets of experiments were performed.

Table II gives details of the operation conditions used in each set of experiments performed.

Figure 5 shows the experimental results obtained from the four sets of experiments (1 to 4) in which the concentration of oxygen in the gas phase was varied in order to compare the formation of blackheart against reaction time. Figure 6 shows the experimental results obtained for the five sets of experiments (4 to 8) in which reaction temperature was varied. Figures 7, 8 and 9 show, respectively, the experimental results for the sets of experiments in which the thickness of the piece

(7, 9, 10, and 11), the content of carbon in the composition (12 to 18) and the content of carbon and ferric oxide in the composition (19 to 23) were varied.

TABLE II Operation conditions used in the sets of experiments performed.

Set No.	Composition No.	P_{O2} (atm)	T (ºC)	$L.10^3$ (m)	$C_{O2}.10^3$ (Kmol/m³)	(Pap)v (Kg/m³).
1	1	0.05	850	10	0.543	1850
2	1	0.10	850	10	1.086	1850
3	1	0.15	850	10	1.629	1850
4	1	0.21	850	10	2.280	1850
5	1	0.21	700	10	2.632	1850
6	1	0.21	750	10	2.503	1850
7	1	0.21	800	10	2.387	1850
8	1	0.21	900	10	2.183	1850
9	1	0.21	800	7	2.387	1850
10	1	0.21	800	12	2.387	1850
11	1	0.21	800	14	2.387	1850
12	2	0.21	850	10	2.280	1920
13	3	0.21	850	10	2.280	1918
14	4	0.21	850	10	2.280	1915
15	5	0.21	850	10	2.280	1915
16	6	0.21	850	10	2.280	1920
17	7	0.2	1 850	10	2.280	1908
18	8	0.21	850	10	2.280	1913
19	9	0.21	850	10	2.280	1963
20	10	0.21	850	10	2.280	1981
21	11	0.21	850	10	2.280	1982
22	12	0.21	850	10	2.280	1979
23	4	0.21	850	10	2.280	1976

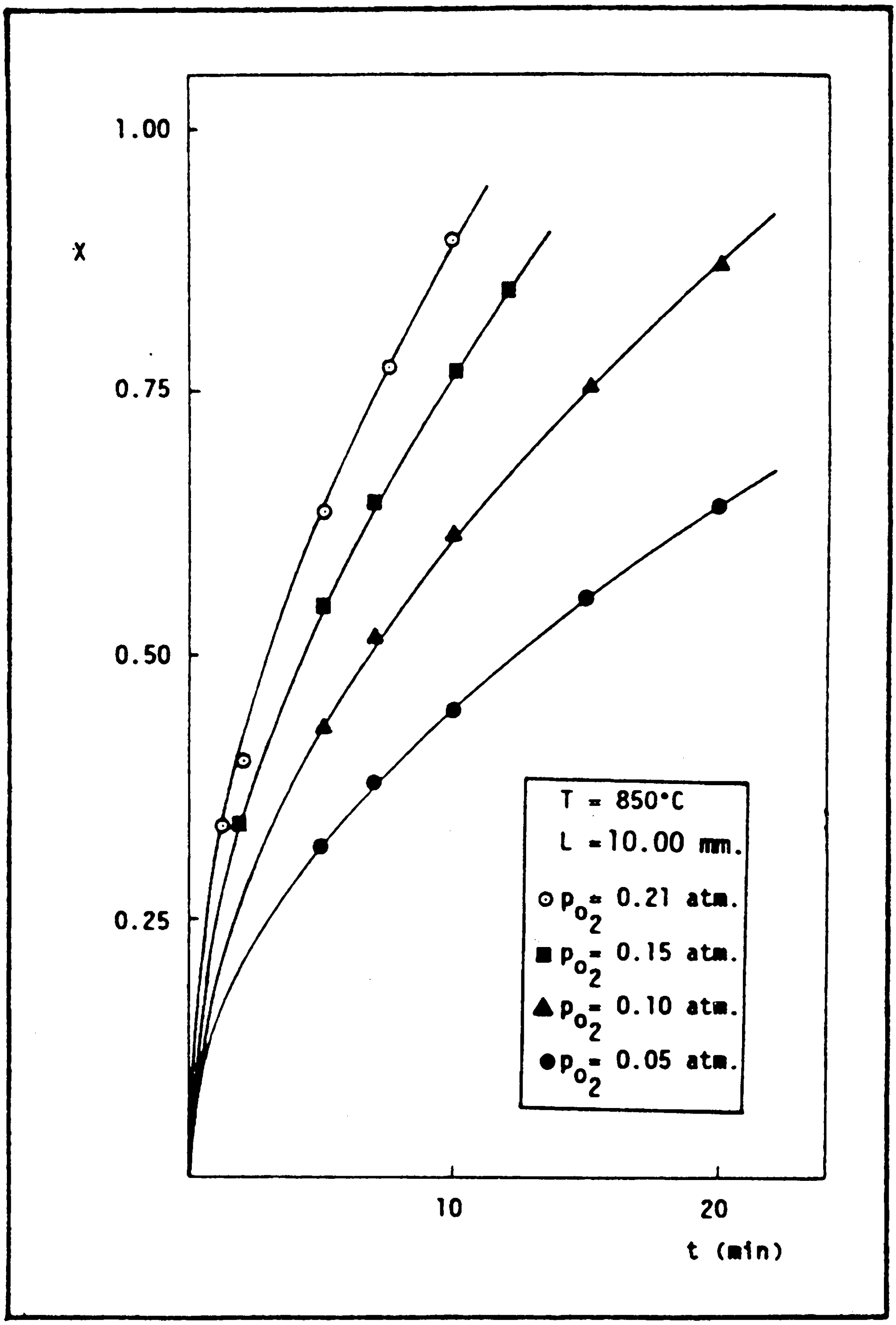

Figure 5. Variation of degree of formation of black heart with reaction time: influence of concentration of O2 in the gaseous phase.

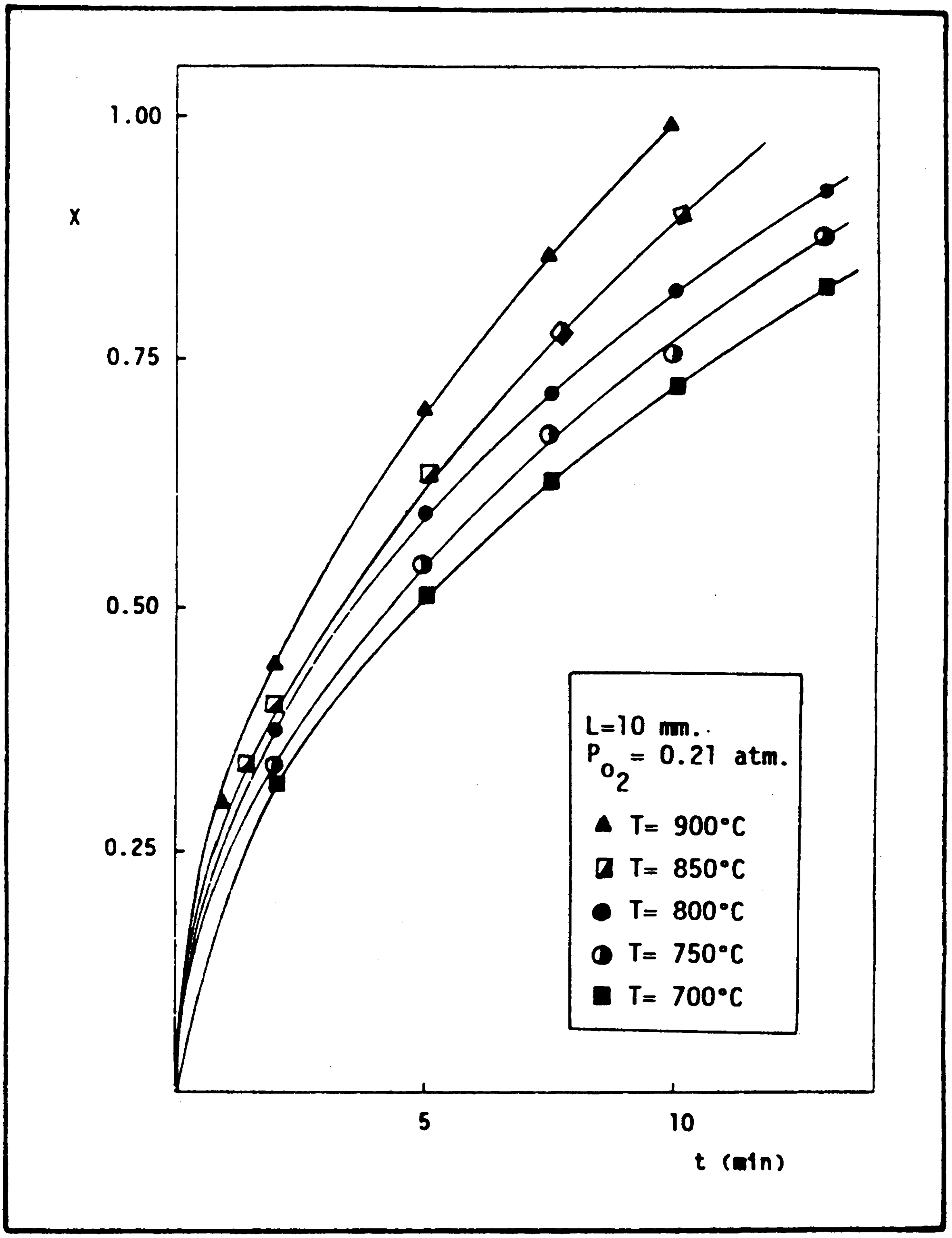

Figure 6. Variation of degree of formation of blackheart with reaction time: influence of temperature.

