

AN ASSESSMENT OF SMELTING REDUCTION PROCESSES IN THE PRODUCTION
OF Fe-Cr-C ALLOYS

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ABSTRACT

The use of energy produced by the combustion of coal and oxygen instead of the electro-thermal energy used in conventional processes for the production of iron-chromium-carbon alloys was studied by the use of a computer programme of mass and energy balances.

These processes feature the injection of coal and oxygen (and possibly inert gases and hydro-carbons) onto or into a bath of molten alloy. Part of the coal is used for the reduction reactions, leaving the surplus coal to be combusted to generate heat. A problem associated with these processes, some of which were considered in this work, is that much of the energy input of that part of the coal used for heat generation leaves the smelter as sensible and chemical heat via the off-gases.

For these processes to become attractive economically, the quantity of off-gas produced must be minimized and utilized to the best advantage. The significance of the pre-heating temperature, the degree of pre-reduction of the charge, and the degree of post-combustion of the gases in the smelter on the demand for coal and oxygen is examined, and some optimum conditions for the combination of the smelter with pre-heating or pre-reduction operations, or both of these, are defined.

Since the gaseous reduction of chromite by carbon monoxide and hydrogen is not practicable, commercial practice involves the reduction of chromite in the form of composite pellets by carbon at temperatures ranging from 1500 to 1750 K.

As an alternative to the rotary kiln, an externally heated shaft furnace - charged with a mixture of chromite and coal is proposed.

GENERAL DESCRIPTION OF THE PRODUCTION OF FERROCHROMIUM ALLOYS

The high-carbon ferrochromium of international commerce - also called charge chrome - has a typical composition of 52 to 55 per cent Cr, 34 to 37 per cent Fe, 6 to 8 per cent C, and 3 to 5 per cent Si. At present it is produced mainly in three-phase submerged-arc furnaces. In South Africa, chromite that typically analyses 43 to 46 per cent Cr_2O_3 , 16 to 20 per cent FeO, 6 to 7.5 per cent Fe_2O_3 , 2.5 to 3.5 per cent SiO_2 , 11 to 12 per cent MgO, and 14 to 15 per cent Al_2O_3 is employed. The carbonaceous reductant is a coke or char, which is produced from a bituminous coal containing 57 per cent fixed C, 12 per cent ash, 28.5 per cent volatile material, and 2.5 per cent moisture.

The electrical energy required per ton of alloy produced by this route is 3500 to 4000 kW.h. This high consumption, coupled with increased electricity costs, has led to a consideration of methods whereby its use may be decreased by the substitution of alternative energy sources.

The options for the reduction of electrical-energy consumptions are:

- (1) pre-heating of the charge of ore, reductant, and fluxes,
- (2) pre-reduction of the charge, and
- (3) the use of the energy produced by the combustion of a suitable fuel and oxygen for the replacement of part or all of the electrical energy required in smelting.

The Council for Mineral Technology (Mintek) has devised a computer programme for mass and energy balances, called CHEMHEAT, which it uses to evaluate each of the electrical-energy saving steps in an attempt to define optimum combinations of these options.

In the present work, the energy unit kilowatt hour per ton of molten alloy is used to facilitate comparisons with the dominant electrical process. Gas volumes are given in normal cubic metres (Nm^3) at 760 mm Hg and 273 K.

PRE-HEATING

In the iron and steel industry, travelling grates, rotary kilns, fluidized beds, and shaft furnaces are employed for the pre-heating (usually associated with the pre-reduction) of raw materials. In the ferrochromium industry, the rotary kiln has gained the greatest acceptance for the pre-heating and pre-reduction.

The Outokumpu Oy process employs a vertical shaft, the upper part of which is heated by fuel-oil burners to harden chromite pellets that are subsequently pre-heated in a rotary kiln. In that kiln the heat is supplied by the combustion of the off-gases from the closed submerged-arc electrical furnace. A vertical annular shaft fired with fuel gas and air is employed by Kuramoto Iron Works of Nippon Kokan (NKK) in Japan to harden chromite pellets before charging them hot to an electrical furnace.

