Abstract

The cement industry faces a unique challenge in reducing greenhouse gas emissions owing to the large amount, 5% of global total, of process emissions originating from the calcination of limestone. Oxygen combustion is considered the most promising technological option as the energy penalty for capturing the CO$_2$ is only associated with the fuel, as opposed to post combustion capture where sorbent regeneration is required for both fuel and process CO$_2$. While more attractive, the implementation of oxygen combustion and the necessary flue gas recycling, will alter process conditions. As a result, significant research is required to produce a viable design for the complete conversion to oxygen combustion. The conversion will require modifications to every component of the plant with the exception of the quarry and finish grinding sections. The plant boundary will also expand to include an oxygen production facility and a CO$_2$ compression station. While the cost of the additions can be quantified, the final cost will be a balance between the modifications and revenues from increased production.

Keywords: cement; oxygen combustion; carbon dioxide; plant modifications.

1. Introduction

The cement industry, like all others, is facing pressure to find technological solutions to the greenhouse gas emissions resultant from their activities. While all industries face challenges in reaching these goals, the cement industry is in a unique situation. The consumption of cement, on a per capita basis, is second only to water and there is no ready substitute. In addition, the majority of greenhouse gases produced during the manufacturing of the product occur via the calcination of limestone, the dominant source material. As a result, the greenhouse gas emissions from cement production are divided between calcination (50%) and fuel consumption (40%) with the remainder as indirect emissions from electricity production and vehicular traffic (10%) (Hendriks, et al., 1999). The emissions are associated with clinker production, which is produced at temperatures above 1,400°C and is the dominant (90%) component of Ordinary Portland Cement (OPC). Current efforts by the cement industry have focused on reducing the clinker content of cement (blending) and alternate sources of heat for the pyroprocessing (alternate fuels) (CSI, 2002). These measures are cost effective but cannot provide the deep reductions necessary for
climate stabilization. In order to achieve near zero emissions, technologies that prevent the release of virtually all plant emissions are required.

Carbon capture and storage (CCS) technologies currently being considered by the power industry can be applied to the cement industry and are a reasonable place to start. The IPCC lists three categories of CCS options for large point source emitters in their special report; pre-combustion, post combustion and oxygen combustion (IPCC, 2005). Pre-combustion can be referred to a “de-carbonizing” the fuel, which has limited applications in the cement industry owing to the large volume of process emissions. In effect, the benefits of separating the carbon upstream of the kiln would be negated by the release of the calcination CO2 during combustion, which would require scrubbing to achieve reductions greater than 50%. Post combustion capture is readily applicable to cement plants after sufficient cleaning of the kiln exhaust. The removal of CO2 using a sorbent does not allow for the differentiation of the two origins of the CO2, calcination and combustion, in the kiln. The sorbent must remove them both and as a result, the regeneration penalty must also be paid. While technically feasible, and potentially the only retrofit option, post combustion capture may result in excessive sorbent regeneration penalties. In oxygen combustion, the amount of oxygen produced (the penalty) is only indirectly tied to the calcination CO2. It is produced in sufficient quantities to completely oxidize the fuel, the calcination CO2 is captured by default. As a result, the cement industry is considered the best location for the use of oxygen for CCS (Gronkvist, et al., 2006). Oxygen enrichment is already practiced in the cement industry as a method to increase production from existing kilns (Wrampe and Rolseth, 1976). Oxygen combustion therefore combines a theoretically lower energy penalty with an increase in production.

2. Clinker production in atmospheres dominated by CO2

Oxygen combustion appears to be a promising choice for the cement industry but brings its own challenges. In oxyfuel systems, exhaust gas is returned to the burning zone to compensate for the lost thermal ballast provided by the nitrogen in air. The result is that the CO2 concentration in the kiln will rise from 20-30% to over 80%. The effect of raising the partial pressure of CO2 on the calcination (thermal decomposition) of limestone has been understood for almost a century (Johnston, 1910). The temperature at which the reaction proceeds rises from 670°C at pCO2=0 to 900°C at 1 bar. The reaction type also changes from a gradual onset to threshold reaction. At low partial pressures, the rate of decomposition increases until it the reaction is complete. By contrast, under high partial pressures, there is no reaction until the threshold temperature is reached. If the temperature drops below the threshold, the lime promptly returns to limestone through the carbonation reaction. Considering a modern pre-calciner design, carbonation would send the heat released up the exhaust stack and the resultant limestone towards the burning zone to be calcined a second time. This possibility places a strong emphasis on maintaining the temperature profile between the calciner and the kiln.

