Callide
Oxyfuel Project

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Final Results

March 2018

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SUPPORTED BY

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1   Summary

The Callide Oxyfuel project was undertaken in three parts: Stage 1 – Demonstration of oxyfuel CO_2 capture; Stage 2 – assessment of CO_2 storage options and potential in Queensland and CO_2 injection testing; and Stage 3 – Project wrap up and commercialisation. The work and outcomes of these three phases are summarised below.

1.1   Oxyfuel Combustion & CO_2 Capture

1.1.1   General

The Callide Oxyfuel Project Stage 1 had two (2) major deliverables:

(i)   The design, construction and commissioning of the Callide Oxyfuel Boiler, Air Separation Units and CO_2 Capture plant; followed by
(ii)   Operation and maintenance of the plant to complete an extensive R&D program in order to –
   - lay the foundations for future applications of Oxyfuel technology; and to
   - demonstrate 10,000 hours of Oxyfuel operation and at least 4000 hours of industrial operation of the CO_2 capture plant.

The operational phase of the Oxyfuel boiler commenced in March 2012, and for the CO_2 Capture Plant in December 2012. When the demonstration phase had been concluded on 6th March 2015, the following operational statistics had been achieved:

   - Boiler Operation   15,397 hours
   - Total Generation (air + oxy-firing)   14,815 hours
   - Oxyfuel operation   10,268 hours
   - CO_2 capture Plant (Industrial Operation)   5,661 hours
   - Continuous generation   815 hours
   - Continuous Oxyfuel operation   627 hours

Over the duration of the operating phase of the project, the following coals and coal blends were utilised:

   - Callide coal – Medium ash, high volatile, sub-hydrous semi-bituminous coal
   - Minerva coal – Medium ash, high volatile, medium swelling, bituminous coal
   - Curragh (25%)/Callide (75%) blend coal – where Curragh coal is a low ash, medium volatile bituminous coal with very low ash fusibility temperatures.
   - Baralaba (25%)/Callide (75%) blend coal – where Baralaba coal has similar geological origins as Curragh coal but had been heat affected by volcanic activity during coalification, and may be described as low ash, semi-anthracite/anthracite coal, with low ash fusibility temperatures.

Specific tonnages used were Callide coal – 265,000 t; Minerva coal – 714 t; Baralaba coal – 616 t in 2 campaigns; and Curragh coal – 400 t.

Essentially, the R&D program was focussed on assessing the reliability of the Oxyfuel boiler and CO_2 capture plant; and in measuring the physical performance of the plant, characterising the combustion behaviour of coals under oxy-firing conditions, and in characterising the CO_2 capture plant performance.

1.1.2   Air Separation Units (ASU)

Oxygen at an average rate of 19,000 Nm^3/h @ 98% O_2 purity was supplied with two Air Liquide Sigma-L ASUs. This standard plant yielded acceptable reliability with the main issues being around expansion turbine coolers. Operationally, there were frequent nuisance issues with the analysers associated with the plant (mostly the Hydrocarbon Analyser) and initially – unacceptably long lead times to run the ASUs back up to full production following an outage. However, forced outages were rare and operator engagement with the plant was minimal.

1.1.3   Oxyfuel Boiler

The Oxyfuel boiler was a first-of-a-kind plant and was subject to a number of issues during hot commissioning and in the first year of operation. However, throughout the demonstration phase, plant and process improvements were made such that in the final 6 to 12 months of operation overall Unit Reliability of 90% was achieved.

The main unreliability issues were Master Fuel Trips arising from furnace pressure fluctuations and burner instability caused by O_2 flow control to the boiler, and sub-optimum set-up of Primary gas flow/pressure versus secondary gas flow/pressure on the recycled flue gas loop. These conditions were exacerbated by poor coal quality. However, these issues were largely redressed during the demonstration phase. In terms of physical plant, reliability was impacted by several tube failures within the Flue Gas Low Pressure Heater (FGLPH) – used to cool the flue gas exiting the Secondary Gas Heater on its way to the Fabric Filters for particulate control – caused by localised fly ash erosion.

In terms of Availability, notwithstanding the forced outages, the design output of the unit was also restrained at times due to: poor coal quality, limitations in O_2 supply because of reduced capacity of the Air Separation units under certain ambient conditions, greater pressure drop through the mills in oxy-firing mode, and certain limitations in induced draft fan capacity.

The combustion- and environmental-performance test programs, supported by updates to the logic to facilitate combustion control, clearly demonstrated the overall ease of operation and transition from air- to oxy-mode and back, the robust and high combustion efficiency achievable with oxy-combustion, and significant reduction (~ 60%) in NOx the specific emission rate.

From a system operations perspective, the oxyfuel boiler achieved a turn-down to 50 - 55% Load Factor depending on the burner configuration; acceptable ramp-up and ramp-down rates; significant reductions in mode transition duration (from 1½ hours for each mode transition to slightly above ½ hour); and acceptable run-back rates. Moreover, other important contributions from the oxyfuel boiler demonstration program included an assessment of the high-temperature corrosion performance of a range of alloy materials used for ultra super-critical (USC) boiler applications, as well as a characterisation of the performance of a range of steels in the low temperature corrosive environments associated with Oxyfuel boilers.

1.1.4 CO_2 Purification Unit (CPU)

The cryogenic CO_2 capture plant generally referred to as the CO_2 Purification Unit (CPU) was designed to deliver a net production of ~ 75 t/day of 99.9% pure CO_2 at 16.2 bar(A) and minus 30 °C. The gross production rate of the CPU was as per design of 100 t/day when the plant was operating normally.   In addition, the cold-box section of the CPU was designed by Air Liquide as a developmental step in their cryogenic technology for CO_2 capture.

1.1.5   Concluding Comments

Overall, important technical and cost information was obtained, critically assessed, and synthesised into a number of scientific papers, public reports, and most importantly an in-house Technical Manual; as the basis for future larger scale Oxyfuel plants with CO_2 capture.

In the case of the Oxyfuel boiler, it should be noted that what is singular about this project is that the demonstration was able to advance the technology from combustion of 100 kg of coal/hour in a pilot-scale test furnace in Japan to 20,000 kg of coal /hour in the modified 30 MW boiler at Callide A Power Station – in one technological step.

1.2 CO_2 Injection & Storage

1.2.1   General

The Callide Oxyfuel Project Stage 2 was concerned with two major activities: appraisal and assessment of the CO_2 storage potential of geological formations in South East Queensland; and with the more specific goal of injecting small quantities of CO_2 product from Callide A in order to advance the science and to improve the *bona fides* of geological storage of CO_2.

1.2.2 CO_2 Storage Assessments

The original ambition of the Callide Oxyfuel Project was to undertake a larger scale storage test of greater than 10,000 t CO_2 in a nearby saline aquifer. The work done in the feasibility and Front-End Engineering Design (FEED) study phases of the project indicated some prospect, not well characterised, of suitable storage sites in the Northern Denison Trough.

From the commencement of the Project in May 2008, a series of studies were undertaken to seek out and assess the potential for CO_2 storage in sandstone formations within a nominal 200 km radius of the Callide A facility. This was ultimately extended to 300 km. The formations considered were as follows:

- Permian age - Natural Gas reservoirs associated with the Northern and Southern Denison Trough Anticlines which run North (position some 200 – 300 km west of the Callide A site)
- Permian age – Saline aquifers at greater depth on the periphery of the Denison Trough anticlines
- Jurassic Age – Precipice sandstone in the southern part of the Taroom Trough running from Wandoan in the south to Moura 100 km west of the Callide A site.
- Jurassic age – Precipice sandstone (primarily) and Hutton sandstone (secondarily) towards the base of the Surat Basin in South East Queensland.

The overall conclusions, in the context of these studies, are as follows:

- The Denison Trough Natural Gas fields and adjacent saline aquifers have limited potential to support large scale CO_2 storage projects in Queensland.
- Resource competition with natural gas producers is problematic because of the risk of breakthrough of CO_2 in the natural gas product.
- The storage potential of deeper coal seam gas resources in Queensland is limited, and there is considerable uncertainty around, and consequential resistance to the idea, of enhanced coal bed methane recovery.
- The Surat Basin Jurassic sandstone aquifers, in particular the Precipice sandstone, offer a very large potential storage medium (> 900 Mt CO_2) within the available GHG tenements.
- Significant concerns are present amongst the public and politicians about the efficacy of geological storage of CO_2, especially where there is a potential for any kind of impact on groundwater; as is the case in the Surat Basin.

1.2.3 CO_2 Injection Test

In 2014 from October to December, a series of injections of Callide Oxyfuel CO_2 product were made through CO2CRC Well No 2 into the Paaratte sandstone formation at a depth of ~ 1440 m. This formation lies within the Otway Basin 200 km to the South West of Melbourne (near Nirranda South off the Great Ocean Road).

The injection trials involved road transport in a nominal 15 t Isotainer from Callide to Nirranda South (some 1300 km). The trials where conducted in two phases:

(i)   Injection of formation water saturated with CO_2 product – pure and with added impurities – to assess the geochemical effect of the impurities on the formation rock in terms of dissolution of minerals, precipitation and water quality.
(ii)   Injection of pure CO_2, and CO_2-saturated formation water, to assess the CO_2 saturation level (pore volume) occupied by the CO_2 in these tests – referred to as a Residual Saturation Test.

The primary benefit of the injection test was to advance scientific knowledge on two fronts: the effect of CO_2 impurities such as SO_2, NO_2 and O_2 on rock formation that is saturated with water; and the improvement in measurement of residual saturation testing; all of which are very important considerations in designing, permitting and operating large scale CO_2 geological storage facilities.

Phase 1 involved initial production of water from the formation, followed by injection of water (100.2 t) and pure Callide Oxyfuel CO_2 (5.2 t), with 3 weeks soaking time interspersed with small water productions for scientific analysis. The injection was then repeated with 100t water and 4.5 t of Callide Oxyfuel CO_2 with added impurities (9 ppm NO_2, 67 ppm SO_2 and 6150 ppm O_2). In the first injection, Strontium and Bromide Tracers were added and on the second injection, Lithium and Fluorescein tracers.

A slight impact was observed on the formation water by the action of the added NO_2, SO_2 and O_2; the O_2 being the more significant component. However, the effects were not significant particularly given the natural buffering capacity of the formation water.

An additional important element of the geochemical (dissolution) experiments was to compare the results with Geochemical models (Geochemists Work Bench and TOUGHREACT ECO$_2$N). The purpose of the modelling was to predict water-rock interactions leading to changes in water composition, mineral dissolution rates, and precipitation of secondary minerals all of which have important practical consequences to CO$_2$ injection rates, storage volume, retention, and environmental outcomes.

The geochemical models in both cases predict only a very slight (insignificant) impact of CO$_2$ impurities on the formation water due to the inherent buffering capacity of the formation water. In other words, the effect of NO$_2$ and SO$_2$ is to slightly decrease the formation water pH (probably 0.1 pH units) with dissolution of Iron-bearing and Feldspar minerals, but with a comparable and balancing precipitation of ankerite and Mg-rich siderite.

The fate of impurities added to the Callide Oxyfuel CO$_2$ was also evaluated on the basis of the Reduction-Oxidation (redox) state of the system. This approach utilises the so called Pourbaix diagrams which can be used to depict the equilibrium between a certain mineral and the reactive component of that mineral as a function of Voltage Potential versus pH. This work highlighted the importance of O$_2$ as an oxidizing agent leading to dissolution of pyrite (and perhaps other iron-based minerals) which should be taken into consideration in future projects.

1.3   Commercialisation & Future Directions

1.3.1   Commercialisation

One of the key inputs to the Commonwealth Funding Deed embodied within a formal IP Management Plan was the Project IP Commercialisation Strategy that targeted the following activities:

• Leveraging from member relationships
• Leveraging off international relationships
• Promotion of Proof-of-Concept
• Diffusion and Exchange

In the wrap up of the Callide Oxyfuel Project, three important documents were prepared to support the future commercialisation of the Callide Oxyfuel Project IP, namely:

• Patent Agreement – which acknowledges Background IP owned by IHI and JPower (preceding the Callide Oxyfuel Project), and the title, rights and interest of all the project participants in Patents taken out by IHI on behalf of the Project partners.
• Manufacturing Licence Agreement between the Callide Oxyfuel Project Parties and IHI which defines Project IP and grants IHI worldwide perpetual non-exclusive rights to utilise, incorporate and sub-license Project IP for commercialisation purposes.
• Project IP Commercialisation Agreement intended to be an overarching Agreement that sets out the terms upon which the project parties are entitled to commercialise Project IP in the future.

1.3.2   Further Work and Future Directions

Significant experience and learnings were achieved from the demonstration, but in addition potential improvements or ideas that could not be tested at Callide A have also been identified. These improvements and ideas include:

(i)   Consideration in the future of the option of partial oxyfuel operation which will facilitate a lower risk approach to the development of larger scale oxyfuel boilers.
(ii)   Improved integration of the ASUs with the oxyfuel boiler by inclusion if Liquid O_2 (LOX) storage.
(iii)   Further developments and studies of the control system concept, mode transition and interaction between the ASU, oxyfuel boiler and CO_2 capture plant.
(iv)   Improved process and heat integration between the ASU, Oxyfuel boiler and CO_2 capture plant. In addition to the system integration and optimisations referred to above, specific further work has been identified for the main process units: ASU, Oxyfuel Boiler and CO_2 capture plant.

Moreover, it may be noted that what has been particularly significant in the last few years has been work undertaken in several countries to develop International Standards on carbon capture and storage. Of particular note, ISO Technical Committee 265 was established in recent years in recognition of the importance of standardisation to support coal trade, CCS technology development, and global commitments to reduce greenhouse gas emissions. There are five (5) general areas being covered by ISO/TC 265:

(i)   Carbon dioxide capture systems, technologies and processes
(ii)   Pipeline transport systems
(iii)   Geological storage
(iv)   Quantification and Verification, Vocabulary (cross cutting terms)
(v)   Other standards such as for Enhanced Oil Recovery.

This report includes an overview of these ISO developments, recognising: (i) their importance in the field of CCS; and (ii) that two member companies of the Callide Oxyfuel Project (namely CS Energy and IHI Corporation) are on various ISO/TC265 working groups and have provided input to the development of these standards drawing particularly on the knowledge and learnings from the Callide Oxyfuel demonstration.

Finally, in consideration of published work on the future direction for CCS and oxyfuel combustion, it may be noted that there have been a small number of international reports, principally prepared by the IEA GHG Programme or the IEA Clean Coal Centre, which represent detailed literature reviews or specific studies on the primary CO_2 capture technologies: Post-combustion capture, Pre-combustion capture, and Oxyfuel Combustion capture. These documents are referenced in this Report.

