Decarbonization of steel production: alternative Direct Reduced Iron and CCS

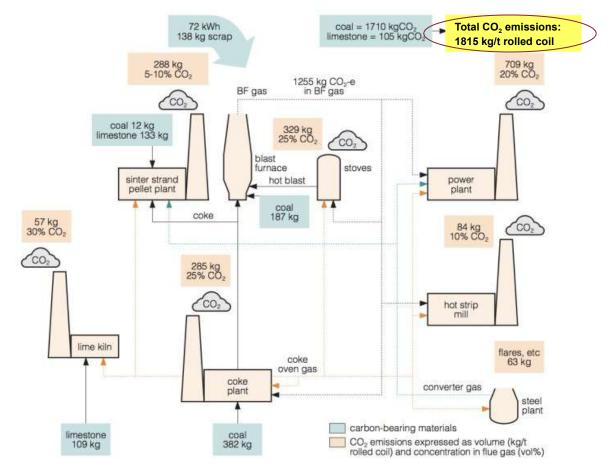
Prof. Giorgio Vilardi Ing. Antonio Trinca



Steel production routes



 Laplace Conseil, "Impacts of energy market developments on the steel industry," 74th Sess. OECD Steel Comm., no. July, pp. 1–2, 2013



 Bui et al, 'Carbon capture and storage (CCS): the way forward', Energy Environ. Sci., 2018,11, 5, The Royal Society of Chemistry, 10.1039/C7EE02342A.

- Coking making:
 - Coke dry quenching: 27 kgCO₂/t_{coke}
 - COG Recovery: 6-9 GJ/t_{coke}
 - Biomass and waste materials: the amount of wood and waste plastics that can be added to the coking coal blend is currently limited to less than 2 wt.% due to detrimental effects on coke quality.
- Sintering:
 - Waste Heat recovery and Off-gas recirculation: 60 kgCO₂/t_{sinter}
 - Waste fuels: 19.5 kgCO₂/t_{sinter}
 - Biochar/Charcoal: Up to 20-30% can be used in the sintering bed.
- Cavaliere, P., & Cavaliere, P. (2019). *Clean ironmaking and steelmaking processes: Efficient technologies for greenhouse emissions abatement* (pp. 1-37). Springer International Publishing..

- Blast Furnace
 - Injection of:
 - COG: saving on coke
 - \circ Oil: 50 kgCO₂/t_{HM}
 - \circ Natural Gas: 55 kgCO₂/t_{HM}

The furnace temperature limits the maximum injection rates. NG has a large effect on the flame temperature cooling with respect to other fuels, so, O_2 enrichment is required.

- H_2 : up to 40%
- Plastic waste: The substitution of coke is limited to a maximum of around 40% since the injectants are unable to give the physical support for iron ore provided by coke.
- Biomass
- Cavaliere, P., & Cavaliere, P. (2019). *Clean ironmaking and steelmaking processes: Efficient technologies for greenhouse emissions abatement* (pp. 1-37). Springer International Publishing..

Coke cannot be completely eliminated in the BF operations; its minimum rate is in the order of <u>200 kg/t_{HM}</u>



• Cavaliere, P., & Cavaliere, P. (2019). *Clean ironmaking and steelmaking processes: Efficient technologies for greenhouse emissions abatement* (pp. 1-37). Springer International Publishing..

HydroMetallurgy

Smelting Reduction

Direct Reduced Iron –

Hydrogen Smelting Reduction









HydroMetallurgy
 Acid Leaching

iron dissolution:

$$Fe_2O_3(s) + 3H_2C_2O_4(aq) \rightarrow Fe_2(C_2O_4)_3(aq) + 3H_2O$$
(1)

photochemical reduction:

$$Fe_2(C_2O_4)_3(aq) + 4H_2O \rightarrow 2FeC_2O_4 \cdot 2H_2O(s) + 2CO_2(g)$$
(2)