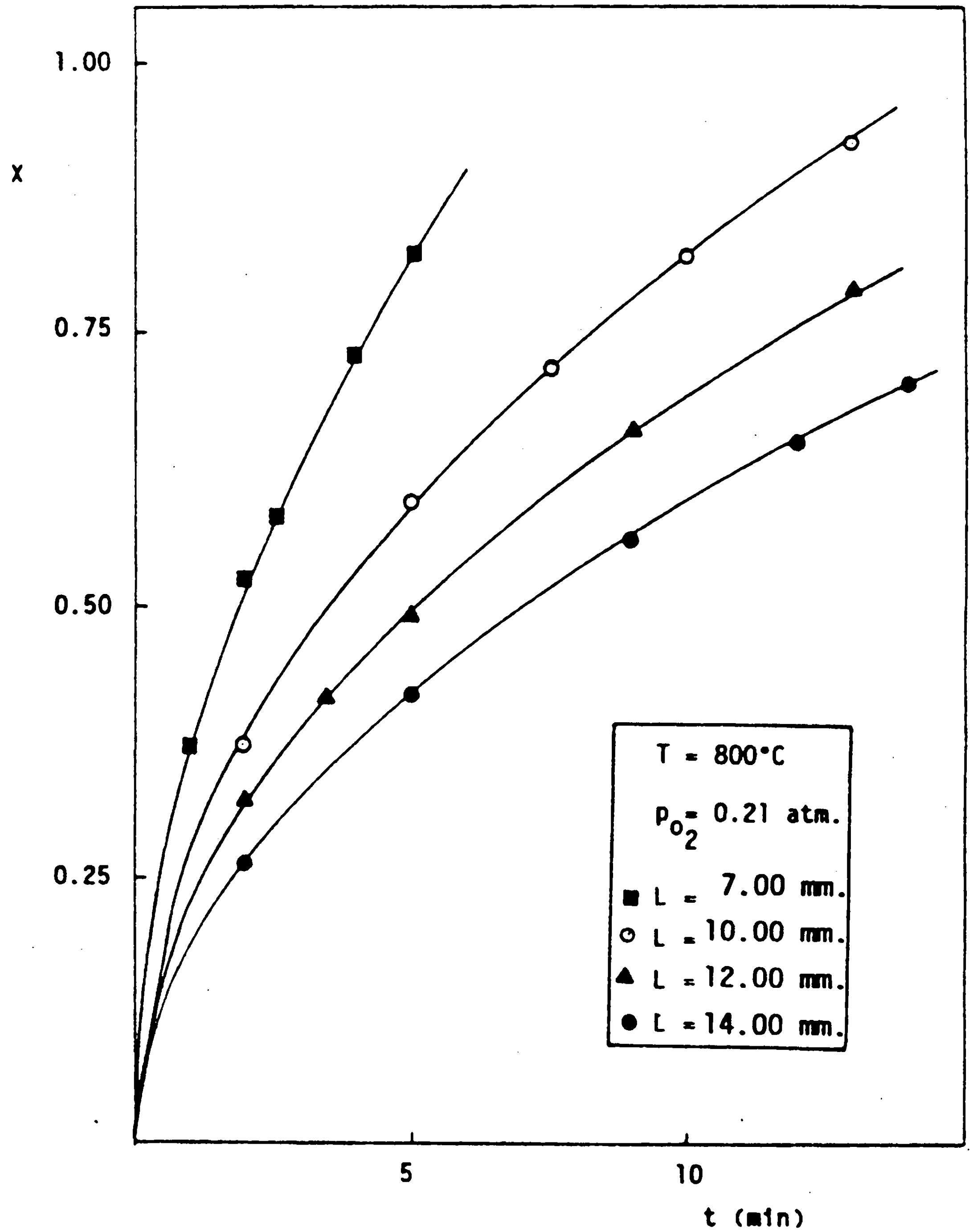

Figure 7. Variation of degree of formation of blackheart with reaction time: influence of thickness of piece.

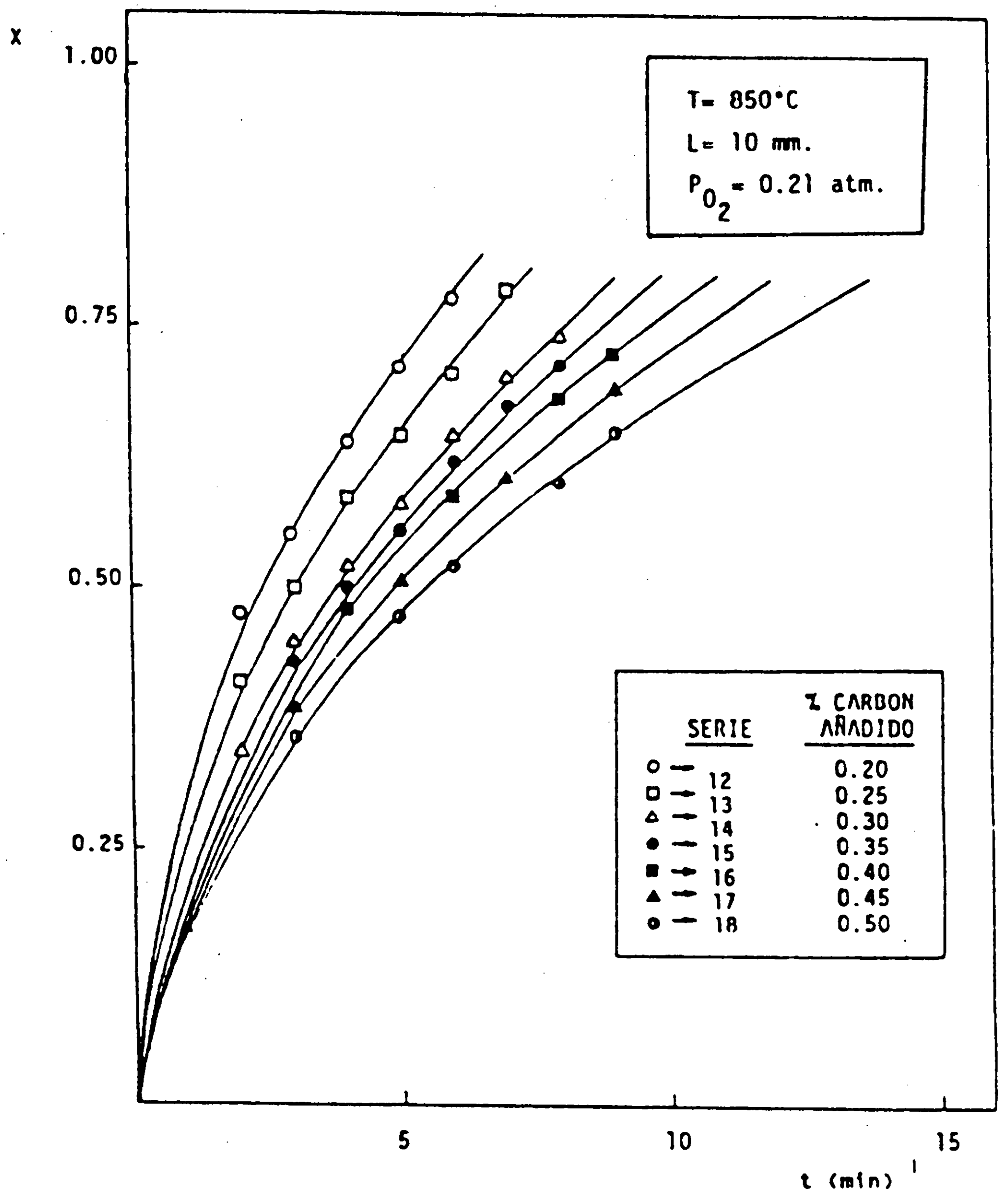

Figure 8. Variation of degree of formation of blackheart with reaction time: influence of carbon content in initial composition.

