

## Zero Emission Oxyfuel Power Generation for CO<sub>2</sub> Capture

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### ABSTRACT

Advanced power plant designs will play a major role in the reduction of carbon dioxide emissions from fossil fuel-based power generation. Foster Wheeler is developing advanced power plant designs of boilers, which capture CO<sub>2</sub> and achieve zero emission of all other pollutants. In oxyfuel combustion, the oxidant, air, is replaced by nearly pure oxygen from an air separation unit (ASU) and recycled flue gas to produce a flue gas stream, which is nearly all CO<sub>2</sub> and H<sub>2</sub>O.

Foster Wheeler has developed a new process, where all vent gas streams from the CO<sub>2</sub> purification unit flow back to the boiler. A pressure swing adsorption (PSA) process is applied to the vent gas, where only nitrogen, argon, and oxygen (N<sub>2</sub>+Ar+O<sub>2</sub>) pass through the PSA, and all other gases (including part of the N<sub>2</sub>+Ar+O<sub>2</sub> regenerated from the adsorption process) are recirculated back to boiler. In addition, flue-gas recirculation is incorporated in the power plant design to control furnace temperature and to optimize boiler operation. This PSA and flue gas recirculations virtually eliminate any emissions by enhancing pollutant re-burning and re-capturing in the boiler. Simulation results indicate that all major pollutants including NO<sub>x</sub>, SO<sub>x</sub>, and CO are either consumed in the boiler or captured in downstream equipment.

The zero-emission process removes 100% of the CO<sub>2</sub> and achieves zero power plant emission. NO<sub>x</sub> control, under this process, does not require any conventional DeNO<sub>x</sub> processes, such as SCR or SNCR, and it potentially relaxes the requirements for combustion staging. Furthermore, due to recycling of the vent gas, required ASU oxygen purity and excess oxygen may be reduced. Consequently, the cost of CO<sub>2</sub> removal is decreased. This approach is applicable for both Greenfield and retrofit applications.

### INTRODUCTION

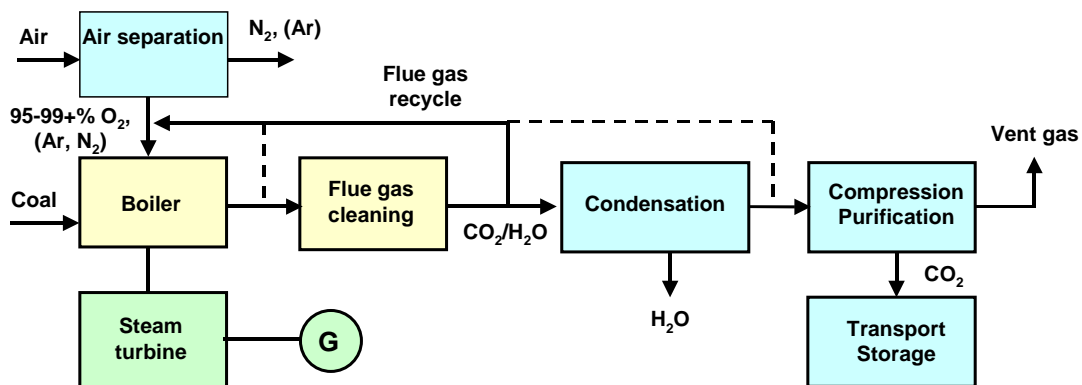
With the abundance of coal for power generation, solutions need to be developed for controlling pollutant emissions including the greenhouse gas, CO<sub>2</sub>. In the short term, power plant efficiency improvements can reduce CO<sub>2</sub> emissions. However, carbon capture and sequestration (CCS) will be required to provide a long term solution for virtually eliminating CO<sub>2</sub> emissions from fossil fuel fired power generation; oxyfuel combustion represents a favorable CCS method among the variety of potential CO<sub>2</sub> capture technologies. Foster Wheeler is developing power plants, with Flexi-Burn<sup>®</sup> technology for both pulverized coal (PC) and circulation fluidized bed (CFB) boilers, as its CCS solution to address CO<sub>2</sub> emissions based on both bench and pilot scale experimental tests (PC and CFB, as well as material testing) and through system level integration and evaluation. One of goals for the improvement of oxyfuel combustion is to combine CO<sub>2</sub>

capture and sequestration with other emission controls to form power generation with zero emissions of atmospheric and condensate pollutants and to reduce costs. It is a challenge but also an opportunity for power industry.

