DRI UPDATE

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Experience and Developments of the ENERGIRON DR Technology for H$_2$ Use

Pablo Duarte, Tenova HYL., Mexico.

Abstract

The trend of the steelmaking industry is in the direction of decarbonisation to comply not only with environmental regulations but with a sustainable approach for steel production. Current actions of steelmaking industry, as part of the decarbonisation of global and specifically Europe's economy, is towards intensive steel scrap recycling as part of the circular economy, and to hydrogen-based iron reduction as a long-term substitute for carbon-based processes.

The ENERGIRON technology scheme (the innovative DRI Technology jointly developed by Tenova and Danieli) has been characterized by the inspiration of innovation. Starting by installing the first gas based direct reduction in the 1950's at industrial scale in Hylsa steelmaking facilities in Monterrey, using H$_2$ rich gas (in a ratio of H$_2$/CO ~5) as reducing gas, incorporating selective CO$_2$ removal for increasing process scheme efficiency while reducing energy consumption and providing practical solution for CO$_2$ capture and commercialization (CCU), developing the ZR (reformerless) scheme for further process efficiency while producing high-Carbon DRI (>3%C) since more than 20 years ago, using the breakthrough reliable Hytemp® System for hot DRI transport and EAF feeding by environmental friendly, totally enclosed pneumatic transport, and developing schemes for intensive H$_2$ use. This paper is focused on the benefits and advantages on H$_2$ use through the ENERGIRON process for Carbon Direct Avoidance (CDA) as compared to other proposals.

Introduction

As compared to the coal-based BF-BOF route, any energy source providing hydrogen (H$_2$) and carbon monoxide (CO) can be used as reducing agent for iron oxides reduction in the DR process. This makes DRI-EAF (or DRI-OSBF) the best available technological solution for decarbonisation of the steelmaking industry. The simplified process configuration when using H$_2$, makes the DR process very efficient in terms of energy consumption and scheme simplicity. The expected energy consumption for the ENERGIRON DR process is reduced from 10,2 GJ/t DRI with natural gas (NG) to as low as 6,6 GJ/tDRI with H$_2$ for process plus additional 1,6 GJ/tDRI as fuel and about 25 kWh/tDRI for the core plant. This exceptionally low electricity consumption is not only because of the H$_2$ use but also due to the high operation pressure of the ENERGIRON system (≥6 barA @ top gas).

On the other hand, in the EAF meltshop, to overcome the negative effect of the gangue in DRI, by feeding high-metallised, hot DRI to the EAF, the power consumption is significantly reduced

to figures very close to the case of 100% scrap melting, overcoming the negative effect of the gangue content in the DRI. Typical power consumption for a charge of 80% hot DRI and 20% scrap is about 400 kWh/tLS. Feeding high percentages of DRI is required for production of high-end quality steels.
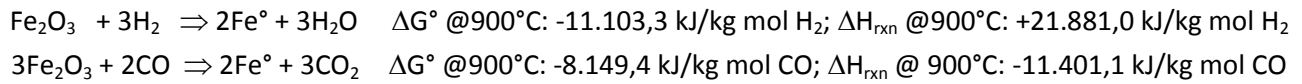
Sustainable H_2 generation is based on the application of electrolyzers, using power from renewable sources (i.e. eolic, solar PV) and eliminating carbon footprint (CDA) for ironmaking and steelmaking (Figure 1). For this industrial application, H_2 shall be generated by high efficiency electrolyzers, There are different available electrolysers technologies, such as: Atmospheric Alkaline Electrolysers (AAE), Proton Exchange Membranes (PEM) and High Temperature Electrolysers (HTE), being the first a mature technology in the MW range for industrial use.

