



The calculation of an internal energy balance in the smelting of calcium carbide

by G.W. Healy*

Synopsis

The smelting of calcium carbide has always been plagued by eruptions, too often with serious injury or loss of life. To find their causes, the author calculated an internal energy balance using 1992 data for CaC₂ and CaO, and older data for the remaining items. The heat content of the charge, and that of the hot gases formed at the reduction temperature, showed that only a fraction of its heat content can be supplied by these gases. Laboratory data on the electrical resistivity of fine mixtures of coke and non-conductive solids were extrapolated to a commercial carbide charge, and then used to calculate the heat produced by current flowing through the mix from the electrode surface to the hearth, which, under favourable conditions, sufficed to bring the charge to 1900 K and higher, at which temperatures reduction could take place.

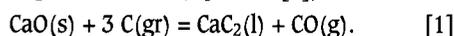
Introduction

The smelting of calcium carbide (as also of standard ferromanganese) has always been plagued by explosions and eruptions, too often with serious injuries and even with loss of life such as that of the engineer who was taking a short-cut past a carbide furnace in Niagara in 1963 just when it erupted, killing him instantly¹; and two cases in South Africa in the 1980s, where two men were burnt during an eruption, and one while tapping a furnace, all dying within three days².

At that time, the writer was engaged on a study of eruptions in a ferromanganese furnace^{3,4}, where it appeared that these resulted from insufficient preheating of the mix, so that the furnace produced manganese vapour, which, on condensing and reacting in the mix, could supply the needed energy.

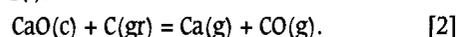
He then turned to a study of calcium carbide smelting, making a series of thermodynamic calculations and energy balances in an attempt to understand how this comes about, which was submitted to the *South African Journal of Mining and Metallurgy* in 1994. He had offered a paper on this subject to the Electric Furnace Conference in 1992 and 1993, which was rejected, but was accepted and was published as 'Carbide Smelting without Eruptions'⁵ in November 1994 and will appear in the Proceedings. The first reference in it is to the South African paper, and many of the criticisms of the reviewers were included. Now the present revision adds further changes and, it is hoped, improvements.

The accepted reaction for calcium carbide is the reduction of burnt lime with coke in a submerged-arc furnace to make a liquid product containing 83 to 85 per cent CaC₂ by weight, melting near 2300 K (equation [1]):



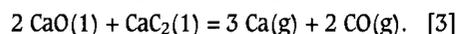
The free energy in this reaction becomes zero at 1970 K but, as the mix melts near 2350 K, this temperature is accepted. Reduction at 1970 K consumes 487 MJ, and heating of the product and melting increase the theoretical energy to 590 MJ/kg-mol, or 7670 MJ/t containing about 13 kg-mol of CaC₂ and 3 kg-mol of CaO. When reacted with water, a kilogram of carbide produces around 300 litres of acetylene, C₂H₂.

If the furnace makes calcium gas instead of CaC₂(l), the reaction is



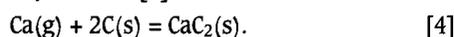
Its free energy becomes zero at 2280 K, but the same temperature of 2350 K is assumed as for reaction [1]. The heat of reaction is 709 MJ, as compared with 590 MJ for reaction [1].

The reaction suggested by the writer¹ for the accident in Niagara assumed that the mix was not feeding down properly to the melting zone, with the result that the entire energy input worked on the liquids already present there:



The free energy of this goes to zero at 2360 K, again close to that of reaction [1]. The heat of reaction [3] is 1331 MJ, or 444 per mole of calcium, which is smaller than reaction [2], because so much energy has already been stored in the molten materials.

The calcium gas produced by reaction [2] or [3] may react exothermically with carbon in the mix to make carbide, each reaction using up 2 mol of carbon, which then need not be heated to the high temperature; however, the carbide does have to be heated and melted. The energy from this cycle supplies about the same energy to the remaining mix that was not provided by the hot carbon monoxide gases passing through it. However, if the mix is sufficiently conductive, it may be heated by I^2R energy, supplementing the small heat content of the gas, and, in the case of carbide, being augmented by any calcium produced by reaction [2] or [3], and forming CaC₂ by reaction [4]:



The heat effect of this, after allowance is made for the energy needed to reheat the carbide formed, is about the right amount to make up the heat deficiency in the mix.

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Smelting of calcium carbide

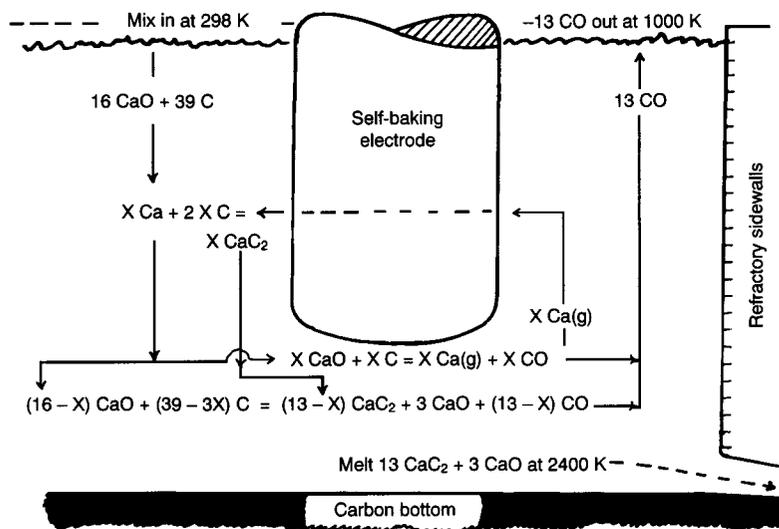


Figure 1—Schematic representation of an electrode making 1t of calcium carbide containing 13 kg-mol of CaC_2 from 16 mol of CaO and 39 mol of C

Necessary conditions were adequate conductivity and freedom from fines. When these conditions are not met, a part of the CaO may be reduced to calcium vapour rather than CaC_2 . At around 2350 K, this calcium gas can rise and react exothermically with carbon in the mix to form solid CaC_2 within it, supplying the missing energy to the rest of the charge. Unfortunately, this high-calcium gas, if it fails to encounter enough carbon in a charge of low porosity, may blow a channel to the furnace top and react there with air or moisture to cause explosions; or else can blow out of an opened taphole, injuring the tapping crew. So the old rule to minimize fines in the mix is still the essential way to ensure a safe and profitable operation.

