The Earth Institute at Columbia University

The Reduced Emission Oxygen Kiln

A White Paper Report for the Cement Sustainability Initiative of the World Business Council on Sustainable Development

July 31, 2008

Lenfest Center for Sustainable Energy
Columbia University in New York
Report No. 2008.01

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July 31, 2008

Re: A Reduced Emission Oxygen Kiln

Dear Dr. Klee,

We are pleased to submit our white paper report on the Reduced Emission Oxygen (REO) kiln. The document outlines the basic technology and the operational differences between the REO kiln and a conventional cement plant. We trust that you will find the results as exciting as we do and look forward moving this next generation cement technology to market.

The REO kiln represents a paradigm shift in cement production that aims to capture virtually all greenhouse gas emissions from the facility while increasing production and energy efficiency. The process will consume more electrical energy, for oxygen production and carbon dioxide compression, but we anticipate significant reductions in category pollutants such as acid gases and particulates.

We thank you for your support in this endeavor and look forward to future collaborations. Please do not hesitate to contact us if we may be of further assistance.

Sincerely,

Frank Zeman

Authors Statement

The cement industry is challenged with developing methods for reducing anthropogenic emissions of carbon dioxide to the atmosphere at a cost that does not suffocate growth. While some technologies can be retrofitted to existing plants, we look forward to the next generation of cement plant that improve efficiency while significantly reducing emissions of greenhouse gases and other category pollutants. Such a facility could be based on oxygen combustion and would represent a paradigm shift from existing technology. The objective of this report is to propose a roadmap for this next generation plant and to highlight potential areas of future research. We do not presume to think that we have identified every opportunity and challenge associated with these plants. Furthermore, we welcome comments and constructive criticism, and believe that the scientific and cement community can move forward together in a cooperative and productive manner. We recognize that issues related to competition among cement companies may limit information sharing but hope that we can help encourage as much cooperation as possible. There will certainly be much experimental and design work prior to the implementation of any such technology and we look forward to participating in collaborations that make real progress towards a sustainable future for cement producers worldwide.

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List of Abbreviations

ASU	air separation unit
B_c	width of cyclone inlet duct
CCS	Carbon Capture and Storage
D_{pth}	particle size where 50% is collected by cyclone
IPCC	Intergovernmental Panel on Climate Change
ITM	Ion Transfer Membrane (Hot O_2 Production)
K	Degree Kelvin (K=^{o}C + 273.15)
kWh	kilowatt hour (3.6 MJ)
MJ	Mega Joule (one million joules)
Mt	Mega tonne (one million tonnes)
N_s	effective number of spirals in a cyclone
Nm^3	volume expressed as cubic meters at 25^{o}C and 1 bar
REO	Reduced Emission Oxygen
tonne	mass equivalent to 1,000 kilograms
tpd	metric tonne per day
v_{in}	inlet velocity of cyclone
μ_g	gas viscosity
ρ_g	gas density
ρ_s	solid density

Introduction

Ongoing scientific research into the effects of anthropogenic carbon dioxide (CO_2) emissions is expected to result in ever increasing restrictions on greenhouse gas emissions with the potential for a net zero carbon economy well before the end of the century. Initially, carbon constraints will cause a reduction in the growth of emissions, rapidly approaching constant rates of global emission. Over decades, the rate of emissions should start to drop and gradually trend to less than 30% of current global emissions. Even then, the CO_2 concentration in the atmosphere will still be rising also much more slowly than today (Lackner 2005). In the near term, the focus of these emissions reductions is directed towards large, point source emitters, most prominently coal-fired power plants. Cement plants are included in this group and are second only to the power sector in terms of the number of facilities and total greenhouse gas emissions. The Intergovernmental Panel on Climate Change (IPCC) special report on Carbon Capture and Storage (CCS) estimates that cement manufacturing produces 932 Mt CO_2 per year from fossil fuel use at 1,175 facilities (Table TS.2) (IPCC 2005). It should be noted that the IPCC only considered emitters in excess of 0.1 Mt of CO_2 per year and does not include CO_2 generated from the calcination of the raw meal (a mixture of calcite, silica and oxides of iron and aluminum). This threshold is the equivalent of a 300 tonnes per day (tpd) clinker kiln, which is smaller than the vast majority of existing kilns.

The production of hydraulic clinker dates back to 1818 with the work of Louis Vicat and the initial patent by Joseph Aspdin in 1824 (Wilcox 1995). As can be expected, the early works were inefficient, with the rotary kiln invented almost 60 years later. Improving the efficiency of cement production is one way to effectively reduce CO_2 emissions. Indeed a 30% improvement in energy efficiency for clinker, and therefore cement, production has been observed from 1970 to 1995 (Cembureau 1998, Worrell et al. 2000). The energy associated with cement production has decreased from 7.9 to 5.6 Mega joules (MJ) per kilogram (kg) of cement while the energy associated with clinker production has decreased from 4.9 to 3.7 MJ per kg clinker. The rate of efficiency improvement was thought to have flattened as the industry "reaches the limit of available technical means (Cembureau 1998)." Modern dry pre-calciner kilns have improved with some requiring approximately 2.5 MJ per kg of clinker (Hegerland et al. 2006). For reference, the theoretical minimum energy required to produce clinker is approximately 1.75 MJ per kg (Hendriks et al. 1999). Using a lime saturation factor (ratio of lime to remaining components of raw meal) of unity, we notice that the energy penalty is dominated by the calcination or thermal decomposition of limestone, the dominant raw material in clinker production. The clinker formation reactions themselves are net exothermic, i.e. produce heat, and do not contribute to the thermal load of the plant (Locher 2002). Currently, the greenhouse gas emissions from a modern dry cement plant are associated with the calcination reaction (50%), fuel use to maintain kiln temperatures (40%) and electricity consumption (10%) (Hendriks et al. 1999). Unless otherwise stated, clinker refers to the kiln product and cement refers to Ordinary Portland Cement (90% clinker, 10% gypsum).

One of the proposed methods for moving past the limits of current technology is to increase the amount of alternate fuels in clinker production and blending in cement production. Alternate fuels are energy sources not having a fossil origin (WBCSD 2002).

Such fuels are generally waste materials from other industries and can help reduce greenhouse gas emissions directly associated with the cement industry. If these fuels contain fossil carbon, as for example in waste tires, the carbon is typically not charged to the cement plant. Fuels that contain biogenic carbon, i.e. carbon that was originally removed from the atmosphere through photosynthesis, are generally considered carbon neutral or as not contributing to anthropogenic climate change.

Blending or reducing the clinker portion of cement is a method of indirectly reducing the greenhouse gas emissions from the calcination reaction. Blending with natural pozzolanic materials and/or industrial wastes, such as blast furnace slag, reduces the amount of clinker and therefore CO_2 emissions per unit of cement. Both are effective options for reducing the greenhouse gas emissions from cement manufacturing. However, both options might suffer from scale up issues should they be implemented industry wide.

The ultimate challenge remains to devise technological methods to prevent the release of fossil and calcination CO_2 to the atmosphere during the production of clinker. A revolutionary approach may be required to drive CO_2 emissions toward zero. This report examines one such technology, the Reduced Emission Oxygen (REO) Kiln. This technology is based on the concept of oxygen combustion and replaces the air currently used in cement kilns with a mixture of pure oxygen and exhaust CO_2 recycled back to the kiln. Industrial oxygen is typically produced in excess of 90% purity in a dedicated facility. The resulting gaseous outflows from a REO kiln are rich in CO_2 and can be readily processed for transport to a CO_2 disposal site. If the CO_2 is disposed of taking advantage of the CO_2 storage processes suggested by the IPCC (IPCC 2005), the net carbon emissions can be greatly reduced, eventually trending to zero.

In this report, we outline the basic technology behind oxygen blown kilns and delineate changes from the conventional design that require further work. The cement industry has been previously suggested as the most efficient location to use oxygen combustion for CCS purposes (Gronkvist et al. 2006, Hendriks et al. 1999). The challenges associated with this concept will be discussed later in the report.

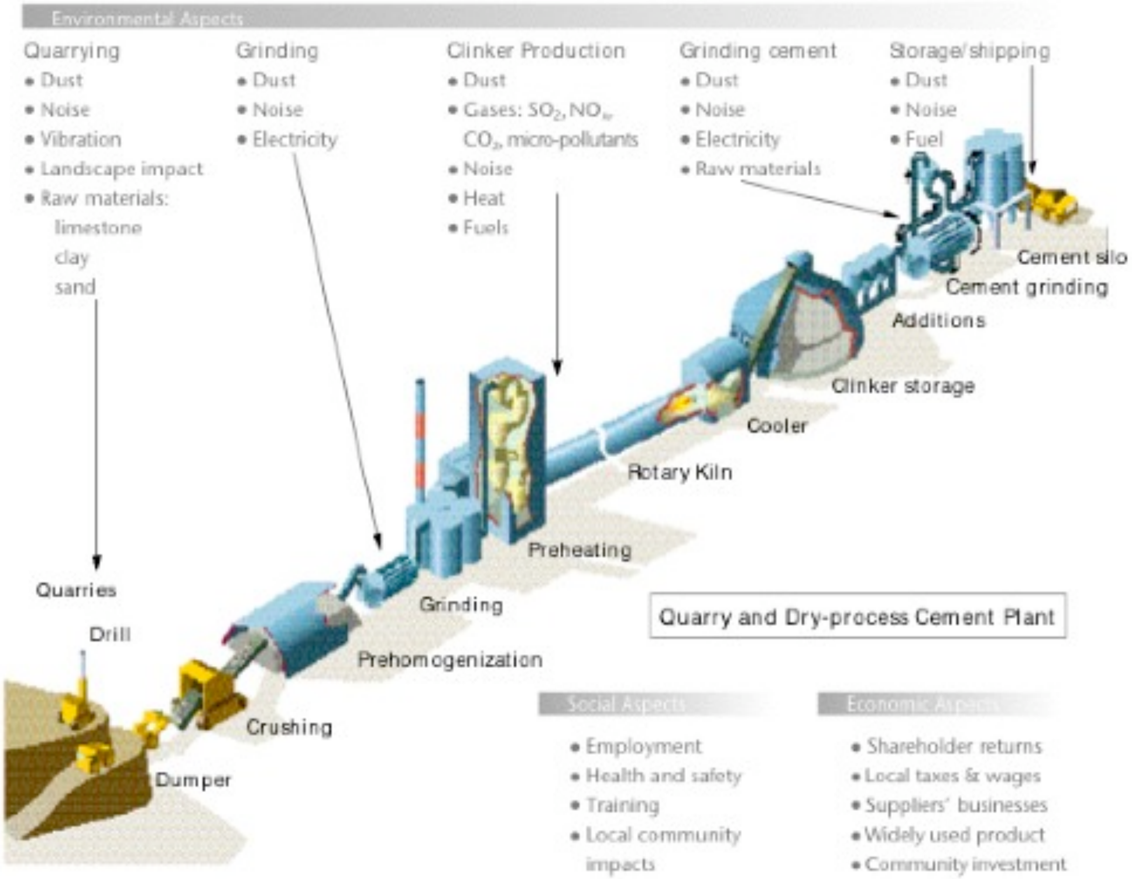

Figure 1: Overview of Conventional Cement Plant with pertinent

A brief overview of the cement manufacturing process, shown schematically in Figure 1, is provided to establish terminology used in this report. Ordinary Portland Cement (OPC), a common form of cement, is a mixture of approximately 90% clinker and 10% gypsum ($CaSO_4$). Gypsum is usually purchased while the clinker is produced on site and is the source of the majority of the greenhouse gas emissions. Clinker is produced by heating minerals to 1,500^{o}C, typically in a rotary kiln. The minerals are quarried then passed through grinding and mixing stages to produce a uniform material termed raw meal. The objective is to produce raw meal containing approximately 80.5% calcium carbonate ($CaCO_3$), 14% sand (SiO_2), 4% aluminum oxide (Al_2O_3) and 1.5% hematite (Fe_2O_3). The raw meal is fed into a pre-heater tower where a series of cyclones transfer heat from the hot exhaust gases to the incoming meal. The first reaction to occur (at 800^{o}C) is the conversion of calcium carbonate to calcium oxide (CaO), which releases the CO_2 bound in the mineral. The heating continues until the series of clinker forming chemical reactions take place between 1,300^{o}C and 1,500^{o}C. Clinker consists of tri-calcium silicate (C_3S or alite), di-calcium silicate (C_2S or belite) as well as smaller amounts of tri-calcium aluminate (C_3A) and iron compounds (C_4AF). In cement industry nomenclature, C refers to lime (CaO), S to SiO_2, A to Al_2O_3 and F to Fe_2O_3. The hot clinker falls from the kiln onto a grate cooler where combustion air is blown through the moving bed to cool the clinker and transfer heat back to the kiln.

Overview of CCS

The concept of oxygen combustion has been chosen as the basis for a new technology we call the Reduced Emission Oxygen (REO) Kiln. We provide a brief overview of carbon capture and storage technologies to clarify the reasoning behind the selection. A schematic representation of the three main options available to cement manufacturing facilities is presented in Figure 2. The European Cement Research Academy (ECRA) has produced a detailed discussion of CCS as related to the cement industry (ECRA 2007).

