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THE POTENTIAL FOR USE OF IRON CARBIDE AS AN ELECTRIC FURNACE RAW MATERIAL

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Introduction

There has become increasing interest in and need for low-residual iron unit sources for use in electric furnaces, as the use of electric furnaces to produce steel for flat products has increased. This has increased the potential for various direct reduced iron products to enter the market. One such product is iron carbide, Fe_3C . This paper will examine the use of such material in the charge mix for an electric furnace.

Theory

Iron carbide is a compound with a small heat of formation (1,2). It is therefore not extremely stable at steelmaking temperatures, and dissociates easily. In a steel bath with low carbon content, such as from molten scrap containing, say, 0.2% C, it dissolves quickly, since it contains the stoichiometric 6.8% C and therefore the driving force for dissolution is large. The carbon liberated in the bath is thus available to react with oxygen from either an oxygen lance, an exothermic reaction, or from residual iron oxide contained in the carbide feed. As Swanson(3) has indicated, the anticipated material from a commercial iron carbide process will have some Fe_3O_4 in it, so that that source of oxygen will be intimately mixed with the carbon from the carbide and will therefore react readily to form CO and Fe, an endothermic reaction. The thermal effects of these reactions can be calculated, along with the energy to bring the material to steelmaking temperatures. This theoretical data can be combined with other thermodynamic data(4,5) to build a mathematical model of the melting process. Such a model can be used to study the effects of the use of iron carbide and other direct reduced materials on the performance of an EAF.

The basis of such a model was published by Geiger(5) in 1980, and the basic equations have not changed since that time. Many refinements are possible to the basic model, which consists of simultaneous material and energy balances that must be satisfied, along with restrictions that can be placed on the amounts of the various materials that can be

used In the charge. The energy balance must be closed by assuming a value for the heat losses from the furnace, McIntyre and Landry(6) have recently published a review of the energy balances in EAF'S, and Garbutt(7) has recently published energy balances on two arc furnaces, and estimates of the heat losses may be made from their data. Thus, the basic equations(6) are altered by the presence of iron carbide only by the addition of the energy terms to heat and dissolve the carbide and the energy to react with iron oxide. The carbon balance, of course, includes the carbon from the carbide or DRI as a source of carbon, as well as or in place of the carbon from coke or other carbon sources in the charge. The Iron balance includes the iron units from iron carbide and from DRI in the iron balance, and any gangue material that comes with the carbide or DRI is in either the silica or lime balance. Minor amounts of other acid or basic gangue constituents are lumped In with these materials in the balances. Table I gives the list of the basic reactions assumed. and Table II gives the basic equations used.

Such a linear programming model can be used to study the effects of various limits on residuals, sulfur, or phosphorous, or on the mix of materials that can be used in the charge to a furnace. It can also be used to compare the potential energy consumption of the process with different mixes of raw materials, for a given level of heat loss. Many other refinements of the model could be made, to take account of special practices, such as foamy slag, post-combustion lances and the like. While not precisely accurate, it can give a good indication of the magnitude of the effects expected. The results can be tuned to a particular furnace. The primary method of doing this will be to adjust the heat loss term, which will be more or less constant for a given furnace as long as heat times are similar. The comparison of the effects of changes in charge practice will therefore be valid.

For purposes of this model, assumptions of the chemical analyses and costs of raw materials and products have to be made. Those used in this case are given in Table III. The basis for the solution is the production of 1 tonne of steel,

Results of Calculations

The calculations result in solutions to the energy and material balances that satisfy all the equations simultaneously, and at minimum cost, given the constraints put on the use of various materials and the assumed costs used. (Other solutions for each case are, of course possible, but will always result in a higher total cost for materials and energy.) The electrical energy requirement to provide whatever energy is needed, in addition to the chemical energy from carbon oxidation, is clearly affected by the energy needed to carry out the reduction of whatever iron oxide is charged to the furnace, either in DRI, HBI, or iron carbide materials. The more of this oxide is added., the more electricity is needed. Typically, the use of DRI has required about 1 to 1.5 Kwh/tonne additional energy per 1

percent DRI in the charge(5,8), and the calculations for a 93% metallized DRI agree with this (Figure 1). Figure 1 also illustrates the reduction in electrical energy required as iron carbide containing 4% Fe_3O_4 is added to the charge.

