Advanced Carbon Capture for steel industries integrated in CCUS Clusters

Innovation Action

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Grant Agreement No 884418.

D1.10 Public report on DISPLACE technology (Task 1.4.2)

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1 Version log

Version	Date	Released by	Nature of Change
0.9	12/23	L. Lücking	1st version
0.99	02/25	J.A.Z. Pieterse	2nd version for internal review
1.0	03/25	J.A.Z. Pieterse	Final version for review

2 Definition and acronyms

Acronyms	Definitions
BFG	Blast Furnace Gas
CASOH	Calcium Assisted Steel mill Off-Gas Hydrogen Production
DISPLACE	Downstream Integrated Steel Production with advanced CO_2 capture
CCR	Carbon Capture Rate
CP	CO_2 Purity
SEWGS	Sorption Enhanced Water Gas Shift
S/C	Steam to carbon ratio for the desorption

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3 Introduction

According to the IPCC report, the capture of CO_2 from the traditional production of iron and steel industry is a crucial element in order to reduce global emissions. Currently the steel industry makes up around 8% of the anthropomorphic CO_2 emissions. This is where the C^4U project (Advanced Carbon Capture for steel industries integrated in CCUS Clusters) aims to contribute to the global effort to reduce carbon emissions by developing a portfolio of CO_2 capture technologies for the carbon intense furnace off-gasses. The capture technologies must be developed and practically tested to high Technology Readiness Level (TRL) to identify the optimal integration solutions delivering the minimum cost and energy consumption.

C^4U elevates from TRL5 to TRL7 two highly energy-efficient high-temperature solid-sorbent CO_2 capture technologies for decarbonizing blast furnace gas and other carbon containing gases. By combining the technologies CASOH (Calcium Assisted Steel mill Off-Gas Hydrogen Production) and DISPLACE (high-temperature sorption-displacement process for CO_2 recovery) these two technologies will target up to 90% of the total emissions from the steel plant that come from a variety of sources. During the CASOH process the steel-works arising gasses are transformed into heat suitable for in-plant heat demands and a H_2-rich product, which is integrated with steel-works internal processes or used for the external production of added value products. Additionally, flue gasses originating from oxy-fuel firing to provide process heat to reheating ovens are decarbonized using DISPLACE technology. This public summary report focuses on the DISPLACE campaigns performed in Lulea Sweden and Petten, Netherlands demonstrating the use of a H_2 rich fuel for reheating purposes and DISPLACE process for decarbonization.

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4 DISPLACE technology

The DISPLACE technology works on the principle of concentration swing. The general layout of the unit typically consists of 6 columns filled with an unique K-promoted hydrotalcite type sorbent with both CO_2 and steam uptake capacity. The columns are interlinked for recycling feed and steam (as shown on *Figure 1*) and can be fed Feed and Steam separately. Each column goes through the steps indicated in the Figure 1, with adsorption being performed co-currently and desorption being done counter-currently.

The columns of the unit are operated isobarically while the adsorption and regeneration is achieved through changes in the concentration/partial pressure of CO_2 and steam. As a result, the CO_2 product is obtained at increased pressure, decreasing the subsequent compression energy. Moreover, because of the isobaric operation, the system does not have to be designed for fatigue. This concentration swing is accomplished by the sorbents characteristic of having a shared adsorption site for CO_2 and steam, which allows for deep regeneration in the presence of steam. Because CO_2 adsorption and steam desorption on the one hand and CO_2 desorption and steam adsorption on the other hand occur simultaneously, the associated heat effects lead to near isothermal operation of the system.

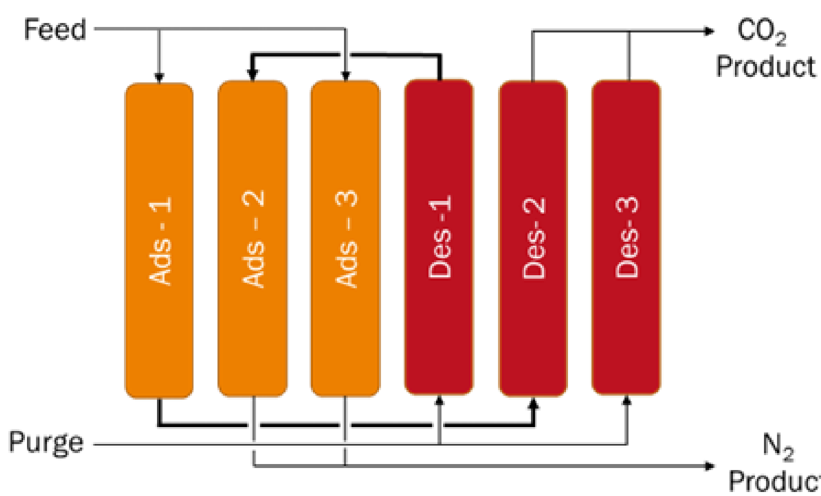

Figure 1 – Cycle design of a 6 column DISPLACE unit.

