CANSOLV TECHNOLOGIES INC.

R&D Department

NCCC Piloting of DC103 with Coal Combustion Flue Gas

REVISION STATUS			Sign-Offs		
Rev.	Date	Description (Implemented/Issued for Review/Complete)	Approved	Reviewed	Custodian
R0	October 14, 2014	Final Report for NCCC Campaign (CANSOLV DC103 Testing)	Paul-Emmanuel Just	Ajay Singh	Matthew Campbell
R0NC	March 29, 2017	Non Confidential Version			Paul-Emmanuel Just

Section 1 – Introduction & Objectives

In 2014 a DC103 testing campaign took place at the NCCC piloting facility in Wilsonville, AL. A total of 325 hours of steady state operation occurred between June 26 and July 17 2014. This testing campaign was established to help further understand the impact of acid mist aerosols on amine emissions. The experimentation included several objectives which are summarized below:

Objectives

1. Confirmation of the overall CO_2 capture performance using CANSOLV DC103 with standard coal combustion flue gas. That is flue gas with a CO_2 inlet concentration similar to 11 vol % dry basis. The main process parameters that have been optimized were (CO_2 Removal and Stripping Factor):

2. Characterization of coal combustion flue gas entering & exiting the CO_2 absorber. This entailed 3 measurements (i) ELPI + measurement by Laborelec where the total aerosol and PM concentration and size distribution was determined. (ii) Measurement of SO_3 entering the CO_2 absorber.

3. Assessment of CANSOLV DC103 amine emissions exiting the CO_2 absorber (outlet of water wash section).

4. Evaluation of the aerosol and amine capture with two different demisters installed at the outlet of the water wash section. The two demisters evaluated were the Sulzer 9033 standard demister and the Sulzer 9797 high efficiency demister.

6. Adjustment of Process temperatures and conditions to understand the impact on amine emissions.
- With intercooler on
- With intercooler off
- With hotter lean amine temperature
- With demister water spray

Each of the above objectives will be discussed in various sections throughout this report. The sections to be covered in this document are:

Section 2 -- Summary of CO_2 capture plant performance
Section 3 -- NCCC Data Quality Assurance
Section 4 -- Summary of results for Laborelec ELPI+ measurements
Section 5 -- Summary of results for SO_3, DC103 amine emission and MEA (past) measurements
Section 7 – Conclusions

Section 2 – Summary of CO_2 capture plant performance

A requirement of this testing campaign was to have steady state and optimal CO_2 Capture performance before any of the ELPI+ or gas sampling measurements would be conducted. This was a requirement to get the process conditions tuned closely to what would be expected for a commercial project. Table 1 summarizes the process conditions which were defined as the optimal conditions for the CANSOLV DC103 solvent with the NCCC plant and flue gas composition.

Table 1: Optimized CANSOLV DC103 Testing Conditions

Optimized CANSOLV DC103 Testing Conditions		
Number of Absorber Packing Sections	#	3
Bottom Intercooler	On/Off	On
Top Intercooler	On/Off	Off
Flue Gas Flowrate	lbs/hr	5000
Flue Gas Temperature	^oC	46
Flue Gas CO_2 Concentration[1]	vol % dry	10.8
Lean Amine Circulation Rate	lbs/hr	10400
Lean Amine Temperature	^oC	45.6
Amine Temperature Outlet from Intercooler	^oC	33
Water Wash Circulation Rate	lbs/hr	10000
Water Wash Liquid Temperature	^oC	43
Steam Flowrate[2]	lbs/hr	930
Rich Amine Temperature to Regenerator	^oC	114
Rich Amine Pressure to Regenerator	psig	50
Regenerator Pressure	psig	14.5
1 normal power plant load CO_2 = 10.8 vol%, high power plant load CO_2 = 11.8 vol %		
2 Steam Flowrate directly from flowmeter (condensate validation results shown in Section 3)		

As shown in Table 1, the CANSOLV DC103 process was optimized for liquid flowrate and steam flowrate with a fixed amount of absorber packing (3 packing sections) and the bottom intercooler turned on. The amine temperature return to the absorber from the intercooler was 33 ^oC. It should be noted that the reported steam flowrate is the measured value from the NCCC steam flowmeter. The accuracy of this measurement was assessed with condensate calibrations and the results are shown in Section 3. The steam verifications tests demonstrated that the steam flowrate reported from the flowmeter was 6.6 % lower than condensate verifications. Therefore in this section all parameters influenced by steam flowrate have been increased by 6.6 %.

Figure 1 & Figure 2 summarizes the CO_2 removal and stripping factor measured at the NCCC during the total 325 hours of operation. Figure 1 & Figure 2 are results on the absorber side and stripper side, respectively. The absorber side calculations utilize the gas flowrate entering the CO_2 absorber and absorber inlet and outlet CO_2 concentration measurements. The stripper side calculations utilize the gas flowrate entering the CO_2 absorber, absorber inlet CO_2 concentration and CO_2 product gas flowrate leaving the stripper. Both absorber and stripper side calculations for CO_2 removal and stripping factor are shown in this section to give the reader a sense for the uncertainty with the plant measurements.