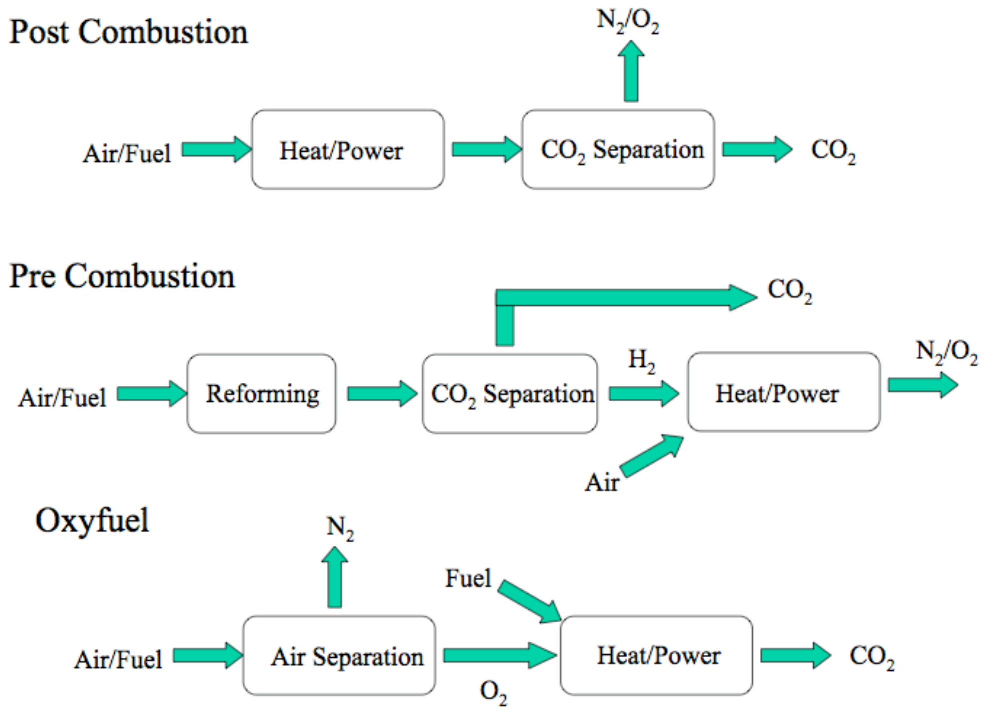

Figure 2: Overview of CCS for Industrial Processes

There are three general pathways for recovering CO_2 from mixed gas streams at cement plants ("heat/power" box in Figure 2), post-combustion, pre-combustion and oxyfuel combustion. As their names imply, post-combustion refers to removal of CO_2 from the kiln exhaust gases, pre-combustion refers to separation of the carbon from the fuel prior to combustion in air and oxyfuel avoids the mixing of fuel and nitrogen (N_2) by providing oxygen (O_2) as a concentrated stream rather than in air. Each form of CCS involves a gas separation process and the technology choice will depend on whether it is easier to separate CO_2 from N_2 (post combustion), H_2 from CO_2 (pre combustion) or O_2 from N_2 (oxygen combustion).

Compared to fuel combustion processes, cement kilns require half the oxygen per unit CO_2 captured. As a result, they are considered the optimum location for oxyfuel combustion. This conclusion is a result of the dual origin of the CO_2 produced in the kiln. CO_2 is produced both from the oxidation of fuel and the decomposition of limestone. The fuel CO_2 is generated in the kiln while the calcination CO_2 is “released” from limestone inside the kiln. By released we mean that the CO_2 can be viewed as “preformed” in the lime stone; its production does not require oxygen as in the combustion of the fuel. This distinction is important when considering methods for CCS.

The concept of pre-combustion capture is to avoid mixing CO_2 with air by transferring the chemical energy to hydrogen prior to combustion. Such a strategy would avoid the production of combustion CO_2 in the kiln but would not address the CO_2 from the calcination, resulting in two streams containing CO_2. The second stream would still be contaminated by nitrogen unless the combustion took place in pure oxygen. For this reason, pre-combustion capture is of limited potential for cement applications, a conclusion that is also supported by ECRA.

Post combustion capture can be viewed as another stage in the gas clean-up process. It would be located downstream of the NO_x and SO_x removal and cannot differentiate between the two forms of CO_2. As such, the regeneration penalty must be paid for both calcination and combustion CO_2. In oxygen combustion, oxygen would be produced in amounts sufficient for combusting the fuel with the exhaust gas containing both the fuel related and the calcination related CO_2. Given that 50% of the CO_2 results from calcination, it is expected that oxygen combustion could reduce the energy penalty for capturing CO_2 by a similar amount. If oxygen combustion and post-combustion capture are competitive in the case of a power plant, oxygen combustion should have a noticeable advantage in the case of a cement kiln. The oxygen demand scales with the fuel consumption, whereas the post combustion energy consumption scales with the amount of CO_2 produced.

The REO kiln removes air from the cement manufacturing process by using oxygen rather than air to combust the fuel. The absence of air removes the thermal ballast provided by the nitrogen and CO_2 must be recycled from the exhaust stack to control flame temperatures. As a result, the exhaust gases leaving the kiln are dominated by CO_2 with the excess CO_2 ready for compression and storage. The absence of the nitrogen, which would be present if combustion occurred in air, is also expected to significantly reduce NO_x production and simplify SO_x removal. Nitrogen may still enter the kiln through leakage, or be introduced with the fuel, especially biomass and petcoke, or be carried in with organic matter contained in the raw meal. Sulfur removal can be effected during the compression and cleanup of the CO_2 and may not even be necessary if a nearby storage site can handle the additional contaminants. There is, for example, a large body of experience in handling of acid gases, mixtures of CO_2, SO_2 and H_2S, in the oil fields of Alberta, Canada.

Carbon Capture and Storage at Cement Plants

Since the early 1990's, several attempts have been made to assess the potential for reducing greenhouse gas emissions from the cement manufacturing process. Work toward estimating the potential for reducing CO_2 emissions from the cement industry started with a review of the process and potential design improvements. Hendriks et al. (Hendriks et al. 1999) estimated that the cement industry released 5% of all global CO_2 emissions in 1995. 50% of the CO_2 emissions related to cement manufacture are from calcination, 40% from the associated combustion and the remainder from the cement plant's electricity consumption. The calcination emissions accounted for 3% of the global CO_2 in 1995 and have risen to 3.5% in 2002 (Marland et al. 2005). The possible pathways for CO_2 reductions were listed as energy efficiency improvements, use of best available technology, fuel switching, lower clinker/cement ratio, alternative cements and flue gas scrubbing. In considering flue gas scrubbing, it was observed that typical CO_2 concentrations range from 14-33%. Given these high concentrations, Hendriks et al. considered oxygen combustion with a CO_2 sweep gas a logical choice.

At present there is no experience with cement manufacturing using pure oxygen. However, the use of oxygen enhanced combustion is practiced in the cement industry and leads to efficiency and production increases (Marin et al. 2001). The use of alternative feedstock was not mentioned in this report. Alternative feedstock's can be viewed as materials that do not contain carbonates and hence do not generate calcination CO_2. One such material is wollastonite, a natural calcium silicate (Kojima et al. 1999). The wollastonite can replace up to 30% of the limestone and results in a 24% reduction of CO_2 emissions. The drawback is the small quantities of globally accessible wollastonite.

Any attempt to ascertain the feasibility of CO_2 mitigation begins with an analysis of the energy consumption of the process. Detailed analyses of the energy consumption and the potential for improvements in energy efficiency have been performed (Worrell et al. 2000, Worrell et al. 2001). The technical information that follows is taken from those reports. As mentioned earlier, the thermodynamic minimum energy for clinker production is 1.76 MJ per kg while the most efficient kilns consume 2.5 MJ of fuel energy per kg of clinker, an efficiency of 70%. Electrical energy is also consumed at various stages in the process further reducing the efficiency. A schematic of the cement making process is presented in Figure 3, along with electrical and fuel consumption for one particular set of technologies. The technologies used include crushing using a roller crusher, raw meal grinding in a vertical mill, a dry (short) precalciner kiln and finish grinding in a ball mill/separator (Worrell et al. 2001). Worrell et al. list many technologies that range from 66 to 107 kWh per tonne cement (70-113 kWh/t clinker). The same author, in an earlier work, lists the electricity consumption of the dry process as 145 kWh/t cement (Worrell et al. 2000). The range of values highlights the variability of the cement manufacturing processes. The purpose of listing the electricity is to provide a comparison point for the increase associated with oxygen production and CO_2 compression. To that end, electricity consumption can be assumed to be on the order of 100 kWh per tonne cement. The primary energy required for electricity generation is calculated based on a conversion efficiency of 33%. There is also 10 kWh/t of clinker consumed by auxiliary equipment, e.g. conveyor belts, and in the cement bagging plant.

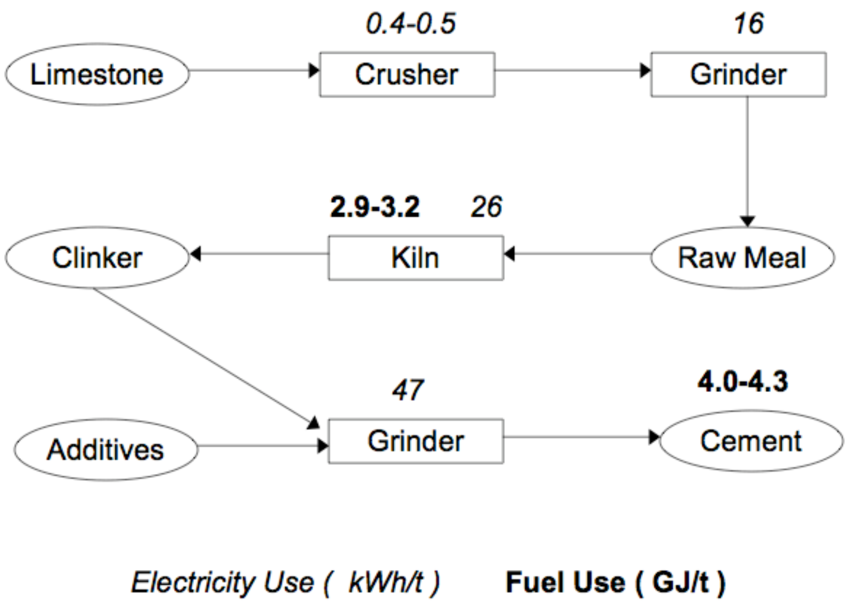

Figure 3: Schematic of cement manufacturing with energy consumption

Recalling that 1 kWh is 3.6 MJ and assuming 33% electrical generation efficiency, we can compare the importance of the various steps. This data, shown as a percentage of the total plant consumption (4.14 GJ), is presented in Table 1. While electrical energy use is not negligible, the thermal energy used in the kiln dominates.

Table 1: Primary Energy Consumption of Cement Plant Components

Crusher	Raw Mill	Kiln (elec.)	Kiln (thermal)	Grinder	Bagger
0.1%	4.2%	6.8%	73.9%	12.4%	2.6%

The focus on using alternative cement materials that “result in lower total CO_2 emissions per unit volume of concrete of equivalent performance” (Gartner 2004) suggests a disinterest in carbon dioxide capture, likely due to cost factors. Gartner highlights that concrete is the most widely used material on earth, based on $1.7x10^9$ tonnes of cement produced each year resulting in over 6 km^3 of concrete. He also doubts that process research will yield significant energy efficiency improvements. In addition, the electricity emissions (1.2 GJ primary energy per tonne of clinker) are not trivial. Gartner concludes that it is not feasible to make the amount of Portland cement using raw materials other than limestone. Instead, he presents four methods for reducing fuel consumption; improving kiln shell insulation, reducing clinkering times and temperatures, reducing the volume of exhaust gas, and reducing the lime saturation factor. In terms of blending, the three most promising alternative cements are pozzolan based (reactive aluminosilicates), calcium sulfo-aluminate based, and calcium sulfate based cements. The use of blending agents will require similar performance characteristics and likely need to have better performance, as they could be more expensive.

Consistently, four pathways to reducing CO_2 emissions from the cement industry are considered; increasing efficiency, alternative fuels, blending and carbon capture. We will not consider blending or alternative fuels as our work is focused on the clinker manufacturing process. The most effective efficiency improvements have been ranked by Worrell et al. (Worrell et al. 2000) and the top ten are listed in Table 2. The carbon reductions refer to annual amounts for the US cement industry. A measure is deemed effective if its cost falls below the average weighted energy supply cost, which was $2/GJ in 1994 discounted at 30%. This fuel cost is no longer relevant for natural gas or oil.

Table 2: Emission reduction through efficiency improvement

Rank	Measure	Reduction (ktC)	Cost ($/GJ saved)	Simple Payback Period (years)
1	Wet to pre-calciner kiln	1009	8.03	13.0
2	Process control system	361	2.32	4.3
3	Conversion to pre-calciner kiln	338	6.67	12.5
4	Add pre-heater	261	6.46	12.1
5	Preventative maintenance	219	0.04	0.1
6	Add pre-calciner to pre-heater	210	4.69	5.4
7	Clinker cooling grate	163	0.68	1.3
8	Use waste fuels	120	0.50	0.9
9	High efficiency roller mill	117	20.74	>25
10	Conversion to semi-wet kiln	104	0.56	0.9

Examining the results in Table 2 we can extract some important information. The most effective improvement involves switching from the worst to the best available technology and includes most of the other improvements. The efficiency measures ranked 3,4,6 and 7 involve heat recovery from the kiln. Measures 2 & 5 can be viewed as advanced operations that reduced error and variability. The final three measures can be summarized as reducing the fossil carbon content, the electricity consumption and the amount of evaporation required for clinker production.

