

Oxycombustion Flue Gas Measurements from Coal Fired Plants: Analytical Challenges



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Presentation Outline

- Oxy-combustion for Power Generation
- Demonstration Project Objectives
- Analytical Challenges
- Analysis Campaign Results
- Summary



Presentation Outline

□ Oxy-combustion for Power Generation

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Clean Coal Combustion

- Coal is the most abundant fuel
 - Lowest cost for fuel production
- Impact of CO₂ on global warming is still under intense debate
 - Coal is the **most** carbon intensive fuel
 - Economical means of carbon management important to coal's future use



Clean Coal Combustion

- Clean coal development is very important to reduce CO₂ emissions in the environment.
 - Electricity production can generate significant amounts of CO₂ emission contribution to almost 39% of WW emission.
- Carbon Capture and Sequestration (CCS) can reduce the CO₂ emission by
 - Injecting CO₂ at high pressure under ground for geological storage
 - Enhanced oil recovery applications

T. Chaubey, P. Terrien, J-P. Tranier, R. Prabhakar and A. Delebecque, "Greenhouse Gas Capture and Mitigation Techniques for Different Industries" in "CO2 Summit: Technology and Opportunity", Frank Zhu, UOP, LLC, USA Eds, ECI Symposium Series, Volume P12 (2010).

Most Viable Options

■ Main options for capturing carbon from coal-fired systems

1. Flue gas scrubbing with amine
 - Most mature, but requires significant scale-up
2. Integrated gasification combined cycle (IGCC)
 - Greenfield option that has long been favored
 - Major scale-up of water shift reactor and H₂ burning gas turbine as well as proof of reliability
 - Costs have been much higher than anticipated, and performance estimates have fallen far short of expectations

M. McDonald, D. DeVault, R. Varagani, "Oxy-combustion in Pulverized Coal Power Plants for Carbon Dioxide Concentration", Presented at 2007 Electric Power Conference, Chicago, May 2007

Most Viable Options

■ Main options for capturing carbon from coal-fired systems

3. Oxy-Coal combustion

- Commercially available equipment
- Oxygen mixing, control of flue gas flow O_2 mixture and heat transfer performance must be optimized
- Predicted to have the highest overall efficiency and promises to be the low-cost option

■ OCC more readily deployable for capture and storage of CO_2

M. McDonald, D. DeVault, R. Varagani, "Oxy-combustion in Pulverized Coal Power Plants for Carbon Dioxide Concentration", Presented at 2007 Electric Power Conference, Chicago, May 2007

What is Oxy-Coal Combustion?

- Uses O_2 as the oxidant rather than air diluted with recycled flue gas in the combustion process
 - Combustion with pure O_2 would result in too high of a flame temperature for the boiler
 - Dilute with recycled flue gas
 - Yields a flue gas stream primarily of CO_2 and H_2O
 - After removal of H_2O , nearly pure CO_2 stream can be produced
- It is assumed that:
 - NO_x , CO , unburned hydrocarbons, and SO_x do not interfere with the sequestration process
- However, impurities need to be reduced to prevent corrosion
 - Transportation, piping, etc...

