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Demonstrating the Effect of the NO₂ Concentration in Flue Gas on CESAR1 Degradation Using Pilot Plant Data

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Abstract

Amine solvent degradation is a major research topic in post-combustion carbon capture currently, as it has a large effect on the total cost and practical operability of carbon capture systems. This study focuses on the effect of NO₂ concentration in the flue gas on CESAR1 degradation using pilot plant data from multiple sources. CESAR1 is an aqueous blend consisting of 3M aminomethyl-propanol (AMP) and 1.5M piperazine (PZ). Long campaign pilot data (months/years) is especially relevant for solvent stability and durability studies as longer pilot campaigns give good insight in these parameters with exposure to real flue gases.

The main campaign in this study is the six week pilot campaign TNO has performed at Umicore Hoboken in Antwerp, Belgium, a non-ferrous metals recycling site of Umicore. TNO's miniplant (a mobile pilot carbon capture system) has been attached to a slip-stream of the flue gas of Umicore's smelter process for a six week campaign using CESAR1 as the capture solvent. An interesting characteristic of this flue gas downstream of the sulfuric acid plant, connected to the smelter off-gas system, is the high NO₂ concentration (up to 50 ppm). This is a higher concentration than what is normally reported in other campaigns (ca. 0-3 ppm) and is a result of an upstream catalyst bed for the conversion of SO₂ to SO₃. Consequently the NO₂/NO_x ratio is also high (90-95%). It is therefore interesting to compare the results of the Umicore campaign to other longer campaigns using CESAR1, such as RWE and TCM [1], [2] in terms of oxidative degradation and nitrosamine formation. The RWE campaign with CESAR1 is one of the longest pilot campaigns ever performed for post-combustion carbon capture, with 3 years of stable operation of their pilot using a single solvent inventory (with refills). Additionally, the test campaign at TCM using the CESAR1 solvent describes the effect of NO₂ on the solvent degradation rate for two different concentrations of NO₂ in the flue gas (0.5 ppm and 2.35 ppm).

Figure 1 shows the ammonia concentration at the absorber outlet during the smelter campaign at Umicore. Ammonia emissions can be used as a proxy for oxidative degradation for many amines including AMP and PZ. The ammonia concentration is increasing throughout the campaign, indicating increasing oxidative degradation rates. Near the end of the campaign, the concentration seems to stabilize around 50 mg/Nm³, which is very high for the CESAR1 solvent

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compared to other campaigns. RWE and TCM indicate ammonia emission in the range of 2-4 mg/Nm³ [3], [4], so it is expected that the degradation rate in the Umicore campaign is much higher than the RWE and TCM campaigns, around 20 times based on the ammonia emission rates.

This is further strengthened by Figure 2 and Figure 3, where component accumulation rates between the Umicore campaign and the RWE and TCM campaigns respectively are compared. This is done for the reported components from each campaign that overlap in both analysis, and are expressed as a ratio. The accumulation rate that this ratio is based on, is expressed as mass of component accumulated (mg) in the liquid phase per volume of flue gas treated (Nm³), instead of per mass of solvent (kg). This is done to circumvent the influence of the specific liquid inventory (which might be different between campaigns) on the results. Expressing it per Nm³ of flue gas treated by the capture system directly links the mass accumulated to the amount of flue gas (and impurities like NO₂). The accumulation rates for all measured components between both campaigns are much higher in the Umicore campaign compared to both the RWE and TCM campaigns. This leads to accumulation ratios ranging from 3-24 (Umicore/other campaign) for the different components.

