

DET NORSKE VERITAS CERTIFICATION AS

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Att: CDM Executive Board

Your ref.: CDM Ref 1174 Our ref.: TRIKA/MLEH Date: 22 January 2008

## Response to request for review "Project for the catalytic reduction of N20 emissions with a secondary catalyst

inside the ammonia reactor of the N3 nitric acid plant at Haifa Chemicals Ltd., Israel'' (Ref. no. 1174)

Dear Members of the CDM Executive Board,

We refer to the requests for review raised by three Board members concerning DNV's request for issuance for CER's for the monitoring periodic 3 December 2007 to 24 May 2008 for project activity 1174 "Project for the catalytic reduction of N2O emissions with a secondary catalyst inside the ammonia reactor of the N3 nitric acid plant at Haifa Chemicals Ltd., Israel" (UNFCCC Ref. No. 1174) project and we would like to provide the following initial response to the issues raised by the requests for review. We also refer to the response provided by the project participants.

The DOE verified that the gauze composition of ammonia oxidation catalyst in the project campaign is different from the baseline campaign. However, the PP did not re-establish the baseline emission factor nor did it use the IPCC default value of 4.5 kg N2O/tHNO3 as stipulated by the methodology. Further substantiation and clarification is required on the DOE's statement that the difference in catalyst composition is not regarded as significant based on a research showing that no significant change in conversion of NH3 to NO is observed for rhodium content in the range 3-10%, and thus no significant effect on N2O is expected, since this in not in line with the methodology.

DNV is referring the methodology (extract from AM0034):

If the nitric acid plant operator has changed the composition of the ammonia oxidation catalyst in a project campaign to a composition not used in the baseline campaign, the project proponent could:

1) Repeat the baseline campaign to determine a new baseline emissions factor (tN2O/tHNO3), compare it to the previous baseline emissions factor and adopt the lower figure as EFBL, or 2) Set the baseline emissions factor to the conservative IPCC default emission factor for N2O from nitric acid plants which have not installed N2O destruction measures (4.5 kg-N2O / t HNO3).

DNV has accepted the baseline campaign (354) based on the argument of this being the most conservative approach since this campaign results in the lowest  $N_2O$  emissions. This approach is according to the

methodology (point 1 above) since the two campaigns (355 and 356) with the same catalyst composition as used in the project campaigns results in higher  $N_2O$  emissions than for the baseline campaign (354) /3/.

The project participants have provided DNV with the full analysis and calculation of  $EF_{BL}$  in accordance with AM0034 for all three campaigns (354, 355 and 356) /5/. These have been checked by DNV and it is confirmed higher emissions factors  $EF_{BL}$  (9.26kg and 10.16kg respectively for campaign 355 and 356) than the emission factor for the previous campaign (354 -7.6 kgN<sub>2</sub>O/tHNO<sub>3</sub>). Hence, it is acceptable and a conservative approach to use the  $EF_{BL}$  resulting from campaign no. 354 as the applicable  $EF_{BL}$  for the subsequent project campaigns of this project activity.

In addition to this conclusion, DNV provides the following information to justify its decision to accept campaign no. 354 as the baseline campaign even though the gauze composition differs slightly from the composition used in the project campaigns.

DNV is referring to the submitted verification report chapter 3.6 "Quality of Evidence to Determine Emission Reductions" /1/ where the following were described:

"It was observed during the site visit that the gauze composition used in the baseline campaign was slightly different to the gauze composition used in the project campaign and a corrective action was requested in monitoring period 1. The project participant has provided sufficient evidence from referenced sources of information together with process data from the N3 nitric acid plant where the N2O concentration in the stack gas from two intermediate campaigns (with 95/5 Pt/Rh gauzes installed as in the project campaign) operated without secondary catalyst werecompared with the N2O concentration measured during the baseline campaign (with 97/3 Pt/Rhgauze installed). The information provided is sufficient to state with reasonable level of assurance that if a difference is to be expected in N2O concentration by changing the gauze composition from 97/3 Pt/Rh gauzes to 95/5 Pt/Rh gauzes the observation will be an increased level of N2O concentration, hence the change in the gauze composition is regarded conservative".

