

STEELMAKING WITH IRON CARBIDE

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Introduction:

The concept of using iron carbide in steelmaking is not new. Tests were run several decades ago, using carbide made from ore, in steelmaking furnaces. The problem was that at that time, the need for the product was not clear and the economics of production were not favorable. In the early 1970's Frank M. Stephens, Jr., conceived the basis for the present process, and considerable development work has been done during the past decade to bring the carbide production process to its present state, with the first commercial unit now under construction.

Carbide Production:

The process utilizes the following overall reaction to produce Fe₃C from ore:



Figure 1 shows a flow sheet of the process. Hydrogen gas from a natural gas reformer is blended with natural gas to form the make-up gas for the process. The process gas is recirculated in a closed loop through the fluid bed reactor, a cyclone to remove most of the entrained solids, a heat exchanger, a packed tower to remove reaction product water, and back through the heat exchanger to a fired heater, and finally through the reactor again. The closed loop nature of the process means that virtually 100% of the process reagents are utilized by the process. The only exception is that a small "bleed" stream of the process gas is burned as fuel in the reheating step, in order to maintain the level of inerts in the process gas at an acceptable level. The quantity of the bleed stream is entirely dependent on the concentration of inert gases in the fuel supply.

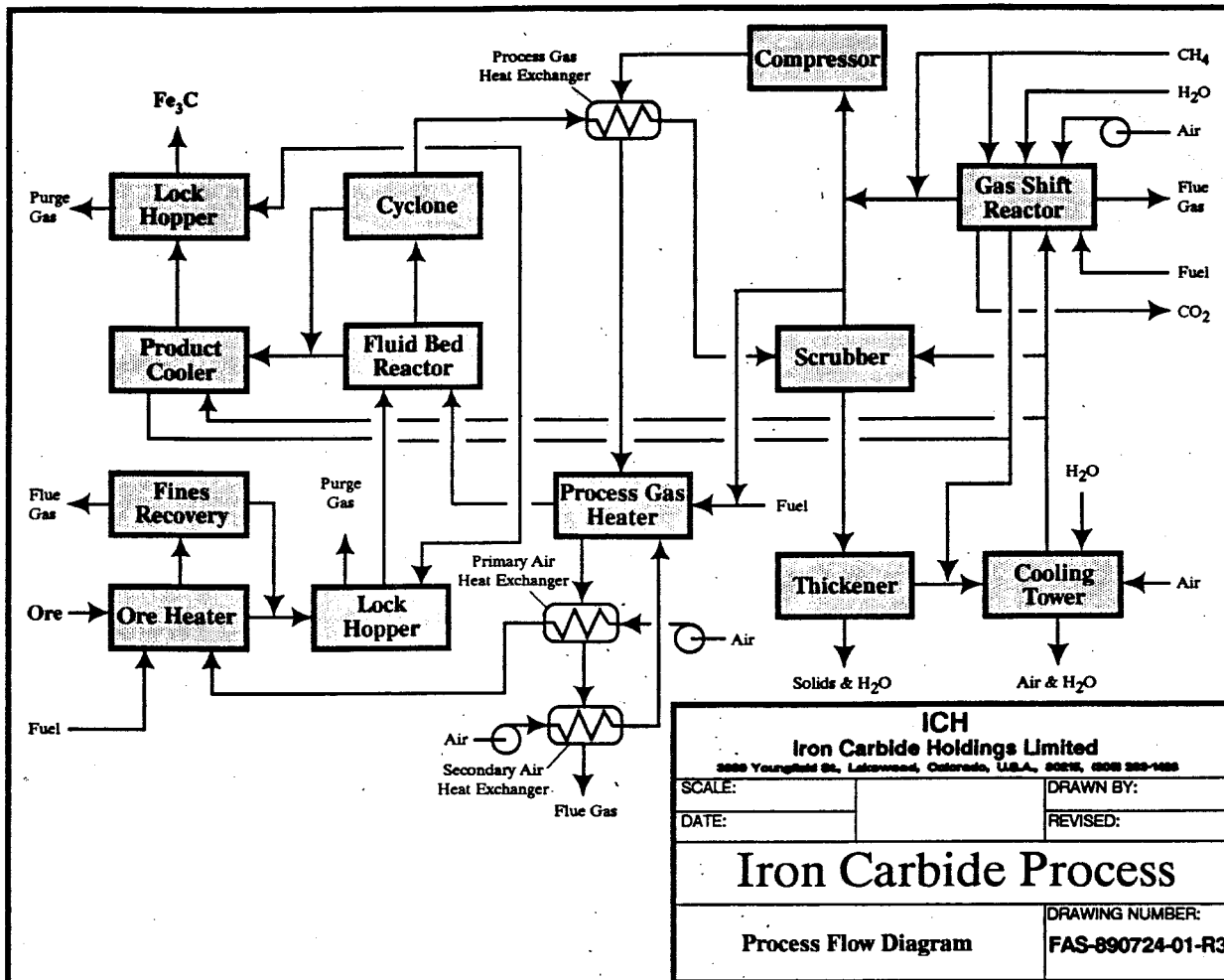


Figure 1: Process Flow Diagram for the Iron Carbide Process.