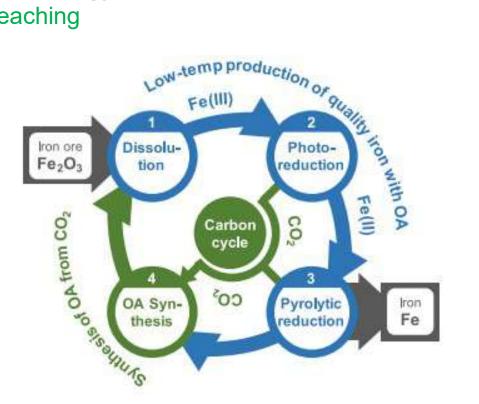
pyrolytic reduction:

$$FeC_2O_4 \cdot 2H_2O(s) + H_2 \rightarrow Fe(s) + CO(g) + CO_2(s) + 3H_2O$$
(3)

WGS: $CO + H_2O \rightarrow CO_2 + H_2$ (4)

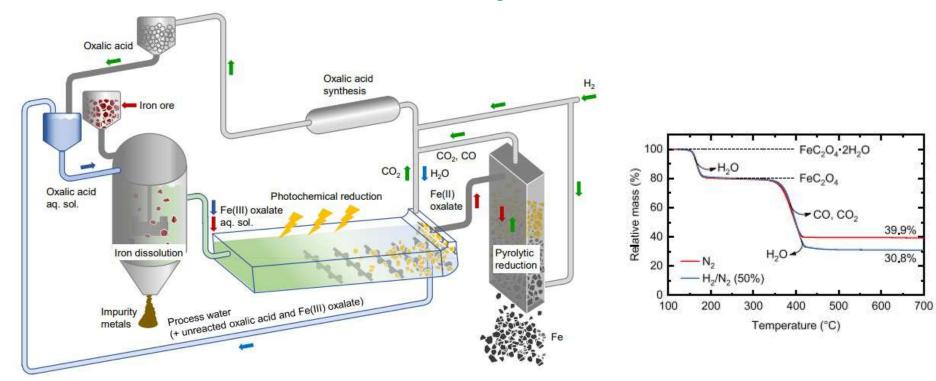
oxalic acid synthesis: $2CO_2 + H_2 \rightarrow H_2C_2O_4$ (5)

net reaction: $Fe_2O_3 + 3H_2 \rightarrow 2Fe + 3H_2O$ (6)



 Santawaja, P., Kudo, S., Mori, A., Tahara, A., Asano, S., & Hayashi, J. I. (2020). Sustainable iron-making using oxalic acid: the concept, a brief review of key reactions, and an experimental demonstration of the ironmaking process. ACS Sustainable Chemistry & Engineering, 8(35), 13292-13301.

HydroMetallurgy
 Acid Leaching



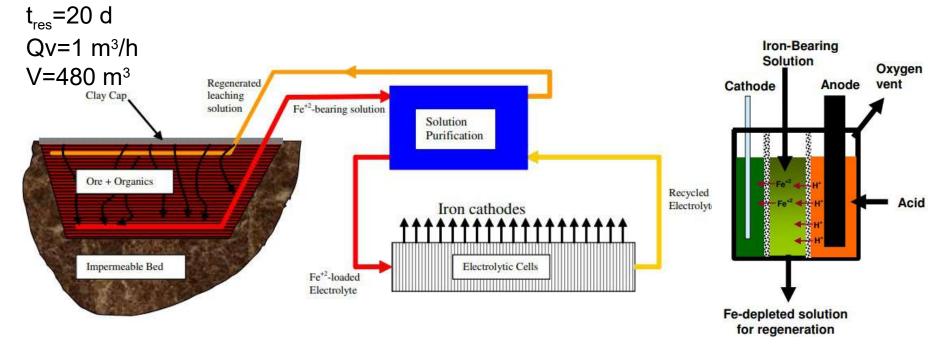
 Santawaja, P., Kudo, S., Mori, A., Tahara, A., Asano, S., & Hayashi, J. I. (2020). Sustainable iron-making using oxalic acid: the concept, a brief review of key reactions, and an experimental demonstration of the ironmaking process. ACS Sustainable Chemistry & Engineering, 8(35), 13292-13301.

- HydroMetallurgy
 Acid Leaching
- Iron purity (on a metal basis): 80.5–99.7 wt %
- Feedstocks consisting of 33.9–93.3 wt % iron
- Highest temperature: **500** °C
- Availability of diverse feedstocks
- The photochemical reduction needed **6 h** to reach full conversion, with the area fraction of solution surface exposed to light being **17%**
- Iron productivity **0.5 ton-Fe/day/m**³ (5–6 h and 0.4–0.5 mol-Fe/L)

• Santawaja, P., Kudo, S., Mori, A., Tahara, A., Asano, S., & Hayashi, J. I. (2020). Sustainable iron-making using oxalic acid: the concept, a brief review of key reactions, and an experimental demonstration of the iron-making process. ACS Sustainable Chemistry & Engineering, 8(35), 13292-13301.

