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A White Paper

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The Impact of Oxygen on Reducing CO₂ Emissions in Blast Furnace Ironmaking

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EXECUTIVE SUMMARY

Modern integrated steelmaking is based on the Basic Oxygen Process (BOP) which requires large amounts of molten iron (“hot metal”) from a blast furnace as a starting material. The blast furnace requires large amounts of metallurgical coke as a fuel, reductant, and internal structural support to provide stable passages for the furnace hot blast. The cokemaking ovens and blast furnaces together account for the vast majority of the carbon footprint of an integrated mill. Cokemaking ovens are also tightly regulated for health-based emissions, making coke increasingly expensive.

In recent years, blast furnace operators have added high levels of oxygen enrichment to the hot blast. The highly enriched blast increases productivity and allows operators to replace part of the expensive coke with secondary fuels, such as pulverized coal and natural gas, injected with the blast. Because the temperature profile in the furnace must be kept within a narrow window, the rates of oxygen enrichment and secondary fuel injection must be closely linked.^{1,2}

Determining the impact of blast oxygen enrichment with secondary fuel injection on the carbon footprint of the integrated mill requires following the paths taken by the carbon in the coal supply to the coke oven, the carbon in the secondary fuel supply to the blast furnace, and the carbon consumed in making power for oxygen production. Additional complications in this calculation arise since both the coke oven and blast furnace produce by-product fuel gases that are used by the steelmaker to generate power to supplement purchases from the electrical grid. Changes in coke oven and blast furnace operation that alter the power generation rate from by-product fuels will change the mill’s demand for power from the grid and the associated carbon release from those external sources.

Process Overview

Carbon in cokemaking coal – Metallurgical coke is produced from coal by two processes, by-product coke ovens and heat recovery coke ovens. By-product ovens convert most of the coal volatiles into a by-product fuel gas (coke oven gas, COG), but some of the volatiles

are converted into useful chemicals. As a result, about 6% of the carbon from the coal is sequestered in by-product cokemaking. This process currently produces about 75% of the coke in the U.S.^{3,4} Heat recovery ovens burn the coal volatiles and convert that heat into electricity, and so all of the carbon from the coal is eventually released as CO₂ in this process. Heat recovery ovens currently produce about 25% of the coke in the U.S. Both processes also yield fine coke particles, called coke breeze, which are too small to be used in the blast furnace and are used for other combustion processes. More details on the products produced in cokemaking are found in reference 5.

Since oxygen enrichment of the hot blast combined with secondary fuel injection lowers coke rate, it also leads to lower production of coke breeze and coke oven derived electricity (either from surplus COG sent from a by-product oven to a boiler or produced directly from a heat recovery oven). The coke breeze must be replaced by another solid fuel, while the power must be replaced by power from the grid. For this calculation the coke breeze replacement is assumed to release the same mass of carbon.

Carbon in blast furnace secondary fuel – At the blast furnace, all carbon from secondary fuels is released in addition to carbon from coke. The carbon is converted in the blast furnace into CO and CO₂ contained in the blast furnace gas (BFG), a by-product fuel leaving the process, or is dissolved in the molten iron. Table I shows the typical replacement ratio for secondary fuels. These replacement ratios represent the mass ratio of coke removed from the blast furnace operation

Table I – Secondary fuel replacement ratios and CO₂ release

Fuel	Replacement ratio lb coke / lb fuel ^{6,7}	CO ₂ released lb / lb fuel ⁸
Coal	0.90	2.86
Natural gas	1.25	2.75
Oil	1.10	3.15
Tar	1.00	3.37

to the mass of secondary fuel added. The selected values are slightly conservative within the ranges given in the references. Table I also shows the CO₂ released by these secondary fuels.

Carbon from power for blast enrichment oxygen – The manufacture and distribution of oxygen at 580 psig requires 363 kWh / ton O₂.⁹ The U.S. average CO₂ emission from power generation is 1.300 lb CO₂ / kWh.¹⁰ The resulting CO₂ emission from the manufacture and distribution of oxygen is 0.236 t CO₂ / t O₂.