Figure 4 shows the accumulation rates for N-nitrosopiperazine, piperazin-2-one and 4,4-dimethyl-2-oxazolidinone between all campaigns (from these products, only piperazin-2-one is reported in the RWE campaign) as a function of the NO₂ amount potentially taken up from the flue gas. At Umicore, a Fourier transform infrared (FTIR) device was installed at the inlet and outlet of the pilot plant, and accurate uptake rates could be calculated. For TCM and RWE, the assumption is made that all NO₂ reported in the inlet is absorbed into the solvent. For N-nitrosopiperazine, a nitrosamine degradation product of PZ, an increasing trend is observed using the TCM and Umicore data. This can be expected, since NO₂ can react directly with piperazine to form N-nitrosopiperazine [5]. What is more interesting, is that piperazin-2-one, an oxidative degradation product of piperazine, follows a similar trend. From this data, it therefore seems that NO₂ is enhancing/catalysing the oxidative degradation of PZ [5]. For 4,4-dimethyl-2-oxazolidinone, a major oxidative degradation product of AMP [2], this effect seems less pronounced, but the degradation rate in the Umicore campaign is still several times higher (5-7 times) than the TCM campaign.

It must be noted that 3 of 4 datapoints per component does not allow for definitive conclusions on the exact effect of NO₂, it however gives a strong indication. Based on these results, it is therefore hypothesized that the concentration of NO₂ in the flue gas has a large effect on oxidative degradation of CESAR1, and should be taken into account when designing CO₂ capture processes using the CESAR1 solvent. It is not yet clear how this effect translates to other solvents, for instance, primary amines like mono-ethanolamine (MEA).

The final submission will provide a more detailed discussion on the results of the Umicore campaign and the comparison to the RWE and TCM campaigns.

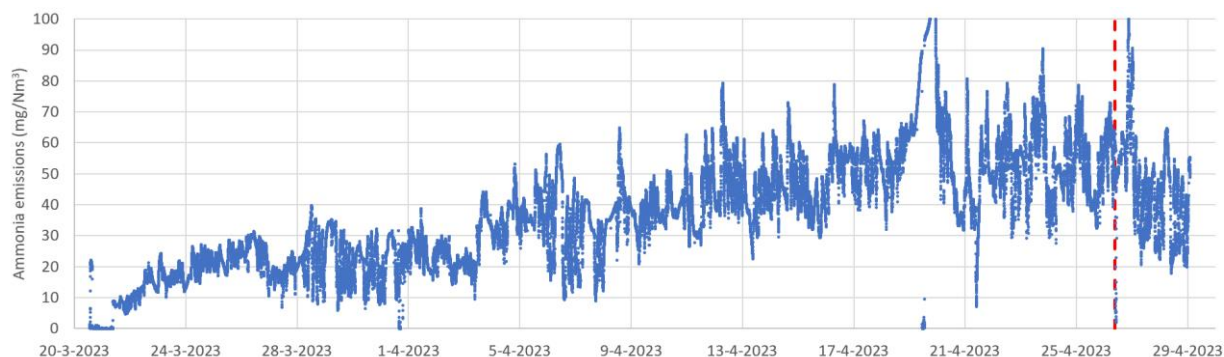


Figure 1, ammonia emissions measured at the absorber outlet during the smelter campaign at Umicore. The red line indicates the time at which some dynamic tests were performed, after which the plant was not operating stable anymore.