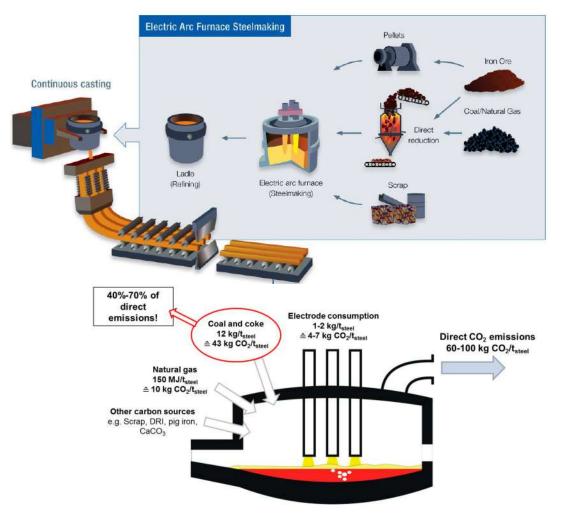
- HydroMetallurgy
 Bio Leaching
- <u>Geobacter metallireducens</u>, <u>Shewanella putrefaciens</u> and <u>L. ferriphilum</u> reduce Fe⁺³ to Fe⁺² under anaerobic conditions
- No need for coke
- Energy consumption reduction by 2,080 MJ/t of iron compared to the blast furnace
- The CO₂ directly emitted by the process entirely from biomass
- Efficiency of 93.85% iron was achieved with <u>L. ferriphilum</u>, at 313 K at the end of 20 days
- TC, E. (2005). Direct Biohydrometallurgical Extraction of Iron from Ore. Final Technical Report (No. INIS-US--0697). Michigan Technological University (United States). Funding organisation: US Department of Energy (United States)

HydroMetallurgy
 Bio Leaching

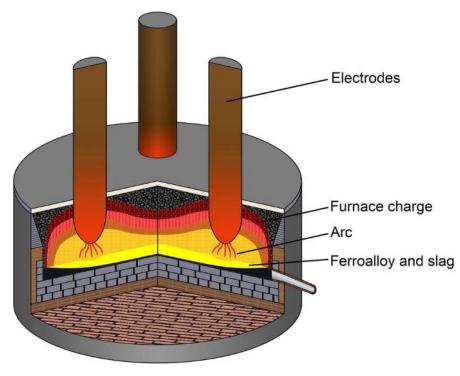


- TC, E. (2005). Direct Biohydrometallurgical Extraction of Iron from Ore. Final Technical Report (No. INIS-US--0697). Michigan Technological University (United States). Funding organisation: US Department of Energy (United States)
- Prabhu, S. V., Ramesh, G., Adugna, A. T., Beyan, S. M., & Assefa, K. G. (2019). Kinetics of iron bioleaching using isolated Leptospirillum ferriphilum: effect of temperature. International Journal of Innovative Technology and Exploring Engineering, 8, 76-81.

• <u>Smelting Reduction</u> <u>Electric Arc Furnace</u>



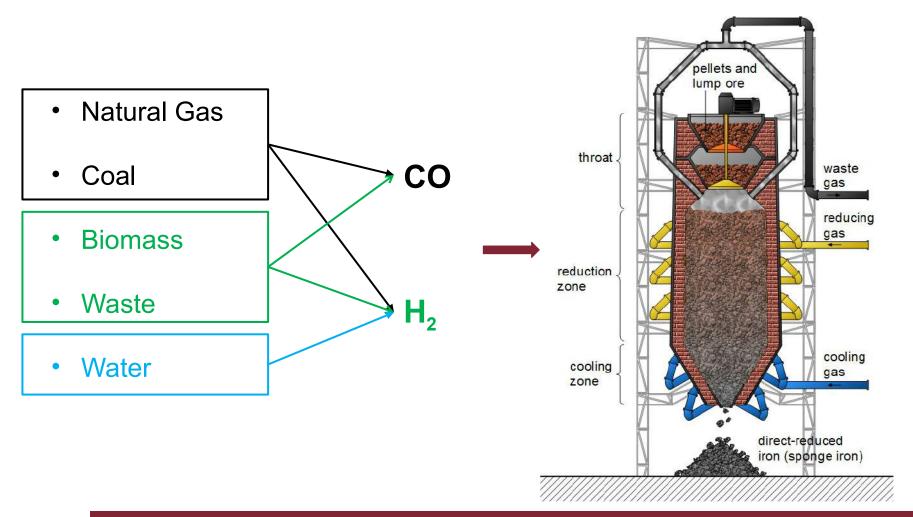
<u>Smelting Reduction</u> <u>Submerged Arc Furnace</u>