Oxyfuel combustion has made significant progress through system level integration studies and pilot scale tests (Ref. 6). Figure 1 shows a simplified process flow diagram of an oxyfuel combustion power plant (Ref. 1), which consists of an air separation unit (ASU) for oxygen supply, a power plant with PC or CFB boiler under oxy-firing with gas recirculation for temperature control, and a CO<sub>2</sub> compression and purification unit (CPU) for meeting the requirement and specification of CO<sub>2</sub> transport and sequestration. Hot and/or cold gas recirculation is required for the proper boiler operation. For the PC boiler, the SO<sub>x</sub> in the primary recirculation gas (PG), sent to mill, needs to be removed to avoid acid gas condensation. The H<sub>2</sub>O in PG also needs to be reduced for proper fuel drying in the mill. Hot gas recirculation (before fluegas clean up) to improve cycle efficiency is also possible as shown in Figure 1 (Ref. 8). It is noted that conventional wet flue gas desulfurization (FGD) does not remove heat; instead, it converts gas sensible heat to latent heat by water evaporation. This water vapor needs to be condensed out downstream of FGD, which essentially shifts the gas cooling to a cooler at a very low LMTD without any heat recovery. To avoid this evaporation and condensation, wet-end heat exchangers are applied before and inside the FGD to recover the heat for improved system efficiency and more efficient cooling of the gas to reduce the cooling water requirement.

In oxyfuel combustion, CO<sub>2</sub> is produced and concentrated by fuel combustion with oxygen and recycled flue gas in a N<sub>2</sub>-free environment. Because of air separation and energy stored in compressed CO<sub>2</sub> there are certain penalties associated with CO<sub>2</sub> capture and sequestration. It has been noted that in spite of whether CO<sub>2</sub> is captured or not, the penalty exists just for oxyfuel combustion itself due to the requirement of pure oxygen from ASU for combustion. Thus for CO<sub>2</sub> removal, considering more than half of penalty (ASU+CPU) comes from ASU, it is more economic to capture as much CO<sub>2</sub> as possible.

Inert gases in the CO<sub>2</sub> stream to the CPU are vented during CO<sub>2</sub> purification and compression. Because of the partial pressure of CO<sub>2</sub>, a certain amount of CO<sub>2</sub> will be vented with inert gases together. This limits the efficiency of CO<sub>2</sub> recovery and increases the CO<sub>2</sub> removal penalty. As a result, for better CO<sub>2</sub> removal efficiency, it is desirable to increase fluegas CO<sub>2</sub> concentration,



**Figure 1 Block flow diagram of oxyfuel combustion for CO<sub>2</sub> removal**

which can be done by reducing the concentration of the inert gases in CO<sub>2</sub> stream, such as by raising oxygen purity from the ASU, sealing the boiler to avoid air ingress, and firing with low excess oxygen -- all of which incur extra cost. But even with substantial efforts to increase CO<sub>2</sub> purity, the inert gases in the CO<sub>2</sub> stream cannot be fully avoided, and a nearly 100% CO<sub>2</sub> removal is still not reachable for such a once-through CO<sub>2</sub> capture process.

An alternative way to enhance CO<sub>2</sub> capture is to reduce or capture CO<sub>2</sub> from the vent gas. In considering the costs of upgrading the ASU and CPU, further investment for recovery of CO<sub>2</sub> from the vent gas becomes economically favorable. Any method which can separate CO<sub>2</sub> from the vent gas or separate inert gas from CO<sub>2</sub> can be applied to recover extra CO<sub>2</sub> and improve CO<sub>2</sub> removal efficiency. Such methods include membrane method by Air Products to recover the extra CO<sub>2</sub> and O<sub>2</sub> from vent gas to boiler (Ref. 2), and VPSA method by Praxair to recover the extra CO<sub>2</sub> from the vent gas and recycle it inside the CPU. Both of these enhance CO<sub>2</sub> recovery efficiency and reduce the penalty of CO<sub>2</sub> removal.

