

THE FERROMANGANESE PROCESS - MATERIAL AND ENERGY BALANCE

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ABSTRACT

The production of high carbon ferromanganese in electric furnaces is discussed based on a staged materials and energy balance. Attention is focused on coke and energy consumption dependent on available oxygen in the manganese ore, relative reactivities of ore and coke, and on moisture content and decomposition of carbonate fluxes. The importance of the energy consuming Boudouard reaction ($\text{CO}_2 + \text{C} = 2\text{CO}$) is emphasised. Manganese vapour and alkali circulation may contribute considerably to energy transfer within the furnace, carrying energy from the hot smelting zone to the colder zones where solid state reduction takes place.

INTRODUCTION

Several manganese-containing ferroalloys are produced. The most commonly used is high-carbon ferromanganese (HC FeMn). This alloy is either produced in blast furnaces or in electric furnaces. The electric furnace process, however, is far more flexible than the blast furnace, in that slags can be further processed to silikomanganese and refined ferromanganese. The choice of process is also dependent on the relative price of electricity and coke.

In three-phase submerged arc furnaces the electrodes are buried in the charge material. The raw materials are heated and the manganese oxides prereduced by hot CO gas from the reaction zones deeper in the furnace. The exothermic reactions contributes favourably to the heat required. Efficient production of HC FeMn depends on the degree of prereduction that occurs in the upper region of the furnace.

The raw materials are manganese ores, coke and fluxes such as limestone, dolomitic limestone and quartzite. The raw materials are often stored outdoor, and the water content, including chemically bound water in the manganese ores, may therefore be high, up to 10%.

In this paper attention is focused on carbon and energy consumption in the ferromanganese process and on process mechanisms. A staged material and energy balance is discussed and the effects of carbon reactivity, manganese ore reducibility, available oxygen (O/Mn-ratio), alkali circulation and content of moisture and carbonates in raw materials will be discussed.

PROCESS CHEMISTRY

The temperature on top of the charge varies from furnace to furnace, but is usually between 200 and 250°C in closed furnaces. Evaporation of water in the charge mixture will take place:



Some of the evaporated water will react according to reaction (2):



This reaction runs to the right at temperatures below 700°C. There is always some hydrogen gas in manganese furnace off-gases, for example 5%, which tells us that this reaction takes place. One reason might possibly be that chemically bound water in the manganese ore is evaporated at temperatures between 300-400°C where reaction (2) may proceed. Another source of hydrogen is volatiles in the coke.

Decomposition of carbonates added as flux to the charge will take place, MgCO_3 at about 400°C and CaCO_3 at about 900°C:



One reaction which may occur is the precipitation of soot around 500 to 600°C:



This soot will mainly be precipitated on the ore and will be carried to higher temperatures where it again is gasified. This closed-circuit circulation does not affect the overall stoichiometry of the process and has little effect on the coke consumption, but it will eventually carry some heat from the lower to the upper part of the furnace.

Alkali oxides, K_2O and Na_2O , enter the furnace with the manganese ores and to a smaller extent with the coke and the carbonate fluxes. In the smelting zone some of it will be reduced to metal vapour which follows the gas flow to colder regions. Here it is reoxidised and reacts with the gas to form alkali carbonates:



This circulation of alkalis will carry heat from the smelting zone to the preheating and prereduction zones. The alkali circulation will be further discussed later.

The possibility of some manganese circulation should also be mentioned. However, due to the low manganese vapour pressure at these temperatures, little manganese is probably circulating between the melting and prereduction zone.

The higher manganese oxides which predominate in manganese ores (MnO_2 , Mn_2O_3 and Mn_3O_4) are relatively unstable and are easily reduced in solid state in presence of CO.



Gas reduction of the higher Mn-oxides are exothermic reactions, and a considerable amount of heat is produced, thereby preheating the charge materials in the furnace. The extent of gas reduction is reflected by the furnace off-gas CO_2/CO -ratio.

Solid Mn_3O_4 converts easily to MnO in presence of CO according to reaction (9). The equilibrium CO/CO_2 -ratio is $8 \cdot 10^{-5}$ at 1000°C . The CO-gas reduction of Mn_3O_4 is thus a question of kinetics and rather than thermodynamics.