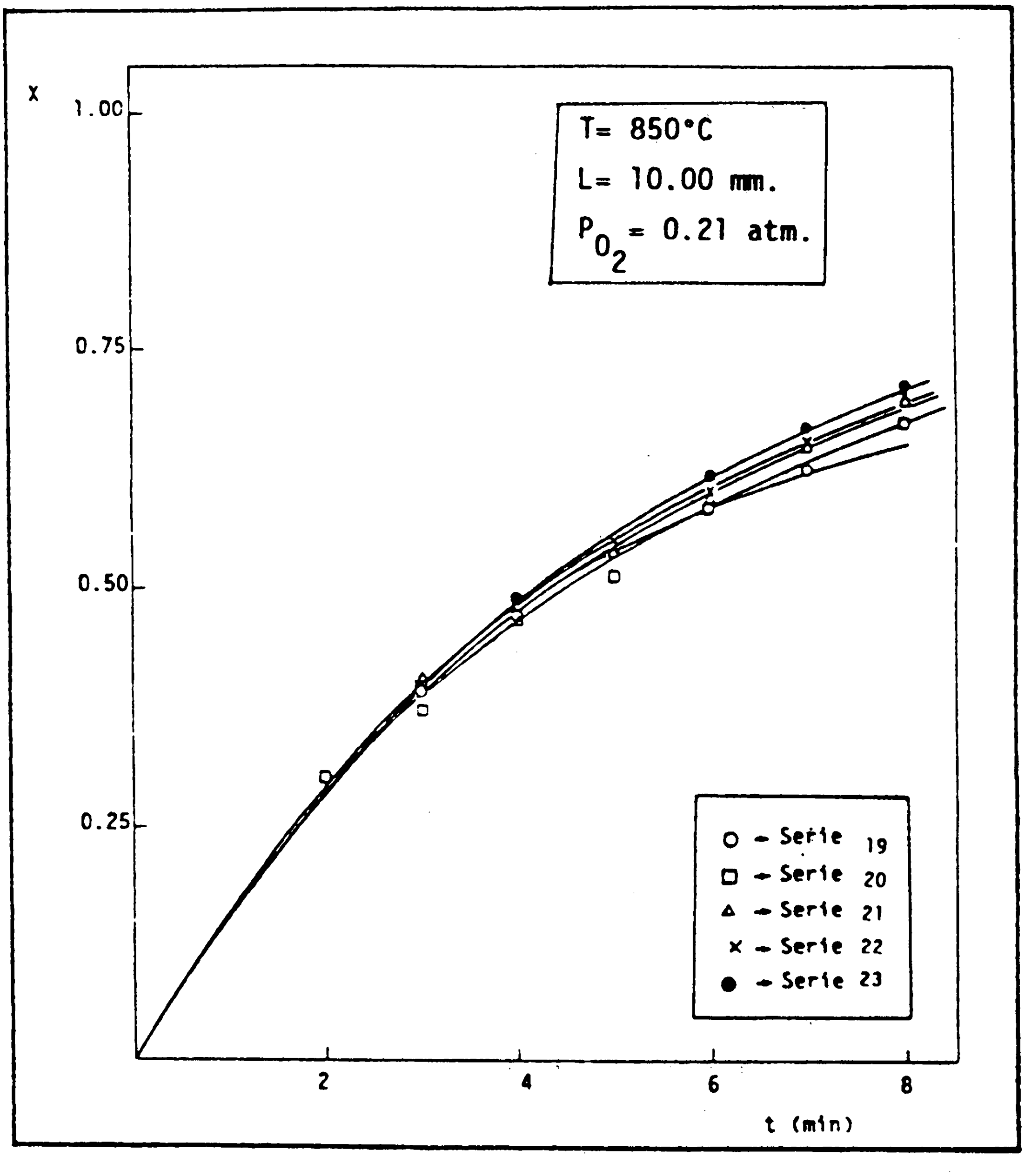

Figure 9. Variation of degree of formation of Blackheart with reaction time: influence of carbon and Fe2O3 content in initial composition.

4.1 STUDY OF THE INFLUENCE OF O2 CONTENT IN REACTING GAS MIXTURE

To check if the results correspond to equation (2) the results from experiments 1 to 4 (table II, figure 5) were plotted on rectangular co-ordinates, in the form X2 against t (figure 10); the result was straight lines which pass close to the origin as the value obtained for A is within experimental error. Consequently, no reasoning can be made about the possible variation of parameter A in equation (2) with the concentration of O2 in the reacting gas mixture. It is observed that the slope of the straight lines increases with O2 content, as was expected. Seeing as the straight lines obtained practically pass through the origin and no monotonic tendency is observed in the variation of A, the results were adjusted to an equation of the form:

$$X2 = M.\, t \qquad (4)$$

where

$$M = [(8.C^{o}O^{2}.Def)/(\ Pc.L^{2})] \qquad (5)$$

in accordance with equation (2). Equation (4) only makes sense, from a theoretical point of view if, from practically the start of the reaction, the diffusion stage is the controller of the overall velocity of the reaction process.

Inserting the experimental results into equation (4), values for M and lineal regression coefficients, specified in table III, were obtained. Given that the parameters L, ρc, Def, T, composition of the mixture and pressing conditions were maintained constant in these experiments, the plotting of M against CoO2 on double logarithmic paper should give a straight line with a slope of one, if equation (5) is true. Figure 11 shows this graph which effectively results in a straight line of equation:

$$\log M = 1.380 + 0.936 \log CO^{2} \qquad r2 = 0.997$$

The slope obtained (0.936), bearing in mind unavoidable experimental error, allows us to assume that the kinetics of the chemical stage can be considered of prime importance with respect to the oxygen. Therefore, the influence of oxygen content in the reacting gas mixture on the overall speed of reaction of blackheart is adequately expressed by equation (2).

TABLE III Variation of M in eq. (4) with the content of O2 in the gaseous phase.

Series No.	PO_2 (atm)	CO_2 (Kmol/m³)	M (min⁻¹)	r^2
1	0.05	$0.543.10^{-3}$	0.021309	0.9999
2	0.10	$1.086.10^{-3}$	0.038717	0.9990
3	0.15	$1.629.10^{-3}$	0.062269	0.9990
4	0.21	$2.280.10^{-3}$	0.079192	0.9998

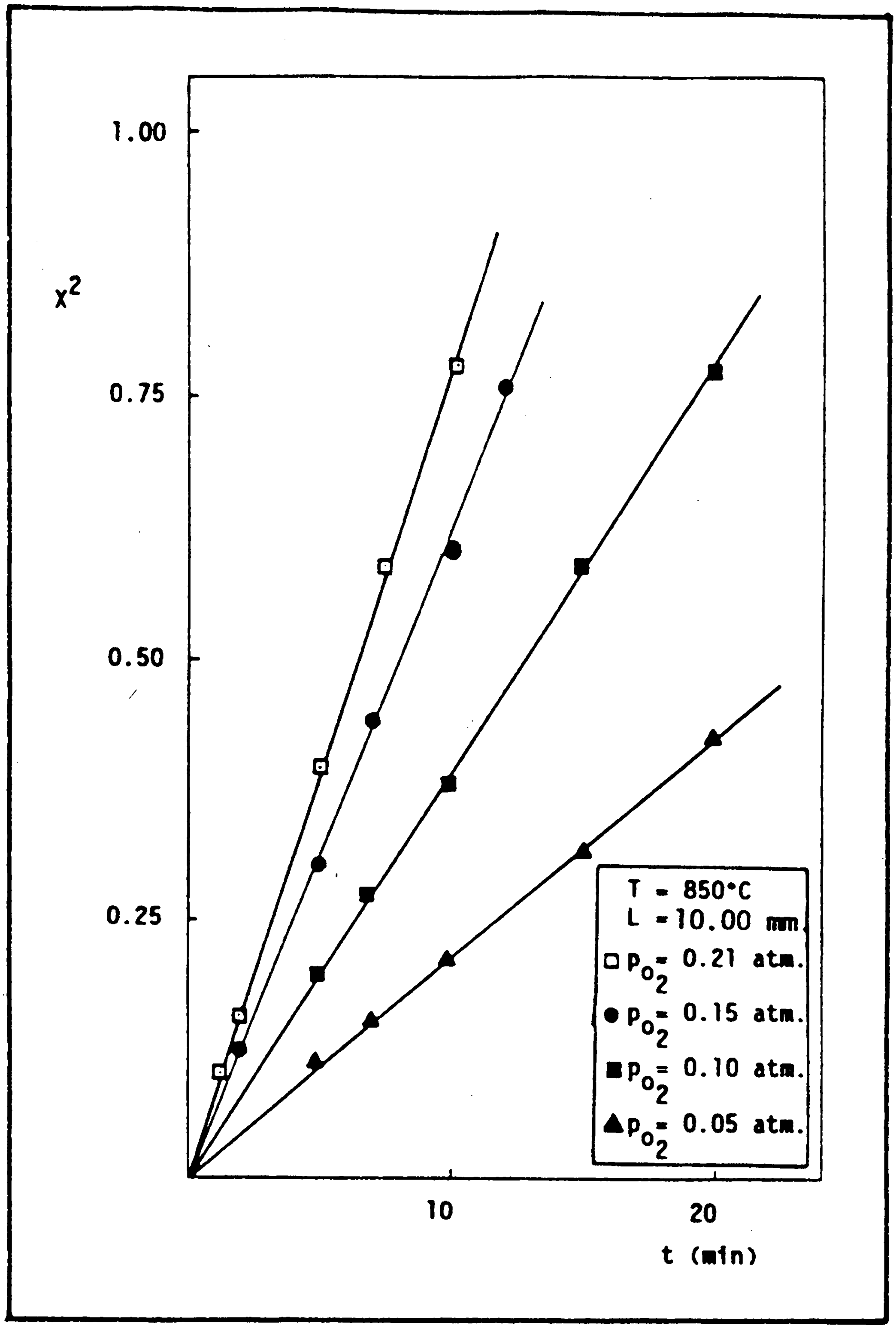

Fig. 10. Adaptation of experimental results for different concentrations of O2 in the reacting mixture to Equation [4].

