

IRON ORE TO STEEL VIA THE IRON CARBIDE ROUTE: AN ANALYSIS OF THE ENVIRONMENTAL IMPACTS OF THE ROUTE

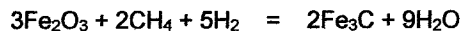
Gordon H. Geiger
Qualitech Steel Corporation

INTRODUCTION

There is much consternation by some scientists about global warming, presumed to be caused by an accumulation of CO₂ in the atmosphere. Since only a few measurement locations are inferred to represent the atmosphere over the entire globe and since there is never any statistical representation of the error in the measurements over decades of time, and since there is no way to establish whether the observed variability in CO₂ analysis or temperatures over the past century is within the normal variability the earth might be expected to exhibit (as the occurrence of several ice ages over the post millennia have demonstrated), there is reason to seriously question the position of so-called environmentalists who would create economic havoc through various schemes to limit CO₂ evolution from industry.

Indeed, the assumption that incoming solar radiation is constant and that the warming effect is due to the very small amount of CO₂ in the atmosphere trapping and reradiating energy may be completely wrong and the effect may be due to variability in radiation from the sun itself, which is after all, undergoing its own "combustion", with solar flares and sunspots as evidence. Nevertheless, we can look at the fact that iron and steel production is a significant contributor to global CO₂ evolution and consider what might be done.

Iron carbide is a new metallic charge material for steelmaking. It is produced from iron ore fines and natural gas, and has a significant carbon content, capturing the carbon atom from the overall reaction leading to its formation:



This carbon atom is carried into the steel furnace and when reacted with gaseous oxygen generates heat that contributes to its melting. In the electric furnace it still requires electricity to melt and may be used in various amounts. However, if the energy from the combustion of the carbon to CO₂ can be captured, it is theoretically possible to melt the entire charge of iron carbide to make steel. While this has not yet been done, considerable design work has been done and patents issued on a practical design. In the case where this heat is captured, in the proposed Carbide-to-Steel (CTS) process, it will be shown here that a significant reduction in the evolution of the most important greenhouse gas, CO₂, is possible, relative to any other steelmaking routes based on iron ore.

UNIT CO₂ EVOLUTION

In order to compare various routes to steel, it is necessary to estimate the evolution of CO₂ from the most important sources of energy and chemical reductants and reactants used in various processes. Table I lists the evolution of CO₂ from burning natural gas, oil and coal: from generating and transporting electricity made from steam generated from fossil fuels; from generating gaseous oxygen; and from burning limestone to produce burnt lime. These are based on well known industrial efficiencies of energy conversion.

From these, the CO₂ evolution from various metallurgical unit processes can be estimated. For example, the iron ore pelletizing process in a grate-kiln process, uses oil fuel and electricity, but in order to get to the pellet machine, iron ore has to be ground to a fine size, usually concentrated, and then pelleted, all of which requires electricity. When all of these steps are added, the CO₂ evolution for production of a tonne of pellets can be estimated, Table 2.

This process can be followed for each unit operation, and the amounts of each unit of material required to produce a tonne of liquid steel can then be multiplied by the unit consumption to compute the total CO₂ evolution per tonne of liquid steel (TLS). For example, the current primary route to steel is iron ore to either sinter or pellets, combined with coke produced from coal, to make hot metal containing carbon, which is mixed with 25% scrap and converted to steel in the basic oxygen process. Working back to the hot metal requirement (.75 tonne) and the coke requirement for that hot metal (.375 tonne), and the pellet requirement (1.125 tonne), the CO₂ evolution per tonne of low-carbon steel is found to be 2010 kg CO₂/TLS, Table 6, using a 100% pellet charge to the blast furnace. Using sinter, the total is 2088 kg CO₂/TLS, in good agreement with Yagi and Akiyama's (1) data for Japanese blast furnaces.

It is interesting to examine other coal-based ore-based processes. The Corex process puts out 3080 kg CO₂/tonne of hot metal containing about 2.5%C, which when fed with pellets and refined in a BOF (using less scrap) results in 3089 kg CO₂/TLS, (Table 6). Yogi and Akiyama (1) have also analyzed direct smelting reduction processes which use coal instead of coke and found that they generate between 1 and 2 times as much as the pellet-coke-blast furnace route to pig iron, which is what they all make. The AISI Direct Ironmaking process is reported to make about 1750 kg CO₂/tonne. Where combined with refining to steel, the result is still higher than the BF-BOF route. Thus while attempting to avoid the environmental problems associated with building and operating coke ovens, these processes have often worsened the CO₂ evolution problem.