2   Introduction

The Callide Oxyfuel Project achieved Financial Close on the 20th March 2008 with the execution of a Project Joint Venture Agreement, Project Funding Agreement with ACALET, Commonwealth Funding Deed, and formal establishment of Oxyfuel Technologies Pty Ltd (as Agent for the project participants) and Callide Oxyfuel Services Pty Ltd and the project Management Company.

The Project Partners, namely CS Energy/Queensland Government, Glencore, Schlumberger (Carbon Storage Solutions), IHI, Mitsui & Co and JPower, provided equity to the project; and the COAL21 Program (under ACALET) and the Commonwealth Government provided funding. All revenues from electricity generation were used to offset operating and maintenance costs.

In May 2014, the Global CCS Institute published the *Callide Oxyfuel Project – Lessons Learned* report which outlined described the Project objectives, structure, permitting and contracting strategy; presented a technical description and results from the project from the work done from March 2012 to March 2015; and also presented material on safety and hazardous area assessments. This report, entitled *Callide Oxyfuel Project – Final Results* is intended to add to the information provided in the Lessons Learned Report primarily by presenting an overview of the results from the entire program dealing with the demonstration of Oxyfuel combustion capture, results of geological storage injection tests conducted with Callide Oxyfuel CO_2 product, and to wrap up with an outline on the commercialisation activities of the project and future directions.

3   Results

3.1   Air Separation Units

Two Air Liquide Sigma-L Air Separation Units (ASUs) were installed at Callide A for the Callide Oxyfuel Project to supply a nominal 9,600 Nm^3/h of pure oxygen each (i.e., 19,200 Nm^3/h) at Gaseous Oxygen (GOX) purity of $\geq$ 98% purity and at pressure of 1.8 bar(A), to meet the full load (30 MWe) requirements of the boiler when in Oxy-fuel mode (Figure 1). These ASUs were installed and commissioned constructed between April 2010 and December 2011, and commissioning was completed on 27 February 2012.
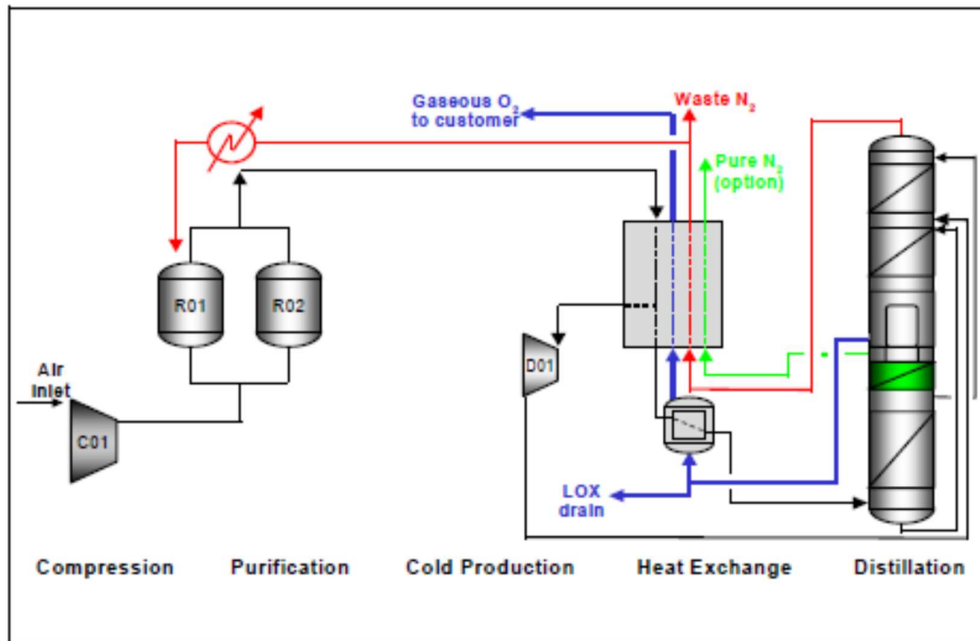
Figure 1 - Schematic of the Sigma-L Air Separation Unit (Courtesy Air Liquide)

The ASU acceptance tests were completed in May 2012 and a second performance test was carried out in February 2015 towards the end of the Oxyfuel demonstration phase. The results of the performance tests were acceptable; the only issue being that the power consumption was slightly above guarantee.

During hot weather periods (typically from November to March), the output of the ASUs was slightly limited as expected.

Over the 3-year operating period of the ASUs, following resolution and elimination of nuisance trip causes during the commissioning phase, forced outages (< 2.0%) were limited to a few minor plant items, O_2 and Hydrocarbon analyser faults, and protection trips arising from 11 kV voltage variation in the electrical supply from the grid. Moreover, the internal condition of the ASU parts was found to be very good on final inspection in March/April 2015.

3.2   Oxyfuel Combustion

The basic concept of oxyfuel combustion is shown schematically in Figure 2. The main parts of the boiler that were modified for oxyfuel combustion are shown in Figure 3, which have been described in detail previously by Spero (2014) in the GCCSI – Lessons Learned Report.
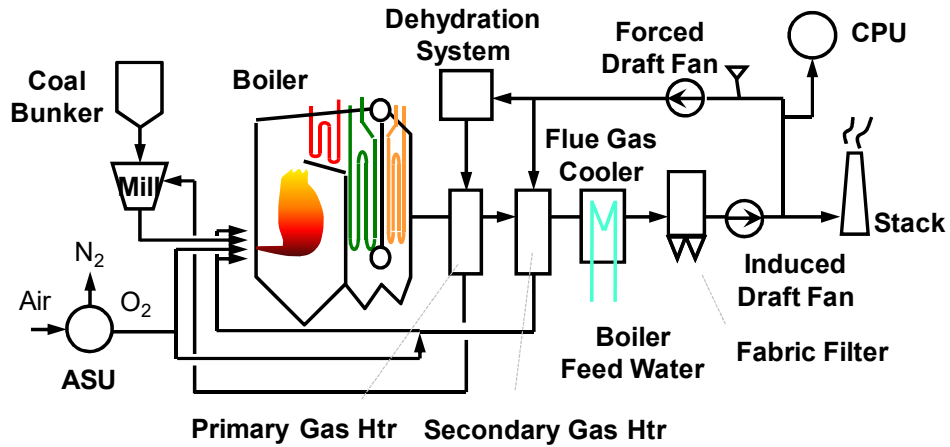
Figure 2 - Schematic of Callide Oxyfuel boiler retrofit

Figure 3 – Photo of Callide Oxyfuel boiler showing retrofit paths and flue gas flue directions

3.2.1 Oxyfuel Boiler Construction & Commissioning

After February 2011, following completion of the basic refurbishment of the original air-fired boiler (Callide A Unit No. 4) initial commissioning work was carried out in Air-mode on the following: upgraded ICMS and Boiler Safety System; refurbished steam turbine; and new equipment including the cooling water system from Cooling Tower No. 4, Gas Recirculation Fan/Forced Draft Fan (GRF), Primary Air/Gas Heater (PAH/PGH), Low NOx Burners (Row A), duct network and new dampers, and Flue Gas Low Pressure Heater (FGLPH). This commissioning work was done in air-mode from March 2011 to November 2011 and included a refiring of the boiler in April 2011.

Commissioning of the oxy-firing capability was carried out from November 2011, with hot commissioning being performed from February 2012 to May 2012; with 1st oxy-firing achieved on the 13 April 2012.

From May 2012, the oxy-combustion R&D phase commenced and was concluded in March 2015 with successful achievement of the important goal of 10,000 hours of oxy-firing operation and completion of the agreed R&D test program.

3.2.2 Test Coals

The oxy-combustion test program utilised the following coals:

- Callide coal – Medium ash, high volatile, sub-hydrous, semi-bituminous coal
- Minerva coal – Medium ash, high volatile, bituminous coal
- Curragh (25%)/Callide (75%) blend coal – where Curragh coal is a low ash, medium volatile bituminous coal with low ash fusibility temperatures.
- Baralaba (25%)/Callide (75%) blend coal – where Baralaba coal has similar geological origins as Curragh coal but had been heat affected by volcanic activity during coalification, and may be described as low ash, semi-anthracite/anthracite coal, with low ash fusibility temperatures.

Over the 3-year operating period (10,200 hours oxy-firing + 4,600 hours air-firing), the following coal tonnages were burned:

Callide coal   265,000 t (from Apr. 2011 – Mar. 2015)
Minerva coal   714 t (in Dec. 2012)
Baralaba coal   216 t (Dec. 2012), 400 t (Nov. 2014 & Feb. 2015)
Curragh coal   400 t (Jan. & Feb. 2015)

3.2.3 Oxyfuel Boiler Key Operational Statistics

The key operational milestone dates recorded for the project are as follows (Table 1).

Table 1 – Callide Oxyfuel Project key operational milestone dates

First fire after retrofit	23rd March, 2011
Start the operational record	12th March, 2012
First O_2 injection to boiler	12th March, 2012
First oxyfuel operation (Fully close of air intake damper)	19th March, 2012
First oxyfuel operation mode	17th May, 2012
First sending the oxyfuel flue gas to CPU	14th September, 2012
First CO_2 production in CPU	11th December, 2012
First product CO_2 sending to tank	14th February, 2013
Achievement of 4000 hours of industrial operation for CPU	15th September, 2014
Achievement of 10000 hours operation for oxyfuel mode	1st February, 2015
Demonstration completed	6th March, 2015

Key operational statistics were as follows (Table 2).

Table 2 – Callide Oxyfuel Project key operational statistics

Boiler operation	15,397 hours
Generation	14,815 hours
O_2 supply to boiler	10,687 hours
Oxyfuel operation	10,268 hours
Sending oxyfuel flue gas to CPU	7,445 hours
HIO of CPU	5,661 hours
Continuous generation	815 hours 37 minutes
Continuous oxyfuel operation	627 hours 46 minutes
Number of start-stop for plant	180
Number of Air to Oxy mode transition	159
Number of Oxy to Air mode transition	61

3.2.4 Oxyfuel Reliability

Overall Unit Reliability (UR) is defined as 100 – Forced Outage Rate (FOR) where FOR is defined as the % of scheduled operating time that the plant is out of service due to unexpected problems or failures. Oxyfuel Reliability (OR) is a subset of UR.

In the final 6 to 12 months of operation, Unit Reliability of 90% was achieved, with a corresponding Oxyfuel Reliability of over 80%. Unit reliability was impacted by the age the coal-fired boiler with a number of issues arising around steam turbine vibration, as well as many forced outages caused by foreign material in the coal (such as large rocks and blocks of wood) as well as ongoing issues due to poor coal – meaning high ash/low calorific value or too fine leading to poor handleability – as compared to the design coal specification. It is important to note that Oxyfuel reliability includes the boiler forced outages as well as any ASU forced outages, as well as outages associated with Oxy-firing specific plant items.

Overall, for a first-of-a-kind oxyfuel power plant, and considering that the Oxyfuel boiler and associated steam turbine/generator were originally commissioned in 1972, the reliability statistics achieved are acceptable.

The causes of plant failure in oxy-firing mode are summarised in Figure 4.
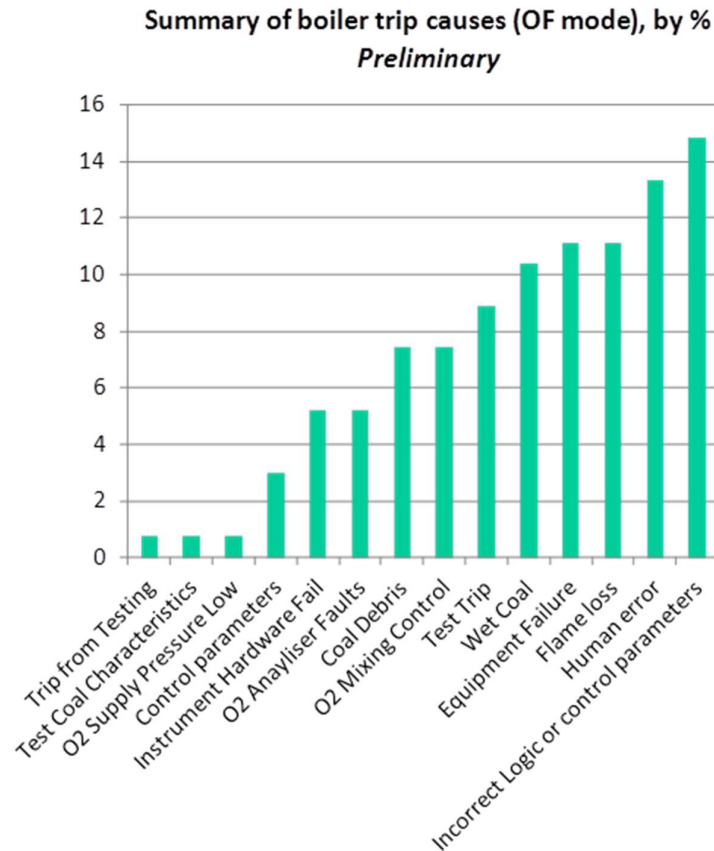
Figure 4 – Oxyfuel boiler causes of plant trips in oxy-mode (as % out of 100)

It may be noted that:

- The boiler was originally designed for HHV 20 MJ/kg (16% Ash); actual coal burned was 17 – 18.5 MJ/kg (24 – 27% ash); which had a significant impact on reliability, especially in oxy-mode.
- Other causes associated with oxy-firing mode were certain equipment failures, human error, O_2 flow control issues and sub-optimum logic.
- Logic issues were largely resolved during the 3-year demonstration phase, and overall reliability of the boiler in oxyfuel mode improved significantly with experience.

3.2.5 Oxyfuel Boiler Performance

A number of specific test campaigns were conducted to evaluate the performance characteristics of the boiler. These tests were as follows.

June to December 2012 – Initial performance testing

The initial performance testing of the Oxyfuel boiler in 2012 verified the following outcomes:

- Air-firing operation from 18 to 30 MW
- Oxy-firing operation from 24 to 29 MW with Boiler inlet O_2 of 25 to 29% without limitation
- Oxy-firing operation with H_2O remover in bypass (October 2012); noting the observed increased likelihood of acid dew point corrosion (particularly for the primary gas ductwork to the mills and downstream PF pipes) due to increase in flue gas moisture content in the presence of SO_2 and SO_3; and ~ 10% reduction in flue gas CO_2 concentration.
- Maximum boiler air-ingress rate of 7 mass % (which was the design value)
- Main-steam temperature, furnace heat absorption and associated parameters within acceptable limits of the design.
- Oxy-firing flue gas composition (SOx, NOx, CO_2 etc) within the expected range at the given load achieved.
- Maximum CO_2 measured during the initial performance testing was 67 vol. % (dry) at 29 MW although subsequent boiler optimisation yielded flue gas concentration as high as 70%; noting the design flue gas CO_2 of 68.2 vol. % (dry) at 30 MW load.