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5 Campaigns

Within the C4U project we were able to demonstrate the DISPLACE technology on large-scale with real steel-off gases. In order to show the full functionality of not only the DISPLACE technology but also the newly built furnace, three campaigns were performed: (1) Demonstration of carbon-free steel slab reheating, (2) Large scale DISPLACE operation on real steel off-gases, (3) Detailed DISPLACE operation at bench-scale for detailed data generation to tune the model for DISPLACE operation.

The large scale campaigns were performed in Luleå, Sweden where a direct pipeline to the SSAB steel mill site allows for real gas demonstration of the technology. The pilot set-up consists of a single column separation unit originally built for the STEPWISE[1] project and a newly built furnace for the C4U project. The campaigns ran for 9 weeks with 24/7 operation and an additional 550 hr commissioning.

5.1 H_2-rich reheat furnace

The effect of using the H_2-rich fuel for reheating purposes within the integrated steel mill was demonstrated at the pilot plant in Luleå, Sweden, using the STEPWISE decarbonization technology to produce a H_2-rich fuel from BFG. This fuel was then oxy-combusted in a chamber furnace for the reheating of various steel samples.

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[1] STEPWISE is a project that has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 640769

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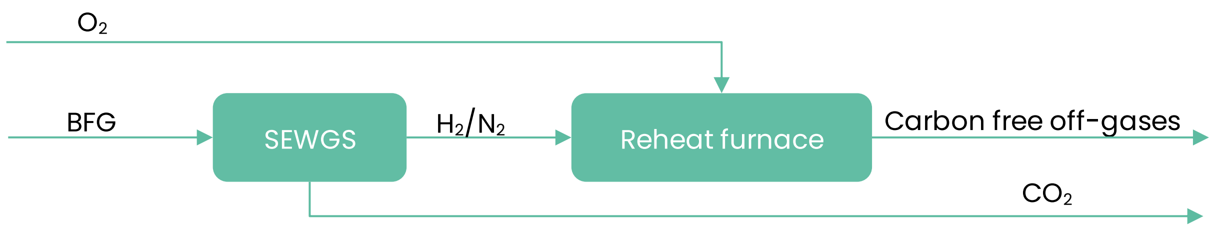

Figure 2 – Scheme of the furnace and SEWGS integration for the H_2-rich reheat furnace campaign

For the first time the STEPWISE decarbonization technology is integrated with scaling and descaling properties of steel.

In the STEPWISE section, the novel KISUMA sorbent was demonstrated. The STEPWISE single column unit was operated at a CCR of >90% and a steam/CO_2 ratio of 1.0 to 1.2 mol/mol. The decarbonization section produced a H_2/N_2 rich fuel having a carbon-slip as low as 0.5 mol%dry and up to 3.0 to 4.2 mol%dry carbon-slip, depending on the specific conditions envisioned for the metal sample tests. This performance resulted from tuning of the cycle operation for the STEPWISE technology. The campaign resulted in various operational points that serve as input for validation of the TNO proprietary model.

After tuning of the furnace feeding system, all planned steal sample heating tests were performed. These tests varied in steel grade, C-clip level, O_2 content and reheating temperature. The highest amount of oxides were formed at the highest temperature and the highest O_2 level. Moreover, the oxidation grade for the samples was higher for the lower C-slip level in the fuel.

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5.2 DISPLACE

The DISPLACE technology is a spin-out from the Sorption Enhanced Water Gas Shift (SEWGS) technology developed at TNO, Netherlands. The DISPLACE technology stands out due to its high-temperature separation and high pressure CO_2 product stream. The separation (Figure 3) is achieved through a concentration swing process, which can be operated isobarically. The main integration of this separation unit is downstream an oxy-fired reheat furnace of the steel slaps, which leads to a CO_2/N_2 off-gas.

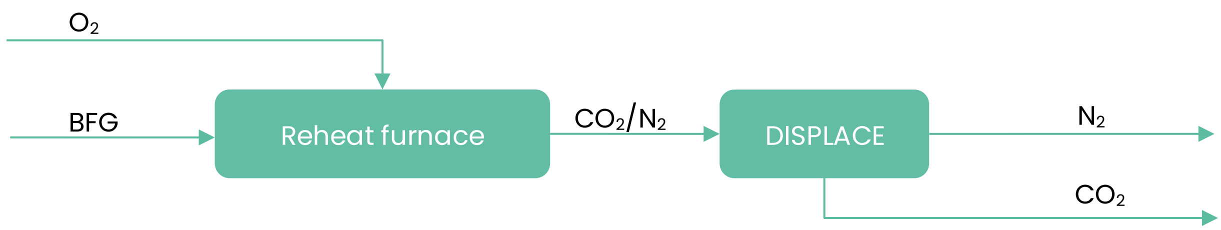

Figure 3 – Scheme of the furnace and DISPLACE integration for the DISPLACE campaign

