IEAGHG SEMINAR ON CONTROL OF NITROSAMINE FORMATION IN CO_2 CAPTURE PLANTS: REPORT ON MEETING

Report: 2011/5

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INTERNATIONAL ENERGY AGENCY

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Further information or copies of the report can be obtained by contacting IEAGHG at:

IEAGHG, Orchard Business Centre,
Stoke Orchard, Cheltenham,
GLOS., GL52 7RZ, UK
Tel: +44(0) 1242 680753 Fax: +44 (0)1242 680758
E-mail: mail@ieaghg.org
Internet: www.ieaghg.org

IEAGHG Seminar on Control of Nitrosamine Formation in CO_2 Capture Plants:
Report on Meeting

1st–2nd February 2011, Zeche Zollverein, Essen, Germany

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1 Background

The environmental impact of CO_2 capture plants is an area where the IEAGHG remains committed to facilitating discussion amongst the academic community, technology suppliers and utility companies. Following on from a successful workshop, Environmental Impacts of Amine Emission during Post-Combustion Capture, in 2010, the IEAGHG held the above seminar to discuss the potential for, and control of formation of nitrosamines in the capture plant process. E.ON, Gassnova and GdF Suez co-sponsored the seminar held at the Zeche Zollverein world heritage site near Essen, Germany. Sixty of the world's leading technical experts from 13 different countries representing academia, technology suppliers and the utility sector were in attendance.

The potential for nitrosamine formation in CO_2 capture plant by the side reaction of amines with NO_2 is now part of the public debate on CCS. In the public domain, there is significant uncertainty as to the expected levels of nitrosamine formation in capture processes and the potential for emission of these harmful compounds to the environment. Gaining widespread public support for CCS is very important for its successful implementation and this seminar provided a forum for experts to discuss this particular issue and find a way forward in order to address it. Key topics were nitrosamine formation pathways, verified measurement techniques and methods to minimise the formation of nitrosamines in the process. Considering the above mentioned motivation, this workshop was held aiming to answer the following questions:

- What inputs can we expect in terms of NO_2 levels and amine quality?
- How to improve the reliability and plausibility of nitrosamine analysis?
- What level of accuracy is possible in nitrosamine detection?
- Which concentration of nitrosamine can be expected until the first reclaimer operation?
- How can nitrosamine levels be minimized?
- How likely is the formation of volatile nitrosamine?
- How can we move forward with providing reliable information to the public?

2 Programme

The programme of the meeting consisted of two half days, which covered the following topics:

- Amine production and quality.
- The expected levels of NO_2 in the flue gas entering the capture process.
- Nitrosamine measurement, analytical instruments and accuracy.
- Measures and approaches to control NA formation.

- Volatility of NA in the CO_2 capture plants.

3 Presentations Summaries and Discussion

3.1 Welcome and introduction, Mohammad Abu Zahra, IEAGHG and Joost van Dijk, E.ON Generation GmbH

Mohammad Abu Zahra welcomed the delegates on behalf of IEAGHG and hoped for a fruitful and interactive workshop. Followed this Mohammad gave a short introduction to the IEAGHG, explaining the background of the programme and its members and sponsors. The background and origination of the workshop were explained, touching briefly on the main aims of the workshop and the reasons for international activity on the control of nitrosamine formation in CO_2 capture plants.

In his opening presentation, Joost van Dijk, Chief Operating Officer, Steam Fleet of E.ON Generation highlighted the importance of CCS in the fight against climate change and its flexibility and cost advantages as a key source of low CO_2 energy in the future. He encouraged the attendees to have open-minded discussions: "A joint engagement of academia, suppliers and future operators ensures a successful further development of this key technology."

3.2 Amine quality for CO_2 capture, Georg Sieder and Oliver Molt, BASF SE

The presentation from BASF SE, the world's largest chemical supplier, discussed the cost dependencies of amines along with current impurities present in technical grade amines. BASF also commented that global uptake of amine-based post-combustion capture would significantly increase the global demand for amine products. Regarding the formation of nitrosamine (NA), it was stressed that no NA is formed during the production process of the CO_2 capture solvents and the fact that the type of amine influences the formation of nitrosamine. All types of amines forms NAs, but yields are significantly different (primary and tertiary << secondary amines).