The reaction proceeds relatively slowly, so residence times in the reactor are long in comparison to roasting processes, but can be optimized by variations in temperature and pressure. The fluid bed is one of the advantages of the process, because the process can utilize fine ores directly, limiting the feed preparation needed. The ideal feed is a hematite ore sized between 1.0 and 0.1 mm. The overall reaction is slightly endothermic, so both the ore and the process gas must be preheated to temperatures slightly above the operating temperature of the bed to compensate for the heat of reaction. This also means that the process is inherently stable, and will cool down if those preheat temperatures are not maintained. Another characteristic of the process that differs from the past experience with fluid beds in iron ore reduction processes is that it operates at a relatively low temperature. This results in two advantages; it is thermally efficient, and there is no tendency for particle sticking and defluidization. In all of the operation of 2 ft. and 6 ft. diameter pilot plants there was never any problem with the bed fluidization. The carbide itself does not soften or melt at temperatures anywhere near the operating temperature of the bed, so it does not stick to anything. The quantity of heat required to produce a ton of carbide product is around

12 MM Btu's, about the same as most direct reduction processes. The product, however has an energy value in the steelmaking furnace, so the net energy to make steel via iron carbide is less than other routes. The product typically contains some residual iron oxide, Fe_3O_4 , and whatever gangue minerals that were in the concentrate feed. The process is designed to achieve 93% conversion of the oxide to carbide. Since the carbide is magnetic, it is possible to use dry magnetic separation to clean up the product, and gangue levels of 2% have been achieved on feed material that contained 5% gangue. A typical product analysis expected from a Canadian concentrate would be:

| | |
|-----------|-----|
| Fe_3C | 93% |
| Fe_3O_4 | 4% |
| Gangue | 3% |

This means that the material contains 6.3% carbon (as carbide) and 1% oxygen.

Another advantage is that the product is not pyrophoric. This makes storage and transportation easier in comparison to other products, and reduces the production cost by avoiding passivation treatment. The particle size of the product is only slightly smaller than that of the feed. While it might be possible to briquette it, this has not been done and is not recommended. It would require a binder, which often introduces impurities, such as hydrogen and sulfur, and the particles are not deformable, making the strength of such briquettes totally dependent on the binder. In any case since the carbide has a high melting point, and in practice dissolves in molten steel rather like sugar in coffee, it is preferable to introduce it into steel furnaces as a finely divided material. While this requires some additional equipment in EAF shops, it is a relatively small capital investment, and does not detract from the other advantages.

Steelmaking:

Iron carbide is an ideal material for steelmaking. It is low in residuals, contains no sulfur, is not pyrophoric, and is finely divided, which allows it to dissolve or melt rapidly. It can be injected into electric furnaces easily, and iron unit recovery is excellent; since it has excess carbon relative to any remaining iron oxide, reduction of the oxide is always complete. The loss to slag is restricted to that in equilibrium with the final carbon level in the bath, and there is effectively no loss in the form of entrained metal in the slag. Tests in four different plants have confirmed its usefulness in this mode.

The real potential of iron carbide, however, lies in its possible use as the sole feed for a conceptual new, continuous steelmaking process⁽¹⁾. In this process, iron carbide is fed into a reactor similar to that employed by the QSL process for lead production (Figure 2). The carbon is removed from the bath using oxygen, burned to CO_2 , and liquid steel is tapped continuously from the discharge end, while counter currently flowing slag is tapped from