The importance of managing the heat produced in the kiln can be quantified using the concept of exergy. Exergy is a measure of the energy available in the system to do work.

The exergy potential associated with each kiln output stream are presented in Table 3 (Camdali et al. 2004) and highlight the importance of heat recovery. The enthalpy refers to heat contained in the various material streams with the lost enthalpy radiated through the kiln shell. The analysis suggests that further gains in efficiency will be realized by improvements in heat recovery from the pre-heater and kiln shell. These values are similar to another study on an Indonesian cement plant which found stack gases and kiln walls as the most suitable for energy recovery (Rasul et al. 2005).

Table 3: Enthalpy and Exergy losses from a cement kiln

Material Stream	Clinker	Dust	Stack Gases	Lost
Enthalpy (%)	83.8	6.0	8.1	2.1
Exergy (%)	18.8	1.1	44.5	35.6

An energy audit on another cement kiln found that 40% of the input energy left the kiln as sensible heat. The flue gas carried away 19%, the cooler stack lost 6% and the kiln shell the remaining 15% (Engin & Ari 2005). The larger shell losses in the Engin paper are a result of higher exterior wall temperatures (308^{o}C) as compared to the Camdali paper (200^{o}C). Engin also found that 1 MW of power could be generated from the stack gases at a 600 tonne clinker per day facility. This is 40 kWh per tonne of clinker or 45% of the electrical requirement shown in Figure 3. The higher kiln surface temperature leads to 3 MW of sensible heat recovery, which could be used for pre-heating. Other literature suggests that along with heat recovery from the flue gas, using secondary air to cool the clinker and limiting air infiltration will reduce energy consumption (Wilson & Iten 1976).

Efforts to estimate the cost of capturing the CO_2 from the cement kiln exhausts have naturally focused on amine absorption systems. One study used the ASPEN computer modeling software to simulate capturing 85% of the CO_2 from a cement plant (Alie et al. 2005). The flue gas was simplified to CO_2 and nitrogen. Alie et al found the re-boiler duty, the dominant energy penalty, to be 177 kJ/mol of CO_2. This value is in line with estimates of monoethanolamine (MEA) capture in the literature (Desideri & Paolucci 1999). However, the result depends on the assumption that flue gas impurities have been reduced to the levels shown in Table 4.

Table 4: Pollutant remediation required for MEA (from Hegerland et al. 2006)

Component	Kiln Outlet	Target	Reduction	Treatment
SO_2	200 mg/Nm^3	12 mg/Nm^3	94%	Sea Water
O_2	8 vol%	<1.5 vol%[1]		
NO_2	64 ppmv	Not specified		SNCR
Dust	40 g/Nm^3	15mg/Nm^3	99.9%	Dust filters
Heat	350-400°C	50°C	85%	Heat Recovery

[1] Hegerland lists this value as ">1.5 vol%" yet MEA deterioration is positively correlated with O_2 concentration (5% at 6% O_2) (Uyanga & Idem 2007); we assume "<1.5 vol%" was intended.

Another capture study on a cement plant in Norway found that MEA was the preferred solution (Hegerland et al. 2006). Hegerland considered the possibility of oxygen blown kilns and MEA scrubbing. The selection of MEA over oxygen was based on a previous Norcem study that determined "for retrofit of an existing installation, amine absorption is the only viable option." The study notes that significant gas clean up is required and that any failures in the cleanup system will cause significant MEA degradation. The pollutants and required mitigation are shown in Table 4. The flue gas also contains 8 mg/Nm^3 of HCl that will be captured with the SO_2. The kiln exhaust gas is assumed to contain 20% CO_2.

The cost estimate by Hegerland et al. uses a natural gas price of \$4/GJ and notes that if the price climbs above \$4.50/GJ then coal is the more cost effective fuel. It is worth noting that switching to coal would double the CO_2 produced by the boiler. The cement kiln produces 307,000 Nm^3/h of flue gas. The CO_2 produced by the boiler was fed to the MEA capture system to limit fugitive emissions. The final cost estimate is \$55 USD per tonne of CO_2 captured. This is more expensive than the Accelerate Weathering of Limestone (AWL) system which estimates costs below \$30 USD/tonne (Rau et al. 2006). Rau et al also suggested using the Cement Kiln Dust (CKD) as an alkalinity source for CO_2 capture. This assumes that the CKD is so fine that if re-introduced into the kiln, it would exit through the stack. This could potentially capture ~10% of the CO_2 generated depending on the efficiency of the plant (Wilson & Iten 1976). There is no mention of the kinetics or scale of the AWL reactor in the paper by Rau et al.

Oxygen Combustion

The use of high purity oxygen in cement manufacturing has been considered for many years because of the associated increase in production (Wrampe & Rolseth 1976). Wrampe and Rolseth showed that adding oxygen to the kiln increases the cement production of the plant. They found that the optimum oxygen content of the combustion air was 22-23% by volume, slightly higher than normal air (21%). The dominant factor controlling this level is the temperature profile in the kiln. The use of oxygen did not always improve fuel efficiency based on their sample of 4 dry plants. The change in specific fuel requirements varied from +1.4% to -15.1%. Wrampe and Rolseth found the production increase ranged from 17-22% over three dry cement plants. In this work we will use an estimated production increase of 15% for the oxygen combustion system. This technology is not a direct proxy for oxygen combustion with sweep gas but does set reasonable starting points for the O_2/CO_2 mixture.

The amount of oxygen required will depend on the specific fuel consumption of the plant. In this work we consider a modern, pre-calciner plant consuming 3,200 kJ per kg of clinker (Engin & Ari 2005, Hendriks et al. 1999). We further assume that the combustion of fossil fuels yields approximately 400 kJ per mol O_2. Using these values we estimate the oxygen demand as 0.20 Nm^3 O_2 per kg clinker. The amount of electricity required to produce cryogenic oxygen is around 1 MJ_e per Nm^3 or 25 kJ_e per mole of O_2. The additional electrical demand associated with oxygen combustion is then 0.20 MJ_e per kg of clinker or 56 kWh per tonne of clinker. Including the extra production, the effective penalty is 48 kWh per tonne of clinker. The current electrical load on a cement plant is 100 kWh per tonne (Figure 3) and the addition of an ASU would increase this to 138 kWh per tonne or by 58%. It should be noted that this does not include the electrical energy required to compress the CO_2 prior to transportation and storage.

Comparison of Post Combustion vs. Oxyfuel

A comparison of these two technologies begins with a discussion on the origin of the CO_2 targeted by the capture technology. A post combustion system can be viewed as a filter on the downstream end of a process that aims to capture 85-90% of CO_2 contained in the exhaust stream. In this sense, there is no differentiation between CO_2 from calcination and oxidation. Oxygen combustion is an upstream modification where high purity oxygen is produced for reaction with the fuel at the burner end of the kiln. Here, attention is only paid to the oxidation CO_2 with an excess of O_2 needed to prevent reducing conditions in the kiln. Given that the portion of CO_2 from fuel oxidation is less than half of the total CO_2, we expect the energy penalty associated with oxygen combustion to be proportionately less than post combustion capture.

These observations can be confirmed by comparing a post combustion MEA system with the equivalent oxygen fired kiln. Hegerland et al. performed a concept study for a coal fired, 1.4 Mt per year cement plant in Norway using the MEA system (Hegerland et al. 2006). The cement plant is expected to produce 0.9 Mt CO_2 per year or 103 $tCO_2\ hr^{-1}$. Emissions from electricity consumed on site are not considered but are small as much of Norway's electricity is derived from hydropower. The MEA system requires a boiler, fired with either coal (145 MW) or natural gas (122 MW), for regenerating the sorbent. The exhaust gases from the boiler are fed, with the cement kiln gases, into the MEA capture system. As a result, the capture system handles 143 $tCO_2\ hr^{-1}$ using coal and 123 $tCO_2\ hr^{-1}$ using natural gas. The objective is to capture 85% of the CO_2 entering the MEA tower resulting in net emissions of 25 $tCO_2\ hr^{-1}$ using coal and 22 $tCO_2\ hr^{-1}$ with natural gas. Compared to the original amount of CO_2 exiting the kiln, the capture efficiency would be 76% for coal and 79% for natural gas.

A kiln fired with oxygen would require a cryogenic air separation unit (ASU) to produce the oxygen of combustion. Cryogenic air separation is currently the most economical methods for producing large amounts (>1,000 m^3 hr^{-1}) of oxygen (Kirschner 2002). We assume that the 44% of the CO_2 exiting the kiln is from the fuel (coal or petcoke), which results in 0.4 Mt CO_2 per year or 46 tCO_2 hr^{-1}. The amount of oxygen needed can thus be estimated at 33 tO_2 hr^{-1} using the ratio of the respective molar masses (32/44). A cryogenic ASU requires 25 kJ_e/mol O_2 or in this case 7.3 MW of electricity (Perry & Green 1997). Using representative emissions factors from the IPCC Special Report, the electricity used would result in emissions of 5.5 tCO_2 hr^{-1} for coal electricity and 4.7 tCO_2 hr^{-1} for a natural gas combined cycle system. Assuming a negligible amount of dilution from air leakage, the capture efficiency of the oxygen kiln ranges between 95% and 97%. There is also an 80% reduction in exhaust stack freight (mass flow) and a 20-40% reduction in the amount of CO_2 sent to storage owing to the absence of a boiler. In terms of mass balance of CO_2 and capture efficiency, oxygen combustion looks promising. A conceptual outline for an oxygen-fired kiln, termed Reduced Emission Oxygen (REO) kiln, has been previously presented (Zeman & Lackner 2006).

Technological Challenges of Oxygen Combustion

Clinker Production in a CO_2 atmosphere

Changing the composition of the gas phase inside the kiln will affect the gas properties. Some of the changes may be beneficial but others may result in performance variations, especially with items like blowers and internal draft (I.D.) fans. Pertinent gas parameters and the relative change, from N_2 to CO_2, are presented in Table 5.

Table 5: Select Properties of N_2 and CO_2 at 300K and 1 bar

Property	Units	N_2	CO_2	Change (%)
Density	g/L	1.12	1.76	+57
Heat Capacity	J/mol K	29.2	37.1	+27
Heat Capacity[1]	J/mol K	34.8	58.4	+68
Thermal Conductivity	mW/m K	26.0	16.8	-35

[1] At 1,500K and 1 bar

The changes in the heat transfer and combustion characteristics in the burning zone of the kiln will be similar to those studied in the power generation industry (Buhre et al. 2005). These include a higher portion of oxygen required to reach similar adiabatic flame temperatures; higher gas emissivities (ability to radiate energy) owing the larger concentration of tri-atomic gases; reduced gas volume in kiln (higher heat capacity); higher concentrations of impurities due to recycling; and reduced volume of excess air. The benefit for carbon capture is that the conversion to oxygen combustion produces an exhaust stream of concentrated CO_2 that is ready for disposal. A co-reduction of NO_x is also expected because of the reduced availability of N_2 in the kiln.

The gas properties can be used to estimate the flow in a kiln converted to oxygen combustion. Based on the literature, the optimum oxygen content for combustion in an O_2/N_2 environment is 23% (Wrampe & Rolseth 1976). Using the specific heat capacities shown in Table 5, the inert portion (0.77) is reduced by at least 28% when switching from N_2 to CO_2. The equivalent CO_2 fraction is then 0.61, which means that the same amount of oxygen is now 28% of the flow. Buhre el al. suggests the optimal O_2 proportion is slightly higher at 30% (Buhre et al. 2005). The stack freight is reduced by approximately 80%, as most of the gases are recycled back to the burner. Buhre et al. also note that heat transfer should increase for the same adiabatic flame temperature.

Experiments were conducted to investigate the effect of switching clinker production from an atmosphere dominated by nitrogen to carbon dioxide as a result of conversion to oxygen combustion (Zeman 2008). The initial experiments investigated the effect on the calcination reaction. This reaction is of particular relevance as it is the first reaction in the clinker manufacturing process (Hewlett 2001, Locher 2002). The experiments were performed using a Netzsch STA 409 PC Luxx thermo gravimetric analyzer (TGA). The gas flow was controlled by two Aalborg GFC17 flow meters with flow rate kept at a constant 100 mL/min for the nitrogen and carbon dioxide experiments. The gases used were “bone dry” grade but not ultra high purity. The temperature profile consisted of a 10K/min ramp to 910°C with a 10 min dwell at 110°C and a 25 min dwell at 910°C.