## **ZERO EMISSION DESCRIPTION**

A new multi-emissions control process producing zero emissions was originally developed by Foster Wheeler in 2007 and has been steadily improved over the last three years. Note that in this paper the term, “emissions”, refers specifically to all gaseous and liquid pollutants (SO<sub>x</sub>, NO<sub>x</sub>, CO, CO<sub>2</sub>, VOC, HCl, Hg etc.). This new zero emission process employs vent gas treatment to enhance CO<sub>2</sub> capture, where a PSA type sorbent bed is applied to adsorb CO<sub>2</sub> and the other gases at vent gas condition, which is very similar to the hydrogen purification method in hydrogen production through reforming. The un-adsorbed or less adsorbed gases, mainly purified Ar, N<sub>2</sub> and O<sub>2</sub> are purged, or forwarded to ASU (if oxygen concentration is high enough to save ASU power and if Ar concentration is low enough to avoid accumulation in system). The PSA adsorbed gases with all emission components including CO<sub>2</sub> are released by pressure reduction (flashing) and, after coolant recovery, forwarded to boiler as part of recirculation gases, where any emission gases will flow through the boiler and undergo re-burn and re-capture processes during gas recirculation.

During research, it has been found (Ref. 3) that recirculating flue gas through the boiler induces re-burn and re-capture of many pollutants. For example, the NO<sub>x</sub> in recirculation gas can be well destroyed (nearly 100%) in the high temperature zone under fuel rich conditions, and about 60-70% destroyed under fuel lean conditions. Furthermore, SO<sub>3</sub> can be reversely converted back to SO<sub>2</sub> in the high temperature zone. CO and VOC in the recirculation gas are primarily burned out in the high temperature zone and will not cause any accumulation in circulation. This re-burning brings another advantage that the boiler can be operated at low excess oxygen despite the CO level as long as the UBC (unburned carbon) is not significantly increased. These re-burn effects greatly reduce the concentration of emission components in gas. The re-capture is another function induced by gas recirculation, where gases pass repetitively through emission control devices such as for SO<sub>x</sub> capture. The vent gas, flowing through the boiler, becomes part of recirculation gas and undergoes both re-burn and re-capture. Without the re-burn and re-capture, gas components reach 4-5 times higher due to N<sub>2</sub> dilution free combustion.

To avoid ice formation during CO<sub>2</sub> condensation at low temperature, the gas moisture in the CO<sub>2</sub> stream has to be removed before cold box, which is done by a sorbent bed before cooling. It has been noted that part of gases, including SO<sub>x</sub> and NO<sub>x</sub>, are also possibly adsorbed (Ref. 4) by the sorbent bed during gas drying, where the extent of adsorptions depends upon the sorbent applied. Based on the present zero emission approach, the regenerated gas stream from this sorbent bed is also forwarded to the boiler island and treated as part of recirculation gas.

The natural acidic condensate drained from the CPU is directly forwarded back to the scrubber as makeup water without additional treatment, where those acid components in condensate will be captured and neutralized (Figure 2).

This configuration is a system with closed loops to emission components, producing only purified (N<sub>2</sub>+Ar+O<sub>2</sub>) gas, solid related gypsum (PC) or solid drain (CFB), and purified CO<sub>2</sub>. This process does not require a sharp cut or separation by PSA and can reach 100% CO<sub>2</sub> removal. It does not require any deNO<sub>x</sub> process as NO<sub>x</sub> can be adsorbed with CO<sub>2</sub> together by PSA. For the same reason, the emissions control of VOC, CO and other pollutants are complete if they can be adsorbed by PSA and recirculated back to boiler after regeneration.