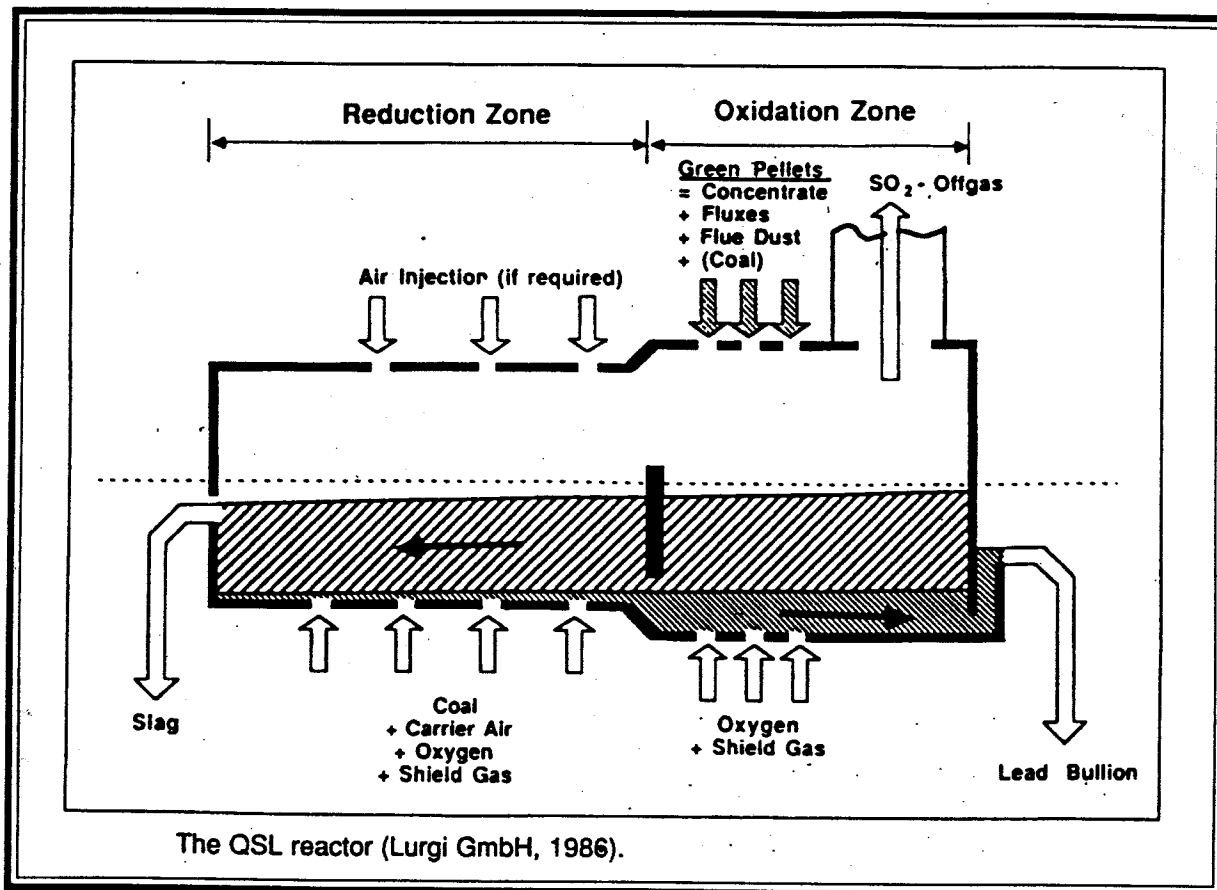


Figure 2: Reactor used by the QSL process for lead production.

the opposite end. The heat and material balances for such a process indicate that the process is possible. In this paper we will examine them, and discuss the benefits, as well as the design problems to be addressed.

The steelmaking vessel is assumed to be cylindrical in cross-section, considerably longer than it is wide (Figure 3). As a comparison, the QSL reactor for lead is four (4) meters in diameter and forty-two (42) meters in length. The vessel is designed to rotate 90 in one direction, so as to bring the bottom tuyeres out of the bath for maintenance. It is also built on a slight incline from one end to the other, to ensure the flow of slag relative to the metal bath. It is not in motion during operation, lest any comparison with the Kaldo process be thought appropriate. Savard-Lee type injectors for oxygen or inert gas are located along the bottom, and post-combustion lances are located in the roof, also spaced along the length of the vessel. Carbide can be fed either through a roof port, through an end port, or through submerged injectors. Figure 4 shows the entire system. The "carbide" feed can either come directly from the carbide production process at near its exit temperature of 500°C or it can be preheated by the process exhaust gases, which have enough energy in them to bring it to 500°C.

Figure 3: Steelmaking vessel for continuous production using iron carbide feed.