Calcination in atmospheres dominated by CO2 is also known to produce highly sintered lime (Garcia-Labiano, et al., 2002). Sintering is a surface phenomenon that reduces the surface area of the lime particles. The effect of the higher CO2 partial pressures on the production of clinker has been investigated (Zeman, 2008). Synthetic raw meal, a mixture of calcite and silica with aluminum and ferrous oxides, was heated to various temperature set points in a muffle furnace. After each test, the mass loss and B.E.T. surface area was measured. The testing confirmed the the change in the calcination reaction. The mass loss was delayed to 900°C in the CO2 environment with total calcination by 1,100°C. The sample also showed slight (≤15%) mass loss below the calcination temperature, which may be a function of the apparatus or direct belite formation. A similar temperature shift was seen in the surface area measurements with the peak surface area delayed until the onset of calcination. The raw meal heated in a CO2 environment developed 66% less surface area, at the peak, than the air burned sample. The sintering caused by the high temperatures resulted in similar surface areas by 1,200°C. The change in gas composition results in less surface area as the sample is heated from 600-1,100°C. Future investigations will investigate whether this loss of surface area, a proxy for reaction sites, affects the formation of low temperature calcium silicates. Additional experiments demonstrated that no carbonation of the free lime in the clinker occurs during cooling in a CO2 environment. This supports the use of CO2, recycled from the exhaust, as the cooling fluid in the clinker cooler section of the plant.
3. The Reduced Emission Oxygen (REO) Kiln

A complete review of the changes induced by converting a conventional cement kiln to oxygen combustion is necessary to ensure the feasibility of the design. The work presented here summarizes a report written by the author for the Cement Sustainability Initiative of the World Business Council on Sustainable Development (Zeman and Lackner, 2008). As a first step, a preliminary review of each component of the existing plant is done in order to list the areas requiring further investigation. Starting with a process schematic of the new facility, shown in Figure 1, we can identify the changes required.

Figure 1: Process Schematic of Reduced Emission Oxygen Kiln. Note: CO₂ compression station not shown.

It is important to note that efforts to reduce greenhouse gas emissions from the cement industry cannot alter the product. Clinker, as the dominant component of OPC, is a ubiquitous construction product that must maintain the same engineering parameters as produced by existing kilns. Post combustion systems do have the advantage of being completely separate from the process. As suggested by Figure 1, the fundamental components of the REO kiln mirror existing plants. The centerpiece is a burning zone where combustion drives the clinker formation reactions. The kiln itself must be suitable for molten reactions and will still have a pre heater and cooler to transfer heat between incoming and outgoing materials. The additions to the plant site include an oxygen production facility, CO₂ compression station and a conduit to return exhaust gases to the burner end. There will also be an unknown amount of other design changes associated with these process alterations. Figure 1 also highlights the potential for gasification in the new design, shown as the Carbonaceous Fuel-Waste block. The REO kiln design makes available oxygen, CO₂ and heat for gasification purposes. While not mandatory, there is the potential to produce a consistent fuel stream from a variety for fuels. Operational variability is the current challenge with the use of alternative fuels.