Oxyfuel Combustion Test Campaign Results (Dec. 2012 – Mar. 2015)

(i) Combustion and Environmental Testing December 2012

Comprehensive combustion and environmental performance testing of the boiler was conducted in December 2012 and involved systematic measurements of coal quality inputs, PF size distribution, furnace observations, furnace and fly ash sampling and testing, and sampling and analysis of flue gas and waste water streams.

The outcomes of this test campaign were presented to the IEA GHG Conference in Spain in 2013 and published through the Global CCS Institute in May 2014 with incorporation of additional material.

The campaign utilised Callide Coal and included trials with Minerva coal as well as Minerva-Callide (25%/75%) blend coal and Baralaba-Callide (25%/75%) blend coal. The overarching objective of these tests was to characterise the performance of the Oxyfuel boiler in oxy-mode versus air-mode and to obtain the first performance measures of the CPU which had then just been commissioned.

These tests reconfirmed the performance of the oxy-fuel boiler as measured during the initial operations phase, and verified the following comparing oxy-firing to air-firing:

- Significant improvement in combustion efficiency, measured as a reduction in Carbon in ash (typically 50% reduction);
- Significant reduction in NOx mass emission rate (mg NOx/MJ fuel) – typically a 60% reduction; and
- Slight reduction in particulate specific emission rates (mg/kWh).

(ii)   Baralaba-Callide and Curragh-Callide Blend Tests

The combustion and environmental performance tests of December 2012 were supplemented by additional blend coal tests in November 2014 and January/February 2015.

These tests provided further data and characterisation of the performance of the Oxyfuel boiler as well as more varied flue gas composition for testing of the CPU.

(iii)   Summary of Combustion Test Results

The Callide Oxyfuel burner and air register arrangement is shown in Figure 5.
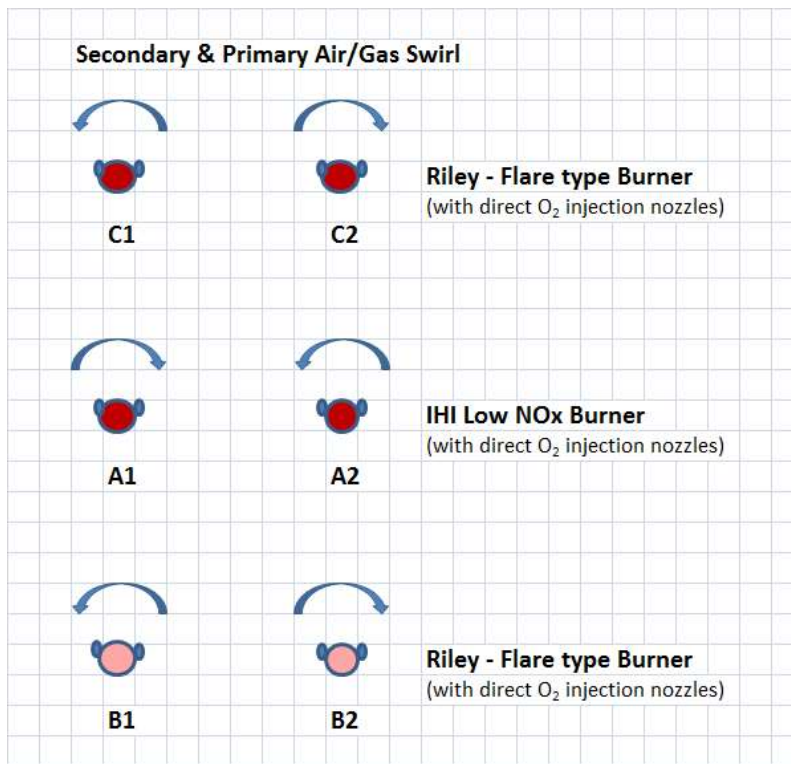
Figure 5 – Callide Oxyfuel boiler – burner arrangement (including 2 direct O_2 injection nozzles/burner) and direction of swirl

As shown in Figure 6, significant improvement was observed in combustion efficiency in OF mode with test burners including low NOx burners, largely due to the elevated boiler inlet O_2 and the increase in residence time in Boiler Oxy-firing/Air-firing ~ 1.3. Injection of direct O_2 (up to 10% of requirement) slightly improves combustion efficiency but also increases flame temperature and reduces flame length with some impact of furnace heat adsorption.
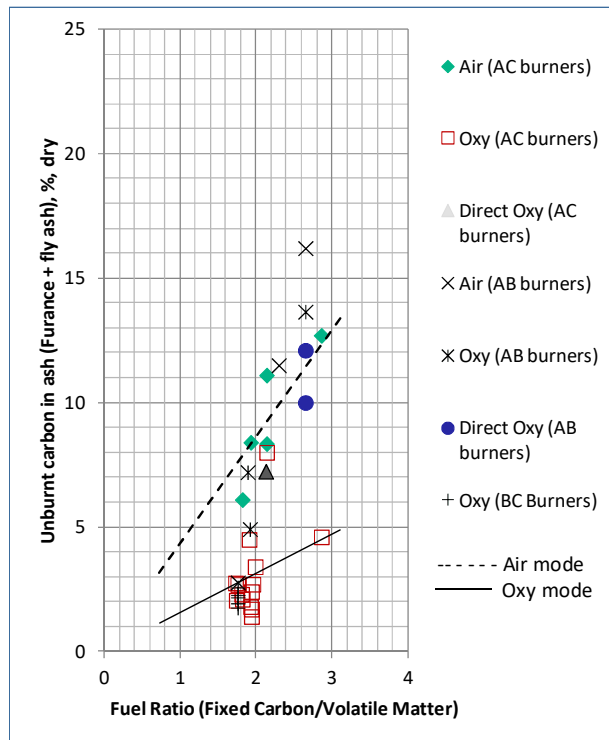
Figure 6 – Callide Oxyfuel boiler, comparison of oxy-firing versus air-firing

Typically, a 60% reduction was observed in NOx specific emission rate, for example, for Callide coal, typical reduction was from ~ 4.7 g NOx/kWh down to ~ 2 g NOx/kWh. Moreover, a slight reduction in Particulate emissions was observed: Air (0.3 – 0.375 mg/kWh) → Oxy (0.25 – 0.34 mg/kWh), due to removal in the H_2O remover vessel (refer to Figures 2 and 3).

The studies also examined the effect of unit load on Flue Gas CO_2 which is an important parameter for the effective operation of the CPU (Figure 7). The following summary points may be noted:
- Boiler inlet O_2 range in oxy-mode is 24% to 30%
- Boiler exit O_2 range in oxy-mode is 2.0 to 3.5 vol% (wet) at 28-30 MWe
- Actual boiler exit O_2 on average is a little higher than set point
- Boiler exit O_2 increased with decreasing load (as usual)
- Overall air ingress was within the design limit of 7 mass %
- Maximum CO_2 achieved was 71 vol. % (dry), limited by: 98% purity O_2; higher actual boiler exit-O_2 than set point; small level of air ingress through ID and GRF fan seals, and air used to pulse fabric filters.

It should be noted in Figure 7 that the design of the CPU was based on a concentration of CO_2 in the feed gas of 68.2 (vol. %, dry) when operating at 30 MWe (maximum continuous rating).
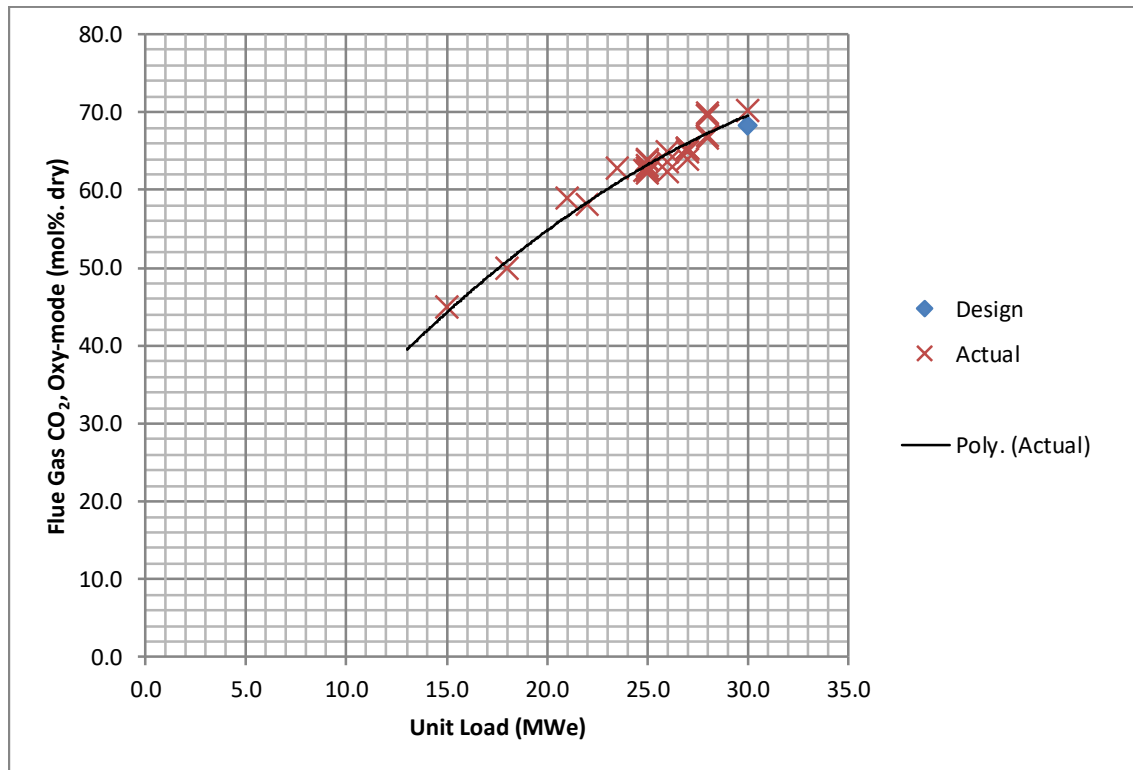
Figure 7 – Callide Oxyfuel boiler, effect of Unit load on flue gas CO_2 concentration

(iv) Combustion Performance with Direct O_2 Injection

Tests were conducted in December 2012, September 2014, November 2014 and January 2015 with the 5 coals described earlier to evaluate the oxy-firing combustion and boiler performance with and without direct-O_2 injection. In these tests, the overall boiler inlet O_2 was maintained (typically 6.3 – 6.5 kg/s) but a portion of the O_2 was injected into the furnace through a probe within the burner barrel, by proportion ranging from 5% (0.3 kg/s) to 12% (0.8 kg/s).

The net result of the direct O_2 injection, confirmed over a Load range of 24 to 29 MW and A-B and C-A mill combinations, was as follows:

- For lower levels of Direct-O_2 injection (around 10%), no significant effect on oxy-firing performance was evident.
- For higher levels of Direct O_2 (say 10%), NOx increased by 20 – 40% and Carbon-in-ash decreased by about 10%.
- Flame condition (brightness and ignition point), and furnace heat absorption was improved as evidenced by a notable reduction in Desuperheater spray flow.

(v) In-Furnace Measurement and Simulation

The purpose of the In-Furnace measurements and simulation was to clarify the characteristics of the pulverised coal combustion and the performance of the boiler under oxy-firing conditions, in order to validate IHI's furnace simulation model as a tool for large-scale Oxyfuel boiler design.

The following conditions were applied for the in-furnace measurement (October 2013).

Table 3 – Plant condition for in-furnace measurements

Combustion mode	Air combustion	Oxyfuel combustion
Output (MW)	28.0	28.0
Mode	Coordination	Coordination
Inlet O_2 (wet vol. %)	As contained in atmosphere	24.5, 27.0, 30.0
Usage of burner (Position of air register)	C burners (35) A burners (40)	C burners (30) A burners (30)

Measurements taken included: gas temperature and gas composition from various parts of the furnace, furnace incident heat flux, and PF sampling.

The key findings from the results were as follows:

- In oxy-firing, steam flow rate is a few percent lower than in air-firing and boiler outlet gas temperature is 20 °C to 30 °C lower. The boiler outlet gas temperature is reduced by increasing inlet-O_2 indicating more complete burnout.

- In the case of 30% inlet-O_2, heat flux within the lower combustion zone of the furnace is generally higher whereas the gas temperature at the furnace exit (above the Nose) is lower, compared to the condition where boiler inlet O_2 < 30%. These results confirm that combustion is more intense in the lower part of the furnace due to the higher inlet O_2 (as would be expected) which results in increased heat transfer in that part, and consequently (downstream) a reduced furnace exit gas temperature.

- The behaviour of gas composition in the furnace has been studied by evaluating the data at each area of the furnace. These data will contribute to the upgrade and validation of boiler CFD models.

- Pulverized coal (PC) size distribution for testing conducted in October 2013 shows that the PF size distribution was somewhat finer in oxy-mode compared to air-mode. In the December 2012 tests, a similar trend was observed but not as marked. The reason is probably because the actual (true) volumetric flow rate of primary gas (or primary air) through the mills is slightly higher in the oxy-firing case. This is because the primary gas + PC temperature is higher at the mill outlet in the Oxyfuel case and the Δp across the mill is higher in the Oxy-firing case so one can surmise that the residence time of coal in the mill is slightly longer in the Oxy-firing case compared to the air-firing case hence the finer grind.

- The primary gas flows are more variable in the case of A mill compared to B&C mills, probably because of the lower back pressure on the PF system due to the configuration of the A (low NOx) burners. The same trend was observed in the December 2012 trials.

- Carbon-in-ash under oxy-firing conditions is almost half the level observed under air-firing conditions indicating a significant improvement in coal burn-out.

- In oxy-firing mode, the concentration of CO_2 in the boiler outlet flue gas is basically unaffected by the concentration of O_2 in the boiler inlet within the normal operating range of 23.5 to 30.0 mol. %, wet. The reason is that the boiler inlet O_2 is a function of the flue gas

recycle (higher recycle yields lower boiler inlet O_2), but the overall O_2 consumed in combustion of the coal is controlled by the O_2 flow from the Air Separation Units in response to the measured Boiler Exit O_2.

- During the in-furnace testing in October 2013, it was observed that the PC size distribution (mean size) was finer for C mill compared to A mill. However, more generally, taking into consideration the PC size distributions observed in December 2012 (Combustion and Environmental Tests) no specific conclusion can be drawn as the mill performance is very much dependent on the condition of the mill internals, which are changed out in regular minor and major mill services.