GREENHOUSE EFFECTS OF STEELMAKING ACTIVITIES

TABLE 1 – CO₂ FROM ENERGY SOURCES AND REAGENTS

<u>Activity</u>	<u>Unit</u>	<u>Assumptions</u>		<u>lb CO₂/Unit</u>	<u>kgCO₂/Unit</u>
Natural Gas	scf	359scf/16 lbs CH ₄		0.12	0.056
Natural Gas	MMBTU	1,000 BTU/scf CH ₄		122.56	55.710
Coal	MMBTU	80%C, 11,000 BTU/lb		266.67	121.212
Coal	lb	80%C, 11,000 BTU/lb		2.93	1.333
Oil	MMBTU	18,000 BTU/lb and 86%C		175.19	79.630
Electricity	kwh	Oil-Based, BTU/kwh	9,500	1.66	0.756
Electricity	kwh	Coal-Based, BTU/kwh	9,500	2.53	1.152
Electricity	kwh	Gas-Based, BTU/kwh	9,500	1.16	0.529
Oxygen	scf	Coal-Based Electricity, kwh/scfO ₂	1.6	0.041	0.018
Oxygen	scf	Oil-Based Electricity, kwh/scfO ₂	1.6	0.027	0.012
Oxygen	scf	Gas-Based Electricity, kwh/scfO ₂	1.6	0.019	0.008
Burnt Lime	lb	Natural Gas	0.860	0.391	

TABLE 2 - CO₂ FROM ORE-BASED PROCESSES

<u>Activity</u>	<u>Unit</u>	<u>Assumptions</u>		<u>lbCO₂/ton</u>	<u>kgCO₂/tonne</u>
Coke	ton	Recovery ovens, fuel MMBTU/ton	2	245	123
	ton	Recovery ovens, scf evolved CH ₄ gas	6,462	792	396
	ton	Recovery ovens, scf evolved CO gas	1,836	220	110
		Total per coke ton		1267	629
Pellets	ton	Electricity to concentrate, kwh/ton, coal base	100	253	127
		Fuel, ore from magnetite, MMBTU oil	0.45	79	39
		Fuel, ore from hematite, MMBTU oil	0.9		0
		Electricity to pelletize, kwh/ton	25	63	32
		Total per pellet ton		396	198
Sinter	ton	Fuel used, MMBTU/ton	0.28	34	17
		Coke breeze charged, lbs/ton	86	284	142
		Electricity, kwh from oil	29	48	24
		Limestone used, lbs/ton	230	181	90
		Total per sinter ton		547	273
Blast Furnace	NTHM	Carbon rate, lbs/NTHM	1,000	3,355	1,678
		Electricity, kwh/NTHM	50	83	42
		Sinter used, tons/NTHM	0		
		Limestone rate, lbs/NTHM	150	118	59
		Pellet rate, tons pellets/NTHM	1.45		0
		Total per hot metal ton		3,566	1,779
BOF	ton	lbs Hot Metal/ton steel	1,550	253	126
		%C in Hot Metal	4.5		
		Tap Carbon, %	0.05		
		Oxygen, scf/ton steel	1,977	80	40
		Lime, lbs/ton	120	103	52
		Total per BOF ton		436	218

The assumptions for each unit operation affect the overall result, of course. In this paper, the assumptions are based on the most practical results the author could find, but the reader can see the assumptions and make his own modifications. Nevertheless, the general conclusions will not likely be changed.

The rotary hearth type processes such as FASTMET 0 and INMETCO do not produce a liquid product, so before making steel, more energy must be added to compare these to the smelting reduction processes. The CO₂ evolution from the FASTMET process is given in Table 3.

The gas-based shaft processes such as Midrex and Hyl III have similar CO₂ evolution, 621 kg CO₂/tonne of DRI, (Table 3). Of course, the need for pellets adds to the totals at the DRI stage. In Table 6, it has been assumed that the charge to the Midrex shaft is 50% pellets and 50% lump ore. With more pellets in the charge, the routes using DRI to make steel would evolve more CO₂.

The use of fines-based reduction processes such as iron carbide, FIOR, and CIRCORED, eliminates the

CO₂ evolution involved with pellet formation, but of course can only work on high-grade ores that do not have to be ground fine for concentration. They also evolve CO₂ during H₂ production. Table 3 illustrates the CO₂ evolution expected from the QSC/KHI iron carbide process: 651 kg CO₂/tonne of carbide.