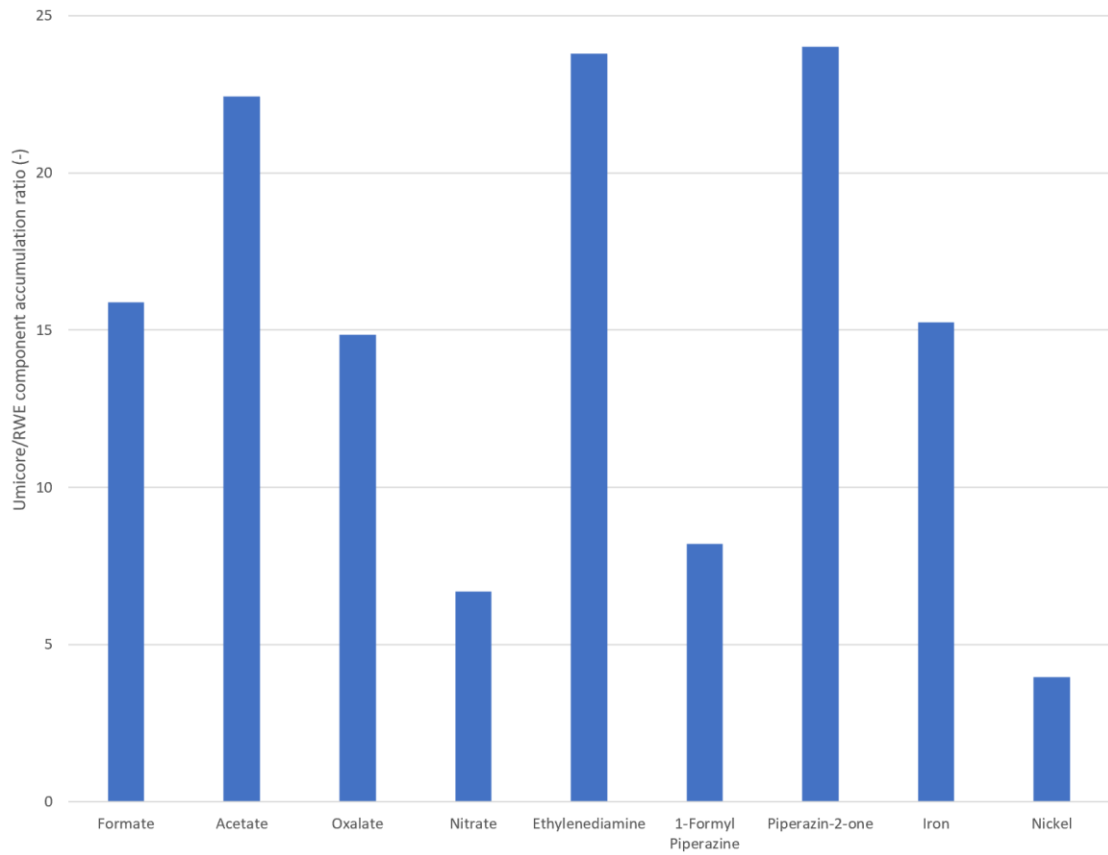


Figure 2, component accumulation ratios of components measured in both the RWE and Umicore campaigns