After the temperature has increased to about 1000°C the reaction on the coke surface is sufficiently rapid to make the ore reduction (9) and the **Boudouard reaction** (10) to run simultaneously. Thus, CO_2 formed by the reduction of Mn_3O_4 may react with carbon to give the overall reaction (11):



The Boudouard reaction (10) is strongly endothermic, and as a result the "direct reduction" of Mn_3O_4 (11) is also endothermic.

Iron is always present in manganese ores. Reduction of the iron oxides runs parallel to the reduction of manganese oxides. Complete reduction in solid state to sponge iron is possible.





Further gas reduction of MnO to manganese metal, analogous to sponge iron formation, is not possible. Reduction of MnO is far more difficult than that of FeO. Considerable melting of the remaining oxide mixture starts at about 1250°C. The average temperature in the smelting reduction zone will normally be around 1400-1450°C. The final reduction to liquid metal will take place with solid carbon in the "coke bed". In addition some silica and alkali compounds are reduced and carbon is dissolved in the metal up to carbon saturation.



STAGED MATERIAL AND HEAT BALANCE

A staged material and heat balance is shown in Figure 1. The furnace is divided in four zones which are defined as follows:

Zone 1 Drying and calcination zone, including the low temperature reduction $\text{MnO}_2 \Rightarrow \text{Mn}_2\text{O}_3$. Some hydrogen formation by the watergas reaction¹. MgCO_3 in dolomitic limestone is decomposed.

Zone 2 Gas reduction zone where Mn_2O_3 is reduced to Mn_3O_4 and partly to MnO.

Zone 3 Direct reduction zone where Mn-ore reduction (9) and the Boudouard reaction (10) run simultaneously. Iron oxide is reduced, $\text{Fe}_3\text{O}_4 \Rightarrow \text{Fe}$ and CaCO_3 in dolomitic limestone is decomposed.

Zone 4 Smelting reduction zone where MnO dissolved in slag is partly reduced to liquid metal. Some silica is also reduced, and some carbon is dissolved in the metal.

¹ Hydrogen in the off-gas may also originate from volatiles in coke and electrode paste.