The use of electric furnaces to melt scrap is obviously the route that evolves the least CO₂, but it is not as little as some might think. Table 4 shows that the typical practice used today for high speed melting, involving the use of oxy-fuel burners, oxygen and burnt lime, results in 641 kg CO₂/TSL. It is useful to examine the effect of other charge mixes to the EAF on the evolution Of CO₂/TSL. For instance, we at Qualitech intend to use 40% iron carbide and 60% scrap in our EAF charge. This will result in evolving 689 kg CO₂/TSL (1379 lbs. CO₂/TSL). However, when combined with the CO₂ evolution from production of 0-45 tonnes of iron carbide, results in 982 kg CO₂/TSL for this steelmaking route, Table 6. If 80% Midrex DRI is melted in an EAF, with scrap, the CO₂ evolution from the EAF is 1196 kg CO₂/tonne (2393 lbs. CO₂/TSL), but overall, the total is 1912 kg CO₂/TSL.

TABLE 3 - CO₂ EVOLUTION FROM COREX AND IRON CARBIDE PROCESSES

Activity	Unit	Assumption		lb CO ₂ /ton	kg CO ₂ /tonne
Corex	NTHM	Coal, (950 kg/tonne) lbs	1,900	5,573	2,787
		Electricity, kwh/ton	54	63	31
		Oxygen, scf/ton	16,371	305	152
		Limestone, lbs/ton	500	220	110
		Pellets, 1.5 tons/NTHM			
Total				6,161	3,080
Iron Carbide	ton	MMBTU Natural Gas/ton	9	1,103	552
		Electricity, kwh/ton, from natural gas	170	198	99
		Total		1,301	651

TABLE 4 - CO₂ EMISSIONS FROM EAF MELTING

Unit		lb CO ₂ /TSL		lb CO ₂ /TSL		lb CO ₂ /TSL		lb CO ₂ /TSL	
ton	Fraction scrap	1	0.65	0.25				0.55	
	Fraction DRI	0	0	0.85				0	
	Fraction iron carbide	0	0.45	0				0	
	Fraction liquid pig iron	0	0					0.55	
	Lbs Carbon charged/ton	15	55	54	198	75	275	22	81
kwh	Electricity, kwh/ton	420	1,064	380	963	750	1,900	350	887
scf	SCF Natural gas/ton	350	43	350	43	350	43	300	37
scf	Oxygen, scf/ton	1,500	61	2,200	89	2,000	81	1,800	73
lb	Lime, lbs/ton	70	60	100	86	110	95	90	77
EAF Total - lb CO₂/t/s			1,283		1,379		2,394		1,156
EAF Total - kg CO₂/tonne			641		689		1,196		578

TABLE 5 – CO ₂ EVOLUTION FROM SHAFT & ROTARY HEARTH PROCESSES					
			lb CO ₂ /ton	kg CO ₂ /tonne	
Midrex DRI	ton	MMBTU gas fuel used/ton	9	1,103	552
		Pellets, ton/ton	0.72		0
		Lump ore, ton/ton	0.75		0
		Electricity, kwh/ton, gas-based	120	140	70
		Total		1,243	622
Fastmet	ton	Lbs coal/ton	660	1,936	968
		MMBTU natural gas/ton	2.4	292	146
		Kwh/ton	90	228	114
		Total		2,456	1,228
Inmetco	ton	Kwh/ton in submerged are	100	253	127
		Total		253	127
CO₂ EMISSIONS FROM CARBIDE-TO-STEEL PROCESS					
Carbide-to-steel ton steel		Electricity, kwh/ton	15	25	12
		scf natural gas/ton	902.01	111	55
		Carbon from 1.6 ton Iron Carbide, lb/ton	120.64	442	221
		Oxygen, scf/ton	4879.2	91	45
		Total		669	333