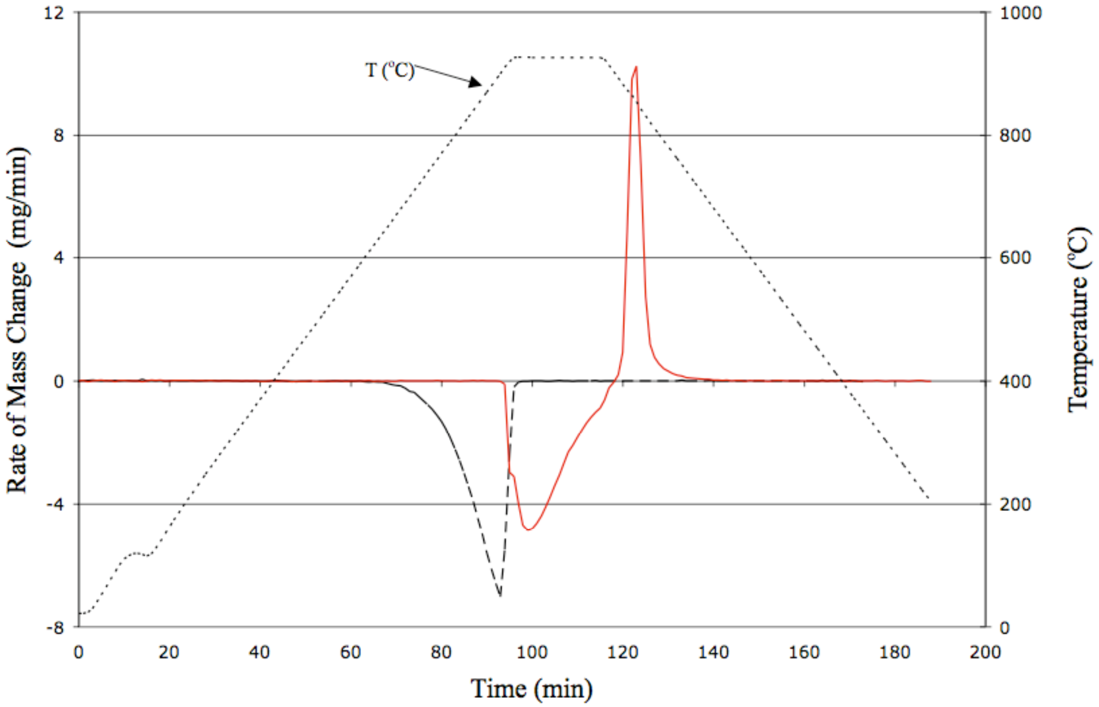

Figure 4: $CaCO_3$ Calcination Reaction in N_2 and CO_2 Atmospheres

The results of TGA analysis on calcite samples are presented in Figure 4. The figure shows the rate of mass change for the calcination reaction, presented in equation 1, and the carbonation reaction or the calcination reaction in reverse.

$$CaCO_3 \leftrightarrow CaO + CO_{2(g)} \qquad \Delta H^o = 165 \text{ kJ/mol; } T=900^oC \qquad (1)$$

As expected the presence of CO_2 delays the calcination to 900°C, however, Figure 4 contains two other pieces of information pertinent to cement production. First, the reaction profile changes from a gradual onset to a “threshold” type reaction with the peak reaction rate highest at the onset and then decreasing to completion. The peak rate was reduced by 30% from 7.0 mg min^{-1} in N_2 to 4.8 mg min^{-1} in CO_2. Second, re-carbonation occurs immediately after the temperature drops below 900°C at a higher rate of 10 mg min^{-1}. The potential of immediate re-carbonation will place an emphasis on a stable temperature profile between the pre-calciner and the kiln. Any re-carbonation will necessitate re-calcination, which may significantly diminish overall plant efficiency. The threshold type reaction may also dampen enhanced $CaCO_3$ disassociation in the presence of alkali salts. The higher CO_2 partial pressure in the pre-heater may also lead to the formation of alkali carbonates.

Clinker Formation Experiments

Experiments were conducted to determine the effect of changing atmospheres on clinker formation using a high temperature (1,500^{o}C) resistive heating (muffle) furnace (Zeman 2008). The furnace was a Carbolite STF 15/180 240V single-phase tube furnace with a 150 mm heating zone. The working tube consisted of a mullite cylinder 915 mm in length with an internal diameter of 52.5 mm. The total mass of the synthetic raw meal used was 446g consisting of 80.5% calcite ($CaCO_3$), 14.4% silica (SiO_2), 3.7% aluminum oxide (Al_2O_3) and 1.4% iron oxide (Fe_2O_3). The mixture used produces a silica ratio (SR) of 2.8, an alumina ratio of 2.64 and a lime saturation factor (LSF) of 0.99. The mass of the samples used in each experiment ranged from 2-4g with the exception of the surface area (B.E.T.) experiments, where 0.1g was used.

The first experiments using the tube furnace focused on changes in the mass and sintering profile. These changes were measured as the raw meal was heated from 600^{o}C to 1,450^{o}C. An experiment consisted of placing a fresh sample of raw meal in a sample dish and heating to the desired temperature with 30 mL/min of the appropriate gas. The results are presented in Figure 5. The line marked “Expected” refers to the mass loss that would result from complete calcination of the limestone portion of the raw meal. In the case of experiments in the CO_2 atmosphere, the gas flow was switched to nitrogen during cooling to avoid re-carbonation.

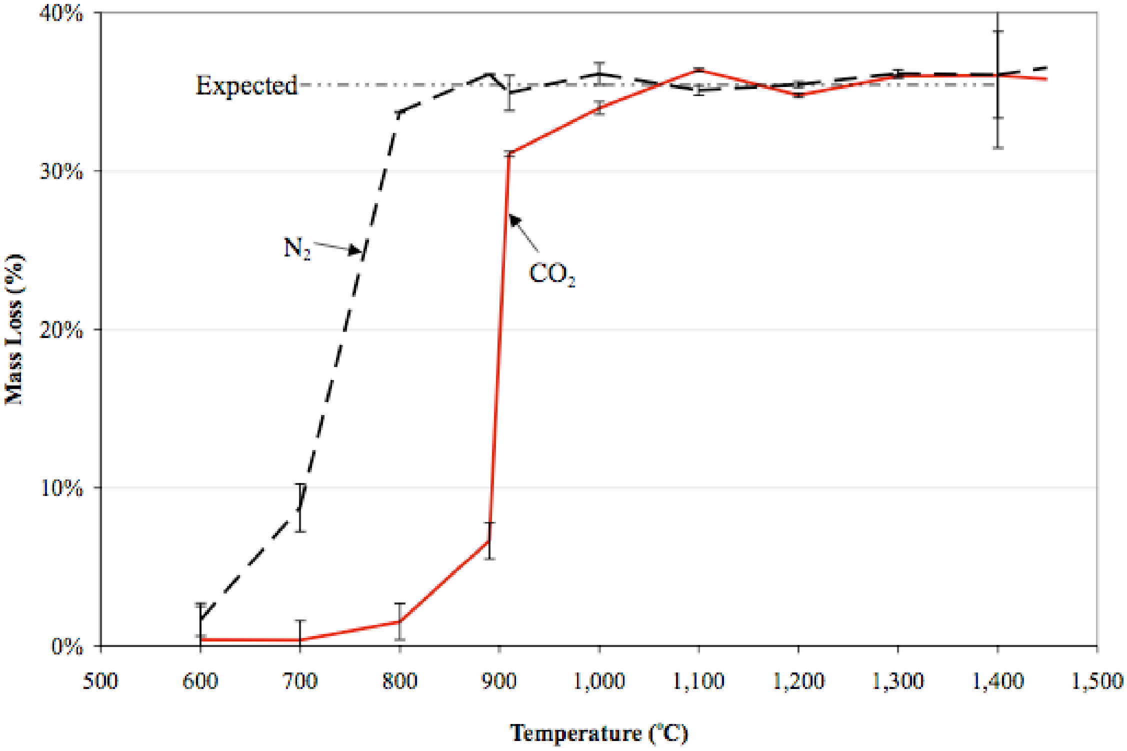

Figure 5: Raw meal mass loss during heating to clinker formation temperatures

The results of the mass loss curves support the experimental results of Figure 5. In it, we see a similar delay in the onset of the mass loss (release of gaseous CO_2 during calcination). In a nitrogen atmosphere, the raw meal begins to release CO_2 almost immediately and nears completion by 800°C. In contrast, in an atmosphere dominated by CO_2, the mass loss is delayed until temperatures reach 890°C. The release of CO_2 nears completion at temperatures above 1,100°C. In both cases, the mass loss expected from calcination of the calcite portion of the raw meal is attained by 1,300°C. The error bars in

Figure 5 refer to the difference in mass of the sample dish before and after the run. Figure 5 shows a small amount of mass loss (15%) in the CO_2 environment at temperatures below 890°C, which is not supported by Figure 4. CO_2 can also be evolved from the raw meal via the formation of belite according to equation 2.

$$2CaCO_3 + SiO_2 \rightarrow 2(CaO)\bullet SiO_2 + 2CO_{2(g)} \quad \Delta H^o = 65\ kJ/mol;\ T=700^oC \qquad (2)$$

The enthalpy of reaction is listed, for both equation 1 and 2, in units of kJ/mol CO_2. A comparison shows that belite formation requires one third the heat input of calcination. While much more experimentation is required to delineate the amount of belite formed, the reaction may potentially reduced the thermal load by 10% assuming the 15% mass loss shown in Figure 5 is attributable to equation 2.

The specific surface area of the samples was measured using the B.E.T. analysis method on a Gemini V device calibrated using Acetylene Black. The measurement of surface area produced a BET value of 76 m^2/g as compared to the expected value of 80 m^2/g. The difference, 5%, exceeded the error provided by the Gemini V, an average of 2.3%, and was used as the representative error. The results are presented in Figure 6. The BET measurements show the delayed onset of the calcination reaction as well as a noticeable difference in specific surface area. The decrease in surface area throughout the calcination reaction in a CO_2 environment is expected given the evidence in the literature regarding the effects of gaseous CO_2 on sintering of lime. Figure 6 also shows that once temperatures reach 1,200°C, the available surface area is similar for both environments. The reduced surface area may affect low temperature belite (C_2S) formation. The literature states that the most important phase of clinker formation is the molten phase at temperatures above 1,300°C (Hewlett 2001), which appears to be unaffected.

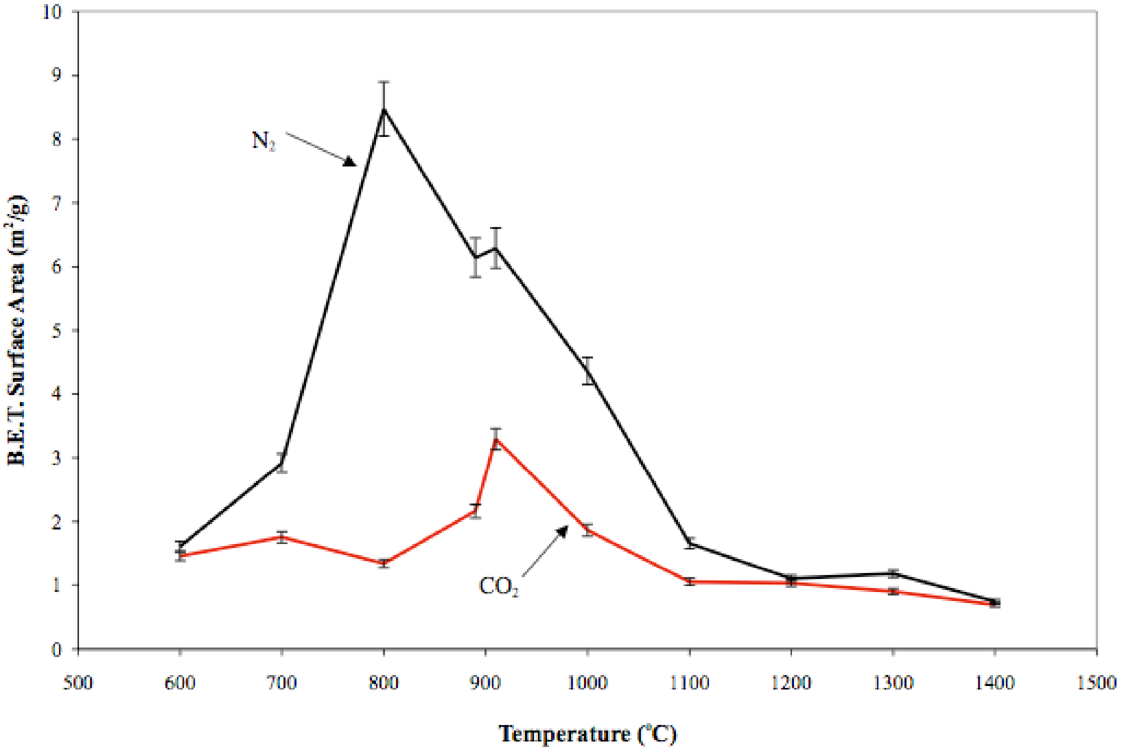

Figure 6: BET Measurements on raw meal heated in atmospheres of N_2 and CO_2

The potential for re-carbonation in a clinker cooler operating in a CO_2 environment was also investigated. Re-carbonation refers to the conversion of free lime (CaO) back to $CaCO_3$ through absorption of gaseous CO_2. The experiments involved heating the raw meal to 1,450°C and cooling (30°C/min) without switching to an inert gas like N_2. In the CO_2 atmosphere case this resulted in the reactants being available for carbonation in the temperature range of 400-900°C. The results are presented in Figure 7.

