

Callide Oxyfuel Project: Overview of Commissioning Experience

Chris Spero (CS Energy), Toshihiko Yamada (IHI), Graeme Rees (GLP),
Philippe Court (Air Liquide)

OCC3

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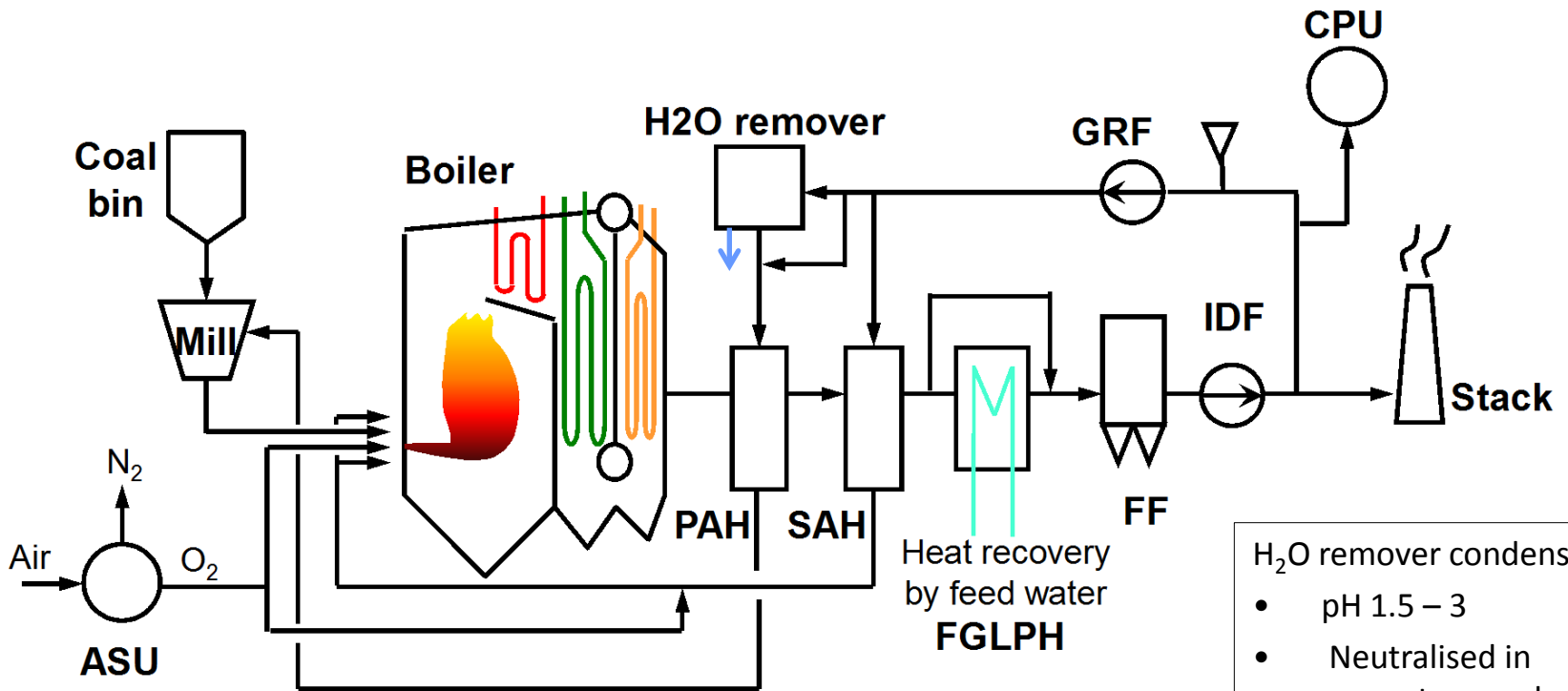
Presentation Overview

- Purpose of the presentation is to provide an overview of the Callide Oxyfuel boiler and CO₂ capture plant (CPU) commissioning experience and outcomes
- Items covered include:
 - Process overview and mass balance data
 - Environmental approvals
 - Hazardous area assessments (toxic gas release)
 - Oxy-combustion process overview and commissioning outcomes
 - CPU process overview and commissioning outcomes
 - Concluding comments

Callide Oxyfuel Project – Milestones achieved

- 1st Oxyfiring – 12 Mar. 2012
- 1st full Oxyfuel mode – 19 Mar. 2012
- 1st flue gas to CO₂ Capture Plant (Low Press. section) – 14 Sep. 2012
- Oxyfuel operation without H₂O remover - 2 Weeks in Early Oct12
- 1st Liquid CO₂ 11 Dec. 2012
- Oxyfuel demonstration - Over 3650 hours as at end August 2013
- CO₂ capture – Over 1100 hours as at end August 2013
- Overall budget = AUD 235 million
- Operation funded to end of 2014
- Safety – Zero Lost Time Injuries