*Figure 1. Carbon-free steelmaking route based on ENERGIRON ZR Process*
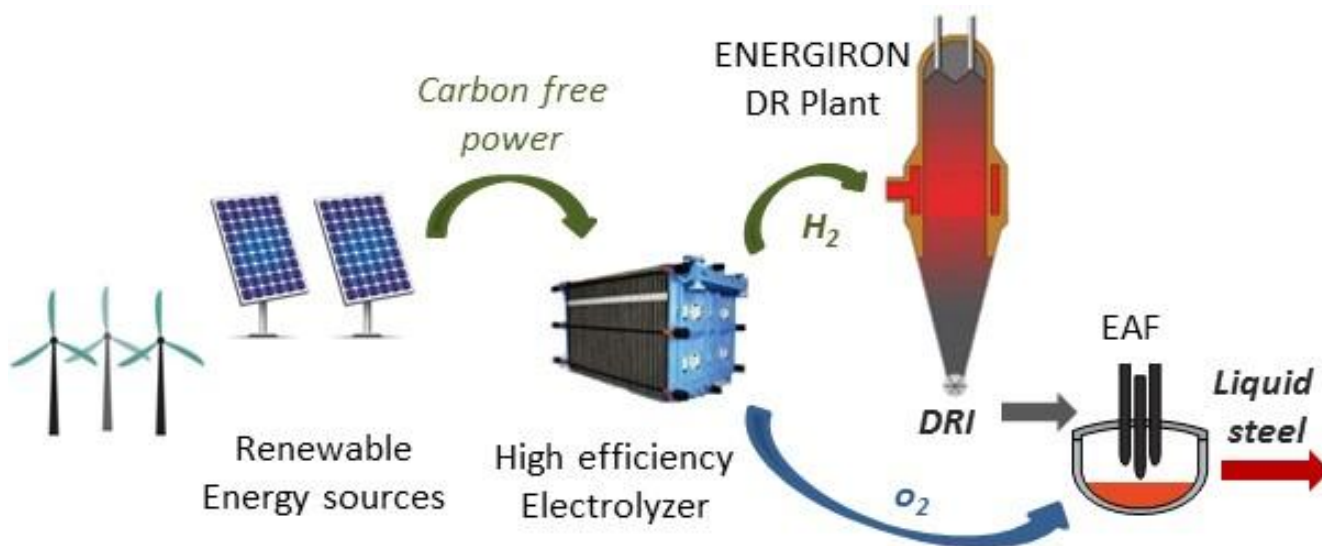
Reduction of iron ores with H_2

The gas reducing agents are CO, H_2 and mixtures of both. Thermodynamics of iron oxides, dealing primarily with equilibrium between iron oxides, CO and H_2, provides the potential for a reduction reaction to occur. This is indicated by the Gibbs Free Energy ($\Delta G°$):

$Fe_2O_3 + 3H_2 \Rightarrow 2Fe° + 3H_2O$ $\Delta G°$ @900°C: -11.103,3 kJ/kg mol H_2; ΔH_{rxn} @900°C: +21.881,0 kJ/kg mol H_2

$3Fe_2O_3 + 2CO \Rightarrow 2Fe° + 3CO_2$ $\Delta G°$ @900°C: -8.149,4 kJ/kg mol CO; ΔH_{rxn} @ 900°C: -11.401,1 kJ/kg mol CO

As observed, thermodynamically H_2 reduces iron oxide easily than CO, as per change of Gibbs free energy [2]. On the other hand, the exothermic or endothermic behavior is indicated by the enthalpy change (ΔH_{rxn}) of the corresponding reactions.

Figure 2. Change of reduction degrees with time for CO:H_2: 0:1; CO:H_2: 1:0

a) Reduction degree (%)-H2 @ 1273°K   b) Reduction degree (%)-CO @1273°K
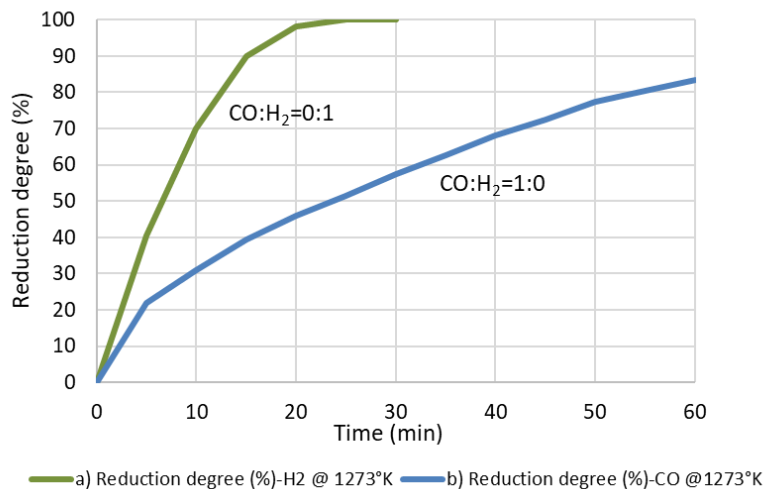
Kinetically, the effect of temperature on the extent of iron ore reduction has been investigated using gases with different H_2/CO ratios [3]. The changes of reduction degree at 1000°C for CO/H_2 ratios of 1:0 and 0:1, are indicated in Figure 2. In general, the higher the temperature the faster the extent of the reduction process, whether the reducing agent is H_2 or CO. However, the reduction of iron ore with H_2 is more than 4 times faster as compared to CO; i.e. 98% reduction in ~20 min vs. 83% reduction in 60 min at 1000°C. Reasons are:

1) the equilibrium of H_2 decreases with increasing temperature because it is an endothermal reaction, leading to a higher reducing potential at high temperature, and as a result, the driving force of the reduction reaction is enhanced;

2) the high temperature contributes to a high mass transfer coefficient.

On the other hand, iron ore reduction with CO requires lower reducing gas temperature because of the exothermal reaction behavior, and kinetically is much slower than the reduction with H_2.

The ENERGIRON ZR Process

The ENERGIRON ZR process, as shown in Figure 2, is a major step in reducing the size and improving the efficiency of direct reduction plants [1]. The same ZR process scheme configuration can be used for any application, regardless of whether using NG, H_2, reformed gas from external steam/NG reformer, syngas from coal gasifiers, or COG, depending on availability. As indicated in Figure 2, the ENERGIRON ZR scheme can produce cold DRI (CDRI), hot DRI (HDRI) which can be directly fed to: 1) Hytemp® System for transport and direct feeding to an adjacent EAF, 2) to briquetting presses for production of HBI and 3) to a proprietary Tenova OSBF melter for production of hot metal/pig iron. The latter is a breakthrough approach for production of hot metal using NG as reducing agent, decreasing to <50% the carbon footprint as compared to the conventional coal-based BF while keeping BOF downstream steelmaking unchanged.

Figure 2. ENERGIRON ZR Process scheme
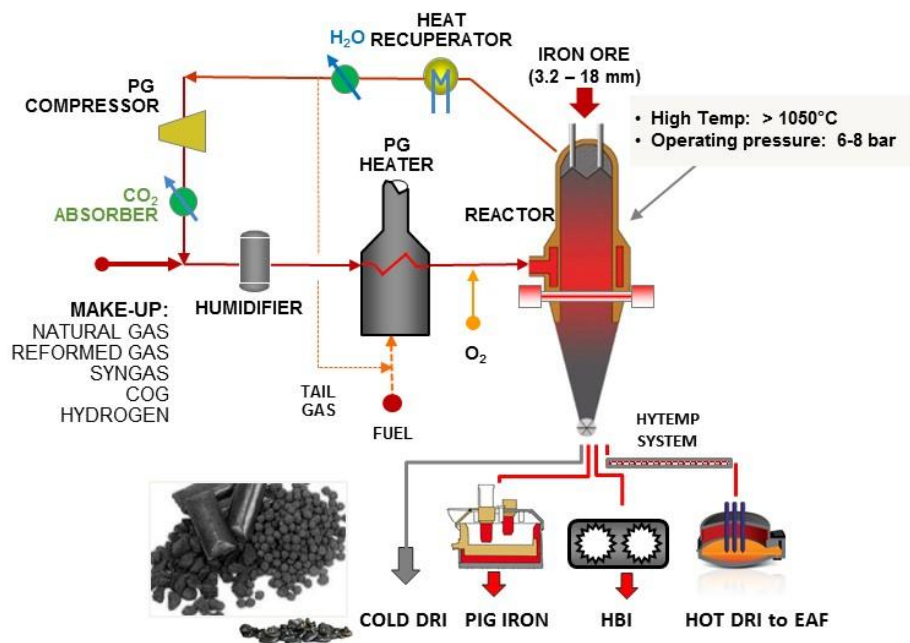
Long lasting experience with Hydrogen