The reduction of the oxide in DRI also requires that additional carbon, in the form of coke, be added to provide the reductant. If not added, the recovery of iron units from DRI decreases. And when added, the coke brings with it additional silica and sulfur as well as requiring energy to dissolve. In the case of iron carbide, the need for extra coke is eliminated, if the conversion of oxide ore to carbide is complete enough. With a 4% Fe_3O_4 content, there is only 1% oxygen in the material, so that only 0.75% carbon is required to react with it, leaving over 5% carbon free to participate in the normal carbon - oxygen reaction or to reduce FeO in the slag. This helps explain the observation of additional recovery of iron from the slag(3). As the degree of conversion of the ore to carbide decreases, however, eventually the point is reached where all of the carbon is consumed in the oxide reduction process. The point at which the energy effect is neutral, where the available energy from normal carbon oxidation is offset by the energy to reduce the oxide in the material is at 88% conversion of the hematite ore to carbide. If the conversion to carbide is less than that, there will be an energy penalty, similar to that for DRI.

Figures 2 and 3 Illustrate some typical results of the linear programming calculations. It is interesting to note that there is a price ratio of iron carbide to DRI at which the choice of carbide or DRI changes (carbide's extra value for energy content alone is on the order of \$7 when electricity costs \$0.04), and also that the desirability of the use of carbide changes with the cost of electricity, clearly becoming more desirable as the cost of electricity increases. Care should be taken, however, in interpreting these data, because in some cases, the use of a minimum or maximum amount of one material or another was restricted, or the chemistry of the material was altered to study its effect. The reason for showing them is to illustrate the point that (1) the substitution is complicated by many factors, and (2) combinations of DRI and iron carbide can make economic sense.

Reported Experience

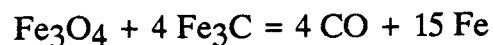
As has been reported, (3,9,10,11) iron carbide product from pilot plant tests has been tested in five electric arc furnaces, ranging from 4 tonne to 110 tonne. The percentages of material used ranged from 11% to 50%. The material was Injected with either nitrogen or air as the carrier gas(3.15), or was added in bulk. Injection rates varied from 10 to 400 kg/min(3.9.10) in all cases, iron yields were reported to be very good, and no significant problems were encountered, except in one case,, where oxygen was used as the carrier gas in a relatively small diameter lance pipe, and lance plugging was reported. Since the average particle size(3) was between 0. 15 and 0.2 mm the time to dissolve can be estimated using the model of Wright and Baldock (10.12). The time is less than one second. Laboratory tests have confirmed this.

As; noted by others(3), the material from the pilot plants was not fully converted to carbide, with an excessive amount of iron oxide present, resulting in the expected negative thermal effects,, but nevertheless giving very good iron yields. Since the commercial product is expected to be of higher quality, there is no reason to believe that the thermal effects will be other than as predicted by the mathematical model presented above. Of course the predicted beneficial energy effects of the material do require that the carbon from the carbide be oxidized with oxygen, If the material is simply injected, and no oxygen is blown in simultaneously or immediately afterwards, the bath will be cooled due to having to provide the energy to heat the carbide up to the bath temperature. It is suggested that the injection should be carried out via a submerged lance through the side wall and a separate oxygen lance be utilized to oxidize the dissolved carbon more or less simultaneously.

The question of how much carbide can be injected is often raised One answer can be found in the experience with the injection of DRI fines at Hamburger Stahlwerk(13). These fines are injected at a rate of 1500 Kg./min with a potential of 2000 Kg/min, through a 100mm lance. The carrier gas in this case is air, but because of the potential for hydrogen generation from moisture in the air, the DRI material in the storage vessels has to be kept under inert process gas. This precaution should not be needed for iron carbide. There is no reason why similar rates of injection cannot be utilized with Iron carbide,, and multiple lances could increase the total injection rate. As noted above either nitrogen or air can be used as the carrier gas..

The effects of iron carbide injection on lowering nitrogen levels in the steel have been noted elsewhere(3,14,15), Table IV summarizes the results(14). The total volume of CO from the carbide particles depends on how much carbide is injected. Assuming that all of the carbon from the carbide will be evolved as CO, injection of 0.1 tonne of carbide per 1 tonne of steel will result in 0.000875 tonnes of CO evolved, or 132 ft³ per tonne. Compare this to the typical evolution of 50 to 180 ft³ of CO per ton for EAF decarburization practices. Figure 4 relates the total change in nitrogen level to the total evolution of CO for various EAF practices(14).