A travelling-grate kiln, heated by the off-gas of

the pre-reduction kiln is used at the plant of Consolidated Metallurgical Industries (CMI) at Lydenburg, South Africa to dry and harden composite pellets made from chromite-ore and coke fines. These pellets are subsequently pre-reduced in a coal-fired rotary kiln(1).

Figure 1 presents a plot of the savings of unit energy consumption (in kilowatt hours per ton), as a function of pre-heating temperatures up to 1500 K. Two cases are presented, viz ore alone, and the total charge of ore, coke, and flux. This energy saving therefore has to be met from an alternative source.

The maximum energy saving at 1500 K for pre-heating of the whole charge represents 880 kW.h per ton of alloy - a reduction of some 26 per cent from 3350 kW.h/t predicted by the CHEMHEAT programme for no pre-heating.

PRE-REDUCTION

Composite pellets (chromite and coke fines) are currently pre-reduced in a rotary kiln fired by pulverized coal and air at the CMI plant in South Africa. The degree of pre-reduction attained is about 55 per cent for chromium and 80 per cent for iron.

A recent Kawasaki patent(2) describes the pre-reduction of chromite in a fluidized-bed reactor by the introduction of methane together with hot reducing gas.

The shaft furnace is widely used in the iron and steel industry for the gaseous reduction of iron-ore pellets and lumps, e.g. Midrex or Hyl processes. There is no practical process for the gaseous reduction of chromite in a shaft furnace because of the different reduction characteristics of chromite and

iron ores. The solid-state reduction of iron oxides by CO and H_2 proceeds to nearly 100 per cent at a satisfactory rate in the temperature range between 1000 and 1300 K in the presence of up to 35 per cent of the oxidant gases produced (CO_2 and H_2O). The gaseous reduction of chromite by CO in the absence of carbon starts at about 1500 K at a slow rate, and stops when the CO_2 level reaches 0.1 per cent (3).

The theoretical energy requirement for the production of one ton of 55 per cent chromium alloy at 1500 K in the solid state is calculated to be about 2600 kW.h of which (Figure 1) about 880 kW.h represents the energy necessary to heat the reactants to the process temperature. If this energy is to be met solely by the complete combustion of a coal of a heating value of 25 MJ/kg (7 kW.h/kg), the minimum coal requirement will be about 370 kg of

coal per ton of alloy produced. Carbon is also required for the reduction reactions and for the formation of carbides. The mass of carbon required is about 350 kg per ton of alloy; this is equivalent to 432 kg of coke containing 81 per cent fixed carbon or 376 kg of coke containing 93 per cent fixed carbon. If the energy required for pre-reduction is to be supplied from the sensible heat of a hot gas with a C_p of 0.407×10^{-3} kW.h/Nm³ per degree in the temperature range between 1750 and 1500 K, then the volume of gas required will be

about 23 000 Nm³ per ton of alloy.

Figure 2 represents a plot of energy consumption (kilowatt hours per ton of alloy) versus the degree of pre-reduction of chromium for charge temperatures of ambient, 1300 K and 1500 K. The net energy saved by pre-reduction in these three cases is shown in Figure 3. This energy is approximately that required for the solid-state pre-reduction operation where, for example, silicon is not reduced.

MELTING AND SMELTING

Completion of the reduction reactions and separation of the alloy from the slag usually takes place in electric-arc furnaces (open-, submerged-, or plasma-arc furnaces), but can be conducted in a coal-oxygen smelter.

Electric Smelting

Electric-arc furnaces are commonly used at present for the final smelting of charges that have been subjected to various degrees of pre-heating and pre-reduction. The off-gas of these furnaces - mostly CO - has a heating value of 3 to 3.5 kW.h/Nm³, the quantity of off-gas depending essentially on the degree of pre-reduction of the charge, as shown in Figure 4.

