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Oxyfuel derived CO₂ compression experiments with NO_x, SO_x and mercury removal – Experiments involving compression of slip-streams from the Callide Oxyfuel Project (COP)

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Abstract

Oxyfuel combustion is a CO₂ capture technology which is approaching commercial demonstration. Of practical interest is the use of the compression circuit to allow low-cost cleaning options for various flue gas impurities. This work has focussed on three species - NO_x, SO_x and Hg – and their removal during compression of “real” oxyfuel flue gas sampled as a slip stream from the demonstration Callide Oxyfuel Project. The flue gas slip stream was compressed using a bench-scale piston compressor developed to allow measurements of impurity concentrations after each compression stage using adjustable pressures. Several operating configurations were investigated including variable pressures from 5-30bar, interstage temperature changes and flow rate. Slip streams taken before and after SO_x removal allowed the impact of mixed NO_x/SO_x gases to also be investigated. The results from the “real” oxyfuel flue gas experiments for the three species were similar to those performed in the laboratory using synthetic flue gas and reported previously. The capture of SO₂ was found to be greater at low pressures than NO_x capture, with 90% removal of SO₂ by a pressure of 10 bar, with NO_x capture extending to higher pressures. The effect of residence time during compression had the greatest influence at higher pressures (>10bar) where the kinetic rate of NO oxidation to NO₂ increases less with pressure increase. Capture of NO_x was increased from 55% to 75% by doubling the residence time in the compressor and could be further extended to 83% by increasing back end pressure from 24 bar to 30 bar. Lowering the temperature during compression produced the greatest NO_x and Hg capture. Overall, the results indicate that capture of mercury during compression occurred as a consequence of high pressure, longer residence time and concentration of NO₂.

Introduction

The increase in anthropogenic CO₂ emissions has been linked to climate change and one of the largest sources of CO₂ is the generation of electricity [1]. Currently coal fired power stations produce 42% of the world's electricity [2] and coal combustion accounts for 43% of the world's CO₂ emissions [3]. However, with the world's population predicted to increase to 8.2 billion by 2030, the rising demand for electricity is expected to increase the need for coal fired power generation [4]. Oxy-fuel combustion is one CO₂ capture technology which reduces the emission from coal fired power utilities and allows safe storage of the CO₂ in deep underground aquifers.

Oxy-fuel technology is based on the combustion of coal in a mixture of O₂ and recycled flue gas, producing a flue gas rich in CO₂ which is then compressed, liquefied and injected underground. The technology has been significantly reviewed as it moves towards demonstration [5-9]. With the recycle of flue gas, oxyfuel systems are known to produce higher impurity levels and these gas cleaning challenges can be met with a number of plant configurations [10]. Traditional gas cleaning units (such as FGD's for SO_x removal) have been shown to operate to similar performance capabilities as in air fired conditions [11, 12]. However, a particular benefit of oxyfuel combustion (and of considerable interest) is the passive removal of impurities during CO₂ compression.

Air Products have demonstrated the potential removal of SO_x and NO_x during compression using the well-known lead chamber process [13, 14]. Other systems, such as LINDE's compression plant at Vattenfall's Oxyfuel Pilot at Schwarze Pumpe [11, 15] and the University of Hamburg's Oxyfuel pilot plant [16] have already demonstrated that acidic condensates as low as pH of 0.8 can be formed by compressing oxyfuel flue gas containing NO_x. However, little work has been performed on mercury removal in an oxyfuel CPU. Mercury (as gaseous Hg⁰), must be substantially removed prior to the CO₂ liquefaction, as brazed aluminium heat exchangers used in the process are well known to be corroded in the presence of mercury [17]. From the natural gas industry, the current permissible limit on Hg concentration entering a brazed aluminium heat exchanger is 0.01 µg/m³, corresponding to the current limit of measurement. A summary of typical Hg concentrations is given on Table 1. Given that Hg concentrations exiting an oxy-fuel boiler are between 2.7 - 45 µg/m³ [18, 19], this suggests that a significant level of cleaning is required prior to CO₂ liquefaction. It has been previously theorised that flue gas borne mercury (present as Hg⁰) will be absorbed in the nitric acid formed from compressing the raw CO₂ from an oxyfuel system [20]. However, a recent study on mercury behaviour in pressurised systems found that the dominant removal pathway was by reaction with NO₂ in the gas phase [21]. Without NO₂ as a gaseous oxidiser, Hg⁰ was both absorbed and desorbed as a dissolved gas.

