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Application of sorption enhanced water gas shift for carbon capture in integrated steelworks

"Matteo Gazzani*, Matteo Romano, Giampaolo Manzolini" [a*]

[a]*Politecnico di Milano, Department of Energy, via Lambruschini 4, Milano*

Abstract

In integrated steelworks a large fraction of total CO_2 is emitted from the power plant, where carbon-rich blast furnace gas (BFG) is burned to produce electricity by means of a steam cycle or a gas-steam combined cycle. The aim of the present paper is to assess the potential of Sorption Enhanced Water Gas Shift (SEWGS) process for CO_2 capture from blast furnace gas. Firstly, a reference combined cycle applied to blast furnace steel plant is defined. Mass flow rate and composition of the steel plant off-gas used as fuel in the combined cycle have been derived from a large integrated steel plant. Then, the application of the SEWGS process is investigated and compared to a reference monoethanolamine (MEA)-based post-combustion absorption option. Two different SEWGS plant layouts are proposed together with two different sorbents. SEWGS achieves 85% of CO_2 avoided with electric efficiency of 39% with the advanced sorbent.

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"CO2 capture; Blast furnace; CO2 capture for industrial processes; SEWGS; Integrated Steelworks"

Nomenclature

BFG	Blast Furnace Gas
BOFG	Blast Oxygen Furnace Gas
COG	Coke Oven Gas
MEA	MonoEthanol Amine
NGCC	Natural Gas Combined Cycle

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[*] Corresponding author. Tel.: +39 02 23993935;
E-mail address: matteo.gazzani@mail.polimi.it

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SEWGS Sorption Enhanced Water Gas Shift

1. Introduction

Steel industry is the most energy-intensive manufacturing sector accounting for 10-15 % of total industrial energy consumption [1]. Being based on fossil fuels and electricity utilization, it accounts for large anthropogenic CO_2 emission, estimated at 1500-1600 MtonneCO_2 year. During last 10 years, steel industry has experienced a large production increase almost doubling the year yield reaching about 1400 Mtonne; developing countries like China, India and Brazil played the main role in this sharp growth. Assuming that the steel demand will continuously rise in the next years, carbon mitigation has to be applied to steel industry as well as power plant.

Specific CO_2 emission depends on several parameters whose most important are: type of steel production process, energy efficiency of the considered process, country base electric energy system and type of fuel adopted for iron conversion. World steel production is based on two main processes: blast furnace and electric arc furnace. The first accounts for around 60% of the market while the second provides around 35%; the remaining 5% is based on alternative processes.

As far as integrated steelworks are concerned, the energy interdependency of the different process is complex; example of the input and output flows is shown in Fig. 1. Therefore, it results that several CO_2 capture solutions can be investigated and applied with different levels of integration with the plant. Early CO_2 capture opportunities are based on blast furnace redesign such as i) CO-rich top gas recycling in the furnace and ii) direct reduction of iron ore through hydrogen. Both these processes aims to reduce the CO_2 produced directly in the iron making process. Another option, which is investigated in this paper, is to mitigate CO_2 emissions by applying carbon capture to the bottoming power cycle which is typically included in integrated steelworks. This solution would allow reducing the CO_2 emission to almost half of the base case without requiring changes in the steel production process. Moreover it could better harness the know-how being developed in the power production area.

Blast furnace steel plant is characterised by the production of process-gases that can be recovered and adopted as energy source both for the plant demand and for grid power production. As shown in Fig. 1, the enriched gas mixture comes from three different processes: i) the blast furnace itself, which is the main gas producer, ii) the coke oven plant and iii) the basic oxygen furnace. Power plants play an important role in integrated steelworks as they consume the excess process gases and provide the necessary steam and power to all the key processes. The gas mixture burnt in the power plant accounts for about 50% of the total gas production.

Historically, blast furnace steel plants have been integrated with conventional steam cycle power plants where the steam generated from burning off-gas was expanded in a steam turbine. The steam generator in such a configuration is generally fed also with other fuels like natural gas or oil; internal steam demand is met with turbine bleedings. The relatively simple arrangement can achieve a high level of availability and is designed to use process gases with low calorific value, mainly BF gas. Recently, this plant layout has been discarded in favour of a more efficient combined cycle.