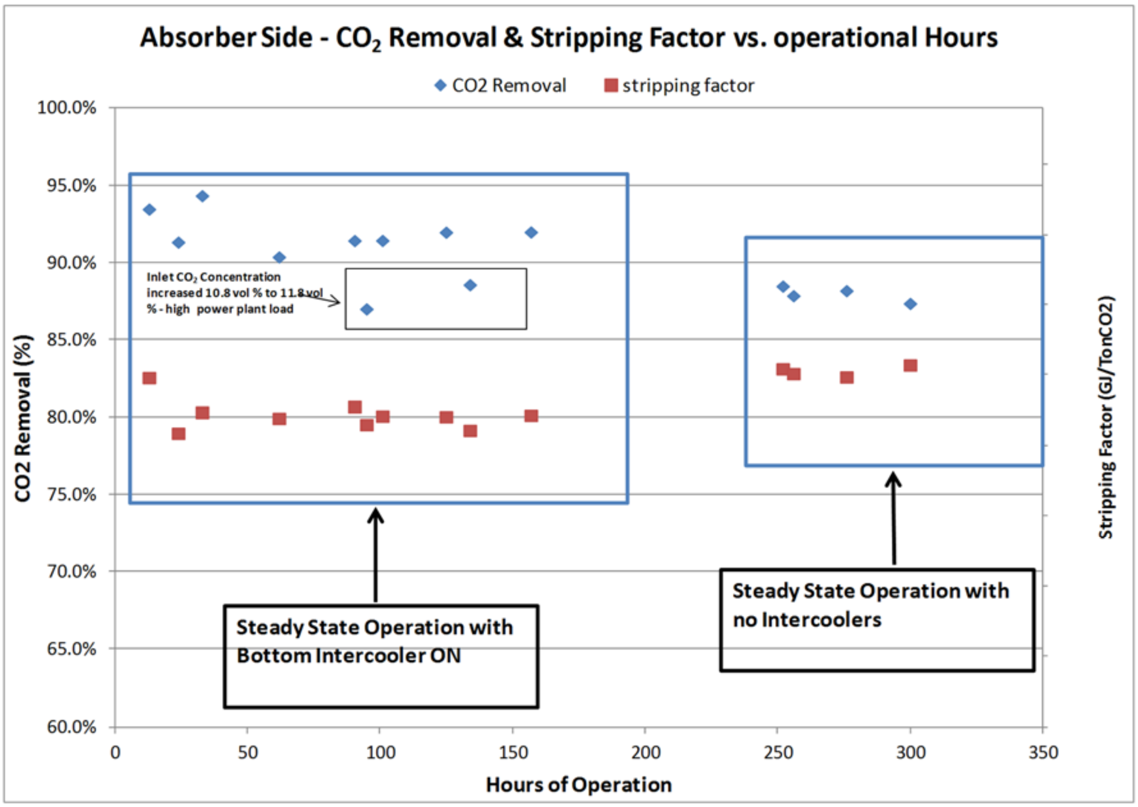

Figure 1: Absorber Side CO_2 Removal & Stripping Factor Performance versus Operational hours