The application of these concepts to the present problem leads to the idealized situation displayed in Figure 1, which shows the flow of 16 kg-mol of CaO and 39 kg-mol of carbon to produce 1 t of liquid carbide containing about 13 CaC_2 and 3 CaO , neglecting the small effect of impurity oxides.

In the work described here, the heat contents of the mix and of the gases flowing counter-current to it were first calculated, and the heats of fusion of CaO and CaC_2 were derived from the binary phase diagram. Next, the free energy and heat of formation for CaC_2 and CaO were selected from the literature. Then, data on the resistivity of mixtures of coke and an insulating solid (in this case burnt lime) were correlated against the particle size. A model of the conducting mix around one electrode was invented and used to calculate the current flowing through the mix and its heat effect. These depend on the voltage drop between the electrode and the high-temperature zone, which was calculated from an energy balance for the reactions taking place at high temperature in the production of either CaC_2 or calcium. The difference from the total voltage drop in the 50 MW furnace used gave the voltage drop through the mix, and the energy developed there could then be calculated.

Heat content of the mix and gases

The mix composition was taken from Robiette⁶ based on thermodynamic data from Pankratz and others^{7,8} to give the energy needed to heat the mix to 1900 K. At this point, the impurities MgO , SiO_2 , and Al_2O_3 , and of CaO , begin to be reduced by carbon to metal and CO , and the reaction is completed at 2350 K by the reduction and melting of the carbide and CaO so that the furnace can be tapped.

If the CaC_2 has been reduced there, the major portion of the gas, 13 kg-mol of CO , coming from the reduction of 13 CaO to CaC_2 , will rise in the mix. Additional CO is added from the reduction of alumina, silica, and magnesia, the last to Mg gas and CO . These hot gases rise through the mix, joined by CO_2 from the decomposition of calcium carbonate in the lime at 1200 K, and from the reduction of ferric oxide by CO , and finally by some moisture vapour from the coke charged, which is assumed to have been dried to 3 per cent. This gas has a total of 1160 MJ added to it and analyses 7.9% CO_2 , 85.3% CO , 1.1% Mg fume, and 5.7% H_2O .

It leaves the furnace at 1000 K, extrapolated from measurements in the off-gas mains from a 50 MW furnace according to Frye⁹. As its heat content is then 390 MJ, the difference transferred to the mix is 770 MJ, 25 per cent of the 3100 MJ for heating the mix to 1900 K and reducing MgO to Mg and CO gases; hence, the need to consider how the remaining 2330 MJ are to be supplied.

The heat content of the mix, augmented by heats of reduction of MgO , SiO_2 , and Al_2O_3 , is shown in Figure 2 as the solid line, while the heat content of the gases starting with 13 CO from the reduction of CaO to CaC_2 is shown by the broken line.

The energy of reduction of CaO is required, together with the heats of fusion of CaC_2 and of CaO that go into the final commercial carbide, for the calculation of the high-temperature energy needed in the arc zone.

Thermodynamic data required

Heats of fusion of CaC_2 and CaO

Figure 3 shows a phase diagram of the CaO - CaC_2 binary system after Juza¹⁰, which was published in 1961. It is in complete disagreement with an attempt by Ruff¹¹ in 1921, which had been used by the writer in his 1965 paper. The later diagram is preferred because much had been learnt about high-temperature research in the

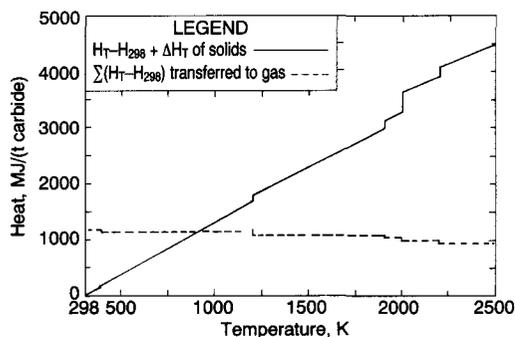


Figure 2—The heat content of the descending solid mix plus the heats of reduction of the impurities (solid line) and the heat content of the rising gases (broken line) versus the temperature of the solids

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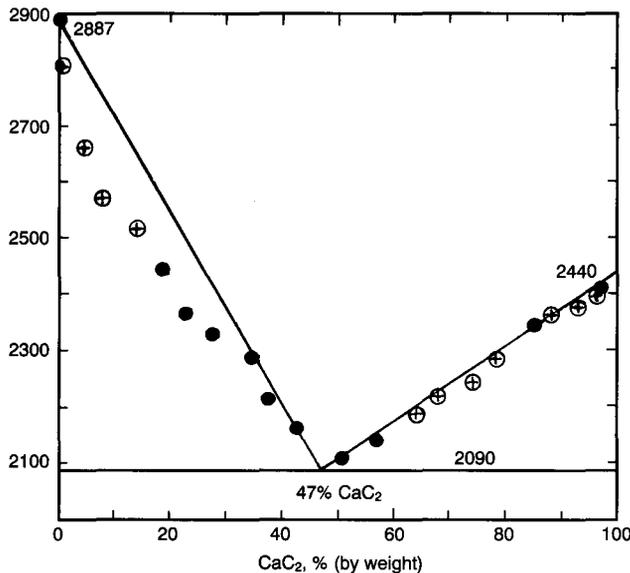