Oxyfuel process schematic

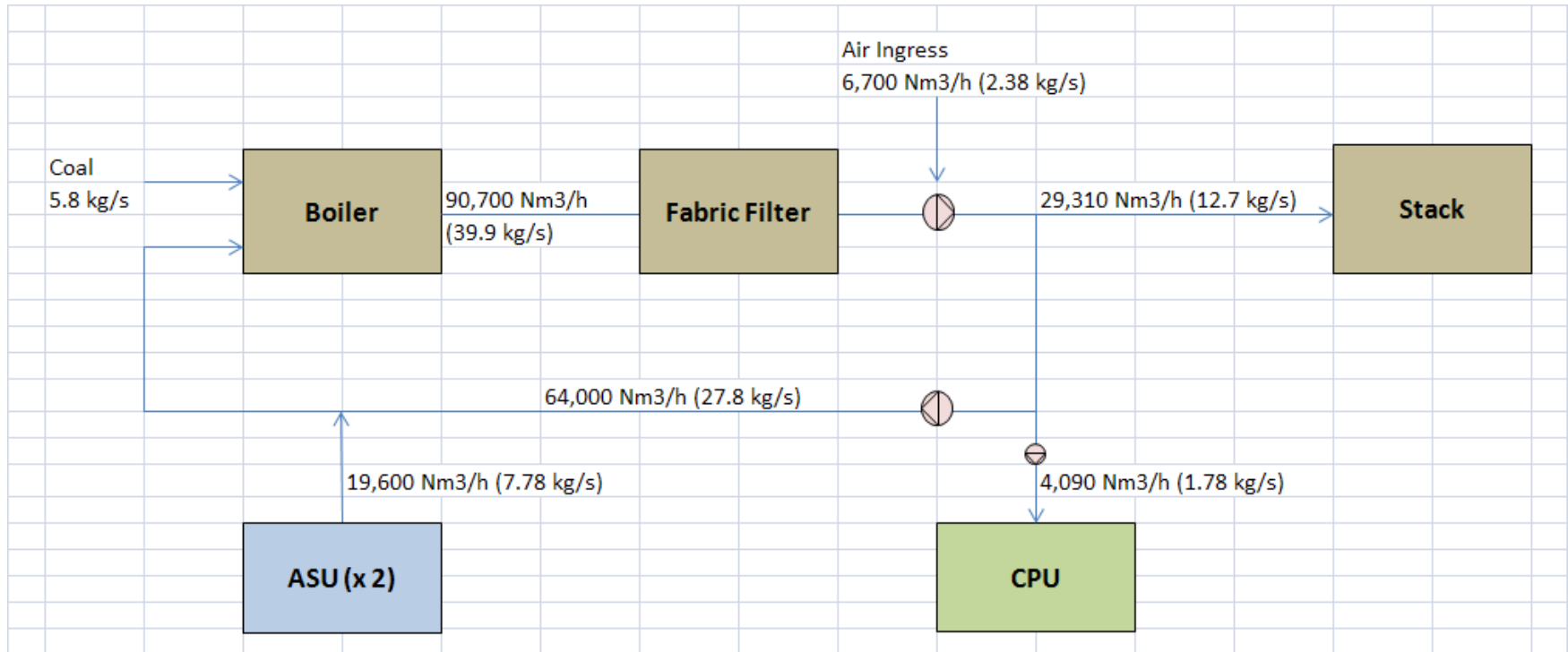


H₂O remover condensate:

- pH 1.5 – 3
- Neutralised in separate vessel with 30 – 50% caustic

Boiler/Stack/CO2CPU - Flue gas mass balance

Indicative at 30 MWe (100% load factor)



COP – Environmental Authority

Boiler (CA4)

- Coal sulfur ≤ 0.35 mass % as-received (monthly average)
- Particulates ≤ 100 mg/Nm³ (@ 12% CO₂) on 4 hour moving average (80% of a given month) – 1 registered release point (CA2 – Stack)
- NOx - Continuous monitoring:
 - Air mode ≤ 850 ppmv (normalised to 7% O₂) – 1 registered release point (CA2 - Stack)
 - Oxy-mode ≤ 70 g/s (1 hour moving average) as measured by CEMS on stack inlet

ASUs (CA5 & CA6)

- No licence limits

CPU (CA7)

- There is one major release point for normal operation which is positioned above the coldbox. Other vents exist for start-up and emergency discharge.
- NOx limited to 70 g/s as reference level at the stack inlet (Release Point CA2)

Overall site

- Limits on runoff, stormwater and seepage: pH 6.5 – 9.0; Dissolved O₂ > 2 mg/L; Suspended Sol. ≤ 100 mg/L; Total dissolved solids ≤ 1450 mg/L; Chloride (Cl) ≤ 400 mg/L.
- Process waters are treated on site and discharged with ash to the ash dam.
- Agreed by Minutes of Meeting with the EPA that plant performance data will be scientifically published in the public interest.