The energy - sensible and combustion - of the off-gas of the electric-arc furnace that is available for pre-heating of the charge depends on the heat-transfer efficiency of the pre-heating reactor, which is defined as:

$$\frac{\text{Energy transferred to the charge}}{\text{Sensible+combustion energies of the off-gas}} \times 100.$$

The energy recovery for heat-transfer efficiencies of 100 per cent, 50 per cent, and 30 per cent are shown in Figure 5.

Figure 6 is a combination of Figures 5 and 1, from which the maximum attainable pre-heating temperature of the charge at a heat-transfer efficiency of 30 per cent for the pre-heater can be determined, and hence the energy recovery that is feasible.

Coal-oxygen Smelting

The chemical energy obtained from the combustion of coal and oxygen can be used for the smelting of chromium ore that has been subjected to various degrees of pre-heating and pre-reduction to ferro-chromium(4-6), as shown in Figure 7.

The volume of the off-gas of these smelters depends not only on the degree of pre-reduction of the charge but on the pre-heating temperature, the quality of the ore, coal, and fluxes, the quantity of the fluxes, the process and off-gas temperatures, and the degree of post-combustion of the off-gas in the smelter. Post-combustion is defined as:

$$\eta_{CO} = \frac{\%CO_2}{\%CO + \%CO_2} \times 100.$$

Figure 8 shows, for a typical case the mass of coal and the volume of oxygen required, and the volume of

the off-gas produced by a coal-oxygen smelter charged with pre-heated, pre-reduced composite pellets. The pellets, which had been made from an initial charge mass of 1850 kg of chromite and 487 kg of coke fines to have a total mass of 1800 kg after pre-reduction (55 per cent reduction of Cr and 80 per cent reduction of Fe), had been pre-heated at 1300 K. The degree of post-combustion of the off-gas was from 5 to 30 per cent. The basis is the production of one ton of alloy at process and off-gas temperatures of 2000 and 1900 K respectively. The slag basicity, defined as

$$\frac{\%CaO + \%MgO}{\%SiO_2}$$

is about 1. The heating value of the off-gas depends on the degree of post-combustion and varies from 3.13 to 2.33 kW.h/Nm³.

The large amounts of off-gas with a high potential for energy recovery that arise from these processes and, in particular, the costs associated with this energy source makes it economically necessary to use them for drying, pre-heating and pre-reduction.

The pre-heating temperatures were varied between 300 and 1300 K and so was the degree of pre-reduction (0 to 100 per cent of Cr) at a degree of post-combustion of the gas of 25 per cent while the other process conditions were kept unchanged. Figure 9 shows the resultant volumes of off-gas, which have a constant heating value of about 2.5 kw.h/Nm³.

The dependence of the off-gas energies for a charge pre-heated to 1300 K (the lowest curve of Figure 9) under the previous process conditions on the degree of pre-reduction of the charge is illustrated in Figure 10. It is assumed that the off-gas enters the pre-treatment reactor at 1900 K and leaves at 600 K. The sum of both energies and half of this sum, representing heat-transfer efficiencies of 100 and 50 per cent, are also shown in Figure 10.

Figure 11 is a combination of Figures 10 and 3, and represents the maximum achievable degree of pre-reduction of Cr at heat-transfer efficiencies of 100 and 50 per cent by the utilization of the energy from the smelter off-gas under the process conditions defined.

If higher degrees of post-combustion are employed in the smelter, the heating value of the off-gas falls to the point where the contribution of energy due to the combustion of the gas is small. The

sensible heat of the off-gas is, however, still available.

The dependence of the volume of the off-gas per ton of alloy produced in a coal-oxygen smelter charged with unreduced but pre-heated materials is shown in Figure 12 as a function of the degree of post-combustion of the gas of between 30 to 80 per cent. It also demonstrates the demand for coke and oxygen for a charge pre-heated to 1200 K.