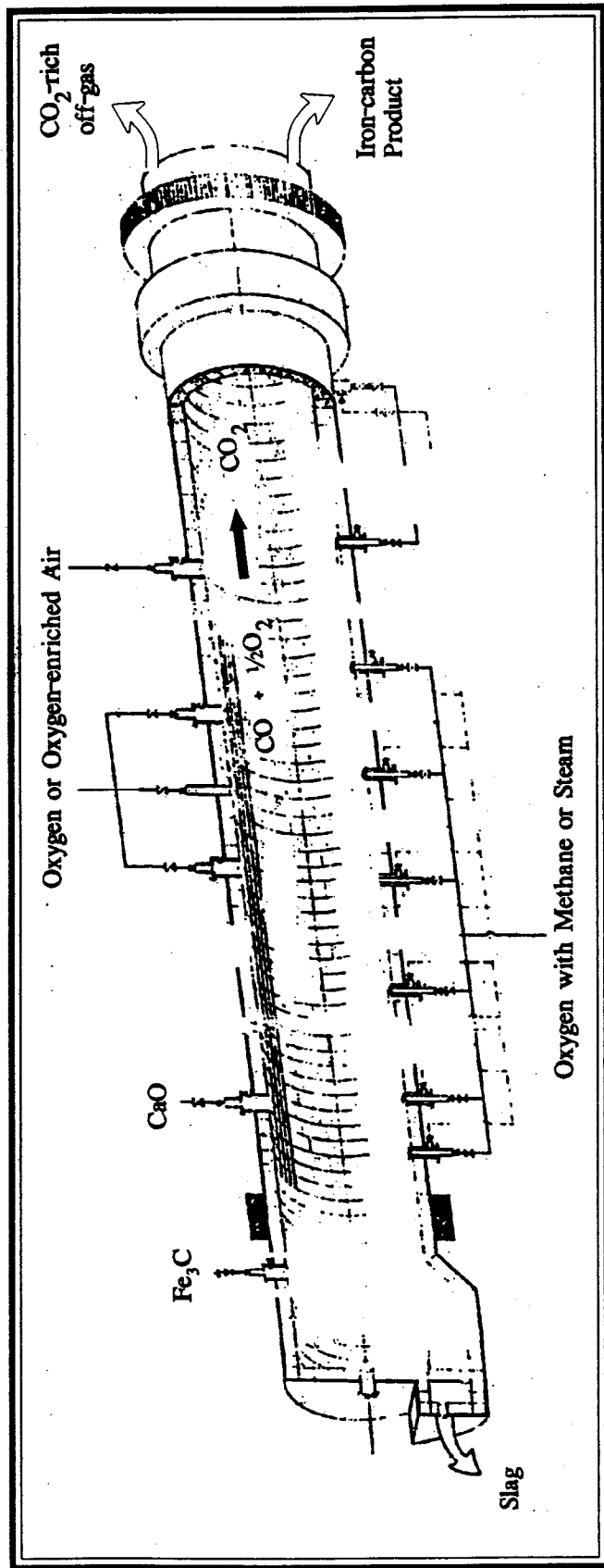
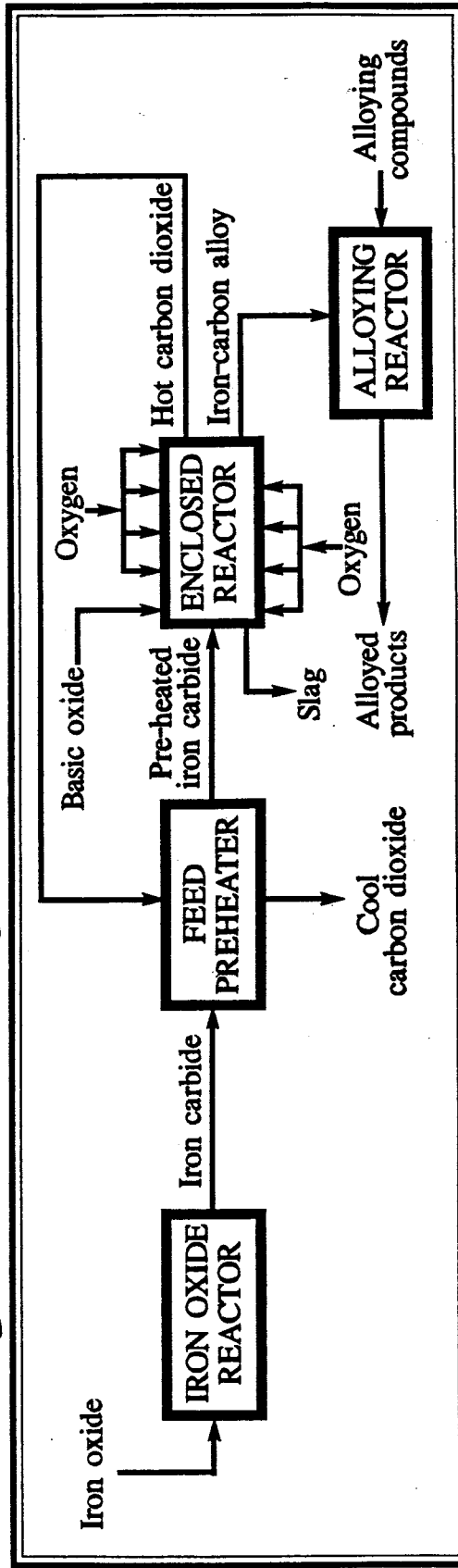


Figure 4: Schematic diagram of the entire continuous steelmaking system.



The reactions in the QSL lead process involve the roasting of lead sulfide concentrate to lead oxide, and the reduction of lead oxide to lead metal, all in the single vessel. This requires that a significant oxygen potential gradient be maintained in steady state from one end of the vessel to the other, since the roasting reaction requires a high oxygen potential, and reduction requires the opposite. The reduction is accomplished at the slag discharge end, using finely divided coal injected through the Savard-Lee injectors. The lead oxide-rich slag is quite corrosive to refractories, so chrome-magnesite refractory has been used. The slag flows counter-current to the lead bath and as the lead oxide is progressively reduced, it exits the vessel with a low PbO content. The roasting reaction is highly exothermic, and the CO from the reduction reaction is post-combusted with oxygen, releasing even more heat.