For this demonstration of the DISPLACE technology, BFG was oxy-fired in a chamber furnace, the off-gas was compressed, heated and fed to the STEPWISE column. This column is operated isobarically with steam as regeneration feed. The isobaric operation allows for a higher pressure CO_2 product. The DISPLACE technology is demonstrated using a similar type of sorbent as the SEWGS technology, which in this case was state of the art sorbents from Kisuma Chemicals as well as recycled sorbent from the preceding project (FreSMe: https://cinea.ec.europa.eu/featured-projects/fresme_en).

During the DISPLACE campaign pilot operational data was gathered for model validation with the aim for cyclic operation at substantial CO_2 slippage during adsorption and steam breakthrough during regeneration. CO_2 purities of up to 99% were achieved during the campaign.

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5.3 Bench-scale campaign for performance mapping

A third, smaller-scale campaign was conducted at TNO in Petten, Netherlands to map the performance of the DISPLACE technology for a range of compositions, temperatures and pressure levels. The small-scale was chosen as it allowed a more flexible choice of settings.

The majority of the results from the campaign were used as input into the model, however, the campaign also proved that the technology is able to reach carbon capture ratios of above 95% and CO_2 purities of up to 99%. The technology best operation range is at 5 to 15 bara and 300 to 400 °C. The performance of the process is dependent of the steam to carbon ratio and improves with more steam. Similarly, the performance increases with higher system pressure and higher temperature.

6 Modelling

Using the results from the two DISPLACE campaigns, the TNO model was subsequently updated to the unique operating regime of the DISPLACE technology. For this purpose, the isotherm of the sorbent was fitted to capacity measurements of the small-scale campaign. Figure 4 shows the parity plot of the fitted isotherm compared to the measured results. The updated model

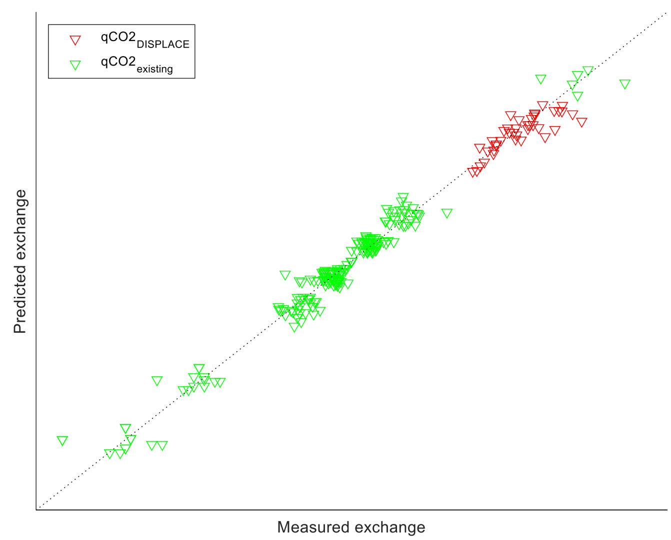

Figure 4 – Parity plot of the fitted isotherm

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was validated against cyclic data and allows the fine-tuning of a cycle and DISPLACE reactor sizing for use of oxy-firing in reheating furnaces.

7 CO_2 purity analysis for pipeline and storage

During the DISPLACE campaign, detailed concentration measurements were performed in the flue gases upstream the DISPLACE reactor and downstream in the CO_2 exhaust. The measurements are based on a new sampling method that uses multilayer bags, tested at INERIS, and accurate gas analysis techniques provided by TNO. The flue gases contained less than 10-20 ppm of minor species like NO, NO_2, SO_2, COS and H_2S (below the detection limits). The CO_2 stream contains more than about 98.5% ±0.5% of CO_2 suggesting a high performance for a single column system during the campaigning at SWERIM. The other components are nitrogen (1.4%) and oxygen (0.1%).

Further testing evidenced that the O_2 in the CO_2 product resulted from air ingress during sampling and cycle tuning. The sorbent material does not adsorb O_2.

8 Characterization of materials

8.1 Sorbent

K-promoted hydrotalcite type sorbent with both CO_2 and steam uptake capacity was used in the DISPLACE technology. Pellet degradation is not observed in the optimized sorbent material used in the DISPLACE demonstration in C4U.