- Furnace simulation results were compared with the actual in-furnace measurement results where some differences in gas temperature and heat flux were noted. However, overall the simulation can recreate the distribution of gas temperature in the furnace and incident heat flux on the furnace walls based on the actual operation data; except for the burner region where it is not possible to take reliable measurements due to fluctuations in flame conditions.

(vi) Turn-down Tests (Minimum Load)

An important capability of a coal-fired power plant is the turn-down capability, meaning what minimum load can be achieved without oil support and maintaining stable operation. The Callide A Boiler in air-firing mode can be turned down to 40% Load Factor (12 MWe). Following some logic modifications to allow the Secondary Air/Gas Inlet Damper to be opened by a few percent more, trials were carried out in oxy-firing mode at Callide A in 2014 as follows:

- January 2014 - Mills A&B
- July 2014 – Mills C&B
- August 2014 – Mills C & A

The initial trial in January 2014 was conduction with A&B mill combination and with Boiler Inlet O_2 of 27% (wet) and 24% (wet); noting that burners A1 and A2 are IHI low NOX burner technology. This test campaign demonstrated that a minimum load of 16 MW coal be achieved with A&B mills provided that the recycled flue gas flow rate was reduced from 3.1 m^3/s (24% boiler inlet O_2) to 2.9 m^3/s (27 % boiler inlet O_2) to provide additional margin to the SAH for controllability.

In July 2014, the turndown testing was repeated with the standard burner C&B mill combinations and reduced recycled flue gas flow rate. A minimum load of 15 MW (50% Load) with stable operation was achieved. Oil igniters on each burner were also put into service to confirm operating characteristics. Finally, the turn down test was repeated at the higher Recycled Flue Gas (RFG) rate of 3.1 m^3/s, and again a minimum stable load of 15 MW was achieved.

In August 2014, the turndown testing was repeated with C&A mill combinations with similar conditions as before. In this case a minimum stable load of 16 MW was achieved.

(vii) Ramp Rate Tests (Rate Change)

Load ramp-up and ramp-down tests were performed in August 2014 to confirm the operational flexibility of the boiler. For the purposes of the tests, improved O_2 control logic at the mixing valve was implemented.

Load ramp tests were successfully conducted with C&A mill combination and A&B mill combination over a range of ramp rates: 0.3, 0.6, 0.9 and 1.2 MW/min over various load ranges representing normal utility boiler ramp rate ranges.

Stable boiler operation and stable steam plant was confirmed.

(viii) Staged Combustion Tests (2 Burner)

Traditional air-firing boilers have utilised two-stage combustion in order to reduce NOx emission effectively without external de-NOx systems (for example, selective catalyst reactor called SCR). The purpose of COP two-stage test was to evaluate the efficacy of two-stage combustion for NOx reduction in oxy-fuel operation. For this trial, the upper burner ports (C1 and C2) were used to simulate staged air ports. These tests were conducted from 6 – 8th November 2014.

 The key findings from these staged combustion tests were as follows:

- In both air- and oxy-firing modes, NOx reduction was observed when air or RFG flow into C row burner increased with changing burner air register position and with increased opening of the windbox damper.

- In oxy-firing mode, the effect of NOx reduction was higher at 27 MW load than that at 23 MW load. Typical NOx reductions achieved by the staged combustion, depending on windbox conditions and air register settings, was up to about 16%.

- However, as expected the reduction in NOx from staged combustion was associated with an increase in carbon-in ash (UBC). The degree of change is less in oxy-mode (2.4% UBC increase to 3.8% UBC) than that in air mode (7.1% UBC increase to 10.2% UBC).

(ix) Run-Back Test

A series of run-back tests were conducted in February 2015 in order to determine the maximum, safe run-back rate (de-load rate) in oxy-firing mode. A rapid run-back rate is considered to be highly advantageous in order to avoid certain unit trips; in other words maintain boiler safety by rapidly de-loading the unit rather than revert to a complete boiler trip.

The tests conducted involved a unit run-back from 24 MW down to 18 MW at rates of 3 MW/min to 10 MW/min.

The tests were successfully completed for each run; however, it was noted that some further logic development would be beneficial to optimise the run-back rate for oxy-firing to match the rate achieved in air-firing mode and to ensure more stable and safe conditions for large-scale Oxyfuel boiler applications.

(x) New O_2 Logic (for mode transition time and combustion stability)

One of the main issues impacting on the performance of the Oxyfuel boiler was the control of O_2 from the Air Separation Units into the Secondary Gas flue gas recycle duct via the O_2 mixing valve;

which was evident in the fluctuation in O_2 flow rate in response to furnace O_2 demand and Boiler Exit O_2. Accordingly, significant effort went into the optimisation of O_2 flow control in order to achieve:

- Stable mode transition especially at lower load (24 MW).
- Reduction in the mode transition time
- Improved boiler inlet and boiler outlet O_2.

Specific measures implemented included a simplification of the O_2 mixing valve control logic, installation of a separate Proportional-Integral (PI) controller, direct control of the mixing valve based on actual O_2 flow rate measurement rather than a calculated O_2 flow rate, and upper and lower limitations in the O_2 valve position to avoid rapid fluctuations. These modifications which were not fully implemented until after September 2014 resulted in a significant improvement in O_2 mixing valve control evidenced by improved stability and response to O_2 demand at the boiler inlet and outlet and a reduction in the mode transition times from a nominal 1½ hours to 30 minutes. In addition, the operation mode could then be selected from "Coordination" or "Boiler Load Set Point - BLSP" during combustion mode transition to provide additional operational flexibility.

(xi) High Temperature (Fireside) Corrosion Tests

It is well documented in the literature that important issues affecting the service life of boiler tube materials especially in ultra super-critical steam environments (steam temperature regime > 600 °C) include: (i) oxidation; (ii) sulphurisation; (iii) high temperature fireside corrosion by aggressive coal ash particularly containing alkali metals; and (iv) fireside carburization by CO_2 concentrated in the flue gas or by carbonate associated with fine ash deposits.

For the Callide A facility, in the high temperature parts of the boiler, comparing oxy-firing conditions to air-firing conditions, one can expect no significant change in the molar concentration of O_2 but rather a significant increase in molar concentration (and therefore partial pressure) of CO_2, H_2O and SO_2 which are known to increase the propensity for high-temperature corrosion of alloys. Moreover, at Callide A, whilst there may be a high proportion of Iron in the coal (as Siderite in the pulverised coal) which may contribute to furnace ash (slag) deposits, the proportions of alkali metals (Na^+, K^+) are quite low.

In the present work a series of in-situ high temperature (fireside) corrosion tests were performed to investigate the corrosion behaviour of a range of materials in actual flue gas, based on simulated surface temperatures in the actual air-combustion and oxy-combustion conditions.

Two types of high temperature corrosion probe where manufactured and installed via ports on the side walls of the furnace in front of the Secondary (or Pendant) Super Heater. The probe materials and surface temperatures used were selected to simulate conditions for Ultra Super-Critical boilers.

The specific results are commercial in confidence, but it may be noted that high temperature corrosion rates observed under the Callide oxyfuel operating conditions (at times air-firing and at other times oxy-firing mode) were not different to rates observed in present day large-scale utility ultra super-critical coal power plants for equivalent levels of coal sulfur, chlorine, etc.

(xii) Low Temperature (Flue Gas) Corrosion Tests

The objective of the testing was to evaluate the performance of various ferrous materials used or likely to be used in oxy-fuel boiler service, where low temperature corrosion environments may exist. Accordingly, coupons were fixed within ductwork downstream of the boiler at three locations as follows.

Table 4 – Callide Oxyfuel boiler flue gas conditions for low temperature corrosion tests

	Secondary Gas Heater Inlet (RFG side)	Primary Gas Heater Inlet (RFG side)	Flue Gas Cooler Outlet (FGLPH)
Gas Temperature (°C)	150	45	155
Gas composition (vol. %)			
H_2O (vol%, wet)	23	8.5	23
CO_2 (vol%, wet)	50	60	50
O_2 (vol% wet)	3.4	4.0	3.4
N_2 + Ar (vol%, wet)	23.4	27.3	23.4
CO ppmv (wet)	200	240	200
SO_2 ppmv (wet)	730	870	730
SO_3 ppmv (wet)	0.5 - 5	< 0.1	0.5 - 5
NO ppmv (wet)	820	980	820
NO_2 ppmv (wet)	50	< 1	50
Cl ppmv (wet)	35	< 5	35

Notes: RFG – Recycled Flue Gas; FGLPH – Flue gas low pressure heater

The corrosion coupons were in service from January to March 2015 for a total period of 1730 hours (1265 hours in oxy-mode and 465 hours in air mode). Five alloys used in boiler ductwork construction were tested: SS400 – low alloy construction steel; S10 low alloy steel used in sulfuric acid dew point environments; mild steel (1020); and 316 SS and Duplex 2205 Ferritic-Austenitic stainless steel. The results indicated superior performance of the 316 SS and Duplex 2205 as shown in Figure 8.
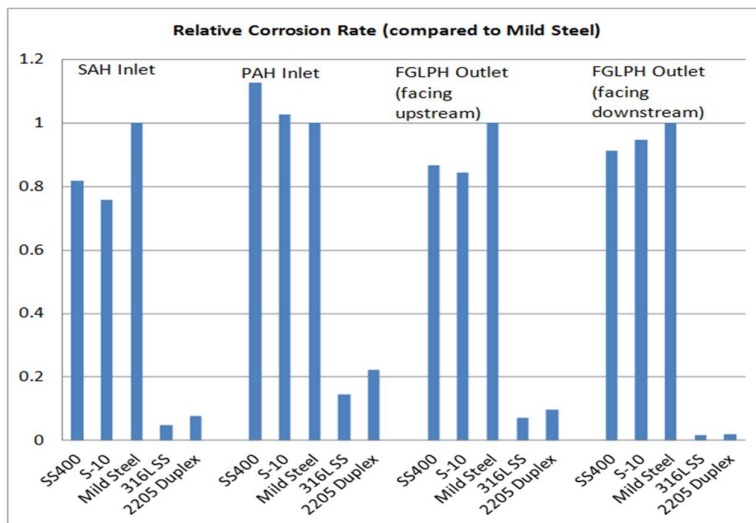
Figure 8 – Callide Oxyfuel boiler, low temperature flue gas corrosion test results

(xiii) Characterisation of Furnace Ash Deposits

As part of the final inspection of the boiler in March 2015, ash deposits were collected from within the superheater area of the boiler (Figure 9), consisting of the following deposits (also shown in Figure 10):

- Sintered ash deposits from the 1st row of tubes at the inlet of the secondary (pendant) superheater, noting that there were no deposits at all after the first row.
- Sintered ash deposits from the 1st row of tubes at the inlet of the primary superheater, noting that the deposits were mainly across the centre of the PSH.
- Sintered ash deposits from a few central tubes in the 2nd row of the PSH; noting that there were no deposits beyond the 2nd row of tubes.
- The internal surfaces of the furnace itself were quite clean and essentially devoid of any ash deposits.
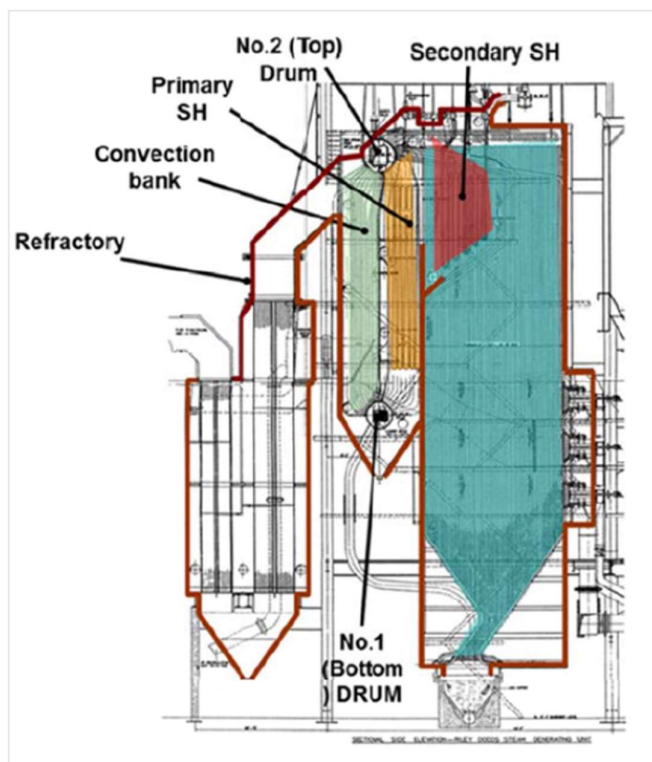
Figure 9 - Side view of the Callide Oxyfuel boiler

It may be noted that essentially the deposits corresponded to some 3 years of operation as the furnace internals had not been cleaned during the demonstration program.

The characterisation of these deposits indicated that each was formed from preferential deposition of iron-rich particles and particles originating from clays. Overall it was concluded that oxy-combustion did not have a notable impact on the behaviour of the coal ash in combustion for the Callide A plant.

	Sintered ash deposit removed from an inlet tube (1st row) of the Secondary Super Heater. There was very little ash deposition on the front of the SSH and no ash deposition at all beyond the 1st row of tubes. The ash deposit was sintered and relatively easy to remove from the tube.
	Sintered ash deposit removed from an inlet tube (1st row) of the Primary Superheater. There was very little ash deposition on the front of the PSH, only on a few tubes is the central area of the inlet face. The ash deposit was sintered and relatively easy to remove from the tube.
	Sintered ash deposit removed from an inlet tube (2st row) of the Primary Superheater, restricted mainly to the central area of the inlet face. There was no ash deposition beyond the 2nd row. The ash deposit was sintered and relatively easy to remove from the tube.

Figure 10 – Callide Oxyfuel boiler, furnace ash deposits

3.3 CO$_2$ Capture Plant (CO$_2$ Purification Unit – CPU)

3.3.1 CPU Design/Plant Description

The basic design of the CO$_2$ Purification Unit (CPU) was provided by Air Liquide (France); the detailed design was provided in part by Air Liquide Engineering (especially the non-condensable stripper) and by GLP Plant (Australia). The cryogenic CPU was designed to deliver a net production of ~ 75 t/day of 99.9% pure CO$_2$ at 16.2 bar (A) and -30 °C for transportation in road tankers.

The gross CPU production rate is nominally 100 t/day but approximately 25% of the CO$_2$ product is recycled and utilised within the process; mainly within the Coldbox to achieve the separation of inert gases (O$_2$, N$_2$, Ar), residual hydrocarbons (mostly CO), and removal of any residual SO$_2$ and NO/NO$_2$ from the CO$_2$ product.