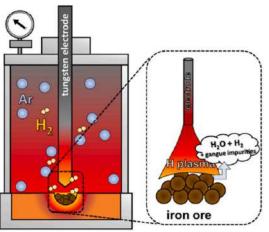
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Direct Reduced Iron



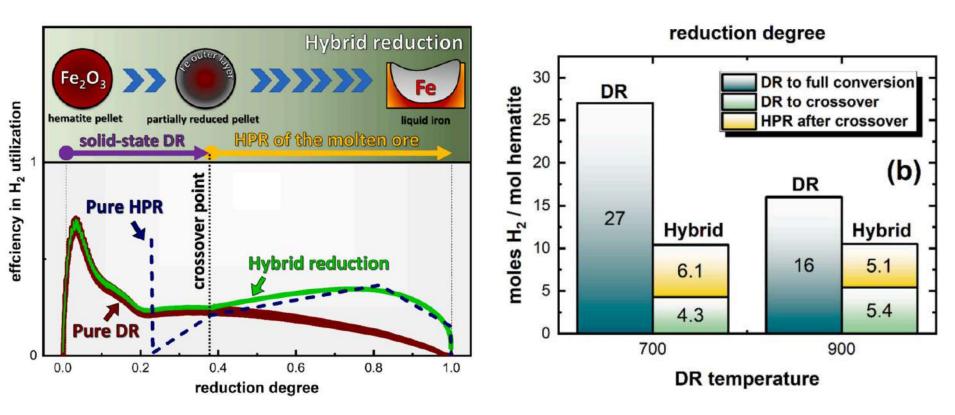
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- Hydrogen Smelting Reduction
- Simultaneous reduction and melting
- Reduction potential of <u>atomic</u> and <u>ionic</u> H₂ present in H₂ plasma is, respectively, 3 and 15 times higher than molecular H₂
- 2000-2600 °C at the interface between the plasma arc and the oxide melt
- Close to 100% reduction



- Souza Filho, I. R., Springer, H., Ma, Y., Mahajan, A., da Silva, C. C., Kulse, M., & Raabe, D. (2022). Green steel at its crossroads: Hybrid hydrogen-based reduction of iron ores. Journal of Cleaner Production, 340, 130805.
- Behera, P.R., Bhoi, B., Paramguru, R.K. et al. Hydrogen Plasma Smelting Reduction of Fe2O3. Metall Mater Trans B 50, 262–270 (2019). https://doi.org/10.1007/s11663-018-1464-8

Hydrogen Smelting Reduction



 Souza Filho, I. R., Springer, H., Ma, Y., Mahajan, A., da Silva, C. C., Kulse, M., & Raabe, D. (2022). Green steel at its crossroads: Hybrid hydrogen-based reduction of iron ores. Journal of Cleaner Production, 340, 130805.



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Carbon Capture in the Steel Industry

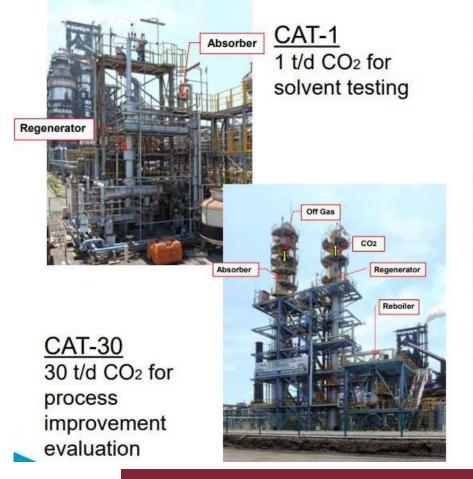
- \succ CO₂ removal consists of:
 - PSA, VPSA
 - VSPA/PSA + Cryogenic Separation
 - Chemical Absorption