While the gas conduit must physically be attached to the kiln ends, the oxygen and CO₂ compression stations can be located within the plant boundaries. Currently, the most cost effective method for producing the quantity of oxygen required for complete conversion is a cryogenic air separation unit (ASU) (Kirschner, 2002). An ASU is a self-contained unit that would not be integrated into the facility. It can be viewed as a “black box” that produces dry oxygen and nitrogen. The ASU will add to the electrical load of the plant and assuming a fuel energy of 400 kJ/mol O₂, the additional energy penalty will be 48 kWh per tonne clinker. One important question is the allowable Argon content for CO₂ storage, as higher oxygen purity levels require a more complex ASU. Oxygen production using Ion Transfer Membranes (ITMs) is a novel technology still in the pilot stages that involves heating air to 900°C in order remove the oxygen, via mixed conductor membranes (Stein, et al., 2002). At this time, ASUs are considered more
likely as they are commercially available. The CO\textsubscript{2} compression stations will also be a “stand alone” structure although heat recovery from the intercoolers may be possible. The heat recovered could be introduced into the raw meal grinding circuit instead of the stack gases.

The remainder of this section is devoted to discussing how the main components of the cement plant will be affected by the complete conversion to oxygen combustion. The components are presented in order from the feed end with a view towards identifying the dominant physical changes and potential solutions. The discussion is based on a multi stage pre heater, pre calciner short dry kiln consuming less than 3 MJ/kg of clinker. Many of the changes are a function of the different gas properties, some listed in Table 1, between Nitrogen (N\textsubscript{2}) and CO\textsubscript{2}. The most pertinent are the changes in density, specific heat capacity and thermal conductivity.

Table 1: Select Properties of Gaseous Nitrogen and Carbon Dioxide

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>N\textsubscript{2}</th>
<th>CO\textsubscript{2}</th>
<th>Change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>g/L</td>
<td>1.12</td>
<td>1.76</td>
<td>+57</td>
</tr>
<tr>
<td>Heat Capacity\textsuperscript{1}</td>
<td>J/mol K</td>
<td>29.2-34.8</td>
<td>37.1-58.4</td>
<td>+27-68</td>
</tr>
<tr>
<td>Therm. Conductivity\textsuperscript{1}</td>
<td>M W/m K</td>
<td>26.0</td>
<td>16.8</td>
<td>-35</td>
</tr>
</tbody>
</table>

\textsuperscript{1} for range 298-1,500K

3.1. Pre Heater

The function of the pre heater tower in modern cement plants is to transfer heat from the hot exhaust gases to the incoming raw meal. The tower consists of a series of cyclones connected by vertical conduits. The raw meal is introduced into the vertical shaft where it is entrained in the gas exiting the cyclone below. The two then enter a cyclone and the procedure repeated. The performance of both the vertical shaft mixer and cyclone are dependent on the velocity of gas flow. The switch of thermal ballast from N\textsubscript{2} to CO\textsubscript{2} will result in a reduction in velocity due to the reduced mass flow and volumetric flow. A reduction in velocity is expected owing to the higher heat capacity, which reduces the mass required in the kiln, and the higher density, which reduces the volume per unit mass. When considering a new plant, it may be possible to affect the same separation pattern by keeping the ratio of relevant cyclone parameters constant. The size of particle separated by the cyclone (D\textsubscript{pth}) is a function of the inlet velocity (v\textsubscript{in}), the width of the entrance (w\textsubscript{en}) and the number of spirals (N\textsubscript{s}) according to equation 1 (Perry and Green, 1997).

\[ D_{pth} \propto w_{in} N_s^{-1} v_{in}^{-1} \] (1)

Given that the design changes may be significant, completely novel methods of heat exchange can also be considered.

The efficiency of the pre heater will also be affected by the reduction in thermal conductivity resulting from the change in gas properties. The reduction in heat transfer with each collision between solid and gas particles can be offset by increasing the residence time, although this would further reduce gas velocities. There are four relevant velocities to the proper function of a pre heater. These are the velocity required to remove the exhaust gases from the kiln, transfer heat from the gases to the solids, transport the raw meal between cyclones and allow satisfactory solid separation in the cyclone. The modified or novel design must accomplish all these tasks.