The overall configuration of the CPU is shown schematically (in simplified form) below.
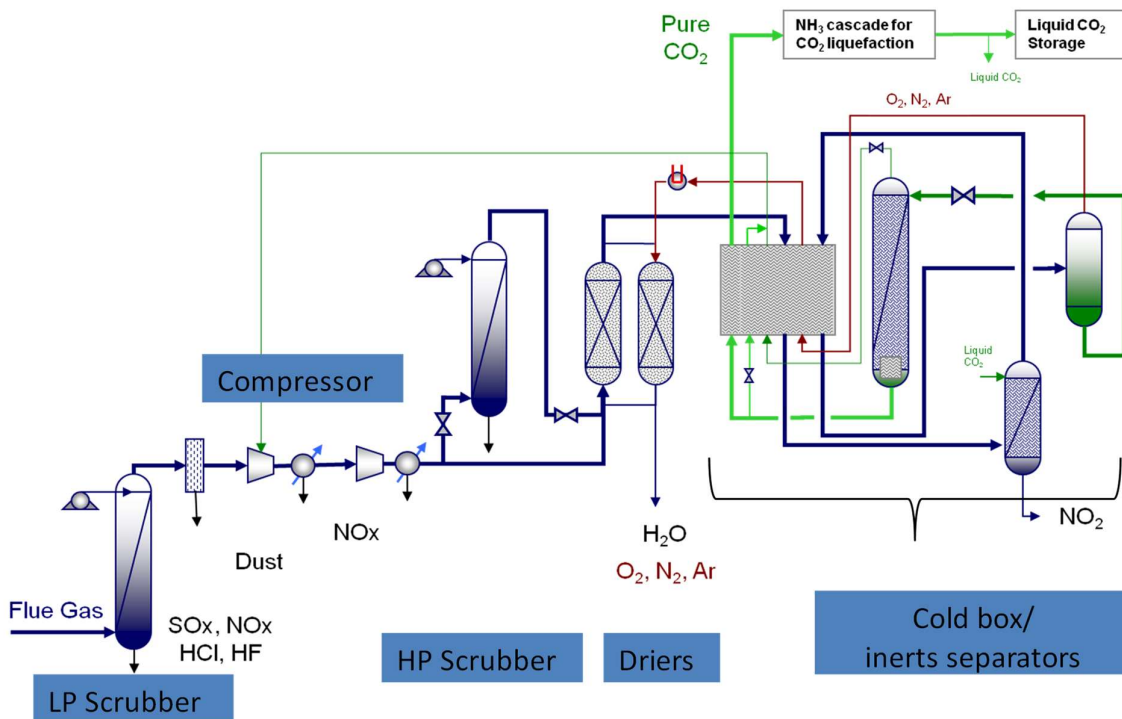
Figure 11 – Simplified schematic of the Callide Oxyfuel CO$_2$ Purification Unit (CPU)

The design basis of the CPU is as follows:

- The low-pressure section consists of a Quencher and Low-Pressure Scrubber, utilising Caustic Soda (NaOH) wash to remove SOx to less than 20 ppm, all the NO$_2$ and some portion of NO according to solubility.

- A blower draws the flue gas from the Oxyfuel boiler recirculation duct through the scrubbers and then pushes the flue gas through dynamic and static particulate filters to achieve a final dust burden of < 0.02 mg/Nm^3.
- The centrifugal compressor was selected on the basis that this would represent the type of equipment that would be used in a large-scale CPU (compared to a lower cost less efficient screw compressor).
- Downstream, there is a HP cooler and scrubber utilising chilled water to further remove acid gases, followed by a Temperature Swing Adsorption Drier system to reduce the dew point to less than minus 80 °C.
- The final purification of the CO_2 product is achieved in the coldbox consisting of several separation vessels and large heat exchanger. This system was designed for a Flue Gas CO_2 concentration [CO_2] of 80% compared to the actual feed gas [CO_2] at the compressor inlet of around 70%, and for this reason a portion of the CO_2 product is recycled back to the compressor as previously described.
- A novel feature of the Air Liquide Coldbox (non-condensable stripper) design was the inclusion of the deNOx column which was an evolution of previous ALE coldbox designs trialled elsewhere; together with the requirement to recycle product CO_2, significantly compromised the overall CO_2 capture rate achieved across the CPU.
- The final step is the liquefaction of the pure CO_2 via the CO_2 liquefier; coupled with an Ammonia Refrigeration cycle.

3.3.2   CPU Construction and Commissioning

The construction of the CPU was undertaken by GLP Plant and the commissioning jointly by GLP Plant and Air Liquide (France) from April 2010 to December 2011, with Practical Completion awarded in March 2012. The main commissioning issues were around optimising the performance of the Coldbox, but overall the commissioning went smoothly and the logic worked well.

3.3.3   CPU Operating Statistics

Flue gas was first sent to the CPU from the Oxyfuel boiler in October 2012, the first operation of the Coldbox was in December 2012 and the first liquid CO_2 was produced in February 2013. In the meantime, the first major test campaign was conducted in December 2012 to provide an initial characterisation of the CPU performance.

Specific equipment hours were as follows:
- Flue gas to the CPU   7446 h
- Compressor operation   ~ 7000 h
- CO_2 to liquefier   1961 h
- CPU Hours of Industrial operation   5661 h

It is very important to note that because there was no CO_2 off-take, the use of the liquefier was limited and most of the Coldbox CO_2 product was by necessity vented over the CPU 2½ year operating period; and consequently, there were only 1961 h of CO_2 to the Liquefier.

3.3.4 CPU Reliability

Throughout the commissioning and operating phases of the CPU, some 200 trips/events were recorded mostly in the earlier phases of the operation. The available trip data indicates the following statistics by CPU plant area (Figure 12).
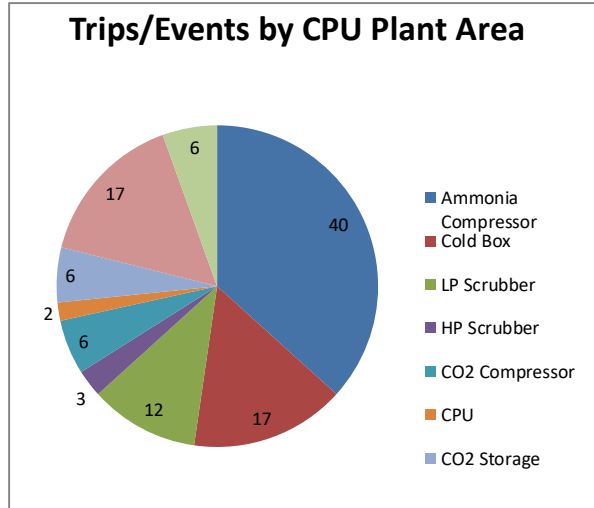
Figure 12 – Callide Oxyfuel CPU trips/events

The coldbox itself exhibited a high level of reliability as indicated in Figure 13, with most trip events being as a protection response to upstream causes.
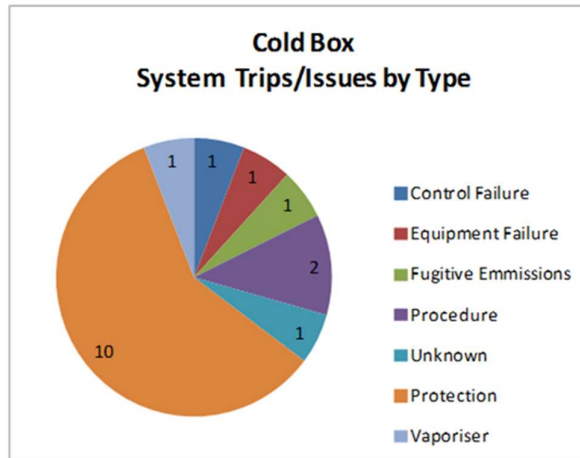
Figure 13 – Callide Oxyfuel CPU coldbox trips/issues by type

In addition, it may be noted that trip events on the CPU were relatively easily and quickly rectified; for example, it was found that several the pumps originally supplied used to recirculate cooling water, caustic soda and liquid CO_2 were of an inferior make and were progressively replaced with more reliable pumps. The main plant items themselves were very reliable and required no significant maintenance activity.

In the final 6 months of the CPU operation, trip events were rare and the Forced Outage Rate is estimated to have been < 1%.

3.3.5 CPU Performance

Plant performance was assessed through several specific test campaigns with Air Liquide (referred to as Passenger Tests), and also on an ongoing basis in parallel with the Oxyfuel Boiler tests utilising COSPL with specialists from the JV partners and support from the University of Newcastle, Macquarie University, HRL Ltd, and Techno Tugos (Japan).

These tests were used to determine the behaviour/elimination of particulates, acid gas and inert gases as the flue gas moved from the low-pressure scrubber area to the exit of the Coldbox (see Tables 5 and 6). These data show the progressive removal of impurities such as SOx, NOx and Mercury primarily as condensate although as shown in Figure 11, some NO_2 is vented from the Coldbox; with the net result being almost pure CO_2.

Various other tests and measurements were made to determine the CO_2 capture rate from the process. On this point, the following may be noted:

1. The CPU Coldbox was designed primarily as a demonstration of the final removal of SOx and NOx to very low levels from the CO_2; it was not designed to demonstrate or achieve high CO_2 recovery.
2. The design point for the CPU (as a complete system) was 67% CO_2 recovery for Feed Gas CO_2 of 68 vol.% (dry); with full NOx removal (to < 15 ppm).
3. Actual CO_2 recoveries for the design Feed Gas CO_2 were around 60% overall for the complete system.
4. The extrapolated CO_2 recovery without NOx removal in the Coldbox was estimated to be in the range of 78 to 84%.
5. For the Coldbox itself, CO_2 recovery was > 80%.

Table 5 – Callide Oxyfuel CPU, analysis of process condensates

Parameter	Unit of Meas.	H₂O Remover (Oxyfuel Boiler)		Raw Water	Quencher	LP Scrubber	Compressor		HP Scrubber	CPU Drier
		Pre-cooler	Cooler				Intercooler	Final cooler		Various steps
pH		1.8 - 2.0	1.9 - 2.2	~7	~7	7.5 - 8	< 1.5	< 1.5	0.5 - 1	< 0.01 - 0.6
Total Dissolved Salts	mg/L	1000 - 1200	850 - 1050	100 - 150	5,000 - 6,000	1,000 - 2,000	< 5	< 5	up to 1,000	
Total Alkalinity	mg/L as CaCO3	< 1	< 1	< 10	1,500 - 2,000	1,000 - 1,500	< 1	< 1	< 1	
Sulfate as SO4	mg/L	130 - 500	90 - 400	10 - 20	3,000 - 4,000	< 100 - 2,000	< 1	< 1	10 - 30	
Sulfite as SO3	mg/L	up to 10	60 - 110							
Chloride	mg/L	130 - 700	80 - 400	10	50 - 100	<50	< 1	< 1	10 - 50	
Nitrate + Nitrite as N	mg/L	< 5	< 5	ND	< 5	< 5	up to 25,000	up to 25,000	1,500 - 15,000	100,000 - 194,000 (all as NO3)
Mercury (Hg)	µg/L	2 - 4	2 - 3	ND	up to 15	< 0.1	20 - 50	up to 10	< 2.5	60 - 75

Table 6 – Callide Oxyfuel CPU performance data for various gas components

SOx	Quencher Column pH setpoint: 7.06; LP Scrubber pH setpoint: 7.5 SOx captured as Sulfate. > 99% of SOx in the flue gas is removed in the Quencher. The product from the LP scrubber has < 20 ppm SOx. Caustic Soda consumption: 17.8 kg/g in the Quencher and 12.9 kg/h in the LP Scrubber.
HCl HF	99 – 100% HCl removed in the Quencher. LP scrubber outlet is < 2 ppm. Any chloride found in the HP scrubber has come from the make-up raw water. Quencher 22 mg/L; LP scrubber and beyond 0 mg/L.
CO	Feed Flue gas: Burners B& C CO < 50 ppm Burners A&B or Burners A&C CO > 500 − 2400 ppm unstable Quencher — LP Scrubber — Compressor — Driers — HP Chiller/Scrubber — Coldbox Flue gas 4536 Nm^3/h CO 1047 ppm CO flow 3.6 Nm^3/h 2.5 Nm^3 CO/h 3.2 Nm^3 CO/h 2.3 Nm^3 CO/h Product 0 Nm^3 CO/h MP Recycle: 0.3 Nm^3 CO/h Regen + vent 2.3 Nm^3 CO/h
Hg	Two forms of Mercury (Hg) are present: Reduced form Hg^{2+} and Oxidised form Hg° (from 1&2 July 2016): CPU inlet 11 µg/Nm^3 Quencher Outlet 3.6 µg/Nm^3 LP Scrubber outlet 1.4 µg/Nm^3 Compressor outlet < 0.08 µg/Nm^3 Target for Brazed Al Heat Exchangers: < 1 µg/Nm^3
NOx	Flue gas Feed NOx is dependent on burner arrangement in the boiler. For high NOx (B & C mill combination): NOx ~ 750 ppm dry (1540 mg/Nm^3) Quencher — LP Scrubber — Compressor — Driers — HP Chiller/Scrubber — Coldbox Flue gas 4536 Nm^3/h NOx 750 ppm 1540 mg/Nm^3 1540 mg/Nm^3 600 mg/Nm^3 300 mg/Nm^3 Product 15 mg/Nm^3 MP Recycle: 45 mg/Nm^3 Regen + vent 250 mg/Nm^3 Effect of HP Chiller versus HP Scrubber: Chiller ON / HP Scrubber OFF ■ 20130702 NO ■ 20130702 NO2 ■ 20130604 NO ■ 20130604 NO2 NOx partial flow (Nm3/h) vs C371 Outlet, Chiller Outlet, HP Scrubber Outlet

3.3.6   CPU Final Inspection

In March/April 2015, a final inspection was undertaken of the CPU. This inspection revealed no notable damage to any of the parts of the CPU. Further inspection during dismantlement of the plant also did not reveal any significant plant degradation.

3.4 CO_2 Injection & Storage

3.4.1   General

The Callide Oxyfuel Project Stage 2 was concerned with two major activities: appraisal and assessment of the CO_2 storage potential of geological formations in South East Queensland; and with the more specific goal of injecting small quantities of CO_2 product from Callide A in order to advance the science and to improve the *bona fides* of geological storage of CO_2.