Gaseous fuel can be injected through the tuyeres if the local heat demands require it. The gases exiting the vessel are concentrated in SO₂ and CO₂, requiring a smaller than average gas treatment and sulfuric acid plant. The overall process is essentially autogenous. Successful operation of the full-scale process has been achieved at the plants of Berzelius Stolberg and Korean Zinc⁽²⁾.

The steelmaking process presented here is essentially simpler than the lead process, since it requires only oxidation and not reduction. There will naturally be an oxygen potential gradient, since the carbide feed will form a high carbon content bath at the feed end of the reactor, and will reduce the iron oxide content of the slag at that end to a low level prior to its discharge. The carbon level will progressively be reduced by oxygen injection as the bath moves toward the discharge end. The carbon monoxide (CO) released from the bath will be burned to carbon dioxide (CO₂) in the space above the bath. At the discharge end, the iron bath will have been reduced to the carbon level desired for steel grades. The iron-carbon bath will be tapped into ladles which will go to ladle treatment stations for alloying and ladle treatment. Since there is no arc involved, hydrogen and nitrogen levels should be low comparable to those from a Q-BOP furnace, and since there is no sulfur entering the system, desulfurization should not be needed. Therefore, ladle treatment should be simple.

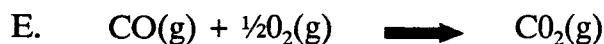
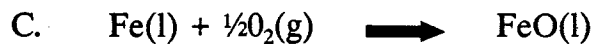
Can a carbon gradient be maintained along the length of such a reactor? Howard Worner presented data recently, based on test work done in the 1960's, that showed that such a carbon gradient was able to be maintained in steady-state in the WORCRA process reactor, in which more complicated reduction and oxidation was accomplished⁽³⁾. The fact that the lead process works, in steady state, in a more thermodynamically difficult process is further evidence that such a gradient, in the relatively simpler process envisioned here, can be achieved. This possibility is helped by the fact that there can be adequate spacing between bottom injectors, coupled with the net flow in one direction, of the bath, to allow the process to work as a series of mixer-settlers. The initial belief in the case of the QSL process that a series of dams would be needed to prevent backmixing has proven to be wrong, and the dams are being removed from that vessel.

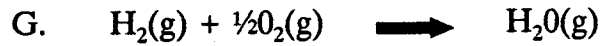
The energy and material balances are based on the following assumptions:

1. The iron carbide has 4 to 6% Fe_3O_4 , 90 to 92% Fe_3C , 3% SiO_2 , 1% $(\text{Ca},\text{Mg})\text{O}$, and enters the reactor at either 25°C (77°F) or 500°C (932°F).
2. The steel has a carbon content between 0.1 and 0.4% and leaves the vessel at 1600°C (2912°F). All calculations result in the production of 1.0 metric tonne of liquid steel.
3. The slag has a CaO/SiO_2 ratio of 2, and leaves the reactor at 1650°C (3002°F). The slag FeO composition depends on carbon content of the steel according to:

| %C | %FeO |
|------|------|
| 0.05 | 35 |
| 0.10 | 25 |
| 0.20 | 12 |
| 0.40 | 6 |

4. The off-gases leave the reactor at 1727°C (3140°F).
5. The ratio of O_2 to CH_4 injected through the tuyeres is 10:1.
6. If the temperature of the flame in the freeboard space is too high using pure oxygen, oxygen enriched air can be used. In that case N_2 increases the gas volume and absorbs some of the heat.
7. If not enough heat is available to satisfy the heat balance additional natural gas can be injected into the freeboard via oxyfuel burners to supply the additional heat required.
8. FeO in dust equals 1% of steel produced.
9. The reactions that take place are:





The balances that must be satisfied are:

H. Fe balance:

$$\begin{aligned} W_{\text{Fe}} \text{ in } \text{Fe}_3\text{C} + W_{\text{Fe}} \text{ in } \text{Fe}_3\text{O}_4 \\ = W_{\text{Fe}} \text{ in steel} + W_{\text{Fe}} \text{ as FeO in slag} + W_{\text{Fe}} \text{ in dust} \end{aligned}$$

I. Carbon balance:

$$W_{\text{C}} \text{ in } \text{Fe}_3\text{C} = W_{\text{C}} \text{ in steel} + W_{\text{C}} \text{ in } \text{CO}_2 + W_{\text{C}} \text{ in CO}$$