The better than average results cannot be explained by considering only the total CO evolution per tonne, nor do they reflect the rate at which these levels were achieved, which was very fast. Both the rate effect and the better than average total effect are the result of the tremendous surface area created by the reaction of the carbon and oxygen associated with each particle of iron carbide, since each particle contains some iron oxide and carbide, the reaction



liberates CO. Depending on the amount of oxide present, the relative volumes of gas bubbles from this source are important, compared to that from ordinary oxygen injection. If each particle contains 1% oxygen in the form of 4% Fe₃O₄, and it is all reacted with Fe₃C to form CO, then each particle, which weighs about 1x10⁻⁵ grams, will form an 1x10⁻³ cm³ CO bubble, with a surface area of 5.5x10⁻² Cm² per bubble. At an injection rate of 400 Kq per minute, this would result in generation of a total surface area of CO bubbles of about 2x10⁹ cm²/min. There are no correlations that independently predict the surface areas from gases normally injected through submerged lances. However, there are correlations that predict the volumetric mass transfer coefficient, which is the product of total bubble area, A, times mass transfer coefficient, k_L, and there are independent estimates of k_L, and so the area A can be inferred for submerged lance injection. The data for estimating the volumetric coefficient are not very consistent, and seem not to have been measured for the exact conditions in the EAF, but if one uses the highest value reported for injected gas-metal systems, on the order of 10³ cm³/sec. for the volumetric coefficient, and the data of Takahashi, et al(16) for a typical value of k_L of 3x10⁻²cm/sec. for nitrogen desorption, the area of gas-liquid interface from a lance pipe blowing oxygen into a bath can be estimated to be on the order of 10⁴- 10⁵ cm². For the same k_L, the volumetric mass transfer coefficient for the case with fine bubbles from iron carbide can be estimated to be on the order of 10⁷ cm³/sec. Therefore, the potential for reaction to remove nitrogen (and presumably also hydrogen) is quite probably several orders of magnitude greater, since the kinetics are proportional to the volumetric mass transfer coefficient according to

$$d(\%N)/dt = C*(k_L * A)[(\%N)_{equil} - (\%N)_t]$$

Another factor to consider is that the smaller the bubbles, the longer the residence time. The bubbles formed at the end of a typical submerged oxygen lance are estimated to be on the order of 10 mm in diameter(17). From Stokes law, the rise velocity (the inverse of the residence time in the bath) is proportional to the square of the bubble radii. For bubbles from iron carbide particles, the ratio of terminal velocities to those from a lance is about 0.004, or it takes 250 times longer for a bubble originating from a carbide particle to rise to the surface than it does for a bubble from an oxygen lance injected at the same depth. This, in turn, allows for the nitrogen content of the bubble to come much closer to equilibrium than is achieved in the usual rising bubble, In the present case, 34 ppm N is in equilibrium with 0.005 atm of N₂, a very small amount in each CO bubble, indicating that equilibrium was probably reached relatively quickly, in contrast to the probable lack of reaching equilibrium in most gaseous injection processes.

Finally, the presence of excess carbon and low sulfur content in the vicinity of the bubbles formed from the carbide particles enhances the rate of nitrogen desorption by ensuring a low oxygen and sulfur activity at the bubble interface, both of which are well

known to poison the interface and inhibit nitrogen transfer.

The outstanding results relative to the same CO evolution may be explained by the sum of all of the above factors, the combination of smaller bubbles, which result in much greater surface area for nitrogen absorption, combined with a longer residence time in the bath, and the low oxygen and sulfur potentials.