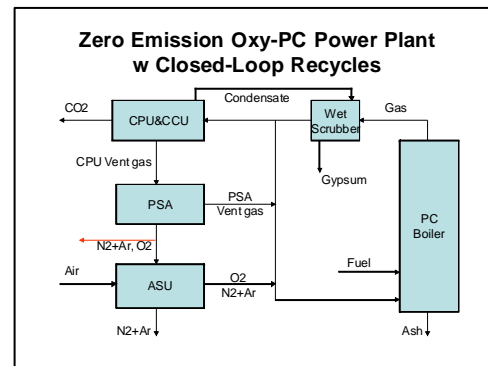


Figure 2 – Zero emission oxyfuel power plant

The key point of this zero-emission approach is the vent gas recirculation to boiler island to form a closed loop system of the emission components, where any separation methods to separate and re-circulate emission components to boiler island are applicable. The PSA method applied here is just an example.

The key for success to this zero emission approach is a sorbent bed to purify (N<sub>2</sub>+Ar) and to send all emission gases to the boiler island. Recently, CO<sub>2</sub> adsorption has become a hot topic for CO<sub>2</sub> removal aiming at reducing energy penalty from regeneration and lowering capital costs (Ref. 7). Different sorbents such as active carbon, molecular sieve, and zeolite (Ref. 5), have been tested. Research is required to find a good sorbent which selectively adsorbs or absorbs CO<sub>2</sub> from fluegas while possessing a high capacity in loading in term of lb-CO<sub>2</sub>/lb-sorbent to lower sorbent circulation rate and the extra heat requirement for regeneration. The purity of regenerated CO<sub>2</sub> from adsorption relies highly on the CO<sub>2</sub> selectivity during adsorptions. The relative CO<sub>2</sub> selectivity therefore becomes important for sorbent evaluation and development.

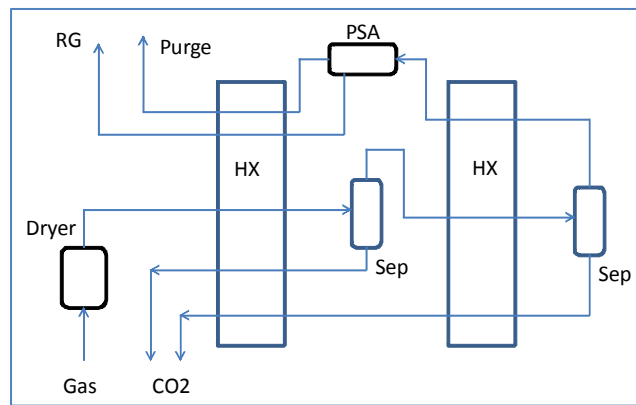
For vent gas treatment, the present zero emission approach uses a PSA, which functions as a guarding device to prevent any emission components to be vented. Since the regenerated gas from the vent gas treatment will be forwarded to the boiler island as part of recirculation gas for emission control, the PSA used in the zero emission process prefers, but does not require, a high selectivity of CO<sub>2</sub> from the other gases. Instead, it just requires a good selectivity between (Ar+N<sub>2</sub>) and the other gases to reduce PSA size.

The attractiveness of the vent gas treatment by PSA is that it not only increases CO<sub>2</sub> recovery efficiency to 100% with reduced cost per CO<sub>2</sub> removal, but also forms closed loops for the emission components to reach true zero emissions. This zero emission approach also allows relaxation of boiler operational parameters, such as low excess oxygen, in spite of potentially high CO concentration. Furthermore, the zero emission system can better tolerate the ingress of air into CO<sub>2</sub> stream as well as a low ASU oxygen purity, which reduces ASU auxiliary power and cost.

## MODELING

This zero emission concept is applicable for both PC and CFB power plants. A nominal 450 MWe oxyfuel PC boiler was applied for analysis. The furnace performance is simulated by Foster Wheeler 3-D CFD furnace models, which include calculations for SO<sub>x</sub>, NO<sub>x</sub> and CO as well as UBC under different excess oxygen levels and gas recirculation rates. The effects of the re-burn and re-capture from gas recirculation are included in the modeling. The over-fired air (OFA) has been turned off due to application of the zero emission where the furnace itself functions for NO<sub>x</sub> reduction. The system heat and material balances are simulated by Aspen Plus<sup>®</sup> commercial software. A fixed total gas recirculation rate was maintained in the model for the parametric study.