During the first verification period DNV raised a CAR since it was observed a change in gauze composition in the project campaign (Pt/Rh 95/5) compared to the baseline campaign (No. 354 Pt/Rh 97/3). The PP responded to the CAR by providing a document with an analysis of available information from the literature/2/. This document includes a description of the effect of rhodium content on the formation of rhodium oxide as follows:

Rhodium content in ammonia oxidation catalyst gauzes (primary catalyst) is likely to lead to the formation of Rhodium oxide ( $Rh_2O_3$ ) which can have noticeable impacts on the conversion efficiency of a nitric acid plant. Rh-oxide forms permanent, needle like crystals on the gauzes. The formation of Rh-oxide will depend on the concentration of Rh-oxide in the gauze as well as the operating temperature and pressure of the nitric acid plant.<sup>1</sup>

Rh-oxide on the gauzes generally leads to lower conversion efficiency of Ammonia to  $NO/NO_X$  and hence higher N<sub>2</sub>O from the primary catalyst. Rh-oxide is expected to be formed especially when the plant operates below certain threshold for temperature and pressure (see graph below). For example, a plant operating with gauzes containing 8% Rhodium and operating at 6 bar would be expected to show Rh-oxide formation at temperatures below 900°C.

<sup>&</sup>lt;sup>1</sup> F. Sperner, W. Hohmann, "Rhodium-Platinum Gauzes for Ammonia Oxidation", W.C. Heraeus GmbH, Platinum Metals Review, 1976, 20, (1), 12-20



Graph showing the Rh2O3 formation dependence on pressure and temperature<sup>1</sup>

As explained by the PP the N<sub>2</sub>O abatement catalyst installation was postponed for two campaigns until the registration of the project activity became imminent. Hence, data from two campaigns (No. 355 and 356 with primary catalyst Pt/Rh 95/5) without installed N<sub>2</sub>O abatement catalyst were available in addition to the data for the selected baseline campaign and the raw data was provided to DNV /3/. The formation of N<sub>2</sub>O needs to be seen in relation to the risk of rhodium oxide being formed. The risk can be assessed by studying the operating conditions of the ammonia oxidation reactor together with the gauze composition. DNV studied the N<sub>2</sub>O emission level and the ammonia oxidation parameters (ammonia flow, temperature, pressure for these campaigns) and made comparison to the baseline campaign (No. 354). The ammonia oxidation temperature and pressure during the baseline campaign and campaign No. 355 and no. 356 are given in the below graphs.

 $<sup>^{1}</sup>$  W.C. Heraeus, taken from Nitro Technologies presentation given by M.W. Gorywoda on 01.07.2002





It can be seen from the graph that the ammonia oxidation pressure is within the range 10 to 11.5 bar. For gauzes with 5% Rh the graph (F. Sperner, W. Hohmann) suggests a Rh-oxide formation threshold of approx. 895°C. For gauzes with 3% Rh it can be expected the threshold to be 870-880 °C from extrapolation. The baseline campaign (354) is operating at a temperature above the threshold temperature and thus the formation of rhodium oxide in the baseline campaign is less likely than the situation for campaign 355 and even more for 356 where the temperature during part of the campaign was below the threshold temperature.

This theoretical analysis is consistent to the observed level of  $N_2O$  concentration in the stack gas as seen from the below graph. It is seen that the  $N_2O$  concentration is lower for the baseline campaign (354) than the two following campaigns (355 and 356).



From this analysis it can be seen that the effect of changing the rhodium content from 3% to 5% will increase the risk of formation of rhodium oxide and thus the formation of  $N_2O$  when ammonia oxidation temperature is below the threshold temperature.

