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Carbon Capture Demonstration at Irving Oil Whitegate Refinery

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Abstract

The refining industry is a highly energy-intensive sector with direct CO₂ emissions varying from 100 to 200 kg CO₂/tonne oil. CCUS can assist in reducing CO₂-related emissions, however, the main challenge is that there are several relatively small sources with various levels of CO₂ concentration, from which this greenhouse gas must be captured. Within the REALISE project, which stands for Refinery-Adapted Cluster-Integrated Strategy to Enable Full-Chain CCUS Implementation, the integration of a multi-absorber concept for capturing CO₂ from different stacks is investigated. In this work, TNO's miniplant, an ATEX-compliant small-scale pilot plant, has been employed to capture CO₂ using the novel HS-3 (aqueous mixture of 40wt% of 1-(2-Hydroxyethyl)pyrrolidine, 1-(2HE)PRLD, and 15wt% of 3-amino-1-propanol, 3AIP) solvent from both synthetic and real flue gas from Irving Oil Whitegate refinery. Results regarding the overall performance of HS-3 solvent, including ease-of-operation, capture capacity, degradation and emissions are presented, indicating that the solvent is easy to use and operate with, without precipitation issues. However, it seems to have slow mass transfer, and high volatile emissions due to one of its containing amines.

Keywords: post-combustion carbon capture; demonstration; pilot campaign; refinery; HS-3 solvent

1. Introduction

The refining industry is a highly energy-intensive sector with direct CO₂ emissions varying from 100 to 200 kg CO₂/tonne oil. Primary challenge related to CCUS lies in having several relatively small sources with various levels of CO₂ concentration, from which this greenhouse gas must be captured. To address this challenge, the REALISE project was initiated with the goal to demonstrate a Refinery-Adapted Cluster-Integrated Strategy to Enable Full-Chain

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CCUS Implementation, through the integration of a multi-absorber concept for capturing CO₂ from different stacks [1], [2]. Within REALISE, CO₂ capture technology has been demonstrated both in the lab and on-site at Irving Oil Whitegate Refinery using TNO's mobile small-scale pilot plant and the novel HS-3 solvent, an aqueous mixture of 40wt% of 1-(2-Hydroxyethyl)pyrrolidine, *1-(2HE)PRLD*, and 15wt% of 3-amino-1-propanol, *3AIP*.

The aim of this work is to apply CO₂ capture technology based on HS-3 solvent in multiple stacks of a refinery, with no change of solvent inventory, in order to investigate the multi-absorber concept and stress-test the performance and stability of the solvent at real industrial conditions. The technology has been demonstrated at the Irving Oil Whitegate Refinery, County Cork, Ireland. This refinery is Ireland's only oil refinery, and is a critical part of Ireland's energy infrastructure. It has a capacity of 75,000 barrels of oil per day, sufficient to provide 40 percent of Ireland's fuel requirements. It was commissioned in 1959 and produces a range of products, including renewable diesel.

HS-3 solvent was developed in the HiperCap project [3], [4]. In order to gain further understanding of HS-3 solvent qualities and de-risk the operation of CO₂ capture on-site at the Irving Oil Whitegate Refinery, demonstration activities were initially performed in TNO's lab with synthetic flue gas. Following the installation and commissioning of the pilot plant on-site, the testing started in April 2022 and continued until September 2022. The materials and methods used as well as the findings of the demonstration work are presented hereafter.

2. Materials and Methods

2.1. ATEX-compliant small-scale pilot plant

A small-scale mobile pilot plant, called miniplant, has been used for the demonstration activities. The miniplant was designed and built by TNO, having a capacity to process up to 5 Nm³/h gas and producing up to 25 kg CO₂/day. Various carbon capture-related technologies, such as specific solvents, solvent management and emission mitigation technologies, are brought up to TRL 5 and 6 (Technology readiness Level) when tested in the miniplant in the lab and on-site, respectively. In addition, it is ATEX-compliant, meaning that it complies with the European ATEX (ATMOSPHERES EXPLLOSIVES) regulations in order to ensure safe operations in environments where gaseous combustible materials may be present, such as refineries. Moreover, the miniplant is fully automated allowing for continuous operation, whereas during the on-site work, it is operated and controlled remotely by TNO, requiring minimum intervention on-site. A picture of the miniplant is shown in Fig. 1.

The miniplant is equipped with 4.3 m packing height in the absorber and 1.9 m in the stripper, connected to each other with a cross heat exchanger (HX). Three washes are used: one serves as a direct contact cooler, called a quench, for flue gas conditioning and removal of impurities (i.e. SO_x) and two water washes in both absorber and stripper top for water balance and amine losses control. The solvent inventory is ~25L. The flue gas entering the plant is a slipstream of ~4 m³/h from the flue gas undergoing treatment.

2.2. Flue gas

The demonstration activities took place using both synthetic flue gas and real flue gas from the refinery. The synthetic flue gas was a mixture of air and CO₂ (CAS: 124-38-9, purity >99.7vol%). The test with the synthetic flue gas was performed in a short campaign with the miniplant located at TNO's premises in Delft, the Netherlands. The aim was to determine the operation parameters (L/G ratio, stripping pressure, temperature profile etc.) for the different flue gases met at the refinery, and, overall, de-risk the operations during the on-site demonstration.

Real flue gas was used during the on-site campaigns at the Irving Oil Whitegate Refinery. There are 15 emission points in the refinery, 4 of which were selected to capture CO₂ from. The main selection criteria were: their distance between the stack and the miniplant's location inside the refinery, the number of impurities and, most importantly, their CO₂ content. Regarding impurities, the flue gas from the selected stacks includes various concentrations of particles, SO_x, NO_x, O₂ and CO₂ in order to stress-test the performance and chemical stability of HS-3 solvent. Since analytical work is still on-going, only the results of testing with the flue gas of the first stack are presented in this work.

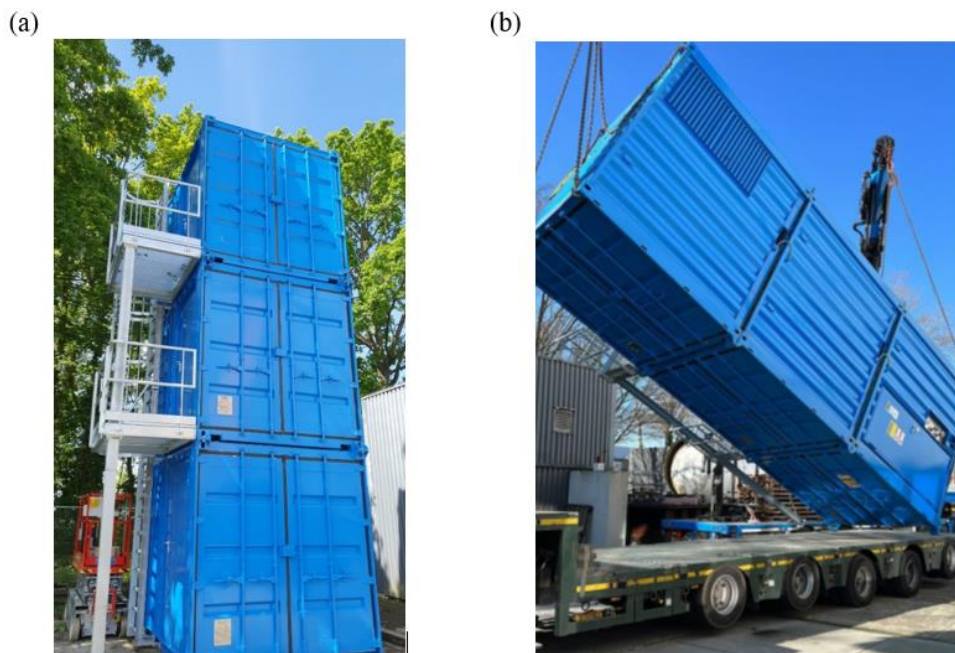


Fig. 1. (a) Miniplant standing; (b) Easy transportation of the miniplant.