Historically, the steelmaking route based on DR-EAF has always been characterized using H_2. The ENERGIRON technology using reformed gas as source of reducing gas, includes a conventional steam/NG reformer. The off line reformer used for DR plants is based standard technology with hundreds of references in DR and hydrogen plants; there are more than 40 HYL/ENERGIRON

plants having used this type of NG reformers. For any reformer, H_2 is produced in different concentration, depending on the oxidants ratio being used; i.e.

$$CH_4 + H_2O = 3H_2 + CO$$

$$CH_4 + CO_2 = 2H_2 + 2CO$$
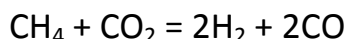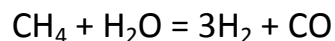
Typical operation characteristics for the ENERGIRON plants and for the DR competing technology (Midrex) are shown in Table 1.

These industrial operating data reflect the long-lasting industrial experience of ENERGIRON plants with intensive use of H_2 for DRI production.

Table 1. Characteristics of reformed gas in DR technologies

Parameter related to H_2	ENERGIRON	Other DR technology
H_2O/C ratio in NG Reformer	2.0 – 2.5	1.5
H_2/CO ratio in reducing gas	4 – 5	1.7
%H_2 to reactor (% vol.)	~70%	~55%

In addition to the vast industrial experience using H_2, in the 1990's, Tenova HYL carried out extensive tests at pilot plant (Figure 3) with ≥ 90% (vol.) H_2; producing H_2 from reformed gas from the industrial DR plant by water shifting and CO_2 removal. The demonstration/pilot plant at Hylsa Monterrey had a production rate of 36-tonne DRI/day with all flexibilities to produce: CDRI, HDRI for HBI production and HDRI for direct pneumatic transport to an adjacent pilot plant EAF.

This plant also included all capabilities for synthesis of all type of reducing gases; from 100% H_2 to 100% CO, including reformed gas, typical COG and gases from coal gasification. In fact, the ZR scheme was developed and demonstrated in this facility during the 1980's. The experimental campaign included 15 different process conditions, depending on the DRI type and quality to be achieved.

- For CDRI conditions, some minimum required amount of NG was injected to the conical/cooling zone of the reactor. The following results were achieved: Metallization of 94%-96%, %C content of ~1,0%. H_2 has been controlled in a range of ~90% vol.
- For the HDRI, HBI was produced to prevent fast re-oxidation due to low %C. Metallization of 94%-96% and %C obtained between 0,2% – 0,8% being the latter for the condition of some NG injection to the reduction circuit. H_2 was also controlled in ~90% vol.

These tests provided all necessary information to define:

- Process and design parameters mainly related to optimized flow-temperature correlation.
- DRI quality in terms of metallization and carbon content.
- Optimization of operating pressure, reactor L/D ratio, solids residence time (τ), to consistently achieve the DRI quality, determination of fluidization factor (f) to ensuring proper gas velocities and distribution through the solids bed, among others for the proper gas distribution and design of the scheme for H_2 utilization.

These campaigns at demonstration/pilot plant tests with highest H_2 volumes providing the fact that the ENERGIRON process is already fit for the use of 100% H_2, when needed. All required data for design and operation under this condition is available and can be directly applicable to any existing and/or new DR plant installation.

*Figure 3. HYL Pilot Plant tests campaigns with ≥90% (vol.) H_2*

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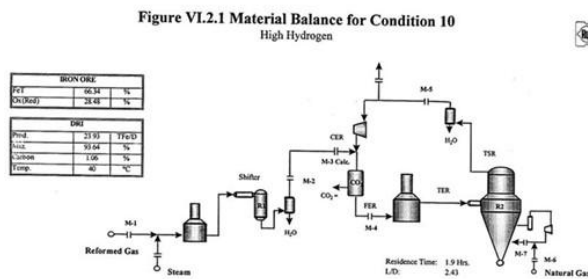
**Scheme with high H_2 use and energy consumption figures**

For the case of H_2, the same ZR scheme applies. The only difference is that, for H_2 utilization higher than ~73% (energy) or ~90% vol. at reactor inlet, the scheme is simplified by-passing the selective CO_2 removal system. For higher H_2 concentrations, any carbon input to the system, via NG, along with other components like N_2, are eliminated through the tail gas purge from the system, which is used as fuel in the gas heater (Figure 4).