It can be seen that, at high degrees of the post-combustion of the gas, the volume of the off-gas produced is not influenced much by the pre-heating temperature of the charge and, at the 80

per cent post-combustion level, the gas volume is about 1100 Nm³ per ton of alloy or about half that produced at a post-combustion of 30 per cent. As the mean heat capacity (C_p) of the gas is 0.7×10^{-3} kW.h/Nm³ per degree, because of the increase in the CO₂ content, the utilization of the sensible heat of the 1100 Nm³ of off-gas (per ton of alloy) at 1900 K depends on the outlet temperature of the gas from the pre-heating reactor, as shown in Figure 13.

Figure 14, which is a combination of Figures 13 and 3, demonstrates the maximum pre-heating temperature of the charge that can be achieved by utilization of the energy of the smelter off-gas in a pre-heater.

DISCUSSION

Pre-heating

In general, pre-heating is an attractive option. It can be deduced from Figure 1 that an average of about 45 kW.h/t can be saved for each 100 degrees of pre-heating temperature if only the ore is pre-heated, and about 70 kW.h/t if the total charge is pre-heated.

If a rotary kiln is employed, the movement of the charge can be arranged to be countercurrent to that of the hot gas; where composite pellets are used, the low-level heat can be used to dry and harden the pellets. When a fluidized bed is employed with a fine ore, the operation is not countercurrent unless multiple stages are used. A temperature limit of 1430 K is found when coal is present with the ore. Without coal, 1700 K is achieved(7). This operation may involve the combustion of, for example, the off-gas from a plasma furnace treating an unreduced charge. A single-bed fluidized reactor operating under these conditions has a thermal efficiency of about 30 to 35 per cent and can, according to Figure 6, pre-heat the ore to 1700 K or the whole charge to 1300 K.

Although the countercurrent rotary kiln has a higher thermal efficiency than the fluidized bed (45 to 80 per cent is reported for a wide range of applications(8)), the difference in energy savings is probably not sufficient to justify the much greater capital and operating costs.

Pre-reduction

For a charge fed at ambient temperature, a 1 per

cent increase in the degree of chromium reduction will result in an energy saving of about 21 kW.h/t in the subsequent smelting (Figure 3). If the charge has been pre-heated to 1500 K, the saving due to pre-reduction falls to about 16.5 kW.h/t.

Unlike pre-heating, which is limited by the amount of energy that can be transferred to the smelter owing to constraints on the pre-heating temperature, pre-reduction up to 100 per cent is theoretically possible. However, because of the slow rate of reduction of chromite, especially at high degrees of reduction, pre-reduction in a rotary kiln is usually limited to about 55 per cent of the chromium.

As already mentioned, the use of the shaft furnace for the pre-reduction of chromite has not been reported as yet. A possibility for development along these lines is the adaptation of the Kinglor-Metor (K-M) process(9), which was developed for iron-ore reduction in the 1970s, to the pre-reduction of chromite. In this process, the shaft is heated externally by the combustion of any fuel (smelter off-gas can be used as well as the shaft top-gas), and combustion can be substantially complete. The shaft would be charged with a prepared mixture of finely divided chromite and coal or coke. During its passage down the shaft, the charge sinters and contracts, thus being relatively free from friction with the walls of the shaft and hence undergoing a high degree of pre-reduction. Such a process would be well suited to a coal-oxygen smelter using moderate degrees of post-combustion (about 25 per cent).

ACKNOWLEDGEMENTS

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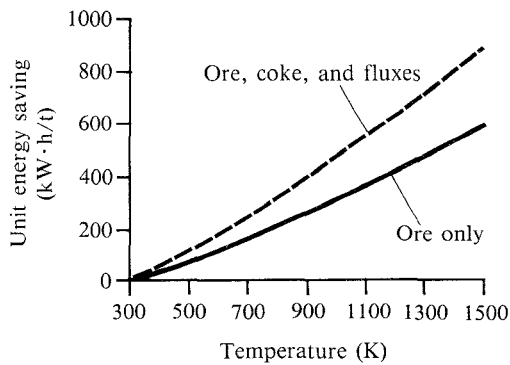