Another observation by all who have tested the material is that while there is a vigorous boil, it is quite controlled, and steady and occurs throughout the surface of the bath quite soon after the start of injection. Of particular relevance to this observation is the comparison with the work of Meischner and Gmoehling(19). They reported observations on mixing phenomena for a process in which a finely divided gas-releasing material, diamide lime, ($\text{CaCO}_3 + \text{C}$), was injected into hot metal. "The decomposition of the carbonate disintegrates the bubbles formed by the carrier gas, avoiding the bubble entrapped passage of reagent through the melt. As the bubbles' move upward through the liquid, the momentum spreads and the dissipated energy density decreases. Some bubbles may therefore coagulate before reaching the surface. This region of less intensive turbulence corresponds to the "bubble-swarm" reactor used in chemical engineering. It is in this region where the main momentum transfer to the liquid takes place which is responsible for inducing the bulk circulation of the liquid. This 'gas-lift pump'-effect is much smoother and regular with small bubbles than with large ones"(19) in their case, which resulted in much improved desulfurization, they estimated that their initial bubble size was around 0.03 mm diameter. Since theory tells us that the dissipated energy, W, per unit volume of liquid is related to the diameter of the rising bubble to the $-5/2$ power, it can be calculated that the ratio of energy dissipated by bubbles of the size estimated from iron carbide, 0.6mm, to that from bubbles from a normal oxygen lance, 10mm, is on the order of 164 times greater. This can account for the very rapid mixing observed in trials in the electric arc furnaces.

It should be pointed out that the injection of powdered material itself results in significant energy for stirring also. Koros, et al(20), demonstrated this by measuring the mixing time in an 170 ton electric furnace when 450 Kg/min of lime were injected with $1.3 \text{ Nm}^3 \text{ N}_2/\text{min}$. The mixing time was 2.5 minutes, compared to 4 minutes for the injection of $3.5 \text{ Nm}^3/\text{min}$ of argon alone. Filar, Bartos and Geiger (21) found similar poor stirring efficiency with argon injection alone into 100 ton heats of stainless steel, where argon flow rates of 1.74 and $7.4 \text{ Nm}^3/\text{min}$ were inadequate to mix stainless steel in 5 minutes and 9 minutes respectively, and not until a flow rate of $11.0 \text{ Nm}^3/\text{min}$, was mixing achieved in 4 minutes,

Conclusion

In conclusion, iron carbide can be considered to be an excellent raw material for use in electric furnaces. It is easily handled, non-pyrophoric, as free of residuals as is the ore used, free of sulfur, and only contains phosphorous to the degree the ore does. Commercial material will contain a high enough ratio of carbon to oxygen to provide a net energy addition to the bath, provided the carbon is subsequently oxidized with gaseous oxygen. There is an added benefit of small bubble formation, which aids in providing improved stirring action to the bath and improved nitrogen removal. Finally, Iron carbide can be used in conjunction with other direct reduced iron sources to counteract some of the negative aspects of their use, and provide the benefits mentioned above.

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Table I Reactions Assumed Taking Place

- A. $\text{Fe}_3\text{C}(\text{s}) \rightarrow 3\text{Fe}(\text{l}) + \text{C}$
- B. $4\text{C} + \text{Fe}_3\text{O}_4(\text{l}) \rightarrow 3\text{Fe}(\text{l}) + 4\text{CO}(\text{g})$
- C. $\text{C} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}(\text{g})$
- D. $\text{Fe}(\text{l}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{FeO}(\text{l})$
- E. $\text{C} + \text{FeO}(\text{l}) \rightarrow \text{CO}(\text{g}) + \text{Fe}(\text{l})$
- F. $1.65\text{CaO}(\text{s}) + \text{SiO}_2(\text{l}) \rightarrow 1.65\text{CaO} \cdot \text{SiO}_2 \text{ (Slag)}$
- G. $\text{CO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \text{ (post combustion)}$
- H. $\text{C}(\text{s}) \rightarrow \text{C}$
- I. $\text{Si} + \text{O}_2 \rightarrow \text{SiO}_2(\text{l})$

Table II. Balances That Must Be Satisfied

J. Total balance

$$W_{\text{scrap}} + W_{\text{DRI}} + W_{\text{Fe}_3\text{C}} + W_{\text{CaO}} + W_{\text{Coke}} + W_{\text{Oxygen injected}}$$

$$= W_{\text{Steel tapped}} + W_{\text{Slag}} + W_{\text{CO}} + W_{\text{CO}_2} + W_{\text{dust}}$$

K. Fe balance

$$W_{\text{Fe in Fe}_3\text{C}} + W_{\text{Fe in Fe}_3\text{O}_4} + W_{\text{Fe in scrap}} + W_{\text{Fe in DRI}} + W_{\text{Fe in FeO in DRI}}$$

$$= W_{\text{Fe in steel}} + W_{\text{Fe as FeO in slag}} + W_{\text{Fe in dust}} + W_{\text{Fe in slag}}$$