Carbon from power generation using by-product fuel gases – Surplus COG and BFG are usually fed into boilers and used to make electrical power. The effect of oxygen enrichment on the power generated from COG and BFG is complex. Oxygen enrichment of the hot blast combined with secondary fuel injection increases the production of BFG and lowers the coke consumption of the blast furnace. Lower coke consumption lowers the production of COG if the coke source is a by-product oven and lowers the production

of electrical power if the coke source is a heat recovery oven. The net result may be an increase or a decrease in the power demand of the mill. The impact of oxygen enrichment with fuel injection on the net power demand of the steel mill can be clarified using a two-zone mass and energy model of the blast furnace.

Table II shows the disposition of the by-product gases for a blast furnace without oxygen enrichment and compares this with the disposition at two levels of pulverized coal injection (PCI) and natural gas injection (NGI) calculated by the model. The table shows that oxygen enrichment affects power demand by -60 to +13 kWh / thm. Using the U.S. average CO₂ emission from power generation of 1.300 lb CO₂ / kWh,¹² this would result in -79 to +16 lb CO₂ / thm change in emission from power plants. On average then, there should be little, if any, increase in CO₂ related to power generation from by-product fuels, and ignoring the impact of power generation on the CO₂ emission has no significant effect on the results.

Table II - By-product gas power generation

Basis – 1 ton of hot metal (1 thm = 2000 lb hot metal)

By-product oven	All coke	PCI 201 lb/thm	PCI 275 lb/thm	NGI 120 lb/thm	NGI 190 lb/thm
Coking col required, lb	1569	1267	1187	1325	1209
COG produced, MMBtu	3.77	3.04	2.85	3.18	2.90
BFG export, MMBtu	2.74	3.03	3.30	3.42	4.16
COG + BFG, MMBtu	6.51	6.07	6.15	6.60	7.06
Fuel for coking, MMBtu	(1.90)	(1.54)	(1.44)	(1.61)	(1.47)
Net COG+BFG, MMBtu	4.60	4.53	4.71	4.99	5.60
Boiler power, kWh	323	318	330	350	393
Net power demand, kWh	--	5	(7)	(27)	(70)
Heat recovery oven					
Coking coal required, lb	1627	1313	1231	1373	1253
Coke oven power, kWh	291	234	221	246	224
BFG export, MMBtu	2.74	3.03	3.30	3.42	4.16
Boiler power, kWh	192	213	232	240	292
Total power, kWh	483	447	452	486	516
Net power demand, kWh	--	36	32	(2)	(33)
Overall					
75% by-product / 25% heat recovery					
Net power demand, kWh	--	13	2	(21)	(60)
Net CO ₂ emission, lb	--	16	3	(27)	(79)

Impact of blast oxygen enrichment on CO₂ emission

Operating data for North American blast furnaces supplied by Praxair was drawn from industry sources (see, for example, references 11 and 12). These compilations list for each furnace the annual production (t), the annual operating hours (hr), the coke rate (lb/thm), the fuel injectant type and rate (lb/thm), and the blast oxygen enrichment rate (scfm). The blast oxygen enrichment rate in scfm E is converted to a rate in lb / thm E' using equation (1),

$$E' = \frac{60 E \rho_o H}{P} \quad (1)$$

where ρ_o is the standard density of oxygen (0.0844 lb/scf), H is the annual operating hours listed in the survey, and P is the actual production rate taken from the data.

The coke rate for the equivalent all-coke practice K_o for each furnace is calculated from equation (2),

$$K_o = K_I + \sum_j R_j m_j \quad (2)$$

where K_I is the coke rate with injectant listed in the survey, m_j is the mass of injectant j , and R_j is the replacement ratio for injectant j listed in Table I.

As shown earlier, by-product coke ovens produce 75% of coke, and 94% of the carbon charged to these coke ovens is released as CO₂. Heat recovery coke ovens produce 25% of coke and release all of the charged carbon as CO₂. The CO₂ emission for the all-coke practice CO_{2,K_o} is then given by equation (3)

$$CO_{2,K_o} = 4.321 K_o \quad (3)$$

With blast oxygen enrichment and secondary fuel injection, less coke is needed, and so less by-product fuel is produced. As noted earlier, however, any loss of coke breeze will be made up by consumption of another, similar fuel, and so there is no CO₂ saving related to lower coke breeze production. The CO₂ emission from coke with blast enrichment CO_{2,K_I} is then given by equation (4),

$$CO_{2,K_I} = 3.922 K_I + 0.398 K_o \quad (4)$$

The K_I coefficient in equation (4) represents the CO₂ release from coke, by product fuels, and cokemaking losses, assuming 75% by-product and 25% heat recovery coke production.* The K_o coefficient represents the CO₂ release with enrichment from coke breeze and its replacement fuels.

