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1 Solvent qualification programme (SQP) overview

One of the objectives of the LAUNCH project is to develop and validate a methodology for accelerating degradation, to save on time while still obtaining industrially representative results, and also to test at smaller scale, to save costs and also allow the rig to be transported to the relevant flue gas source if required.

The small-scale LAUNCH rig#2 being tested for solvent qualification is a fully automated CO_2 capture plant designed to de-risk scaling-up of solvent technologies by representing the solvent degradation behaviour of full scale plants. This plant is designed with a small capacity of 1 kg/h of captured CO_2 , or 0.025 tonne per day (tpd). This small rig system, proposed before LAUNCH and further validated within the project, can be used to quantify the formation of degradation products over time. The rig is mobile, has a small footprint (6 m²) and can be easily connected at different industrial sites. This opens up the possibility to qualify solvents using different flue gases. The cost of the LAUNCH rig is estimated at 500 k \in . **Error! Reference source not found.** illustrates LAUNCH rig#2 at TNO.



Figure 1: LAUNCH rig#2 at TNO

To assess the effect of scale in solvent assessment LAUNCH rig#2 results were compared with those from the much larger (~1 tCO₂/day) pilot scale CO₂ capture plant at TERC, shown in Figure 2. The TERC plant is integrated with site combustion facilities including: Grate Boiler/Waste to Energy plant; Gasifier CHP; Biodiesel CHP, Gas Turbine CHP and visiting/future rigs, but for these tests it was fed from a dedicated synthetic gas mixing skid comprising 3 bulk gas streams: CO₂, N₂ and Air, each of 6-300Nm³/h flow rage and with trace gas (NO₂, SO₂) injection capability; this enables the simulation or modulation of a range of combustion/process gases.

The LAUNCH rig#2 and the TERC plant were used to investigate the capability of the much smaller LAUNCH rig#2 to mimic the degradation trends of larger plants as well as to study various strategies to accelerate degradation. Four accelerated degradation techniques were studied: increased oxygen levels in the flue gas, increased solvent concentration, increased stripping temperature, and addition of NOx to the flue gas. For the Baseline campaign, 7.6 vol% oxygen concentration was considered in the flue gas, since this is representative of industrial gases. The accelerated degradation techniques were applied in different operational campaigns:

Campaign name	Description
Baseline	34 wt% MEA, 7.6 vol% O ₂ , 120 °C
Higher O ₂ *	35 wt% MEA, 19.8 vol% O ₂ , 120 °C
Higher O ₂ /MEA	37 wt% MEA, 19.8 vol% O2, 120 °C
Higher O ₂ /stripping T	35 wt% MEA, 19.8 vol% O ₂ , 130 °C
Higher O ₂ /NOx	35 wt% MEA, 19.5 vol% O ₂ , 120 °C, NOx

Table 1: LAUNCH rig comparison test conditions

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2. Results and conclusions

Degradation trends for two major products HEPO and MEA-Urea, in the two rigs are shown in Figure 3. HEGly was another major product, while formic acid was the most dominant acid. Iron concentrations up to 4 mg/kg were seen in TERC and up to 7 mg/kg in the LAUNCH rig#2. In addition, the concentration of zinc (Zn - a known degradation catalyst) in LAUNCH rig#2 tests was possibly significant, sometimes exceeding the Fe concentration; the source of it is suspected to be a heating element in the rig. Zinc and copper construction materials would not normally be expected to be included in the wetted path of amine capture plants. Although it is seen that the LAUNCH rig#2 is capable of predicting the degradation trends and the most significant degradation products as larger rigs, such as TERC, it is noted that when comparing the trends between the two rigs, we see significant differences regarding the accelerated degradation strategy that yields higher degradation. For example, highest HEPO, MEA-Urea and Fe concentration were found at the *Higher O₂/stripping T* campaign in the LAUNCH rig, while this was the case for *Higher O₂/MEA* campaign at TERC. The campaigns were performed with the two rigs in similar, but not identical, conditions, therefore longer tests and operating condition variations, plus the different dissolved metal levels, can possibly explain the differences seen in the degradation trends.



Figure 2: TERC CO₂ capture plant

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Larger pilot units are still required for qualifying solvents regarding process performance (e.g., reboiler energy demand) at varying operational conditions. However, decoupling the two aspects – process and degradation performance – allows for small LAUNCH rigs to be used in long-term degradation campaigns (months), while larger pilots can be used in short-term process performance campaigns (weeks).

A LAUNCH SQP could consist of 2 campaigns, that can be executed within 3-8 months. Estimated operational costs for a 6 months program are 104 k \in , which is in line with LAUNCH's target of 100 k \in , but very dependent on the assumed costs for analytical techniques development – the item with largest uncertainty in this cost estimate.

The LAUNCH SQP is the first attempt that we are aware of on suggesting a methodology for solvent qualification. CO_2 capture technology providers could greatly benefit from a proven SQP, and this would also facilitate investment decisions by end-users, and permit processes from environmental authorities.

SQP campaign	Flue gas	Termination criteria	Solvent sampling	Expected duration
Degradation characterization	Artificial or real. In case of artificial, add NOx to realistic level. In both cases, use increased O ₂ content (close to 20%).	Liquid degradation products account for 5% of the initial solvent N content	Weekly quantification of products. Comprehensive analysis so that mass balance is closed.	500-1000 hours
Benchmarking	Ideally real flue gas. In case of artificial, add NOx to realistic level.	Maximum acceptable solvent loss rate reached (kg/tonco2), based on business case	Weekly quantification of main degradation products	2-6 months

Table 1. LAUNCH Solvent Qualification Protocol

LAUNCH WP reports

Deliverable number(s)	Title
D4.1.1	Final Comparison Report Rig#2 and PACT (TERC)
D.4.1.2/D.4.4.1/D.5.1.2/D4.4.3/D6.2.1	Qualification, drawing and validation of the LAUNCH rigs as a tool for measuring solvent degradation
D4.2.1	Assessing the representativeness of accelerated degradation tests using the LAUNCH rigs and the DNM
D4.3.1 / D5.2.5	Demonstration and assessment of mitigation technologies effectiveness on solvent degradation

Other publications

Akram, Muhammad and Skylogianni, Eirini and Veronezi Figueiredo, Roberta and Monteiro, Juliana and Grimstvedt, Andreas and Vevelstad, Solrun Johanne and Milkowski, Kris and Gibbins, Jon and van Os, Peter and Pourkashanian, Mohamed, *Comparison of TERC and TNO's LR2 CO2 capture rigs for normal and accelerated degradation* (November 17, 2022). Proceedings of the 16th Greenhouse Gas Control Technologies Conference (GHGT-16) 23-24 Oct 2022, Available at SSRN: <u>https://ssrn.com/abstract=4279777</u> or <u>http://dx.doi.org/10.2139/ssrn.4279777</u>

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