L. C balance

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

M. Oxygen balance-

$$W_{\text{O}_2 \text{ in Fe}_3\text{O}_4} + W_{\text{O}_2 \text{ injected}} + W_{\text{O}_2 \text{ in FeO in DRI}}$$

$$= W_{\text{O}_2 \text{ in CO}_2} + W_{\text{O}_2 \text{ in CO}} + W_{\text{O}_2 \text{ in FeO In slag}} + W_{\text{O}_2 \text{ in dust}}$$

N. Silica balance:

$$W_{\text{SiO}_2 \text{ in feed materials}} + W_{\text{SiO}_2 \text{ from scrap oxidation}} = W_{\text{SiO}_2 \text{ in slag}}$$

O. Lime balance

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

P. 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 considered to be at 1873 °K.

$$\begin{aligned}
 & (H_{1873} - H_{298})\text{CaO charged} + (H_{1873} - H_{298})\text{O}_2 + (H_{1873} - H_T)\text{Fe}_3\text{C} + \\
 & (H_{1873} - H_{T \text{ in}})\text{Fe}_3\text{O}_4 \text{ in carbide} + (H_{1873} - H_{T \text{ in}})\text{SiO}_2 + (H_{1873} - T \\
 & \text{in})\text{CaO in carbide} + (H_{1873} - H_{298})\text{Scrap} + (H_{1873} - H_{198})\text{Coke} + (H_{1873} \\
 & - H_{298})\text{Fe in DRI} + (H_{1873} - H_{298})\text{FeO in DRI} + (H_{1873} - H_{298})\text{C in DRI} \\
 & + (\text{Sum of Heats of Reactions A-I})_{1873} + \text{Electrical Energy} + \text{Heat Loss} = 0
 \end{aligned}$$

Table III Assumed Compositions and Costs of Materials

<u>Material</u>	<u>%F e</u>	<u>%Resid</u>	<u>%S</u>	<u>%P</u>	<u>%C</u>	<u>%O</u>	<u>%CaO</u>	<u>%SiO₂</u>	<u>\$/T</u>
Scrap 1	99.3	0.15	0.020	0.025	0.10	0	0	0	120
Scrap 2	98.4	0.75	0.025	0.025	0.20	0	0	0.4	100
Scrap 3	98.7	0.50	0.025	0.025	0.20	0	0	0.4	110
Scrap 4	98.8	0.40	0.025	0.025	0.20	0	0	0	115
Carbide	89.8	0	0	0	6.2*	1*	1.	2.	128
DRI	92.0	0	*	*	1.0	1.5*	2.	3.5	120
Lime	0	0	0	0	0	0	98.	2	50
Coke	0	0	1.0	0	92.	0	0	7.	100

Slag CaO/SiO₂ = 2.0; FeO = 25%; Fe⁰ = 4%.