2.3. HS-3 solvent

HS-3 solvent is a novel solvent developed in HiperCap project [3], [4] and optimized within REALISE in order to be used in the demonstration activities. It is an aqueous mixture of 40wt% of 1-(2-Hydroxyethyl)pyrrolidine, *1-(2HE)PRLD*, (CAS: 2955-88-6) and 15wt% of 3-amino-1-propanol, *3AIP*, (CAS: 156-87-6). The purity of both these non-toxic chemicals was 99 wt%, while demineralized water was used for preparing the solvent. The same solvent inventory that was used for the testing with synthetic flue gas was used in the operation of the miniplant on-site at Irving Oil Whitegate Refinery.

2.4. Analytical methods

A Fourier-transform infrared spectroscopy (FTIR) analyzer (GasMET CX/DX 4000) has been used for the measurement of gas composition. The gas is sampled by means of a heated probe. A short heated line (180 °C) carries the gas from the sampling probe to the FTIR analyzer. The analyzer has been calibrated for standard inorganic components (NH₃, H₂O, SO₂, NO_x, CO, CO₂) and the HS-3 comprising amines, and is equipped with a ZrO₂ sensor for oxygen measurement.

In the synthetic flue gas campaign, mass flow controllers were used to set the inlet gas composition, while the FTIR was mounted in the outlet of the absorber wash. A multiplexer was used to alternate the sampling of gas between the inlet and the outlet of the absorber water wash in order to investigate its removal efficiency. In the real flue gas campaigns on-site, the FTIR was used to measure the gas composition of both absorber inlet and absorber wash outlet. The inlet gas was analyzed at the start of each campaign, while the absorber water wash outlet was measured continuously along the campaigns.

During the campaign in the lab, the amine concentration and CO₂ loading in the liquid samples were analyzed using an FTIR-ATR (Attenuated Total Reflection). It was found that the spectra of *1-(2HE)PRLD* and *3AIP* are overlapping, making therefore possible only the quantification of both amines, and not individually. As a result, total amine is reported in the **Results** section. Solvent samples were taken twice a week, and selected solvent samples were sent to SINTEF's laboratory for analyses. This included Karl Fisher (KF) titration, Total Inorganic Carbon-Total Organic

Carbon (TIC-TOC) for CO₂ loading, Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), oxidative catalytic combustion and chemiluminescence detection (Shimadzu TOC-L CPH TNM-L) for total nitrogen and Liquid Chromatography – Mass Spectrometry/Mass Spectrometry (LC-MSMS) for various degradation products such as amine, urea, amino acids, amides. More details regarding the analytical methods are available in [5]. The selected degradation compounds analyzed in both campaigns described in this work are given in Table 1. In this way, the stability of the solvent and potential corrosion in the pilot plant has been monitored and evaluated along the campaigns by SINTEF and TNO, in order to decide if and when a solvent management technology would be added in the process.

Table 1. Degradation compounds analyzed using LC-MS in this work for both campaigns

Name	CAS	Abb.
3-(methylamino)-1-propanol	42055-15-2	Methyl-AP
1,3-oxazinan-2-one/tetrahydro-2H-1,3-oxazin-2-one	5259-97-2	OZN
N,N'-bis(3-hydroxypropyl)-urea	71466-11-0	AP-urea
pyrrolidine	123-75-1	Pyrrolidine
3-methyl-pyridine	108-99-6	3-MPy
N-(3-hydroxypropyl)-β-alanine	55937-35-4	HPAla
N-(3-hydroxypropyl)-glycine	100747-20-4	HPGly
N-(3-hydroxypropyl)-formamide	49807-74-1	HPF
tetrahydro-1-(3-hydroxypropyl)-2(1H)-pyrimidinone	670227-88-0	tHHPP
3-[(3-aminopropyl)amino]-1-propanol	40226-15-1	APAP

3. Results

3.1. Synthetic flue gas

The campaign with synthetic flue gas using the miniplant has brought the capture technology with HS-3 solvent to TRL 5. During the operation of the miniplant, important parameters, such L/G ratio, stripping pressure, temperature profile etc., were obtained. The campaign was designed in order to study the performance of the solvent and the required operating parameters, based on the flue gas concentration, specifically the CO₂ content, that is expected to be met in an oil refinery. Therefore, various runs were conducted with ~5 vol% and 10.5 vol% CO₂ (dry basis) which are the minimum and maximum expected values, respectively. Information regarding gas and liquid flowrates, temperatures, stripping pressure, solvent loading, capture rates and emissions are provided in Table 2. Capture rates are calculated with three different ways: a) gas side, using the CO₂ measurement into and out of the absorber, b) gas side, using the CO₂ measurement coming into the absorber and out of the stripper, and c) liquid side, based on liquid sample analysis. Due to the limited column diameter (wall effects) and heat losses associated with the small size of the plant, the energy numbers are not representative, therefore, are not reported.

Table 2. Overview of operational parameters used in the demonstration with synthetic gas.