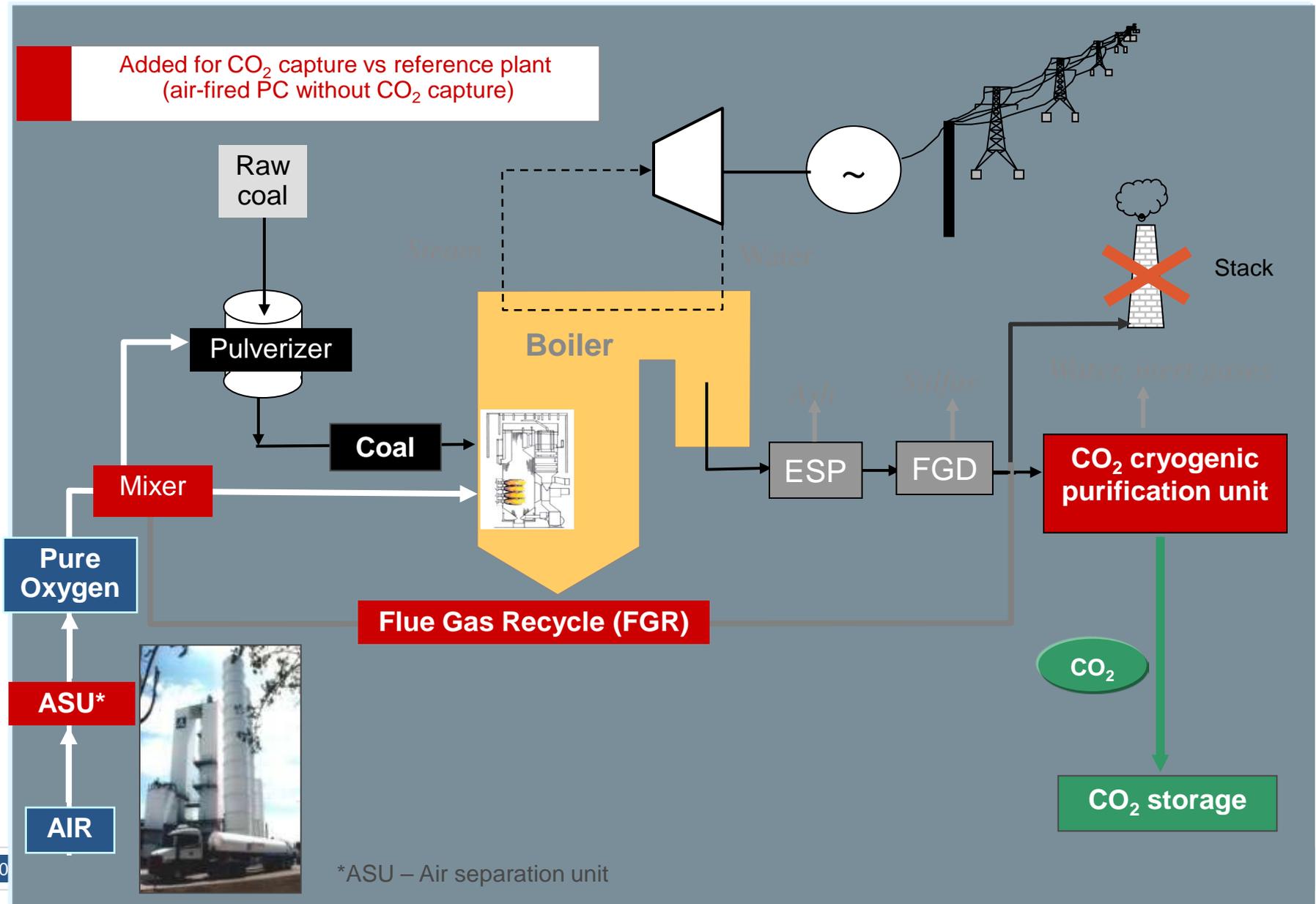


OCC + Sequestration

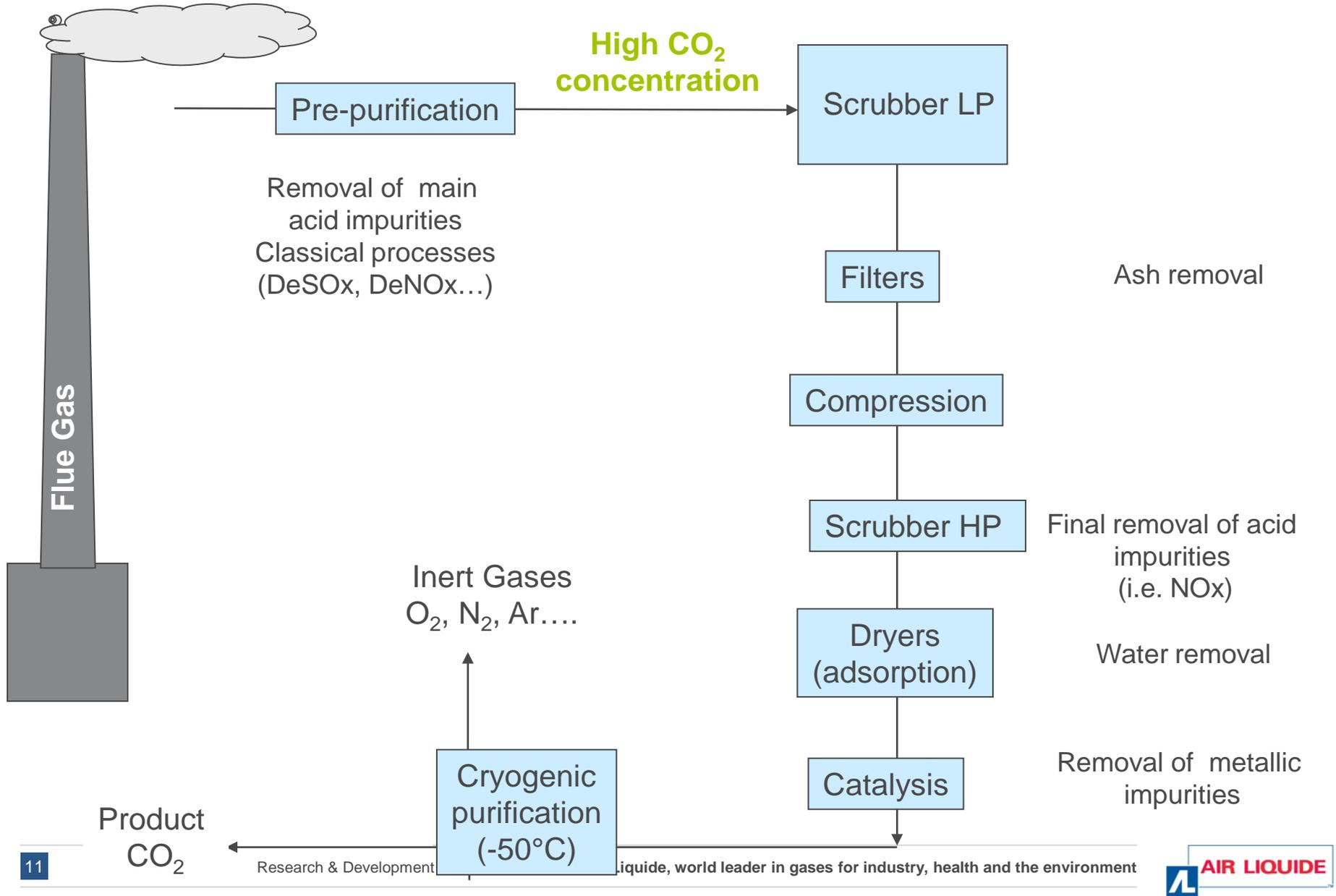
- Oxy-Fuel combustion has significant advantages over traditional air fired plants
 - Flue gas volume is reduced, decreasing the heat loss in the flue gas
 - Concentration of pollutants making separation easier
 - Most of flue gases are condensable making sequestration possible
 - Because air is not used for combustion, NO_x production will be greatly reduced



Oxy-Coal Combustion



Cryogenic Purification Unit (CPU)



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Carbon Capture & Sequestration Demonstration



Callide Australia

- 100 MW demonstration of the complete CCS chain for steam & power production in Australia with hard coal
- Retrofit of existing Callide coal power plant
- 2 x 330 TPD ASU
- Oxy-combustion retrofit
- 75 TPD CO₂ recovery
- Trucking to CO₂ reservoir

Carbon Capture & Sequestration Demonstration

■ Objectives

- Validate “Near Zero Emissions”
- Understand & validate mass balance of “impurities” throughout the entire process
 - Impurity management
 - Particle Matter, SO_x, NO_x, Hg
 - Equipment efficiency
 - Equipment sizing
- Enable **cost reduction and performance improvement for large scale units**
- Provide feed back from operation
 - Corrosion
 - Aging