The CO₂ emission from injected secondary fuels $CO_{2,I}$ is given by equation (5),

$$CO_{2,I} = \sum_j e_j m_j \quad (5)$$

where e_j is the emission factor for injectant j given in Table I.

The CO₂ avoided from cokemaking and ironmaking operations $\Delta CO_{2,1}$ is given by equation (6),

$$\Delta CO_{2,1} = CO_{2,K_o} - CO_{2,K_I} - CO_{2,I} \quad (6)$$

*Although the coke supply to individual furnaces will not follow the overall 75% / 25% split uniformly, that split represents the best available estimate since specific coke ovens and blast furnaces are not directly linked. Blast furnaces supplied by Praxair produce more than 50% of North American hot metal and use both by-product and heat recovery coke extensively, so the error introduced by using a constant split will be small.

The CO₂ emission from oxygen production CO_{2,O₂} is given by equation (7),

$$CO_{2,O_2} = 0.236E' \quad (7)$$

where the coefficient for E' represents 363 kWh / t O₂ power consumed in oxygen production and distribution and the 1.300 lb CO₂ / kWh U.S. average emission factor for power generation.

The net CO₂ saving from blast oxygen enrichment with secondary fuel injection ΔCO₂ is given by equation (8),

$$\Delta CO_2 = \Delta CO_{2,1} - CO_{2,O_2} \quad (8)$$

ANALYSIS OF CO₂ EMISSIONS

Table III shows that from 2000-2008 the ratio of CO₂ emission avoided in cokemaking and ironmaking through blast oxygen enrichment to the CO₂ generated in oxygen production and distribution was 6.29 ± 0.21 during 2000 – 2005 and 5.60 ± 0.33 during 2006 – 2008 in furnaces supplied by Praxair. In 2009 the ratio fell to 4.75. As will be shown below, these changes in the ratio are caused largely by the collective strategic responses of ironmakers to business and economic conditions. A brief discussion of the constraints placed on ironmakers will help explain these responses.

Secondary fuel injection and blast oxygen enrichment have different and complementary effects on the blast furnace. Secondary fuels are injected primarily to lower

coke consumption, with cost and environmental benefits. Fuel injection also lowers temperatures in the furnace. Blast oxygen enrichment raises furnace productivity and raises temperatures in the furnace. Since furnace temperatures must be kept within a narrow window, fuel injection and blast oxygen enrichment are used together. The raceway adiabatic flame temperature (RAFT) is a commonly used benchmark for furnace temperatures. Variations in RAFT of 150°F are considered tolerable with PCI. Because reduction by the hydrogen in the natural gas avoids some of the endothermic Boudouard reaction, there is more flexibility in RAFT with NGI,¹³ although the limits are not widely agreed on. However, since the operating window has a finite width, ironmakers enjoy some flexibility.