Parameter	Unit	# 1	# 2	# 3	# 4	# 5	# 6	# 7	# 8	# 9
<i>Gas and liquid flows</i>										
Air	Nm ³ /h	2.61	3.25	2.61	3.25	3.25	3.25	3.25	3.25	3.25
CO ₂ , dry	vol%	5.4	4.2	5.4	10.5	10.5	10.5	10.5	10.5	10.5
CO ₂ inlet	Nm ³ /h	0.15	0.14	0.15	0.38	0.382	0.38	0.38	0.38	0.38
Liquid inlet (lean)	kg/h	9.0	11.8	9.9	6.9	9.0	11.3	15.0	12.0	15.0
L/G absorber	kg/kg	2.4	2.5	2.6	1.3	1.7	2.2	2.9	2.3	2.9
<i>Temperatures</i>										
Liquid inlet	°C	45.2	45.4	45.1	45.7	44.6	45.2	46.1	45.9	46.1
Gas inlet to absorber	°C	23.9	25.2	23.0	22.7	21.2	25.5	28.0	25.5	26.0
Packing height (bottom = 0 m)	°C	43.7	45.1	43.9	39.9	32.7	42.7	47.7	44.2	46.2
Packing height (0.60 m)	°C	52.4	53.0	53.6	43.1	41.3	50.6	57.1	50.2	55.8
Packing height (1.45 m)	°C	56.9	55.8	57.8	46.4	48.1	56.2	62.8	54.1	61.8
Packing height (2.30 m)	°C	57.8	53.1	55.2	50.3	53.2	60.0	65.3	56.3	64.6
Packing height (3.49 m)	°C	55.2	49.3	49.5	58.1	59.8	65.0	65.7	58.6	65.3
Water wash in	°C	43.2	42.7	40.3	50.1	49.6	52.1	52.6	47.8	52.1
Water wash outlet	°C	28.2	29.4	25.9	28.9	26.3	27.5	31.2	30.1	29.5
Cross HX-rich inlet	°C	36.5	39.6	36.9	30.5	28.3	37.7	43.3	39.0	42.4
Cross HX-rich outlet	°C	91.7	96.1	92.8	84.8	91.0	96.3	101.0	91.8	100.0
Cross HX-lean inlet	°C	106.0	108.0	106.0	98.9	106.0	108.0	110.0	104.0	110.0
Cross HX-lean outlet	°C	39.7	44.3	40.0	33.5	32.6	42.1	48.3	42.5	47.2
Reboiler	°C	120.1	120.1	120.0	120.1	120.1	120.1	120.1	115.3	120.0
<i>Pressure in stripper top</i>	barg	0.85	0.85	0.85	0.85	0.85	0.85	0.85	0.79	0.90
<i>Solvent composition</i>										
Lean - total amine*	wt%	52.46	53.28	52.29	55.82	55.75	55.08	-	53.19	52.34
Lean - H ₂ O	wt%	44.51	43.65	44.65	40.72	40.82	41.49	-	41.72	44.06
Lean - CO ₂	wt%	3.03	3.07	3.06	3.47	3.43	3.42	-	5.08	3.60
Lean – loading**	mol/mol	0.15	0.15	0.15	0.15	0.15	0.16	-	0.24	0.17
Rich - total amine*	wt%	49.69	54.35	50.39	54.23	53.90	53.14	53.44	53.02	48.89
Rich - H ₂ O	wt%	44.96	41.53	44.20	37.57	38.21	39.49	39.50	39.27	44.25
Rich - CO ₂	wt%	5.36	4.12	5.41	8.20	7.89	7.37	7.06	7.71	6.87
Rich – loading**	mol/mol	0.26	0.19	0.26	0.36	0.35	0.33	0.32	0.35	0.34

Capture rate

Gas side (in-out of absorber)	%	100	99	99	65	74	81	86	65	86
Gas side (in-out of stripper)	%	100	-	95	54	67	77	83	55	85
Liquid side***	%	75	-	84	44	55	61	-	43	68

Emissions

1-(2HE)PRLD (before the abs. wash)	mg/Nm ³	1100.0	1420.0	-	-	-	-	-	-	-
3A1P (before the abs. wash)	mg/Nm ³	-	-	-	-	-	-	-	-	-
NH ₃ (before the abs. wash)	mg/Nm ³	11.4	11.8	-	-	-	-	-	-	-
1-(2HE)PRLD (after the abs. wash)	mg/Nm ³	98.7	191.0	-	6.3	14.2	5.3	27.6	8.8	33.0
3A1P (after the abs. wash)	mg/Nm ³	3.0	0.1	-	1.3	4.1	0.1	0.0	0.0	0.0
NH ₃ (after the abs. wash)	mg/Nm ³	8.3	7.2	-	4.8	5.5	3.8	8.0	5.2	9.4

*Due to overlapping FTIR spectra, total amine is measured.

**Due to total amine measurement, the conversion to mol CO₂/mol amine assumes mean amine's molecular weight equal to 104.2 g/mol.

***High uncertainty in composition measurement due to overlapping spectra.

Runs #1 to #3 are conducted with low CO₂ content, ~5 vol% (dry basis). These runs have a slightly different L/G ratio, due to a malfunction of the CO₂ mass flow controller which led to similar L/G ratio when corrected. Looking at the capture rates (when calculated from the gas side), it seems that a large amount of the CO₂ of the flue gas is being captured leading to >95% capture rates. Runs #4 to #9 are conducted with high CO₂ content, 10.5 vol% (dry basis), with Runs #4 to #7 focusing on the effect of increasing the L/G ratio. It is observed that with same gas flow and compositions and increasing liquid flowrate, the capture rate increases. This is expected and is seen for all ways of calculating the capture rate.

Runs #8 and #9 investigate the effect of stripping pressure on the capture capacity of the system. Lowering the pressure from 0.85 barg, which was the base case, to 0.79 barg led to the reboiler temperature being lowered from 120 to 115 °C, and higher lean loading of the solvent, thus lower capture rate. Higher pressure, as it was studied in Run #9, shows negligible deviation in loadings, capture rates and emissions when compared to the run with the same L/G ratio (Run #7). The reason for this is that the temperature did not increase but remained at 120 °C. This is a result of how the miniplant was operated by setting both set-points, one for the pressure on the top of the stripper and one for the reboiler temperature. The stripping pressure is controlled by a pneumatic valve on the top of the stripper, which in this case remained longer closed while operating the reboiler at 120°C in order to meet the desired pressure level.

A difference in the temperature profile in the absorber is shown between the low-CO₂ and the high-CO₂ flue gases, as expected. Runs #1 to #3, which have the lower CO₂ content, exhibit the typical bulge temperature approximately in the middle of the absorber height, while the rest of the runs with the higher CO₂-content appear to have their maximum temperature towards the top of the absorber. This is illustrated in Fig. 2. The location of the bulge depends primarily on CO₂ concentration, capture rate, heat of absorption, L/G ratio and absorber height. For full-height absorbers and fast solvents, the temperature bulge appears in the bottom or in the lower part of the column. Having a temperature bulge higher and on the top of the column indicates slow kinetics while also pointing towards the limited height of the column. This is expected due to the fact that the miniplant is a pilot with limited height, not specifically optimized for HS-3. This can be easily understood from the data in Table 1 where the achieved rich loadings are ~0.23 mol/mol and ~0.34 mol/mol for the low-CO₂ and the high-CO₂ runs, respectively (the maximum loading capacity of the solvent is ~0.5 mol/mol [6]). For comparison reasons, typical lean and rich loadings achieved with the miniplant using aqueous 30 wt% MEA, the benchmark solvent for post-combustion CO₂ capture, are ~0.2 and ~0.45 mol/mol, respectively.

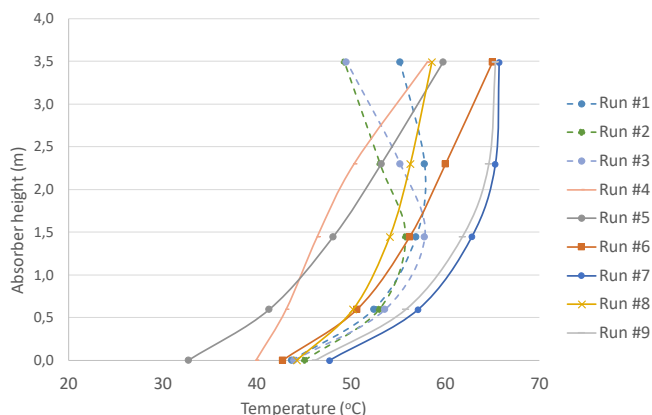


Fig. 2. Temperature profiles in the absorption column. Dashed lines indicate runs with ~5 vol% CO₂, continuous lines indicate runs with 10.5 vol% CO₂ in the flue gas inlet.