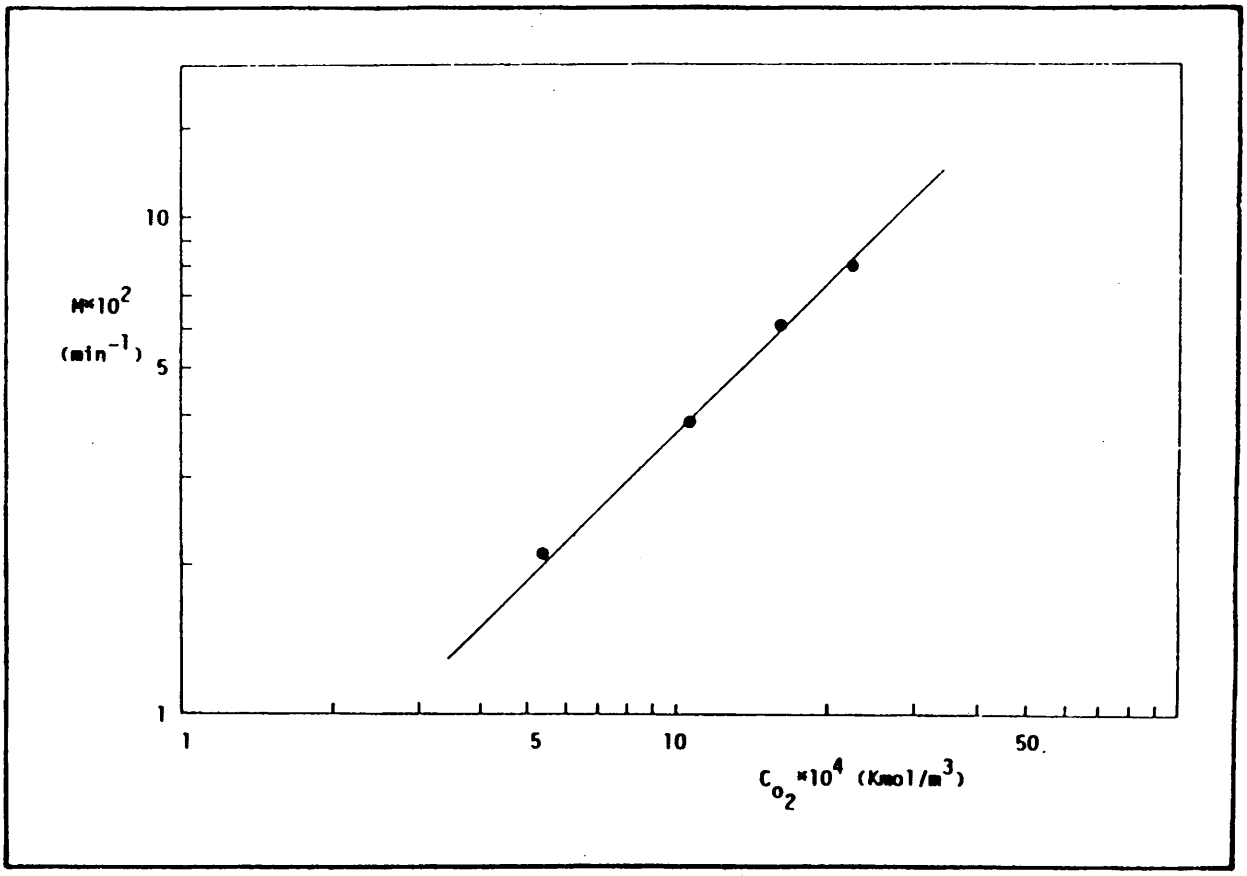

Figure 11. Variation of M in equation [4] with concentration of oxygen in reacting gas.

4.2 STUDY OF THE INFLUENCE OF TEMPERATURE ON OVERALL VELOCITY OF REACTION

Variations of temperature should only affect the parameter Def of equation (2).

Figure 12 shows the results obtained from the series of experiments 4 to 8 (table II, figure 6) in the form X2 against t. The experimental results also corresponded to straight lines (one for each reaction temperature) that pass close to the origin. The adjustment of the experimental values to equation 4 by lineal regression gives values for M and the co-efficients of lineal regression that are presented in Table IV.

Given that ρc, L, composition, pressing conditions and PO2 are maintained constant (although CO2 varies with temperature) in the five sets of experiments, if the effective diffusivity of the oxygen across the oxidised crust of the solid (for relatively small temperature intervals) is inserted into an exponential equation of the form:

$$D_{ef} = Do \, . \, \exp \left[\frac{-E'}{R.T.} \right] \qquad (6)$$

from equations (2) and (6) it results that the slope (M) of the straight lines $X^2 = f(t)$ obtained at different temperatures must be related to this variable by an expression of the form:

$$M = \left[\frac{8.C^{o}_{O2} \, . \, Do}{\rho_c \, . \, L^2} \right] . \exp \left[- \frac{E}{R.T} \right]$$

or :

$$\lambda n \, \frac{M}{C^{o}O2} = \lambda n \left[\frac{8.Do}{\rho_c \, . \, L^2} \right] - \frac{E'}{R.T} \qquad (8)$$

Inserting the experimental results into this equation, we get a straight line of the equation:

$$1n \frac{M}{C^{o}_{O2}} = 7.6878 - 4610 \, . \, \frac{1}{T} \; ; \; r^2 = 0.986 \qquad (9)$$

which can be put in the form:

$$\frac{M}{C^{o}_{O2}} = 2181.60 \, . \, \exp \left[\frac{-4610}{T} \right] \qquad (10)$$

This equation confirms the validity of the empiric correlation (6) for representing the influence of temperature of oxidation of blackheart on the speed at which this process takes place. The values obtained for E'/R = 4610 and for [(8.Do)/(c . L2)] = 2181.6 are only valid for operation conditions and compositions studied. In other cases, it will be necessary to carry out a few experiments to determine the values of these parameters.

TABLE IV Variation of M in equation (4) with reaction temperature.

Series No.	$C^{o}_{02}\cdot10^{3}$ (Kmol/m^{3})	T (K)	M (min^{-1})	M/C^{o}_{02} (m^{3}/Kmol.min)	r^{2}
8	2.183	1173	0.099818	45.7251	0.9999
4	2.280	1123	0.079192	34.7333	0.999
7	2.387	1073	0.067132	28.1240	0.998
6	2.503	1023	0.058843	23.5090	0.999
5	2.632	973	0.052872	20.0881	0.9999