There are many different CPU configurations presented in the literature. For the parametric study of the potential gains of the zero emission process, a common CO<sub>2</sub> purification process with two-stage CO<sub>2</sub> condensation was applied (Figure 3). To recover as much energy as possible, both streams exiting from the PSA pass through the cold box for coolant recovery. The purified CO<sub>2</sub>



**Figure 3 - Block diagram of CO<sub>2</sub> purification by condensation**

streams are then compressed to an end pressure of 2000 psia. Regenerated gases from PSA and dryer are treated as part of recirculation gases. Flashing of the purified vent gas (N<sub>2</sub>+Ar+O<sub>2</sub>) for cooling is produced by gas expansion at low temperature to recover power directly.

There is no test data available for PSA operated at vent gas condition. It has been assumed that the relative selectivity at room temperature can be applied to low temperature, and the O<sub>2</sub>, N<sub>2</sub> and Ar have the same relative selectivity as compared with the other gases for a given sorbent. The PSA adsorption performance, or recovery of (N<sub>2</sub>+Ar+O<sub>2</sub>), can then be obtained by integration of

relative selectivity along sorbent bed, where the total recovery of (N<sub>2</sub>+O<sub>2</sub>+Ar) is affected by the operating pressure and feed composition.

It has been demonstrated that both NO<sub>x</sub> and SO<sub>x</sub> can potentially form acids under high pressure and low temperature during CO<sub>2</sub> compression. In the zero emission process, the acidic CPU condensate forms a closed loop for liquid emission components, where all condensates from the CPU are recycled back to the boiler scrubber. All emission components in liquid will be captured and removed by the scrubber. The condensate, mainly water, is used as makeup water for scrubber operation.

## RESULTS

A parametric study was conducted to evaluate the effect of air ingress, and furnace excess oxygen, and ASU oxygen purity on the zero emission performance in terms of specific power penalty and emissions. The CO<sub>2</sub> capture power penalty depends upon the power plant heat integration, the ASU and CPU configuration and design, and raw CO<sub>2</sub> purity to CPU. For simplicity, a relative specific power penalty (ASU+CPU) per tonne of CO<sub>2</sub> removed is calculated. For comparison, the power penalty without the zero emission process at 3% O<sub>2</sub> in flue gas, 97% ASU O<sub>2</sub> purity, and 8% air ingress is normalized to 100%.

### Effect of air ingress

An important issue in oxyfuel combustion is the air ingress into the boiler since the efficiency of CO<sub>2</sub> removal is highly dependent on CO<sub>2</sub> purity. Air ingress increases not only CO<sub>2</sub> in the vent gas, but also increases power penalty for compression of the inert gases. One of the objectives of the zero-emission is to maximize CO<sub>2</sub> capture in spite of the air ingress.

As is shown in Figure 4, the efficiency of CO<sub>2</sub> removal is greatly impacted by air ingress.