Regarding the capture rates, overall, it is seen that the calculation from the absorber side is always higher than when calculated from the stripper side, with an average deviation of 5% (max 10%, min 0%). This deviation is associated mainly with uncertainties in the FTIR measurement on the top of the absorber wash and the flow measurements both in the absorber and the stripper side. Uncertainties in pressure and temperature also propagate in the calculations through the conversion of volume to normal (Nm³) conditions. The capture rate when calculated based on the liquid analysis is consistently 10% lower than the capture rate from the gas side (stripper). Such deviation is associated to the errors in measurements of liquid flow and, primarily, the liquid sample analysis suffering from high uncertainty due to, among other, overlapping spectra. Overall, there is higher confidence on the calculation of the capture rate from the stripper side due to the fewer parameters included, and thus lower error propagation in the result.

As far as the emissions are concerned, high amine emissions up to ~200 mg/Nm³ are shown for the low-CO₂ content streams and lower and up to 30 mg/Nm³ for the high-CO₂ content runs. Although the emissions were significantly lower with the high CO₂-content runs, they are still high considering the presence of the water wash. The higher emissions are most likely the result of low loading of the lean solvent (4-5 wt% CO₂). The main contribution to emissions is from *1-(2HE)PRLD*, due to its significantly higher volatility. Furthermore, the efficiency of the water wash was verified for runs #1 and #2 by measuring the gas composition before and after the absorber wash with fresh water being used. It is seen that amine emissions in the order of thousands is decreased to a couple of hundreds, thus offering a ~90% removal in these runs.

In addition, when comparing the total amine wt% measured by the ATR and the sum of the measured concentration of *1-(2HE)PRLD* and *3AIP* (from LC-MS), it is seen that the latter is always higher than the first one by 1-3 wt%. Although this provides insight regarding the reliability of the FTIR-ATR method for the analysis of HS-3 solvent at the given conditions, it does not explain the deviations observed in the capture rates when calculated by the liquid side. The reason is that the difference between the rich and the lean loading is used, therefore any additional error in the quantification of CO₂ would be present in both measurements, yielding the same difference.

During the testing, discoloration was observed in the solvent. Discoloration indicates that the solvent degrades, however to which extent it is occurring is found by analyzing lean samples for degradation compounds. The samples were analyzed using LC-MS for selected degradation products as well as for *1-(2HE)PRLD* and *3AIP*. An overview of the concentration (mmol N/kg) of the selected degradation products is shown in Fig. 3. It is clearly seen that main degradation products are AP-Urea and pyrrolidine which were also observed in cycled set-up for studying degradation [5].

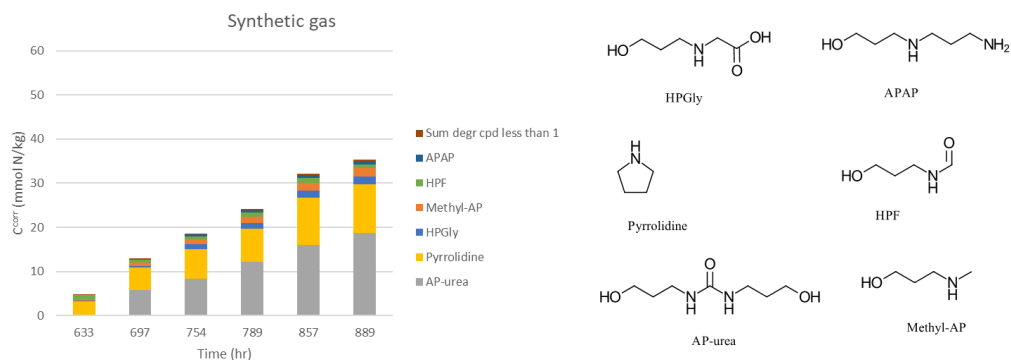


Fig. 3. Distribution of degradation products (AP-urea, Pyrrolidine, HPGly, Methyl-AP, HPF, APAP, HPAIa, OZN and 3-Mpy) in HS-3 after the synthetic gas campaign.

3.2. Real flue gas

The composition of the flue gas was determined by the GasMET FTIR in the start and the end of the campaign of the studied stack, here forth referred to as Stack 1. The measurement lasted for at least 1 hour and/or until stable measurements. Table 3 presents the composition of the flue gas reported in this work. Some fluctuations are expected in the flue gas composition, and this is the reason why a measurement was conducted before and in the end of the campaign. It is noted that the CO₂ content is quite stable, while significant deviations are seen for carbon monoxide and nitrogen oxides. For the calculation of the capture rates, which require the inlet CO₂ concentration, the average of the two values is used. It is noted that due to water condensing in the non-insulated line during the transport of the gas from the stack to the miniplant, the water content measured is expected to be lower than the one out of the stack while specific compounds which are soluble in water, such as NO₂, are expected to appear in lower concentration in the measured stream.

Table 3. Flue gas composition in the start and in the end of campaign with Stack 1.

Component	Unit	Stack 1 (start)	Stack 1 (end)
CO ₂	vol%	5.94	5.33
O ₂	vol%	7.79	7.63
H ₂ O	vol%	1.82	2.06
CO	mg/Nm ³	3.93	90.16
N ₂ O	mg/Nm ³	0.00	0.22
NO	mg/Nm ³	40.19	19.70
NO ₂	mg/Nm ³	0.08	4.01
SO ₂	mg/Nm ³	1.12	0.00
CH ₄	mg/Nm ³	2.07	3.59

The operational parameters in the start and the end of the campaign are given in Table 4, in order to evaluate if any significant effects on the performance of the solvent during that period occurred. When compared to the data obtained during the synthetic gas tests, the main difference in the operational settings is the stripping pressure. The stripping pressure used in the refinery is higher than the ones studied in the lab, with 0.95 barg used compared to the pressures of 0.80-0.90 barg studied in the lab. The reason for this is the fact that, during some unplanned safety shut-downs during the operation start-up, where the stripper top for safety reasons remains open to atmosphere, significant amount of water evaporated risking also high amine carry-over. It is noted that despite the safety shut-downs and, thus quick cooling of the columns, no precipitation issues have been observed. Furthermore, it is observed that the temperatures

are generally lower in the campaigns with real flue gas. This can be explained by the fact that additional lines in lean and rich lines have been added for the demonstration activities in the refinery, where probes made from promising non-metal material have been set in order to study the stability of the material when exposed to degraded HS-3 solvent. As a result, the heat losses increase especially around the cross heat exchanger thus leading to also lower absorber temperatures.

Table 4. Overview of operational parameters used in the demonstration with real flue gas in the start and in the end of campaign with Stack 1.