Fig. 1.—Energy saved by pre-heating

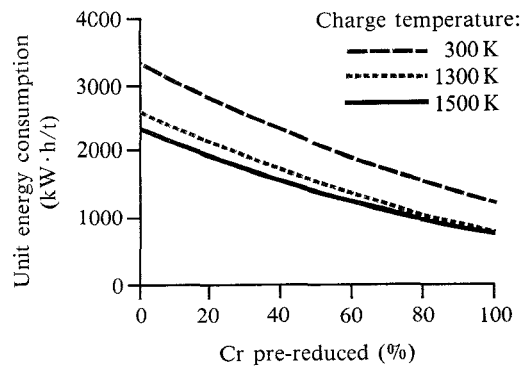


Fig. 2.—Dependence of energy requirement on pre-reduction

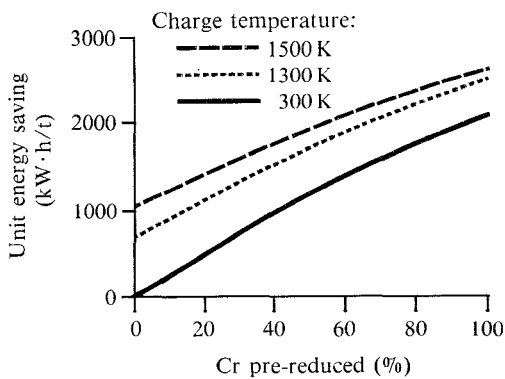


Fig. 3.—Energy saved by pre-reduction

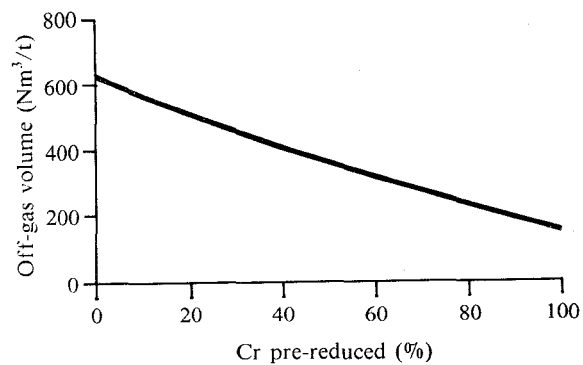


Fig. 4.—Off-gas volume versus degree of pre-reduction in an EAF

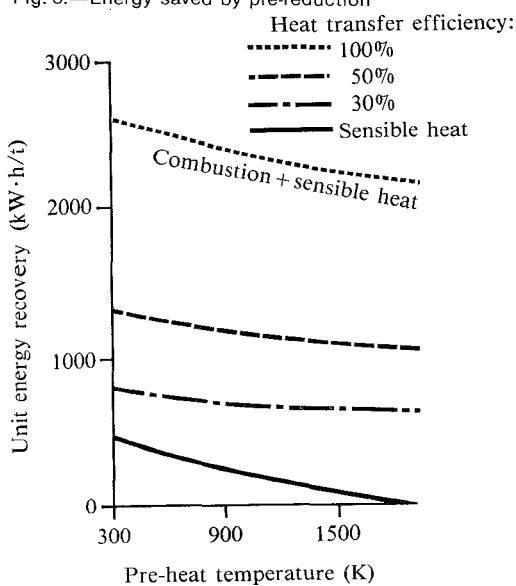