TABLE 6 - TOTAL CO EMISSIONS FOR VARIOUS ROUTES TO LIQUID STEEL							
					Total Lbs CO ₂ /TLS	Total kg CO ₂ /tonne	
Unit consumption/ton steel	Iron Ore to	Pellet to	Coke to	Blast Furnace	to BOF		
lbs CO ₂ per ton material		1,125	0.375	0.75	1		
lbs CO ₂ per ton steel		396	1,257	3,556	436	4,020	2,010
		445	472	2,667	436		
Unit consumption/ton steel	Iron Ore to	Pellet to	Corex to	BOF			
lbs CO ₂ per ton material		1,275	0.85	1			
lbs CO ₂ per ton steel		396	6,161	436		6,177	3,089
		504	5,237	436			
Unit consumption/ton steel	Iron Ore to	Pellet to	Midrex to	EAF			
lbs CO ₂ per ton material		0.66	0.88	1			
lbs CO ₂ per ton steel		396	1,243	2,393		3,748	1,874
		261	1,094	2,393			
Unit consumption/ton steel	Scrap to	EAF					
lbs CO ₂ per ton steel	1.1	1				1,283	641
		1,283					
Unit consumption/ton steel	Scrap + 40% Iron Carbide to	EAF					
lbs CO ₂ per ton material	0.65	0.45	1				
lbs CO ₂ per ton steel	0	1,301	1,379		1,964	982	
		585	1,379				
Unit consumption/ton steel	Scrap +	Fastmet	to EAF				
lbs CO ₂ per ton material	0.55	0.55	1				
lbs CO ₂ per ton steel		2,456	2,393		3,744	1,872	
		1,351	2,393				
Unit consumption/ton steel	Scrap +	Inmetco	to EAF				
lbs CO ₂ per ton material	0.55	0.55	1				
lbs CO ₂ per ton steel		2,709	1,154		2,644	1,322	
		1,490	1,154				
Unit consumption/ton steel	Iron Ore to	Iron Carbide to	Carbide-to-Steel				
lbs CO ₂ per ton material		1.16	1				
lbs CO ₂ per ton steel		1,301	669		2,178	1,089	
		1,509	669				

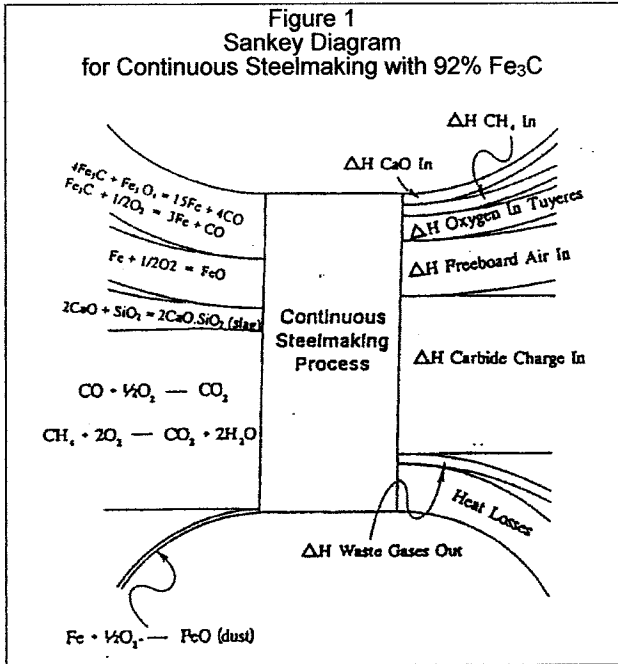
DEVELOPMENT OF CARBIDE-TO-STEEL PROCESS DESIGN

In 1993 a paper was presented (2) based on a patent granted in 1992 (3) outlining a process to take iron carbide and melt-dissolve it and refine the carbon out in a continuous reactor, a la the Queneau-Schuhmann process reactor for lead melting and refining. The heat balance, Fig. 1, showed that if most of the carbon was burned to CO₂, and the heat transferred to the bath, the process could be autogenous, requiring no other energy input to take iron carbide from its process at 600 C and make steel with 0.05%C. This was a totally theoretical picture with a lot of assumptions, particularly with respect to heat transfer.

Working with US Steel and Praxair researchers, we reviewed the original process and reconsidered the overall energy balance. We looked at many vessel shapes. One thing became

apparent rather quickly: when iron carbide is dissolved in a molten iron bath, the iron oxide remaining in each particle will react with the carbon from the carbide to form CO, in addition to the production of CO by decarburization with gaseous oxygen. The number of CO bubbles create a tremendous stirring energy - as has been observed by those of us who have used iron carbide. This energy is so high that it rapidly homogenizes the bath, (Table 7), and QSL configuration of the continuous reactor from further consideration. it is impossible to create a stable carbon gradient within a vessel into which "iron carbide" is being injected. This effectively eliminated the QSL configuration of the continuous reactor from further consideration.