Oxyfuel Boiler & CPU – Hazardous area assessment (1)

- Hazardous Area is an area in which a toxic or flammable gas atmosphere is or may be expected to be present in quantities such as to require special precautions.
- Potential hazards with the ASUs, Boiler and CPU can arise from:
 - Coal dust clouds exceeding 50 mg/Nm³)
 - Uncontrolled release of flue gas (predominantly CO₂ but also containing SO_x, NO_x, CO)
 - Controlled release of flue gas from registered release points including main vents, PSVs and TSVs
 - Controlled and uncontrolled release of Ammonia from the refrigeration plant
- Hazardous areas are divided into three zones (Zone 0, 1 & 2) according to the likelihood of a toxic or flammable gas being present and their persistence/frequency.
- Assessments methodology applied is as per AS/NZS/IEC 60079.10.1:2009 (Annex A & B).
- Oxyfuel boiler has 1 registered release point – the Stack.
- CPU area has 1 major release point for normal operation and several other release points for start-up and emergency operation.

Oxyfuel Boiler & CPU – Hazardous area assessment (2)

	OSHA STEL (ppm)	Australian MSDS STEL (ppm)	LEL (ppm)	UEL (ppm)
CO ₂	5,000	30,000		
CO	50			
NO	25	35		
NO ₂	5			
SO ₂	5	5		
SO ₃	0.28			
NH ₃		35	148,000 (14.8 mol. %)	250,000 (25 mol. %)
STEL - Short Term Exposure Limit				
LEL - Lower Explosion Limit				
UEL - Upper Explosion Limit				

O₂ is also a potential hazard:

O₂ < 19 mol %

O₂ > 23 mol %

Assessment Methodology

- Determine release rate for each gas component (choked or un-choked flow, initial concentration, T, p).
- Determine local conditions (ambient temperature, ventilated or enclosed), and select a Safety Factor according to the Standard.
- Determine theoretical concentration within the affected envelope.
- Select a certain size of leak (eg., around the circumference of a flange/gasket pipe section), and calculate the theoretical release rate and concentration.
- Compare the concentration with the STEL or Explosion limits (SAFE or UNSAFE).

Oxyfuel Boiler & CPU – Hazardous area assessment (3)