In section 2 the reference cases with and without carbon capture are defined; in section 3 SEWGS is described together with its integration in the overall plant; in section 4 methodology and assumptions are reported whilst sections 5and 6 are dedicated to results and conclusions.

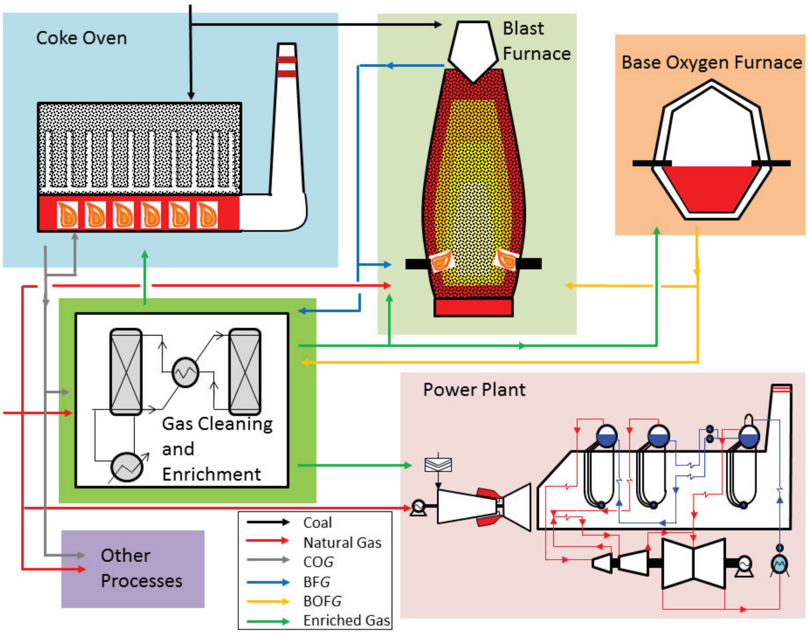

Fig. 1. Overall layout of an integrated steel plant with the main gas streams exchanged.

2. Reference cases with and without capture

In order to evaluate SEWGS as innovative CO_2 capture process in steel plants, two reference cases with and without capture have been developed. Reference cases are based on pure blast furnace feeding and combined cycle performances derived from data of commercial plants. In order to simplify the final comparison and to avoid misleading interpretations of the performance of the different configurations assessed, no blending with natural gas is considered before combustion. It has been assumed to adopt one GT and one HRSG as the steel-off gas production cannot feed two large size combined plants. BF gas cleaning is carried out inside the steel plant battery limit where the gas is available at ambient conditions. The considered GT is a generic F class with no TIT de-rating due to the low LHV of the fuel; this hypothesis, even though significant for performances calculations, is applied to all the considered plant, with and without capture, in order not to affect the comparison.

2.1. NGCC no capture

A commercial plant for blast furnace application based on EBTF [2] was modelled (named NGCC REF). Gas turbine is fuelled with steel mill off-gas. Compared to pure NG fuelled plant, a significant amount of power is required for the steel-off gas compression as gas is available at ambient pressure; no further significant penalties have been applied.

Steel mill off-gas mass flow and composition have been derived from a large, state-of–the-art integrated steel plant. It has been supposed to keep a constant steel mill off-gas production. HRSG and steam turbine data refer to EBTF assumptions. Stack temperature has been set at 80°C. The condensing pressure is set at 0.048 bar, assuming the use of a cooling tower. The resulting net power output is 319.2 MW with a net electric efficiency of 52.3% and specific CO_2 emission of 1338 g/kWh.