3.4.2 CO_2 Storage Assessments

From the commencement of the Project in May 2008, a series of studies was undertaken to seek out and assess the potential for CO_2 storage in sandstone formations within a nominal 200 km radius of the Callide A facility. This was ultimately extended to 300 km. The formations considered were as follows:

- Permian age - Natural Gas reservoirs associated with the Northern and Southern Denison Trough Anticlines some 200 – 300 km west of the Callide A site, which run North.
- Permian age – Saline aquifers at greater depth on the periphery of the Denison Trough anticlines.
- Jurassic Age – Precipice sandstone in the southern part of the Taroom Trough running north from Wandoan to Moura 100 km west of the Callide A site.
- Jurassic age – Precipice sandstone (primarily) and Hutton sandstone (secondarily) towards the base of the Surat Basin in South East Queensland.

As reported by Spero (2014), the overall conclusions in the context of these studies were as follows:

- The Denison Trough Natural Gas fields and adjacent saline aquifers have limited potential to support large scale CO_2 storage projects in Queensland.
- Resource competition with natural gas producers is problematic because of the risk of breakthrough of CO_2 in the natural gas product.
- The storage potential of deeper coal seam gas resources in Queensland is limited, and there is considerable uncertainty around, and consequential resistance to the idea of enhanced coal bed methane recovery.
- The Surat Basin Jurassic sandstone aquifers, in particular the Precipice sandstone, offer a very large potential storage medium (> 900 Mt CO_2) within the available GHG tenements.
- Significant concerns are present amongst the public and politicians about the efficacy of geological storage of CO_2, especially where there is a potential for any kind of impact on groundwater; as is the case in the Surat Basin.

3.4.3 CO_2 Injection Test

In 2014 from October to December, a series of injections of Callide Oxyfuel CO_2 product were made through CO2CRC Well No 2 into the Paaratte sandstone formation at a depth of ~ 1440 m within the Otway Basin 200 km to the South West of Melbourne (near Nirranda South off the Great Ocean Road) – Figure 14 and Figure 15.
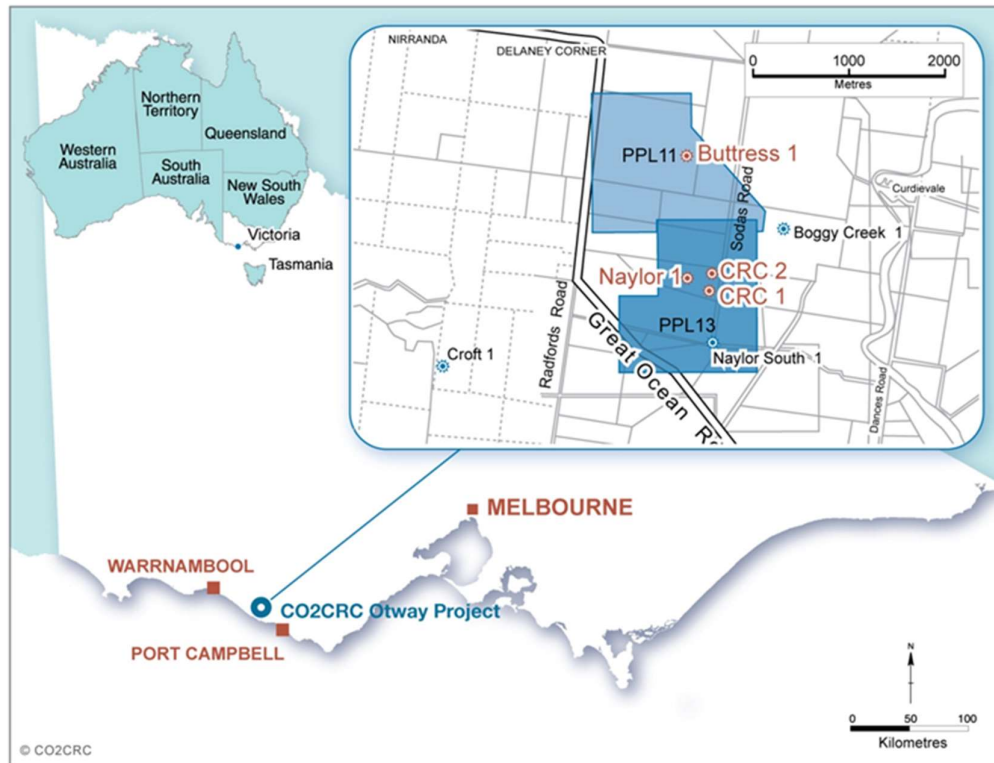
Figure 14 – Location of CO2CRC Otway Basin CO_2 storage site (Courtesy of CO2CRC)

The injection trials involved road transport in a nominal 15 t Isotainer from Callide A COP site (Figure 16) to Nirranda South (some 1300 km). The trials were conducted in two phases:

(i)   Phase 1 injection of formation water saturated with CO_2 product; pure CO_2 and CO_2 with added impurities – to assess the geochemical effect of the impurities on the formation rock in terms of dissolution of minerals, precipitation and water quality.

(ii) Phase 2 injection of pure CO_2 and CO_2-saturated formation water to assess the CO_2 saturation level (pore volume) occupied by the CO_2 in these tests – known as a Residual Saturation Test.

The primary benefit of the injection test was to advance scientific knowledge on two fronts: the effect of CO_2 impurities such as SO_2, NO_2 and O_2 on rock formation that is saturated with water; and the improvement in measurement of residual saturation testing; all of which are very important considerations in designing, permitting and operating large scale CO_2 geological storage facilities.

Figure 15 – Layout of CO2CRC Otway Basin Storage test site, as at December 2014 (Courtesy CO2CRC)

Figure 16 – Loading Liquid CO_2 into an Isotainer from the Callide A CO_2 storage tank (October 2014)

Geochemical tests (Phase 1)

Phase 1 involved initial production of water from the formation, followed by injection of water (100.2 t) and pure Callide Oxyfuel CO_2 (5.2 t), with 3 weeks soaking time interspersed with small water productions for scientific analysis. The injection was then repeated with 100t water and 4.5 t of Callide Oxyfuel CO_2 with added impurities (9 ppm NO_2, 67 ppm SO_2 and 6150 ppm O_2). In the first injection, Strontium and Bromide Tracers were added and on the second injection, Lithium and Fluorescein tracers were added.

A slight impact was observed on the formation water by the action of the added NO_2, SO_2 and O_2; the O_2 being the more significant component. However, the effects were not significant particularly given the natural buffering capacity of the formation water (Vu et al 2018; Black et al, 2018).

An additional important element of the geochemical (dissolution) experiments was to compare the results with Geochemical models (Geochemists Work Bench and TOUGHREACT ECO_2N). The purpose of the modelling was to predict water-rock interactions leading to changes in water composition, mineral dissolution rates, and precipitation of secondary minerals all of which have important practical consequences to CO_2 injection rates, storage volume, retention, and environmental outcomes.

The geochemical models in both cases predict only a very slight (insignificant) impact of CO_2 impurities on the formation water due to the inherent buffering capacity of the formation water (Todaka & Xu, 2017; Vu et al, 2018). In other words, the effect of NO_2 and SO_2 is a very slight decrease in pH (probably 0.1 pH units) with dissolution of Iron-bearing and Feldspar minerals, but with a comparable and balancing precipitation of ankerite and Mg-rich siderite.

The fate of impurities added to the Callide Oxyfuel CO_2 was also evaluated on the basis of the Reduction-Oxidation (redox) state of the system (Vu et al, 2018). This approach utilises the so called Pourbaix diagrams which can be used to depict the equilibrium between a certain mineral and the reactive component of that mineral as a function of Voltage Potential versus pH. This work highlighted the importance of O_2 as an oxidizing agent leading to dissolution of pyrite (and perhaps other iron-based minerals) which should be taken into consideration in future projects.

Residual Saturation Test (Phase 2)

An important method of CO_2 storage is by the mechanism of residual trapping whereby the supercritical CO_2 in a non-continuous condition is retained in the pores within the rock matrix as shown in the following general schematic.
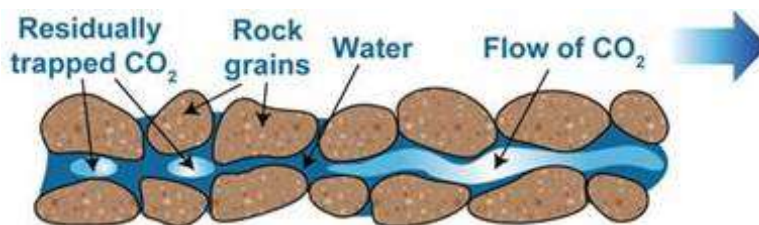
Figure 17 – Schematic indicating the mechanism of residual trapping of CO_2 in porous rock (Courtesy CO2CRC)

Residual CO_2 Saturation Testing gives an indication of the fraction of pore space in which the CO_2 is trapped following injection, determined by gamma ray detection in response to the interaction of the formation to pulse neutron bombardment. The method is referred to as the Residual Saturation Sigma Log (sum of the gamma ray detection, Σ), and involved the following steps:

- Baseline Sigma logging of the formation
- Logging after injection of pure CO_2
- Logging after injection of CO_2 saturated water

In the Residual Saturation Test, 21 t of Callide Oxyfuel CO_2 together with an additional 50 t of CO_2 supplied from BOC were injected into the formation, essentially for permanent storage.

The test results indicated CO_2 filled a fraction of 0.4 to 0.6 of the pore space near the well after injection of pure CO_2, reducing to a fraction of 0.1 to 0.2 of the pore space following subsequent water injection. The remaining fraction of pore space contains formation water. Saturation computation results were found to be dependent on which output was used in determining the fluid saturations. In this experiment, Thermal Porosity Hydrogen Index (TPHI) which is a measure obtained from the ratio of the Near to Far neutron capture, was used to compute saturations instead of Sigma Measurement (SIGM), as SIGM is prone to statistical error in low water salinities (~900ppm) during the SIGM to Saturation conversion process.

Observations and Recommendations for Further Work

Finally, it may be noted that the injection test experiments have yielded several important observations and recommendations for further work, as summarised below:

- The analysis of CO_2 impurities by different techniques gave different results and this needs to be addressed in the future projects. In addition, a better knowledge of impurity partitioning into the liquid CO_2 source is required so that an exact concentration of impurities (such as NO_x and SO_2) can be assessed. Further CO2CRC recommends laboratory experiments involving mixing of CO_2 and impurities in gas cylinders to simulate road transport conditions in order to: (a) monitor potential gas partitioning between phases; (b) determine gas reactivity with the transport container, surface facility materials and well bore sampling materials; and (c) improve the analysis of gas impurities in CO_2.

- Buffering capacity (dissolved carbonate alkalinity) plays an important role in mitigating the influences of acidification (due to the injection of NO_x and SO_2) on mineral dissolutions. Future experimental and modelling studies should consistently account for alkalinity in order to predict and interpret pH correctly.

- The importance of O_2 as an oxidizing agent leading to the dissolution of pyrite was observed in this injection study and should be considered in future projects. Sulphide minerals like pyrite are common particularly in organic-rich rocks such as coals and may be enriched in heavy metals, which may become mobilised during pyrite oxidation.

- The scope of this field test was limited to the study of fluid-rock reactions involving impurities within a given siliciclastic reservoir. Ideally, site-specific reactive transport

simulations at reservoir scale will be required to fully understand the reactivity of impurities in different parts of the reservoir and over time.

- There is a further need to better understand the impact of impurities on sealing intra-formational shales and coals, particularly the potentially associated mobilisation of heavy metals. Equally, the role of impurities on well bore cements and steels requires further studies.

- The CO_2 injection results show that typical (shallow) groundwater tracers need to be applied with caution when studying the hydrodynamics in a CO_2 storage reservoir, warranting further investigations.

4   Costing Studies

One of the key objectives of the Callide Oxyfuel Project was to assess the costs of the technology and consider the implications for large scale commercial Oxyfuel CO_2 capture projects. These items are considered in this section.

4.1   Capital Costs

The Callide Oxyfuel Project Capital Costs are summarised below. These data include an extrapolation to 2017 A$ assuming a CPI of 1.5% per year.

Table 7 – Summary of Callide Oxyfuel Capital Costs (rounded)

CAPEX	BOILER – Air-firing refurbishment (30 MWe)	ASU (660 t/day)	BOILER – Oxyfuel Retrofit (30 MWe)	CPU (75 t/day)
2012 AU$ (excludes pre-commissioning costs)	9,300	52,500	47,100	29,500
2017 AU$ (1.5% CPI) - rounded	10,000	56,500	50,800	31,700
Unit Capital Cost (2017 data)	$330/kW	$3,577/kW		$425/TPD CO_2

A cost extrapolation for large scale plant was estimated using the "Rule of Sixth Tenths" which can be used to obtain costs of different capacity plant if a base cost is known, and is expressed as follows:

$$C_B = C_A \left(\frac{S_B}{S_A}\right)^N$$

Where C_B = approximate cost ($) of equipment having size S_B
C_A = known cost ($) of equipment having corresponding size S_A (same units as S_B)
S_B/S_A is the ratio known as *size factor*, dimensionless.
N = *size exponent* (taken as 0.6 in the *rule of sixth tenths*)

For specific plant, the *size exponent* varies, e.g., Industrial boilers (all sizes) is typically 0.5; large belt conveyors, 0.65; fabric filters, 0.68; heat exchangers, 0.53 – 0.62; hammer mills, 0.85; roll mills, 0.65. Overall, a *size exponent* of 0.6 was considered to be reasonable.

Applying the Rule of Sixth Tenths to the data above and normalising the data to a unit cost, the following results for a Retrofit to a 420 MW Super-Critical Boiler such as a unit at Callide C, Tarong North or Millmerran Power Stations with 2.8 Mtpa CO_2 capture were estimated at **$1990/kW** (rounded).

Inclusion of CO_2 pipeline transport and geological storage would increase the overall capital cost by about 2.5% to ~ $2045/kW.

4.2   Operating and Maintenance Costs

A summary of the Callide Oxyfuel operating and maintenance (O&M) costs for the actual operating period (March 2012 to March 2015) are summarised below.

Table 8 – Callide Oxyfuel Project, plant O&M costs

Cost component	ASU ($/MWh)	Boiler ($/MWh)	CPU ($/MWh) – extrapolated for full CO_2 recovery

Fuel cost
  Coal
  Fuel oil
		30
		2.0	

O&M costs (non-fuel)	3.9	30	~ 4.1
Total	**3.9**	**62**	**~ 4.1**

What is evident from the costing data is that even for the Callide Oxyfuel Project, the O&M costs for the ASU and CPU plant are relatively small. In the case of the Oxyfuel boiler, about ½ of the O&M costs were fuel costs. In addition, the operating labour and site staff costs were very high, but in fact if the boiler were 420 MW as opposed to 30 MW, the number of operating staff and site staff would increase from a total of about 25 persons to not more than 50, compared with an increase in the scale of the plant by a factor of > 10 times.

