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## SO<sub>2</sub> effect on oxidative degradation of monoethanolamine for post combustion CO<sub>2</sub> capture

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### 1. Introduction

The most conventional amine used in the post combustion capture technology, based on chemical absorption, is monoethanolamine (MEA). Depending on the composition of the flue gas to be treated, several mechanisms of amine degradation occur. This leads to a loss of CO<sub>2</sub> absorption capacity and may give rise to products that are environmentally difficult to dispose of. Results from CO<sub>2</sub> capture pilot plants showed that oxidative degradation due to the presence of oxygen in the flue gas is the main degradation pathway [1], [2]. Furthermore, MEA degrades when exposed to a flue gas containing an amount of sulfur dioxide (SO<sub>2</sub>). Until now there is not a clear statement about the effect of SO<sub>2</sub> on oxidative degradation of MEA. [3], [4] and [5] reported that the increase of SO<sub>2</sub> concentration leads to more MEA degradation. In addition, SO<sub>2</sub> can compete with CO<sub>2</sub> to react with MEA, which delays the inhibitory role of CO<sub>2</sub> on the MEA oxidative degradation. [5] also noticed based on a comparison between the reaction orders that the degradation of the amine is influenced much more by the presence of SO<sub>2</sub> than O<sub>2</sub>. [6], [7] and [8], however, reported that the degradation rate was inversely affected by the increase of SO<sub>2</sub> concentration. The goal of this study is to identify the impact of the presence of SO<sub>2</sub> on the oxidative degradation of MEA.

### 2. Materials and methods

This study was conducted in the Degradation Test Rig (DTR) which was developed at the University of Liège [9]. Its main particularity is to allow a batch operating mode on the liquid side with a continuous gas feed flowing through the liquid under pressure. In addition, the gas bubbling occurs through a hollow-shaft agitator that allows for a better dispersion of the gas phase into the liquid phase. Typically, 300 g of 30 wt % MEA is weighted into the reaction vessel. The accelerated laboratory experiments were performed for 48h at 120 °C, 4 barg and 800 rpm with a gas flow rate of 160 Nml/min. The composition of gas feed is presented in Table 1.

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Table 1: Gas feed composition

Test	1	2	3	4	5	6	7
O <sub>2</sub> (%)	0	5	5	5	5	5	5
N <sub>2</sub> /SO <sub>2</sub> (%)	100	95	75	50	25	10	0
N <sub>2</sub> (%)	0	0	20	45	70	85	95
SO <sub>2</sub> (ppm)	200	200	150	100	50	20	0

After 48h, the experiment is completed, and a sample is taken for analysis. The high-performance liquid chromatography (HPLC) technique was adopted as a method for determination of final MEA concentration. The main compounds in degradation experiments samples are identified and quantified using the gas chromatography method coupled with FID detector.

### 3. Experimental results and discussions

#### 3.1. Identification of MEA degradation products

As mentioned above, the presence of oxygen in the flue gas leads to MEA degradation. Degraded MEA Samples from tests 2, 6 and 7 are analyzed and the obtained results are presented in figure 1. It can be seen that in the presence of 5% of O<sub>2</sub> with and without the presence of SO<sub>2</sub>, the identified degradation products are the same. Consequently, the SO<sub>2</sub> therefore seems not to affect the oxidative degradation mechanisms. Furthermore, it was noticed that the SO<sub>2</sub> in the absence of O<sub>2</sub> does not induce degradation of MEA. This observation is in line with the result reported in [10]