2.2. NGCC with MEA post combustion capture

As far as carbon capture is concerned, a reference case with post combustion capture was developed (named *MEA CAP*): CO_2 capture is based on amine technology which represents the commercial ready technology for carbon capture. Ancillary consumptions for the absorption cycle have been specifically calculated and optimized by varying the L/G ratio: the high CO_2 content in the exhaust gas slightly reduces the specific heat duty for MEA regeneration than fossil fuel plants. The CO_2 capture section is simulated with ASPEN Plus® ver.7.2 adopting the RK-SOAVE equation of state with the default coefficients. The resulting MEA-solvent regeneration energy is about 3.5 MJ/kg_{CO2} which is also consistent with recent work on post-combustion capture from steel mill [3]. It has been found that, because of the large CO_2 mass flow compared to the heating value, the steam produced in the HRSG does not allow reaching high carbon capture values even with the adoption of a back pressure turbine configuration, where all the steam expanded is condensed in the MEA stripper reboiler. Therefore, part of exhaust gases after the HRSG are directly sent to the stack, bypassing the CO_2 capture section. Size (or number) of the absorber of the MEA plant is hence reduced with respect to a case where all the flue gas are treated. With the considered bypass configuration, 90% of carbon is removed from 45% of the total flue gases, the remaining 55% being directly sent to the stack. Although other configurations have been considered where the entire flue gases are treated, the selected configuration seems to be the best compromise between performances and capital costs. The resulting net power output is 235.9 MW with a net electric efficiency of 38.7% and CO_2 emissions of 870.4 g/kWh.

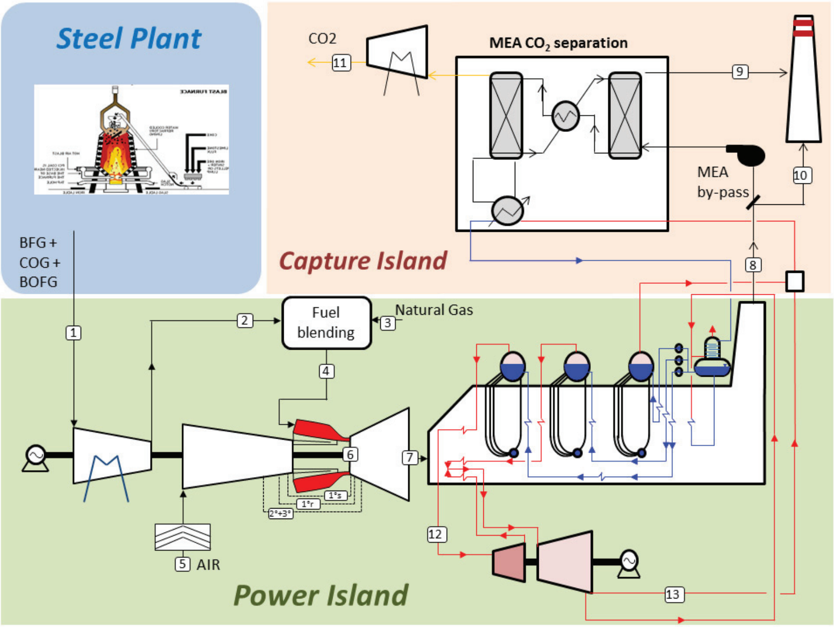

Fig. 2 Plant layout of the reference case with CO_2 capture by MEA

3. Sorption Enhanced Water Gas Shift

The combination of high temperature equilibrium reactions with pressure swing adsorption (PSA) processes was investigated in the 1990s by Air Products and Chemicals Inc., and then developed in CO_2 Capture Project (CCP) [4], in Cachet Framework Programme 6 (FP6) [5]. Recently, it has been further developed in the CAESAR FP7 project for natural gas, coal and blast furnace applications [6]. SEWGS comprises multiple fixed beds operating in parallel that adsorb CO_2 at high temperature and pressure, and release it at low pressure. The combination of CO conversion and CO_2 removal enhances H_2 production and the purity of the stream feeding the Gas Turbine (GT) combustor, whilst a separate CO_2 by-product can be recovered from the adsorbent by regenerating the bed with high temperature steam [7]. This stream can then be compressed and sequestered without further clean-up. The advantages of combining the water gas shift reaction with separation of CO_2 are:

- High hydrogen and CO_2 recovery: in SEWGS, almost all the CO is converted and hydrogen recovery is maximized, while conventional WGS section leaves larger fractions of unconverted CO, leading to lower hydrogen and CO_2 recoveries.
- Better heat integration: CO_2 is captured at high temperature, while in conventional pre-combustion systems the capture is performed at ambient or even sub-ambient temperatures with thermodynamic disadvantages.