Presentation Outline

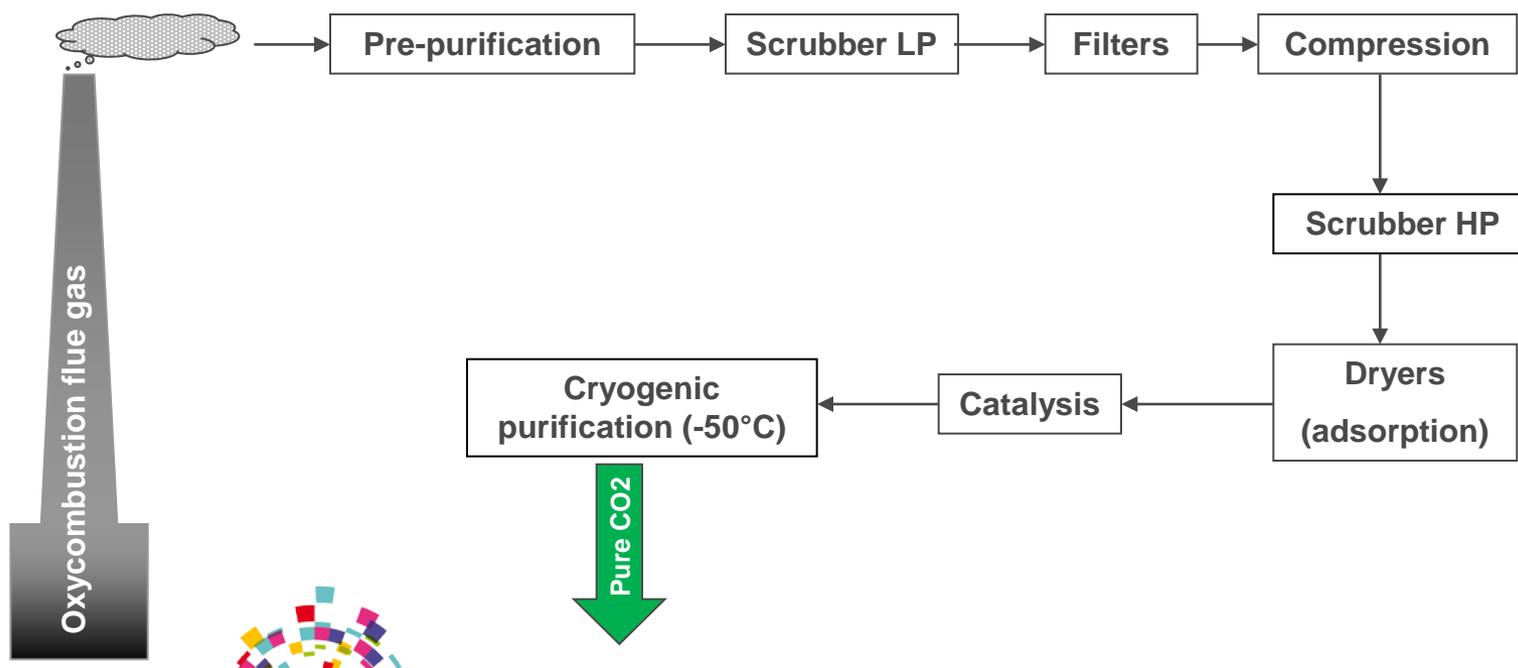
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Analytical Challenges

■ Understand flue gas composition at each step of the CPU

CPU	T (°C)	P (bar)	Particulate content (mg.m ³)	Moisture content (%)	CO ₂ (%)	N ₂ (%)	Ar (%)	CO (ppm)	SO ₂ (ppm)	NO (ppm)	NO ₂ (ppm)	O ₂ (%)
Inlet	175	1	50	25	50	25	3	800	700	1600	300	12
Outlet	-27	25	0	0	100	0	0	0	0	0	1	0



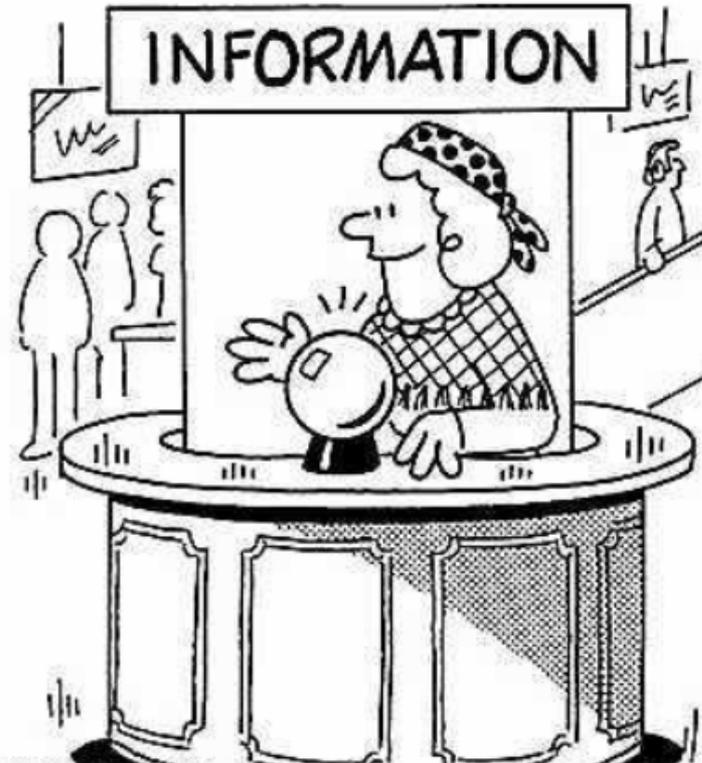
Analytical Challenges

- The analyzers need to be able to analyze multi-component mixtures containing high levels of impurities
 - NO_x, SO_x, H₂O, HCl, etc. in CO₂
- Since the gas composition will change as it progresses through the CPU
 - Analyzers need to detect variations with a high degree of accuracy as gas composition changes



Analytical Challenges

- Reliability of measurements **MUST** be validated for each analytical tool
 - Critical when matrix, temperature & pressure vary significantly



Analytical Challenges – Sampling System

- Sampling system for a CO₂ rich flue gas over the entire process
 - Must be appropriately specified for accurate analysis
 - Wide range of conditions
 - Fast loops for rapid sample transfer
 - Prior to cryogenic purification
 - Heated lines (up to 60 M)
 - Heated sample panels & specific heated sample probes
 - Specific materials for Hg analysis (Teflon, Silcosteel)