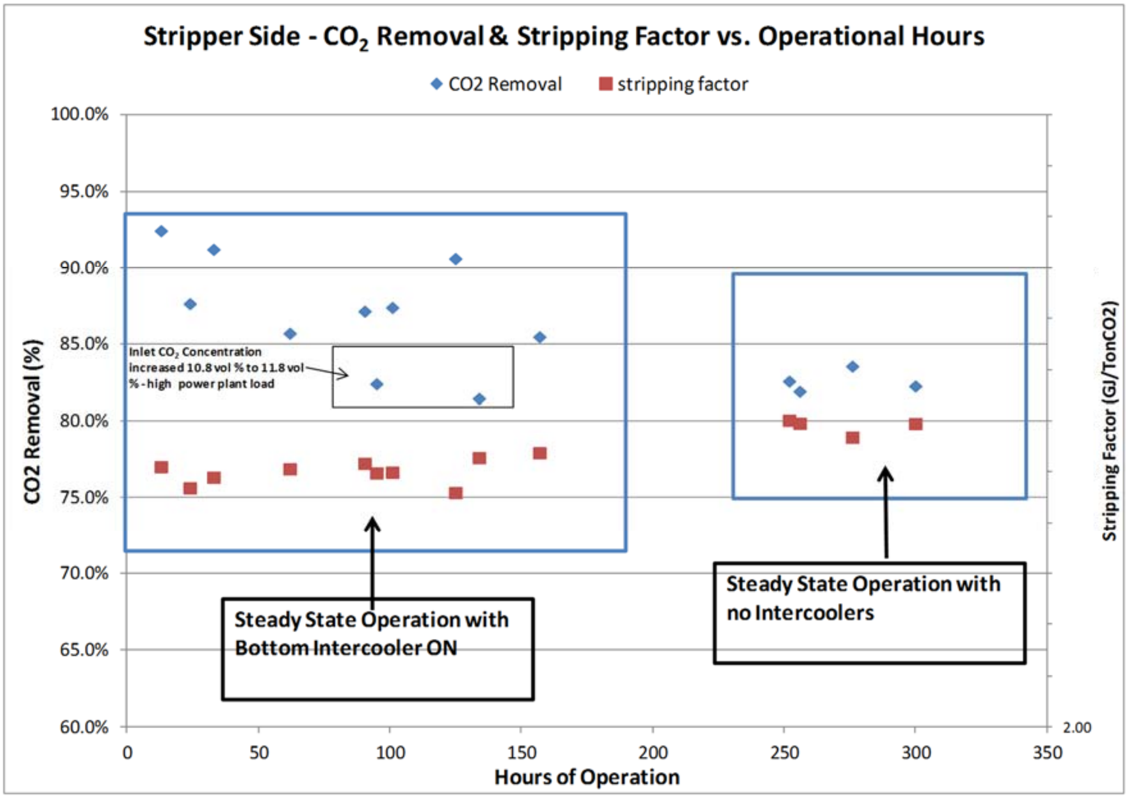

Figure 2: Stripper Side CO_2 Removal & Stripping Factor Performance versus Operational hours

The first important aspect to mention related to Figure 1 & Figure 2 is that optimal steady state operation was achieved around 50 hours of operation. At this point, the configuration with one intercooler in the bottom section of the absorber (3 packing sections) was optimized for energy consumption. After this point in time where the optimized conditions has been established the ELPI^{+} and other gas sampling & monitoring had commenced. Please see Section 4, Section 5 for a summary of gas sampling results.

The average results for the main process parameter calculations (CO_2 removal) are summarized for both absorber and stripper side calculations in Table 2.

Table 2: Average Steady State Performance – Absorber & Stripper Side Comparison

Average Steady State Performance Absorber & Stripper Side Comparison		
CO_2 Removal (Absorber Side)	%	91.5
CO_2 Removal (Stripper Side)	%	87.3
% Difference	% diff.	4.59

The results of Table 2 demonstrate that there is ~ 5 % uncertainty or difference between the absorber side and stripper side calculations. Overall, the absorber side calculations are ~ 5 % more optimistic than the stripper side calculations.

The impact of power plant load on CO_2 removal and stripping factor can also be understood by viewing Figure 1 & Figure 2. As NCCC power plant load increases the inlet CO_2 concentration raises from ~ 10.8 vol % CO_2 dry to ~ 11.8 vol % CO_2 dry. The results for CO_2 capture performance demonstrate a reduction of CO_2 removal by ~ 5 % at this high load condition. However, the stripping factor remains unchanged, since the total CO_2 captured remains the same, the only difference is that more CO_2 is being sent to the absorber. This reduction of CO_2 removal at higher inlet CO_2 concentration indicates that the liquid flowrate is at the point near maximum loading where no or very little additional CO_2 can be loaded.

An additional aspect from Figure 1 & Figure 2 is the impact of the bottom intercooler on overall process performance. As can be seen, when the bottom intercooler is turned off the CO_2 removal decreases by approximately 5 %. This loss of CO_2 capture performance also translates into an increase of stripping factor by ~ 5 %. The comparison for with and without intercooler was done with plant operation at normal power plant load (Inlet CO_2 concentration ~ 10.8 vol % dry). It should be noted that one test with no intercoolers was performed with an increased lean amine temperature from 45 ^{o}C to 60 ^{o}C. The results demonstrated no significant difference in CO_2 removal and/or stripping factor.

Section 3 – NCCC Data Quality Assurance

Data quality assurance is an important part of any piloting or demonstration campaign.

For the NCCC capture plant it was decided to double check a few critical instruments to ensure that readings and uncertainties were deemed to be acceptable. The most critical instruments which sometimes have issues are steam flowmeter and gas analyzers. Specific attention throughout this campaign was made to ensure that these instruments were performing reasonably well. Table 3 summarizes the accuracy of the steam flowmeter used during this piloting campaign. The accuracy is determined by comparing steam flowrate measurements versus the weight accumulation of steam condensate over a certain period of time.

Table 3: Steam Flowmeter Verification

Steam Flowmeter Verification			
Verification Test	Steam Flowmeter FI20250	Condensate Accumulation Rate	% Difference
#	lbs/hr	lbs/hr	%
1	932	1020	8.65
2	934	1000	6.55
3	934	980	4.74
		Average Difference	6.65

The results demonstrate the steam flowrate measured by the flowmeter is on average 6.65 % lower than the actual flowrate measured by condensate accumulation. This underestimate of steam has been corrected in Section 2.