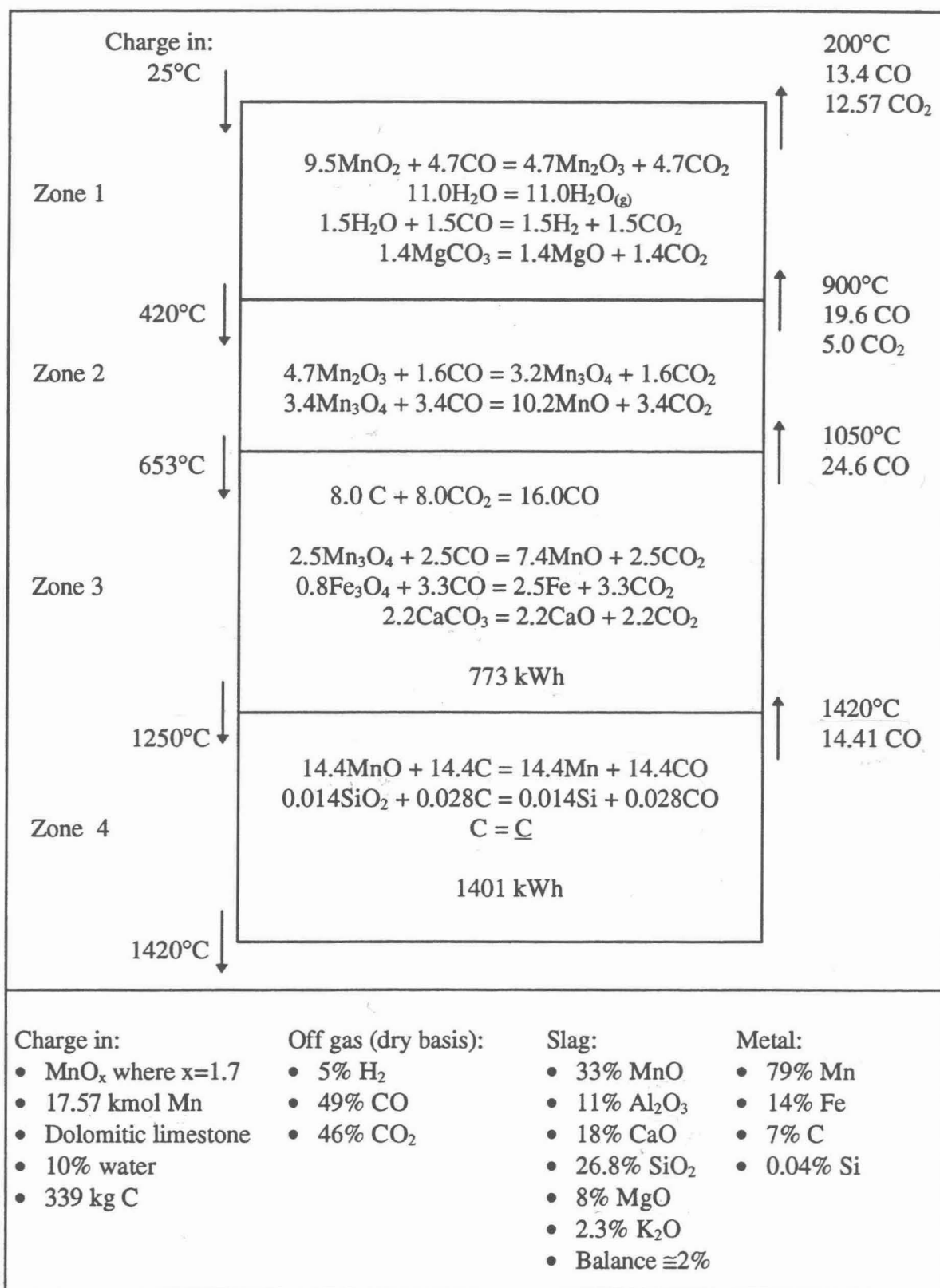


Figure 1. A staged heat and material balance for the ferromanganese process.

Raw materials are mixed for production of 1 ton of HC FeMn and 685 kg of slag with compositions as shown. Other assumptions are that 339 kg of carbon is used. The off-gas temperature is 200°C and the slag and metal temperature 1420°C. The hot gas leaving the smelting zone has a temperature of 1420°C, and its temperature is assumed to be 1050°C when it enters zone 2. The burden temperature is estimated to be 1250°C when it enters the smelting zone. This gives a burden temperature of 653°C between zone 2 and 3. If the gas temperature is 900°C at the junction between zone 1 and 2, the burden temperature will be 420°C. Heat exchange with hot gases and exothermic heat from reduction of MnO_2 will in this case be sufficient for complete drying and decomposition of hydrates and MgCO_3 . The different zones may overlap in industrial furnaces.

When heat losses are disregarded, there is an energy deficiency of 773 and 1401 kWh in zone 3 and 4 respectively. The total external energy requirement is then 2174 kWh/ton of alloy. Assuming a thermal and electrical efficiency of 80% (due to energy losses in transformers, conductors and electrodes and radiation/convection heat losses from the furnace shell), the total registered energy consumption will be about 2700 kWh/ton.

Carbonates in the burden have a double effect, first requiring energy for decomposition, 154 kWh, and next to increase energy and coke consumption according to the Boudouard reaction (10). In the example shown in Figure 1 this accounts for additionally 106 kWh and 26.4 kg of carbon.

The reactions in the smelting zone are well defined and independent on raw material properties. Energy requirement and carbon consumption in this zone is therefore fixed whereas the carbon and energy requirement in the direct reduction zone 3 varies, especially with the relative reactivities of ore and coke. In any case, energy requirement in the direct reduction zone will always account for a considerable share of the total energy input to the process. There are several ways in which this energy may be supplied:

- 1) Ohmic energy production due to current flowing directly between the electrodes. In FeSi production this is about 1% [1]. In FeMn furnaces it is estimated to be smaller, and ohmic energy will not be a significant contribution.
- 2) Heat transfer, mainly by diffusion and radiation from the coke bed where the main part of the electric energy is released.
- 3) Circulation of alkalis and Mn-vapour carrying heat from the smelting zone to the prereduction zones.

The alkali contents in manganese ores are often very high, in some ores up to 1.8% as K_2O . This is more than ten times the normal content in iron ores. According to Forsberg [2] the 'ignition temperature' of coke in the iron blast furnace is significantly lowered by alkalis, from 900-1000°C to 700-800°C, due to a catalytic effect. It is also established that circulating alkalis in the iron blast furnace increases the coke consumption.