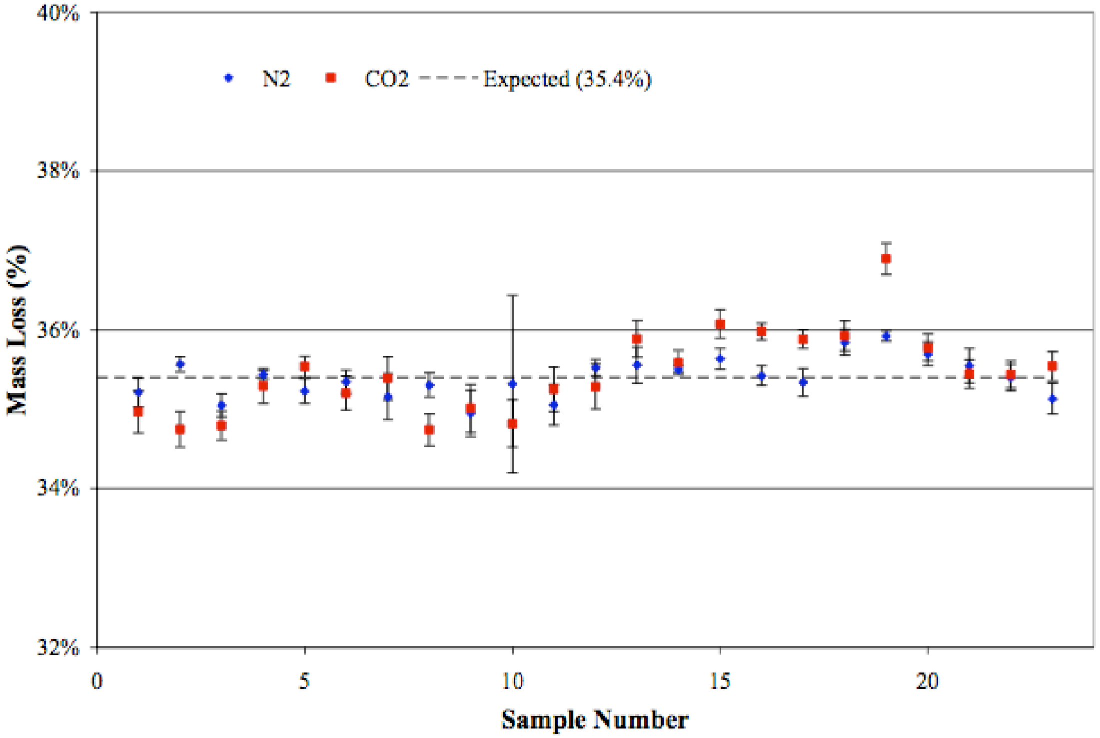

Figure 7: Results of Re-carbonation Experiments in N_2 and CO_2

The results show no clear trend that would indicate gaseous CO_2 is reacting with the clinker or free lime. In the N_2 environment, the average mass loss was 35.4±0.2% while in the CO_2 environment the average was 35.5±0.2%. The expected mass loss value (35.4%) is based on the composition of the raw meal. The variation around this value can be attributed to imperfect mixing of the reagents. The absence of any re-carbonation is likely a function of the reduction in specific surface area induced by the high temperatures and the formation of the calcium silicate compounds that limit the availability of lime.

One can conclude that re-carbonation of the clinker in the cooler is not a serious concern. It is not necessary to switch from a CO_2 atmosphere to a CO_2 free atmosphere, which would likely introduce major losses in the CO_2 capture efficiency.

The Reduced Emission Oxygen Kiln

The removal of air from the cement manufacturing process will produce some profound changes in the design of the kiln. It is expected that the main components, the pre-heater, kiln and clinker cooler, will function in a similar manner while using different fluids. In this manner, conventional rotary kilns may be converted, through retrofitting, into Reduced Emission Oxygen (REO) kilns. In this section we introduce the basic design of the REO kiln and compare it to a conventional kiln. The comparison serves to highlight the components that will require modification and future research. A simplified schematic of the REO kiln is presented in Figure 8.

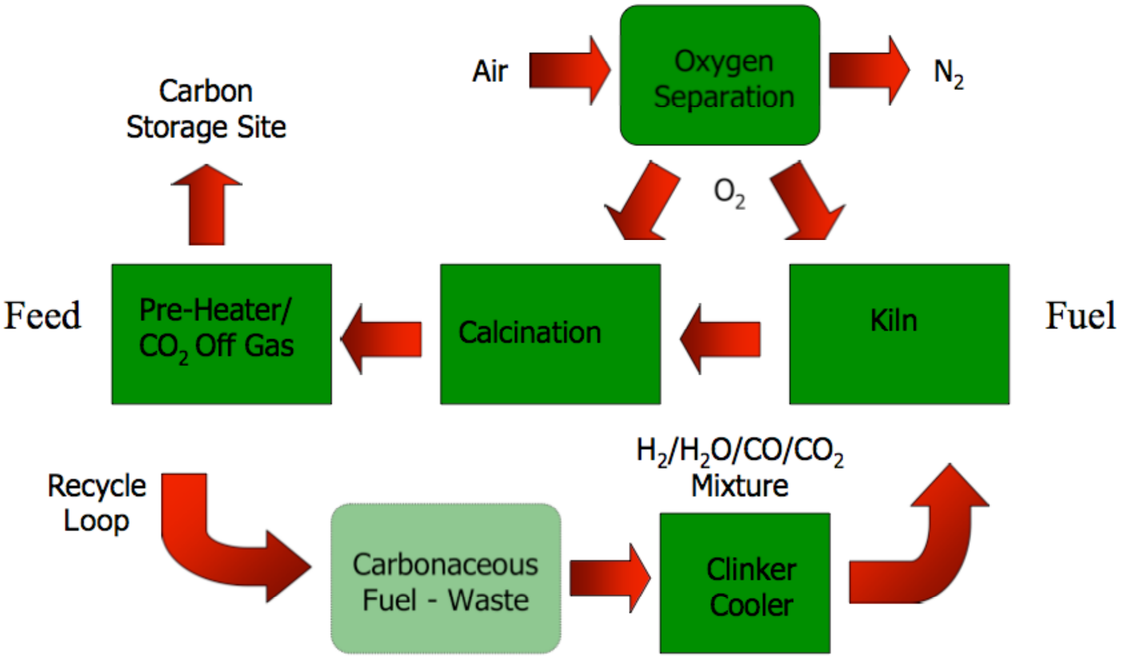

Figure 8: Process Components in REO Kiln

Baseline System

The basic blocks of the cement kiln are present in Figure 8 with the addition of an oxygen separation or production step. The REO kiln will have a clinker-burning zone where temperatures reach 1,450^{o}C along with a pre-calciner operating at slightly elevated temperatures (925^{o}C) as compared to a conventional pre-calciner (850^{o}C). A pre-heater will also be present for transferring heat from the outgoing kiln gases to the incoming raw meal. The noticeable difference is that the gas stream will have a higher density (+57%) owing to the absence of nitrogen and the dominance of CO_2. The clinker cooler will also be of a similar design with an O_2/CO_2 mixture rather than air as the working fluid. The cooler warrants closer attention as the cooling gases may be hotter than ambient air, which may increase the amount of secondary cooling or vent air. The two novel components are the oxygen production facility and a fuel preprocessing facility.

Oxygen production and integration

Oxygen production will occur on site, as this is the most cost effective method for a consumer the size of a cement plant. The size of the oxygen facility will of course depend on the plant. As a rough guide we estimate the amount per tonne of clinker produced. Using the average energy consumption per unit clinker (3.2 MJ kg^{-1}) and the heat produced per unit of oxygen consumed (0.4 MJ mol^{-1}), we can estimate the oxygen requirement as 8 mole O_2 or 0.20 m^3 per kg of clinker. This value can be converted to 200 m^3 per tonne of clinker. The capital cost of an ASU plant is \$6 per 100 m^3 adding \$12 to the cost of a tonne of clinker, not including operational (electricity) costs.

Approximately 25 kJ_e is needed to produce one mole of oxygen, which can be converted to 56 kWh per tonne of clinker, 48 kWh considering production improvements. The electricity required for oxygen production would increase the electricity consumption of the plant by 54% according to Figure 3. These figures are based on a cryogenic Air Separation Unit (ASU) location built expressly for the cement plant and connected via pipeline. The actual electricity increase may be lower owing to the associated increase in clinker production.

Oxygen can also be produced using novel technologies such as an Ion Transport Membrane (ITM). One of the significant advantages of ITM oxygen production is that it can be a net producer of electricity rather than a consumer. The oxygen is separated from the air by transport across a non-porous, mixed conducting ceramic membrane that has both electronic and ionic conductivity at high temperatures ($850^{o}C$) (Stein et al. 2002). The feed air is compressed to 5-20 bar and then heated to temperature to drive the oxygen across the membrane using a chemical potential gradient supplied by a partial pressure difference. The heat can be provided directly, by combustion, or indirectly. After oxygen removal, the remaining air can be heated by further combustion and then expanded through a turbine to produce power. This expansion provides more power than is required for the oxygen compression thus obviating the need for electrical power input. ITM systems are expected to reduce the capital cost of oxygen production by 35% but may increase CO_2 emissions if direct combustion is used for heating the air feed.

Oxygen production facilities are generally designed as separate facilities in order to maximize efficiency. This is particularly true for ASU systems, which cool the feed air to temperatures well below freezing. In order to minimize the cooling duty, the feed and exhaust streams undergo extensive heat exchange leaving the exhaust gas near ambient temperature and pressure. The system removes water and CO_2 from the feed stream to avoid problems during distillation. The ASU would capture 0.75 kg of CO_2 per tonne of clinker, which is a trivial amount (<0.1%) and will not be considered. The exhaust stream of an ASU will be dominated by dry nitrogen with some oxygen and argon. The salient feature is the absence of moisture, which suggests a potential for drying fuel or raw meal. Recalling that one kg of air can hold 15 g of water at 20^oC and that the oxygen required for one tonne of clinker would produce approximately 900 m^3 of Nitrogen, we estimate the evaporation potential of the ASU exhaust at 16 kg H_2O per tonne clinker. Recalling also that 1.5 tonnes of raw meal is required to produce 1 tonne of clinker, the ambient nitrogen exhaust is capable of drying raw meal with moisture content of 1%. In order to dry raw meal containing 6% moisture, the nitrogen would have to be at 50^oC.

Differences from Conventional Kilns

The conversion of a conventional cement manufacturing plant to a REO kiln design will involve design changes to many, if not all, parts of the plant. In this section we outline the expected changes in material flows and design involved in converting a conventional plant, shown in Figure 1, to a REO kiln. The discussion, focused on changes to the conventional design, will be divided into the process components shown in Figure 1 including quarrying, grinding, clinker production, clinker grinding and storage/shipping. The clinker production section has been further subdivided into pre heater, kiln and clinker cooler sections. We do not expect any changes to the quarrying and storage/grinding aspects of the cement manufacturing process. It is also not expected that changes in the electricity consumption patterns will ensue. The electricity consumed, however, is expected to increase and there is the potential to generate electricity on site.

The clinker production portion of Figure 1 encompasses the pre-heater, rotary kiln and clinker cooler as well as the associated fans. Each of these process steps will be affected in a different manner and as such, will be discussed separately. In addition, the REO kiln contains a CO_2 recycle conduit that returns CO_2 from the top of the pre-heater to the clinker cooler. A common thread among them is the absence of air or more specifically the nitrogen contained in air. The gas mixture in these components would consist of a CO_2/O_2 mixture with the CO_2 portion in excess of 70%. There will also be a general effort aimed at reducing leakage in order to avoid dilution of the CO_2.

Pre Heater

The primary function of the cement kiln pre-heater is to transfer heat from the kiln exhaust gases to the incoming raw meal. The pre heating of the raw meal increases the thermal efficiency of the plant thereby reducing operational fuel costs. Kiln exhaust gases are currently dominated by nitrogen as shown in Table 5. The REO kiln design is expected to raise the CO_2 levels from 20-30% to over 90%. As mentioned, changing to a gas stream dominated by CO_2 may adversely affect convective heat transfer, owing to the lower thermal conductivity. In addition, the density of the exhaust gas will increase by 50% affecting the fluid dynamics in the pre heater tower. The actual increase in density will likely be less owing to the presence of steam, whose concentration may increase because of exhaust gas recycling. The increased heat capacity of the gas will result in a decrease in volumetric flow, which would lower the gas velocity for the same tower configuration.

A pre-heater tower consists of a series, usually 4-6, of conduits (riser ducts) and separation cyclones. The raw meal and exhaust gases flow co-currently in the duct to the cyclone, where the solids fall to stage below and the gases rise to the stage above. In the co-current transport, the gas phase lifts the raw meal and carries it to the next stage. CO_2 can be more effective at this than nitrogen owing to its higher density (Clark 2006). Future work must investigate whether the higher density and viscosity compensate for the lower thermal conductivity and gas flow.

$$D_{pth} = \sqrt{\frac{9\mu_g B_c}{\pi N_s v_{in}(\rho_s - \rho_g)}} \qquad (3)$$

The efficiency of the cyclone separators will also be affected by changing the gas composition. Determining the change in the theoretical diameter of particle removed (D_{pth}), as described in equation 3 (pg. 17-28 (Perry & Green 1997)), can provide an indication on those changes. The viscosity, at 327^{o}C, drops 5% from 29.6 μPa s for N_2 to 28.0 μPa s for CO_2 (Lide 2000). The increase in gas density will not affect the cyclone, as the solid density is one thousand times larger. A lower velocity is expected, as volumetrically less CO_2 is present owing to the higher heat capacity. Table 5 shows a 30-60% increase in heat capacity, which suggests a proportionate reduction in velocity for a fixed cross sectional area. In equation 3, the size of particle removed is inversely proportional to the square root of the air velocity and a 30-60% reduction in velocity would suggest a 30-80% increase in the theoretical particle size. Velocity is proportional to the number of spirals (N_s) in the cyclone, which may further increase the size. Reducing the width of the inlet duct (B_c) increase the inlet velocity. Changing the gas density and velocity will affect the pressure drop across the cyclone. The pressure drop is proportional to the density and to the square of the velocity (ρv^2). The net change on the pressure drop across the pre heater tower will depend on the change in velocity required to effect the same dust removal.