J. Oxygen balance:

$$\begin{aligned} W_{\text{O}_2} \text{ in } \text{Fe}_3\text{O}_4 + W_{\text{O}_2} \text{ injected via tuyeres} + W_{\text{O}_2} \text{ injected in freeboard} \\ = W_{\text{O}_2} \text{ in } \text{CO}_2 + W_{\text{O}_2} \text{ in CO} + W_{\text{O}_2} \text{ in } \text{H}_2\text{O} + W_{\text{O}_2} \text{ in FeO in slag} + W_{\text{O}_2} \text{ in dust} \end{aligned}$$

K. Silica balance:

$$W_{\text{SiO}_2} \text{ in feed} = W_{\text{SiO}_2} \text{ in slag}$$

L. Lime balance:

$$W_{\text{CaO}} \text{ in feed} + W_{\text{CaO}} \text{ added} = W_{\text{CaO}} \text{ in slag}$$

M. Hydrogen balance:

$$W_{\text{H}_2} \text{ in } \text{CH}_4 = W_{\text{H}_2} \text{ in } \text{H}_2\text{O} \text{ in off gas}$$

N. Nitrogen balance:

$$W_{\text{N}_2} \text{ in air} = W_{\text{N}_2} \text{ in off gas}$$

- O. **Heat Balance:** The base temperature for the heat balance is taken as 1873°K (1600°C, 2912°F), and all heats of reaction are calculated at that temperature. All reactants are brought to that temperature and the energy required to do so is calculated. All reaction products are then taken to their exit temperatures, and the energy required to do that calculated. In the cases presented here, the gas exit temperature was taken as 1727°C (3140°F).

$$\begin{aligned}
 & (H_{1873} - H_{298})\text{CaO charged} + (H_{1873} - H_{298})\text{O}_2 + (H_{1873} - H_T)\text{Fe}_3\text{C} \\
 & + (H_{1873} - H_{T_{in}})\text{Fe}_3\text{O}_4 + (H_{1873} - H_{T_{in}})\text{SiO}_2 + (H_{1873} - H_{T_{in}})\text{CaO} \\
 & + (H_{1873} - H_{298})\text{CH}_4 + (\text{Sum of Heats of Reactions A-G})_{1873} \\
 & + (H_{T_{gas}} - H_{1873})\text{CO} + (H_{T_{gas}} - H_{1873})\text{CO}_2 + (H_{T_{gas}} - H_{1873})\text{H}_2\text{O} \\
 & + (H_{1923} - H_{1873})\text{slag} + (H_{T_{gas}} - H_{298})\text{N}_2 + (H_{T_{gas}} - H_{1873})\text{FeO dust} \\
 & + \text{Heat Loss} = 0
 \end{aligned}$$

The heat loss is based on the measured heat loss from the QSL reactor and so the heat loss from the reactor is taken as 90000 Kcal/tonne for a vessel producing 30 tonnes per hour. It would be less for a larger production vessel. The balance is closed by calculating the amount of CO that must be left unburned in order to close the balance, or, if not enough energy is available from complete combustion of the CO calculating how much additional CH₄ and O₂ would be needed to close the heat balance.

The output from the simultaneous solution of all of the equations gives the consumption of all materials per tonne of liquid steel and the various energy requirements or contributions from each reaction. Table 1 shows the results for two feed "carbide" compositions and various other conditions. Case 1 shows that the process can be autogenous if the feed carbide is preheated to 500°C and if most of the heat of reactions E and G is transferred to the bath. Figure 5 is a Sankey diagram showing the heat balance for the case where the carbide feed containing 92 percent Fe₃C is preheated to 500°C. Case 2 shows how the balance changes if the postcombustion enriched air is preheated somewhat. Case 3 illustrates what the effect of blowing to a higher tap carbon does to the balances, and Case 4 shows the effect of a lower Fe₃C content in the carbide feed on the balances and the amount of extra CH₄ required. This latter is one reason for the desirability of having as high a degree of conversion of the ore to carbide as possible. If the gangue content is reduced, the heat balance is improved slightly. If the carbon content in the steel is less than 0.2, it is also improved.