Voskoboinikov et al. [3] followed the alkali accumulation in a blast furnace during a change from foundry pig iron- to ferromanganese-production. From the amount of alkalis in the off gas, they found, for steady state conditions, that the circulating alkalis were 204 kg per ton ferromanganese.

This was five times greater than the input of alkalis into the furnace. (204 kg equals 2.2 kmol calculated as K_2O .)

The total burden weight of a 36 MW furnace at Elkem Mangan, PEA is estimated by Sterneland to be about 1700 tons [4]. Accumulation of alkalis was followed after a relining of the furnace, and above 100 tons of K_2O was found to accumulate before a steady state was reached [5]. Assuming that recycling occurs within 50% of the furnace volume, the average K_2O content in the active part of the burden will be as high as 14% when it reaches the smelting zone. As an example, circulation of 5,75 kmol potassium per ton of FeMn will bring the alkali content in the burden up to about 15% K_2O and carry about 770 kWh from the hot to the colder zones. If the alkalis are accumulated in scaffolds, the calculated value of 14% may be too high, but even an alkali content of 5-10% will contribute significantly to the energy transfer. This illustrates the importance of the alkali circulation.

It is difficult to predict the net effect of the alkali circulation as regards energy and carbon consumption. On one hand transfer of heat to the gas reduction zone will extend the height of this zone and thereby increase the retention time. On the other hand we should expect a lowering of the ignition temperature of the coke and an earlier start of the energy and carbon consuming Boudouard reaction (10). In addition to the influence on energy and carbon consumption, it is known from iron production how alkalis reduce the strength of coke and pellets. In addition to crust formation, this reduction of strength will result in less permeability of the burden.

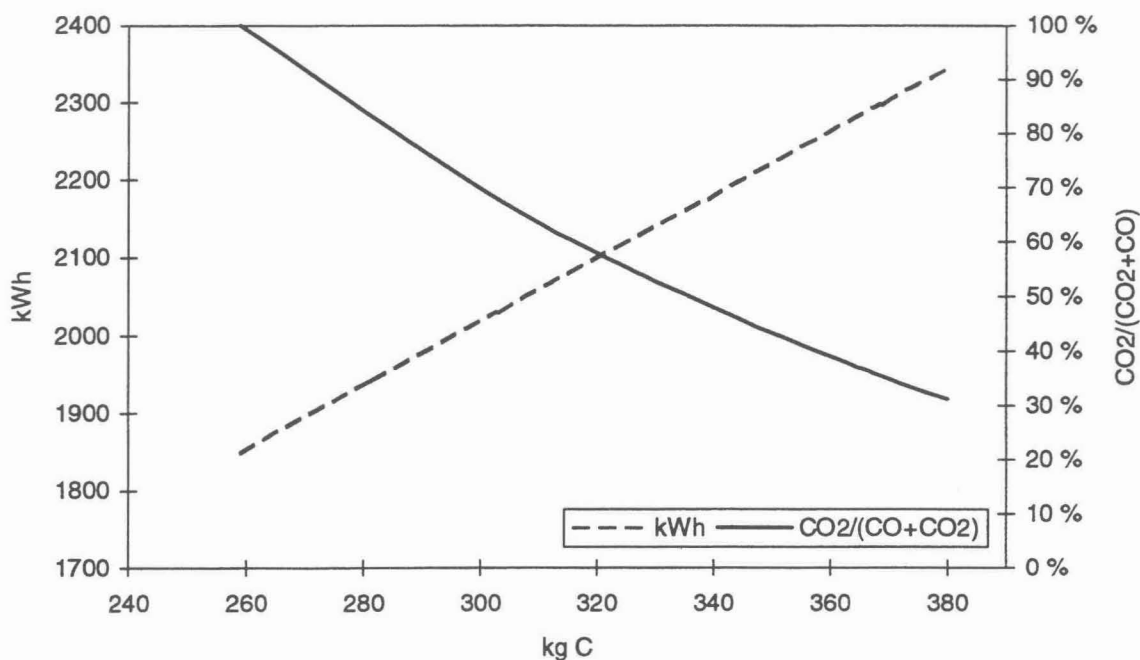


Figure 2. Energy consumption and off gas analyses versus carbon consumption.

There is a close connection between carbon and energy consumption and off-gas analyses as shown in Figure 2. The maximum and minimum amounts of carbon are given by the extent of the Boudouard reaction (10). These are for the ore blend above, 380 and 259 kg respectively. Maximum carbon consumption occurs when no gas reduction takes place, that is when all Mn_3O_4 is reduced in the direct reduction zone 3. Minimum occurs when the ore is completely reduced to MnO in the gas reduction zone. Then the off gas will not contain any CO.