In terms of gas analyzer verifications, calibrations were performed on a daily basis to ensure that the zero and span are matching up with the gas cylinder standards. Table 4 summarizes the outcome of 3 gas analyzer calibrations which were performed throughout the testing campaign.

Table 4: Gas Analyzer Calibrations

Gas Analyser Calibration on July 9th, 2014				
	zero	cylinder standard	span calibration	% Difference
AI20105D CO_2 (vol %)	0	14.79	14.8	0.1
AI20160AA O_2 (vol %)	0	19.96	19.95	0.1
AI20105S SO_2 (ppmv)	0.4	4.90	5.4	10.2
AI20199X NO_2 (ppmv)	0	15.20	15.7	3.3
AI20199Z NO (ppmv)	0	51.20	51.4	0.4
Gas Analyser Calibration on July 1st, 2014				
	zero	cylinder standard	span calibration	% Difference
AI20105D CO_2 (vol %)	0	14.79	14.79	0.0
AI20160AA O_2 (vol %)	0	19.96	19.95	0.1
AI20105S SO_2 (ppmv)	0.4	4.90	4.85	1.0
AI20199X NO_2 (ppmv)	0	15.20	15.25	0.3
AI20199Z NO (ppmv)	0	51.20	51.4	0.4
Gas Analyser Calibration on June 30th, 2014				
	zero	cylinder standard	span calibration	% Difference
AI20105D CO_2 (vol %)	0	14.79	14.8	0.1
AI20160AA O_2 (vol %)	0	19.96	19.95	0.1
AI20105S SO_2 (ppmv)	0.4	4.90	5	2.0
AI20199X NO_2 (ppmv)	0	15.20	15.22	0.1
AI20199Z NO (ppmv)	0	51.20	51.1	0.2

The results demonstrate that both the zero and span have been done appropriately with minimal differences for CO_2, O_2, SO_2, NO_2 and NO measurements.

Section 4 – Summary of results for Laborelec ELPI+ measurements

One of the main objectives of this testing campaign was to arrange for the Belgium Company Laborelec to perform ELPI+ measurements onsite during the DC103 testing campaign. This goal was achieved and Laborelec successfully performed measurements at 3 gas sampling locations throughout the NCCC capture plant.

i. Inlet Flue Gas to the CO_2 Absorber
ii. Outlet Flue Gas from the Water Wash after the standard (9033 Sulzer) demister
iii. Outlet Flue Gas from the Water Wash after the high efficiency (9797 Sulzer) demister[1]

The ELPI+ measurements provided results for aerosols/pm concentration and size distributions at the locations mentioned above. Gathering this information was valuable for multiple reasons as explained below:

i. To assess and characterize the flue gas properties from a typical coal fired power plant with a wet stack arrangement. The wet stack arrangement is defined as the coal combustion flue gas being quenched/cooled directly with water from the prescrubber upstream of the CO_2 absorber.

ii. To assess and characterize the treated flue gas after contact and interaction with the CANSOLV DC103 amine solvent. This was done with the two different demisters, to evaluate the impact of standard and high efficiency demisters on percent droplet capture and amine emissions.

The ELPI+ measurements of aerosol/PM concentration and size distributions for the NCCC flue gas are shown in Figure 3. The results demonstrate no significant difference in aerosol/PM concentration or sizes for the 3 different process locations which have been tested. The total number of aerosol/PM concentration is in the order of 1E7 to 2E7, the majority of aerosol/PM sizes are between 0.1 μm and 0.3 μm. Also there is no significant difference between the results after the standard or high efficiency demister. Based on the very low droplet sizes it would be expected to have no significant aerosol/PM capture with either demister.