This ties the removal of mercury to the absorption of NO_x in compression condensate, and (if successful) could replace the more expensive traditional options such as activated carbon beds. A number of fundamental studies on the compression of oxyfuel flue gas have been reported by the University of Newcastle (UoN) [21-23] with a focus on NO_x and Hg behaviour at higher pressure. The latest study has involved the development and laboratory testing of a bench scale piston compressor to study behaviour under real compression conditions [22]. This fundamental work was undertaken in support of the Callide Oxyfuel Project (COP). This current study details the use the bench scale compressor with real oxyfuel flue gas sampled from slip streams during a two week field campaign at the COP.

TABLE 1. Industrial mercury limits

Mercury Limit	Concentration $\mu\text{g}/\text{Nm}^3$	Note
Expected Hg in flue gas from coal	10-50	Without capture
Occupational Safe Working Limit	10	Based on TWA (8 hour time weighted average)
Australian Gas Quality Standard	1	AEMO Natural Gas Rules ¹
Brazed Aluminium HEX Standard	0.1	ALPEMA recommendation ²
Typical Design Specification for Carbon Bed	0.01	for natural gas processing ^{3,4}
Analytical Limit	0.0001-0.002	Instrument dependent

¹ Australian Energy Market Operator; Gas Quality Standard – System Injection Points 2007 [24]

² Aluminium Plate-Fin Heat Exchanger Manufacturer Association Standards 3rd Edition 2010 [25]

³ Francis, “Brazed Aluminium Heat Exchangers – BAHX- Surveillance, Analysis, Mitigation” [26]

⁴ Santos, “Challenges in Understanding the fate of mercury during oxyfuel combustion” [17]

Experimental

Laboratory piston compression apparatus (continuous gas / continuous liquid)

The apparatus used for evaluating Hg behaviour in oxyfuel was a laboratory scale compression system built from a three stage air compressor (RIX Industries Model SA-3) and modified to allow gas sampling between compression stages and interstage variation of pressure. This apparatus is described elsewhere [22]. Figure 1 shows a diagram of the apparatus using the same gas and Hg feeding system with the addition of a H₂O bubbling saturator prior to entering the compressor. Table 2 provides a summary of the compressor details and its modifications. The compressor was fitted with a variable speed drive to change the gas in-take (ie in effect changing the residence of the gas). After stages 2 and 3 a back pressure regulator, pressure relief valve and pressure gauge were fitted to allow the pressure to be altered within the compression circuit. Sampling of the gas occurred using a dilution system which pulled 9L/min of compressed air through a critical orifice and venturi providing a 0.5bar vacuum for sampling 1L/min of gas through a second orifice. This combination diluted the sample gas by 1:10 and allowed the NO_x analyser to handle high NO₂ concentrations (typically limited to ~100ppm NO₂). A dry gas meter measured the gas flowing out of the compressor after passing through an activated carbon scrubber.

Figure 1. Laboratory compression system with gas feeding system (feeding O₂/N₂/NO, Hg⁰, H₂O), three stage axial piston compression and interstage gas and liquid sampling.

Liquid samples were taken after compression stages 2 and 3 using the moisture separators provided with the compressor. The modifications involved removing the copper cooling coils in favour of flexible high pressure teflon tubing braided with stainless steel and a 300mL 304SS sample cylinder. The liquid sampling modifications are shown in Figure 2. These additions allowed for indirect water cooling of the compressed gas leaving the piston stage and for condensation of water. This step was considered important from the perspective of simulating mixing conditions between gas and liquid prevalent in compression (ie high surface area, wetted walls, condensing droplets). The gas/liquid mix was then directed to the moisture separators, where the liquid was allowed to build-up until reaching a suitable sample volume. The gas exited from the top of the separator and passed through the back pressure regulator and into the next stage (ie either 3rd stage piston or exit). The liquid was sampled in a highly controlled method using a fine needle valve and could be sampled directly into a container or directed towards an air-aspirated sample cylinder (300mL, 304SS). For the field testing at Callide only total liquid samples were taken due to time restraints. The volatile analysis of the liquid condensates typically takes several hours and uses both the NO_x and Hg analysers.

Figure 2. Detailed diagram of interstage compression line showing water condensation, gas-liquid separation and liquid sampling system using controlled de-pressurisation and air aspiration.