	PSA	VPSA	PSA+cryogenic separation+ compression	VPSA+compression + cryogenic separation	Amines+ compression	
CO ₂ -rich gas captured						
CO ₂ (% vol)	79.7	87.2	100	96.3	100	
Suitable for transport and storage?	no	no	yes	yes	yes	
CCS Process						
Electricity consumption (kWh/tCO ₂)	100	105	310	292	170	
Capture Process (kWh/tCO ₂)	100	105	195	160	55	
Compression to 11 MPa for storage (kWh/tCO ₂)	-	-	115	132	115	
Steam consumption (GJ/tCO ₂)	0	0	0	0	3.2	
Total energy consumption (GI/tCO ₂)	0.36	0.38	1.12	1.05	3.81	
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Carbon Capture in the Steel Industry COURSE 50 Programme

CAT-1 & CAT-10

at Nippon Steel Kimitsu Works



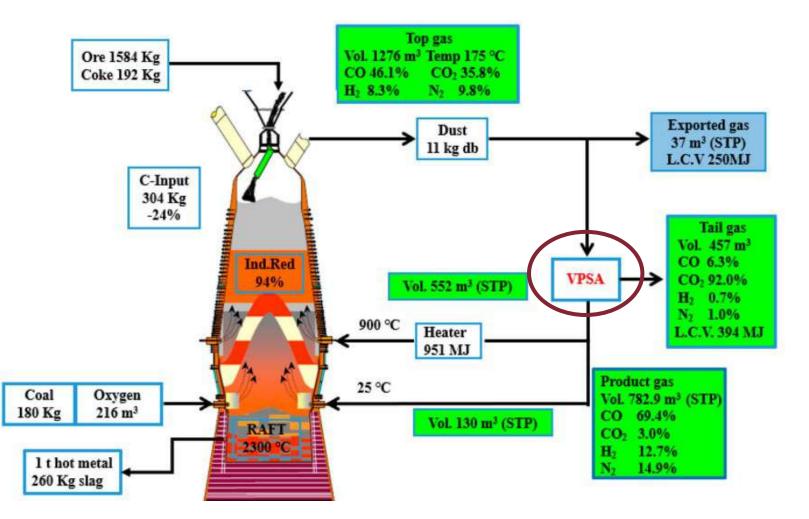
ASCOA at JFE Steel Fukuyama Works



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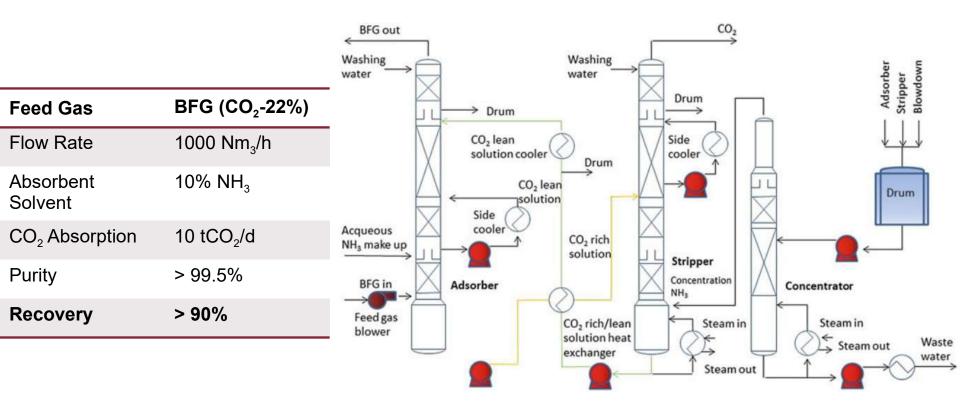
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Carbon Capture in the Steel Industry <u>Ultra-Low CO₂ Steelmaking (ULCOS) Programme</u>