Parameter	Unit	Stack 1 (start)	Stack 1 (end)
<i>Gas and liquid flows</i>			
Gas inlet	Nm ³ /h	3.97	3.95
Liquid inlet (lean)	kg/h	12	11.9
L/G absorber	kg/kg	2.3	2.3
<i>Temperatures</i>			
Liquid inlet	°C	35.8	37.9
Gas inlet to absorber	°C	22.9	24.5
Absorber bottom packing	°C	35.7	34.8
Absorber intermediate (low)	°C	-	-
Absorber intermediate (middle)	°C	48.3	47.7
Absorber intermediate (middle)	°C	-	-
Absorber top of packing	°C	-	-
Water wash in	°C	44.8	45.2
Water wash outlet	°C	28.1	28.2
Cross HX-rich inlet	°C	32.7	31.8
Cross HX-rich outlet	°C	89.2	91
Cross HX-lean inlet	°C	102	102
Cross HX-lean outlet	°C	35.4	35.1
Reboiler	°C	120	120
<i>Pressure in stripper top</i>	barg	0.94	0.95
<i>Capture rate</i>			
Gas side (in-out of absorber)	%	62	58
Gas side (in-out of stripper)	%	60	56
<i>Emissions after abs. wash</i>			
1-(2HE)PRLD	mg/Nm ³	224.0	38.9
3A1P	mg/Nm ³	19.6	19.7
NH ₃	mg/Nm ³	1.3	1.7

Moreover, the capture rate towards the end of the testing, which lasted more than 770 operating hours, seem to slightly drop from ~60% to ~56%. This difference is considered negligible, considering the uncertainty of the operational measurements and possible gas fluctuations. In addition, higher emissions of amine are seen in the start compared to the end of the campaign. This seems peculiar and it might be the result of flue gas fluctuation and higher particle content that might have led to higher aerosol-based emissions.

Results of the solvent analysis during the real flue gas campaign indicate lean loadings of 0.2 mol/mol, rich loadings of 0.41 mol/mol and amine content of ~31 wt% *1-(2HE)PRLD* and 13 wt% *3AIP*. Ignoring the stripping pressure difference, a comparison is attempted with Run #1 since the CO₂ concentration and L/G ratio are more similar than compared to the other runs in the lab. Both lean and rich loadings are lower with the synthetic flue gas, i.e. 0.15 instead of 0.20 for lean loading and 0.26 instead of 0.41 mol/mol for rich loading respectively. The cyclic capacity increases from 0.11 to 0.21, which can hardly be attributed to the somewhat higher CO₂ concentration in the case of the campaign in the refinery. It is likely that the higher cyclic capacity is a result of the lower amine content than the original formulation. The latter was a result of solvent dilution from the water wash during an unplanned safety-shut-down in the start-up of the campaign, that has most likely led to lower viscosity and potentially enhanced mass transfer. It is noted that the capture rate calculated based on these values varies significantly compared to capture rate calculation from the gas side, and actually leads to >100 capture. This is difficult to explain and an investigation is on-going.

The selected degradation compounds (analyzed also for the synthetic gas campaign at TNO) are shown in Fig. 4 for the campaign at Irving with flue gas from stack 1. The solvent samples were additionally analyzed for total nitrogen, and the nitrogen balance for the lean samples from the campaign at Irving with stack 1 is given in Fig. 5. Taken into account the uncertainty, the nitrogen balance is closed, and it is therefore believed that all major degradation compounds with nitrogen are accounted for. The degradation compounds are the same as those observed in the smaller lab-scale set-up where the solvent [5] was tested before demonstration campaigns were started. The order of major degradation compounds are the same for both campaigns with the miniplant as well as what was observed in the laboratory.

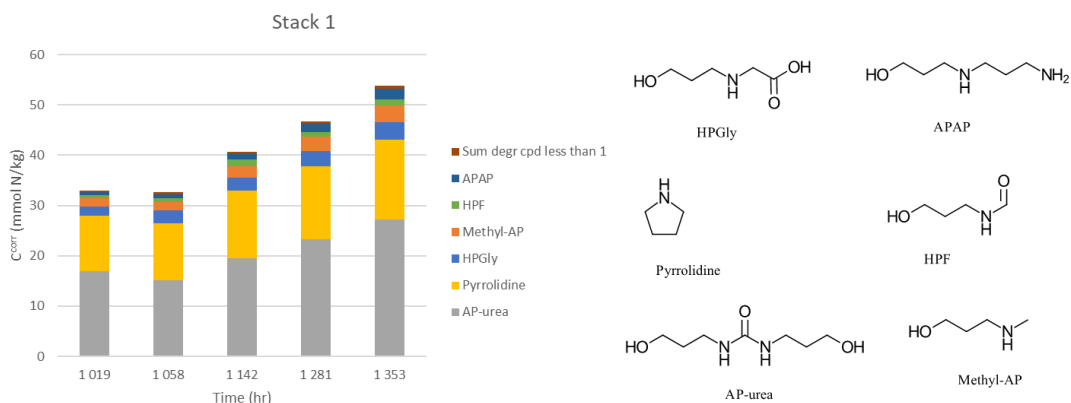


Fig. 4. Distribution of degradation products (AP-urea, Pyrrolidine, HPGly, Methyl-AP, HPF, APAP, HPAla, OZN and 3-Mpy) in HS-3 after the stack 1 gas campaign.

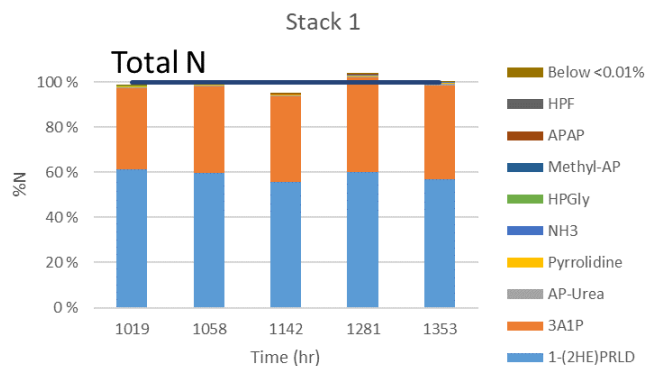


Fig. 5. Nitrogen balance over the lean samples from the stack 1 campaign at Irving.

Metals, while at trace levels in the flue gas, are seen to be detectable in the miniplant solvent 25L inventory overtime. A selected number of miniplant solvent samples has been analyzed for metal content from the real flue gas campaign using ICP-MS, specifically for Fe, Cr and Ni. The obtained data points are presented in Fig. 6. The measured concentrations are below 2 mg/L for Fe and Cr, and below 5 mg/L for Ni in the presence of HS-3 solvent after almost 2 months of operation. The concentration of nickel seems to increase in a fast rate and needs to be followed closely. After approximately 1240 operating hours, the concentration of Fe and Cr seem to slightly decrease and then start the increasing trends again. This is a result of the water balance disruption, which was then slowly corrected.

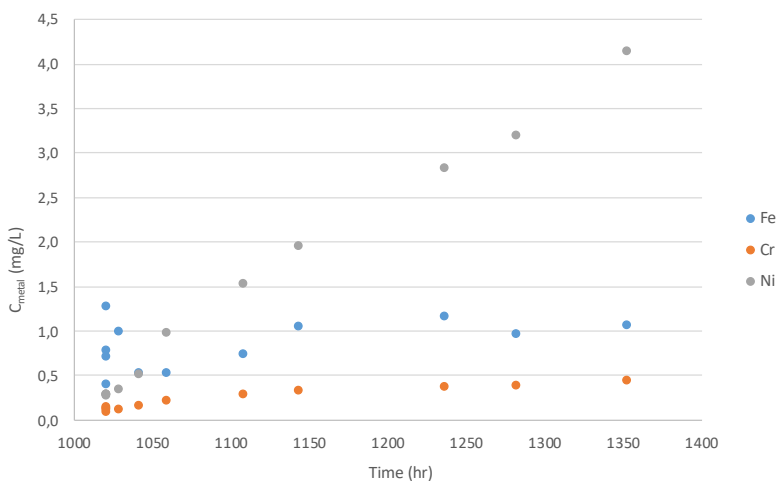


Fig. 6. Metal content change during the campaign with real flue gas.