[1] Sulzer high efficiency demister was installed on June 30th, 2014

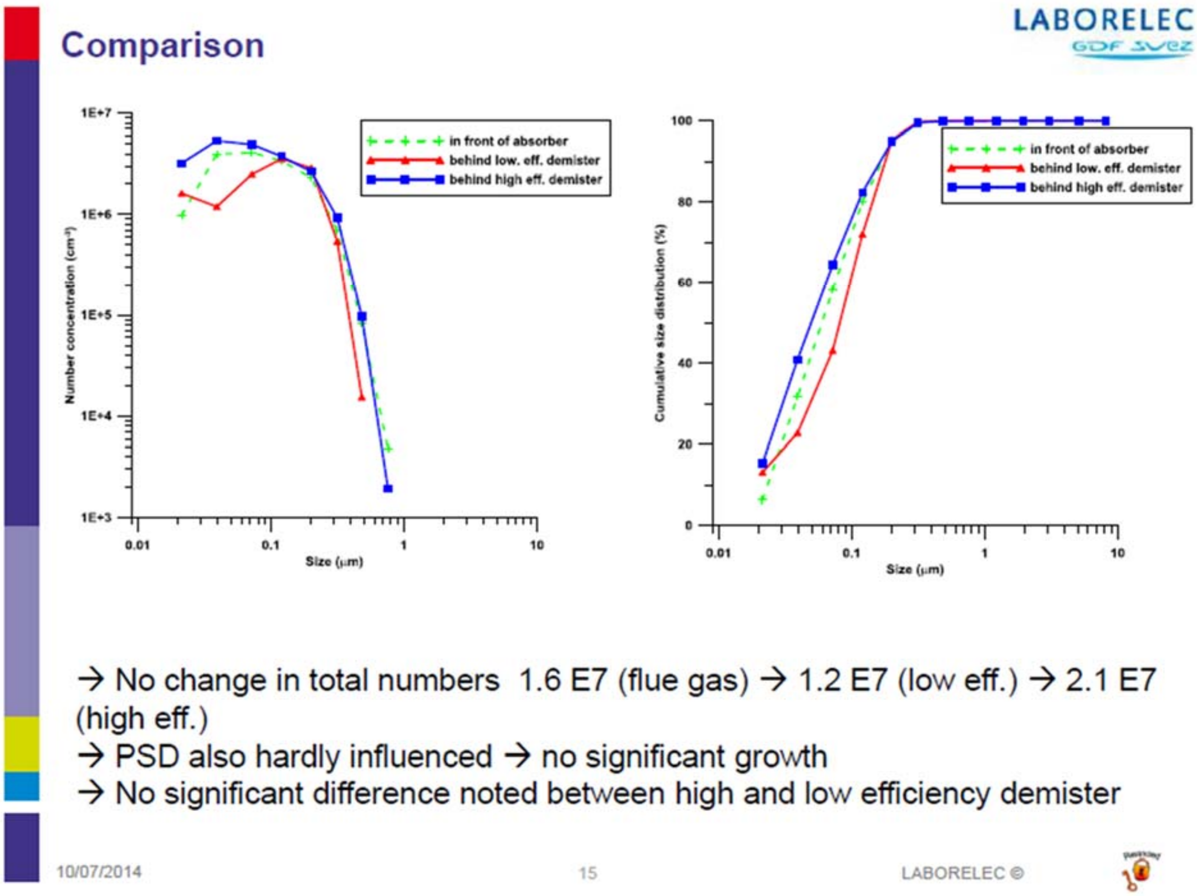

Figure 3: ELPI + Results during DC103 NCCC Campaign

The description of 2 flue gases tested with the ELPI+ instrument and the resulting aerosol concentrations are summarized below.

1) NCCC flue gas = flue gas measured at the NCCC capture plant as part of this study, the coal fired power plant arrangement is a wet stack arrangement. The total aerosol/PM concentrations measured were 1.6 E7, which is in the upper range of all ELPI+ measured performed by Laborelec in the past. Laborelec expects MEA emissions in the range of 100 ppmv to 1000 ppmv.

2) ambient air = During one of the previous ELPI+ testing campaigns in Europe, Laborelec decided to take measurements on ambient air. The air ELPI+ results can be used as a baseline to compare against actual coal combustion flue gases with different lineups and treatments options. As can be observed total aerosol/PM concentrations were quite low for this gas.

Typically, coal combustion flue gases tested with the ELPI$^+$ have measured aerosols/PM which are quite small. According to the size distribution the majority of aerosols/pm is less than 0.3 μm. The NCCC plant actually had the largest aerosols/PM and the majority was still between 0.1 μm and 0.3 μm. For CANSOLV DC103 there has been no change in aerosol/PM size at the outlet of the absorber, because this solvent is a low volatility solvent. However, if an amine such as MEA, a higher volatility solvent is tested, the aerosol/PM size at the outlet of the absorber would be significantly larger.

Based on the above discussion it would be recommended for NCCC to perform additional Laborolec ELPI+ measurements with MEA as CO_2 capture solvent. This information will demonstrate if higher volatility solvents grow more considerably throughout the absorption process.

Section 5 – Summary of results for SO_3 and amine emissions measurements

During the CANSOLV DC103 piloting campaign at NCCC in Wilsonville, Alabama several gas emission monitoring tests were done. The two major types of gas sampling and analysis performed were (1) SO_3 concentration measurements at the inlet of the CO_2 absorber & (2) Amine emission monitoring at the outlet of the water wash section. The SO_3 concentration was measured by the Controlled Condensation Method and measurements were taken on each day that amine emission measurements were conducted. This was done to observe the relationship between variation of inlet SO_3 concentration and amine emissions.

The amine emission measurements were evaluated with an impinger train developed SRI. The sampling system developed by SRI is shown in 4. The gas is extracted isokinetically to obtain a representative gas sample. An ice bath removes both droplets and condensable vapor constituents in a Modified EPA Method 5 (MM5) sample system. Contact between liquid and gas is minimized and gas is never bubbled through liquid. One of the impingers has an impaction plate to help collect small droplets.