The decrease in the thermal conductivity of the exhaust gases will also affect the efficiency of the pre heater tower. The reduction is expected to lead to less heat transfer during each collision between the gas and solid particles. Heat transfer can be improved by increasing the residence time between stages, a result of lower velocities mentioned above. The minimum velocity will be set by the size of the raw meal particles, in order to maintain fluidization, and the exhaust flow from the kiln. If the latter is limiting, some of the gases can be ducted to bypass the pre heater tower. The appropriate operating conditions will be determined by site specific criteria such as raw meal grinding, duct size in pre heater and increases in production capacity.

The requirements discussed above suggest that there are four relevant velocities in the pre heater tower. These are the velocities required to remove the combustion gases from the kiln, transfer heat from the gases to solids, to transport the raw meal to the next cyclone and allow satisfactory solid separation in the cyclone. The changes induced by switching to gases dominated by CO_2 may necessitate a technological alternative to the existing multi stage cyclone design.

Increasing the partial pressure of CO_2 in the pre-heater will have the effect of enhancing re-carbonation of the lime migrating up the tower. The migration of particles is caused by the efficiency of the bottom stage cyclones being less than 100%. If we use a bottom stage efficiency of 85% we can determine the upper limit for extra energy consumption due to re-carbonation. An 85% efficiency cyclone leaves 0.18 kg of raw meal in the tower per kg of clinker produced. At 65% CaO, the energy penalty associated with re-calcination of the lime is 218 kJ per kg of clinker assuming full re-carbonation. The extra energy amounts to a 7% increase in thermal input for a kiln consuming 3,200 kJ per kg of clinker. Increasing the efficiency of the bottom stage cyclone can reduce the amount of thermal energy lost. The optimum operational point is the balance between the thermal load saved by increasing the efficiency and the increased pressure drop across the tower caused by the high efficiency cyclone.

Pre-Calciner

Even though the function of the pre-calciner would not change, the concentration of CO_2 would increase from 20-30% to potentially 90% or higher owing to absence of N_2. The effect of increasing the partial pressure of CO_2 on the calcination reaction has been known for almost one hundred years (Johnston 1910). The temperature at which the calcination occurs will rise from 800-850^{o}C in a conventional kiln to 900^{o}C in the REO Kiln. The operational temperature of the pre calciner would rise accordingly. The energy required to calcine the calcium carbonate would remain constant (180 kJ mol^{-1} CaO). More energy may be required to raise the gas temperatures to 900^{o}C, which may require more fuel and oxygen to be diverted from the primary burner.

The impact of changing the temperature of the pre calciner is to change the temperature profile in the kiln. Raising the temperature in the pre calciner will flatten the profile, i.e. reduce the difference between the pre-calciner and burning zone in the kiln. Given that the gas phase is dominated by CO_2 the temperature profile must be kept steady to avoid re-carbonation of the lime. Temperatures below 900°C between the pre-calciner and the burning zone could result in re-carbonation. This would significantly increase the energy consumption of the kiln, as calcination is the most endothermic reaction and all of the raw meal can re-carbonate at this stage. The higher temperature in the pre calciner would also increase heat loss through the walls of the pre calciner.

Some cement plants include bypass systems to control chloride and alkali cycles between the kiln and pre-heater. The system operates by removing a small percent (1-5%) of the kiln exhaust gas and then quenching it to crystallize alkali chloride compounds. The quenching is accomplished by mixing the exhaust gas with an excess of ambient air. Such a system could be implemented in a REO kiln design but would lead to fugitive emissions. Given that 80% of the kiln exhaust is recycled CO_2, the 1-5% removal would constitute fugitive CO_2 emissions of 5-25%. Alternatively, novel methods for controlling cycles of volatile compounds must be found.

Kiln

The implementation of a REO kiln design for clinker production will drastically change the gas composition in the kiln. The use of concentrated oxygen results in the removal of nitrogen, which acts as a thermal ballast during the combustion process. The absence of thermal ballast would result in kiln temperatures high enough (>2000°C) to cause structural damage to the kiln. CO_2 would therefore be recycled from the exhaust stack to the kiln to act as the ballast. Changing the dominant gas from nitrogen to CO_2 will alter the gas properties in the kiln. A comparison of some properties of the two gases is presented in Table 5.

The effect of these changes is being studied by the power generation industry as oxygen combustion is considered a possible method for capturing CO_2 emissions. Changes to the combustion conditions will include a higher portion of oxygen to reach similar adiabatic flame temperatures; higher gas emissivities owing to larger concentrations of tri-atomic gases; reduced gas volume owing to higher heat capacity; higher concentration of impurities due to recycling; and reduced volume of excess air (Buhre et al. 2005). Buhre et al. suggest the gas feed should consist of 30% oxygen although this may be reduced as a result of the higher emissivities especially if water vapor is present.

Research into oxygen combustion has focused on boilers for power generation (IPCC 2005). Results obtained to date suggest the technology is feasible (Buhre et al. 2005). Buhre et al identified heat transfer, gaseous emissions, ash issues and flame characteristics as the dominant issues moving forward. In all cases, the pilot studies showed that heat transfer conditions in an air fired facility could be duplicated in the oxygen facility. It was noted that radiative heat transfer increased slightly with a drop in convective heat transfer. The result may be an increase in kiln shell temperature and heat loss through the kiln wall. The studies also showed an increase in sulfur dioxide (SO_2) concentrations, caused by the recycled exhaust gases, with the potential for corrosion. Given the high CaO content of raw meal, the potential exists for in-situ gypsum formation with deposition in the kiln or inclusion in the clinker. Higher concentration of trace elements, such as mercury and cadmium, can also be expected. The emission of nitrogen compounds (NO_x) was significantly reduced in most cases. The overall combustion performance is affected by leakage of air into the combustion zone.

One important difference between cement kilns and power boilers is the rotation of the kiln. The rotation of the kiln results in the potential for leakage at both ends, particularly at the feed end. The hood is typically at negative pressure, which results in air infiltration. There is also leakage out of the kiln system, which can account for 4% of the mass balance for the plant (Rasul et al. 2005). Either case is detrimental to the objectives of the REO kiln. Hood infiltration would reduce efficiency by introducing cold air into the combustion zone, diluting the CO_2 stream and increasing NO_x formation. Leakage out of the system would result in fugitive CO_2 emissions and increase the cost per tonne CO_2 captured.

Leakage can be reduced by preventative maintenance aimed at plugging holes in the skin of the pre heater and cooler. Encasing the kiln in a non-structural sheath that is gas tight and slightly pressurized with CO_2 can reduce the leakage from the rotation of the kiln. The sheath would isolate the kiln from the environment and ensure that hood infiltration does not dilute the CO_2 content. While leakage and dilution may be reduced, the sheath would restrict convective heat transfer from the shell wall to the environment. The result could be excessive shell temperatures. Currently, the outside temperature of a kiln shell can exceed 300°C. In order to minimize damage to the shell, an active heat management system would be required for the sheath. The high shell temperature suggests a system based on water evaporation and condensation may be feasible. The heat radiated, totaling 3% of the energy balance, would be harnessed for use elsewhere in the plant. A schematic of a possible configuration of a kiln shell cooler system is shown in Figure 9.

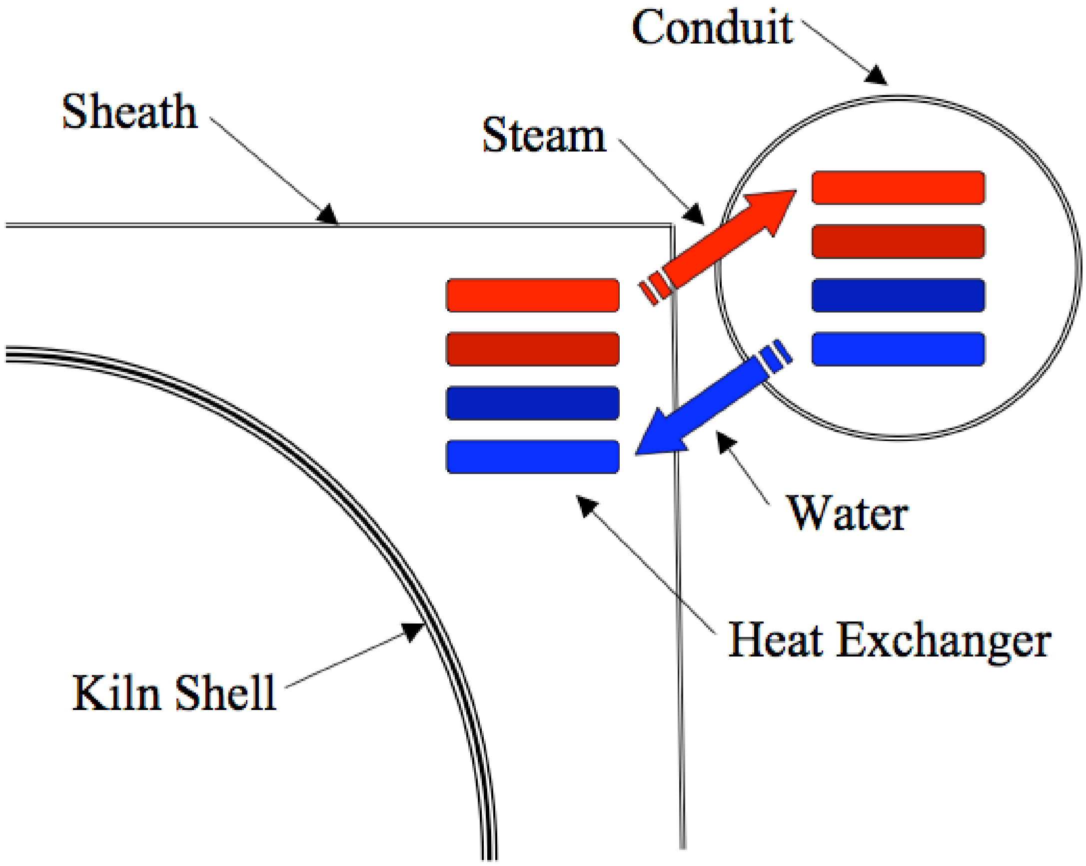

Figure 9: Schematic of Kiln Shell Cooler

The system would consist of two heat exchangers, one located inside the sheath and one outside. Water would flow, possibly by gravity, from the external to the internal heat exchanger where it is evaporated by the heat from the shell. The steam would flow to the external heat exchanger were it would be condensed back to water. The external heat exchanger could be contained in a conduit, as shown, which would allow heat transfer to a designated fluid. Alternatively, the heat could be discharged to the atmosphere by blowing ambient air through the heat exchanger. However, there is typically use for low grade heat in drying and preparing the input streams. If the heat is used to raise the temperature of the input streams, the overall efficiency of the kiln is enhanced.

The use of industrial oxygen in the kiln places an economic incentive on minimizing the amount of excess oxygen exiting the kiln and pre-calciner. The economic cost of producing the oxygen will require tighter control over the reducing and oxidizing conditions in the kiln. In addition, CO_2 can be viewed as an oxygen source through its reduction to carbon monoxide (CO). Reducing conditions can be localized owing to placement of the flame in the load.

Clinker Cooler

The function of the clinker cooler is to lower the temperature of the hot clinker exiting the kiln (~1,200^{o}C) down to more manageable levels (200^{o}C). A secondary function is to recover heat from the cooling process and transfer it to the kiln via secondary and tertiary air feeds. Typically, ambient air (20^{o}C) enters the cooler below the clinker bed and is blown upwards through the bed before entering the kiln. The REO kiln design uses CO_2 from the exhaust stack for clinker cooling as opposed to air. The exhaust gas exiting the top of the pre heater is hotter (over 250^{o}C) than ambient levels and will not be able to remove as much heat. In addition, CO_2 has a different heat capacity that air, consisting of oxygen and nitrogen.

The specific heat capacity of the gas is a measure of how much energy must be absorbed per unit mass to raise the temperature by one degree. The specific heat capacities, at constant pressure, for the gas mixtures relevant to cement manufacturing and the REO kiln are presented in Figure 10. We can see from the figure that the heat capacity of CO_2 is higher than that of air. Furthermore, the heat capacity rises faster with temperature than that of air. The net effect is that it will take more energy to raise a cooler gas dominated by CO_2 to the same secondary air temperature currently seen in the kiln. We can estimate that it would take 42% more energy for the 20% O_2/ 80% CO_2 mixture and 52% for CO_2 alone using a target air temperature of 625°C. Ambient air enters the cooler at 20°C while CO_2 from the pre heater would enter at elevated temperatures. We can also estimate the allowable entry temperature that would result in the same heat absorption and secondary air temperature. The maximum inlet temperature for the O_2/CO_2 mixture is 220°C and 250°C for CO_2 alone. This is a good approximation for the re-circulated CO_2.