3.2. Pre Calciner

The pre calciner is a combustion zone at the base of the pre heater tower that thermally decomposes the limestone in the raw meal prior to entry into the kiln. Fuel and tertiary air, from the cooler, are injected into a riser duct with the resultant oxidation converting limestone to lime. The pre calciner currently operates at temperatures above 800°C, however, the rise in CO\textsubscript{2} partial pressure that accompanies oxygen combustion will necessitate operation above 900°C. The thermodynamic energy penalty associated with calcination will not change although more energy may be required to heat the flue gases the additional 100°C. The larger concerns for the new calciner conditions are
the temperature profile and separation efficiency of the bottom cyclone. These concerns both stem from the change in the calcination reaction type in a CO₂ environment from gradual to threshold. Once calcined, the raw meal moves up the pre heater tower and is separated in the first cyclone. The solids are sent to the kiln and the gases up the tower. The possibility of re-carbonation of the lime if the temperature drops below 900°C is a concern as it results in heat rising up the tower and limestone heading to the kiln. The additional energy required to re-calcine the raw meal will lower plant efficiency. A similar concern exists for the lower cyclone of the tower, generally with the lowest separation efficiency (85%). Assuming full carbonation, the raw meal migrating up the tower will raise the specific energy demand by 0.2 MJ per kg of clinker or 6%. The redesigned pre calciner will have to consider the increased likelihood of re-carbonation.

3.3. Kiln

The primary function of the kiln is to heat the raw meal to 1,450°C in order synthesize the clinker compounds. The removal of N₂ and its substitution with CO₂ recycled from the exhaust will drastically alter the gas composition inside the kiln. While CO₂ is not an active component in the clinker forming reactions, it remains to be shown that the clinker mineralization will not be affected. The unknown is derived from the effects of re-circulating exhaust gases, and all their impurities, back to the burner. Work on oxygen combustion in the power sector, although not directly applicable, has shown a higher concentration of oxygen is needed to reach similar adiabatic flame temperatures, higher gas emissivities owing to larger concentration of tri-atomic gases, reduced gas volumes owing to higher heat capacities, higher concentration of impurities from recycled gases and lower concentration of excess air (Buhre, et al., 2005). It was also noticed that radiative heat transfer increased slightly while convective transfer decreased. This may affect kiln shell temperatures.

A large difference between the generation of power and the production of cement is the reactor itself. The use of a rotary kiln results in leakage into the combustion zone. The rotating kiln contacts fixed ends at the fuel and feed ends with the hood (fuel) pressure negative. In addition, some kilns operate an alkali bypass circuit to control the concentration of chlorides in the kiln. The bypass operates off a slip stream from the kiln exhaust and vents those gases to the atmosphere after precipitation of the salts. In oxygen combustion, the infiltration of outside air would result a reduction in efficiency and dilution of the CO₂ concentration in the kiln. Loss of CO₂ through leakage or venting would reduce the amount captured and therefore increase the unit cost of capture. While a concerted effort at plugging holes will reduce leakage alternatives will be needed for infiltration and venting. Once possibility is to encase the kiln in a non-structural sheath that is charged with CO₂. The immediate effect is to eliminate the convective cooling of the exterior of the kiln shell. It may be possible to introduce a heat recovery system based on evaporation, exterior temperatures exceeds 300°C, and recover 3% of the kiln energy for use as low grade heat. The alkali bypass system could be indirectly cooled with the CO₂ returned to the kiln.

3.4. Clinker Cooler

The clinker cooler is another heat transfer device except this time the transfer is from the outgoing clinker to the incoming gases. The majority of the heat is transferred from the clinker to the nitrogen, which has now been removed. The higher heat capacity of the CO₂ should improve heat transfer by maintaining a larger temperature gradient between the solids and gases. The lower thermal conductivity may offset this and similar to all other aspects of the work, it must be validated through experimentation. The CO₂ used to cool the clinker would be recovered from the exhaust and will contain impurities. Corrosion will likely be the largest concern with impurities and the addition of a gas clean up step may be necessary. Conventional coolers have a supplemental air loop that completes the clinker cooling and is vented to the atmosphere. The feasibility of this additional gas loop in the CO₂ cooler would depend on the ability to separate the cooler into two distinct zones; one charged with CO₂ feeding gases into the kiln and the other cooling the clinker and being vented, with possible heat recovery, to the atmosphere. This could be accomplished using an enhanced over grate curtain that prevents gas exchange between the two zones. An alternative would be to recycle CO₂ within the cooler. This refers to using CO₂ as in a counter current heat exchanger where it passes through the clinker bed more than once on its way to the burner. Consideration can also be given to introducing the CO₂ into the cooler above ambient temperatures, which reduces
the heat recovery in the recycle loop and potentially increases the overall efficiency of the plant. The final design of the clinker cooler will balance the necessary cooling of the clinker with the desire to maximize plant efficiency.