Figure 5

Sankey Diagram

for Continuous Steelmaking with 92% Fe₃C

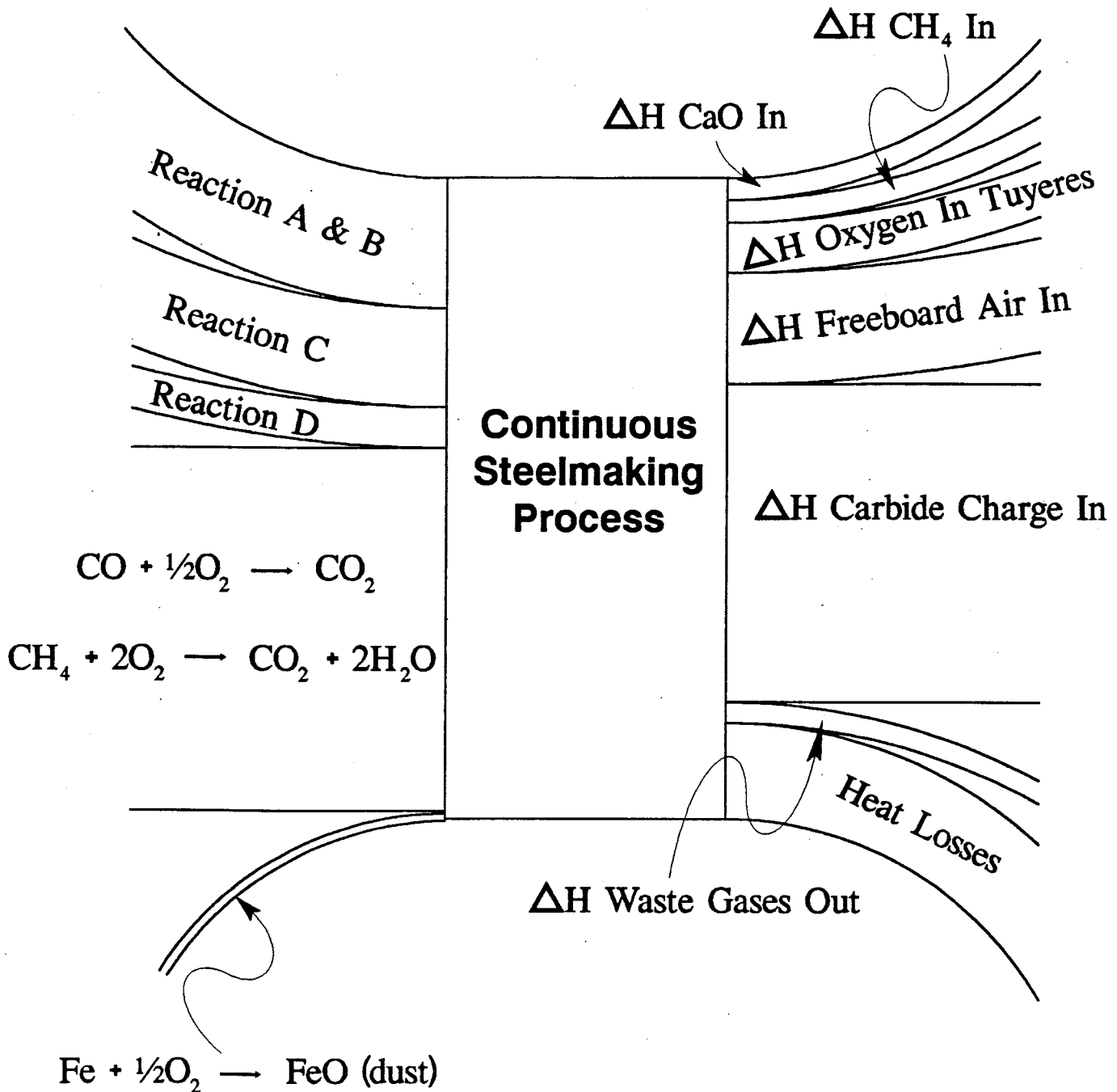


TABLE 1

| Results of Calculated Material and Energy Balances. | | | | |
|---|--------|--------|--------|--------|
| (Basis Is production of 1000 Kg. liquid steel. Carbide refers to raw material in Assumption 1.) | | | | |
| | Case 1 | Case 2 | Case 3 | Case 4 |
| % C in Steel | 0.2 | 0.2 | 0.3 | 0.2 |
| % Fe ₃ C in Carbide | 92 | 92 | 92 | 90 |
| % Fe ₃ O ₄ in Carbide | 4 | 4 | 4 | 6 |
| Temperature of Carbide (C) | 500 | 500 | 500 | 500 |
| Temperature of Air (C) | 25 | 327 | 25 | 25 |
| N ₂ /O ₂ Volume Ratio in Air | 2:33 | 2:33 | 1:50 | 2:33 |

| | | | | |
|--|------|------|------|------|
| Charge Wt. Carbide (Kg) | 1149 | 1149 | 1141 | 1154 |
| Charge Wt. Lime (Kg) | 57 | 57 | 57 | 58 |
| Total Oxygen req'd (Kg) | 222 | 213 | 206 | 254 |
| Weight Methane req'd (Kg) | 12 | 12 | 11 | 18 |
| Weight N ₂ in Air (Kg) | 209 | 193 | 122 | 233 |
| Weight Steel (Kg) | 1000 | 1000 | 1000 | 1000 |
| Weight Slag (Kg) | 121 | 121 | 112 | 122 |
| Weight CO ₂ out | 282 | 261 | 256 | 313 |
| Weight CO out | 2 | 15 | 14 | 0 |
| Weight N ₂ out | 209 | 193 | 122 | 233 |
| Weight H ₂ O out | 27 | 27 | 25 | 38 |
| Weight Dust out | 10 | 10 | 10 | 10 |
| Heat Req'd by Input Materials (Mcal.) | 512 | 482 | 467 | 526 |
| Heat Req'd in Output Materials (Mcal.) | 24 | 22 | 19 | 24 |
| Heat of Reactions (Mcal.) | -626 | -594 | -576 | -640 |
| Heat Loss (Mcal.) | 90 | 90 | 90 | 90 |