4. Conclusions and Future Work

CO₂ capture using HS-3 solvent has been successfully demonstrated both in the laboratory with synthetic gas (TRL 5) and at Irving Oil Whitegate Refinery in Ireland with real flue gas (TRL 6). TNO's miniplant, an ATEX-compliant small-scale pilot plant, has been employed to capture CO₂ from the flue gas of various sources of the Irving Oil Whitegate refinery. The results of one of them is presented in this work, in addition to the results from laboratory testing. The flue gases have varying content of CO₂, O₂ and other impurities in order to degrade and stress-test as much as possible the stability of the solvent. The results so far indicate that the solvent is easy to use, since it is non-toxic and did not precipitate, even during unplanned shut-downs. The solvent seems to show slow mass transfer, and another point of attention is the volatility of one of its containing amines, 1-(2HE)PRLD, leading to significant emissions of the component, despite the use of water wash. Removal efficiency of emissions above 90% of the water wash has been shown.

In the analytical front, it was found that the FTIR-ATR method is not suitable for analyzing liquid samples of HS-3 due to overlapping spectra of the main amines, therefore other type of more complex analysis such as LC-MS should be used. The same degradation compounds were found in both campaigns, in agreement with what has been observed previously in a smaller cycled degradation rig, and the major components were AP-urea and pyrrolidine. The nitrogen balance over the liquid samples was closed, indicating that all major degradation compounds with nitrogen have been accounted for. The results of the metal content analysis during the first 1300 operating hours with synthetic and real flue gas, which was done to investigate any corrosion-related issues, show overall low metal concentrations. On-going analytical work will provide more information regarding the performance of the solvent and behavior when exposed to specific impurities.

The miniplant operation has been performed in order to demonstrate the technology in a refinery and to degrade the solvent, after which the whole solvent inventory will be sent to SINTEF's pilot plant in Tiller, Norway. By testing the solvent in this larger CO₂ capture plant, representative energy numbers will be obtained. In addition, 5 L of the miniplant's solvent inventory will be used for developing a reclaiming strategy for a two-amine solvent (one of which is volatile).

Acknowledgements

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CARBON CAPTURE DEMONSTRATION AT IRVING OIL WHITEGATE REFINERY

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1. Introduction

The refining industry is a highly energy-intensive sector with direct CO₂ emissions varying from 100 to 200 kg CO₂/tonne oil. Primary challenge related to CCUS lies in having several relatively small sources with various levels of CO₂ concentration, from which this greenhouse gas must be captured. Within the REALISE project, a Refinery-Adapted Cluster-Integrated Strategy to Enable Full-Chain CCUS Implementation will be developed, through the integration of a multi-absorber concept for capturing CO₂ from different stacks [1], [2]. CO₂ capture technology has been demonstrated both in the lab and on-site at Irving Oil Whitegate Refinery using TNO's mobile small-scale pilot plant and the novel HS-3 solvent. HS-3 is an aqueous mixture of 40wt% of 1-(2-Hydroxyethyl)pyrrolidine, 1-(2HE)PRLD, and 15wt% of 3-amino-1-propanol, 3A1P, developed in the HiperCap project [3].

2. Materials and Methods

A small-scale mobile pilot plant, called miniplant, has been used for the demonstration activities (Fig. 1). It was designed and built by TNO, it is fully automated and can be accessed remotely, with capacity to process up to 5 Nm³/h gas and producing up to 25 kg CO₂ /day. The miniplant is ATEX-compliant, meaning that it complies with the European ATEX (ATmosphères EXplosives) regulations in order to ensure safe operations in environments where gaseous combustible materials may be present, such as refineries.

The demonstration activities took place using both synthetic flue gas and real flue gas from the refinery. The synthetic flue gas was a mixture of air and CO₂, and 9 runs were conducted in order to determine the operational setting to be used in the refinery; Runs #1-#3 with ~5 vol% CO₂ and Runs #4-#9 with 10.5 vol% CO₂. CO₂ was captured from 4 different real flue gases at the Irving Oil Whitegate Refinery, selected based on their distance between the stack and the miniplant's location inside the refinery, the number of impurities and, most importantly, their CO₂ content. Regarding impurities, the flue gas from the selected stacks includes various concentrations of particles, SO_x, NO_x, O₂ and CO₂ in order to stress-test the performance and chemical stability of HS-3 solvent. Since analytical work is still on-going, only the results of testing from with the flue gas of the first stack are presented in this work. The gas contained ~5.8 vol% CO₂, ~7.7 vol% O₂, 3-90 mg/Nm³ CO, 22-40 mg/Nm³ NO_x, ~1 mg/Nm³ SO_x and 2-4 mg/Nm³ CH₄.



Fig. 1: TNO's small-scale ATEX-compliant mobile pilot plant

A Fourier-transform infrared spectroscopy (FTIR) analyzer was used for the gas composition measurement of the inlet gas and the outlet gas of the absorber wash. Liquid analysis included FTIR-ATR (Attenuated Total Reflection) during the synthetic gas testing, Karl Fisher (KF) titration, Total Inorganic Carbon-Total Organic Carbon (TIC-TOC), Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), oxidative catalytic combustion and chemiluminescence detection (TOC-L CPH TNM-L) for total nitrogen and Liquid Chromatography – Mass Spectrometry/Mass Spectrometry (LC-MSMS) for various degradation products such as amine, urea, amino acids, amides. More details regarding the analytical methods are available in [4].

3. Results

Synthetic flue gas

The tests were conducted using 40°C lean solvent temperature, 120°C reboiler temperature, and 0.85 barg stripping pressure. The findings of the testing show that in Runs #1 to #3 (low CO₂ content), a large amount of the CO₂ of the flue gas was captured leading to >95% capture rates. Runs #4 to #9 (high CO₂ content) indicate lower capture rates varying from 50 to 85% capture, increasing with increasing liquid flowrate and with same gas flow and compositions. The effect of stripping pressure was also investigated and it was seen that lowering the pressure led to higher lean loading of the solvent, thus lower capture rate.

By studying the temperature profile in the absorber of the runs, a difference is shown between the low-CO₂ and the high-CO₂ runs, with Runs #1 to #3 exhibiting the typical bulge temperature approximately in the middle of the absorber height, while the rest of the runs appear to have their maximum temperature towards the top of the absorber (Fig. 2). Having a temperature bulge higher and on the top of the column indicates slow kinetics while also pointing towards the limited height of the column. This is expected due to the fact that the miniplant is a pilot with limited height, not specifically optimized for HS-3.