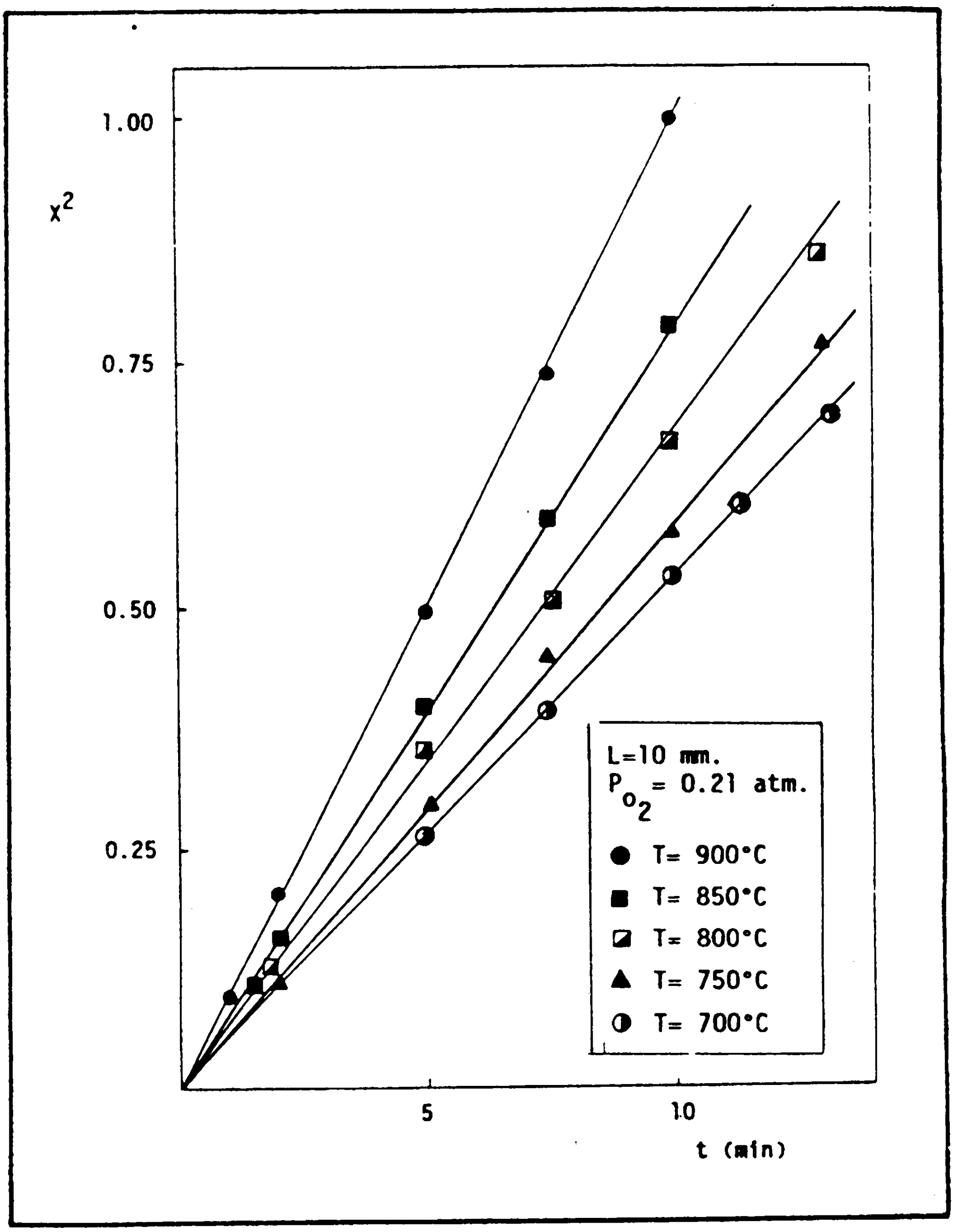

Fig. 12 Adapation of experimental results obtained at different reaction temperatures to equation [4].

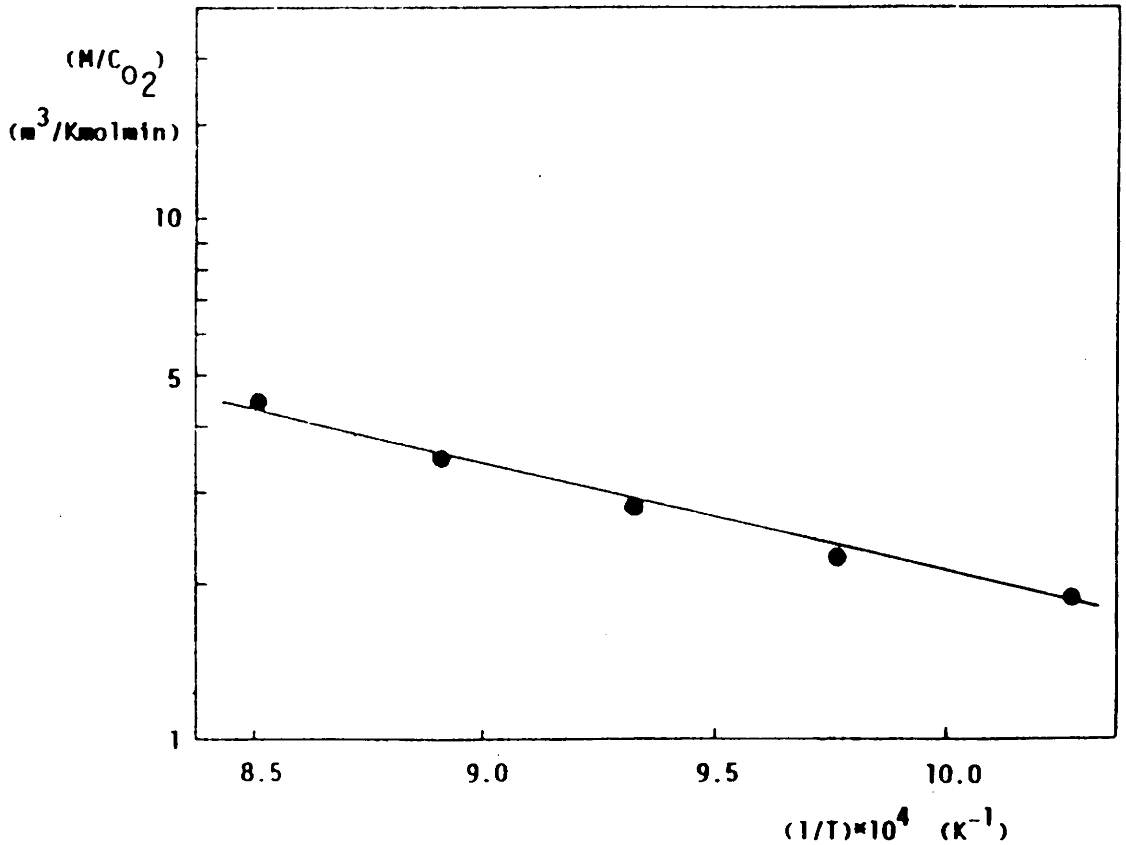

Fig. 13 Variation of M in equation (4) with reaction temperature.

4.3 STUDY ON THE INFLUENCE OF THICKNESS OF THE PIECE

Figure 4 shows experimental results obtained in four sets of experiments (table II, figure 7) performed with samples of different thicknesses (series 7, 9, 10 and 11) in the form X2 = f(t). As can be seen, the straight lines obtained also correspond well to equation (4), and the slope M increases as the thickness decreases, as equation (2) predicts. According to this equation, the following must be true:

$$M = B/L2 \qquad (11)$$

the constant B includes the group of parameters ρ_c, C^oO2 and Def, since these were maintained constant during these experiments.

Table V gives details of the slopes (M) obtained for each straight line with the corresponding value of L. Figure 15 shows the obtained values of M plotted against the corresponding values for 1/2. It can be seen that the result is a straight line that passes through the origin and whose equation is :

$$M = 6.70812.10^{-6}/L^2 \qquad (12)$$

this equation demonstrates the validity of equation (2) for predicting the influence of thickness of the piece on the speed of oxidation of blackheart.

TABLE V

Series No.	$C^o_{O2}.10^3$ (Kmol/m^3)	T (K)	L.10^3 (m)	M (min^{-1})	r^2
9	2.387	1073	7	0.135206	0.9999
7	2.387	1073	10	0.067132	0.998
10	2.387	1073	12	0.048244	0.9999
11	2.387	1073	14	0.035397	0.9999