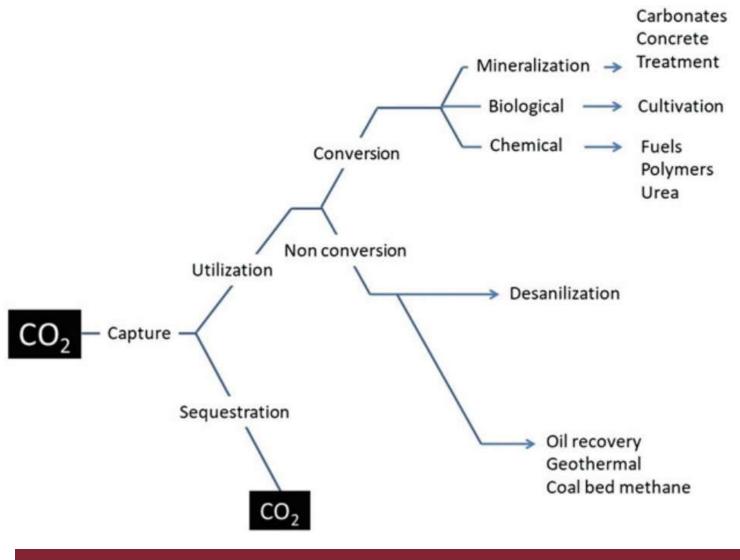


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Carbon Capture in the Steel Industry POSCO Programme

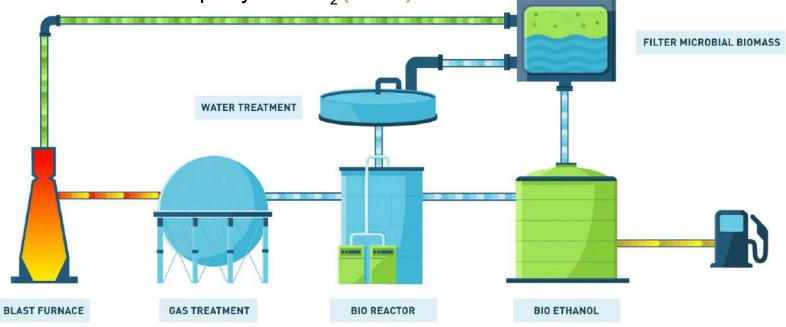


Carbon Capture in the Steel Industry



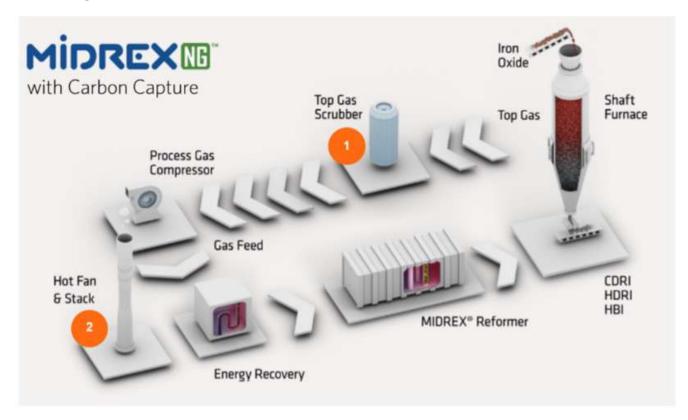
Carbon Capture in the Steel Industry Steelanol Programme

- 165 M€ investment
- 80 million liters of bioethanol annually
- Every 2.3 tons of CO₂ captured equals one ton of ethanol
- Reduction of 5 Mt per year CO₂ (-60%)