TABLE 2 Summary of Compressor Details and Modifications

	Initial System	Modifications
Description	RIX Industries Model SA-3 oil free, three stage, axial piston air compressor, designed for SCUBA tank filling	
Functional	3HP electric motor Maximum pressure 248bar 3CFM flow rate at a speed of 2300RPM	2HP max after fitting with variable speed drive Pressure Gauges + control to 40 bar, relief valve to 50bar 2CFM
Compressor	Piston Size: 1 st stage ~60mm diameter 2 nd stage ~25mm diameter 3 rd stage ~12mm diameter Stroke ~24mm Oil free Cooling: Forced air fan	Air cooling coils removed, gas sample point added to 1 st stage Condensers and interstage pressure controls + added gas sampling point to 2 nd & 3 rd stage Water cooled
Gas Analysis	Thermoscientific 42i-HL Chemiluminescent NOx Analyser (0-1000ppm range) Ohiolumex RA-915+ Hg ⁰ Analyser (0-20,000ng/m ³ range) M&H Dilution System (1:10 critical orifice + venturi sampling) Testo Flue Gas Analyser 350XL (for FEED) (O ₂ , CO, NO, NO ₂ , SO ₂)	Furnace System added for thermal conversion of gaseous Hg ²⁺ at 700°C Connected to interstage sample points with ON/OFF and needle valves for flow regulation

	Bosch Wideband O ₂ Sensor Accutherm Dry Gas meter (0-60L/min, pulse output every 10L)	
Liquid Analysis	Horiba pH probe (calibrated range pH 1-7) Horiba Nitrate probe (calibrated to 2000mg/L NO ₃ ⁻) Dionex Ion Chromatograph (calibrated to 500mg/L NO ₃ ⁻) Hg content in liquid "Volatile" NO _x + Hg in liquid tested using gas analyser system (see Figure 2)	Dilution required Use of KMnO ₄ /H ₂ O ₂ for total N & nitrite, dilution required Dilution required Used SnCl ₂ /HCL injection into liquid combined with M&H Dilution System+ Ohio Lumex RA-915+ Hg ₀ gas analyser above

Comment on NO_x gas analysis

The analytical method used for NO_x gas analysis was based on chemiluminescent detection. These units are the commonly used systems in commercial application. This method detects a total NO_x and uses a convertor to provide the difference between total NO_x and NO₂. In this case the NO₂ difference signal may be comprised of other N species, of which N₂O₄ is expected to be measured as 2xNO₂ (due to the equilibrium between NO₂/N₂O₄) and amounts of N₂O₃, N₂O, HNO₃, HNO₂ (all of which may be detected to varying yet unquantifiable degrees). It should also be noted that the gas measurements are made at atmospheric pressure after exiting the pressure vessels. It is expected that this may also have an influence on species such as N₂O₄, N₂O₃ and HNO₂. As such the term NO₂ is used here with the understanding that other species may be present and future work should be focussed on clarifying the presence and quantification of these gases.

Callide Oxy-fuel Project Field Trial – Compression of real flue gas

The field trial of the laboratory compressor was undertaken over a two week period in October 2013 with the following aims:

- 1) Determine the effect of SO₂ on NO_x conversion during compression
- 2) Determine the influence of residence time under pressure
- 3) Determine the influence of temperature on NO_x conversion
- 4) Compare laboratory compression results to actual gas measurements on the Callide CPU

The effect of SO₂ during compression was expected to be associated with reactions with the

NO₂ via the lead chamber mechanism, rapidly producing H₂SO₄ and NO (ie NO₂ acting as an oxidiser) with the overall impact being to reduce Hg conversion in compression. The concentration of SO₂ was altered by selectively sampling from before and after the low pressure caustic scrubbers. Figure 3 shows the Callide CPU diagram with slip stream sample point indicated. The high SO_x slip stream was taken at the inlet of the quench column, where flue gas enters the column directly from the boiler block at ~150°C, containing high moisture (~22% H₂O) and high particle concentration (~150mg/Nm³). The slip stream was sampled by flexible ~12mm PFA tubing, which has a high thermal resistance and low Hg absorption. Sampling of the high SO_x stream occurred without heated lines and thus was cooled and partially condensed out into a large impinger and dust filter prior to entry into the compressor. The residence time of the gas passing through the laboratory compression system was controlled by changing the speed of the drive motor which in turn altered the compressor intake. Overall, the low flow rate tests were performed at ~10L/min (STP) and the high flow rates were ~20L/min (STP). The effect of temperature was examined by cooling down the two condensing units placed after the 2nd and 3rd stage pistons. These condensers typically sat in a bucket of water allowed to stay at ambient temperature (~34°C), however a full testing day was performed with iced water, with the level of ice maintained in the bucket throughout the testing period allowing a constant measured temperature of ~0°C.

The laboratory compression system and associated analytical instruments were located down on the CPU bench between the caustic scrubbers and the Air Separation Unit. A photograph taken from a nearby observation point shows the UoN set-up location relative to the Callide Oxyfuel Plant is shown in Figure 4. A high top van was used to house the analytical equipment (eg computers, gas analysers) and a gazebo was erected to house the compressor system and associated sampling equipment. A summary of sampling activities is given in Table 3.