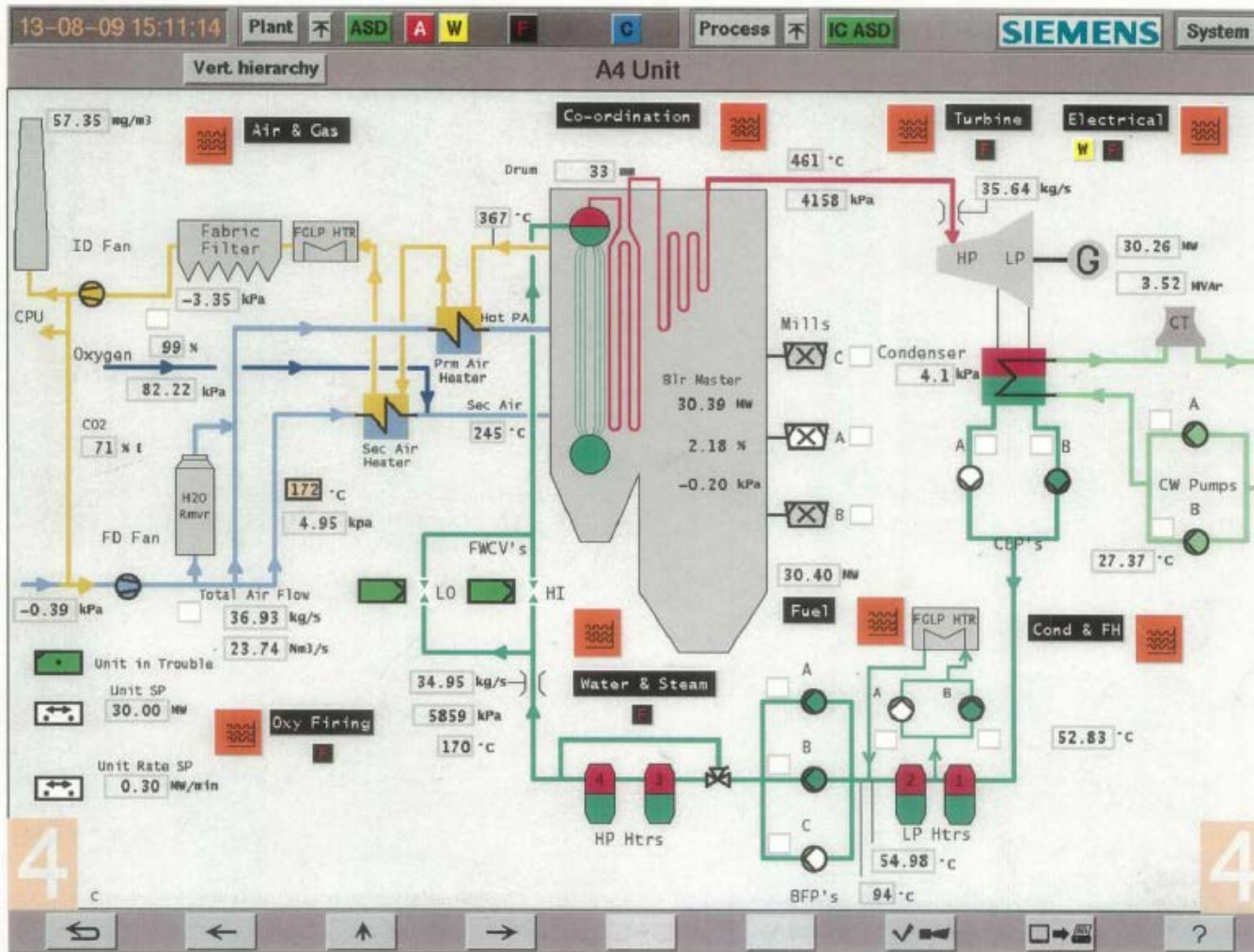
Safe Guards

- Operators do plant walk-downs every shift.
- Fixed CO₂ detectors in CPU compressor house have been installed (3 measurement points) as well as inside the Process and Air Liquide R&D Modins (used for process control and monitoring gas analysis).
- Personal CO₂ monitors must be worn around boiler in oxy-firing mode.
- Personal CO₂ and NO₂ monitors must be worn in CPU plant area.

Commissioning experience

- Some leaks have occurred due to material failures on old boiler heat recovery sections (e.g., Secondary Air/Gas Heater); which have been repaired.
- Actual measurements of gas concentrations due to leaks within affected zone are generally as predicted using the AS/NZS/IEC 60079.10.1:2009 modelling approach.

Oxyfuel boiler - overview



30 MWe (100% Load Factor)

Oxy-firing mode change sequence

Actual data (at 28 MWe)

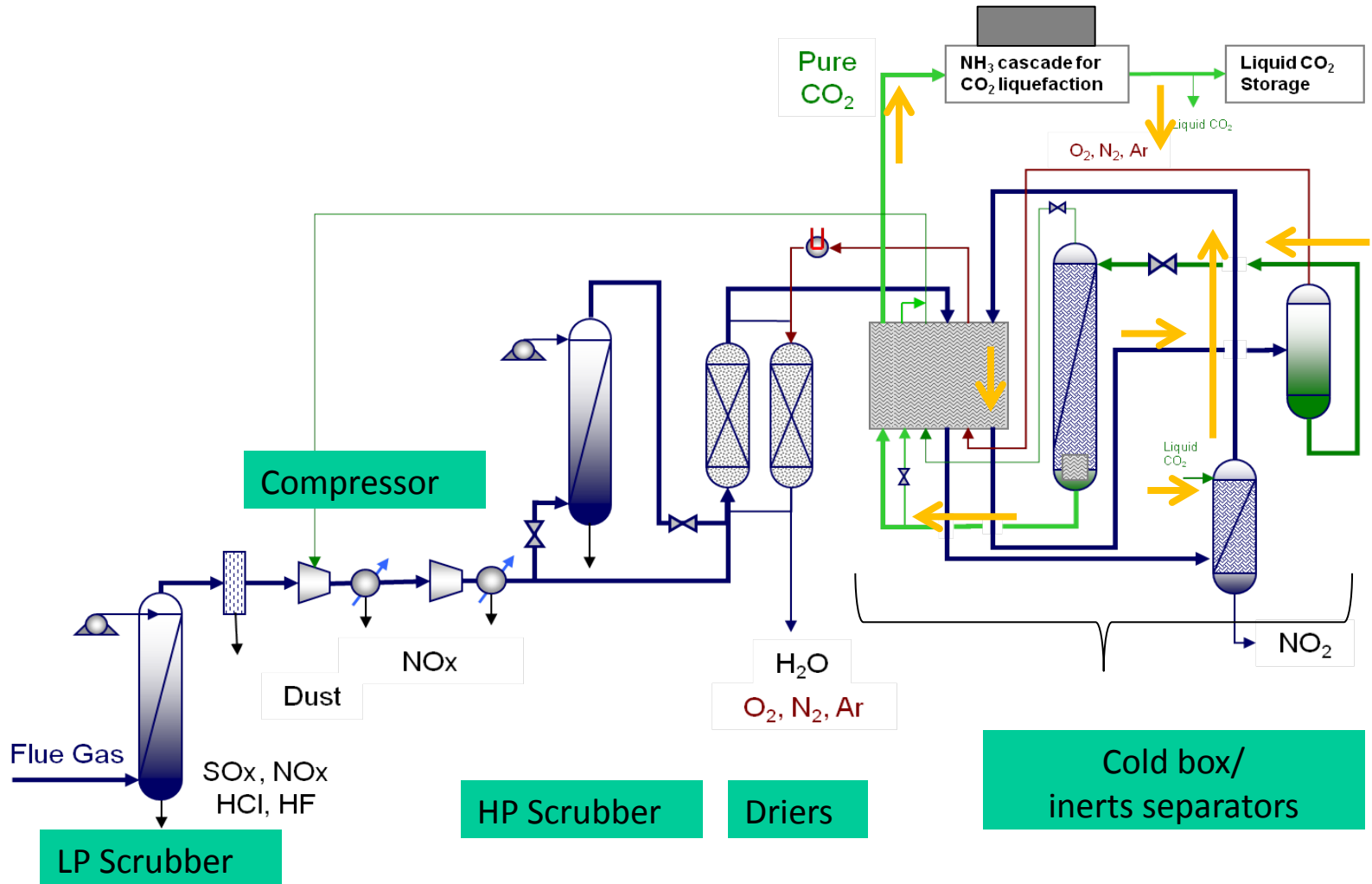
Flue Gas Composition		Air-Firing mode	O2 Sequence	RFG Mode	Oxy-mode
O2	vol %, dry	4.5	6.0	6.8	5.4
CO2	vol %, dry	15.0	16.2	59.9	72.2
CO	ppm, dry	20	20	12	12
SO2	ppm, dry	220	230	800	890
NO	ppm, dry	550	720	1195	965
NO2	ppm, dry	9	10	45	46
H2O	vol %	8	8.5	20.5	21.6