3.3 Expected NO_2 levels at the inlet of CO_2 capture plants, Bernd Schallert, E.ON

In the presentation of E.ON it was shown that NO_2 is effectively removed by a wet flue gas desulphurisation system, but re-oxidation of NO to NO_2 is favoured under the conditions found at a typical FGD outlet. During recent tests using power plant flue gases, E.ON have found that lower temperature and higher O_2 concentration favour the formation of NO_2. The intensive scrubbing of FGD plants reduce the NOx concentrations by approximately 2% but a re-oxidation occurs immediately. Therefore, small amounts of NO_2 (approximately 1 mg/m^3) are likely to occur at the inlet of the CO_2 capture plant, if an additional control of NO_2 immediately upstream of the capture plant is installed (pre-scrubber or DCC).

3.4 Plausibility of total and individual nitrosamine measurements and improvements, Matthias Frischmann, Henkel

The Henkel presentation discussed the different methods for detecting nitrosamines and for monitoring nitrosamine formation. Two different NA detection available methodologies were discussed: the total NNO and the individual NNO determination. The total NNO methodology will detect all nitrosamines, it will give a worst case values but the source of NNO remains unknown. On the other hand, the individual NNO methodology will identify the sources of NNO.

The results of the campaign to monitor nitrosamine formation were presented. Diethanolamine (DEA) was used to monitor the formation of N-Nitrosdiethanolamine (NDELA). The results showed excellent correlation of total NNO and individual NDELA determination and that both techniques are applicable for determination of nitrosamine content as long as NDELA is the predominant reaction product.

3.5 Nitrosamine analysis: challenges and approaches in CO_2 capture, Kolbjørn Zahlsen, SINTEF

The SINTEF presentation discussed different method to detect nitrosamines. The presentation started with an overview of available mass spectrometric laboratory, which could be used to analyse and identify chemicals with special focus on those could be used to determine NA.

Two methods to detect NA have been developed: GC-MS-NCD and LC-MS-MS-QQQ. The first method has been developed for screening of known and unknown NA on a group bases. However, the LC-MS-MS-QQQ methods have been developed for quantitative analysis of detected nitrosamine with a high specificity and sensitivity. The table below summarised the validation data for both of these detection methods.

Parameter	***NCD***	***MS***	***GC-MS-MS-QQQ***
Specificity	+++	+++	++++
Linearity	>1000	> 1000	>10000
Accuracy	ND	ND	ND
Precision	RSD < 20%	RSD < 20%	RSD < 5%
LOD (instrumental)	< 100 ng/ml	< 500 ng/ml	< 10 ng/ml
Matrices	S/WW/FG	S/WW/FG	S/WW/FG

3.6 Statoil's approach to nitrosamines, Steinar Pedersen, Statoil

Following a report by the Norwegian Institute for Air Research, NILU, suggesting the potential formation of nitrosamine from atmospheric amine emissions, there has been significant governmental and media pressure in Norway around this issue. As a result Statoil have embarked on

a research programme investigating nitrosamine formation in the capture process and from atmospheric amine emissions using laboratory analysis, atmospheric studies and pilot plant testing.

The formation of secondary amine (DEA) and the nitrosamine (NDELA) in primary amine (MEA) solvent were investigated. It was found that DEA could be formed from primary amine and the formation of DEA is dependent on the O_2 and NO_2 concentrations, the higher O_2 and NO_2, the higher DEA formation. NDELA was formed and detected in the washing water and no major NDELA was detected in the gas phase. Most of the NDELA is washed in the washing section, however, the removal of NA in the washing section and the quantity of NA escaped to the atmosphere depend on the NA volatility. The MEA primary amine will not form stable NA in the atmosphere.