Figure 3—Phase diagram of the CaO–CaC₂ system after Juza¹⁰

intervening forty years. In addition, Ruff had used only commercial carbide, while Juza also worked with synthetic material. Both, operating in vertical Tamann furnaces, had considerable trouble in deciding whether or not their samples were molten, which they judged by the resistance of the samples to stirring with a graphite rod. Juza showed solid points in his diagram for those he felt sure were molten, and open circles enclosing a plus-sign for the doubtful ones.

Their evidence suggests that CaC₂ and CaO form a liquid that is approximately ideal, with no solid solution. If so, heats and entropies of fusion can be calculated when the fusion temperatures and the eutectic concentrations and temperature are known from the binary diagram, where CaC₂ melts at 2440 K, the eutectic temperature is 2090 K at 57 weight per cent CaC₂ (a molar fraction of 0,57), and CaO melts at 2887 K according to Levin¹². At the eutectic, the molar fraction of CaO is 0,463. In the consideration of CaC₂, the free energy of fusion at the melting point is

$$H_{\text{carb}} - 2440 S_{\text{carb}} = 0 \quad [5]$$

and at the eutectic it is

$$-2090 R \ln 0,537 = H_{\text{carb}} - 2090 S_{\text{carb}} \quad [6]$$

Inserting $H_{\text{carb}} = 2887 S_{\text{carb}}$ from [5] into [4], one gets

$$\begin{aligned} -2090 R \ln 0,537 &= (2440 - 2090) S_{\text{carb}} \\ &= 350 S_{\text{carb}} \end{aligned} \quad [7]$$

Hence, for $R = 8,314$ in the S.I. system, one gets $S_{\text{carb}} = 30,87$ J/K and $H_{\text{carb}} = 75,320$ J per g-mol.

The analogous calculation for CaO, which melts at 2887 K, gives the free energy of fusion as

$$H_{\text{CaO}} - 2887 S_{\text{CaO}} = 0, \quad [8]$$

and at the eutectic

$$\begin{aligned} -2090 \times 87,314 \times \ln 0,463 \\ = (2887 - 2090) S_{\text{CaO}} = 797 S_{\text{CaO}} \end{aligned} \quad [9]$$

$S_{\text{CaO}} = 16,788$ J/K and $H_{\text{CaO}} = 48,470$ J per g-mol.

Kubaschewski and Alcock¹³ proposed an approach to the estimation of the entropies of fusion of ordered metals and of oxides, suggesting 2,5 to 3,5 cal, or 10,5 to 14,6 J/g-atom, for the metal, and 2 to 3 cal, or 8,4 to 12,6 J/g-atom, for the entropy of fusion of the oxides. The entropy of 30,87 per mol CaC₂, or 10,3 per g-atom, is close to the lower limit of 10,5 recommended for metals, and that calculated above for CaO, 16,8 J/mol or 8,4 per g-atom, is at the lower limit of the range for oxides. Thus, the calculations based on an ideal solution with no solid solubility lead to reasonable estimates for both the carbide and the oxide.

Thermodynamic data for CaC₂, CaO, and CO

In view of the temperature of 1000 K for the gases leaving the mix, it seems sufficient to consider thermodynamic data above the melting temperature of calcium (1112 K) for use in the solid CaC₂ and CaO regions. Selected data for these were taken from Richardson¹⁴ (1953) and the same data from Kubaschewski and Alcock¹³, still in the calory system in 1979 as are those in Turkdogan's¹⁵ 1980 book. Terkel Rosenqvist's second edition¹⁶ of 1983 gives data in kJ/g-mol in graphical form, and this is used here as a source for $H_T - H_{298}$, which is given up to 1873 K, extrapolated to the melting temperature of 2440 K, and extended with greater error to 3000 K.

ΔH_T^\ddagger is calculated from this by use of Kirchhoff's law:

for CaC₂,

$$\begin{aligned} \Delta H_T^\ddagger &= (\Delta H_{298}^\circ + \Delta H_T^\circ - \Delta H_{298}^\circ \text{ of CaC}_2) \\ &- (\Delta H_T^\circ - \Delta H_{298}^\circ \text{ of Ca} + 2 \text{ C}) \end{aligned} \quad [10]$$

and for CaO,

$$\begin{aligned} \Delta H_T^\ddagger &= (\Delta H_{298}^\circ + \Delta H_T^\circ - \Delta H_{298}^\circ \text{ of CaO}) \\ &- (\Delta H_T^\circ - \Delta H_{298}^\circ \text{ of Ca} + 0,5 \text{ O}_2). \end{aligned} \quad [11]$$

For the Gibbs free energy of formation of CaC₂, the more recent measurements of Ono *et al.*¹⁷, whose data were obtained from 1223 to 1673 K, are accepted for the entire liquid calcium range from 1112 to 1757 K, because the heat term of free-energy equations generally changes little as long as there is no change in state:

$$\begin{aligned} \text{Ca}(1) + 2 \text{ C} &= \text{CaC}_2(\text{s}); \Delta G^\circ = \\ &-(0,011 \pm 0,001) T - (90,10 \pm 0,5). \end{aligned} \quad [12]$$

These are given in Table I in MJ/kg-mol.