Analytical Challenges – Sampling System

- Cryogenic Purification
 - Stainless steel tubing
 - Headed sample panels
 - Vaporizer



Analyzers

■ Prior to cryogenic purification

- Multicomponent system from Sick Maihak (MCS) including ZrO_2 oxygen probe
- Mercury analyzer from PS Analytical

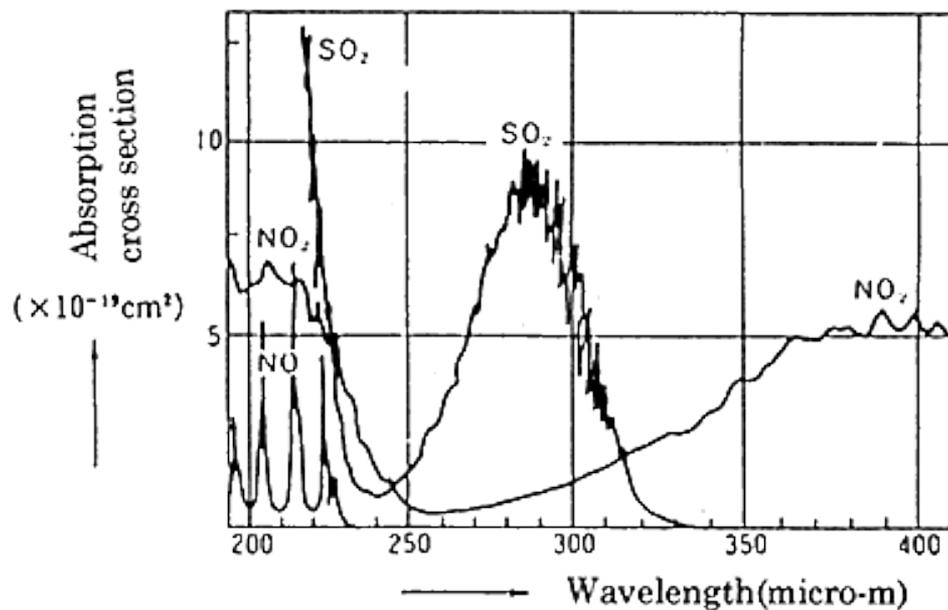
■ After cryogenic purification

- NO_x with an Environment SA TOPAZE
 - Additional NO_x analyzer is necessary to reach lower dL anticipated
- Air gases: Varian micro GC
- Multicomponent system from Sick Maihak



Analytical Challenges

- Cross interferences MUST be known and corrected for prior to on-site analysis



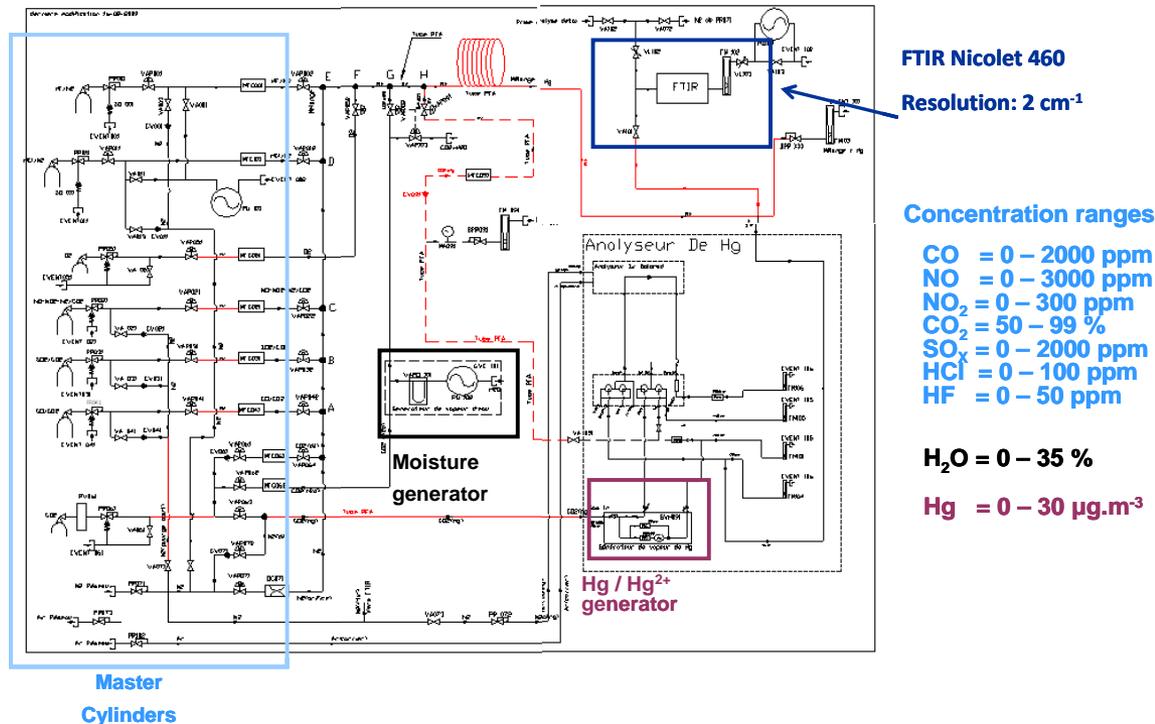
Cross Interference Identification

■ Synthetic gas generator

- Composition representative of the oxy-combustion flue gas at each step of the process

- NO, NO₂, SO₂, HF, HCl, O₂, N₂, H₂O, CO₂ and Hg

- Performance of analyzers can be correctly evaluated



Synthetic Gas Generator

- To control the synthetic gas composition, a quantification method based on FTIR was developed
- Concentration ranges correspond to anticipated in the demonstration project
- Validated with multicomponent “certified” mixtures



Global Uncertainty

- Measurement uncertainty
 - Calibration gas mixture uncertainty
 - Calibration curve uncertainty

Sources	μ
Concentration	Value on certificate
MFC	0.1% FS + 0.5% RD 0.29%
Peak area	$(\sigma/\sqrt{n})/A$
Calibration Curve	Component dependant

σ = standard deviation, A = peak area, n = number of replicates



Global Uncertainty

- For the uncertainty of the calibration curve, uncertainties in dilution must also be calculated