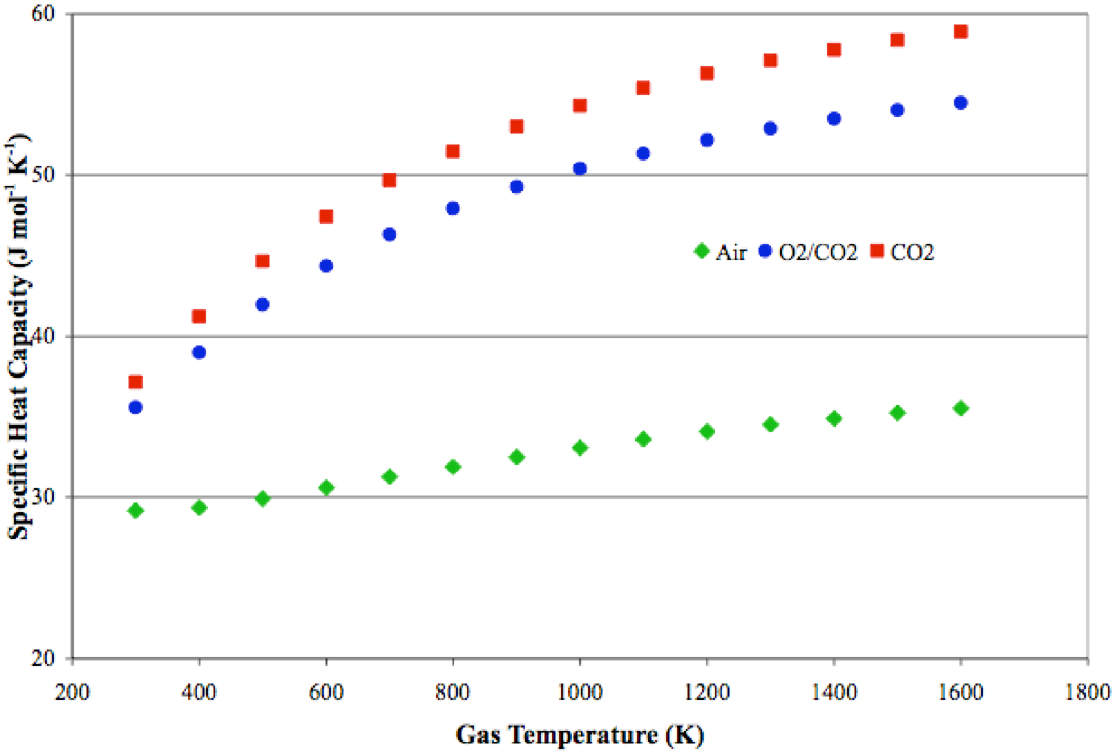

Figure 10: Heat Capacities of Potential Cooler Gases

The fact that we are recycling CO_2 from the pre heater introduces another degree of freedom, the cooler gas inlet temperature, which allows for optimized operation of the clinker cooler. If the recycled gas stream is cooled to ambient temperatures then the average temperature gradient between the hot clinker and the gas would be greater than in a conventional cooler, owing to the higher heat capacity. The steeper gradient would be expected to enhance heat transfer.

Clinker coolers also exhaust vent air to the atmosphere, potentially 30% of the cooling air. Venting is necessary as the amount of cooling air required for the clinker exceeds the amount of combustion air required for the kiln. The amount of vent air is affected by the efficiency of the kiln and the amount of primary air, which is not derived from the clinker cooler. The use of recycled CO_2 in the REO Kiln precludes any venting to the atmosphere as this would result in both CO_2 emissions and material loss from the kiln. Potential solutions may involve inserting a gas barrier into the cooler similar in nature, but less permeable, to the overgrate curtain. One possible solution is to use the higher heat capacity of the CO_2 to remove more heat from the clinker. In this method, the recycled CO_2 is cooled to ambient temperatures and fed into the downstream section of the cooler. Upon exiting the clinker bed, the CO_2 is reused in the upstream portion of the cooler. Analogous to a counter flow heat exchanger, the feasibility is tied to eliminating gas exchange between the upper and lower section of the cooler. Another option is to use air in the lower section of the cooler without venting it to the atmosphere. The hot air could be used in the grinding mill or fed to an ITM oxygen facility. If the dry nitrogen were used then it could be fed to the grinding circuit. Here as well, the feasibility depends on dividing the cooler into two sections that do not exchange significant amounts of gas. Another approach would use CO_2 and recycle some of the CO_2 for a second round of cooling. The heat can be removed in a separate cooling system where the heat is used to produce steam.

It is clear from these discussions that efficient heat transfer from the CO_2 released from the kiln to raise the temperature of the feed and air streams and cool the clinker is important in a well-designed system. In addition, it may be advantageous to use some heat to create steam for the operation of a power plant.

Recycle Loop

The use of exhaust CO_2 as thermal ballast in the burning zone of the kiln necessitates a conduit to return a portion of the exhaust gases from the pre heater to the burner. The recycle loop is a new addition to the cement plant that returns CO_2 and heat from the pre heater to the clinker cooler. The dominant design considerations for the recycle loop are corrosion and heat loss. The brief discussion surrounding the recycle loop is not intended to diminish the engineering challenges associated with effectively returning CO_2 to the clinker cooler. The effectiveness of the loop is contingent on minimizing the heat lost to the environment and maintenance costs of equipment in contact with the gases.

In modern pre calciner kilns, the exhaust gases leave the top of the pre heater at temperatures ranging from 300 to 360^{o}C depending on the number of stages. Traditionally, these hot gases are sent to the grinding mill to dry the raw meal prior to entry in the pre heater. In this discussion we consider a gas stream containing CO_2, dust,

O_2 with the potential for gases such as SO_2, NO_x, Argon (Ar) and N_2. At the exit of the pre heater tower all of the exhaust gases are collected rather than sent to the grinding mill or vented to the atmosphere. At this point, an excess of CO_2 is present equivalent to the amount generated though combustion and calcination. Prior to being sent to storage, the excess CO_2 must be scrubbed to remove dust and impurities. At this time, a choice exists between scrubbing the entire gas stream or diverting the excess CO_2 and sending the ballast CO_2 to the clinker cooler raw. The advantage of clean up after diversion is the reduced size, and cost, of scrubbing equipment. This does not preclude a separate scrubber prior to the cooler, which can be of a different nature than that for the compression.

The excess CO_2 will require cooling prior to and during compression. Given the high temperature of the exhaust, heat recovery for use elsewhere in the plant (e.g. raw meal drying) is worth consideration. Again, this can be done before or after diverting the excess CO_2 to the compression station. The decision will likely be affected by cost considerations and the ability to provide an end use for the heat. It is worth noting that CO_2 compression requires the condensation of water vapor, which increases the amount of low temperature heat recovery, which can be used for drying incoming raw meal.

CO_2 Compression Station

The objective of capturing the CO_2 from the cement plant is to prevent its release to the atmosphere. Once captured, the CO_2 must be compressed prior to transport to the storage site. We will consider the compression of CO_2 to 80 bar, at which point it liquefies. Beyond 80 bar, the additional energy required for further compression is three orders of magnitude smaller, per bar, than that required to reach 80 bar (Blok et al. 1997). Blok et al. estimated the electrical energy penalty for compression to 80 bar at 281 kJ_e per kg CO_2 at a pump efficiency of 70%. A cement plant will have to compress the combustion and calcination CO_2.

Earlier we estimated the oxygen requirement at 0.20 Nm^3 per kg of clinker. This can be converted to a mass of 0.35 kg CO_2 to which we add 0.53 kg CO_2 from calcination of the limestone. The total CO_2 requiring compression is therefore 0.88 kg CO_2 per kg clinker. The electrical load associated with this level of compression is 247 kJ_e per kg of clinker, which is equivalent to 69 kWh per tonne of clinker. This is added to the existing electrical load from Figure 3 (90 kWh per tonne) and the load associated with oxygen production (48 kWh per tonne). We therefore estimate that the total load for the REO kiln is about 207 kWh per tonne of clinker, an increase of 130% over a conventional plant.

While the compression of CO_2 will add to the electrical load of the process it will also add to the heat available. Considering the amount of energy consumed by the compressors (69 kWh/t clinker) we can estimate the heat released. Assuming all of the energy is transferred to the CO_2, the compression will release approximately 300 MJ of heat. That amount of heat is capable of evaporating 135 kg of water per tonne of clinker, equivalent to a raw meal moisture content of 9%. Potentially, there is enough energy available in the compression step to dry the input meal.

Coal Mill

Cement plants fired using solid fuels have on-site grinding plants, not shown in Figure 1, to prepare the fuel, often coal or petcoke. These fuels have high radiative heat transfer owing to a bright flame and lower fuel costs with the potential disadvantage of high sulfur content and CO_2 emissions. We consider both direct fired kilns where ground coal from the mill is fed directly to the burner and indirect fired kilns where the coal accumulates in a bin prior to injection in the burning zone. Coal mills use air to fluidize the coal after grinding and to evaporate any moisture. If hot air, either from the cooler or pre-heater, is used then external air is mixed in to control the inlet and outlet temperature of the mill. Active temperature control is needed to prevent spontaneous combustion of the coal. Currently, adding ambient air is used to lower temperatures in the mill.

The central challenge with auxiliary systems to the REO Kiln design is to minimize air leakage into the kiln or CO_2 venting to the atmosphere. In an indirect fired system, the transition from open environment on the coal system to the closed system in the kiln can occur at the coal mill or the storage bin. If the transition is located at the bin then no change in coal mill operation occurs. The bin must now operate at atmospheric conditions above the ground coal and CO_2 rich conditions in the feed pipes. This can be accomplished by interlocks or using the coal itself as a vapor barrier with a slight leakage of CO_2 up through the bin. While potentially simpler, an indirect system cannot take advantage of REO kiln operating conditions, as it is isolated from the kiln gases.

Placing the interface at the coal mill inlet would result in the mill being charged with CO_2. A coal mill operating in an inert gas environment could be expected to be inherently safer than one using air. The safety is further enhanced by the endothermic (heat consuming) Boudouard reaction (carbon gasification) shown in equation 4.

$$C + CO_{2(g)} \leftrightarrow 2CO_{(g)} \quad \Delta H^{o} = +170 \text{ kJ/mol}, T = 700^{o}C \qquad (4)$$

The Boudouard reaction does not proceed until 700°C, well beyond operating temperatures of the coal mill. The operational temperature of the coal mill is now a free parameter controlled by the maximum operating temperatures of the equipment as the presence of CO_2 reduces the risk of spontaneous combustion. If the mill is operated at pressure, the carbon gasification reaction proceeds at proportionately higher temperatures. Steam will be present, from the coal drying, and converts to CO_2 and H_2 at similar temperatures (650°C). We assume that the gas stream exiting the coal mill will consist of CO_2 and steam with fluidized coal particles. The temperature of the mixed stream can be in excess of the 70-90°C (Peray 1986) of conventional coal mills.

Given that the fuel mixture will combust upon exiting the burner tip, the possibility of partial gasification of the coal exists in transit from the mill to the burner tip. One possible implementation is autothermal reforming of the coal/CO_2 mixture to induce the Boudouard reaction and convert some of the coal to CO. Some steam gasification can also be expected to occur. The result would be a more reactive fuel mixture entering the burning zone with energy “stored” as CO. The advantage is the improvement for low volatility fuels while the disadvantage is more stringent material requirements in the burner pipe. Given the use of produced oxygen, the appropriate amount of oxygen can be injected directly into the burner pipe, thereby reducing the risk of uncontrolled oxidation.

Safety Concerns

A cement plant built according to the REO kiln design would have structural changes that place an emphasis on operational safety. The changes are both positive and negative. The use of CO_2 as the drying medium in the coal mill may improve safety by reducing the risk of "over drying" in the presence of oxygen. The lack of oxygen in the coal mill would suggest operating at higher temperatures to reduce heat transfer. Components operating at elevated temperatures tend to increase safety hazard for workers. This is particularly true if the thermal load on the kiln shell is increased as a result of increased levels of oxygen.

The exclusion of air from kiln operations will be accompanied by a concerted effort to minimize air leakage into the kiln. The "plugging of holes" will have the side effect of eliminating any outlets for sudden pressure increases. The operational variability inherent in a cement kiln suggests the need for a "pressure release" option in the design. One possibility is to use the sheath as an outlet for sudden pressure increases or instances of kiln "upset". In this case, methods for removing dust pushed into the sheath must be devised.

Increased safety awareness is also needed whenever high purity oxygen is in close proximity to combustible fuels. The areas of concern could include premature mixing, loss of CO_2 ballast, loss of oxygen stream and variability in material streams. It may be necessary to have the oxygen and fuel delivered in separate conduits in order to avoid early combustion, which can be solved by using multi-port burners. Conditions may become unsafe if the oxygen supply to the kiln is interrupted while the fuel continues to be injected. While a prompt halting of the fuel supply is possible, it may be necessary to devise an alternate supply of air to reduce the risks associated with excess fuel combustion owing to the build up. Similar concerns would arise during an interruption in the CO_2 recycle loop that cools the clinker and provides thermal ballast for the kiln. The REO Kiln design may require the ability to substitute air in the clinker cooler and kiln for safe operation. Overall, the tighter control over operating conditions will necessitate contingencies for when conditions deviate from the design.