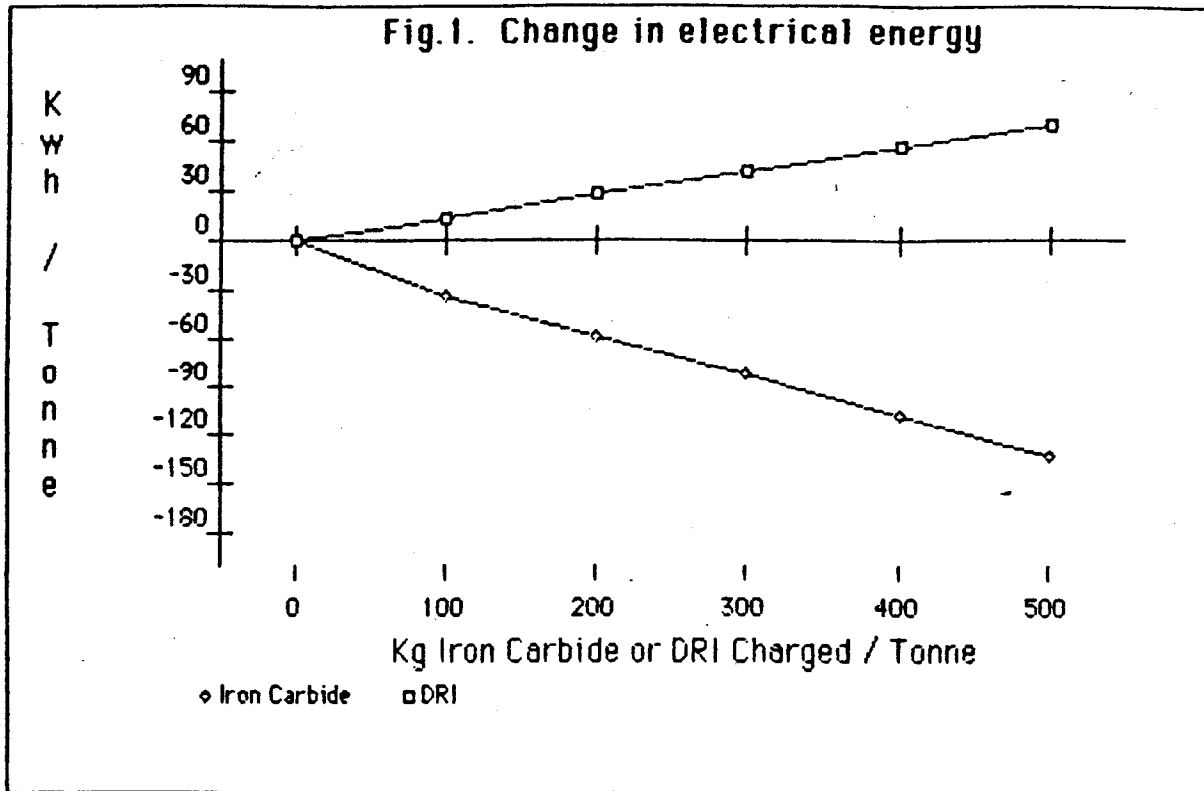
Steel 0.2%C, bal Fe.