The kinetics of the Boudouard reaction have been extensively studied during the years, among others also by Aderbigbe and Szekely [6] and Rosenqvist [7]. The reaction rate is governed by the temperature, the CO- and CO_2 -pressure and the coke reactivity. Within the term reactivity, parameters like sizing, open pore volume and chemical composition of the coke are included. Metallurgical cokes are low in reactivity. Aderbigbe and Szekely [6] studied a metallurgical coke from Inland Steel Company. The rate of the Boudouard reaction was insignificant below 950°C , but increased exponentially with further raising of the temperature.

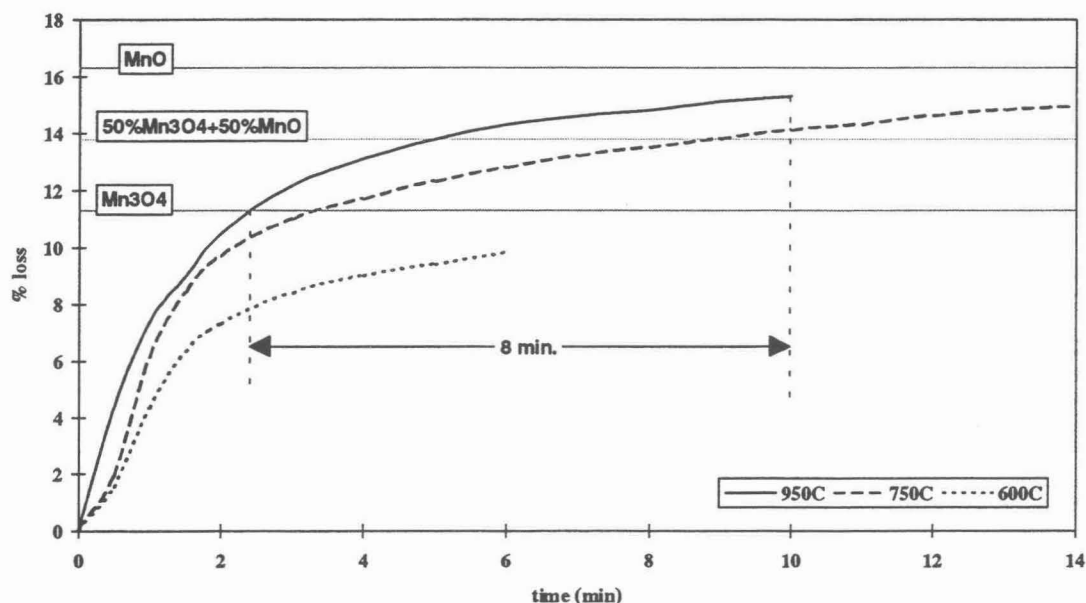


Figure 3. Weight loss of 10-12mm Comilog particles in CO gas, after Ommundsen [8].

The use of highly reducible ores leads to increased indirect reduction of Mn_3O_4 in the gas reduction zone 2 where the rate of the Boudouard reaction still is slow. Several investigations have been carried out to study the kinetics of manganese ore reduction. Ommundsen [8] measured the reduction rate of 10-12 mm Comilog ore particles, see Figure 3. As indicated in the figure 70-80% Mn_3O_4 was reduced to MnO in CO gas within 8 minutes at 950°C and 11 minutes at 750°C (not indicated). The time for complete reduction of Mn_3O_4 , at the same temperatures, is estimated by extrapolation of the curves to 15 and 27 minutes. Assuming a 5 m high furnace and a total retention time of 10 hours, the charge rate is 0.5 m/h. Under such circumstances 10-12 mm Comilog particles should only need a 12.5 cm high reduction zone at 950°C and 22.5 cm at 750°C . Assuming an averaged temperature of 600°C in the gas reduction zone, 2.1 m will be necessary to achieve

complete reduction to MnO . Twice as big particles should need about four times as long reduction time. It follows that a small sized ore with a high reducibility is beneficial.