Conc (ppm)	U _{co} (ppm)	RSD (%)
20.5	2.0	9.6
49.8	1.5	3.0
103.3	3.9	3.7
206.6	6.2	3.0
413.2	25.4	6.2
620.0	31.4	5.1
825.8	25.5	3.1
1034.3	31.0	3.0
2070.0	65.6	3.2

95% confidence interval



Chemiluminescence Based Analyzer

■ TOPAZE 32M from Environment SA

■ NOx analysis

■ Potential interfering species in oxy-fuel combustion gas

- CO₂, H₂O, CO

■ Dedicated to analysis of “dry gas”

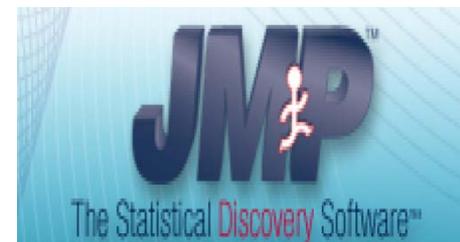
- H₂O does not considered



■ Use “Design of Experiments” to quantify potential interferences

■ A systematic approach to variation of a system

■ *JMP software from SAS*



Chemiluminescence Based Analyzer

Experimental plan based on JMP DOE

Experimental Plan			
Experiment	NOx (ppm)	CO (ppm)	CO ₂ (%)
1	36.3	500	50
2	36.3	20	95
3	554	500	95
4	36.3	500	95
5	556	500	50
6	556	20	50
7	288	260	72.5
8	554	20	95
9	36.3	20	50



Chemiluminescence Based Analyzer

Effect of CO₂ on NOx measurement

Experimental Plan				Experimental Results	
Experiment	NOx (ppm)	CO (ppm)	CO ₂ (%)	NOx (ppm)	Stdev ppm
1	36.3	500	50	35.39	0.52
2	36.3	20	95	30.84	0.07
3	554	500	95	445.89	1.81
4	36.3	500	95	31.10	0.06
5	556	500	50	495.36	2.99
6	550	20	50	497.75	3.09
7	288	260	72.5	250.52	0.11
8	554	20	95	448.08	0.92
9	36.3	20	50	35.86	0.56

- Concentrations of NOx and CO are identical
- Concentration of CO₂ varied

Measured NOx concentration varies by >50ppm from theoretical value

Chemiluminescence Based Analyzer

Effect of CO on NOx measurement

Experimental Plan				Experimental Results	
Experiment	NOx (ppm)	CO (ppm)	CO ₂ (%)	NOx (ppm)	Stdev ppm
1	36.3	500	50	35.39	0.52
2	36.3	20	95	30.84	0.07
3	554	500	95	445.89	1.81
4	36.3	500	95	31.18	0.06
5	556	500	50	495.36	2.99
6	556	20	50	497.75	3.09
7	288	260	72.5	250.52	0.11
8	554	20	95	448.08	0.92
9	36.3	20	50	35.86	0.56

- Concentrations of NOx and CO₂ are identical
- Concentration of CO varied

Negligible variation in measured NOx concentration

Chemiluminescence Based Analyzer

- **Key result:** CO₂ concentration in the gas stream has significant impact on NOx measurement

Summary of Fit		Lack Of Fit			
RSquare	0,999939	Source	DF	Sum of Squares	F Ratio
RSquare Adj	0,999931	Lack Of Fit	3	76,80640	23,0131
Root Mean Square Error	1,745249	Pure Error	35	38,93763	1,1125
Mean of Response	248,327	Total Error	38	115,74403	Max RSq
Observations (or Sum Wgts)	44				1,0000
Sorted Parameter Estimates					
Term	Estimate	Std Error	t Ratio		Prob> t
NOx (ppm)(36,3,555)	219,39314	0,279993	783,57		<,0001*
CO2 (%)(50,95)	-13,97122	0,27998	-49,90		<,0001*
NOx (ppm)*CO2 (%)	-11,49487	0,279979	-41,06		<,0001*
CO (ppm)(20,500)	-0,665191	0,279964	-2,38		0,0226*
NOx (ppm)*CO (ppm)	-0,622579	0,279932	-2,22		0,0322*

Results statistically significant



$$Y(\text{NOx}) = \text{Const} + a[\text{NOx}] + b[\text{CO}_2] + c[\text{NOx}][\text{CO}_2]$$

- CO₂ concentration **must** be known to use the correction



DOE for NDIR Based Measurements

Potential interfering species

Components	Interfering Components						
	NO	NO ₂	CO	CO ₂	SO ₂	HCl	H ₂ O
NO		X	X				X
NO ₂	X					X	X
CO	X						
CO ₂							
SO ₂							X
HCl		X					
H ₂ O	X	X			X		

Validate manufacturers internal corrections



NDIR Based Analyzer: MCS

Experiment		NO (ppm)	NO ₂ (ppm)	SO ₂ (ppm)	CO (ppm)	HCl (ppm)	H ₂ O (%)
4	C _{theo}	100.00	250.00	600.00	550.00	30.00	2.00
	C _{exp}	107.94	246.80	607.21	560.51	25.61	2.81
	σ	0.88	0.56	5.03	0.51	0.67	0.03
14	C _{theo}	100.00	250.00	600.00	50.00	30.00	20.00
	C _{exp}	112.91	206.19	636.34	37.09	24.57	20.11
	σ	0.81	1.17	0.90	01.3	0.32	0.02

10	C _{theo}	1500.00	250.00	50.00	550.00	30.00	20.00
	C _{exp}	1620.03	249.15	50.00	571.30	24.26	19.73
	σ	1.58	2.64	0.36	0.16	0.06	
16	C _{theo}	100.00	250.00	50.00	550.00		20.00
	C _{exp}	113.36	190.76	77.49	580.72	2.00	20.04
	σ	0.77	1.68	6.06	2.02		0.33



DOE for IR Based Measurements

Concentration ranges for DOE

Components	Concentration ranges	
NO (ppm)	100	1500
NO ₂ (ppm)	20	250
CO (ppm)	50	550
SO ₂ (ppm)	50	600
HCl (ppm)	2	30
H ₂ O (%)	2	20