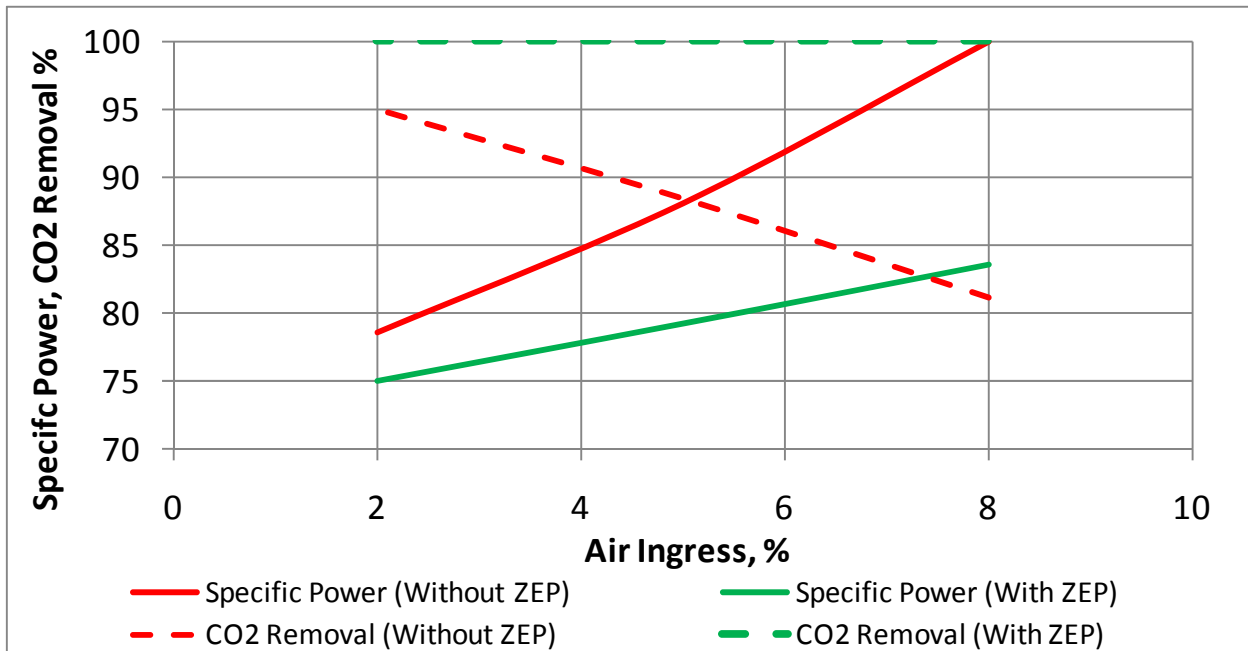


Figure 4 – Specific Power and CO<sub>2</sub> Removal Vs. Air Ingress at 3% Flue Gas O<sub>2</sub>, 97% ASU O<sub>2</sub>

Sealing the boiler to reduce air ingress from 8% to 2% lowers the relative specific power penalty from 100% to 79% without the zero emission process (ZEP), but only from 84% to 75% with the zero emission process. Therefore, incorporating the zero emission process makes the boiler less sensitive to air ingress. Note that the relative specific power penalty at 8% air ingress with ZEP is equivalent to that at 3.6% air ingress without ZEP. Moreover, as shown in Figure 4, the CO<sub>2</sub> removal is 100% at 8% air ingress with ZEP versus only 93% at 3.6% air ingress without ZEP. In fact, with ZEP 100% CO<sub>2</sub> capture is always obtainable in spite of the level of air ingress. Consequently, the application of the ZEP gains more when air ingress is significant, which means that the ZEP technology is well suited to a retrofit application where sealing the existing boiler is a challenging issue.

### Effect of excess O<sub>2</sub>

In oxyfuel combustion, the fuel combustion is enhanced by the high concentration of oxygen in the feed, which benefits fuel burnout and so reduces UBC (unburned carbon). However, because of high CO level in gas due to equilibrium in a high CO<sub>2</sub> environment, certain amount of excess oxygen needs to be maintained to suppress the CO concentration. Low excess oxygen combustion not only reduces oxygen requirement and ASU duty, but also reduces inert gases in CO<sub>2</sub> stream to CPU and thus the vent gas flow and CPU duty. Low excess oxygen reduces NO<sub>x</sub> but increases CO. With application of the zero emission process, recycled CO and NO<sub>x</sub> undergo re-burn. In oxyfiring the over-firing air (OFA) is turned off due to the unnecessary NO<sub>x</sub> control in the furnace. As a result without the OFA and with increased O<sub>2</sub> level in feed, fuel burnout is enhanced. The 3-D furnace model simulations determined that the UBC at 1% O<sub>2</sub> level without OFA in oxy-firing is nearly the same as at 3% O<sub>2</sub> level with OFA in air-firing. Figure 4 and Figure 5 show that reducing the excess oxygen from 3% without ZEP to 1% with ZEP reduces the relative specific power penalty from 100% to 81.5%.