Table III – CO₂ summary

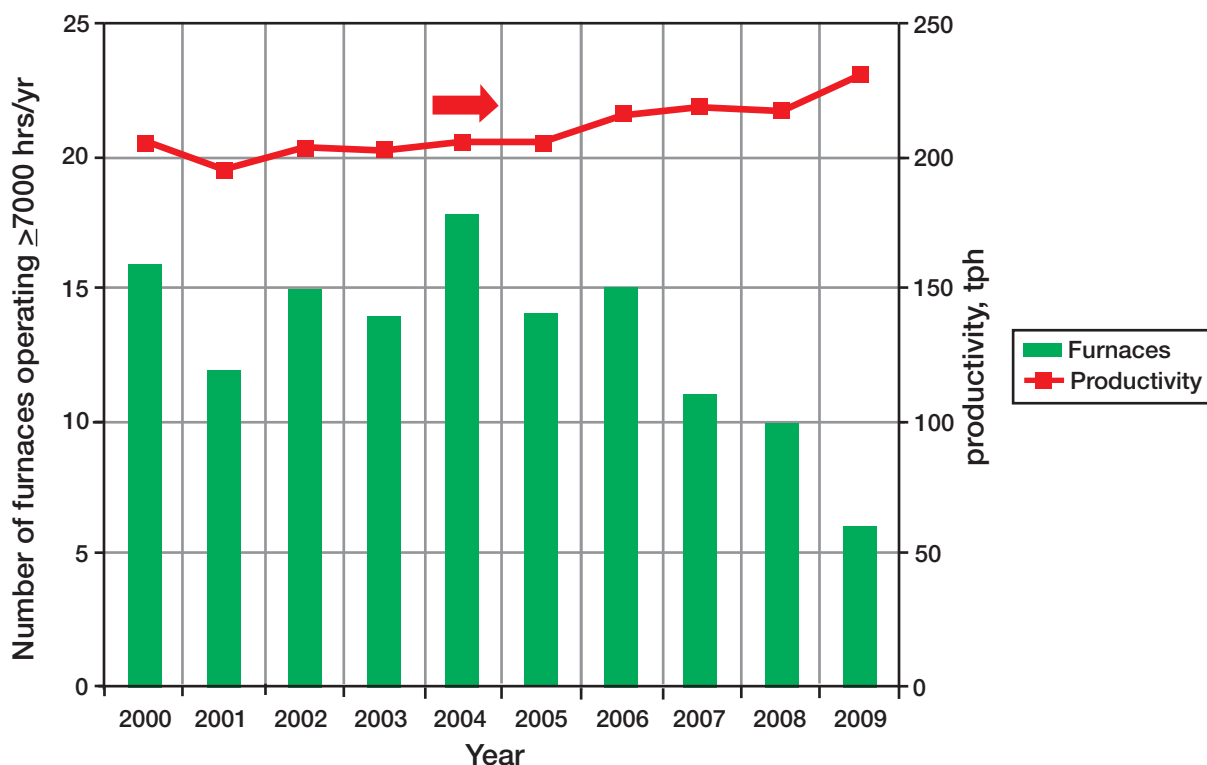
Year	2000	2001	2002	2003	2004
CO ₂ emitted for all-coke practice, MMtpy	63.325	57.026	55.240	58.267	64.387
CO ₂ avoided in cokemaking/ironmaking, MMtpy	3.696	2.593	2.987	2.944	3.976
CO ₂ generated for oxygen, MMtpy	0.589	0.410	0.460	0.454	0.635
Ratio, avoided / generated for oxygen	6.27	6.33	6.49	6.48	6.26
Net CO ₂ saved, MMtpy	3.1027	2.182	2.527	2.490	3.341
Year	2005	2006	2007	2008	2009
CO ₂ emitted for all-coke practice, MMtpy	58.156	64.152	59.841	57.111	39.514
CO ₂ avoided in cokemaking / ironmaking MMtpy	3.282	3.282	3.002	2.795	1.657
CO ₂ generated for oxygen, MMtpy	0.540	0.575	0.507	0.530	0.349
Ratio, avoided / generated for oxygen	6.08	5.71	5.92	5.27	4.75
Net CO ₂ saved, MMtpy	2.742	2.707	2.495	2.265	1.308

Under normal operating conditions, ironmakers minimize costs. They use the highest practical fuel injection rate and the lowest blast oxygen enrichment level that will support that amount of injected fuel. When higher productivity is required, ironmakers increase blast oxygen enrichment beyond the minimum required[†]. When total production falls, ironmakers may need to lower their fuel injection rate to accommodate cokemaking operations.^{††}

Ironmakers' responses to changing conditions are evident in Figure 1, which shows the number of Praxair

supplied furnaces operating for at least 7000 hours (80% utilization) in a year and the average production rate for Praxair supplied furnaces. Normal operating conditions can be seen from 2000 – 2005. In this period, productivity is fairly constant at 200 tph. From 2006 – 2008, a combination of strong demand and high selling prices for steel,¹⁴ increased exports,¹⁵ and planned and unplanned furnace outages¹⁶⁻¹⁸ caused ironmakers to raise furnace productivity to around 215 tph. During this period, oxygen enrichment volumes were high relative to fuel injection rates. In 2009, in response to the

Figure 1 – Number of Praxair furnaces operating at 80% availability (≥ 7000 hrs/yr) and average Praxair furnace productivity.