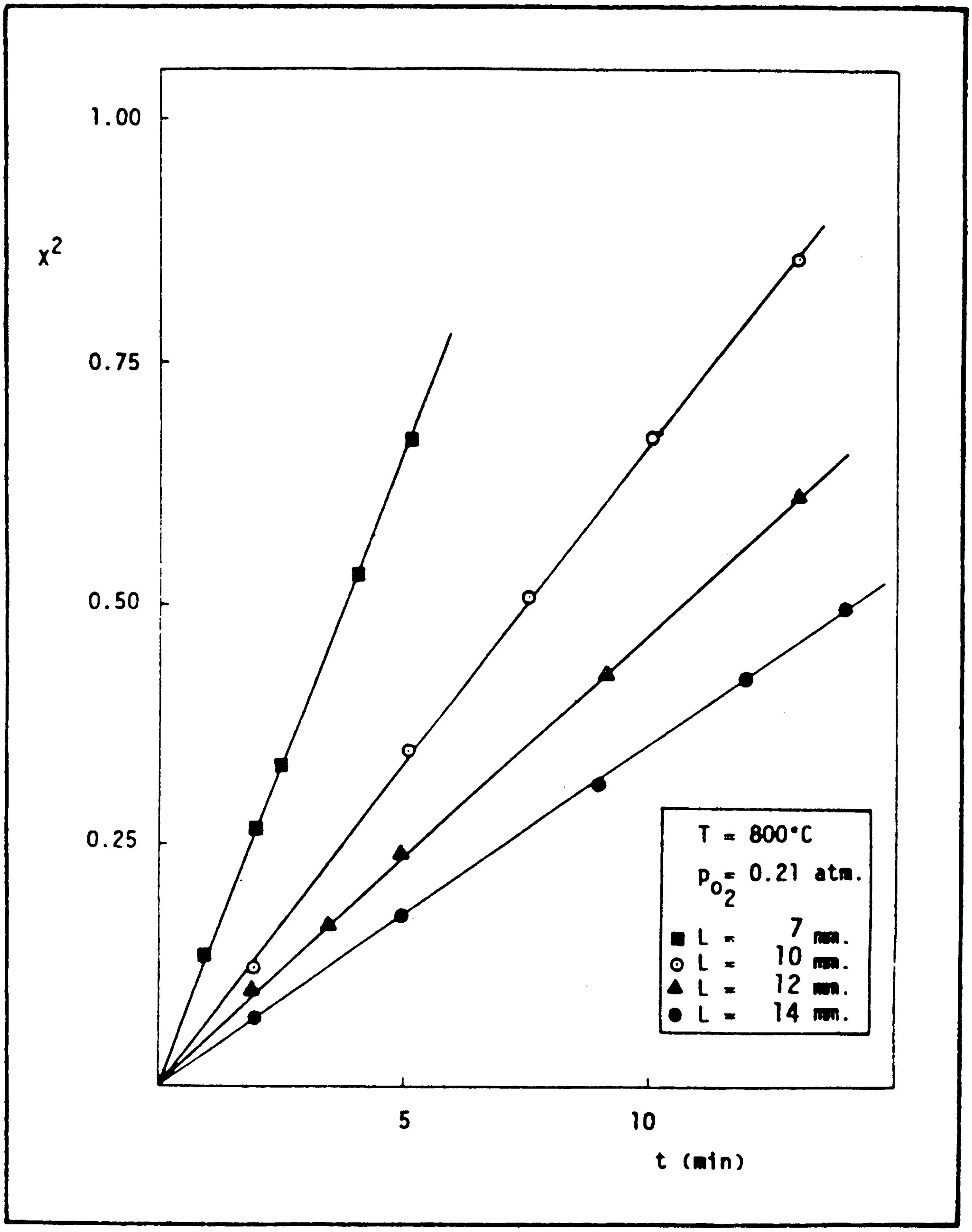

Figure 14. Adaptation of experimental results obtained with samples of different thickness to equation (4).

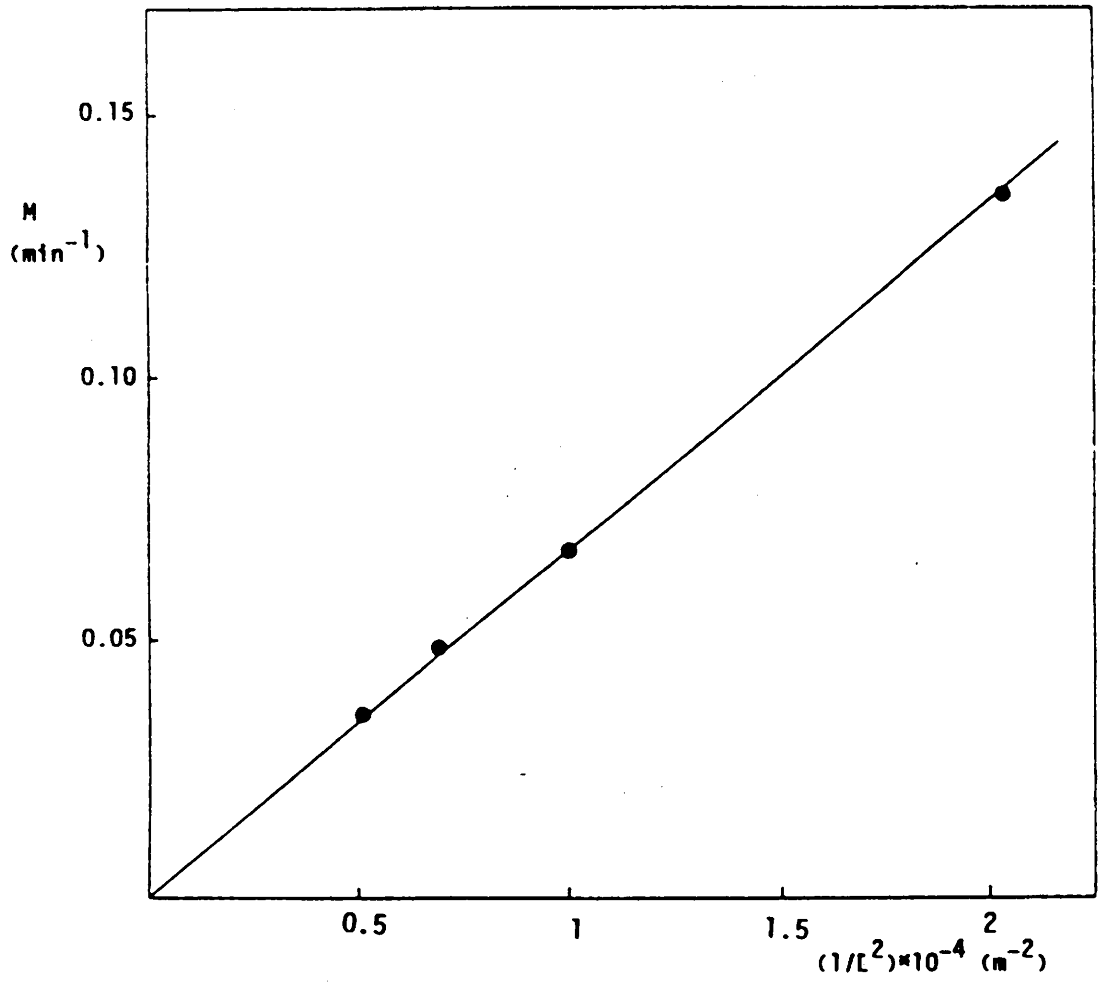

Figure 15. Variation of the parameter M in equation (4) with thickness of the piece.

4.4 STUDY OF THE INFLUENCE OF THE CARBON AND FERRIC OXIDE CONTENT OF THE INITIAL COMPOSITION

i) Influence of Carbon content.

To study the influence of the carbon content on the speed of oxidation of blackheart, seven sets of experiments (series 12 to 18) were carried out with samples containing different proportions of carbon and no ferric oxide (table II, figure 8).

According to equation (2), the content of oxidisable components of blackheart (in these series the only oxidisable component is carbon) should influence the degree of formation or oxidation of blackheart, since X2 is inversely proportional to ρ_c. To verify this, the results obtained are plotted in the form X2 against t, in accordance with the equation (4) (figure 16), this results in straight lines whose slope (M) is given in table VI. It can be seen that the parameter M decreases as the carbon content increases as expected. Assuming that the porous structure of the samples or pieces is not affected by altering the carbon percentage, then Def should have the same value in the seven series of experiments performed at the same temperature, and given that L and CºO2 are maintained constant in these experiments, the following equation must hold true:

$$M = \text{Constant}/\ \rho_c \qquad (13)$$

in accordance with equation (2).

Before checking how the experimental results obtained adapt to equation (2), some considerations must be made about the calculation of c (AtKg of Carbon per m3 of piece). In the experiments performed, this parameter can be calculated from the expression:

$$\rho c = [\frac{m_s.w + m_c}{m_a + m_c}] . \frac{({}_{(}rap)\ v}{12} \qquad (14)$$

in which the possibility that the standard composition may contain some carbon, mixed with the clay and/or feldspar is taken into account. In this equation:

m_s = mass of the standard composition contained in each sample (feldspar + clay + carbon equivalent of the material that may contain it) (Kg/sample).

w = mass fraction of carbon eventually present in standard composition (Kg of C/Kg of solid).

m_c = mass of carbon added to standard composition per sample, in each series of experiments (Kg of C/sample).

(ρ_{ap}) v= apparent density of the unfired pieces (Kg/m3)

From equation (14) the value of ρ_c that corresponds to each amount of carbon added (mc) to the standard composition, as long as the mass fraction of carbon is known (w) initially contained in the standard composition.

When the standard composition is analysed, the value for w is 0.000548 Kg of initial solid. From this value, values of c are calculated, for each series of experiments, and are given in table VI.

According to equation (13), when the values obtained for the parameter M in table VI are plotted against 1/ c, the result should be a straight line passing through the origin, with a positive slope and equal to [(8.CoO2.Def)/L2]. Figure 17 shows the graph obtained from the equation:

$$M = 0.040706/\ \rho_c \qquad (15)$$

which shows that, for compositions free from ferric oxide, equation (2) is representative of the oxidation of blackheart. ρ_c, as indicated above, being AtKg of Carbon per m^3 of volume of the unfired piece, in general, can be calculated from the expression:

$$\rho c = \frac{wc \, . \, (\rho \alpha \pi) \, v}{12} \tag{16}$$

where:

wc = the mass fraction of carbon (equivalent to the carbon and the organic material present) in the unfired piece (total Kg of C/Kg).