Manufacturer implemented corrections are validated

NO results

Sorted Parameter Estimates					
Term	Estimate	Std Error	t Ratio		Prob> t
NO (ppm)(100,1500)	753,0585	0,448661	1678,5		<,0001*
NO (ppm)*H2O (%)	-23,99048	0,372461	-64,41		<,0001*
H2O (%) (2,20)	-18,50257	0,458851	-40,32		<,0001*
CO (ppm)*H2O (%)	-1,890222	0,577166	-3,28		0,0019*
NO2 (ppm)*H2O (%)	-0,944879	0,387723	-2,44		0,0183*
NO2 (ppm) (20,250)	-0,972817	0,474653	-2,05		0,0455*
NO (ppm)*CO (ppm)	0,9858665	0,570782	1,73		0,0901
NO2 (ppm)*CO (ppm)	-0,546852	0,583078	-0,94		0,3526
CO (ppm) (50,800)	-0,339664	0,576601	-0,59		0,5584
NO (ppm)*NO2 (ppm)	0,1019099	0,381728	0,27		0,7905

Mercury Analysis

■ Detection limit validation

■ 0.08 $\mu\text{g}/\text{m}^3$ elemental Hg generated using the calibration system of the mercury analyzer

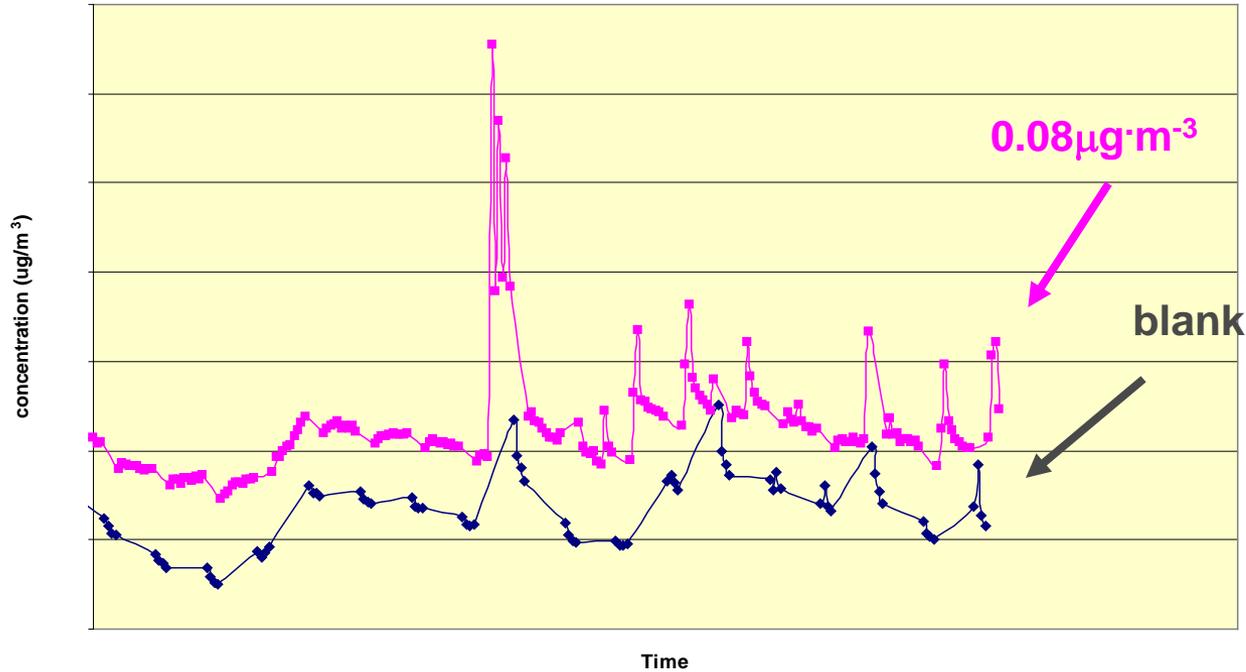
■ Connected to multi-component mixer

■ Measurements made on mercury analyzer

- 10 minute collection time
- Alternating analysis sequence
 - 5 blanks
 - 10 samples



Mercury Analysis



■ Statistical difference between the sample & blank

■ $0.085 \mu\text{g}/\text{m}^3 \pm 0.019$



Mercury Analysis

■ Balance gas comparison

■ HovaCal system used to generate Hg vapor from $\text{Hg}(\text{NO}_3)_2$

■ CO_2 or N_2 was mixed at a total flow of 3 L/min into analyzer

Balance gas	Average concentration ($\mu\text{g}/\text{m}^3$)	Standard deviation ($\mu\text{g}/\text{m}^3$)
N_2	34.5	3.1
CO_2	37.2	3.6

■ Data is statistically insignificant



Mercury Analysis

■ Catalyst conversion rate

- Probe is used to sample gas from process stream
- Contains a catalyst chamber at 700°C
 - Convert Hg^{2+} to Hg^0
- At ambient temperatures, Hg^{2+} will not be converted
 - Can not simultaneously measure Hg^0 & Hg^{2+}

■ Aqueous solutions of oxidized & elemental mercury generated with HovaCal system

■ Same concentrations ($5 \cdot 10^{-6} \text{ g} \cdot \text{mol}^{-1}$)



Mercury Analysis

■ Catalyst conversion rate

■ 30 replicate analyses

	Average concentration ($\mu\text{g}/\text{m}^3$)	Standard deviation ($\mu\text{g}/\text{m}^3$)
Hg ⁰	53.4	4.7
Hg ²⁺	33.8	2.8

■ 60% difference between elemental & oxidized form

■ Hg²⁺ is not totally converted by catalyst

■ Uncertainty of total Hg measurements will be high

■ Looking into alternative solutions

■ Proportion of Hg²⁺ in the flue gas is unknown and conversion efficiency is significantly below 100%