Fig. 5.—Available energy of the off-gas of an EAF

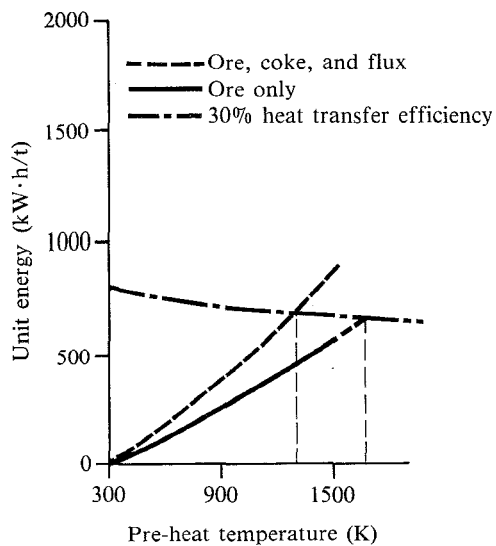


Fig. 6.—Maximum achievable pre-heating temperature by the off-gas of an EAF

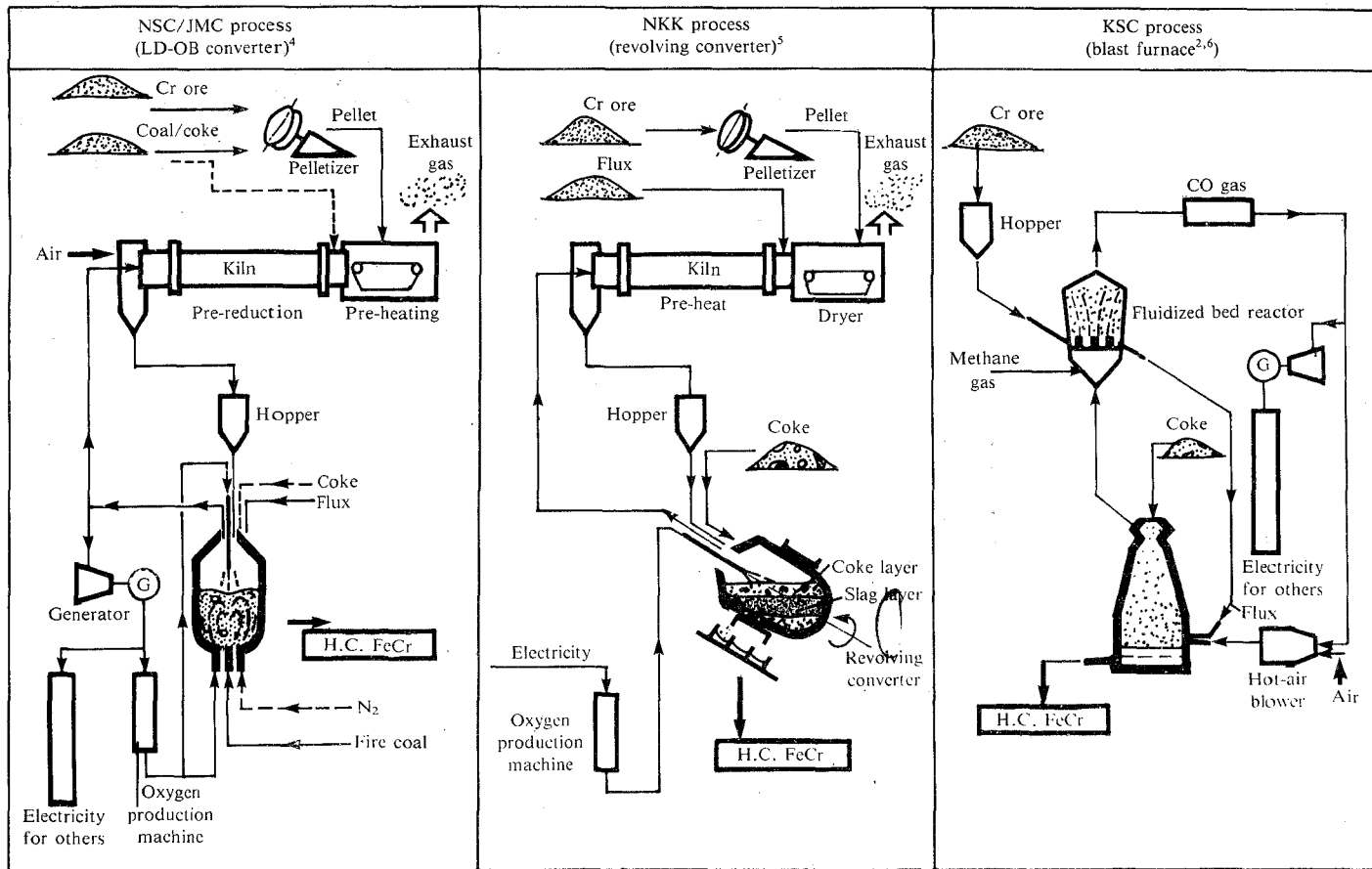


Fig. 7.—FeCr new production processes

GENERAL DESCRIPTION OF THE PRODUCTION OF FERROCHROMIUM ALLOYS

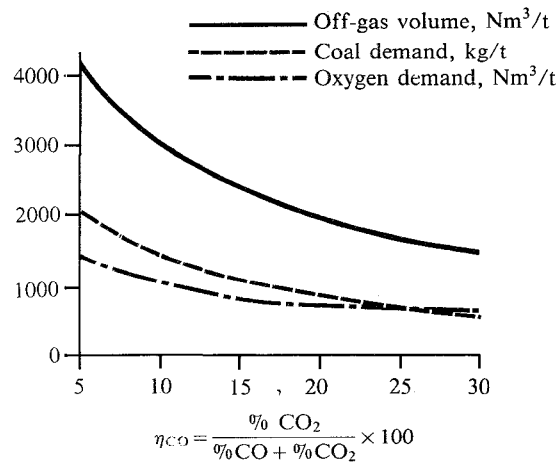