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The DISPLACE campaign also gave the opportunity to evaluate the fate of sulfur on the sorbent after exposure to SO_2-containing flue gas generated by oxy-fuel combustion of BFG. It was found that during cyclic operation very little sulfur is deposited on the sorbent. However, also no significant amounts of SO_2 was detected in the gas phase analysis with the CO_2 product. The most likely explanation is that sulphates are still progressively formed with cyclic operation but only very slowly with the low levels of SO_2 in the feed in C^4U, which in combination with the limited time span of the second campaign complicates its analysis. SO_2 is therefore likely trapped by the sorbent, forming sulphates. Regeneration for these sulphates by reaction to H_2S can be considered, as H_2S is known to reversibly interact with the sorbent.

8.2 Catalyst

Water gas shift (WGS) catalysts are being used commercially in the chemical industry to produce hydrogen at different temperatures to achieve the maximum CO conversion. This type of catalyst (high temperature WGS catalyst) was used in the campaign described in 5.1, upstream the SEWGS unit. The catalyst was proven to be extremely robust for BFG operation and characterization work has shown that the catalyst performance is not impacted with the 15-20 ppm H_2S in the feed.

8.3 Metals

For the first time the STEPWISE decarbonization technology is integrated with scaling and descaling properties of steel. One of the main conclusions of the study of the metal samples is that samples reheated with H_2/N_2 atmosphere suffer a decarburization of the steel in the

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surface of the piece compared with the samples reheated under the BFG atmosphere. This behavior is located on the first 0.5 mm of the sample from the surface. With less carbon on the surface, a part becomes less resistant to tension. Parts that face extreme rotational or alternating forces – structural bolts, for example – are prone to failure if decarburization occurs. Decarburization also involves additional cooling and fracture risks for harder alloy parts. In further studies it is interesting to determine if this degree of decarburization impacts the mechanical properties of the steel. Oxide formation in most of the samples was observed, but not very embedded in the steel structure.

9 Techno-economic analysis of DISPLACE

In an assessment on carbon avoided and cost of carbon avoided DISPLACE was compared with an amine CO_2 removal system (MEA). DISPLACE is superior for higher CO_2-content cases i.e., reheat oven and hot stoves. At lower CO_2 content, i.e. sinter plant, MEA becomes more favourable (Table 1). The arrow up in Table 1 means displace outperforms MEA, arrow down means MEA outperforms DISPLACE. The results are published in Journal of Cleaner production https://doi.org/10.1016/j.jclepro.2025.144739. Advanced analysis on the full integration of the C4U technologies in the steel plant is currently under review with the Journal of greenhouse gas technology.

Table 1. TEA comparing DISPLACE with MEA CO_2 removal system

Application	CO_2 content	CCR	SPECCA	CCA
• Reheating ovens / Hot stoves	44%	↑	↓	↓
• Sinterplant	20%	↑	↑	↑

CCR – carbon capture rate ; SPECCA – Specific Primary Energy Consumption per CO_2 Avoided
CCA – Cost of CO_2 Avoided

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10 Exploitation of C4U technologies

There are significant opportunities to advance C^4U technologies within the steel industry. The Blast Furnace (BF) – Basic Oxygen Furnace (BOF) route remains a key production pathway and is not being phased out. Innovative BF technologies, such as EasyMelt from Paul Wurth, are actively being developed. Meanwhile, alternative production routes, including Electric Arc Furnaces (EAF), still require effective decarbonization strategies. Hydrogen-based Direct Reduced Iron (H_2-DRI) is expected to gain prominence in the future; however, its development presents challenges, and even H_2-DRI will necessitate further decarbonization efforts. Additionally, certain steel grades require specific production methods that depend on carbon-based processes. The ongoing European projects GreenSmith, More4Less, and Remap2 – EMPHATICAL are contributing to the further de-risking and advancement of the technologies.

11 Conclusion

The DISPLACE TRL7 pilot experimental program was successfully completed with 9 weeks 24/7 operation with an additional 550 hr commissioning. The pilot data has refined the understanding of how CO, CO_2 and H_2O interact with the sorbent material. This update significantly improved the insight on both the process models and overall cycle optimization. The demonstration to TRL7 by integrating and demonstrating decarbonization around the steel-plant (i.e. in the reheating ovens) represents an important step closer to the near-complete reduction of total carbon emissions at steel plants. A significant achievement was the successful use of decarbonized steel gas in a reheating process, a world-first in the field. Reheating steel samples using hydrogen as a fuel gas in furnaces does not prohibitively impact the overall microstructure of the metal. However, slight decarburization may occur at the

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surface, warranting further study. Additionally, reheating times and temperatures may vary and must be controlled, as regions of high stress could form due to the resulting microstructures. DISPLACE has shown potential cost savings for decarbonizing a variety of steel mill off-gases, by shifting their chemical energy content towards H_2 and/or by allowing efficient thermal integration of their high temperature off-gases in the steel making process, while generating a separate CO_2 stream for utilization or permanent storage.

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