[†]The productivity benefit from increasing oxygen enrichment within the RAFT window (i.e., independent of fuel injection) results in a lower specific heat loss from the furnace. However, since this loss is only about 1% of the total energy involved in ironmaking, the impact on CO₂ emissions is very small and is ignored here.

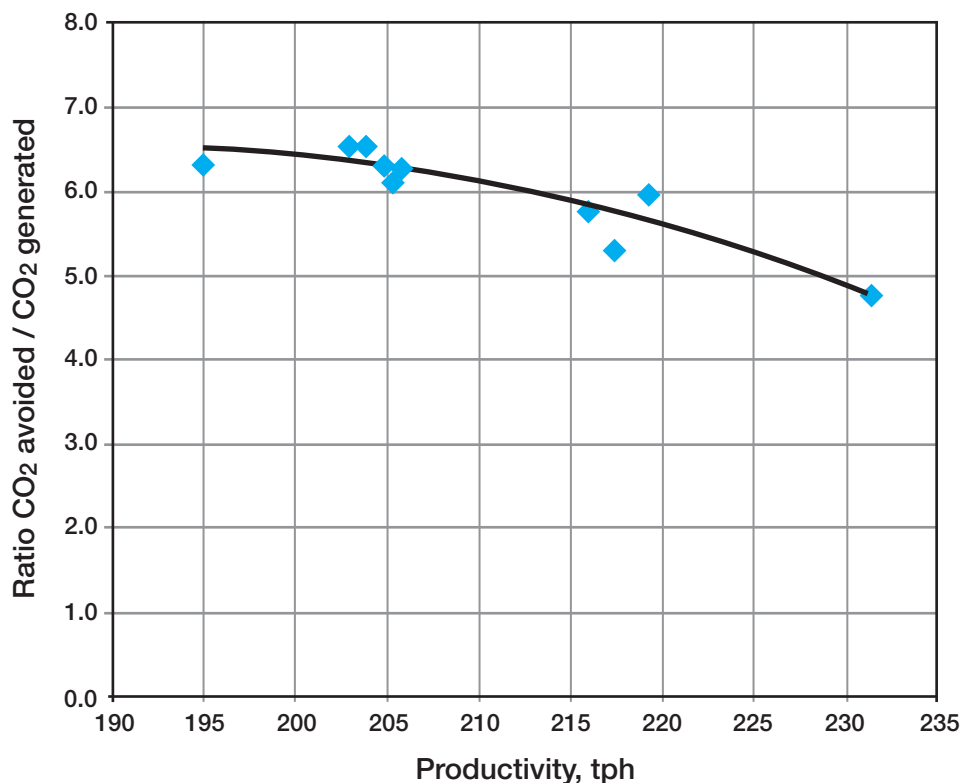
^{††}Heat recovery coke ovens are operated by third parties, and the coke is supplied on a take-or-pay basis. When production falls sharply, fuel injection must be lowered to allow the contracted amount of coke to be consumed. With by-product ovens operated within the steel company there is also incentive to lower fuel injection with falling production since coke oven refractories must remain hot once heated. Lower fuel injection rates may be more economical than heating unused coke ovens or rebuilding cooled ovens.

economic crisis, ironmakers consolidated production into a small number of furnaces (6 operated for ≥ 7000 hours, compared with 10-15 during 2000 – 2008) and pushed these furnaces to productivity rates of 230 tph, 15% higher than the 2000 – 2005 period. This led to an unusual combination of low total production and high productivity (giving high oxygen enrichment levels).

Thus, there appears to be a correlation between furnace productivity and the ratio of CO₂ avoided to CO₂ generated for oxygen production. Figure 2 plots the relationship between the ratio and productivity for the 2000 – 2009 period. The second-order curve shown accounts for 86% of the variation in the data ($R^2 = 0.857$).

Figure 2 – Ratio of CO₂ avoided in cokemaking and ironmaking to CO₂ generated for oxygen production and distribution as function of average productivity for Praxair furnaces.

Regression coefficient for curve $R^2 = 0.857$.



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