Note on Actual Temperature and Pressure (ATP)

Under these testing conditions the flow rates were measured from the compressor exhaust using a dry gas meter. This gas could be considered to have water content under saturated conditions at 30 bar pressure and ambient temperature (34°C) of ~1860ppm, which have been assumed to be negligible. Rather than correct for a lower temperature, these flow rates were set at ambient conditions and reflect the true volumetric flow rate (and hence residence time) at the time of sampling. As such the term ATP here refers to 34°C and 101.3kPa for this study.

Figure 3. Diagram of Callide CPU with gas slipstream sample points (red) for compression apparatus and other samples including liquids (blue) taken during field trial. Note that the 2 compression symbols represent 2 stages of compression each. Condensates are removed after compressor stages 2 and 4.

Figure 4. Photograph of the UoN se-up with the parked white van with analytical equipment relative to the CPU and ASU of the Callide A Power Station, showing the oxy-fuel retrofit.

TABLE 3. Description of sampling points and test operations

Sampling Point and approximate gas conditions [27]	Aim	Samples Taken on Compressor
<u>Scrubber 1 Inlet</u> (CPU feed) Stack conditions ~150°C 19-22% H ₂ O 150-250 mg/Nm ³ dust	High SO _x Low Flow 10L/min (Preliminary)	Full Gas Suite Feed/3 rd /2 nd /1 st stage 0 / 24 / 8 / 3 bar
	High SO _x Low Flow 10L/min	Full Gas Suite Feed/3 rd /2 nd /1 st stage 0 / 24 / 8 / 3 bar 2 nd Stage Suite (5-10bar)
<u>Scrubber 1 Outlet</u> (compressor feed) Clean-cool conditions 35°C 5-7% H ₂ O <0.02 mg/Nm ³ dust	Low SO _x High Flow 20L/min (Preliminary Run)	Full Gas Suite Feed /3 rd /2 nd /1 st stage 0 / <u>30</u> / 8 / 3bar
	Low SO _x High Flow 20L/min	Full Gas Suite Feed/3 rd /2 nd /1 st stage 0 / 24 / 8 / 3bar 2 nd Stage Suite 5-18bar
	Low SO _x Low Flow 10L/min	Full Gas Suite Feed/3 rd /2 nd /1 st stage 0 / 24 / 8 / 3bar
	Low SO _x Low Flow 10L/min ICED condensers	Full Gas Suite Feed/3 rd /2 nd /1 st stage 0 / 24 / 8 / 3bar

Results

Laboratory compression unit field testing

The compression system was run for a total of 5 days, typically obtaining a full suite of analysis over ~6 hours. A typical result is shown in Figure 5, whereby the compression stages are sampled in reverse from 3rd stage to feed in order to avoid the downstream impacts of sampling (ie a reduced gas flow lengthening the residence time in the compressor). Also of note is the asymmetric cycles in the gas concentrations. These fluctuations are considered

typical of real flue gas and ultimately result in longer required sampling periods to obtain sufficient variation. In practice, at least three cycles were considered a minimum before switching the sample. Figure 5 shows that these cyclic variation begin with NO and Hg, in particular the Hg represents variation of ~30%. As the pressure rises from 1st through to 2nd stage the cycles can be observed to pass into the NO₂ as greater amounts of NO was converted, however by the 3rd stage the residence time inside the final stage acts as a blending vessel, smoothing out the cycles. Figure 5 also shows a break in data collection, where the concentrations drop to zero. These periods represent a manual baseline check of the Hg analyser using zero air passed through an activated carbon bed, which was followed by a switch between the Hg sample flowing through the furnace (set at 700°C) to obtain a Hg^{total} or bypassed to obtain the Hg⁰. For every compressor test performed there was no significant difference between Hg^{total} and Hg⁰ observed, suggesting that no oxidised mercury species are present in the sampled gas streams.

Figure 5. Typical gas results for a full suite of compressor operation with sampling from high to low pressure.

Full suite analysis was performed for conditions of high and low flow in the compressor with the low SO_x slip stream, as well as a low flow run from the high SO_x slip stream. These runs used comparable pressures in the three stages of the compressor; namely 1-3bar in the 1st stage, 8-10bar in the 2nd stage and 24bar in the 3rd stage. The 3rd stage pressure of 24 bar was set in order to match the pressure of the Callide CPU compression block. Two other full suite