The liquid collected was then analyzed by GC in the NCCC Laboratories and duplicate samples were analyzed by LCMS in the Shell Cansolv Laboratory.

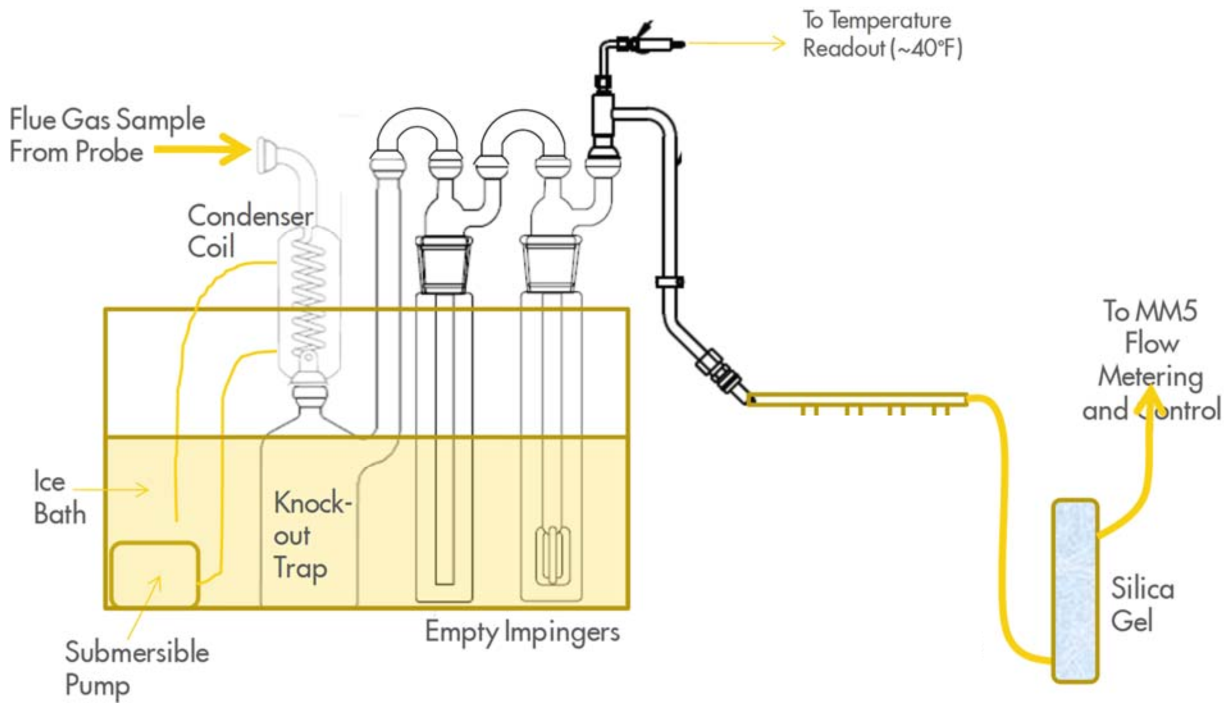

Figure 4: SRI Impinger Train Setup developed for monitoring amine emissions

This section will be split into three categories (1) Past MEA emission results from the NCCC capture plant, (2) Variation of SO_3 concentration measurements over time during DC103 testing & (3) CANSOLV DC103 emission results from DC103 testing.

Section 5.1. Past MEA emission results from the NCCC capture plant

NCCC has published MEA emissions from the same capture plant that was evaluated for CANSOLV DC103. NCCC varied multiple parameters to identify their influence on MEA emissions to stack. The parameters which were varied were:

- Inlet SO_3 concentration to the CO_2 absorber (this varied naturally depending on the coal quality and other upstream operation conditions)
- Number of absorber packing sections (either 2 or 3 packing sections)
- Intercooler(s) on or off, there was the possibility of 0, 1 or 2 intercoolers
- Concentration of MEA in the water wash section

Results for MEA emissions are shown in Table 5.

Table 5: MEA emissions for the NCCC capture plant

Test	Absorber Beds	# of Intercoolers	MEA in Water Wash wt %	MEA Emissions lb/hr	MEA Emissions ppmv
Alabama Bituminous Coal (flue gas SO3 1.8 ppmv)					
1	3	0	1.05	2.1	231
2	3	2	0.98	7.3	802
3	2	1	1.06	4.9	538
4	2	1	0.22	3.8	417
5	2	0	0.92	1.1	121
6	2	1	5.58	5.9	648
Higher Sulfur Illinois Coal (flue gas SO3 3.2 ppmv)					
7	2	0	1.16	1.8	198
8	2	0	1.02	2.1	231
9	2	0	1.08	1.7	187
reference T. Carter - July 10, 2012 NETL CO2 Capture Technology Meeting					

The results demonstrate that MEA emissions vary between 121 ppmv and 802 ppmv. For MEA the emissions seem to be highest with the process configuration with 1 or 2 intercoolers, as highlighted with blue shading in Table 5. It is believed the cooling throughout the absorber is creating additional superstation zones where acid mist droplets can form and grow to enhance MEA emissions. It should be noted that this behavior may only be applicable for high volatility amines such as MEA.