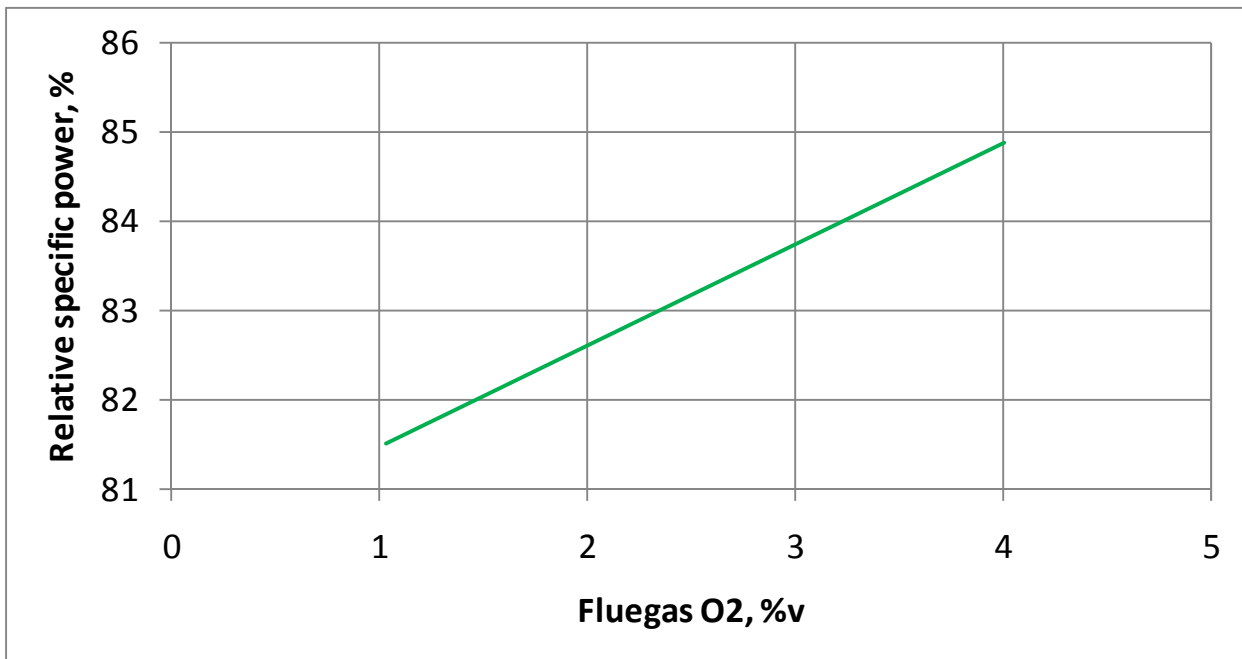


Figure 5 – ZEP Specific Power Vs. Flue Gas O<sub>2</sub> at 8% Air Ingress, 97% ASU O<sub>2</sub>



Changing the O<sub>2</sub> level from 3% to 1% increases the CO level from 3400 ppmv to 5100 ppmv (1600 ppmv air-firing) at furnace exit, and from 280 ppmv to 460 ppmv (154 ppmv air-firing) at boiler exit. Changing the O<sub>2</sub> level from 3% to 1% reduces the NO<sub>x</sub> level by 25%.

### Effect of oxygen purity

High purity oxygen demands more auxiliary power from the ASU, but helps to reduce CPU power and captures more CO<sub>2</sub>. In the literature, the optimum oxygen purity is judged to be at about 96-97%v. Due to vent gas recirculation, ZEP shifts the optimum point to a lower oxygen purity value, which reduces the relative specific power penalty.

Figure 6 shows that relative specific power penalty is relatively insensitive to oxygen purity with a 7% point change in oxygen purity producing only a 1% point change in the relative specific power penalty. This effect indicates that the requirement of high pure oxygen can be relaxed when the ZEP is applied since CO<sub>2</sub> removal is a constant 100%. With ZEP vent gas purification and recirculation, the efficiency of CO<sub>2</sub> capture is decoupled from the ASU, which allows the implementation of advanced oxygen generation processes with low specific power penalty at low oxygen purity.