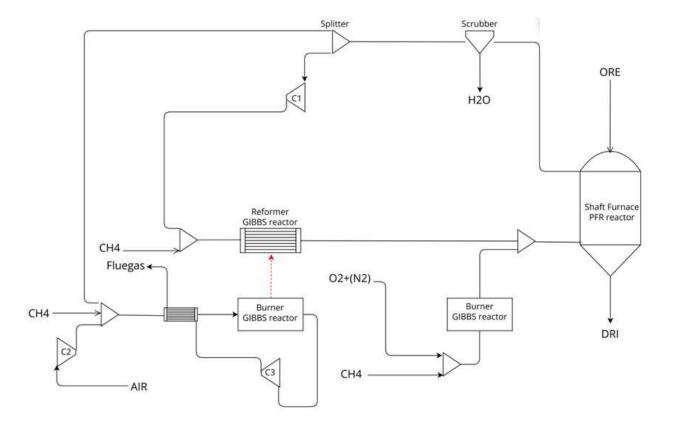


Carbon Capture in DRI MIDREX Process

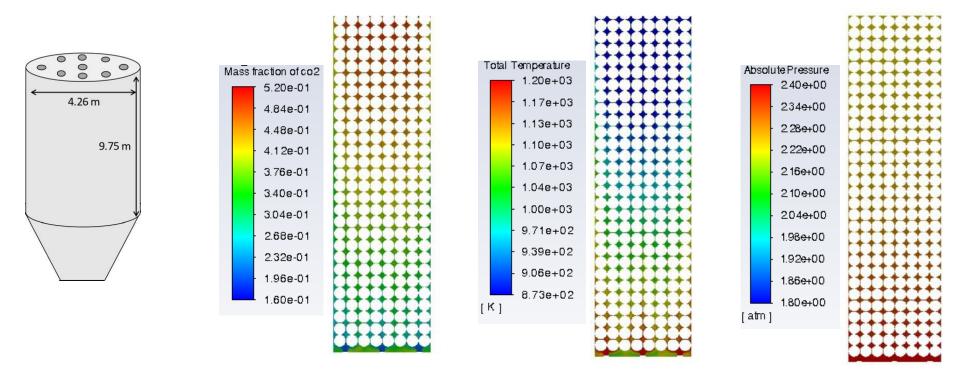
• No standalone Midrex Plant that removes CO₂ from the DRI shaft reactor's off-gas.



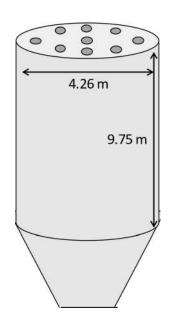
Carbon Capture in DRI MIDREX Process Gilmore Steel Corporation (U.S.A.)

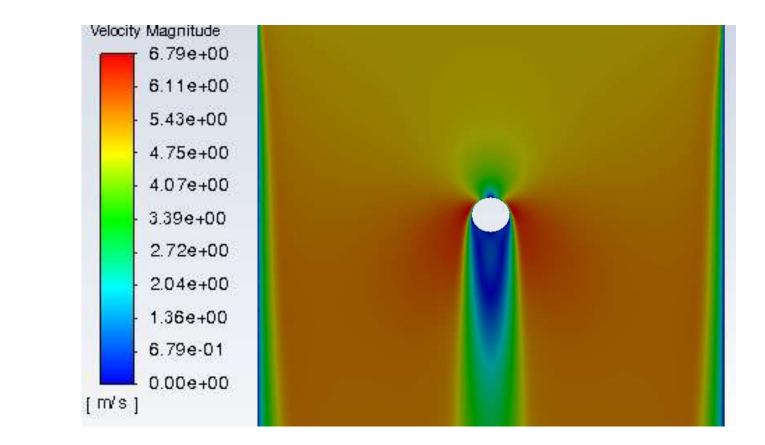


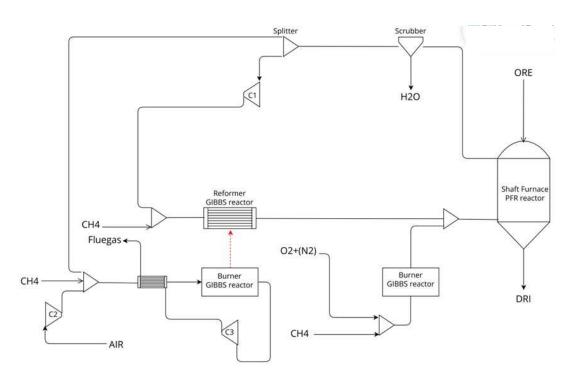
Carbon Capture in DRI MIDREX Process Gilmore Reduction Shaft