Figure 4. ENERGIRON ZR Scheme with H_2 use

Scheme with partial use of H_2 Scheme with ≥90% vol. H_2
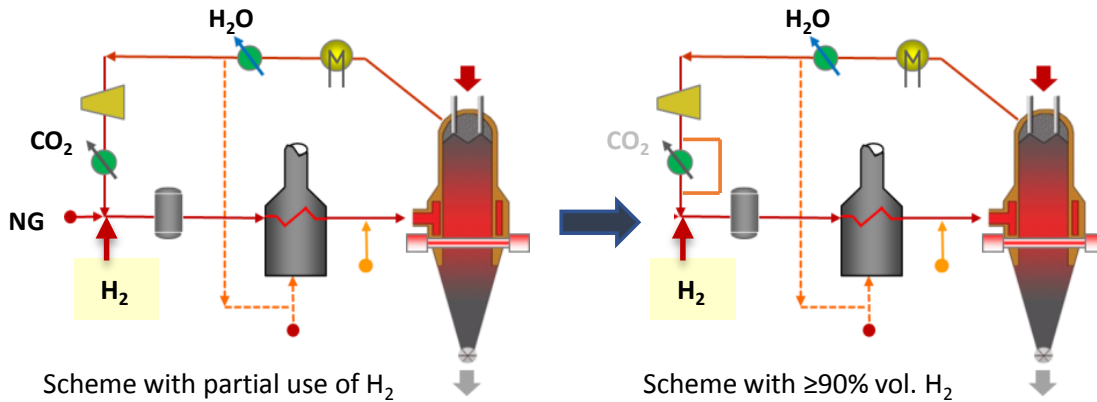
In terms of energy consumption, the impact of H_2 (figures as % of total energy input), as compared to NG is indicated in Figure 7, showing the potential energy credit of the %C in the DRI, when being melted in a EAF.

Figure 7. Energy consumption figures as function of NG/H_2 ratios (% energy input)
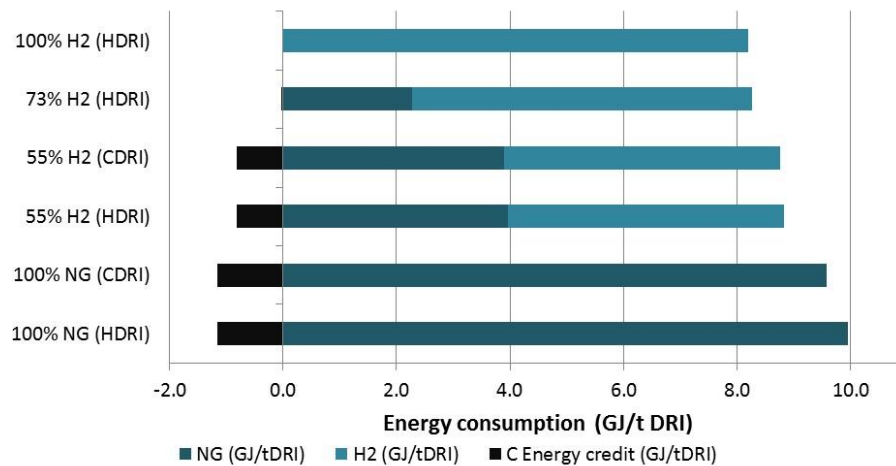
Unique advantage for the use of H$_2$ with high operating pressure

Unique benefits of the ENERGIRON ZR technology for the direct use of H$_2$ is related to the high operating pressure (6-8 bar a), which is reflected in:

- Gas sealing

  Tight sealing is required to prevent any leak of the most diffusible gas in nature. In the ENERGIRON DR plants, the high operating pressure is managed using mechanical sealing for pressurization/depressurization from atmosphere. Mechanical sealing allows higher pressure drop (ΔP) due to friable ores and/or additional fines and is preventing any gas leak/air intake. By this, any additional ΔP is simply handled by the compressor instead of lower gas flow and/or decreasing production rate.