3.5. Recycle Loop

The conduit that returns exhaust gases from the exit of the pre heater tower to the clinker cooler is the only physical addition to the cement kiln. The dominant design concerns are corrosion and heat management. Losing heat to the environment will reduce plant efficiency while excessive corrosion raises plant maintenance costs and indirectly, the cost of CO$_2$ capture. The recycle loop captures the gases that would have been sent to the raw meal grinding circuit and then vented to the atmosphere. At the exit from the pre heater tower, there will be an excess of CO$_2$ equivalent to that produced during combustion and calcination of the raw meal. This portion must be separated and sent to the CO$_2$ compressions station. Prior to compression, these gases will have to be cooled and scrubbed resulting in the construction of a heat recovery/gas clean up facility near the compressors. An option at this point is to increase the size of this facility to accommodate the entire exhaust stream. The cleaned up gas can then be divided accordingly with the appropriate recycle amount sent to the cooler.

The temperature of the exhaust gas leaving the pre heater tower ranges from 300-360°C depending on the number of cyclone stages. Of interest is the ability to return as much heat as possible to the process while minimizing the emission of pollutants and corrosion to equipment. The final design will balance the option of two separate heat recovery/clean up units, which allows for tailoring the exit conditions to the destination versus the economies of scale with a single clean up. The recycling of gases can also allow for a reduction in the number of pre heater stages, which results in a higher exhaust temperature. The preheating of the raw meal would then be accomplished using the heat recovered from the gases sent to storage and the cooling of the compressor station. This option has ramifications for sulfur emissions as the majority of those associated with a cement plant are derived from organic sulfur introduced with the raw meal. A detailed heat balance is necessary to optimize the utilization of all of the heat contained in the exhaust gases.

3.6. CO$_2$ Compression Station

The storage of CO$_2$ will require its compression and transportation in a pipeline. The compression of CO$_2$ is an established technology consuming 281 kJ$_e$ per kg CO$_2$ to reach 80 bar assuming a 70% pump efficiency (Blok, et al., 1997). For a cement plant, we can estimate 0.35 kg CO$_2$ from combustion, based on an O$_2$ demand of 0.2 Nm$^3$, and 0.53 kg CO$_2$ from calcination per kg clinker. The resulting compression demand is 247 kJ$_e$ per kg clinker or 69 kWh per tonne of clinker. The compression of the CO$_2$ will generate heat, which can be used to dry incoming raw meal. Assuming all of the compression energy is transferred to the gas, 300 MJ of heat will be generated capable of evaporating 135 kg of water, which corresponds to raw meal moisture content of 9%. The heat from the compressor can potentially compensate for the diversion of the exhaust gases to the cooler.

3.7. Coal Mill

The coal mill takes the coal feed and grinds it to a size suitable for introduction into the burner. It is a good example of the boundary considerations that will accompany isolating the kiln from the atmosphere. The coal is transported to site under atmospheric conditions and enters the kiln, which is isolated. At some point between those extremes a gas boundary must be established, either before or after the mill. Currently, the coal mill presents a safety hazard as friction from the grinding can heat the coal dust to the point of ignition. To mitigate this risk, ambient air is blown through the mill to control internal temperatures. If the boundary is placed upstream of the coal mill then it would be charged with CO$_2$ rather than air. As a result, oxygen is not present to ignite the coal dust; in addition, the endothermic Boudouard or carbon gasification reaction caps the maximum temperature at 700°C. Steam will also be brought in as moisture on the coal. The resultant mixture of CO$_2$, steam and heat may lead to gasification if the operating temperature of the mill is allowed to rise. In this manner, some of the electrical energy consumed by the mill can be transferred, as sensible heat, to the kiln. The mixture, now potentially containing carbon monoxide (CO) and hydrogen (H$_2$) can also be further treated through the addition of some of the oxygen. Introducing a small
amount of O2 could lead to further CO production. The advantage of this scenario is that the combustion properties of the fuel mixture can be altered to produce the optimum conditions in the clinker formation zone.