For CaO, Wakasugi and Sano¹⁸ reviewed older free-energy data, finding a wide scatter. They used a novel experimental method in which calcium dissolved in silver was equilibrated with carbon monoxide gas.

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Table 1

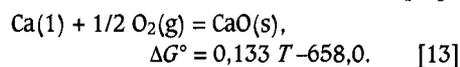
Thermodynamic data for CaC₂, CaO, and CO in kJ/g-mol or MJ/kg-mol (recent data: 17, 18. Old data: 7, 8, 14)

CaC ₂ (c,1) Ca(1) + 2 C = CaC ₂ (s), 1112 to 1757 ¹⁷			
$\Delta G_f^\circ - (0,011) + 0,001 T - (90,10 + 0,5)T^{17}$			
	$H^\circ - H_{298}^\circ$	H_f°	ΔG_f°
1112 to 1757 At 1757 K, Ca(g) = Ca(1) Ca(g) + 2 C(gr) = CaC ₂ (s) 1757 to 2440 K 2240 K CaC ₂ (s) to (1) 2440 to 3000 Ca(g) + 2 C = CaC ₂ (1) 3000 K	0,070 T - 12,8 110 0,080 T - 30,6 165 to 240 0,077 T + 52,1 283	-0,007 T - 50,7 -152,7 0,006 T - 227 75,3 0,007 T - 154 -133	-0,011 T - 90,1 0,083 T - 152,7 0,072 T - 242,8 -0,031 T + 75,3 0,041 T - 167,5 -4,5
CaO (c,1) ^{17,18}			
Temperature	$H_f^\circ - H_{298}^\circ$	H_f° at T	ΔG_f° at T
1112 to 1757 K 1757 Ca(1) to (g) 1757 to 2887 2887 CaO (c) to (1) 2887 to 3000 K 3000 K	0,057 T - 21,0 0,059 T - 26,4 +48,5 0,061 T - 32,21	0,008 T - 652 -153,2 0,017 T - 822,0 +48,5 0,022 T - 785,5	0,133 T - 658,0 ¹⁶ 0,087 T - 152,8 0,220 T - 810,8 -0,017 T + 48,5 0,203 T - 762,3 -153,8
C(gr) + 0,5 O ₂ (g) = CO(g) 2000 to 3000 K, MJ/kg-mol ^{7,8} $\Delta G = 0,0817 T - 122,8$ MJ/kg-mol $H_f^\circ - H_{298}^\circ = 0,0368 T - 16,86$ $H_f^\circ = -0,0085 T - 101,9$			
CaC ₂ melts at 2440 K. $\Delta H_m^\circ = 75,3$ MJ, $\Delta S_m^\circ = 0,31$ MJ/K CaO melts at 2887 K. $\Delta H_m^\circ = 48,5$ MJ, $\Delta S_m^\circ = 0,017$ MJ/K			

References

- HEALY, G.W. Why a carbide furnace erupts. *Proceedings Electric Furnace Conference*, vol. 23. 1965. pp. 62-67; also *J. Metals*, May 1966. pp. 643-647.
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Ono *et al.*¹⁷ used Wakasugi's method to get a figure for the formation of CaO close to their recommended value, as shown in equation [13]:



The energy deficit for preheating of the mix

The energy deficit can be met, at least partially, by resistance heating of the mix, which is the most desirable way; alternatively, by formation of calcium vapour low in the furnace, as in reaction [2] or [3], which increases the probability of eruptions. However, the provision of energy to the mix by the reaction with carbon to make carbide, reaction [4], is less desirable because it results in an increase in the amount of calcium gas in the mix.

The resistivity of the mix is estimated next, followed by the model by which the energy developed in the mix can be calculated.

Resistivity of a mixture of coke and non-conducting material

The resistivity of mixtures of coke and silica over a range of sizes and of volume-fractions of coke was studied by Dijs¹⁹. In the smelting of calcium carbide, the non-conductor is mainly burnt lime (CaO) and the conductor is coke, but the sizes are usually considerably larger than those studied by Dijs. A linear correlation was therefore made between his data (a volume-fraction for carbon of 0,5) and mean sizes (defined as the square root of the product of his conducting and insulating sizes), and is given in equation [14]. This had not been done for the present author's ferro-manganese paper⁴, which used data from Dijs¹⁹.

$$Y - a + bX \pm t_{(0,05,2)}\sigma_Y$$

$$\sqrt{\left\{ \frac{(1-r^2)}{(n-2)} \times \left[1 + n + \frac{(X - X_{ave})^2}{\sigma_x} \right] \right\}^2} \quad [14]$$

where

$$Y = \log_{10} \text{ resistivity, in } \Omega\text{-m; } Y_{ave} = 0,596$$

$$X = \log_{10} \text{ mean diameter of coke and lime, in cm; } X_{ave} = -0,391$$

$$a = -1,76; b = -2,97; \text{ pairs of independent data} = 4$$

Student's $t = 4,30$ at the 0,05 probability level; $n = 4-2$ degrees of freedom

$$r = \text{the correlation coefficient, } -0,967$$

$$\sigma_Y = \text{the standard deviation of log resistivity in } \Omega\text{-m} = -0,319$$

$$\sigma_x = \text{the standard deviation of log mean particle size in cm} = 0,104.$$

Equation [14] can be simplified by the insertion of a single factor for

$$t\sigma_Y \sqrt{1 - \frac{r^2}{(4-2)}} = 4,3 \times 0,319 \times 0,180 = 0,247.$$

Thus,

$$Y(\Omega - m) = -1,76 - 2,97 \times (\log \text{ cm}) \pm 0,247$$

$$\sqrt{5 + \left[\frac{(X + 0,391)}{0,104} \right]^2} \quad [15]$$

The result is shown in Figure 4 by three curves. The straight solid line is for the linear correlation, and the broken curves give the statistically determined plus and minus limits. These were obtained from the variances of the points and the slope, and from the distance from the averages indicated in equation [15].