It can be observed that there are lower MEA emissions when 2 absorber packing sections are used compared to 3 packing section. For 2 packing sections the MEA emissions are measured to be ~ 1.9 times lower than MEA emissions for 3 packing sections. It is believed that for the 2 packing section configuration emissions are lower since there is a dry packing section which can act a filter of the acid mist/ amine aerosols formed throughout the absorber.

The impact of SO_3 concentration on MEA emissions can be assessed by comparing results from Alabama Bituminous coal (1.8 ppmv SO_3) versus High sulfur Illinois coal (3.2 ppmv SO_3). The results demonstrate 1.5 to 2 times higher emissions for the high sulfur Illinois coal.

Section 5.2. SO_3 concentration measurements during the DC103 testing campaign

Figure demonstrates the SO_3 concentration measured by SRI at the inlet to CO_2 absorber process location. The results of SO_3 concentration are plotted against operational time for the CANSOLV DC103 testing. The results demonstrate that the SO_3 concentration varies between 1.8 ppmv and 4.3 ppmv throughout the testing campaign. The variation of SO_3 concentration at the NCCC capture plant is expected to be attributed to the following factors:

1) Variation of coal type and quality throughout testing
2) Frequency and repeatability of trona injection into the dry ESP
3) Conditions for coal combustion

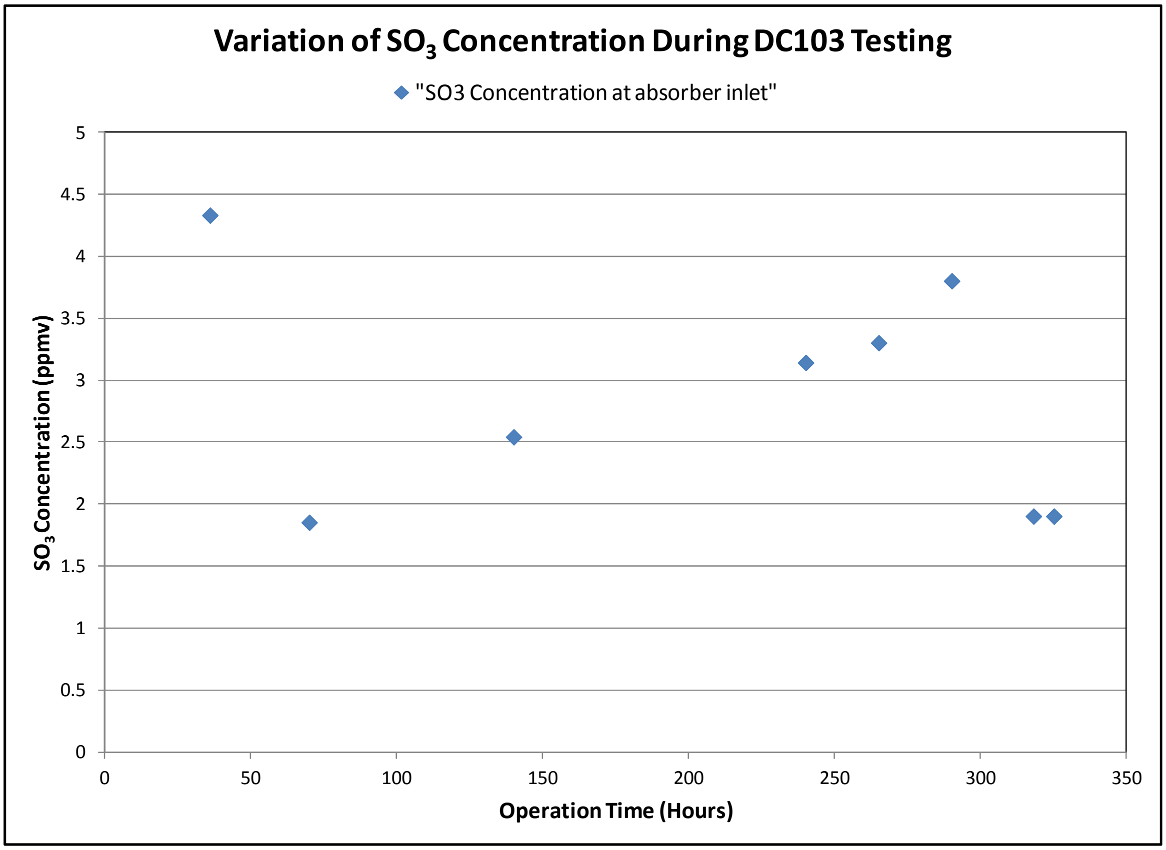

Figure 5: Variation of SO_3 Concentration versus Time (inlet to CO_2 absorber)