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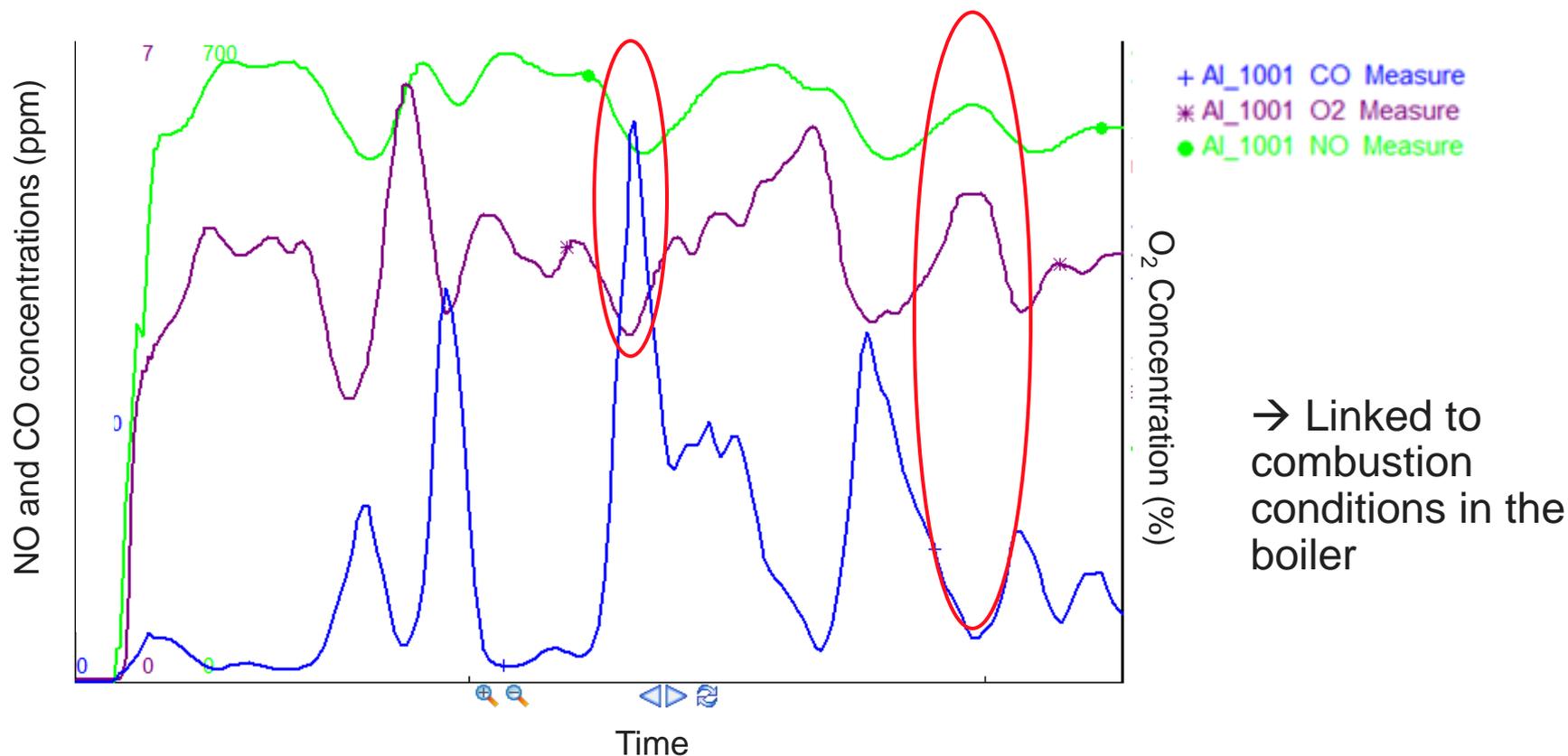
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Analysis Campaigns – Multi-Component Analyzer

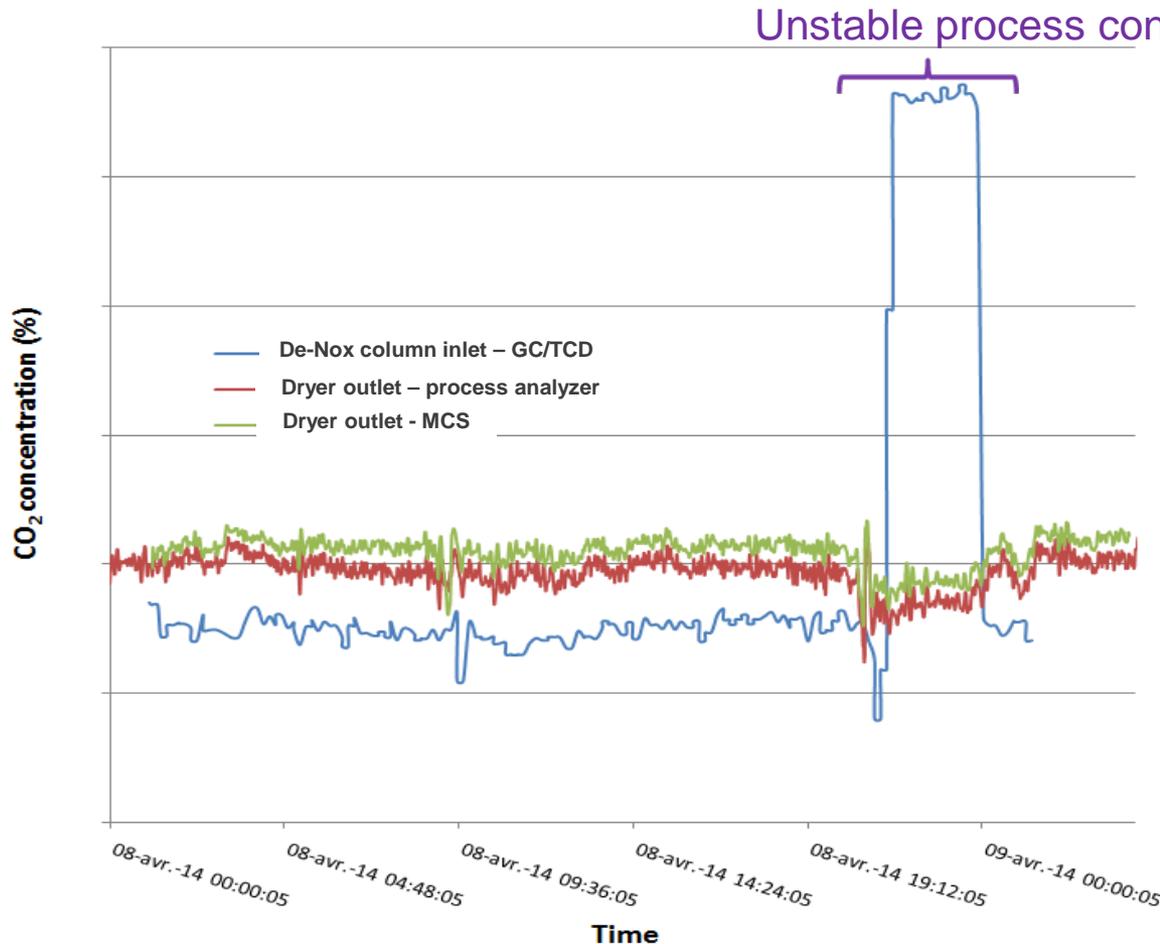
■ Multi-Component analyzer based on NDIR