As a benchmark, plant costings for large scale Oxyfuel plant from the CO2CRC/EPRI Australian Power Generation study (November 2015) provided the following summary.

Table 9 – CO2CRC/EPRI Australian power generation cost study (Nov. 2015)

Cost Component	SC		USC		Oxyfuel (USC)
	No CCS	With CCS	No CCS	With CCS	With CCS
CAPEX A$/kW sent-out	3,000	6,750	3,100	7,000	6,750
Fixed O&M A$/kW-yr	45	55	45	55	55
Variable O&M A$/MWh	2.5	10	2.5	9	12
LCOE $/MWh	76 - 82	157 - 179	77 - 83	157 - 180	158 - 180

On the basis of the cost evaluation of the Callide Oxyfuel Project and comparing with various published sources, it would be reasonable to conclude that the Capital cost of a large scale Oxyfuel retrofit should be around $2000 - $2300/kW including CO_2 storage as indicated in Section 4.1, the overall O&M costs would be between 1.5 to 2.0 times the O&M cost for a Ultra Super-critical coal power plant (without CCS), and the Levelized Cost of Energy should be about 1.5 to 2.0 times the LCOE for USC (without CCS).

5 Callide Oxyfuel Project - Commercialisation Agreements

Within the joint venture, the project partners have in place several instruments to protect ownership of Project IP and to facilitate subsequent commercialisation of oxyfuel Project IP. These instruments are briefly described below.

5.1 Patent Agreement

Over the course of development of Oxyfuel Technology led by IHI Corporation over more than a decade, some Thirteen (13) patents have been developed and successfully lodged and approved. There are four (4) specific patents as listed below granted or in the process of being granted to IHI based on Project IP, for which all the Project Partners share rights under a formal Patent Agreement.

Table 10 – Callide Oxyfuel Project, patents held by IHI for the project participants

Patent No.	Title of Patent	Country
US20120227644A1	Oxygen mixing apparatus for oxygen combustion boiler	US, AU, CA, EP (re-examination request), JP
US20130302739A1	Method and device for controlling operation of oxygen combustion boiler	JP, US, CN, EP (publication), AU, ID (examination request)
US20160169504A1	Exhaust gas cooler steam-generation prevention device for oxygen combustion boiler	JP, WO (released), KR, US, CA (decision pending), MX (applied), AU
JP2016-114309_A	Method and apparatus for controlling inlet temperature of de-dusting apparatus in oxygen combustion boiler equipment	JP, WO

5.2 Manufacturing Licence Agreement

On 15 June 2017, the Callide Oxyfuel Project Parties entered into a Manufacturing Licence Agreement (MLA) with IHI Corporation (the Manufacturing Party) in order to grant IHI Corporation a world-wide perpetual non-exclusive right to the following:

(i) Use the Project IP for the purpose of designing, manufacturing and fabricating, operating and maintaining or other utilization of Project IP Plant for sale to Project IP Plant Purchasers;

(ii) Incorporate Project IP into Project IP Plant; and

(iii) Sublicense, or otherwise grant the right to use, the Project IP as part of the Project IP Plant in a power plant or other fuel burning facility in accordance with the provisions of the Agreement and the Project IP Commercialisation Agreement.

The Manufacturing Licence Agreement defines what is agreed to constitute Project IP, Project IP Plant, and what is excluded from these definitions.

5.3   Project IP Commercialisation Agreement

On 15 June 2017, the Callide Oxyfuel Parties entered into a Project IP Commercialisation Agreement (PIPCA), intended to be an overarching Agreement that sets out the terms upon which the Parties are entitled to commercialise the Project IP.

The PIPCA acknowledges the Callide Oxyfuel Project Parties' ownership rights with respect to Intellectual Property associated with the Project, where Intellectual Property is defined in three categories, as either:

- **Background IP** being, in general terms, Intellectual Property made available for the Project by a Participant – with ownership to remain with the relevant Participant;

- **Project IP** being, in general terms, Intellectual Property that has been developed during the course, and as a part, of the Project – with ownership to be with the participants as tenants in common in proportion to their Participating Share; or

- **Subsequent IP** being, in general terms, Intellectual Property that is created outside the Project by a Participant or its Related Body Corporate as a result of further development of the Project IP or is created on the basis of, or using the, Project IP – with ownership to be with the Participants as tenants in common in proportion to their Participating Share, unless otherwise agreed by the Parties.

Though the PIPCA, each Participant grants to each other Participant, ACALET Contributor and their respective Related Bodies Corporate a non-exclusive, worldwide, royalty free right to use Project IP and Subsequent IP solely for their Internal Purposes.

The PIPCA allows the Participants, ACALET and their Related Bodies Corporate to market the Project IP and encourages the parties to continue to collaborate and work together in a spirit of honesty, integrity and in the common good of all parties to promote and facilitate the commercialisation of Project IP.

6 Oxyfuel Technology - Future Study Items

6.1 General

In the Callide Oxyfuel Project, an industrial (and semi-commercial) 30 MWe oxyfuel power plant with a partial CO_2 capture was demonstrated. There are a number of study items that have not been demonstrated in the Callide Oxyfuel Project towards the goal of commercialization. This section describes a number of technical items that should be studied in the near future to further explore the reliable and economical operation for oxyfuel power plants and CO_2 capture.

6.2 Oxyfuel Power Plant

6.2.1 Background

The basic schematic of the Callide Oxyfuel plant as given below comprises of the following:

- ASU: two x 330 t/day, cryogenic type
- Boiler: 30MWe generating capacity, retrofit to oxyfuel
- CPU: 75 t/day, CO_2 liquefaction plant

Figure 18 – Schematic of the Callide Oxyfuel plant

6.2.2 Partial Oxyfuel Operation

One of the most significant impediments to the large-scale commercialisation of oxyfuel technology is that it is not cost effective to process a side-stream of flue gas (partial CO_2 capture) as is the case for Post Combustion Capture (CO_2 adsorption) technologies. The possibility of a hybrid oxyfuel boiler consisting of for example two (2) boilers each capable of oxy-firing integrated with one (1) steam turbine, in order to reduce costs, is a possible option for partial oxyfuel operation; at least as a transitional technology option.

6.2.3   Integration of ASU and Oxyfuel Boiler

In the Callide Oxyfuel Project, most of the O_2 produced in ASUs were supplied to the boiler, but a small proportion of surplus of O_2 was released to the atmosphere. Power consumption of the ASU is quite large so it is important to minimize power consumption of the ASU without releasing O_2.

The installation of liquefied O_2 tanks at an outlet of ASUs in order to adjust the O_2 supply to an oxyfuel boiler is one of the methods that should be considered for optimising the utilisation of O_2 and the power consumption associated with its production.

6.2.4   Full integration between the Oxyfuel Boiler and CPU

In the Callide Oxyfuel Project, the CPU was sized for only a 10% side-stream of flue gas sufficient for the production of a nominal 75 t/day of CO_2, so most of oxyfuel flue gas was emitted from a stack.

A future commercial plant will need to be fully integrated between an Oxyfuel Boiler and a CPU and further studies of operations and control procedures will be necessary.

6.2.5   Control System

Further developments and studies of the control concept, mode transition or connection procedure among an ASU, an oxyfuel boiler and a CPU will be necessary relating to the above items.

In addition, there are some 'special events' such as a fan trip, master fuel trip (MFT) or run-back for normal power plants, and oxyfuel plants that must be managed safely. In the Callide Oxyfuel Project, the oxyfuel power plant was operated safely after MFT. Simulated run-back operation was also tested, but the simulated run-back test meant rapid load decreasing without stopping mills, ASU and CPU. Generally, recent commercial power plants have dual fan systems and multi-mills system. In case of run-back operation, one fan system and half of mills in the system are stopped to keep the plant operational. For future larger-scale oxyfuel power plants, a train of ASUs and CPUs may be required which will provide for partial operation of the entire oxyfuel CCS power plant when special events occur. This functionality should be studied in the future.

6.2.6   Heat integration between the ASU, Oxyfuel boiler and CPU

One of the main issues for an oxyfuel power plant is the reduced efficiency and increased quantities of cooling water required. Therefore, it will be very important to consider and further study the heat integration between the ASU, Oxyfuel Boiler and CPU in order to increase the efficiency and minimize the amount of water consumption.

6.2.7   Optimisation of the overall process

Future oxyfuel processes will need to be commercially optimised according to the requirements of the coals to be utilised, emission regulations, and impurities in the captured CO_2 product, costs and so on.

6.3 Air Separation Unit (ASU)

6.3.1 Scale-Up

Currently, the maximum capacity of a single ASU is about 5,000 t/day. This capacity corresponds approximately to the amount of O_2 required for a 250 MWe power plant. A train (2 or more ASUs) should be considered for large scale plant operational flexibility and economy.

6.3.2 New O_2 production process

Membrane technology for O_2 production has been developed in the USA and will achieve cost reductions and higher efficiency with time. Integration studies with this type of oxygen separation technology with an Oxyfuel Boiler will be necessary in the future.

6.4 Oxyfuel Boiler

6.4.1 Process/Equipment type

Firing type of boiler

The Callide-A boiler was a front wall firing boiler with six (6) burners and without staging combustion. There are some other firing types of boilers such as tangential firing, stocker firing and fluidized bed firing. Further developments and studies will be needed regarding these firing types.

H_2O remover

In the Callide Oxyfuel Project, a Turbulent Contact Absorber (TCA) type of H_2O remover was installed in order to remove moisture from a primary recycled flue gas. This was a partial H_2O remover.

There are options for more effective types of H_2O remover to be considered, such as the use of a combined low pressure scrubbing system with the CPU.

DeNOx

In the Callide Oxyfuel Project, DeNOx systems in the boiler process were not installed as the accepted technology in Australia is low-NOx burners because of the low density of population and low density residential, commercial and industrial facilities. However, the utilisation of standard DeNOX (catalytic) reduction systems will have important positive impacts on the efficiency and cost of CO_2 capture plants.

DeSOx

In the Callide Oxyfuel Project, DeSOx systems in the boiler process were not installed as the accepted technology in Australia because the domestic coal sulphur content is generally low by international standards and because of the low density of population and low density residential, commercial and industrial facilities. However, the utilisation of standard DeSOX reduction systems will have important positive impacts on the efficiency and cost of CO_2 capture plants.

Vertical/tube type mill

Callide-A boiler used beater type (high speed) mills to pulverize coal. Existing boilers use vertical or tube-ball type mills and recent USC boilers use vertical type mills because of low power consumption; which were not demonstrated at Callide A.

Electrical precipitator

Fabric filtration was used in the Callide Oxyfuel Project, and although widely used around the world, electrostatic precipitators (also widely used) were not demonstrated at Callide A.

Regenerative heat exchanger

In the Callide Oxyfuel Project, tubular type heat exchangers were used. Currently, regenerative heat exchangers are normally used in commercial power plant; which were not demonstrated at Callide A.

Air in-leak prevention system

There was no air in-leak prevention system in the Callide Oxyfuel Project to increase CO_2 concentration in oxyfuel flue gas. The high CO_2 concentration makes it possible to decrease power consumption of flue gas compressors in a CPU process.

Operation-Mill switching

In the Callide Oxyfuel Project, a mill pattern was switched during air firing, not oxyfuel, due to problems of temperature resistance for cold primary piping. Future study and evaluation of mill switching during oxyfuel operation will be necessary.

Fuel

Bituminous coals and diesel oil were burned under oxyfuel condition in the Callide Oxyfuel Project. Oxyfuel technology has a potential to use other fuel such as anthracite coal, woody biomass, petroleum coke and heavy oil.

Scale-Up

The generation capacity of oxyfuel power plant in the Callide Oxyfuel Project was 30 MWe (the world's largest oxyfuel power plant to date). Further developments and studies of scale-up will be needed to commercialize oxyfuel power plant, in particular O_2 duct/piping and mixing points due to the huge amount of O_2, operation flexibility and so on.

Others - Tapping points

Many tapping points to measure pressure, gas component and temperature were installed on the duct wall in the Callide Oxyfuel Project. Several pressure tapping points on low temperature ducts were blocked and several MFTs were caused as a result. In the Project, targeted pressure tapping points were periodically cleaned out as a practical countermeasure.

In future commercial oxyfuel plants, possible countermeasures such as material selection of pipe, addition of permanent dry gas purge system and so on should be considered respectively.

O₂ supply process (O₂ control issue)

In the Callide Oxyfuel Project, one O_2-Mix control valve adjusted O_2 flow rate to control boiler exit O_2. Therefore, it was difficult to adjust or tune O_2 control logic because very fine adjustment was required for one O_2-Mix control valve.

In future commercial plants, one idea is to place both small and large valves and to control the boiler exit O_2 by a combination of both valves.

FGLPH design

In the Callide Oxyfuel Project, erosion of tubes and fins of FGLPH by fly ash was a problem. Contributing factors included: fly ash accumulation upstream resulting in increased flue gas velocity; poor inlet duct flow design; insufficient tube face protection.

Slagging & fouling

In Callide-A boiler, there were no slagging and fouling issues on the furnace wall and super-heater tubes, probably due to the fact that the boiler was single wall fired, there was only 1 set of low-NOx burners, and the furnace was generously sized which meant that good heat pick up was always achieved and furnace exist gas temperatures were always below the minimum ash initial deformation temperature.

However, fully commercial larger-scale boilers are usually marginally designed for economic reasons and are more likely to suffer from ash slagging and fouling; so these factors will need to be re-evaluated in the future.

6.5   CO₂ Purification Unit (CPU)

Scale-Up

The capacity of the CPU in the Callide Oxyfuel Project was 75 t/day representing almost 10% of oxyfuel flue gas. The capacity of 75t/day was equivalent to 3MWe, whereas a scale of 100 times will be needed for commercialization of a CPU. However, it is noted that Air Liquide Engineering (ALE) had evaluated a CPU capacity of 200 MWe class for the proposed FUTUREGEN 2.0 Project in the USA. ALE had indicated publicly that there is no technical barrier to the commercialisation a large-scale CPU in oxyfuel power plants.

7 International CCS Standards & Reports

Under the International Standards Organisation (ISO), Technical Committee 265 (ISO/TC 265) was established several years ago to develop standards relating to carbon dioxide capture, transport and storage. There are several countries including Australia, China, Europe, Japan and the USA that are active participants in ISO/TC 265, recognising the importance of standardisation to support coal trade, CCS technology development, and global commitments to reduce greenhouse gas emissions.