The degree of post-combustion is variable, reaching 100% when all of the CO is combusted. This should be quite possible and can be controlled by the amount of oxygen introduced along the vessel. The heat transfer efficiency required is about ninety-five (95) percent. Is this heat transfer efficiency possible? One of the reasons for the longer vessel, completely enclosed, is that it allows a much greater residence time of the hot gases in the vessel and a larger surface area for radiation heat transfer to take place than does an EAF or BOF-type vessel. In effect, it is more like a kiln, which is a good heat transfer device. Heat transfer efficiency is also enhanced by convection when there is a submerged tuyere that ejects slag and metal into the gas stream. By spacing the tuyeres properly, the opportunity exists for maximizing this transfer. Further, some of the post combustion oxygen can be introduced in the slag layer to enhance heat transfer. Heat transfer efficiencies of between ninety (90) and one hundred (100) percent have been reported by Katayama, et al⁽⁴⁾ for a bath smelting process using a BOF vessel with top and bottom blowing and having a thick slag layer.

Hardle et al⁽⁵⁾ reported heat transfer efficiencies of eighty-five (85) percent for the HISMELT pilot reactor, with post-combustion percents of between forty (40) and sixty (60), with no decrease in efficiency with increasing post-combustion. This vessel is somewhat closer in shape to that of the present concept, but is still not as long in comparison to diameter. While no definitive answer can be given to the question, there seems to be good reason to believe that it may be possible.

If the process works, what will be the benefits? Why should we be interested? The principal driving forces for any process development have to be related to commercial situations. One has to be the possibility of a process that will produce a product less expensively on either/or both an operating or capital cost basis than existing processes. Another has to be that it will solve extraneous problems, such as environmental problems or energy concerns. Referring to the material consumption figures in Table 2, reasonable cost estimates can be made of the operation. The cost of carbide feed will obviously vary, depending on location and gas and ore cost, but a reasonable number would be \$100 per tonne, including depreciation.

TABLE 2

| | Kg/tonne steel | Cost/Kg | Cost/tonne steel |
|-------------|----------------|---------|------------------|
| "Carbide" | 1140 | \$0.10 | \$114 |
| Lime | 60 | 0.05 | 3 |
| Oxygen | 200 | 0.04 | 8 |
| Natural Gas | 10 | 0.10 | 1 |
| | | Total = | \$126 |

Labor should be very low, since only one or two operators are needed, plus some part time maintenance. Allow \$2 for labor and supervision. Refractories will add \$2 or \$3 per ton. Even with some other minor costs, and depreciation on the order of \$5 per ton, one can envision a total cost of liquid steel, including depreciation for all of the plant, from ore to steel, of \$135-140 per metric tonne. The installed capital cost could be between \$225 and \$275 per annual tonne of capacity, for the entire route.

Like the iron carbide production process, the steelmaking process would be environmentally friendly. Since the reactor is enclosed, with no electrode openings or difficult gas hood seals, the volume of gas is kept small; only that generated by oxidation of the carbon. This keeps the size and cost of pollution control equipment low. The gas is completely burned to and is rich in CO₂, which could be recovered for other uses. If air is not used in the freeboard combustion, no NO_x should be formed. Steam could be used as a coolant for the gases instead. Finally, from an environmental standpoint, the total amount of CO₂ released to the atmosphere per ton of liquid steel made is 50% of that from any other present steelmaking route, when the CO₂ from burning coal to produce electricity is considered.

Clearly, this is a proposed process. There are engineering and refractory challenges to be considered and resolved. But they are less daunting than those of any direct smelting process. The volume of slag involved is small, and since no sulfur is introduced with the raw materials or fuel, the reactor could be run with a lower basicity slag, allowing less erosion. The FeO content would only be high at the steel exit end of the vessel, possibly requiring special refractories in that zone. On the other hand, since the vessel can be rotated, the slag erosion area can be exposed rather easily and refractory repair can be done under operation with refractory guns through access ports. Carbide can be introduced through the top, end or via submerged injectors, perhaps located at various points along the vessel. Local heat balances can be optimized to provide for balanced combustion of CO along the vessel. All of these issues must be addressed in the next stage of design, but the potential benefits appear attractive enough to warrant taking the next steps toward reality. ■

References:

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