NOx	ppm, dry @ 7% O2	474	681	1223	907
NOx	ppm, dry @ 12% CO2	447	541	248	168
Flue Gas to Stack	kg/s (wet)	54	59	15.4	14.0
	Nm3/s (wet)	40.8	44.3	9.77	8.48
NOx	g/s	43	61	21	15

Oxyfuel Boiler – Commissioning issues

- Realigning of Boiler Control settings and new Boiler Protection System settings.
- Optimization of the oxy-firing logic.
- Balance of primary gas and secondary gas pressures to obtain optimal combustion conditions.
- Optimization of logic of the O₂ mixing valve between the ASU O₂ valve skid and the branch point on the O₂ injection line upstream of Secondary (Air) Gas heater.
- Minimizing air-ingress (e.g., improving hatch seals on fabric filters).
- Minimizing unreliability associated with some parts of the old plant (e.g., generator cooling air fans, instrument failures, logic hiccups, Secondary air heater internals).
- Managing coal quality (e.g., rocks in coal jamming coal feeders).

Carbon dioxide capture plant



Courtesy of Air Liquide

CPU – Low Pressure Section

Quencher & LP scrubber

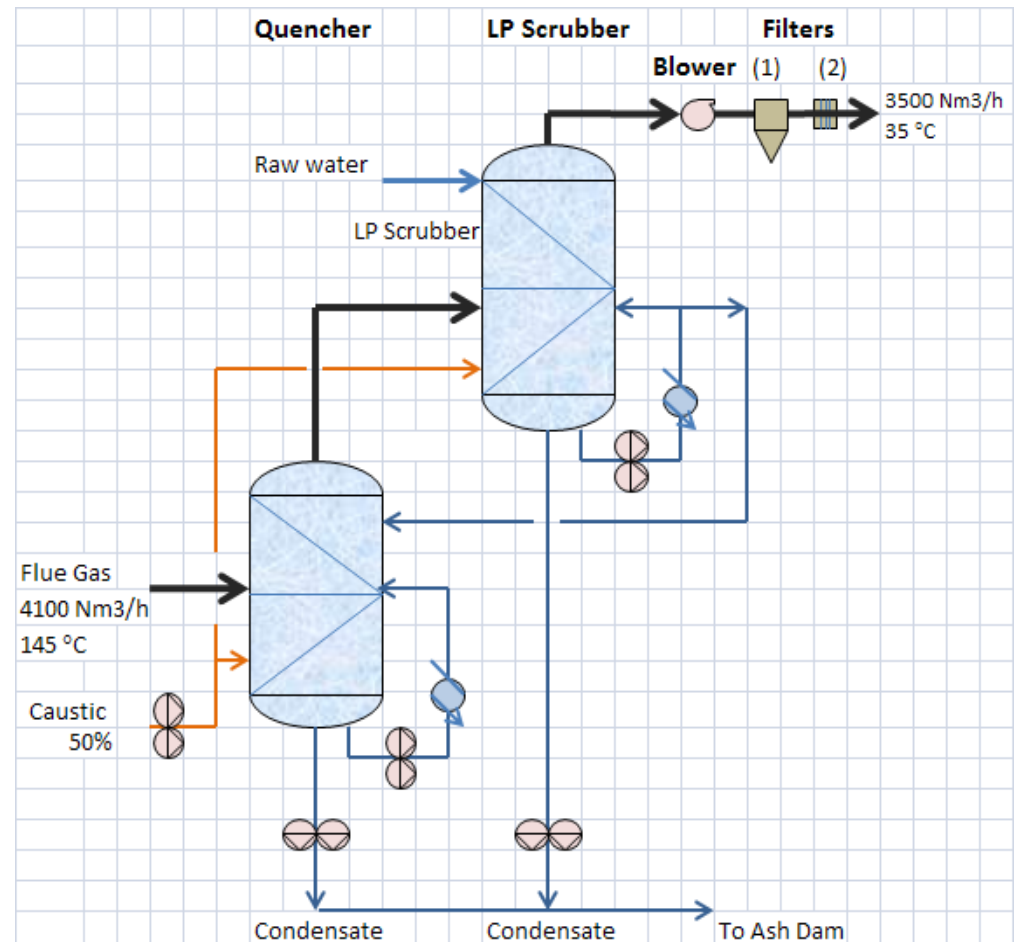
- Cools the gas from up to 145 °C to < 40 °C
- Removes SO_x to < 10 ppm in two stages.
- Caustic soda is used to dose the lower sections of neutralise the flue gas.