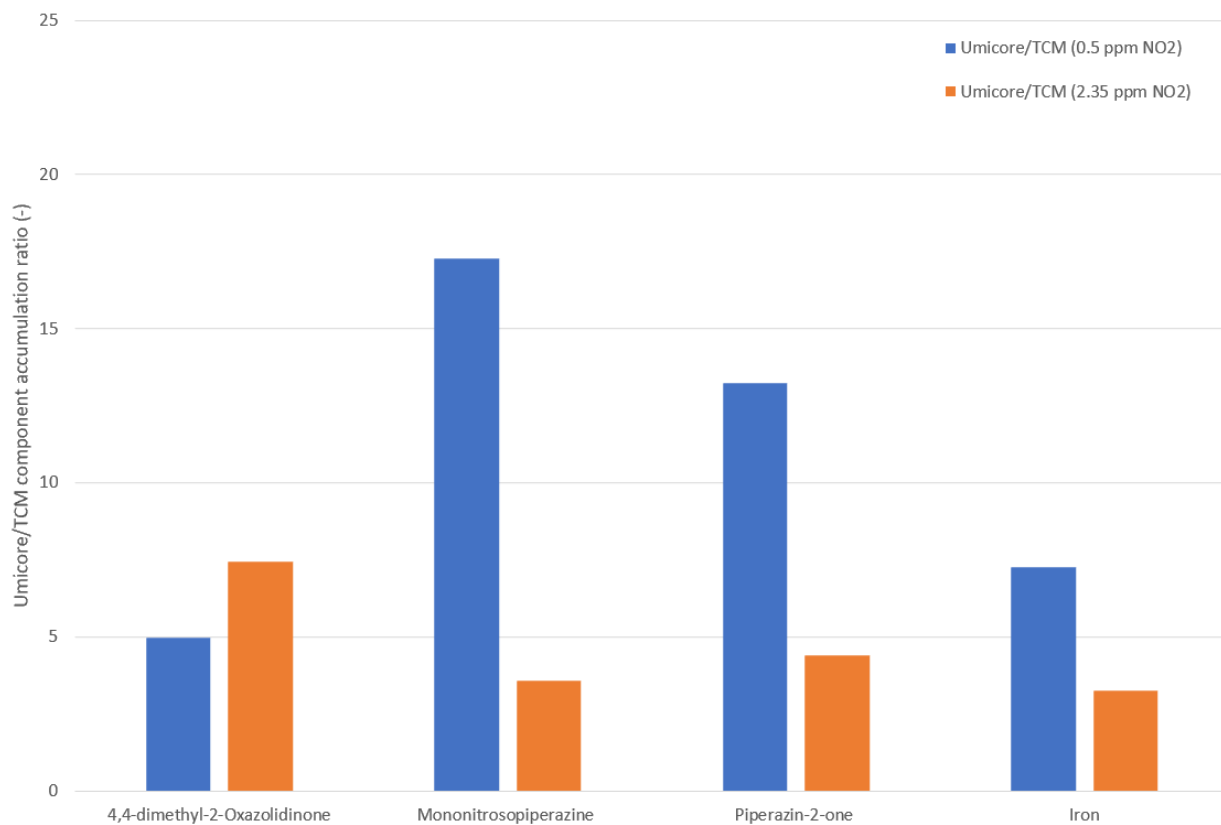


Figure 3, component accumulation ratios of components measured in both the TCM and Umicore campaigns, splitting up the TCM campaign in a low and high NO₂ sub-campaign.

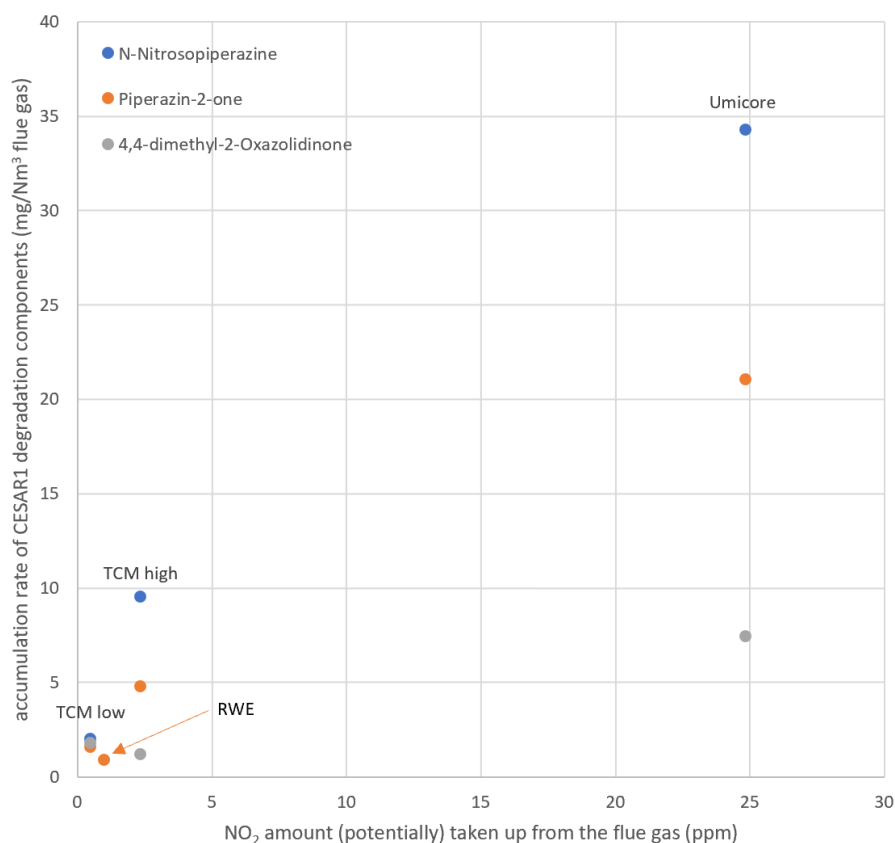


Figure 4, accumulation rate of CESAR1 degradation products as a function of amount of NO₂ taken up from the flue gas for the Umicore, RWE and TCM campaigns, splitting up the TCM campaigns in a low and high NO₂ sub-campaign.

Keywords: Solvent degradation, CESAR1, pilot campaigns, effect of NO₂.

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