- Fluidization and gas distribution

  Regarding the reduction reactor design, there are two fundamental parameters which define the size and geometry of the shaft: 1) the fluidization factor (f) and the solids residence time (τ). The gas velocity of the gas inside any moving bed reduction shaft has the following functionality:

  $$(1)\ V_G = V_{mf} * f = k * [F_{G(act)} * F_S * (M * T)^{1/2}] / [D_i^2 * P^{1/2}]$$

where:

V_G *is the actual gas velocity inside the shaft*

f *is the fluidization factor (<1)*

V_{mf} *is the velocity of minimum fluidization; i.e., the gas velocity*

at which the solids flow is suspended

k *is a function of solids and gas properties, the bed's void*

fraction and particle size distribution

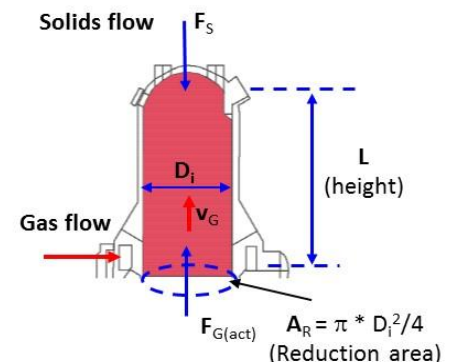$F_{G(act)}$ *= Specific reducing gas flowrate (actual cond.)*

Fs *= Production rate*

M *= Gas molecular weight*

T *= Reducing gas Temperature*

P *= Operating pressure*

Di *= Reactor internal diameter*

On the other hand, the residence time is defined as:

(1) $\tau = V_R / [F_S/\rho_S] = L * A_R / [F_S/\rho_S]$

where:

τ *is the residence time*

V_R, A_R *= volume, area of the cylindrical (reduction) area*

L *= the height of the reactor cylindrical (reduction) section*

ρ_S *= solids density*

The fluidization factor (f) cannot exceed a maximum value and the residence time (τ) is determined from experimental data, leading to the required volume (V_R). Thus once M (M_{H2} =2), solids properties, required reducing gas (F_G) and H_2 temperature (T) are fixed, the only variables to optimize the reactor design are: diameter (D_i) and height (L).

From above equation (1), It can be easily noted that a high operating pressure allows better flexibility in terms of diameter (D_i), height (L), and residence time (τ) for a better gas distribution.

- <u>Effect of high operating pressure on overall power consumption for H_2 scheme</u>

Regarding the recycle gas compressor for, the power requirements is a function of the compression ratio; i.e.

Compression $\propto (P_2/P_1)^k$

For the same ΔP, higher suction pressure at compressor leads to lower power consumption, as observed in Table 2 below.

Table 2. Effect of high operating pressure for High-H_2 scheme (~96% vol.) on power consumption

Parameter @ PG compressor	ENERGIRON	Other DR technology
Suction pressure (bar a)	5,4	1,1
Discharge pressure (bar a)	7,5	3,2
Gas flow (Nm^3/t DRI)	1440	1440
Power (kWh/t DRI)	20	82

The impact on power consumption for PG compressor with H_2 for lower pressure operation is 4 times higher, reflecting the higher overall energy efficiency of the higher operating pressure of ENERGIRON process.

Remarks

- The ENERGIRON ZR process is a proven DR technology for H_2 use:
- Same process scheme for NG and H_2 in any proportion
- All ENERGIRON DR plants with external reformer are already using ~70% H_2 (%vol.).
- Extensive campaigns were carried out in a demonstration plant in the 1990's with >90% H_2.
- ENERGIRON has been the DR technology of choice for projects based on up to 100% *Green* H_2 from renewable energy, like HYBRIT in Sweden and SALCOS in Germany.

References

[1]Pablo Duarte, Markus Dorndorf. METEC & 4th ESTAD 24-28 June 2019. Düsseldorf, Germany. *Technological achievements and experience on H_2 use for DRI production in Energiron Plants.*

[2]Amit Chaterjee; Second edition 2012; *Sponge iron production by direct reduction of iron oxide*.

[3]International Journal of Minerals, Metallurgy and Materials. Volume 22, Number 7, July 2015, Page 1.

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You may Contact : Jorge MARTINEZ Tenova HYL; Monterrey, Mexico; Email; jorge.martinez@tenova.com
Praveen CHATURVEDI; Tenova Technologies Pvt Ltd, India; tel +91 9167725604; Email; hylindia@tenova.com