runs were also performed on the low SO_x slip stream; the first was a high flow condition using 30 bar in the 3rd stage and the other was a low flow condition using the ice in the condenser. A second set of experiments were also performed on the 2nd stage only, typically varying the pressure from 5-18 bar. These fundamental runs were obtained at the high flow condition on the low SO_x slip stream and at the low flow condition on the high SO_x slip stream. The results for these experiments, both full suite analysis and fundamental 2nd stage pressure tests are summarised in Figures 12-14 in terms of NO, NO₂ and Hg. The NO concentration (Figure 6) decreased exponentially with higher pressure, with the rate of conversion becoming slower as concentration is reduced. The majority of the reaction occurs at lower pressure with approximately 68% of the NO converted within the 10 bar pressure range. The apparent scatter in the data was caused by the cyclic variation in the plant and compared to this scatter, the overall impact of the flow rate and SO₂ concentration do not appear to be significant. However, the low SO_x condition did result in a lower NO concentration in the 2nd stage. The iced condensers do appear to show an impact greater than the variability of the data, giving a lower NO concentration throughout the compression range, despite having a higher feed NO. This is expected given that the conversion of NO to NO₂ favours lower temperature.

The formation of NO₂ in Figure 7 shows the opposite in the low pressure region, increasing in concentration up to 10 bar, however the concentrations appear to reach a plateau at higher pressures as the rate of capture becomes increasingly significant. It is in the 3rd stage compression that the NO₂ concentrations show a significant difference between experimental conditions, with the high flow (and thus lower residence time) having the highest NO₂ concentration and therefore the lowest capture rate. The extended 30bar test in the high flow condition suggests that greater capture is possible at higher pressure. The low flow conditions with both high and low SO₂ concentration do not appear to provide significant difference in NO₂ concentration, however both low flow conditions give a lower NO₂ than the high flow condition. It should also be noted that the low SO_x condition also resulted in a higher NO₂ in the 2nd stage. The iced condensers gave the lowest final NO₂ concentration, approximately half the high flow condition.

Of the three gas species, Hg showed the most variation both in its cycles and between testing days. During the course of the testing program, the Callide plant operators and engineers revealed that several return loops from the back of the CPU can be mixed into the incoming feed gas. Largest among these was the use of clean CO₂ product gas to pulse the primary dust filter located after the caustic scrubbers. These pulses were set at approximately every 15 minutes, which is similar to most of the cyclic fluctuations measured in the NO_x concentrations, however the actual pulse rate could be set by operators and this value varied depending on which operator was asked. Figure 8 gives the effect of higher pressure on Hg in the gas stream. As with the NO/NO₂, these numbers are represented as an average for each sample period and therefore appear scattered due to the effect of the cycle trend. As stated earlier, no difference in Hg^{total} and Hg⁰ was observed, proving that all of the Hg is present in the gas stream as elemental Hg. This was consistent with the laboratory results. The effect of pressure is pronounced on the Hg in the gas stream, being systematically reduced with higher pressure. There does not appear to be any clear effect of high flow, but the iced condensers show lower Hg concentration exiting the 2nd stage. This value is the same exiting the 3rd stage, indicating that no capture of Hg occurs in the 3rd stage under the iced condenser condition. It must be stated that not all conditions are represented across the full pressure range, with the low flow / low SO_x missing the 3rd stage Hg measurement and the high SO_x / low flow not included. The incomplete data set for the low flow low SO_x was due to a power

failure, which resulted in a loss of data on the Hg analyser. The high SO_x low flow data set was not included because of the negative influence of the SO₂ on the Hg baseline – a consequence of the high response analyser used.

As a summary of the removal potential during compression, Figure 9 shows the total NO_x and SO_x exiting each pressure setting of the compressor. Within the variability of the data, there appears no clear trend in NO_x between testing conditions in the 2nd stage, however the 3rd stage high pressure region reflects the same trend of the NO₂, with the higher flow producing less capture, followed by the low flow condition and finally the iced condenser producing the greatest NO_x capture. The SO₂ shows a much larger effect from increased pressure, with 80% of the SO₂ captured at 10 bar in the 2nd stage and 96% captured by the 3rd stage. Overall, the impact of SO₂ on NO_x capture does not appear to be significant under these conditions. Furthermore, it was expected that no NO_x capture would occur until the SO₂ was completely removed, but this was not observed, with both SO₂ and NO_x being captured simultaneously.

Figure 6. Removal of NO with pressure

Figure 7. Formation of NO₂ with pressure

Figure 8. Removal of Hg with pressure

Figure 9. Impact of compression pressure on NO_x/SO_x removal

Comparison of Laboratory & Field Results

The field trial results were compared against the previous laboratory results. The previous laboratory results were based on a full suite analysis using controlled NO_x injection between 500-1500ppm NO and controlled Hg injection of 1000ng/m³. Figures 10-12 show these comparisons in terms of the amount of NO converted, the amount total NO_x captured and the amount of Hg captured. The *NO converted* is based on the difference between NO concentrations from the feed NO to each pressure setting. Figure 16 shows that the two high flow cases in the field trials lie on the same conversion trend, approximately 10-15% lower than the low flow case. The 2nd stage low flow condition in the field results corresponds well with the laboratory work performed at the same pressure and flow rate (10L/min), while the 3rd stage low flow condition in the field results corresponds well with the trend in laboratory data despite being at different final pressure settings. The previous 3rd stage laboratory results were performed at 30 bar, rather than 24 bar, however these results are also very close to 100% NO conversion.