Blower

- Draws gas from the oxy-fuel boiler ID Fan outlet and compresses the gas to 110 kPa (abs).

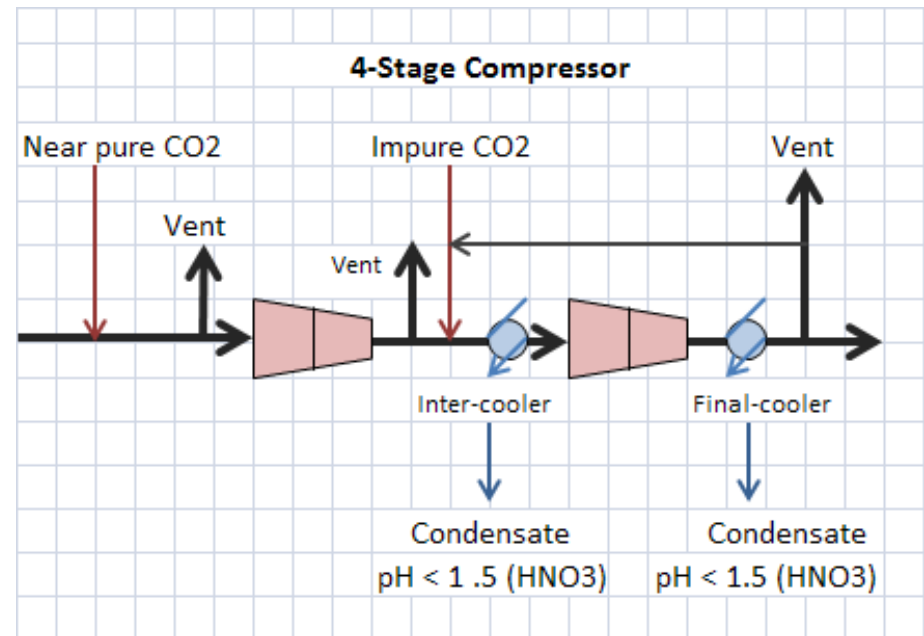
Filters

- Dynamic filter is pulsed with CO₂
- Dust level at Static filter outlet is < 0.02 mg/m³



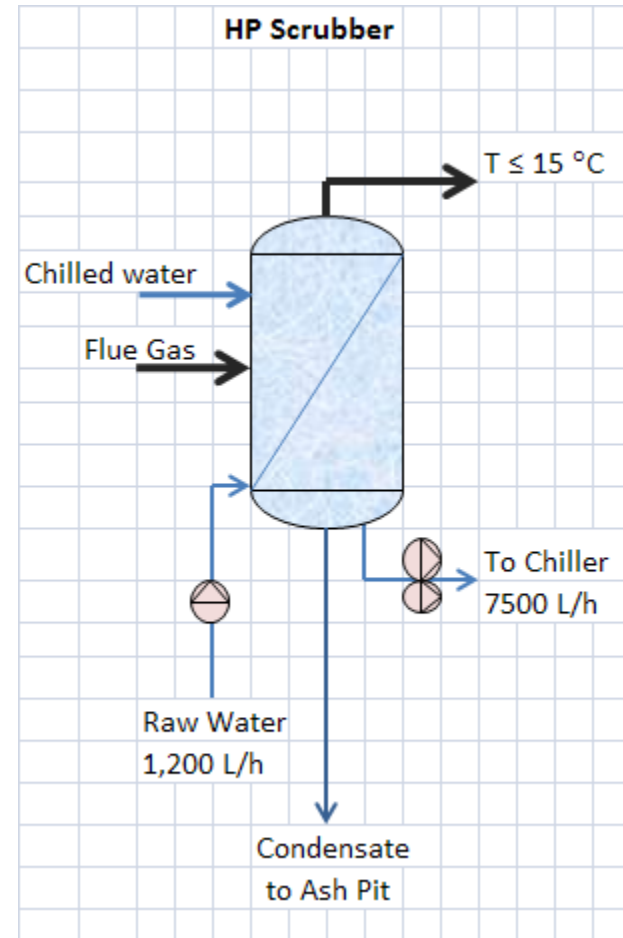
CPU – 4 Stage Centrifugal Compressor

- 4 Stages with coolers after Stage 2 and 4
- Stage 2 ~ 600 kPa (abs)
- Stage 4 ~ 2,500 kPa (abs)
- Acid condensate comprised of Nitric acid with low levels of Nitrous acid.
- Gas can be vented before and after the compressor.
- Commissioning experience is that **Hg is << 0.1 $\mu\text{g}/\text{Nm}^3$** at the compressor outlet.