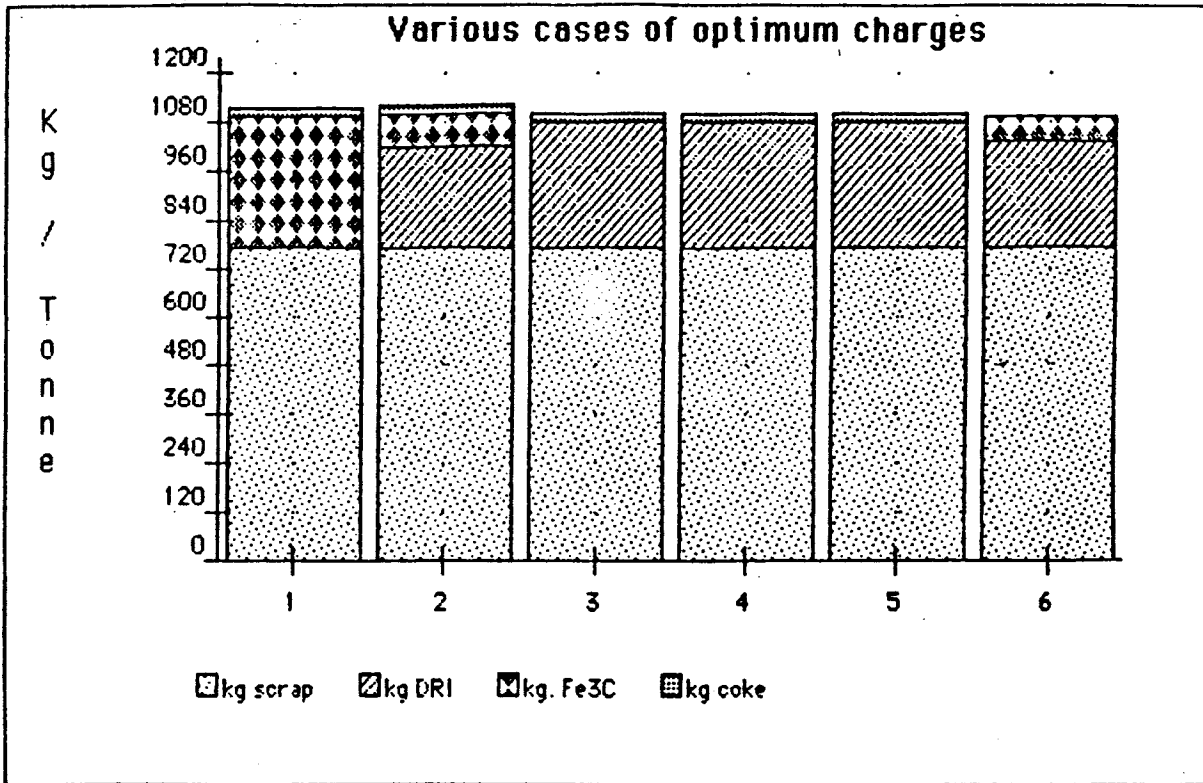
*C as Fe₃C, O as Fe₃O₄

*Depends on source. For Fastmet, assumed 0.15% S, 0% P,
For HBI, assumed 0% S, 0.05% P, O present as FeO in both cases.

Table IV. Furnace Practices Resulting in the Greatest
Removal of Nitrogen After Meltdown(14).

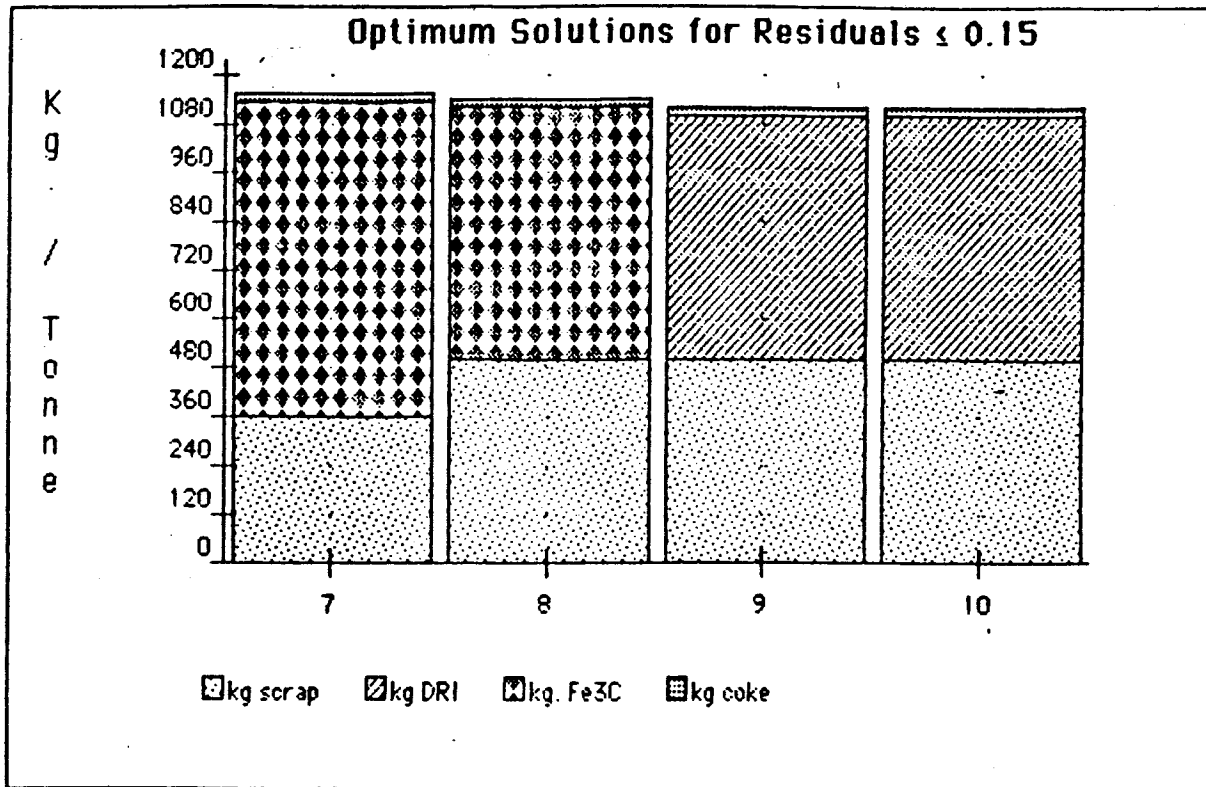
<u>Practice</u>	<u>Nitrogen Content (ppm)</u>		
	<u>Melt-down</u>	<u>Tap</u>	<u>Average Reduction</u>
High Carbon Blowdown	89	59	-30
Medium Carbon Std Practice	87	65	-22
Iron Carbide Injection	82	34	-48





Power Cost, cents	4	4	3	4	5	4
Type DRI	F-met	F-Met	Mid	Mid	Mid	Mid
Price DRI	\$120	110	120	120	120	120
Fe3C -%Fe3O4	4	4	15	15	15	15
Price Fe3C	\$128	128	128	128	128	127
Total Cost, Mat. & Ener.	\$154	153	146	152	157	151

Figure 2. Results of linear programming cases where the amount and types of scrap were fixed at 750 Kg/tonne, and the choice of DRI or Fe3C was unconstrained.