By comparison, the amount of total NO_x removed from the system through compression gives a measure of the capture performance under different conditions. Figure 11 shows the *NO_x captured* for the two data sets. Once again, all results compare well up to 10 bar, however in the higher pressure range the high flow conditions show a lower overall capture rate due to the shorter residence time.

The capture of Hg during compression involves a significant number of variables, in particular the concentration of NO₂, which in turn is affected by residence time, temperature and water condensation. A comparison of Hg capture across the two data sets (Figure 12) shows a relative increase with higher pressure leading to a significant amount (95-100%) of Hg removed at 30 bar. However the data sets diverge during the 2nd stage compression with much higher Hg capture demonstrated in the laboratory testing at high NO_x levels (1000-1500ppm) and much lower results for the low NO_x laboratory tests at 500ppm. A potential reason for this difference is that these laboratory tests were performed in Newcastle during winter when laboratory temperatures were typically below 20°C leading to lower inlet water vapour concentrations and a lower condenser temperature. By comparison the field testing occurred at Callide during spring with ambient air and condenser temperatures of ~34°C. The effect of lower temperature in the field tests can be clearly observed in the iced condenser test which showed a significantly higher capture rate in the 2nd stage compression. In the 3rd stage at 24 bar the iced condenser result shows higher capture than the high flow condition at the same pressure settings gaining approximately 10% higher capture.

Figure 10. Comparison of NO converted during compression between field tests and laboratory results at three different NO feed rates.

Figure 11. Comparison of NO_x captured during compression between field tests, and laboratory results at three different NO feed rates. Laboratory tests were performed at the low flow rate of 10L/min. The high flow tests were performed at 20L/min

Figure 12. Comparison of Hg captured during compression between field tests and laboratory results. Laboratory tests were performed at the low flow rate of 10L/min. The

high flow tests were performed at 20L/min

Discussion

The field trial at the Callide Oxyfuel Project examined three main variables during compression, namely: the effect of SO₂, residence time and temperature. The presence of SO₂ was found to impart a minor reduction on the conversion of NO into NO₂ in the 2nd stage of the compressor but did not affect the amount of NO_x captured. No effect of SO₂ was observed in the 3rd stage most likely because the SO₂ was removed in the 2nd stage. However, SO₂ was found to be readily captured during compression, suggesting that it remains a viable and passive cleaning option. Residence time was shown to have the greatest impact in the 3rd compression stage, with a doubling of flowrate lowering the conversion of NO to NO₂ by 10% and reducing NO_x capture by 20%. Extending the pressure range from 24 bar to 30 bar had a minor impact (+5%) on NO_x captured but higher impact (+12%) on Hg captured.

Recent work presented on the Schwarze Pumpe [28] oxyfuel pilot-plant compared different trials in NO_x and SO_x capture including traditional FGD systems and CPU options (Table 4). Linde, the original suppliers of the Schwarze Pumpe CPU, have undertaken pilot work on their LICONOX process which uses a high pressure scrubber with ammonia water run at approximately pH 7. Passing through the compressor units, the NO_x removal was ~50%, with an additional 25-30% removed in the trial scrubber. The potential benefit of this process was an ability to regenerate the solution to produce N₂. An added benefit was the stabilisation of the solution chemistry enabling better handling of by-products. Air Products have also conducted a pilot trial of their sour gas compression circuit. Under this process, both SO_x and NO_x are included in compression, with SO₂ being preferentially removed in the first column (15bar) and the NO_x being removed in the second column (30bar). The SO₂ oxidation and removal was previously considered due to the catalytic oxidation from NO₂ (forming NO) [20]. However, recent modelling work has suggested that this process occurs in the liquid phase [29], either through the lead chamber process (resulting in NO desorbed from the liquid) or the rashig mechanism (resulting in the formation of N₂O). This liquid phase concept is supported by the field compressor experiments which showed only an influence on NO conversion and no influence on NO₂ or the amount captured from the gas phase. Moreover, in their pilot trials Air Products showed that SO_x capture could be affected by the feed SO_x/NO_x ratio with lower ratios favouring higher capture rates. The SO₂ concentrations during the Air Products testing ranged as high as 2000ppm with NO_x between 180-400ppm. In the Air Products trials, these SO_x/NO_x ratio ranged from 3-11 producing SO₂ capture rates from 100% down to 20%.