A more detailed SEWGS description is reported in [7] [8] and [9]. SEWGS operating conditions adopted in this work, i.e. steam usage for rinse and purge, are derived from CAESAR results specifically calculated for blast furnace gas and are reported in Table 1; values are presented in terms of the required kmols of steam relative to the kmols of total carbon in the feed. Values are reported for two different sorbents named Sorbent Alpha and Sorbent Beta. Both has been developed at ECN laboratories; the first has been extensively tested during the project [10] whilst the second is a new advanced material with adsorption capacity about 100% higher (at CO_2 partial pressure of 6 bara) and recently tested at ECN

Table 1. SEWGS steam consumptions for bed regeneration and hydrogen recover.

Sorbent type	Sorbent Alpha		Sorbent Beta	
SEWGS CCR %	95		95	
Train number	6 trains x 9 vessels		6 trains x 9 vessels	
Purge pressure [bar]	1.1		1.1	
CO_2 purity [%]	99		99	
Steam demand	Rinse	Purge	Rinse	Purge
[mol_{H2O}/mol_{Carbon}]	0.52	0.89	0.20	0.26
Temperature [°C]	400		400	
Pressure [bar]	28.0	1.25	28.0	1.25

The SEWGS reactor, being a pre-combustion technology, introduces large modifications to the integrated power plant but leaves unchanged the steel manufactory island. After the compression, steel mill off-gas enters a conventional high temperature shift reactor (at around 320°C), where the largest part of CO is converted into H_2. Syngas leaving the shift is sent to the SEWGS reactor where the CO conversion is enhanced and CO_2 is adsorbed and separated. Two different streams leave the SEWGS: i) the hydrogen rich flow to be sent to the GT and ii) the CO_2+H_2O flow. Both streams are at high temperature, around 400 °C, improving the GT Joule-Brayton cycle efficiency and allowing large heat recover respectively. As well as the MEA case, the energy penalty for carbon capture is mainly determined by the steam bled from the steam turbine, in this case required for the shift reaction, the hydrogen recovery and the bed regeneration (respectively rinse and purge step).

Two different plant layouts have been investigated:

- SEWGS with intercooled gas compression and saturator (SEWGS SAT), shown in Fig. 3:steel mill off-gas is compressed with intercooling stages with benefits on the compression work;

steam bleedings for shift are substantially reduced adopting a saturator whose water is heated by recovering heat from intercooled compressor, CO_2 cooling and off-gas exiting the compressor. The main drawbacks of this configuration are represented by: i) the temperature swing between the gas compressor and the shift and ii) the stream exiting the SEWGS is not expanded as in [8] and [9] in order to increase the heat to the saturator water. High pressure steam is produced by cooling the hydrogen rich syngas exiting the SEWGS and the rinse steam withdrawn from the hot RH.

- SEWGS with intercooler compressor and expander (SEWGS EXP): steel mill off-gas is compressed in an intercooled compressor modifying the last stage pressure ratio in order to make the gas available at 320°C, suitable for the high temperature shift. The CO_2-steam mixture exiting the SEWGS is expanded till 0.5 bar and cooled by producing IP and LP steam. HP steam is produced in a dedicated section by cooling: i) the syngas leaving the WGS, ii) the H_2-rich stream exiting the SEWGS and iii) the rinse steam withdrawn from the hot RH. This configuration allows a better harness of the sensible energy inside the capture island but requires a higher steam bleed for the WGS process.

All the SEWGS cases are calculated with almost atmospheric purge pressure and 95% of CO_2 recovery from the total amount adsorbed in the bed.