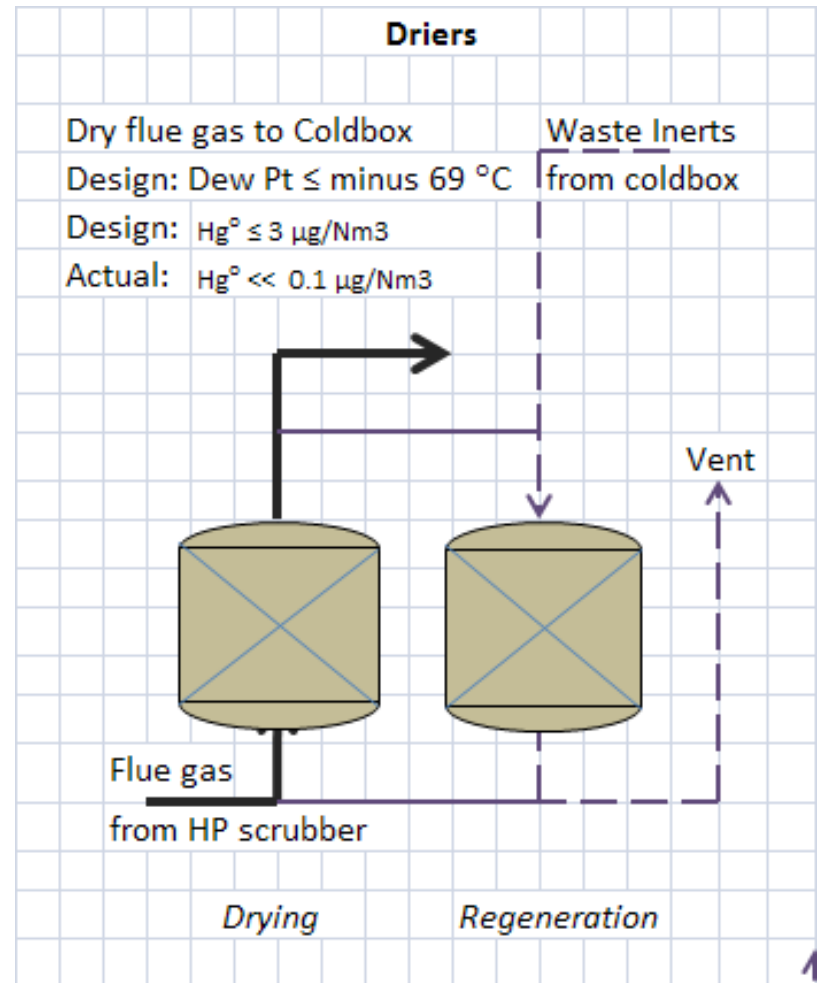
CPU – HP Scrubber (Cooler)

- HP scrubber (cooler) acts as a simple direct cooler to cool the flue gas from the compressor.
- The refrigeration plant provides chilled water at $\sim 7\text{ }^{\circ}\text{C}$ to the HP scrubber.
- Condensate (primarily Nitric acid) is neutralised and discharged to the ash pit.