Power Cost, cents/K.wh	5	4	4	3
Price DRI, \$/tonne	\$120	120	120	120
Price Fe ₃ C, \$/tonne	\$122	122	128	122
Total Cost, Mat. & Ener.	\$161	157	156	151

Figure 3. Results of linear programming cases where the amount of Scrap 1 was limited to 300 Kg/tonne, and other types of scrap and the choice of DRI or Fe₃C was unconstrained, but it was required that total residuals not exceed 0.15%. The Fe₃C was assumed to contain 4%Fe₃O₄.

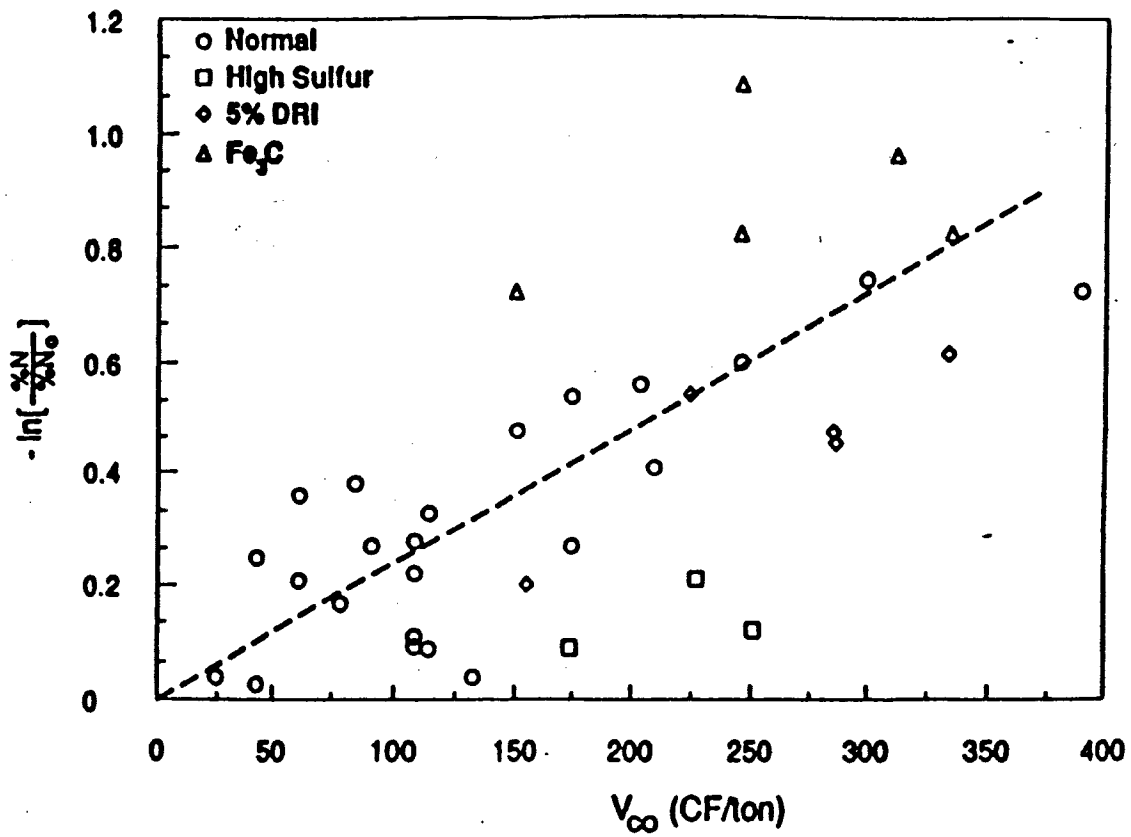


Figure 4. Total nitrogen removal as a function of total CO evolution per ton (14).