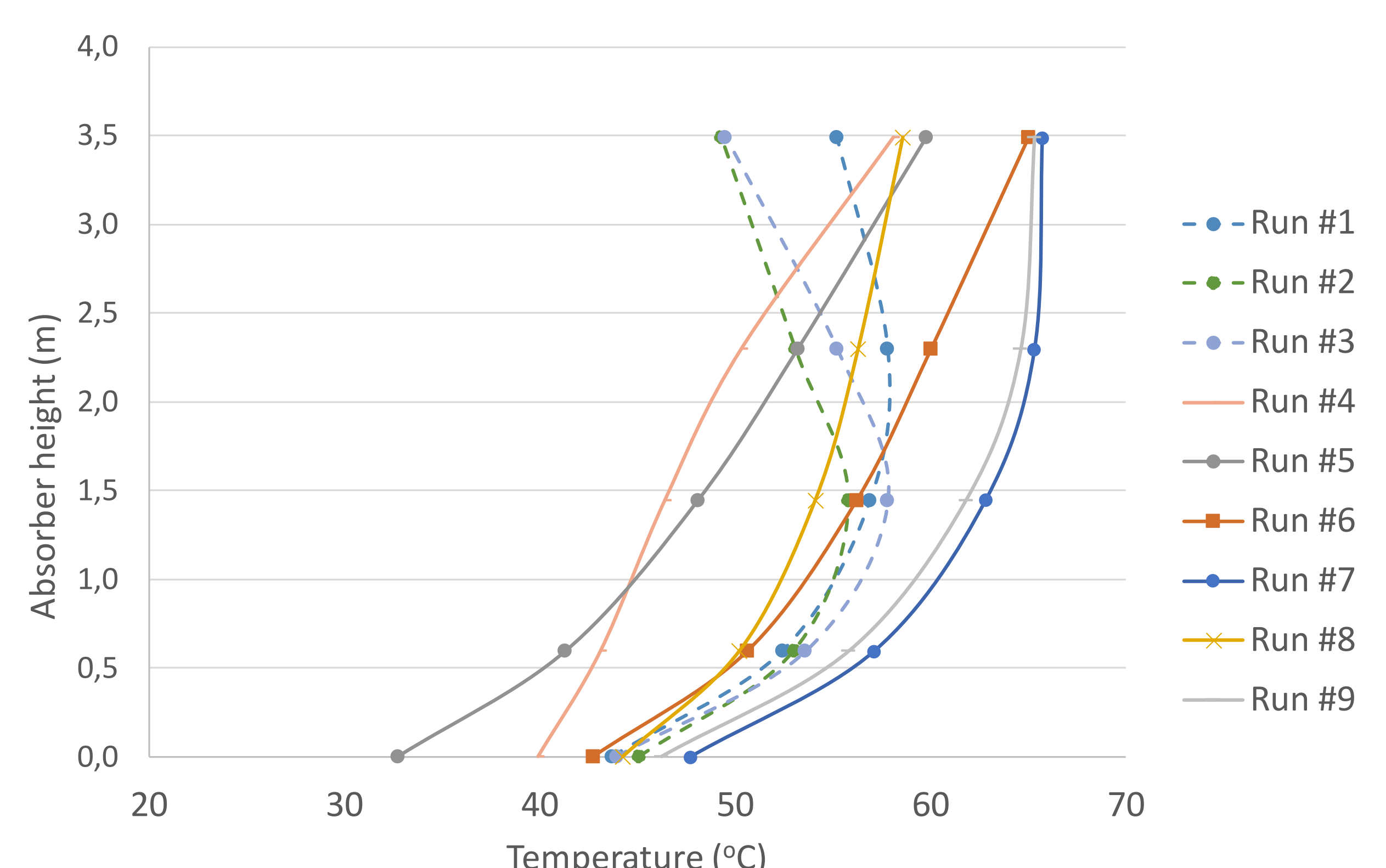


Fig. 2: Temperature profiles in the absorption column. Dashed lines indicate runs with ~5 vol% CO₂, continuous lines indicate runs with 10.5 vol% CO₂ in the flue gas inlet.

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As far as the emissions are concerned, high amine emissions up to ~200 mg/Nm³ were seen for the low-CO₂ content streams and lower and up to 30 mg/Nm³ for the high-CO₂ content runs. Although the emissions were significantly lower with the high CO₂-content runs, they are still high considering the presence of the water wash. The higher emissions are most likely the result of low loading of the lean solvent (4-5 wt% CO₂). The main contribution to emissions is from 1-(2HE)PRLD, due to its significantly higher volatility. Furthermore, the efficiency of the water wash was verified for runs #1 and #2 by measuring the gas composition before and after the absorber wash with fresh water being used. It is seen that amine emissions in the order of thousands is decreased to a couple of hundreds, thus offering a ~90% removal in these runs.

Real flue gas

The operational parameters in the start and the end of the campaign are given in Table 4, in order to evaluate if any significant effects on the performance of the solvent during the testing period occurred. Several unplanned shut-downs took place, leading to sudden temperature drops of the loaded solvent, in which no precipitation issues have been observed.

Table 1: Main operational parameters used in the demonstration with real flue gas in the start and in the end of campaign with Stack 1.

Parameter	Unit	Stack 1 (start)	Stack 1 (end)
<i>Gas and liquid flows</i>			
Gas inlet	Nm ³ /h	3.97	3.95
Liquid inlet (lean)	kg/h	12	11.9
L/G absorber	kg/kg	2.3	2.3
<i>Temperatures</i>			
Solvent inlet (lean)	°C	40	40
Reboiler	°C	120	120
<i>Pressure in stripper top</i>	barg	0.94	0.95
<i>Capture rate</i>			
Gas side (in-out of absorber)	%	62	58
Gas side (in-out of stripper)	%	60	56
<i>Emissions after abs. wash</i>			
1-(2HE)PRLD	mg/Nm ³	224.0	38.9
3A1P	mg/Nm ³	19.6	19.7
NH ₃	mg/Nm ³	1.3	1.7

The capture rate towards the end of the testing, which lasted more than 770 operating hours, seem to slightly drop from ~60% to ~56%. This difference is negligible, considering the uncertainty of the operational measurements and possible gas fluctuations. In addition, higher emissions of amine are seen in the start compared to the end of the campaign. This seems peculiar and it might be the result of flue gas fluctuation and higher particle content that could lead to higher aerosol-based emissions.

Degradation and corrosion

A selected number of lean samples from both the synthetic gas testing and the on-site real flue gas testing was analyzed using LC-MS for selected degradation products as well as for 1-(2HE)PRLD and 3A1P (Fig. 3). The findings are similar for both, showing that the main degradation products are AP-Urea and pyrrolidine, as also shown previously in [4]. The solvent samples were additionally analyzed for total nitrogen. The nitrogen balance was closed indicating that all major degradation compounds with nitrogen are accounted for.