We then focused on how to form the liquid bath and get the energy from CO to CO₂ combustion without having to resort to a batch process. Why a continuous process? This has always been the process metallurgists dream because it results in:



There is a two-stage heat balance that allows the carbon content of the intermediate stream to be varied. The energy balance of the first reactor requires that the CO from the second reactor be burned to CO₂ in the first reactor and the combustion energy be transferred to the bath, along with partial combustion of the carbon in the change to CO and its combustion to CO₂ by post-combustion lances. This is a significant heat transfer problem and results in determining the size of the vessel. Here we relied on the published experience of Hismelt researchers, AISI researchers, and DIOS researchers in Japan that indicated that heat transfer efficiency of 70-90% to slag-metal emulsion could be achieved from combustion of CO in the slag-metal emulsion. This drove us to design vessel with a deep bath with room to create and maintain large slag foam for heat transfer purposes.

On the other hand, the second reactor has to maintain a carbon gradient from 2% C to 0.05%. This means that it has to allow for introduction of controlled oxygen flow at points along it, for enough apart so that their individual turbulence regions do not affect each other. This requires a minimum plug flow velocity of 0.5 m/min. Fluid mechanic modeling combined with kinetic modeling and heat and material balances establishes the combination of oxygen jet flow rate and nozzle size and spacing that allows this (Fig. 3). The result is a long cylindrical reactor with a trough running through it. Which brings me to another fundamental observation that we made. If you try to scale this down, you rapidly run into the fact that if the metal flow is going to be decreased to say, 10 tonne per hour, the channel to maintain 0.5 m/min. has to be 0.044 M² in cross-section. This is so small that when metal is introduced to the reactor, even if it is preheated, a skull will rapidly form and one cannot run the process because the heat balance is dominated by the refractory heat sink. In fact, most high temperature processes in our business cannot be scaled down very well for this reason and, in my opinion, accounts for a lot of the post failures of continuous process pilot plants. The use of batch pot grate tests in iron ore pelletizing, for example, has led to very erroneous results in the sizing of plants (7). Therefore, the design for the smallest plant we believe is feasible, is for 50 tonne/hr.

Table 7
Typical Mixing Energy Intensity
for Stage 1 Reactor

CO evolved from Fe304 reduction	18.41	Nm ³ /min
CO evolved from injected O ₂	89.63	Nm ³ /min
Total CO evolution	108.4	NM ³ /min
Mixing energy, watts / tonne	35542	
Mixing time, sees, based on Nakanishi et al. (4)	12	
Mixing time, sees, based on Kato et al. (5)	22	

- smaller equipment per annual unit of capacity, and therefore, higher capital equipment utilization
- better refractory performance (for fewer thermal cycles)
- it is easier to control a steady state process than a batch process, with regard to product end point

We realize that in going from solid Fe₃C to liquid Fe+0.05% C, there are both endo and exothermic stages. Once liquid, with dissolved carbon, the injection of gaseous oxygen to form CO is mildly exothermic, and there is no need for external energy or fuel to go from 2% to 0.05% C. On the other hand, to go from solid Fe₃C to a liquid iron carbide takes a lot of energy and the process vessel needs to be well mixed all of the time. This led to the concept of a coupled two-stage process, wherein the first stage is a reactor to which iron carbide and oxygen are fed, and which continually discharges an iron-carbon melt to a second reactor, where it is refined to steel evolving CO which, in turn, is injected into the first stage to be burned to CO₂, Fig. 2.(6)

The basic design has been completed, materials specified, and many details thought about. Patents have been applied for and issued all over the world (6) and all that is needed now is to build and test it.

The only energy used is the electricity and natural gas used in Fe₃C production and the electricity to make gaseous oxygen, plus, about 0.9 mm BTU/tonne of natural gas, if cold Fe₃C is used. The total CO₂ evolution would be 334 kg CO₂/tonne. The combined CO₂ evolution from ore to steel would be 1089 ka CO₂/TLS.

Regarding the environment, no SO₂ is released. The production of iron carbide uses methane with no sulphur, so that the feed material has no sulphur.

Reactors to convert iron carbide to steel are completely enclosed, so air ingress is minimized or eliminated, reducing or eliminating NO_x formation and minimizing total exhaust gas volume and capital cost to handle waste gases.