Section 5.3. CANSOLV DC103 emission results (current testing campaign)

During past amine emission surveys performed at NCCC (Section 5.1), it has been proven that amine emissions are considerably influenced by the composition of the flue gas. To evaluate this phenomenon better it was decided for the DC103 test to plan and execute gas emission tests with different quality flue gases. Two different gas types were tested:

(1) Standard Coal Combustion Flue Gas – this is the flue gas with no dilution after the dry ESP, SCR and FGD. The concentration variation of SO_3 in this gas type is described in Section 5.2.

(2) Clean Air – this is atmospheric air around the plant that was used as a benchmark, which is believed to be a good representative of gas with insignificant aerosols or acid mist. Saturated air was sent at appropriate flowrates through the CO_2 Absorber.

The results of DC103 amine emissions to stack during the testing campaign are summarized below in Table 6 . All results are normalized to emissions for DC103 with air (no aerosols or acid mist). The results demonstrate that the DC103 amine emissions with coal flue gas are ranging 95 to 140 times higher than emissions of DC103 with air as the gas source. Regardless of the process conditions the average DC103 emissions with coal flue gas were observed in the same range. This includes changes to the demister type, operation with and without intercooling, increased lean amine temperature and spraying the water wash demister. Different behavior was observed in Section 5.1 for previous MEA emission surveys. This difference of behavior is believed to be attributed to the different volatility of the MEA solvent compared to that of CANSOLV DC103. MEA is a significantly more volatile amine compared to DC103. A solvent with higher volatility will have more amine molecules in the gas phase throughout the absorption process. It is believed if $ELPI^+$ measurements were performed during the MEA campaign that the growth rate of aerosols throughout the absorber would be significantly higher than for DC103. In other words, the growth of aerosols throughout the absorber is attributed to the attraction of amine molecules from the gas phase.

It should be noted that absolute value for emissions of CANSOLV DC103 is significantly lower than MEA, but this is company proprietary information and will not be disclosed.

Table 6: DC103 Amine Emission Results during NCCC piloting campaign (without mitigation)

CANSOLV DC103 Amine Emissions at the Outlet of the NCCC Water Wash Column (To Stack)			
Test	Test Description	SO_3 Concentration	DC103 Emission Ratio to Air Test
#	Conditions	ppmv	Ratio
1	Outlet of standard demister (K9033)	4.3	140
2	Outlet of high efficiency demister (K9797) - trial 1	1.9	143
3	Outlet of high efficiency demister (K9797) - trial 2	2.5	115
4	Outlet of high efficiency demister (K9797) - trial 3	1.9	95
6	No Intercooler - Outlet of high efficiency demister (K9797) -trial 1	3.1	156
7	No Intercooler - Outlet of high efficiency demister (K9797) -trial 2	3.8	202
8	No Intercooler & hot lean amine - Outlet of high efficiency demister (K9797)	3.3	152
9	Outlet of high efficiency demister (K9797) + demister spraying	1.9	98
* Unless mentioned all flue gas emission tests are performed with bottom intercooler on *			

Section 6 – Conclusions

The CANSOLV DC103 solvent was successfully operated for 325 hours at the NCCC pilot plant. The process was optimized with 3 absorber packing sections, one intercooler at the bottom of the absorber and inlet CO_2 gas concentration ~ 11 vol % dry. The CO_2 capture performance (absorber side) yielded an average CO_2 removal of 91.5 %.

In terms of emission monitoring, successful Laborelec (ELPI+) measurements were carried out at 3 different process locations.

i. Inlet Flue Gas to the CO_2 Absorber
ii. Outlet Flue Gas from the Water Wash after the standard (9033 Sulzer) demister
iii. Outlet Flue Gas from the Water Wash after the high efficiency (9797 Sulzer) demister

The results demonstrate the total number of aerosols (# concentration) is in the order of 1E7 to 2E7, the majority of droplet sizes are between 0.1µm and 0.3 µm. Also there is no significant difference between the results at the inlet to absorber, after the standard or high efficiency demister. This is the result of the low aerosol sizes and it was expected to have low or no aerosol capture with either demister.

A correlation of CANSOLV DC103 emissions against inlet SO_3 gas concentrations was also made. The results demonstrated that there are only mild impacts on amine emissions as the SO_3 concentration varies between 1.8 ppmv and 4.3 ppmv. However, there are significant differences comparing amine emissions results for gases with and without SO_3 content. The results with SO_3 in the flue gas were 95 to 140 times higher than the results with air (no SO_3) being the gas type. It should be noted that absolute value for emissions of CANSOLV DC103 is significantly lower than MEA, but this is company proprietary information and will not be disclosed.