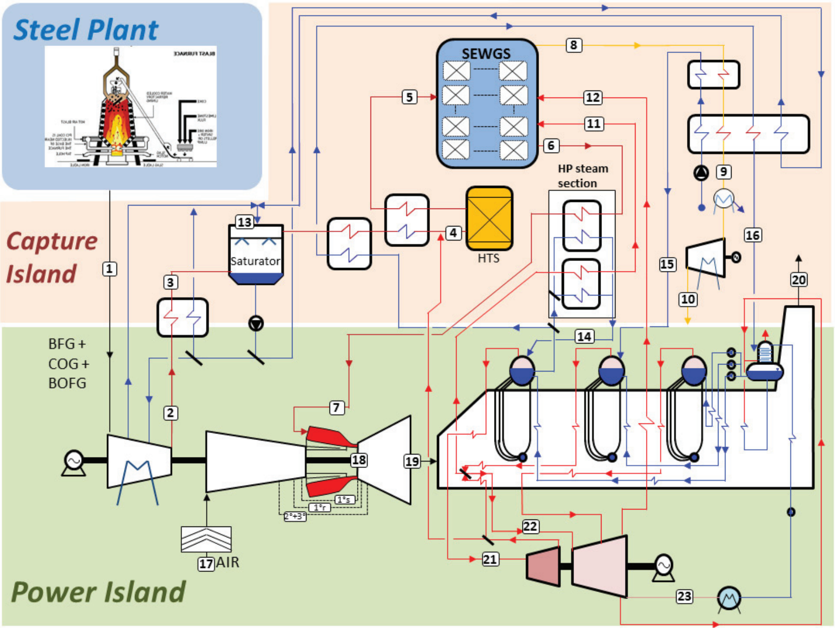

Fig. 3 Plant layout of SEWGS SAT configuration, with intercooled compressor and saturator

4. Methodology and Assumptions

All calculations presented in this paper were carried out with the code GS, developed within the Department of Energy of the Politecnico di Milano and ASPEN Plus™. The GS code can calculate detailed energy and mass balances of a wide variety of plant schemes [11]. The same code is used to compute performance of all the reference cases and has been calibrated with other commercial codes within EBTF. GS implements a pinch analysis for heat recovery steam generator optimization, while for other parts of the plant, heat recovery is carried out by fixing a pinch point in each heat exchanger according to EBTF common definition framework. For CO_2 capture with MEA and CO_2 compression sections, calculations were carried out with ASPEN™. Assumptions used for reported calculations are shown in Table 2.

Table 2. Assumptions

Ambient conditions	15 °C / 1.013 bar / 60% RH			
Air composition, dry molar fraction (%)	N_2 78.08%, CO_2 0.04%, Ar 0.93%, O_2 20.95%			
Rich Blast Furnace Gas				
(BFG + COG)	CH_4	2.10 %	C_2H_4	0.20 %
	CO	21.29 %	C_2H_6	0.07 %
	CO_2	19.57 %	H_2	7.22 %
	C_2H_2	0.01 %	N_2	49.53 %
	O_2	0.02 %		
LHV	3.386 MJ/kg			
Gas turbine (generic F class)				
Pressure ratio	18.1			
TIT	1360 °C			
Pressure loss at inlet	1 kPa			
Generator efficiency	98.7 %			
Mechanical efficiency	99.6 %			
Steam cycle				
Pressure levels, bar	130, 28, 4			
Maximum temperature SH e RH	565 °C			
Pinch, subcooling, approach ΔT	10/5/25 °C			
Condensing pressure	0.048 bar (32 °C)			
Turbine Isentropic efficiency (HP/IP/LP)	92/94/88 %			
Pumps efficiency	70%			
HRSG thermal losses	0.7 % of thermal input			
HRSG pressure losses, gas side	3 kPa			
Power for heat rejection	0.8% of the released heat			
CO_2 separation and compression				
Final delivery pressure	110 bar			
Compressor isentropic efficiency	85%			
Temperature for CO_2 liquefaction	25°C			
Steel gas compressor				
Compressor ratio	28			
Number of intercoolers	2			
Organic efficiency	99.8 %			

All the investigated plants with carbon capture are compared by means of the Specific Primary Energy Consumption for CO_2 Avoided (SPECCA) which measures the energy cost related to CO_2 capture. It is defined as shown in Eq.1:

$$SPECCA = \frac{HR - HR_{REF}}{E_{REF} - E} = \frac{3600 \cdot \left(\frac{1}{\eta} - \frac{1}{\eta_{REF}} \right)}{E_{REF} - E} \qquad (1)$$

Where:

- HR is the heat rate of the plant, expressed in kJ_{LHV}/kWh_{el}
- E is the specific CO_2 emission rate, expressed in kg_{CO2}/kWh_{el}

- REF is the reference case for electricity production without carbon capture, which is the one presented in section 2.