Preheating and prereduction of the burden may be carried out outside the furnace as described for example by Tanabe [9]. The consumption of electric energy will be reduced but additional heat loss from the prereduction unit requires combustion of extra coal and the total carbon consumption will probably not be significantly changed. Contrary to iron production, separate prereduction units are not much used in production of ferromanganese, due to the high investment and operating cost.

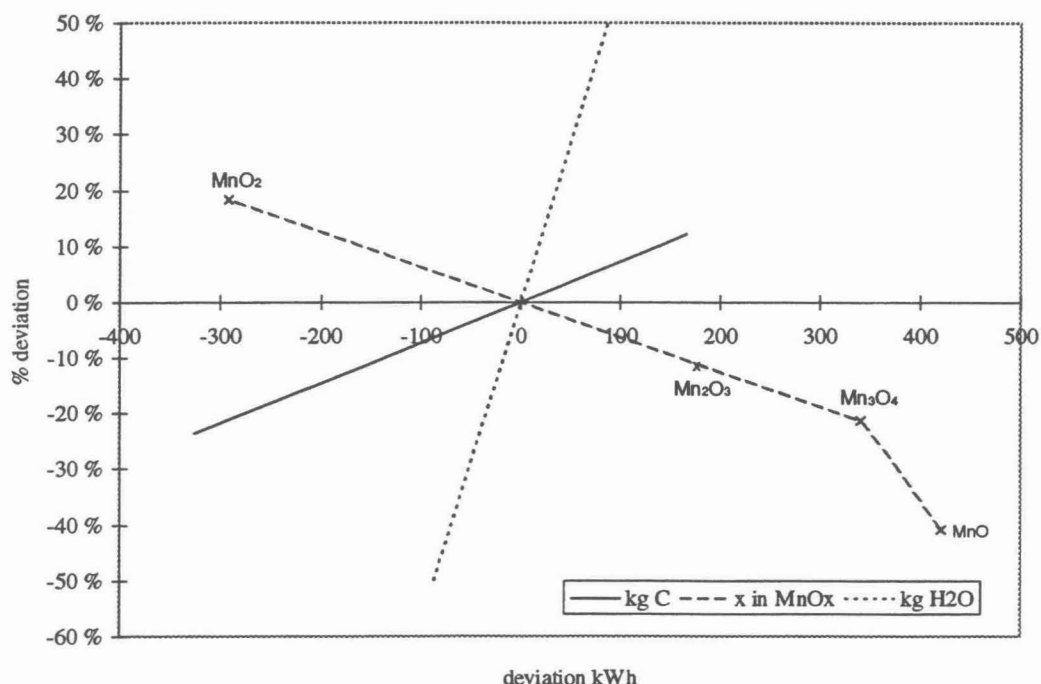


Figure 4. Effect of carbon consumption, oxygen level of ore and moisture content on energy consumption. Point zero represents the charge used in Figure 1, with $\text{MnO}_{1.7}$, 339 kg carbon and 225 kg water, which gives a total consumption of 2174 kWh.

To summarize, the influence of carbon consumption, available oxygen in the ore and moisture content on the electric power consumption is illustrated in Figure 4. The zero point in the figure represents the charge used in Figure 1, with $\text{MnO}_{1.7}$, 339 kg carbon and 225 kg water, which gives a total consumption of 2174 kWh. The figure shows how the energy requirement will change with the parameters mentioned.

An example is given for illustration:

Precalcined dolomitic limestone is used, decreasing the energy consumption with 154 kWh. In addition we change the raw material blend as follows:

- | | |
|--|----------|
| I. The water content is decreased with 50% | -87 kWh |
| II. Reduction of the carbon consumption with 11% due to change in relative reactivities of ore and coke, | -146 kWh |
| III. Increase the oxygen level with 18% by using MnO_2 . | -292 kWh |

These changes together will reduce the power consumption with 679 kWh and result in a total requirement of 1495 kWh per ton of alloy produced. Assuming an 80% efficiency this gives a total of 1869 kWh per ton of alloy produced.

CONCLUSION

A staged material and heat balance for the ferromanganese process have been discussed. It shows how the energy requirement in the furnace is closely connected to the Boudouard reaction. The extent of this reaction depends first of all on the relative reactivities of ore and coke. A highly reducible ore and a low reactive coke will separate the gas reduction zone from the Boudouard reaction, thereby increasing the indirect reduction of Mn_3O_4 and reducing the consumption of carbon and electric energy. These favorable effects may be counteracted by circulating alkalis in the furnace.

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