3.7 Measures to control nitrosamine concentrations, Bernd Schallert, E.ON

E.ON provided further details on their work utilising real flue gases from coal fired power plants to evaluate some potential methods of controlling nitrosamine concentrations in solution. To avoid the formation of nitrosamine; solvent quality, secondary amine concentration and NO_2 concentrations entering the absorber are important. The formation of NA could be reduced by inhibiting the formation of NA, by using competing side reactions (e.g. formation of SN compounds) and by reclaiming the solvent. In addition, the formed NA could be destroyed inside the solvent by UV irradiation. It was found that the formation of NA will go on as long as there is secondary amines concentration available and nitrite concentrations occur. Ascorbic acid as an inhibitor was tested, but found to only be effective in high concentrations. Reclaiming of the solvent will be a sink for NA, but additional countermeasures are still necessary. The effect of UV irradiation of solvent was found to have a significant effect in reducing the concentration of nitrosamines. This work represents a promising step forward to manage nitrosamine levels in the process.

3.8 Emissions from post-combustion CO_2 capture-laboratory research and pilot plant operation, Paul Feron, CSIRO

The CSIRO research activities on CO_2 capture including the 3 pilot plants in Australia were presented as part of CSIRO's integrated PCC program. CSIRO have studied the atmospheric formation of nitrosamines using their dedicated Smog Chamber facilities and have also embarked on a laboratory research programme of studying and detecting nitrosamine formation and stability. Using a synthetic gas mixture resembling a typical flue gas, CSIRO have observed the formation of N-nitrosopiperazine, N-oxopiperazine, piperazinenitramine and dinitrosopiperazine. However, no NA was detected in the Smog chamber. During these studies it was found that UV is effective in destroying nitrosamines and CSIRO intend to investigate nitrosamine formation further on their pilot plants. Future activities also include the validation of the sampling methods, study the NA formation mechanisms, develop NA formation/emission model and extend the Smog chamber studies to assess the solvent degradation in the atmosphere.

3.9 Conclusions and way forward, Hallvard Svendsen, NTNU

Hallvard Svendsen concluded the workshop by highlighting some of the key learning points from the seminar:

- If preventative measures are not taken, nitrosamines could be formed in post-combustion capture plant and maybe emitted (albeit in low concentrations approaching current detection limits). The NA formation was detected during operation with MEA exposed to NOx with NDELA as the main component and also during the emissions measurement done by Statoil at Esbjerg.
- Analytical methods for the detection of nitrosamines are available, but recognised standards regarding sampling, preparation and analysis are still required.
- Production rates of NA are related to inlet gas NOx/NO_2 content, oxygen plays less important role.
- UV irradiation shows promise as a method to mitigate against possible nitrosamine formation.

Hallvard also highlighted possible actions to prevent the NA formation from being a major problem. Such actions include among other: the reduction of NO_2 content entering the absorber, reduce the rate of formation by radical scavenger type additives (e.g. ascorbic acid) and reduce the amount of NA in both the solvent and washing water by UV-decomposition.

The details of a research programme to be undertaken this year to test the efficacy of UV irradiation in limiting nitrosamine concentrations in the laboratory capture pilot plant at NTNU were presented. The outcome of this test campaign will be published in public and expected to include:

- Demonstrate that UV irradiation can be used to control NA level in MEA and DEA containing solvents
- Determine the formation rate of nitrosamines and nitramines
- Optimize the UV radiation for NA decomposition
- Investigate the impact of UV irradiation on the solvent and check the reaction products of UV-decomposition
- Determine the best location of the UV-irradiation
- Estimate time and energy needed for radiation

4 Thanks and Acknowledgements

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5 Contacting the Co-ordinator

IEAGHG organised and coordinated this workshop together with E.On. Queries about the workshop or copies of this report can be obtained by contacting:

- Mohammad Abu Zahra mohammad.abuzahra@ieaghg.org
- Helmut Rode Helmut.Rode@eon.com
- Bernd Schallert Bernd.Schallert@eon.com
- Sian Twinning sian@ieaghg.org.