3.8. Integration and Safety Concerns

A cement plant converted to oxygen combustion would include fundamental changes that affect plant safety in both a positive and negative manner. As part of the Agenda for Action, the member companies of the Cement Sustainability Initiative committed themselves to monitoring and improving worker safety (CSI, 2002). The oxygen plant can improve conditions by reducing the explosion hazard in the coal mill but increases risk by mixing high purity oxygen with fuels and potentially operating the kiln shell at elevated temperatures. Components operating at elevated temperatures tend to increase safety hazards for workers.

The exclusion of air from the kiln will be accompanied by a concerted effort to reduce leakage. The net effect will be to integrate the components of the cement plant even further. The plugging of holes reduces the possible outlets for sudden changes in pressure or material flows. The design may have to consider a pressure release system to handle “kiln upset.” The sheath could be used as a pressure release valve provided some mechanism is installed to allow the removal of dust and debris from inside the sheath. The unexpected shutdown of the oxygen supply will also be a safety hazard, as oxygen could not be re-introduced into the system if there is a build up of fuel in the kiln. In this case, a back up air system may be required to mitigate any explosion hazards.

3.9. Advanced Concepts

The discussion above presents a direct, item-by-item, discussion for converting the best available cement production technology over to a REO kiln design. The process will likely involve a complete reconsideration of the entire plant, which opens the door to innovation not possible under the air fired system. Some, such as electricity production, are currently being used by some plants and could be adapted to the new conditions. We considered electricity production and determined that even if the exhaust is pulled straight from the pre calciner, only 50% of the total electrical demand could be met in this manner. The presence of pure gases, steam and heat, suggest that a gasification facility could be included in the new design. This would help improve fuel stability given the industry trend to alternative fuels. In addition, these fuels could be pre treated to remove pollutants, especially tires. As the global energy infrastructure moves towards ever great pollution restrictions, opportunities will certainly arise for the thermal destruction of wastes made possible by the operating temperature of a cement plant. The challenge for the next generation cement kiln is to produce high quality clinker while maintaining operational flexibility for waste destruction.

4. Conclusions

The greenhouse gas emissions from the global cement industry are second only to the power sector and will eventually require mitigation. While post combustion systems can be retrofitted to existing facilities and do not alter the clinker production process, they can only be an energy burden on the plant and result in a 25% increase in the amount of CO2 sent to storage. Oxygen combustion, on the other hand, fundamentally alters the process with significant potential benefits. Aside from increasing production, which has the potential to offset some of the costs, the recovery of heat from the exhaust stack and improved combustion conditions could increase plant efficiency potentially decreasing the CCS burden. Finding an effective solution, with the lowest cost, is imperative as cement, and therefore clinker, are used ubiquitously and are a key component of global development goals.

The conversion to oxygen combustion will necessitate the addition of an oxygen production facility in addition to the CO2 compressing stations required for CCS. These additions will double the electrical demand of the plant to over 200 kWh per tonne of clinker. Even assuming coal based electricity without CCS, the fugitive emissions from the electricity consumption are significantly less than a post combustion system capturing 85% of the CO2 generated on site. In addition, the conversion process opens exciting new doors for fuel gasification and heat recovery that may improve plant operations, increase safety and reduce the specific fuel consumption. Even today’s best available
technology operates at a thermal efficiency of less than 70%. By returning the exhaust heat to the kiln, reducing the amount of vent air and utilizing the heat radiated from the outside of the kiln shell, the potential exists to significantly increase the thermal efficiency of the process. The avoidance of nitrogen in the kiln also reduces the emphasis on NOx reduction. The solution to this problem has generally been to introduce a low NOx (temperature) burner, which adversely affects clinker quality. The use of oxygen will allow for a short, hot burning zone that will be able to produce consistently high quality clinker.

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