5. Results

The results of the investigated plants are shown in Table 3. The reference case without capture has a net electric efficiency of 52.3% and specific emissions of 1338 g_{CO2}/kWh$_{el}$ which is almost twice the specific emission of an USC plant. This is due to the high CO_2 content of the fuel gas. The post-combustion capture case is largely affected by steam bleeding for solvent amine regeneration leading to about 50% reduction of steam turbine power output. The resulting net electric efficiency is 38.7% with a limited penalization considering the low value of the fuel gas, but with a low CO_2 avoided of only 35%. This is also consistent with the results presented in [3] where the CO_2 capture ratio is below 50%.

The SEWGS case with Sorbent Alpha achieves a good trade-off between thermodynamic and capture performances. This is stressed by the SPECCA which is considerably below the post-combustion case (3 MJ/kg$_{CO2}$ of SEWGS vs. 5 MJ/kg$_{CO2}$ of MEA). The adoption of Sorbent Beta, which has twice the capacity of Sorbernt Alfa, sharply increases the efficiency with a gain of about four percentage points at almost constant carbon avoidance; a higher sorbent capacity reduces the SEWGS steam demand increasing the steam cycle power output of 27 MW. When saturator is adopted the calculated efficiency is 39.3% whilst with the expander it slightly increases to 39.9%. Accordingly, the SPECCA value lowers to 2.0 and 1.9 MJ/kg$_{CO2}$ for *SEWGS SAT* and *SEWGS EXP* respectively. The difference between the two SEWGS layouts is set by: i) the steam cycle, whose power output is higher when the saturator is adopted, ii) the expander, which adds 12 MW to the power production, and iii) the intercooled compressor which increases by 2 MW more when the saturator is not used. In addition to the better efficiency, equipment savings may also be anticipated for the SEWG EXP case, due to the lack of the saturator and the reduced heat transfer surface.

Table 3. Performances of all the considered cases; moving from left to right: NGCC without capture, NGCC with postcombustion capture by MEA, SEWGS with saturator and sorbent Alpha, SEWGS with saturator and sorbent Beta, SEWGS with expander and sorbent beta.

		NGCC ref	MEA	SEWGS SAT alpha	SEWGS SAT beta	SEWGS EXP beta
Gas input	[kg/s]	180	180	180	180	180
Thermal input LHV	[MW]$_{LHV}$	609.5	609.5	609.5	609.5	609.5
POWER PRODUCTION						
Gas Turbine net power	[MW]$_{el}$	199.0	199.0	192.1	189.1	187.3
Steam Cycle gross power	[MW]$_{el}$	123.3	66.6	62.6	90.3	83.4
Expander	[MW]$_{el}$	--	--	--	--	12.6
CONSUMPTIONS						
HRSC pumps	[MW]$_{el}$	1.5	1.5	2.1	2.2	1.7
CO_2 compressor	[MW]$_{el}$	--	19.5	36.0	36.0	37.0
MEA auxiliaries	[MW]$_{el}$	--	8.5	--	--	--
Heat Rejections	[MW]$_{el}$	1.6	0.2	1.5	1.4	1.3
BOP	[MW]$_{el}$	--	--	0.22	0.18	0.05
OVERALL BALANCES						
Power Output	[MW]$_{el}$	319.2	235.9	215.0	239.6	242.9
$\eta_{electric}$	**[%]**	**52.3**	**38.7**	**35.3**	**39.3**	**39.9**
$\Delta\eta$	[%points]	--	-13.7	-17.1	-13.0	-12.5
CO_2 emissions	[g/kWh]	1338.0	870.4	215.6	193.4	190.8

CO_2Avoided	[%]	--	34.9	83.9	85.5	85.7
SPECCA	**[MJ/kg$_{CO2}$]**	**--**	**5.2**	**3.0**	**2.0**	**1.9**

6. Conclusions

In this work, CO_2 mitigation solutions in integrated steel plant with bottoming power generation and pre-combustion capture with SEWGS process were investigated. Different plant layouts with and without carbon capture were considered and performance of SEWGS-based plants was compared to post-combustion carbon capture with MEA one. It was found that SEWGS reaches good performances with around 85% CO_2 avoidance. On the other hand, MEA post combustion configuration does not seem a valuable solution to significantly decrease the CO_2 emissions, due to a carbon capture rate lower than 50%. Among the different SEWGS layouts investigated, the adoption of an intercooled compressor and a CO_2-steam expander featured the best performances.

Acknowledgements

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