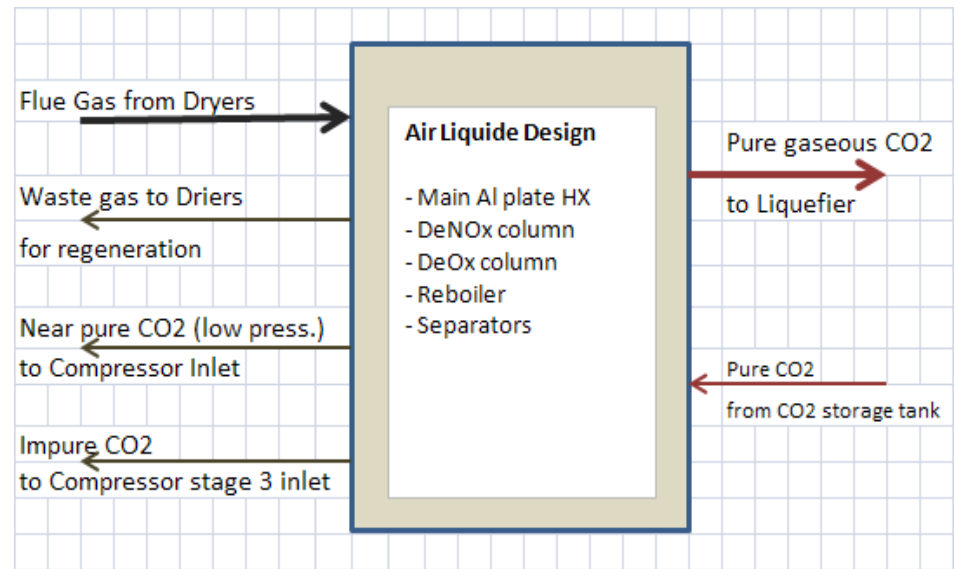
CPU - Dryers

- CPU has two dryers with acid resistant adsorbent.
- Utilises Temperature Swing Absorption principle
- Purpose is to dry the compressed/clean flue gas to very low dew point (typically minus 80 °C), and to remove any final traces of mercury.
- The Dryers are on a 12 hour cycle of adsorption and desorption.
- Desorbed gas, together with other waste gases from the deNOx and DeOx columns are vented from the top of the CPU coldbox.



CPU – Coldbox (CO₂ purification) & Liquefier

- Within the coldbox there is a large brazed-Al heat exchanger, and an array of columns and vessels that are used to purify the flue gas.
- An O₂ set point limit can be applied to the pure gaseous CO₂ prior to sending this to the Liquefier.
- CO₂ liquefier is coupled with an Ammonia Refrigeration plant and sits above the 100 tonne CO₂ storage tank.
- Analysis of LCO₂ product indicates purity exceeding 99.9% CO₂.
- Final CO₂ product is maintained at 1450 to 2300 kPa(abs) and minus 27 °C.



CPU – Process gas quality (actual)

Gas Composition	Unit of Measure	CPU - LP Inlet	CPU - LP Outlet	Product CO2
		From Boiler	To compressor	
Boiler Load Factor	%	80 - 100		
H2O	mol. %	19 - 22	5 - 7	< 20 ppm
O2	mol. %	3 - 5	3.5 - 6	< 30 ppm
CO2	mol. %	50 - 57	58 - 67	> 99.95
CO	ppmv	20 - > 200	25 - > 200	< 10
NO	ppmv	500 - 700	580 - 820	< 2.5
NO2	ppmv	20 - 40	Nil	< 20
SO2	ppmv	800 - 1000	< 10	< 0.1 ppm
SO3	ppmv	10 - 15	< 0.1	< 0.1 ppm
N2 (+ Ar)	mol. %	Balance	Balance	trace
Hg	ppbv	0.3 - 0.5	0.04 - 0.1	< 0.0002
	µg/Nm3	2.7 - 4.9	0.4 - 0.9	< 0.002
Particulates	mg/Nm3 (at 60 - 70% CO2)	150 - 250	< 0.02	nil
	mg/Nm3 (at 12% CO2)	20 - 50	< 0.01	nil

CPU – Process condensates

Data from Dec 2012 trials

Parameter	Unit of Meas.	Raw Water	Quencher	LP Scrubber	Compressor		HP Scrubber
					Intercooler	Final cooler	
pH		~ 7	~ 7	7.5 - 8	< 1.5	< 1.5	0.5 - 1
Total Dissolved Salts	mg/L	100 - 150	5,000 - 6,000	1,000 - 2,000	< 5	< 5	up to 1,000
Tot. Alkalinity	mg/L as CaCO ₃	< 10	1,500 - 2,000	1,000 - 1,500	< 1	< 1	< 1
Sulfate as SO ₄	mg/L	10 - 20	3,000 - 4,000	< 100 - 2,000	< 1	< 1	10 - 30
Chloride	mg/L	10	50 - 100	<50	< 1	< 1	10 - 50
Nitrate + Nitrite as N	mg/L	ND	< 5	< 5	up to 25,000	up to 25,000	1,500 - 15,000
Mercury (Hg)	µg/L	ND	up to 15	< 0.1	20 - 50	up to 10	< 2.5

Commissioning data indicates:

- LP area (caustic wet scrubbers and filters) remove particulates, SO_x, NO₂ and a major portion of trace elements
- NO is converted to NO₂ in the compressor and a significant portion is removed with the intercooler and final cooler condensates as Nitric Acid.
- Almost all the Hg that has passed through the LP area is removed with the compressor condensates.

Concluding comments

- By the end of August 2013, most issues associated with running-in of new plant had been resolved, and reasonably steady operation is anticipated for the remainder of the demonstration phase to the end 2014.
- The commissioning and operation has provided a great deal of knowledge and experience to inform future oxyfuel technology development. It is very important to have the background from R&D and pilot facilities and carefully considered design; but there will always be unforeseen issues in the plant.
- The Project is supporting a number of R&D initiatives that have received funding support from the Australian National Low Emissions Coal Research & Development, Australian Coal Association, NEDO and METI, and is collaborating with FutureGen 2.

Callide Oxyfuel Project – Participants

Oxyfuel Project Partners



Supporting Collaborator



Thank you

for more information: www.callideoxyfuel.com

Callide Oxyfuel Project – Participants

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Australian Government



Queensland
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METI
Ministry of Economy, Trade and Industry

Supporting Collaborator



Thank you

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