Participants of the Callide Oxyfuel Project (CS Energy and IHI Corporation) have been directly involved with the preparation and review of these standards and have provided inputs from the learnings of the Callide Oxyfuel Project to these standards. The standards relating to CCS that have been published, as well as a number of draft standards under development (at the time of writing of this Report), are listed and summarised below to indicate to the reader the good progress being made in this endeavour.

The information presented on the published standards has been derived from a review of the standards themselves as well as information published in: https://www.iso.org/committee/648607/x/catalogue/.

7.1 Carbon Dioxide Capture Systems, Technologies and Processes

Document: *ISO/TR 27912: 2016 Carbon Dioxide Capture – Carbon Dioxide Capture Systems, Technologies and Processes*

Working Group: WG1 (CO_2 Capture)

Published: 2016

This Technical Report describes the principles and information necessary to clarify the CO_2 capture system and provide stakeholders with the guidance and knowledge necessary for the development of a series of standards for CO_2 capture. The technical report also covers technologies, equipment and processes specific to CO_2 capture from the viewpoints of international standardization for implementation of CCS.

The purpose of ISO/TR 27912 is to provide guidance for the development of an ISO document related to CO_2 capture as part of a CCS chain. The Technical Report covers CO_2 capture systems applicable to CO_2 emission sources and their respective boundaries, as well as capture technologies, equipment and processes.

CO_2 capture processes considered include:

- Post-combustion capture in the power industry
- Pre-combustion capture in the power industry
- Oxyfuel combustion power plant with CO_2 capture
- Capture from cement production processes
- CO_2 capture in the iron and steel industry
- Capture from industrial gas production processes

The Technical Report indicates that among combustion-type thermal power generators, coal-fired power generation is expected to expand in many parts of the world including developing countries as an economic source of power. Since coal-fired power generation causes high CO_2 emission, this is considered as a sector in which the practical use of CCS in need to be utilised.

7.2 Pipeline Transportation Systems

Document: *ISO/27913:2016 Carbon Dioxide Capture, Transportation and Geological Storage – Pipeline Transportation Systems*

Working Group: WG2 (CO_2 Capture)

Published: 2016

The objective of this document is to provide requirements and recommendations on certain aspects of safe and reliable design, and construction and operation of pipelines intended for large scale transportation of CO_2 that are not already covered in existing pipeline standards such as ISO 13623, ASME B31.4, EN 1594, AS 2885 or other standards. The document is not standalone but is written to be a supplement to other existing pipeline standards for natural gas or liquids for both onshore and offshore pipelines.

Transportation of CO_2 via ship, rail or road is not covered by this standard.

7.3 Geological Storage

Document: *ISO/FDIS 27914 Carbon Dioxide Capture, Transportation and Geological Storage – Geological Storage*

Working Group: WG3

Approved for Publication in 2017

The objective of this document is to provide recommendations for safe and effective storage of CO_2 in subsurface geological formations through all phases of a storage project life cycle.

It may be noted that this document applies to injection of CO_2 into geological formations for the sole purpose of storage and does not apply to CO_2 injection for hydrocarbon recovery, or storage of CO_2 that occurs in association with carbon dioxide enhanced hydrocarbon recovery (so-called CO_2-EOR).

7.4 Quantification and Verification

Document: ISO/TR 27915:2017 Carbon Dioxide Capture, Transportation and Geological Storage – Quantification and Verification

Working Group: WG4

Published: 2017

ISO/TR 27915 is intended to serve as a reference document for future development of any technical standards that could be approved by TC 265 for the quantification and verification (Q&R) of greenhouse gas emissions and emission reductions from CCS projects. This document is a review of current practices and requirements, for the Q&V of carbon dioxide captured, transported and geologically stored; as well as for direct and indirect GHGs than can arise from integrated CCS project activities associated with injection of carbon dioxide into geological formations. While CO_2 is the primary target of the capture process, other GHGs (such as CH_4) may be entrained in the capture stream, and emissions can include GHG's other than CO_2.

7.5   Vocabulary – Cross Cutting Terms

Document: *ISO/DIS 27917: 2017 Carbon Dioxide Capture, Transportation and Geological Storage – Vocabulary – Cross Cutting Terms*

Working Group: WG5

Published: 2017

The objectives of ISO/DIS 27917 are to provide: (i) a comprehensive list of terms and their definitions for carbon dioxide capture, transportation and geological storage including EOR, in order to facilitate communication among experts and stakeholders; and (ii) the basis for common understanding for all future ISO standards for carbon dioxide capture, transportation and geological storage.

7.6   Other ISO/TC 265 CCS Standards

There are a number of additional standards and documents under ISO/TC 265 that are still under development, as noted below.

Table 11 – Status of ISO Standards under development for CCS
(https://www.iso.org/committee/648607/x/catalogue/)

Standard	Working Group
ISO/FDIS 27916 Carbon Dioxide Capture, Transportation and Geological Storage – Carbon Dioxide Storage Using Enhanced Oil Recovery	ISO TC265/WG6
ISO/DTR 27918 Carbon Dioxide Capture, Transportation and Geological Storage – Lifecycle Risk Management for Integrated CCS Projects	ISO TC265/WG5
ISO/FDIS 27919-1 Carbon Dioxide Capture, Transportation and Geological Storage – Part 1: Performance evaluation methods for post-combustion CO_2 capture integrated with power plant	ISO TC265/WG1
ISO/FDIS 27919-2 Carbon Dioxide Capture, Transportation and Geological Storage – Evaluation procedure to assure and maintain stable performance of post-combustion CO_2 capture plant integrated with a power plant	ISO TC265/WG1
ISO/AWI 27920 Carbon Dioxide Capture, Transportation and Geological Storage – Quantification and Verification	ISO TC265/WG4
ISO/AWI TR 27921 Carbon Dioxide Capture, Transportation and Geological Storage – CO_2 Stream Composition	ISO TC265/WG5

7.7　International Status of CCS and Reports

In 2017, the Global CCS Institute published an update on the global status of CCS with particular reference to plants already constructed or under construction as indicated in the following figure.
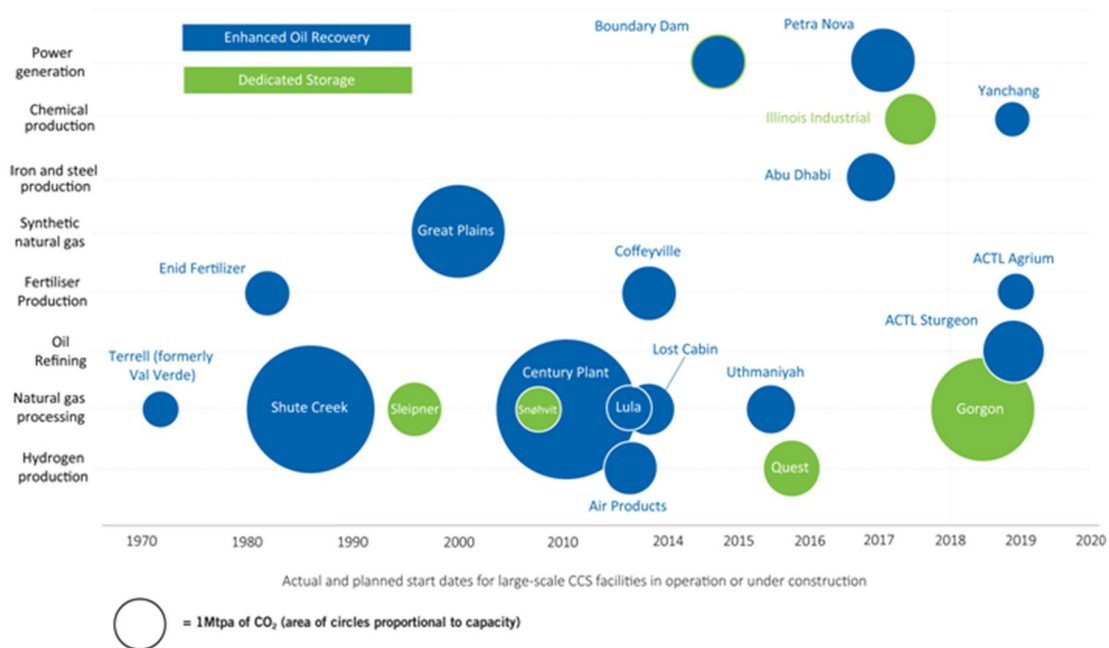

Figure 19 – Actual and planned start dates for large-scale CCS facilities in operation or under construction (GCCSI, 2017)

It is interesting to note that most of these projects have or are being established for the purpose of Enhanced Oil Recovery, or in the case of the Gorgon Project in Western Australia have a CO_2 capture component that is required by Government under the approval conditions of the respective project – but even still have an underlying commercial reason to justify the costs associated with their respective CCS component.

Finally, it may be noted that there are several significant published reports on the options and future direction for CCS and oxyfuel combustion in particular, principally prepared by the IEA GHG Programme or the IEA Clean Coal Centre, which represent detailed literature reviews or specific studies on the primary CO_2 capture technologies: Post-combustion capture, Pre-combustion capture, and Oxyfuel combustion capture (see IEA, 2007; IEA, 2010; IEA, 2012a; IEA 2012b; and IEA, 2016).

8   Conclusion

8.1   The Project

The Callide Oxyfuel Project confirmed that carbon capture technology could be applied to a coal-fired power station to generate electricity with almost no emissions. By capturing CO_2, the project demonstrated that deep cuts could be made to power station emissions to help slow the process of climate change while maintaining the use of fossil fuels as a major energy source.

As one of only a handful of coal-fired low-emission projects in the world to move beyond concept to construction, the project represented several firsts for Australia and the world.

- World's first industrial-scale demonstration of oxyfuel combustion and carbon capture technology
- World's first power station to be retrofitted with oxyfuel carbon capture technology
- First injection of CO_2 underground from an Australian power station
- World's first injection of CO_2 underground from an Oxyfuel power station.

8.2   Project Timeline

The project was conceived in 2003 as an initiative of the Australian Coal Association COAL21, and culminated in a three-year demonstration phase from March 2012 to March 2015 which achieved 14,800 hours of overall Generation into the electricity grid, 10,200 hours of oxyfuel combustion and 5,600 hours of carbon capture.

8.3   Global Partners

As an international joint venture comprising seven partners, the success of the Callide Oxyfuel Project relied on both the individual strengths of its partners, supporters and participants, as well as the group's ability to collaborate effectively to achieve an innovative solution.

The project was a joint venture partnership between CS Energy; ACA Low Emissions Technologies (ACALET); Glencore, Schlumberger Carbon Services; and Japanese participants J-Power, Mitsui & Co., Ltd and IHI Corporation. The project was awarded $63 million from the Commonwealth Government under the Low Emissions Technology Demonstration Fund and received additional financial support from ACALET and the Japanese and Queensland governments, and technical support from JCOAL.

The project was also supported throughout by the Global CCS Institute, and by the Australian National Low Emissions Coal (ANLED R&D) with particular input from the University of Newcastle and Macquarie University.

8.4   The Site

The Callide Oxyfuel Project demonstrated that new technology could be applied to an old power station to produce cleaner electricity. Built in the 1960s, the Callide A Power Station near Biloela in Central Queensland was chosen as the project's demonstration site. Retrofitting the Callide A Power Station with oxyfuel technology represented a low-risk and cost- and time-effective way to demonstrate clean coal technology on an industrial scale, and heralded a new era in the station's history.

8.5 The Technology

The Callide Oxyfuel Project demonstrated the production of electricity from coal with almost no power station emissions to the atmosphere by capturing a major portion of the flue gas CO_2 as liquefied gas, and other waste gases such as oxides of nitrogen (NOx), oxides of sulfur (SOx), and heavy metals in condensate form for dam storage together with the ash. The project involved the following key technologies and activities:

1. Oxyfuel combustion of coal to achieve a 60% to 70% reduction in the actual volume of flue gas and a proportionate increase in the CO_2 concentration.

2. Cryogenic separation and recovery of industrial grade CO_2 from the power station flue gas stream.

3. Assessment of CO_2 storage capacity in Queensland, and injection testing of Callide Oxyfuel CO_2 product.

8.5.1 Oxyfuel Technology

Oxyfuel technology enables coal to be burned more efficiently in oxygen in a power station boiler to produce a significantly reduced stream of waste gas that contains carbon dioxide (CO_2) in a concentrated form. More than 70 percent of the CO_2 from the waste gas can then be extracted in a downstream process using well-established cryogenic technology. Oxyfuel technology can therefore both technically and economically facilitate the capture of CO_2 for subsequent geological storage.

8.5.2 Carbon Capture & Storage

In addition to extracting the CO_2, the cryogenic technology removes other gaseous pollutants and normal coal-fired power station waste products such as fly ash from the waste gas stream. The industrial grade CO_2 product can be transported and stored securely and indefinitely in stable geological formations deep underground, or utilised for enhanced oil recovery from ageing reservoirs, other industrial uses; and with further minor purification can be used in food and beverage applications.

8.6 Sharing Knowledge

8.6.1 Results

One of only a handful of low-emission coal projects in the world, the Callide Oxyfuel Project made a significant contribution to the international carbon capture and storage knowledge bank. The results from the project can be applied to future low-emission projects worldwide aimed at producing cleaner and affordable electricity from fossil fuels. The project achieved:

- 14,800 hours of total generation

- 10,200 hours of oxy-firing operation

- 5,600 hours of CO_2 capture

- 320,000 tonnes of coal burned.

8.6.2　Viable Technology

The project has helped create pathways for the design and construction of larger scale oxyfuel combustion plants with carbon capture, as both 'bolt-on' technology to existing plant or as new-build plant, offering exciting future possibilities. When linked with geological carbon storage, this technology has the potential to reduce CO_2 emissions from coal fired power stations by around 90 per cent, providing a realistic technology option for low-emission electricity generation.　This technology is now ready to be scaled up and is available to be applied to commercial-scale, capture-ready power plants.

8.6.3　Contribution to Global Knowledge

In 2016/17, the joint venture partners consolidated the learnings and data from the demonstration phase of the project in a technical manual, formalised its ownership of four international patents for the oxyfuel technology, and signed a manufacturing licence agreement with IHI Corporation (Japan) to capture royalty benefits from future commercialisation of oxyfuel technology.

Significantly, the joint venture progressed oxyfuel technology from combustion of 100 kg of coal/hour in a pilot-scale test furnace in Japan to 20,000 kg of coal /hour in a modified 30 MW boiler at Callide A Power Station. Over the demonstration phase of the project, some 300 GWhs of electricity were produced and dispatched, powering the equivalent of some 10,000 Queensland homes. The next scale-up would be to full commercial scale (350 MW or larger).

Results and learnings from the project have been published either directly (see Section 10 - Publications), or through its association with research organisations such as Australian National Low Emissions Coal (ANLEC) and the Global CCS Institute.

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