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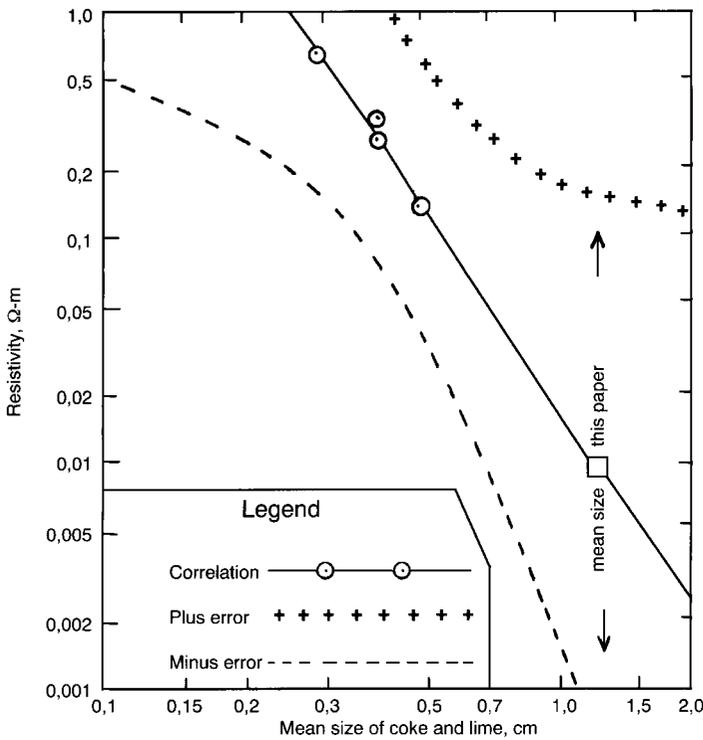


Figure 4—Correlation between mean particle size and resistivity

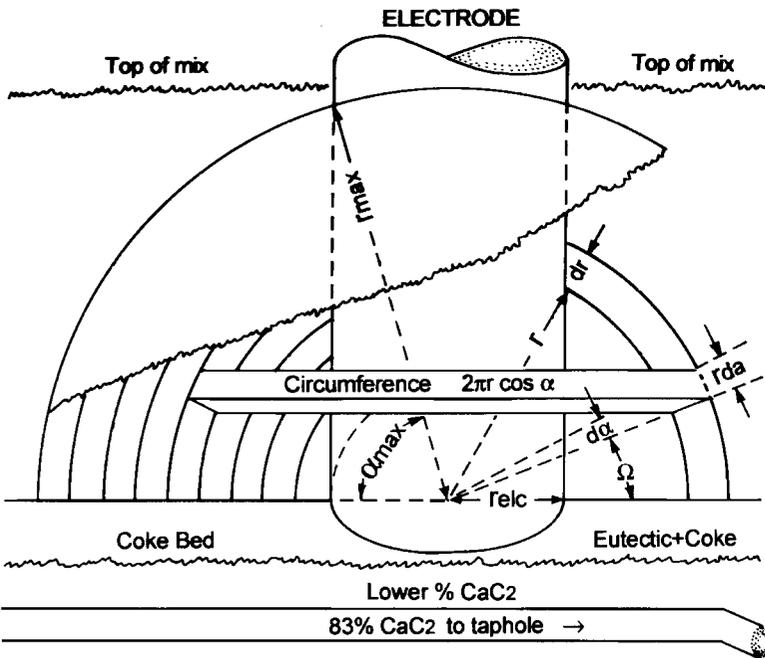


Figure 5—Section through the electrode from Figure 1, showing the assumed path of electrical conduction through the mix

4. HEALY, G.W. How ferromanganese mix resistivity affects manganese gas, carbon balance, and kWh per metric ton. *Proceedings Electric Furnace Conference*, vol. 49, 1991. pp. 251-258.

Based on bulk density data from the writer's files, a mixture of lime and coke of the mixture order given by Robiette⁶ would result in a mean size of coke and lime of 1,23 cm (0,0123 m, 0,4 inch), and a volume fraction of coke of 0,53, which is close enough to the published volume-fraction of 0,5 used in this correlation to be a good approximation.

The result is an average resistivity of 0,01, the plus limit being 0,2 Ω-m and the minus limit 0,0004 Ω-m. These are used in the calculation of electric heating that follows.

It should be noted that, if the mean size decreases, for example by the presence of too many fines in the screened burden, the resistivity will increase and less current will flow through the mix. Figure 4 indicates that, if the size decreases from 1,23 to 1,00 cm, the resistivity will double, from 0,01 to 0,02 Ω-m, and the heating current in the mix will diminish to one-half of its earlier value; hence, the need for meticulous control of the sizing operations. The temptation is always present to cut material costs by the removal of fewer fines. This could result in the loss of a human life because, when the preheat is insufficient, the furnace produces more calcium gas in the hearth, as was shown in the case of manganese, where its vapour was produced⁴.

Calculation of the resistance of the mix and the current flowing through it

The nomenclature for the equations in this section is given at the end of the paper.

Most of the 37 000 A per electrode will flow straight down the electrode shown in Figure 1, but a portion leaves the surface almost normally and then bends down through the mix towards the region of the product and coke bed. The path is simulated by a series of concentric hemispherical shells pierced by the electrode, as shown in Figure 5. Here, the part to the right is a section through the centre line, while the left-hand portion is the exterior of the largest shell along with a horizontal slice of the fifth shell. The example pictured has nine shells.