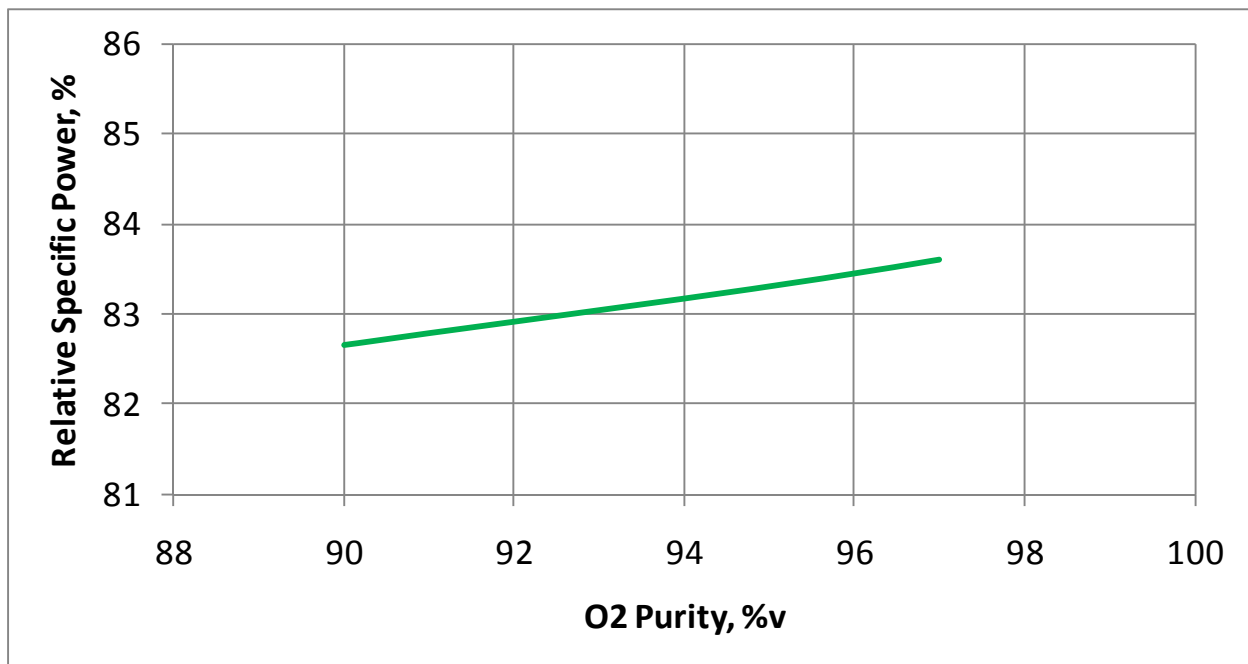


Figure 6 – ZEP Specific Power Vs. Flue Gas O<sub>2</sub> at 8% Air Ingress, 3% Flue Gas O<sub>2</sub>

### CONCLUSIONS

The oxyfuel combustion raw gas to the CPU contains emission components. This raw gas must be treated to meet the end use requirements of the CO<sub>2</sub> stream. The zero emission process eliminates the emission of these gaseous and liquid pollutants by separation at high pressure and recycling pollutants back to the boiler for reburn and recapture. To avoid accumulation of



nitrogen and argon ( $N_2+Ar$ ) in system, a pressure swing adsorption (PSA) process is applied to the vent gas before recirculation, where purified ( $N_2+Ar+O_2$ ) passes through the PSA, and the other gases, including part of the ( $N_2+Ar+O_2$ ) regenerated from the adsorption process, are recirculated back to boiler.

The advantages of this zero emissions process is that it achieves 100%  $CO_2$  removal without increasing the ASU duty, does not require any conventional deNO<sub>x</sub> processes, such as SCR, SNCR or staged combustion, allows the boiler to be operated at low excess oxygen, and does not require high efficiency emission control equipment. Compared to conventional oxyfuel process the zero emission process reduces overall power penalty by 20% or more. This approach is applicable for both Greenfield and retrofit applications.

In summary, the zero emission process achieves 100%  $CO_2$  removal, incurs a relatively low specific power penalty, and readily accommodates advanced oxygen separation techniques

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