- Good results obtained over the whole process on specified sample points
- Correlations found between NO, CO and O₂ concentrations at CPU inlet



Analysis Campaigns – Operation Conditions Influence

- Analysis of the same flue gas at two different sample points
- Different results of CO₂ concentrations depending on process conditions



Importance of:

- sample point location
- process conditions

Analysis Campaign – Multi-component Analyzer

- Multi-Component analyzer based on NDIR
 - Good results obtained over the whole process on specified sample points, however.....
 - Measurement of SO₂ concentration at the LP scrubber outlet gave inconsistent results
 - Process NDIR → >10ppm SO₂
 - Not part of R&D analytical system
 - Other methods → <1ppm
- Consequence
 - High SO₂ level will trip the plant
- Which is the correct value?



Analysis Campaign – Multi-component Analyzer

■ Test with calibration gas cylinders on the process analyzer

Gas Cylinder	SO ₂ reading (ppm _v)	CO ₂ reading (%)
55% CO ₂ balance N ₂	6.6	55.2
75% CO ₂ balance N ₂	24.3	76.8
100% N ₂	0	0

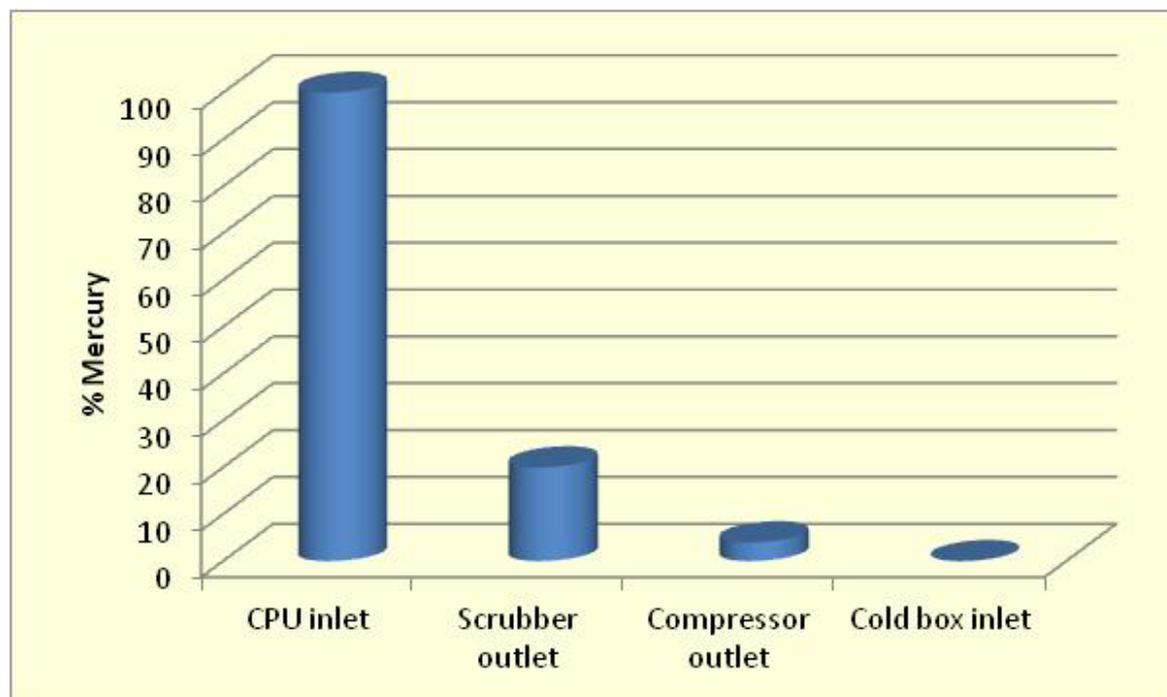
- CO₂ interference → Manufacturer's Correction model underestimated
- Manufacturer contacted and updated correction model installed

Significance of prework clearly validated



Analysis Campaign - Mercury Analysis

- Total mercury analysis from the outlet of the dryers to the CPU inlet
- Different collection times (30 s and 10 min) on the gold trap depending on mercury levels



■ Inlet cold box
 $Hg_{tot} < 0.1 \mu\text{g}/\text{Nm}^3$



Analysis Campaign – CO₂ Product Analysis

■ Ar, O₂, N₂, CO and CO₂ analysis

- Frequent column reconditioning for good resolution of Ar/O₂ peaks
- Determination of % levels O₂ as well as low O₂ concentrations

■ NO/NO_x analysis

- Concentration levels between low ppm to low % levels



Analysis Campaign – CO₂ Product Analysis

■ Results

- Good analytical measurements obtained on site
- **High purity CO₂ achieved at the CPU outlet**

Analysis of the CO₂ gas product

Component	Concentration
CO ₂	>99.9% vol
SO ₂	<1ppm _v
NO _x	<20ppm _v
H ₂ O	<20ppm _v
O ₂	<30ppm _v



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Summary

- Reliable results were obtained owing to prior analyzer evaluation
- Data obtained helped to better understand the CPU
- Performances of the CPU were as expected
- Calide pilot test results are a good contribution to further demonstration projects
- Demonstration of concept with more than 5500 hours of operation



Acknowledgements

Callide
Oxyfuel Project



Research & Development

Opening new ways



THANK YOU FOR YOUR ATTENTION