To check the possible influence of the granulometry of carbon, when the carbon content of a clayey composition is due to the presence of natural carbon, four experiments were performed, adding the same proportion of lignite to the standard mixture but using a different size of granule in each case. No influence is observed on the subsequent speed of oxidation of the resulting blackheart.

TABLE VI Variation of M in equation (4) with carbon content of composition.

Series No.	ρ_c (atKg of C/m^3)	M (min^{-1})	r^2
12	0.4069	0.1006	0.999
13	0.4859	0.0847	0.992
14	0.5645	0.0685	0.996
15	0.6436	0.0636	0.990
16	0.7266	0.0578	0.998
17	0.7990	0.0520	0.990
18	0.8801	0.0452	0.990

ii) Simultaneous influence of carbon and ferric oxide.

It has been observed that, when the samples are prepared from a formulation containing Fe_2O_3 and carbon, the latter. during thermic treatment at temperatures above 650ºC, is oxidised by the oxygen of the Fe_2O_3 which is partially reduced to Fe_3O_4 and/or FeO, while black heart is formed in an inert atmosphere [33]. Consequently, the oxygen necessary to oxidise CO_2 (the remanent carbon in the piece after the formation of blackheart) and the Fe_2O_3, FeO and Fe_3O_4, potentially present, should be equal to the amount required to oxidise the carbon that was initially present in the piece, before it was fired.

If the thermic treatment takes place in the presence of oxygen, the behaviour should be analogous. A part of this oxygen from the oxidising gaseous mixture will be used to oxidise the carbon present and the rest to reoxidise the potential Fe_3O_4 and/or FeO, formed as a consequence of the partial reduction of Fe_2O_3 ,during heating, by the carbon initially present in the sample. To check this hypothesis five sets of experiments were carried out (Series 19 to 23), using different proportions of Fe_2O_3 to carbon (table II, figure 9).

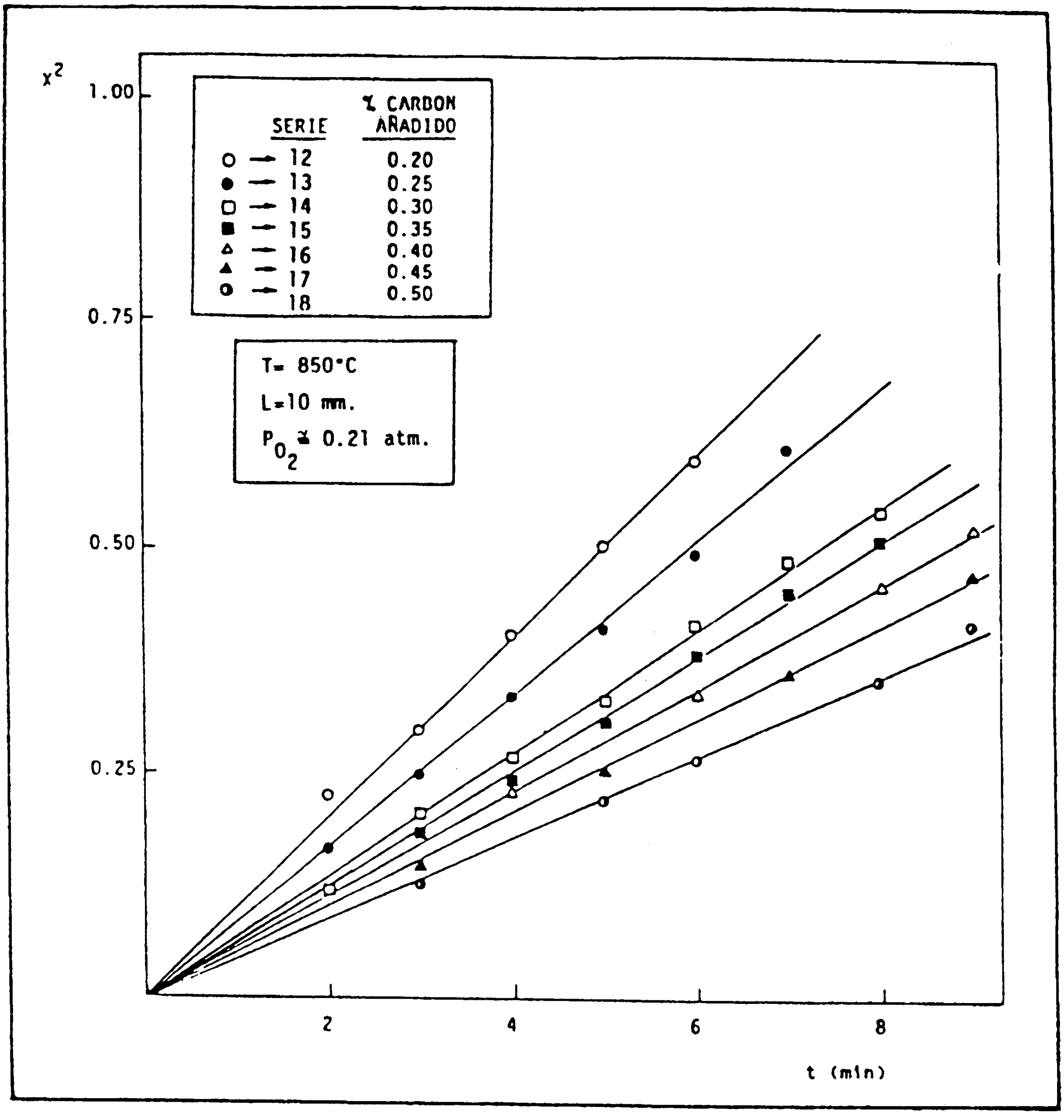

Figure 16. Adaptation of experimental results obtained with samples of different initial carbon contents to equation (4).

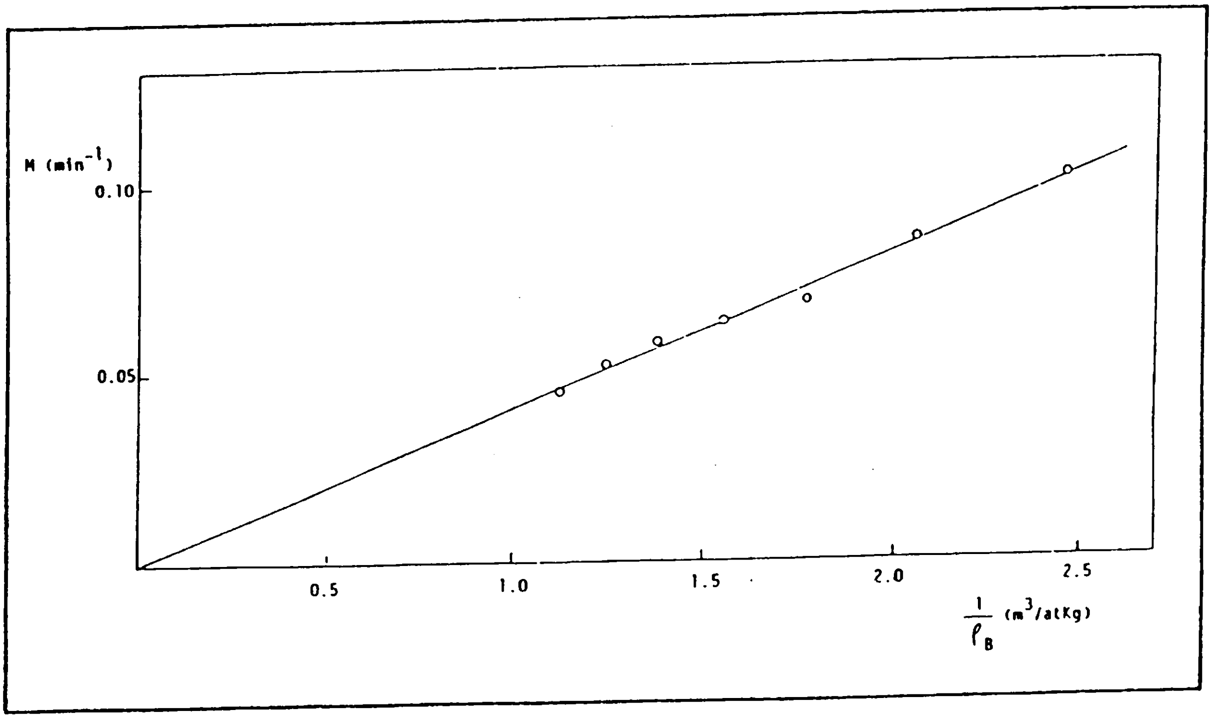

Figure 17. Adaptation of experimental results to equation (13)

Figure 18 shows the results obtained, in the form X^2 against t. Also, the resulting straight lines correspond more to equation (2) than to equation (4). The values obtained for A and M are given in Table VII. If the hypothesis concerned is valid, the molar density of the oxidisable components (the initial carbon) of the blackheart (ρ_c) that appears in equation (2), should be calculated, by analogy to equation (4), from the expression:

$$c = [\frac{m_s.w + mc}{m_s + m_c + m_{Fe2O3}}] . \frac{(rap) v}{12} \qquad (17)$$

where: mFe_2O_3 = mass of Fe_2O_3 added to the standard composition per sample (Kg of Fe_2O_3/ sample).