The procedure is first to find the electrical resistance, dR , to the current flowing through a single shell from the shell radius, r_{shell} , and the angle of the section with the horizontal α . The element of resistance has the circumference $C = \pi r \cos \alpha$ and the width dr . The distance through which the current travels is $L = r d\alpha$. With the resistivity designated by $\rho \Omega\text{-m}$, the element of resistance for one shell is

$$dR_{shell} = \frac{\rho L}{CW} = \frac{\rho r d\alpha}{2\pi r \cos \alpha dr} \quad [16]$$

Cancellation of the r 's and separation of the variables give

$$dR_{shell} = \left(\frac{\rho}{2\pi dr} \right) \times \left(\frac{d\alpha}{\cos \alpha} \right) \quad [17]$$

With the shell width, dr , constant, this is integrated with respect to α between the limits $\alpha = \alpha_{max}$ and $\alpha = \arccos(r_{elec}/r)$:

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5. HEALY, G.W. Carbide smelting without eruptions. *Proceedings Electric Furnace Conference*, vol. 52. To be published mid-1995.
6. ROBIETTE, A.G.E. Electric smelting processes. *The making of calcium carbide*. New York, John Wiley and Sons, Halsted Press, 1973. Chap. 10, pp. 234-253. (Out of print.)
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8. PANKRATZ, L.B., STUVE, J.M., and GOKCEN, N.A. *Thermodynamic data for mineral technology*. Washington D.C., Bureau of Mines, U.S. Government Printing Office, 1984.
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$$R_{\text{shell}} = \left\{ \frac{\rho}{4} dr \right\} \left[\ln \frac{(1 + \sin \alpha_{\text{max}})}{(1 - \sin \alpha_{\text{max}})} \right]. \quad [18]$$

Because of the high conductivity of the electrode compared with that of the mix, the voltage drop between the electrode surface and the hearth will be practically constant. So, the current flowing through the shell becomes

$$d(I A) = \frac{E_{\text{elc}}}{R_{\text{shell}}} = \frac{4 \pi E_{\text{elc}} dr}{\rho \ln \left[\frac{(1 + \sin \alpha_{\text{max}})}{(1 - \sin \alpha_{\text{max}})} \right]}. \quad [19]$$

Although α_{max} is a function of r , no way was found to integrate this expression algebraically to give the total current through all the shells, and consequently a summation was resorted to. If the total steps in the summation are a large number, N , and one looks at the n^{th} one, dr is replaced by

$$\Delta r = \frac{r_{\text{max}} - r_{\text{elc}}}{N} \quad [20]$$

and

$$r = r_{\text{elc}} + \frac{n}{N} (r_{\text{max}} - r_{\text{elc}}). \quad [21]$$

With these changes, the total current through all the shells becomes

$$I_{\text{total}} = \frac{4 \pi E_{\text{elc}} (r_{\text{max}} - r_{\text{elc}})}{\rho} \times \sum_{n=0}^{n=N} \frac{1}{N \ln \left[\frac{(1 + \sin \alpha_{\text{max}})}{(1 - \sin \alpha_{\text{max}})} \right]}. \quad [22]$$

Since $\cos \alpha_{\text{max}} = r_{\text{elc}}/r$, the replacement of r by the expression in equation [21], gives

$$\sin \alpha_{\text{max}} = \sin \left\{ \arccos \left[\frac{1}{1 + \frac{n}{N} \left(\frac{r_{\text{max}}}{r_{\text{elc}}} - 1 \right)} \right] \right\}. \quad [23]$$

This is calculated and inserted into the Σ term of equation [22] so that it can be evaluated as a function of n/N . Since it was found that the Σ term changed but little when more than 10 000 steps were used, this value was employed in the calculation. The value as a function of $r_{\text{max}}/r_{\text{elc}}$ is shown in Figure 6.

Information on the 50 MW furnace used for smelting

Significant data on the calcium carbide furnace described by Frye⁹ are given in Table II. The electrical losses for this are estimated from Foscue²⁰, who gave them as 7,5 per cent of the 18 MW input in 1949. For the present 50 MW furnace, one might expect the electrical losses to be smaller, but the only data he gave are for 50 per cent ferrosilicon furnaces, in which the electrical losses were 6,0 per cent of 12 MW in the 1930s, and only 3,5 per cent of 48 MW in the 1960s. From this one could guess that they would be in the neighborhood of 3,5 per cent \times (7,5 per cent/6,0 per cent) = 4,4 per cent of the input. The author estimated the value of r_{max} needed for the resistance of the mix from Figure 7 of Frye's paper by guessing that the man shown is about 1,75 m tall, giving 2,5 m. This is reasonably close to the depth of the mix, given as 2,7 m above the taphole. As the electrode is about 1,6 m in diameter, $r_{\text{elc}} = 0,8$ m, and $r_{\text{max}}/r_{\text{elc}} = 3,12$ ¹⁹.

Voltage drops for $\text{CaO} + 3\text{C} = \text{CaC}_2 + \text{CO}$

The voltage drop in the energy put into the furnace is shown in Table II. The drop through the mix is needed for the estimation of the energy heating in it. This can be obtained by conversion of the kilowatt-hour value from an energy balance for the high-temperature reactions and calculation of the voltage.

This is first found for the 1900 to 2350 K region applied to reaction [1], in which CaO is smelted to commercial-grade liquid CaC_2 . Table III shows the calculation of the voltage for this reaction.