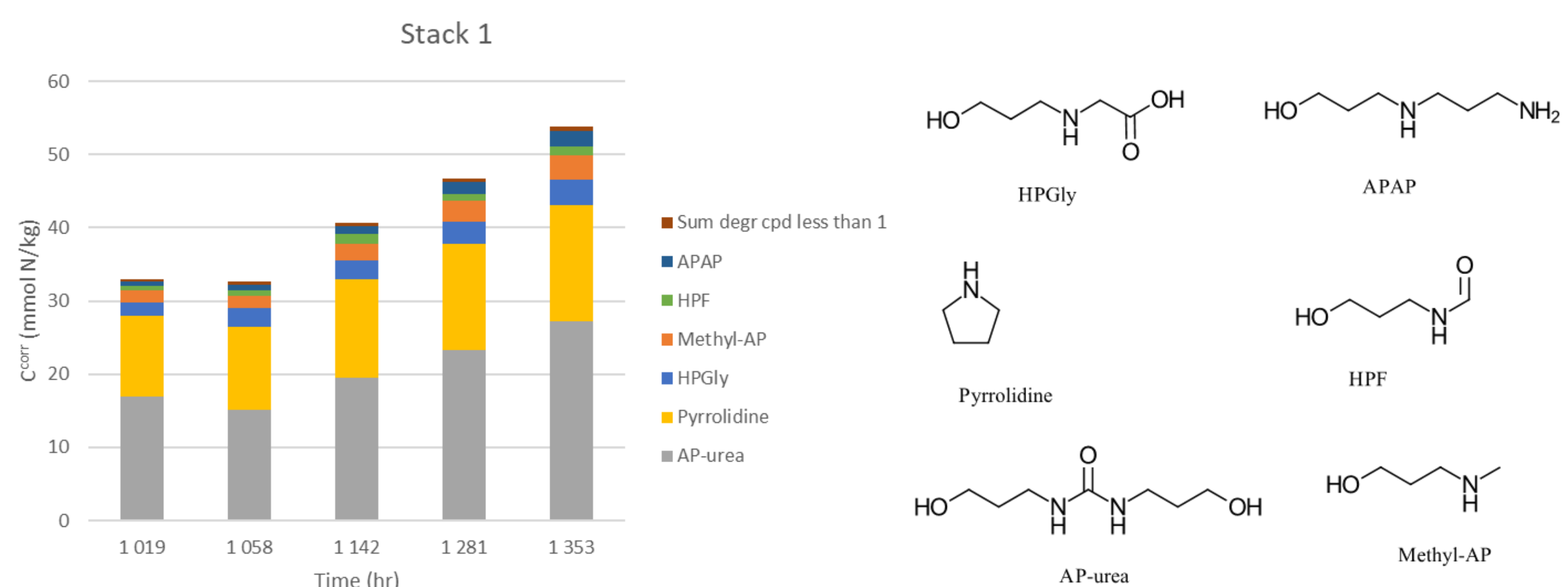


Fig. 3: Distribution of degradation products (AP-urea, Pyrrolidine, HPGly, Methyl-AP, HPF, APAP, HPAIa, OZN and 3-Mpy) in HS-3 during the stack 1 gas campaign.

Metals, while at trace levels in the flue gas, are seen to be detectable in the miniplant solvent 25L inventory overtime. Fig. 4 presents the ICP-MS measurements for Fe, Cr and Ni as a function of testing time. After approximately 1240 operating hours, the concentrations of Fe and Cr seem to slightly decrease and then start the increasing trends again. This is a result of the water balance, which was then slowly corrected.

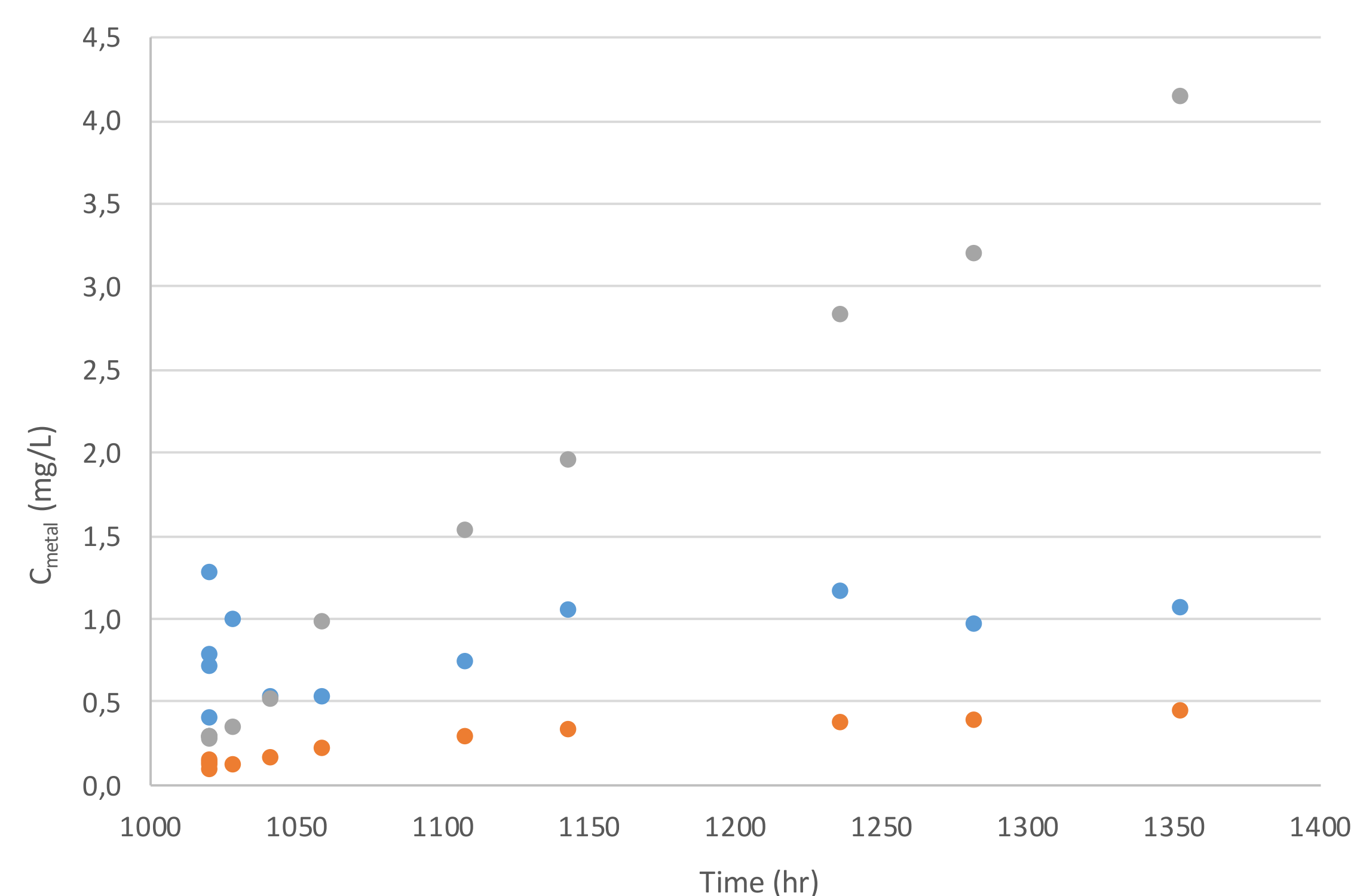


Fig. 4: Metal content change during the campaign with real flue gas.

4. Conclusions

- CO₂ capture using HS-3 solvent has been successfully demonstrated both in the laboratory with synthetic gas (TRL 5) and at Irving Oil Whitegate Refinery in Ireland with real flue gas (TRL 6) using TNO's miniplant.
- The results so far indicate that the solvent is easy to use, since it is non-toxic and did not precipitate, even during unplanned shut-downs.
- The solvent seems to show slow mass transfer, while another point of attention is the volatility of one of its containing amines, 1-(2HE)PRLD, leading to significant emissions of the component.
- In the analytical front, the same degradation compounds were found in the campaigns with both synthetic and real flue gas, also in agreement with what has been observed previously in a smaller cycled degradation rig. The major components were AP-urea and pyrrolidine.
- The results of the metal content analysis during the first 1300 operating hours with synthetic and real flue gas, which was done to investigate any corrosion-related issues, show overall low metal concentrations.
- On-going analytical work will provide more information regarding the performance of the solvent and behavior when exposed to specific impurities.

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