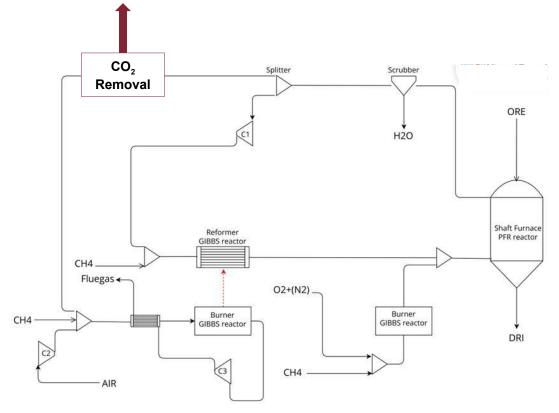
Carbon Capture in tDRI MIDREX Process



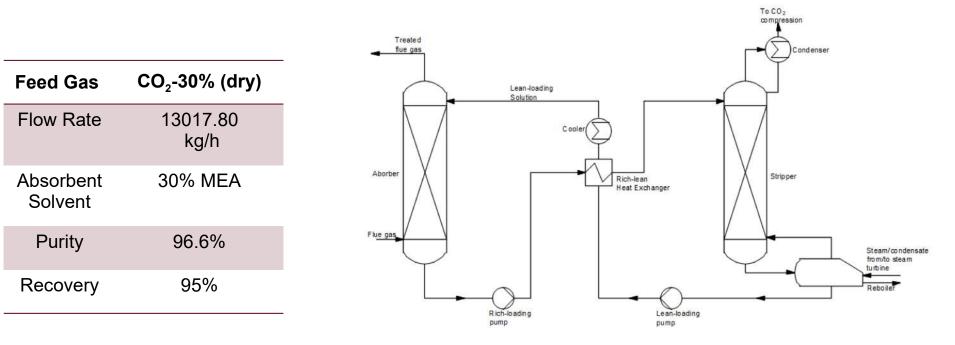




Inlet reducing gas						
Nm³/h	53,862.31					
°C	930					
bar	2.4					
Composition						
%	48.19					
%	25.40					
%	13.85					
%	5.43					
%	7.13					
Outlet gas						
Nm³/h	53,799.74					
°C	660					
Composition						
%	37.04					
%	12.80					
%	17.98					
%	25.13					
%	7.01					
	Nm³/h °C bar Composition % 0% %					



Inlet reducing gas						
Flow rate	Nm³/h	53,862.31				
Temperature	°C	930				
Pressure	bar	2.4				
Composition						
H ₂	%	48.19				
CO	%	25.40				
H ₂ O	%	13.85				
CO ₂	%	5.43				
N ₂ (+CH ₄)	%	7.13				
Outlet gas						
Flowrate	Nm³/h	53,799.74				
Temperature	°C	660				
Composition						
H ₂	%	37.04				
СО	%	12.80				
CO ₂	%	17.98				
H₂O	%	25.13				
$N_2 (+CH_4)$	%	7.01				



Specific Emission (t _{co2} /t _{steel})					
	DRI-NG	DRI-NG+Carbon Capture			
Direct	0.46	0.19			
Equivalent	0.14	0.15			

0.34

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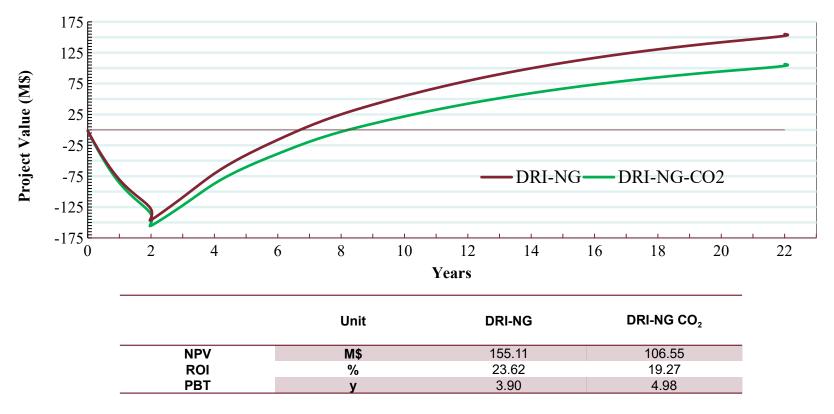
0.60

Total

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Production cost (\$/t):

- Chemical Absorbtion: + 8.7%
- Chemical Absorption + Storage/Transport: +10.5%



Decarbonization of steel production: alternative Direct Reduced Iron and CCS

Prof. Giorgio Vilardi Ing. Antonio Trinca

Research group: <u>https://giorgiovilardi.wixsite.com/dracons</u>



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