In accordance with equation (17), in these series of experiments, given that the apparent density (ap)v (table II) is practically invariable [except in series no. 19 where the samples have a smaller (ap)v], as are the values for ms, w and mc, c should slightly decrease when the quantity of added Fe_2O_3 is increased, which also causes M from equation (2) to increase in amounts of the same order.

Studying the graphs obtained in figure 18, a qualitative agreement with the above can be seen: if the proportion of Fe_2O_3 is increased, the slope of the straight lines increases, which seems to confirm the initial hypothesis.

In order to quantitatively check this conclusion, the equations of the straight lines in figure 18 were determined using lineal regression. In table VII the values obtained for A and M are given, as well as the values calculated for the product M. ρ_c. In accordance with equations (2) and (5), if the variation of M in the five sets of experiments is due only to the changes that c undergoes (since D_{ef}, L and C^o_{O2} were maintained constant), and this parameter can be calculated from equation (17) (in accordance with the assumed hypothesis), the product M. ρ_c should be constant for the five sets of experiments. As can be seen in the last column of Table VII, this product does remain almost constant, although its value slightly increases as the percentage of initial Fe_2O_3 increases. This result confirms the validity of the hypothesis that c can be calculated exclusively from the initial carbon present in the composition, regardless of the presence of Fe_2O_3.

The small differences that are observed between the values for the product M. ρ_c in the five sets of experiments may be due to a slight increase in the porosity of the pieces, that is produced as the proportion of Fe_2O_3 in the composition increases. In fact this last property of the solid could affect the effective diffusivity (D_{ef}) that appears in equation (2) and that could thus affect M.

TABLE VII Variation of the parameter M in equation (2) with the content of both carbon and ferric oxide in the composition.

Series No.	ρ_c (atKg of C/m^3)	A	M (min^{-1})	r^2	M. ρ_c (atKg C/m^3.min)
19	0.5780	-0.0107	0.0583	0.998	0.0337
20	0.5563	-0.0356	0.0615	0.999	0.0342
21	0.5411	-0.0284	0.0637	0.999	0.0345
22	0.5257	-0.0387	0.0664	0.9996	0.0349
23	0.5111	-0.0368	0.0690	0.9994	0.0353

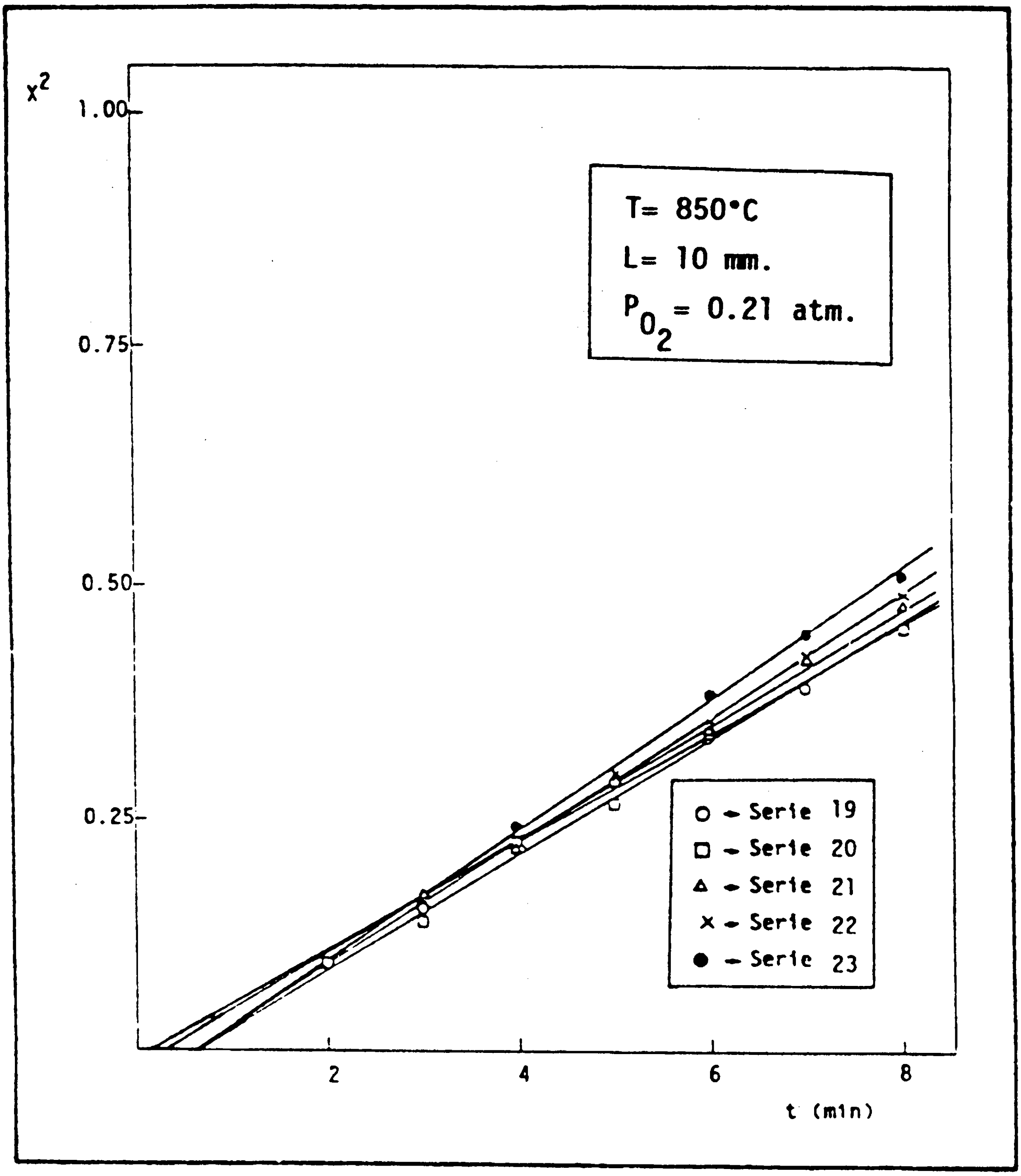

Figure 18. Adaptation of the experimental results obtained with samples containing different relative proportions of Fe2O3 and C.

5. CONCLUSIONS

i) It has been verified that the kinetic model of the unreacted core, applied to a lamina of a very small thickness compared to its other two dimensions, in the case where the controlling stage of the overall reaction process is the diffusion of oxygen across the porous structure of the external layer of oxidised solid, allows the prediction of the speed of oxidation of blackheart which is caused in ceramic pieces prepared from compositions, and at pressing conditions, analogous to those used in the manufacture of ceramic paving.

ii) The equation obtained relates the degree of formation of blackheart (connected to the thickness of the black nucleus that remains unreacted) with the reaction time, temperature, concentration of oxygen, carbon content in the unfired piece, the thickness of the same, and the effective diffusivity of oxygen across the oxidised solid layer, a variable which is closely linked to porous structure of the latter. This equation allows the calculation of the reaction time necessary for the complete oxidation of the blackheart, at pre-established operation conditions, as well as the way in which this variable can be quantitatively affected by the injection of oxygen into the preheating area in the oven, where this oxidation takes place.

iii) The influence of temperature and of the porous structure of the fired piece, both of which are related to the effective diffusivity of oxygen across a solid (D_{ef}), can be determined from a few sets of experiments, for each particular case. In fact, Def depends not only on the composition and method of preparation (degree of milling and dry or wet system) used, but also on the pressing variables (pressure and wetness of pressed powder).

iv) Even though these oxidation experiments were performed using dehydroxylated samples, in which the formation of blackheart had been caused by heating in an inert atmosphere, for a given amount of time, at a temperature at which oxidation would subsequently take place, the results can be perfectly extrapolated to industrial practice. In fact, the piece loses dehydroxylation water as it is heated in the preheating zone of an industrial oven, and the organic material contained turns to coke; at the same time a partial reduction of any Fe_2O^3 initially present may occur. In these circumstances, when the piece reaches temperatures of 700-800ºC, it is usually in the same, or even more favourable, conditions for the oxidation than the pieces with which this study was carried out, at the beginning of each experiment.

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