Fig. 8.—Off-gas volume, coal, and oxygen demand versus degree of post-combustion in a coal-oxygen smelter (charge at 1300 K)

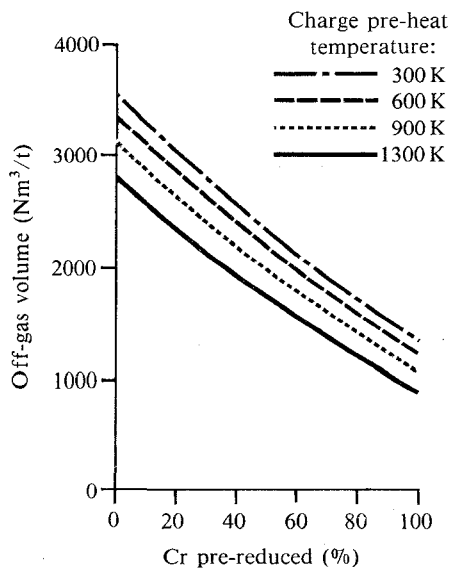


Fig. 9.—Volume of off-gas versus degree of pre-reduction in coal-oxygen smelting ($\eta_{CO} = 25\%$)

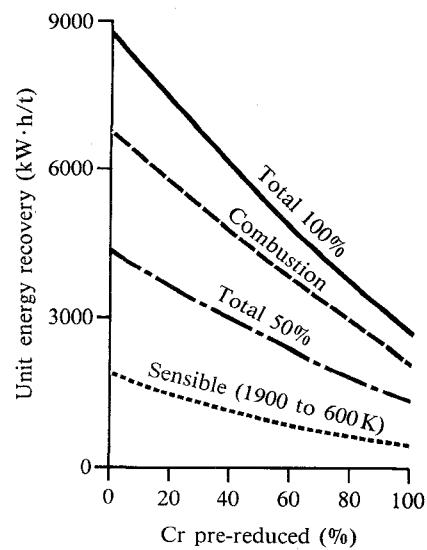


Fig. 10.—Available energy of the off-gas ($\eta_{CO} = 25\%$) versus degree of pre-reduction in coal-oxygen smelting