By comparison, the SO_x/NO_x ratio in the Callide field tests was approximately 1, suggesting that sufficient NO_x would be available for accelerated SO_x capture. The complex chemistry involved in this process is not fully understood, nor is the effect of pressure. However, in both the lead chamber process and the rashig mechanism, a significant amount of H₂SO₄ is required and it remains up to future work to determine whether the use of water or alkaline solutions can effectively buffer the formation of N₂O in mixed SO_x/NO_x conditions under pressure.

Temperature Effects

The effect of lowering temperature from 35°C to 0°C using ICED condensers produced a

significant increase in the amount of NO_x and Hg captured. As previously predicted [30], the oxidation of NO to NO_2 is partially driven by an “activated” NO species which favours lower temperature. The following dimerization of NO_2 to N_2O_4 also favours lower temperature ultimately producing a greater conversion of the feed NO into N_2O_4 . Figure 13 gives the modelled NO conversion to NO_2 and the predicted equilibrium N_2O_4 for both temperatures in the 2nd stage (10 bar). The model shows that the difference in NO conversion between temperatures is relatively small compared to the predicted difference in N_2O_4 concentration. Figure 14 shows the influence that temperature and NO_x concentration has on the gas phase Hg^0 concentration. In both figures, the grey dotted line indicates the residence time inside the second stage of the laboratory compressor. In both temperature cases, the Hg^0 is consumed well before the end of the compression stage. In comparison, the lower temperature also changes the amount of water condensed in each compressor stage – increasing the amount condensed in the second stage from 84% to 98% of the feed H_2O and decreasing the amount in the third stage from 9% down to 1% of the feed H_2O . Despite this reduction, the amount of NO_x captured in the 3rd stage was increased, suggesting that the amount of liquid water formed is not a driving influence in capturing NO_x in the condensate.

The combination of higher NO conversion and higher $\text{NO}_2/\text{N}_2\text{O}_4$ concentrations had the greatest impact on the Hg captured in the 2nd stage. While the literature is scarce on the mechanism of the reaction between Hg and NO_x , the modelled effects of temperature on the NO_x kinetics and equilibrium suggest that N_2O_4 is in fact the likely reactive species as previously suggested [31]. In the previous report [30] the laboratory results indicated that the presence of liquid water was not required for Hg capture, but the capture of NO_x from the gas phase into the liquid retarded the Hg capture. The iced condenser condition in the field tests changed the amount of liquid water present and did not result in a significant increase in extra NO_x captured in the 2nd stage. It did, however, have a large influence on Hg captured, supporting the previous laboratory observations.

Figure 13. Modelled NO conversion and equilibrium N_2O_4 at 10 bar for temperatures of 35°C and 0°C. Greyed dotted line gives approximate residence time in the 2nd stage of the laboratory compressor in the experiments.

Figure 14. Modelled Hg^0 conversion at 10 bar for temperatures of 35°C and 0°C, based on the reaction with N_2O_4 . Greyed dotted line gives approximate residence time in the 2nd stage

of the laboratory compressor.

Practical Implications

Slipstream measurements using actual flue gas taken from the bench-scale compressor agree with synthetic flue gas measurements taken from the bench-scale compressor in the laboratory. The field measurements taken from a slipstream from a real oxy-fuel flue gas showed similar conversion with higher pressure and in terms of actual concentration. The natural cyclic variability of the real flue gas is a feature which could not be replicated in the laboratory.

The impact of SO₂ on NO_x conversion in compression was minor, producing a measurable difference in NO conversion but no difference in NO_x captured. The expectation that SO₂ would react with NO₂ and thus reduce its capture is derived from the work of Air Products, however the ratio of SO_x to NO_x is apparently sufficient to provide the accelerated SO_x capture effect without significant influence. This suggests that passive capture of both SO_x and NO_x during compression is viable providing the operational envelope for N₂O formation is determined (N₂O was not measured in the current campaign).

The amount of Hg that was removed from both the experimental compressor sampling a slip-stream and the Callide CPU satisfy the Hg limit for natural gas compression limit of 10 ng/m³.

The practical implications suggested in previous work [30] on laboratory measurements of synthetic gas are confirmed by the present results on real oxy-fuel gas at the COP.