It must be note that the comment mentioned in the CAR in monitoring period 1 "*The change in composition is not regarded as significant. This is justified by referring to research showing that no significant change in conversion of*  $NH_3$  *to NO is observed for rhodium content in the range 3-10%, and thus no significant effect on*  $N_2O$  *is expected*" is only relevant if the operation conditions are stable and not causing formation of rhodium oxide. The final conclusion of the raised CAR was based on the analysis as presented in detail in this request for review by using the same references as reported in verification report period one and the provided operating data for campaign No. 354, 355 and 356 referenced as /28/ and /29/ in DNVs verification report period 1.

The actual temperature and pressure of stack gas is not reported. Further clarification is required how it can be confirmed that the flow is correctly converted from actual pressures and temperatures.

### **DNV Response:**

DNV refers to the response given by the PP. The TSG and PSG is available at a 2 second monitoring interval. The PP has made available the QAL 2 and AST report for verification. DNV was able to verify that the QAL 2 test and AST test was conducted by an ISO/IEC 17025 accredited test laboratory (SGS). During the QAL 2 and AST tests the correct conversion from measured VSG to standard conditions was audited. The standard reference method (SRM) showed a small deviation to the installed flow meter. The stack gas flow measured with SRM was 32 945 Nm<sup>3</sup>/h and the measured value for the installed meter was 31 764 Nm<sup>3</sup>/h. Correction factors based on this values from the SGS QAL 2 report is 1.0372. It has been verified that the same value is correctly used in the calculation spread sheet for adjusting the total stack gas flow during the monitoring period. The measurement range of the flow meter is appropriate and the measured average flow rate is within the range expected for a nitric acid plant with a capacity of 240 metric tonnes per day.

# The project participant is required to submit all the required monitoring data at the intervals specified by the methodology, not one final value for each of the required parameters.

### **DNV Response:**

DNV is referring to the response given by the project participant (PP) and the submitted verification report chapter 3.4 "Assessment of monitoring parameters" and related Excel files provided from the PP during verification /4/. During the site visit DNV was able to verify that the recording frequency was according to AM00034 by checking the raw data available in the Process Information system at Haifa nitric acid plant 3. The PP attached an excel file with continuously measured monitoring data to the PPs response to this request for review. There are separate folders for historic campaigns, baseline campaign and project campaign. Other required parameters (calculated) is based on the submitted data for monitored parameters and verified as described in the verification report

As N.serve has developed the N.serve Database Management System (N.DBMS) for data handling and processing only the Excel sheet including the emission reductions calculations together with the monitoring report (explaining the queries used for the statistical tests and calculation within the program) were originally submitted for the request of issuance. It should be noted that N.serve has in place routines to ensure that the correct data is used in the N.DBMS program. To ensure that the calculations are done correctly, plausibility checks are done by N.serve using manual Excel calculations on the received data from the plant. For example the average values for the different parameters are calculated by Excel and compared to the results of Query 1 of the N.DBMS calculation.

#### References

- /1/ DNV verification report : "Project for the catalytic reduction of N2O emissions with a secondary catalyst inside the ammonia reactor of the N3 nitric acid plant at Haifa Chemicals Ltd., Israel" (UNFCCC Ref. No. 1174) for the period 23 September to 2 December 2007 and period 3 December to 24 May 2008.
- N.Serve document: Haifa Chemicals N3 and N4 switching of gauze composition from 97/3 to 95/5 (reference /28/ in verification report for period 23 September to 2 December 2007).
- /3/ Excel sheet (filename: N3 355 356\_14 Apr 08) including process data from intermediate campaigns operated with ammonia oxidation catalyst 95/5 Pt/Rh (reference /29/ in verification report period 23 September to 2 December 2007)
- /4/ Excel sheet (filename: N3\_working data 04\_2007-05\_2008\_MS\_080623). Hourly raw data extracted from Haifa Chemicals data acquisition system (PI-system). Reference /4/ in verification report for 2. monioring period.
- /5/ Excel sheet (filename: HC\_N3\_355\_Calc V6 090114\_MS; HC\_N3\_356\_Calc V6 090114\_MS). Raw data and calculations of emission factor accordign to AM0034 v2.

We sincerely hope that the Board accepts our above explanations.

Yours faithfully for DET NORSKE VERITAS CERTIFICATION AS

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