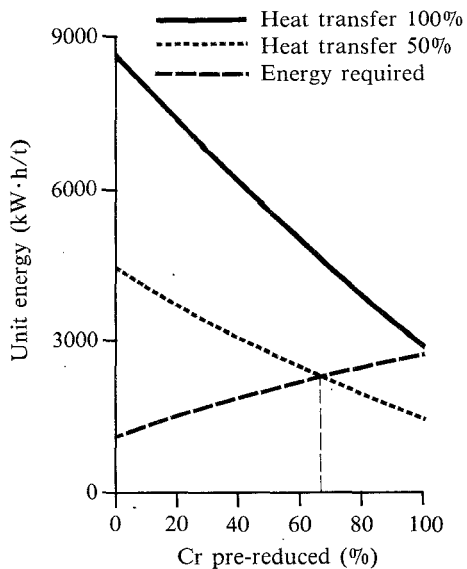


Fig. 11.—Maximum achievable degree of pre-reduction by the off-gas ($\eta_{CO} = 25\%$) of a coal-oxygen smelter

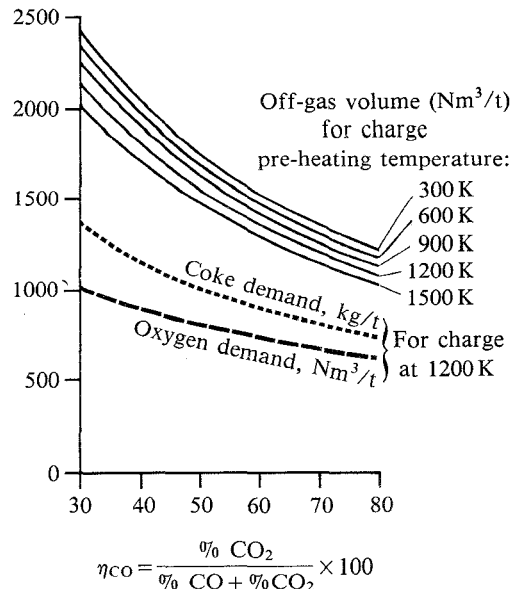


Fig. 12.—Off-gas volume, coke, and oxygen demand versus degree of post-combustion in a coal-oxygen smelter

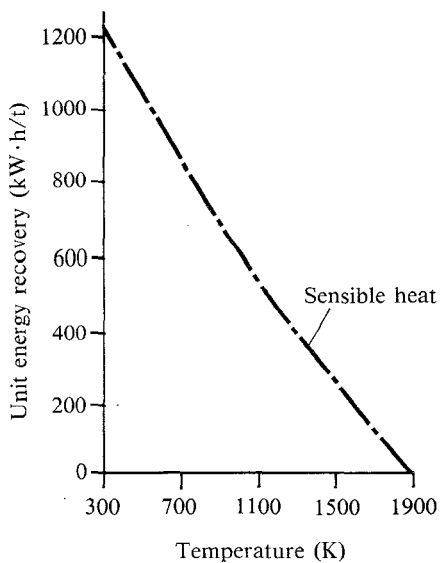


Fig. 13.—Sensible heat of 1100 Nm³/t of off-gas (at 1900 K, $\eta_{CO} = 80\%$) versus gas outlet temperature

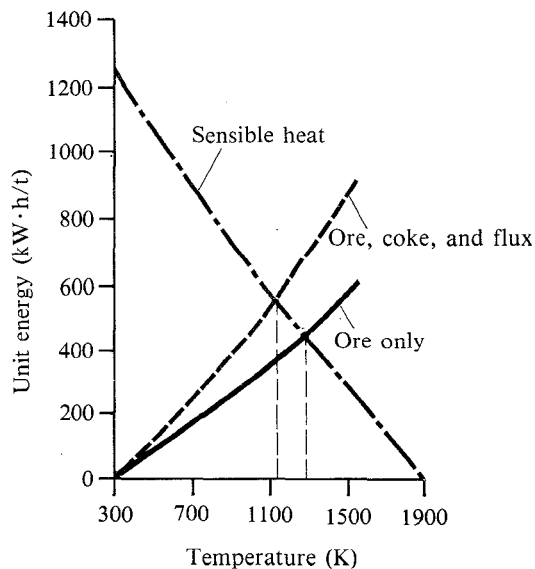


Fig. 14.—Maximum achievable pre-heating temperature by the off-gas (at 1900 K, $\eta_{CO} = 80\%$) of a coal-oxygen smelter