Implications confirmed from previous laboratory work

Gaseous Hg⁰ in the flue gas can be effectively removed from the gas stream using the compression circuit during back-end CO₂ processing. This reduces the risk of mercury corrosion of cryogenic aluminium heat exchangers and suggests that dedicated removal units, such as an activated carbon bed are not necessary in an oxy-fuel circuit. These findings represent a paradigm shift in mercury control for oxy-fuel technology and reduces the emphasis on upstream speciation and capture. Furthermore, this passive gas cleaning option in oxy-fuel is a low cost advantage over other capture technologies such a post-combustion capture which require significant cleaning prior to CO₂ removal.

The main pathway for oxidation occurs in the gas phase with NO₂/N₂O₄, rather than in the acidic condensate. The conditions which enhance NO oxidation are the same as that for Hg oxidation, namely higher pressure and residence time. However, the presence of liquid water in an oxy-fuel compression circuit is both necessary for removing NO_x and a hindrance for removing Hg. This work has shown that Hg⁰ can be dissolved in acidic liquid at high pressure, but does not form a stable salt without the presence of a gaseous oxidiser. Therefore the premature capture of NO_x into the liquid condensates will retard the removal rate of Hg⁰. Future design of back-end oxy-fuel CO₂ processing plants could enhance the Hg oxidation rate by prolonging the residence time prior to intercooling and condensate removal.

The final oxidised Hg product has yet to be identified. This research has shown that Hg⁰ is removed from the gas phase but has yet to identify the product of oxidation. Likely candidate products are a Hg-NO_x salt or HgO, however the valence of the Hg atom affects

solubility, and may well impact the potential removal in the condensate. The results of this work have shown that a significant portion of the gaseous Hg was not removed in the condensate and was not present in the gas as Hg^{2+} . It is therefore possible that the Hg is being deposited in a section of the laboratory compression apparatus which is not being regularly contacted with water or that the compound is not soluble. On a larger scale, this may ultimately present a risk of blockage or a safety hazard during shut-down. Identification of the final oxidised form of Hg under compression conditions will offer insights into its behaviour during compression and ultimately result in better circuit designs to optimise its capture.

Highly acidic condensates represent a corrosion and safety risk. The analysis of the condensates indicated a significantly high acidity which consisted predominantly of HNO_3 . Given that the mass balance closure was relatively poor, there is high possibility that deposition of HNO_3 is occurring in non-wetted sections. Given that observed blockages were found in areas surrounding the back pressure regulators and piston head it is also possible that other NO_x species such as N_2O_5 (a white solid at room temperature) may also be formed. In this work, the blockage was easily removed with water and future design options may take advantage of such solubility to remove potential build-ups. The emission of NO_x gases produced from depressurising the liquid condensates present a potential safety hazard. Liquid condensates from compression should be depressurised in a controlled way to allow off-gassing to be recycled back into the process.

Conclusions

The removal of NO_x , SO_x and Hg during compression of “real” oxyfuel flue gas was investigated using a novel (piston) laboratory compression unit. The unit was previously used under laboratory conditions using a synthetic flue gas and was used on a sampled slipstream of “real” oxy-fuel flue gas derived from the Callide Oxyfuel Project. The field campaign at Callide had four main aims:

- 1) To determine the impact of passively cleaning SO_2 and NO_x in the compression circuit
- 2) To vary the residence time within the compression circuit
- 3) To determine the impact of temperature on NO_x conversion
- 4) To compare the (experimental) compressor results to measured NO_x and Hg concentrations within the Callide CO_2 Processing Unit

It was found that SO_2 had only minor impact on NO conversion and no impact on the capture of NO_x during compression. It was also observed that the SO_2 was removed at a faster rate than the NO_x , obtaining >80% removal by 10 bar. This was found to be consistent with other international pilot trials.

The effect of shorter residence time has confirmed the impact of gas kinetics and was shown to decrease the conversion of NO to NO_2 though this effect was mainly observed in the 3rd compression stage after 60% conversion of NO. The overall capture of NO_x during the compression circuit could be improved from 55% to 75% with a doubling of residence time and further extended to 83% with an increase in pressure from 24 to 30 bar.

A reduction in temperature during high pressure intercooling (using an ICED condenser) had the greatest effect on NO_x capture at higher pressure, while Hg capture was removed at lower pressure. Modelling suggested that the lower temperature produced a higher equilibrium concentration of N₂O₄ which is considered the likely reactant species involved in Hg removal.

Overall, the field measurements taken from the laboratory compressor using real flue gas were found to agree with the previous laboratory measurements. This provides confidence in laboratory experiments to study NO_x/SO_x/Hg mechanisms prevalent in large scale oxyfuel compression. The removal of these flue gas impurities during compression has the potential to reduce the overall cost of oxyfuel and represents a significant advantage that oxy-fuel has over other CCS technologies, such as post-combustion capture, which require removal of impurities prior to entering the CO₂ compressor unit.

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