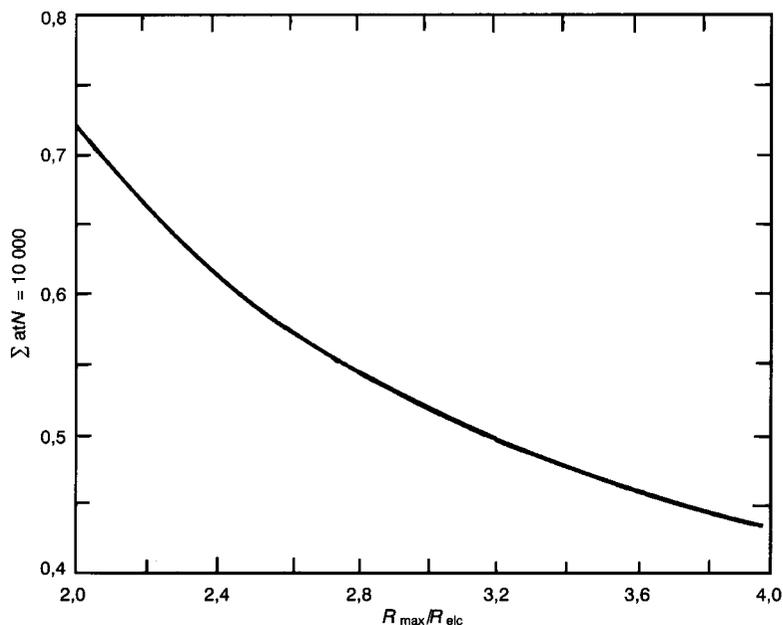


Figure 6—The final values of the summation for insertion in equation [17] for the calculation of the energy developed by the current in the mix

Smelting of calcium carbide

Table II

Data on the 50 MW furnace for calcium carbide^{8,19}

Dimensional data		Operating data	
Shell diameter, inside lining	9,5 m	Operating weight	34,000 kW
Shell depth above taphole	2,7 m	Secondary power	110,000 A
Electrode radius, r_{elec}	0,8 m	Secondary voltage	306 V
$r_{max} = 2,5 \text{ m} = \text{depth of mix}$		Production rate	2850 kWh/t
$r_{max}/r_{elec} = 3,125$		Electricity loss: 4,4% of 2850	125,4 A
$r_{max} - r_{elec} = 1,70 \text{ m}$		Voltage 0,044 x 306	13,5 V
		Smelt + preheat rate	2724,6 kWh
		Voltage (2724,6/2850) x 306	292,5 V
Time per tonne of carbide	0,0838 h	Total	2850 kWh, 306 V

2850 kWh/t divided by 34,000 kWh = 0,0838 h/t
As 1 kWh = 3,60 MJ, the energy input is 10,260 MJ/t

Table III

High-temperature energy balance for $\text{CaO} + 3\text{C} = \text{CaC}_2 + \text{CO}$, MJ/t

Heat CaO, SiO ₂ , Al ₂ O ₃ from 1900 to 2350 K		MJ/(t carbide)
Heat to 2000 and 2200 K		473
Heat carbon for reduction and alloying		445
Bring Fe from 1900, Si and Al from reduction temperatures to 2400 K		26
Decompose SiO ₂ , Al ₂ O ₃ , and CaO	10 869	
Form CO gas	-1769	
Form and melt 13 CaC₂ at -137,6 =	-1789	+7311
Total energy consumption, MJ		8255
Divide by 3,6 to get 2293 kWh or 246,2 V		
Smelt + preheat = 2725 kWh or 292,6 V		
Preheat = 443 kWh or 46,4V		

Table IV

Energy supplied to the mix by the reaction of 1 mol of calcium vapour cooling from 2350 K to a selected temperature

Item	Energy, MJ				
	220,4	220,4	220,4	220,4	220,4
1. Heat content of Ca	220,4	220,4	220,4	220,4	220,4
2. Heat content of CaC ₂ (1)	233,0	233,0	233,0	233,0	233,0
Reaction temperature	1900	1757+	1757-	1112+	1112-
3. Heat in Ca, T_R	211,1	208,1	54,9	39,0	27,5
4. Heat from Ca (items 1 to 3)	-9,3	-12,3	-165,5	-182,4	-192,9
5. 2 C not heated	-22,8	-29,9	-29,9	-62,5	-62,5
6. ΔH of CaC ₂ at T_R	-215,6	-16,5	-63,0	-58,5	-50,2
7. (Heat in CaC ₂ at T_R)	(-121)	(-110,2)	(-110,2)	(-65,0)	(-65,0)
8. Heat, melt CaC ₂ (items 2 to 7)	+111,6	+122,8	+122,8	+168,0	+168,0
9. Total energy, MJ (items 4 + 5 + 6 + 8)	136,1	135,9	135,6	135,4	137,6

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It was assumed that the MgO impurity was reduced to gases at 1900 K. This left SiO₂ and Al₂O₃ to be heated from 1900 to 2000 K and at 2200 K respectively, and these metals to be added to the iron and heated to 2350 K. The 16 mol of CaO must also be heated to 2350 K, at which 13 mol are reduced by 39 mol of carbon to CaC₂ while 3 mol are melted. All of these energies are shown in Table III, and the total is converted to volts, which are deducted from the 292,6 V estimated for the preheating and reduction of the mix from Table II to give a voltage drop through the mix of 46,4 V.

Energy for the making of Ca(g) rather than CaC₂

In the case of reaction [2], $\text{CaO} + \text{C} = \text{Ca(g)} + \text{CO}$, the free energy goes to zero at 2280 K but will seldom occur by itself; it usually occurs in addition to the primary reaction, equation [1], which will govern the temperature at 2350 K. It is assumed that the same mix arrives in the arc zone, but (perhaps because of a local shortage of coke) the product is 13(Ca + CO). Thus, the energy required is obtained by simple removal of the -1789 MJ required for the forming and melting of CaC₂, so that the energy consumption for 13 Ca(g) becomes 10,077 MJ or 2790 kWh with a voltage drop of 300 V, leaving a deficit for the heating of the mix. Indeed, with the same rate of energy input, 2790 kWh would have produced 2790/2293, which is 1,22 times as much carbide as there would have been if reaction [1] had been the only reaction.