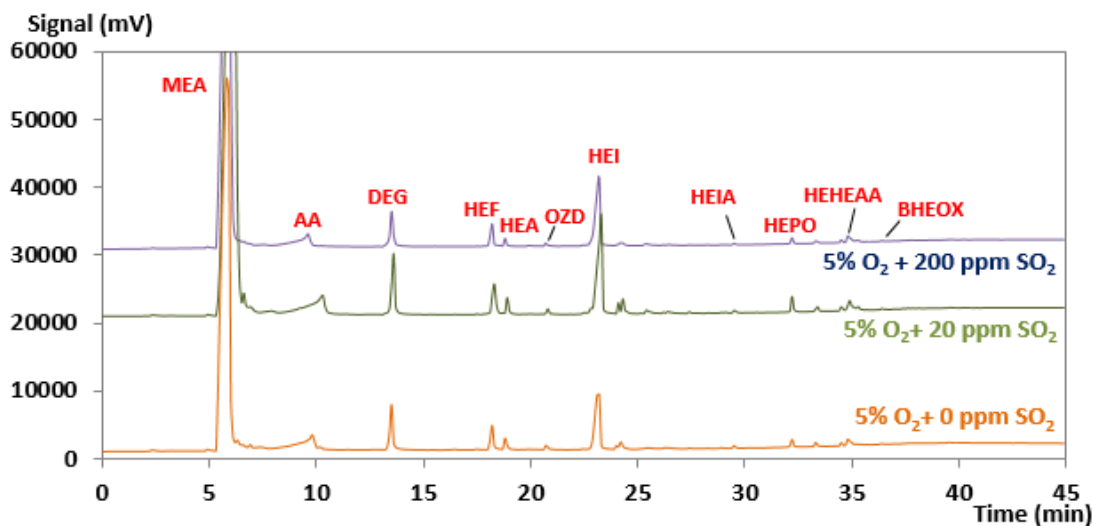


Fig. 1. Comparison of the gas chromatography spectra between test 2, 6 and 7.

#### 3.2. Influence of the presence of SO<sub>2</sub> and O<sub>2</sub> on MEA degradation products

In this section, the effect of the presence of both SO<sub>2</sub> and O<sub>2</sub> on MEA degradation is studied in the Degradation Test Rig. Degraded MEA samples from test 2 to 7 are analyzed by GC-FID and results are presented in figure 2. The MEA concentration decreased after 48 hours of experience for all tests. The decrease of MEA concentration results in the formation of a larger quantity of degradation product. According to [6], the low amount of SO<sub>2</sub> introduced into the solution is not sufficient to scavenge all the dissolved oxygen in solution. It is therefore expected that there will be no significant influence on the rate of degradation. However, a higher SO<sub>2</sub> content would maintain

oxygen in solution at a relatively low level, thus limiting oxidative degradation of the MEA. This conclusion seems consistent with the observations in figure 2.

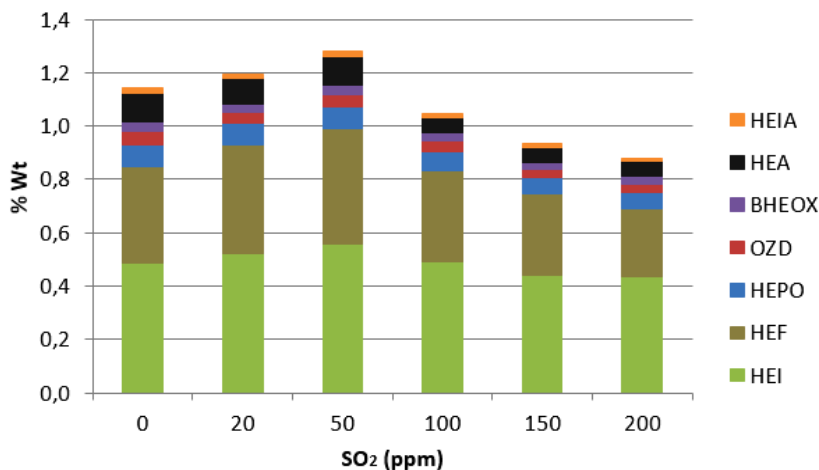


Fig. 2. Degradation products as function of SO<sub>2</sub>.

#### 4. Conclusion

The effect of the presence of SO<sub>2</sub> on the MEA oxidative degradation is studied and below are two of the main conclusions that have been achieved:

- 1) The same degradation products were obtained in the presence of 5% O<sub>2</sub> with and without SO<sub>2</sub>. This allowed us to assume that the oxidative degradation mechanism is not affected by the presence of SO<sub>2</sub>.
- 2) MEA oxidative degradation seems to be reduced with the presence of higher amount of SO<sub>2</sub>. Thus, SO<sub>2</sub> can be considered as a potential inhibitor of MEA oxidative degradation.

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