Figure 2

Flow Sheet for Carbide-to-Steel Process ⁽⁶⁾

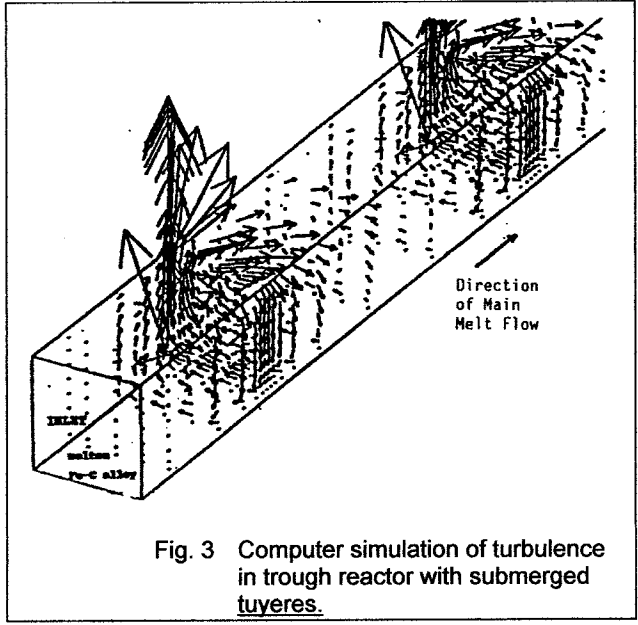
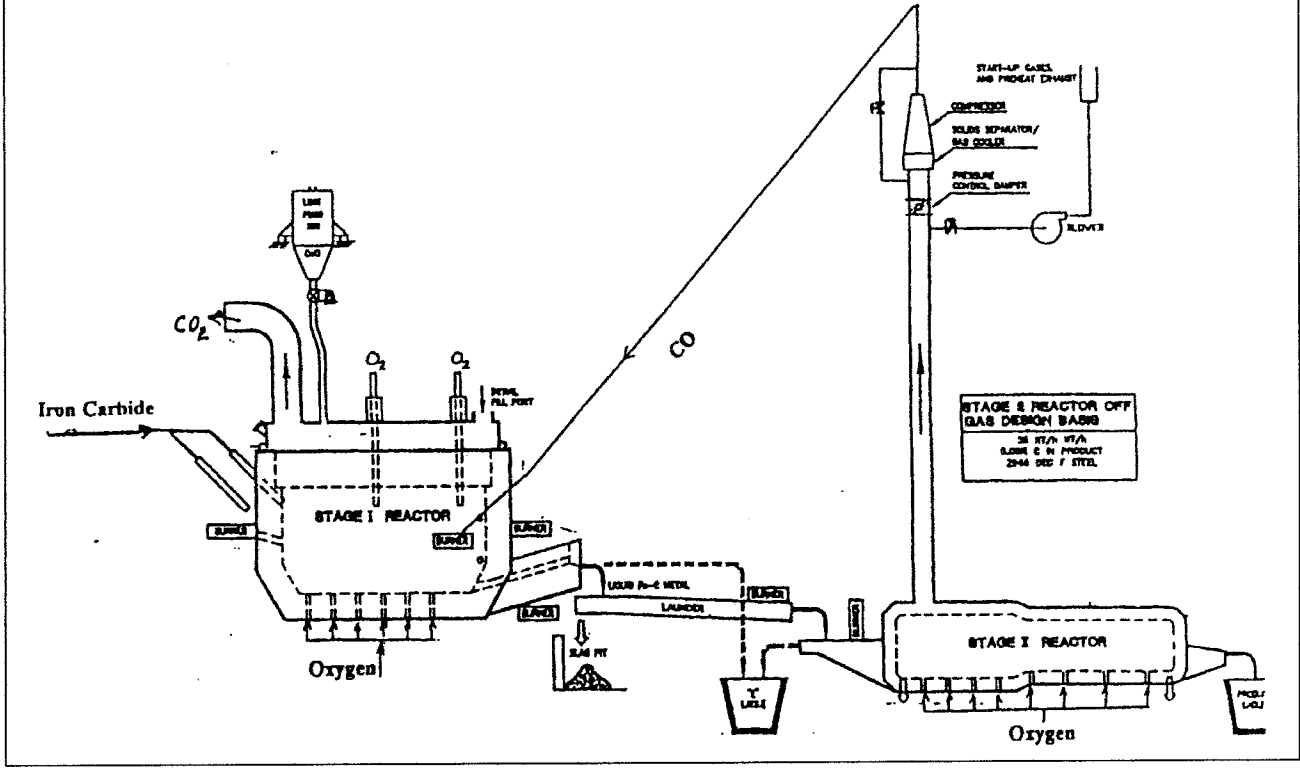


Fig. 3 Computer simulation of turbulence in trough reactor with submerged tuyeres.

Because of not using contaminated scrap or coal, any possible VOC's are eliminated. Total CO₂ emissions are the minimum of any ore-based route to steel.

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