Now, 1 mol of the calcium gas rises in the mix, cooling the mix from 2350 K to a temperature T_R , giving off its sensible heat and then reacting with 2 mol of carbon at T_R to form 1 mol of CaC₂, giving off additional energy to the mix. One must now calculate the cycle in which the calcium gas cools from 2350 K to some lower temperature, reacts there with 2 mol of carbon to make CaC₂, and supplies its heat of formation to the mix. Then, since the mix contains two fewer moles of carbon, credit is taken for their heat content from T_R to 2350 K. Since no information is available on where all this takes place, the heat effect of the cycle is calculated for a variety of reaction temperatures, selecting Ca(g) at 1900 K and, at the boiling point (1757 K), Ca(l) at that temperature, Ca(l) at 1112 K, and finally Ca(s) there. The results are shown in Table IV. The scatter among the values is doubtless due to inaccuracies in the extraction of data for CaC₂ from Table I.

The average value is 136,12 MJ with a standard deviation of 0,78 per mole of calcium reacted in the mix. If 13 mol reacted in this way, the energy supplied to the mix would be 1770 MJ = 492 kWh as compared with 2790 kWh consumed in the making of the calcium gas (Table IV), which is a recovery of 60 per cent of the smelting energy.

Smelting of calcium carbide

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Calculation of heating through the mix

The heating by current flowing from the electrodes to the hearth via the mix can now be estimated. From the correlation of the mix resistivity for the sizes estimated in this study, the resistivity is $0,01 \Omega\text{-m}$ with a considerable deviation, possible values lying between $0,0004$ and $0,2 \Omega\text{-m}$. From the average and the data derived in the calculation of the current flowing through the mix, the following is found for one electrode:

$$I = 4\pi \times E_{\text{elc}}(r_{\text{max}} - r_{\text{elc}}) \times \frac{\Sigma}{\rho} \quad [24]$$

Here, Table III gives the voltage, E , as 46,4, and Table II gives the r factor as $2,5-0,8 = 1,7$. The Σ read from Figure 6 is 0,5 at $r_{\text{max}}/r_{\text{elc}} = 2,5/0,8$. With this, the current becomes

$$I = \frac{4\pi \times 46,4 \times 0,5}{0,01} = 49,562 \text{ A} \quad [25]$$

Multiplying by three electrodes and by the voltage of 46,4 and dividing by 1000 give

$$\text{Power} = \frac{3 \times 49562 \times 46,4}{1000} = 6899 \text{ kW} \quad [26]$$

The power per tonne is obtained by multiplying the kilowattage by 0,0838 hour per tonne:

$$\begin{aligned} \text{Power per tonne} &= 0,0838 \times 6899 \\ &= 578 \text{ kWh/t} \\ &= 2081 \text{ MJ/t} \end{aligned} \quad [27]$$

Summary of heat per tonne of carbide made (13 mol of CaO reduced)

Energy deficit, preheat	
minus energy from gases	3100-770 = 2330 MJ
Normal: I^2R heating	
(equations [25] and [26])	<u>2081 MJ</u>
Remaining deficit	249 MJ
1,83 mol of CaO are reduced to calcium vapour made at 2350 K and are needed to supply the deficit	<u>-249 MJ</u>
Balance	0

Discussion

This study shows that there is fair to good probability that the mix will be heated adequately by the current flowing through it. A deficit will probably be met safely by about 2 mol of Ca per tonne reacting in the mix. This part of the carbide will require 20 per cent more energy than that reduced directly at high temperature but is probably included in the 2850 kWh/t given in Table II. For these conditions to be safe, great care must be taken in the preparation of the mix to maintain good porosity.

In discussing a paper by Scherrer²¹, Frye wrote, 'The question then becomes what to do about the screened material. We, at Calvert City, find ourselves hedging more and more often and using unscreened charge as well as smaller size raw materials. A covered furnace will take only so much material under 1/3 inch (8 mm) before it becomes wild; here again you risk damage to the cover'.

Measures to protect the workers need to be installed, with a safe room on deck as close to the furnace as feasible, and strong enough to withstand an eruption. People who have no urgent need to be there should be banned. I have been told that, after an incident in which a tapper working a second shift died from a blast of gas when he opened the taphole, a water-cooled, remotely controlled drill was installed at the taphole area in a South African plant. Such a drill had been strongly recommended after the wild-cat strike at the Niagara Works in the early 1960s, where all the engineers volunteered (?) to keep the plant running. However, the management decided that such an installation would be too costly. Later, in 1966, a different solution was found by the company which appears to have worked well for many years. This was to screen the mix just before it was charged to the hoppers. The fines were blown down the hollow electrodes right into the arc zone²² by the use of furnace gas.

On risky operations, the men have probably to be alert and well rested. It seems better to shut down temporarily when a replacement worker does not arrive. It is better to forego some production for a few hours than to lose a man working on a second shift.

Nomenclature for equations [16] to [23]

R	Resistance, Ω
ρ	Resistivity of mix, $\Omega\text{-m}$
α	Angle above the coke bed to a conducting element (Figure 5)
α_{max}	Angle between the base and the outside of the electrode
r	Radius of a conducting shell
dr	Thickness of a shell
L	Length of a conducting path = $r d\alpha$
C	Circumference of an element of resistance, $2\pi r \cos \alpha$
W	Width, i.e. the distance through which the current passes = dr ◆