Economic and Policy Considerations

The price of carbon in a carbon-constrained world

The REO Kiln and other technologies or practices that aim to reduce atmospheric emissions of CO_2 from cement manufacturing are spurred by the scientific consensus that anthropogenic climate change requires significant action. The ratification of the Kyoto Protocol can be considered the first political manifestation of this consensus and requires reductions ranging from 5-15% from levels expected in 2008. However, these reductions are limited to the developed nations. Reductions of this size will slow down the rate of increase in atmospheric CO_2 concentration, but it will not lead to stabilization at any reasonable concentration level. Emissions pathways that lead to stabilization call for significant reductions (50%) over the next 50 years and virtual elimination of all emissions by the end of the 21st century. We consider the initial 50 year period for this work and the associated 50% reduction by 2050 (Pacala & Socolow 2004).

The IPCC Special Report on Carbon Capture and Storage is focused on large industrial sources (>0.1 Mt CO_2 annually) that combine to produce over 50% of current global CO_2 emissions (IPCC 2005). These sources are associated with the power, cement, refining, steel and petrochemical industries. A trend to reduce allowable emissions from all these industries evenly would result in an effective price for CO_2 emissions that is set by the marginal cost of the last tonne of CO_2 removed. In such a scenario, industries that can capture CO_2 more readily would have a cost advantage. An alternate scenario is one in which each industry will be held to its own performance standards.

It is noteworthy that 78% of the emissions from the large point source emitters catalogued in the IPCC special report originate from the power industry as opposed to 7% from the cement industry. The cost of capture in the power industry, estimated at $13-74 per tonne CO_2 for new fossil fuel plants, provides a good benchmark for what the cement industry must achieve in order to remain competitive in carbon markets. Given the relatively high percentage of CO_2 in the kiln exhaust, we expect the cement industry to be more cost effective than other industries. If this is the case, the cement industry will have an incentive to capture all its emissions and trade any additional emission reductions in markets such as the European Emission Trading Scheme (ETS) or the Chicago Climate Exchange. Early implementation of a lower cost technology would place cement companies in a strong negotiating and selling position for near term carbon markets.

Carbon credits, carbon taxes and other regulatory tools

There is a vast array of policy options for regulating the emissions of carbon dioxide. In order to move on a path toward stabilizing the atmospheric concentration of carbon dioxide, mandatory emission constraints in some form will be unavoidable. The task is simply to onerous to be accomplished strictly by voluntary compliance. Regulations could be broad-based like an economy-wide cap-and-trade system, or aim at specific technologies in specific industries. While this report cannot discuss all of them, it notes that different implementations will affect the cement industry differently, and have different impacts on the implementation and diffusion of new technology throughout the cement industry. It is therefore important for the cement industry to establish its own approach to the problem in order to make sure that in the larger context regulations are not written in a way that disadvantages the cement industry relative to other industries.

One approach to carbon dioxide emission reductions is a government controlled performance standard on an industry or on particular plant designs. Such performance standards are routinely promulgated in pollution control, for example in the United States, the Environmental Protection Agency has set standards for a variety of emissions referred to as criteria pollutants. The difficulty with such an approach is how to set such standards when the goal in the end amounts to a revolution in the way a particular industry does business. Nevertheless, it has been suggested (e.g. Jeff Sachs private communication) that international performance standards could provide one avenue for international agreements that prevent the wholesale migration of industries from industrialized countries with highly restrictive regulations to countries in which the bulk of the greenhouse gas emissions remain unregulated. While it is difficult to see how a global agreement can be obtained on the price of carbon, it may be easier to set certain performance standards in the handful of industries and few thousand operators that ultimately control the vast majority of all emissions.

Regulations can work alone, or in combination with carbon pricing policies. A price on carbon dioxide emissions is achievable either by taxation or through cap-and-trade like instruments. Again there is a plethora of sub options that need to be considered carefully.

For example, taxes could be levied on fossil fuels as they are produced, in which case the only direct impact on the cement industry is an increase in fuel cost with a potential for similar charges on calcination CO_2. Alternatively, taxes can be levied on the actual emission. In the first approach it would also be necessary to give credit for the sequestration of greenhouse gases. Otherwise one would do no more than drive fossil fuels out of the market. A scenario has been laid out in which fossil fuel producers must purchase or generate certificates of sequestration that match the introduction of carbon into the environment (Lackner et al. 2000). Initially the supply of certificates of sequestration will fall short of demand and is augmented by permits issued by public institutions. In such a scenario, the cement industry could deliver certificates of sequestration to fossil fuel producers, regardless of the source of its own fuel. The sequestration of biomass carbon would also reduce the CO_2 loading of the atmosphere and thus would have the same beneficial effect one could achieve by sequestering carbon dioxide produced from fossil fuels. The approach becomes particularly simple when it comes to waste fuels that could have mixed into them fossil carbon, e.g. in the case of tires that are burned for their heat value. In this case, the fossil carbon in the waste product has been charged at the time of production and one need not separate wastes into bio-derived wastes and petroleum or coal derived wastes.

In general a tax is levied on the emitter or the producer of fossil carbon. A credit is an allocation of carbon that can be sold to another emitter if the initial owner of the credit does not need it. While in the long term the number of available allowances is likely to move toward zero, over the next few decades there will be a substantial amount of CO_2

emissions that are either taxed, or alternatively permitted through allowances. It is possible to outlaw emissions in excess to ever shrinking allowances, or excess emissions are taxed at some prescribed rate. Again it becomes necessary to introduce mechanisms that allow for the recognition of carbon capture and storage as a means of reducing CO_2 emissions.

The cement industry is unique in that it contributes a substantial amount of CO_2 to the world's emission budget, an important part of which is not derived from fossil fuels. More than half of the CO_2 emanating from a cement kiln is due to the CO_2 released during the calcination of limestone. It is therefore likely that specific regulations on cement production will take into account this additional source of greenhouse gases.

The cement industry, with its high concentration of CO_2, would likely benefit from any scheme that allows it to generate credits. For this to be possible, carbon capture and storage (CCS) needs to be recognized as a valid means of reducing carbon dioxide emissions, and a pricing mechanism has been put in place that would allow any one who can reduce CO_2 emissions sufficiently to sell their excess reductions back into a larger market. This would work if fossil fuels are taxed and CCS-generated credits can be sold. This would work, if the industry were given a set of allowances that can be used internally or that could be sold into a wider market, as has been the case in Europe. While each implementation raises questions about price volatility and performance, it is clear that those players who can capture carbon dioxide more cheaply than others can take advantage of the change in the game and sell emissions reductions to those players who have a harder time collecting CO_2.

A carbon credit based implementation could drive innovation toward systems that can capture a substantial fraction of the off-gases coming from a cement plant. The financial incentives in a market that approaches $30 per ton of CO_2 would indeed be very substantial. It is likely that prices will reach this level, as most technologies that can actually store CO_2 will require financial support on this scale.

From the cement industries perspective, the most important set of technologies will revolve around carbon dioxide capture. Capture is unique to the industry as it involves capture from specific plant designs. On the other hand, when it comes to carbon dioxide storage the cement industry is a relatively small player and it is likely that the power industry will work out storage schemes to which the cement industry can add its own carbon dioxide. Since both power plants and cement plants are located near large populations, location issues for cement derived carbon dioxide disposal is not likely to create new problems.

Cost considerations

Estimating the cost of implementing a REO kiln design is not feasible, as the full extent of the required modifications cannot be defined at this stage of the research. There are, however, several aspects of the final design that can be considered. These include the oxygen production facility, the compressors for the CO_2 and the cost of electricity. The cost of CO_2 capture estimated in this section should not be taken as a total cost, as it represents only additions to the cement plant. Establishing this minimum cost allows us to establish both a basement price and the allowable cost of modifications to the plant. The basement price is based on the assumption that a "best case" scenario is one where the cost of plant modifications is exactly offset by increased revenues associated with the expected increase in production induced by oxygen combustion. The allowable cost of modifications is the difference between the cost of plant additions and the cost of CO_2 capture using post combustion capture (MEA) technologies. The value establishes a design limit for future work.

We can use literature estimates to cost the plant additions and establish a minimum cost of capture at a REO Kiln. For comparison purposes, we will use the metrics from the coal fired facility studied by Hegerland et al. (Hegerland et al. 2006). Unless otherwise noted, we have used a financial charge rate of 19% (15% capital + 4% operation and maintenance) amortized over 20 years.

The reference facility produces 1.4 Mt of clinker and 0.9 Mt of CO_2 per year. Assuming that 44% of the CO_2 is associated with combustion (Worrell et al. 2000), we can estimate the oxygen required to combust the appropriate amount of coal at 0.294 Mt O_2 per year or 26,200 m^3 per hour. The large feed rate suggests an on-site cryogenic air separation unit (ASU) would be the most economical choice. Based on the available literature (Dillon et al. 2005, Kirschner 2002), we establish the capital cost of an ASU at \$6/100 m^3 O_2 of annual production. The cost of the oxygen plant is then \$14 million USD or \$3.00 tCO_2^{-1} captured. Similarly, the capital cost of the compression equipment is expected to be between \$7-8 tCO_2^{-1} (Allam et al. 2005, Blok et al. 1997, Hegerland et al. 2006). Compression costs are higher, per tonne of CO_2, than oxygen production, which may be a peculiarity of cement production where two units of CO_2 are produced from each unit of fuel, and therefore oxygen. This has led others to state that cement plants are the most efficient location for oxygen combustion (Gronkvist et al. 2006).

The production of oxygen and compression of CO_2 will require additional electricity, which will result in fugitive CO_2 emissions and additional costs. An ASU consumes 25 kJ_e per mole O_2 (Perry & Green 1997) and CO_2 compression requires 12.5 kJ_e per mole CO_2 (Blok et al. 1997). We use representative values (IPCC 2005) of 0.367 kg CO_2 kWh^{-1} and \$0.037 kWh^{-1} for natural gas power and 0.762 kg CO_2 kWh^{-1} and \$0.046 kWh^{-1} for pulverized coal. Converting the reference plant to oxygen combustion would incur a total electricity cost of \$6.85 tCO_2^{-1} with 0.102 Mt of fugitive CO_2 using coal and \$5.51 tCO_2^{-1} with 0.049 Mt of fugitive CO_2 using natural gas. The fugitive emissions can also be expressed as 11% for a coal boiler and 5% for a natural gas boiler.

Combining these items we arrive at a minimum capture cost of between \$15 and \$18 per tonne of CO_2 captured. Hegerland el al. estimated the cost of capture using an MEA system at \$40 tCO_2^{-1} using a lower capital charge rate of 7% while other suggest a minimum of \$50 tCO_2^{-1} for US plants (Mahasenan et al. 2005). The initial cost estimate for oxygen combustion suggests the technology may be more economical without considering potential increases in production (Wrampe & Rolseth 1976). Additionally, the REO kiln is expected to reduce CO_2 emissions by 90-95% while the MEA system from Hegerland et al. resulted in a 77-78% reduction with an 18-37% increase in the amount of CO_2 sent to storage.

Table 6: Comparison of CCS Options for Cement Plants

Unit (Mt CO_2/year)	Plant Emissions[1]	CCS Emissions[2]	CO_2 to Storage	CO_2 Emitted[3]	CO_2 Avoided (%)
Post Combustion[4]	0.90	0.42	1.05	0.18	80
Oxyfuel	0.90	0.09	0.90	0.09	90

[1]Representing 1.4 Mt/year cement plant operating 306 days per year. [2]Post combustion emissions from MEA boiler fired with coal, Oxyfuel from coal based electricity generation without CCS. [3] Post combustion assuming 85% capture using MEA, Oxyfuel assuming no leakage from plant. [4]Taken from (Hegerland et al. 2006)

Standardized Cement Production

The REO kiln is expected to produce clinker while reducing emissions of CO_2 and other pollutants to the atmosphere. The technology is a response to stricter environmental controls expected in the future. The Kyoto Protocol differentiates between developed and developing countries with emission limits applied to the former. The situation is created wherein cement can be imported, potentially more cheaply, from countries where CO_2 emissions and other environmental concerns are not regulated. Existing conditions with respect to labor and environmental constraints have already given rise to allegations of "dumping" cheap cement through importing.

The need exists, therefore, for market mechanisms to distinguish cement production technologies and emissions profiles useable by cement companies competing against imports. The objective is to establish the emissions profile, in tonnes of CO_2 per tonne of cement, of the imported clinker and apply the relevant emissions cost to the difference. The emissions profile of the imported cement should include the production method and the emissions resulting from transportation. The latter emissions can be estimated using coefficients established by the IPCC amongst others.

The emissions associated with the particular exporting plant or country must also be established. Information obtained from the successful completion of the Agenda for Action provides a base for this system (WBCSD 2002). The Cement CO_2 Protocol (Vanderborght & Brodmann 2001) and any associated database can be used to estimate unit emissions according to the country and kiln technology. Cement companies that are not providing plant data could have location specific averages applied to any exports. The database could also be used to measure progress towards industry targets for emissions reductions.

Advanced Concepts

Application of the REO Kiln technology will change the operating conditions at the cement plant. The most dramatic changes are the addition of a recycle loop that returns exhaust gas to the cooler and the use of pure oxygen in the kiln. Recycling exhaust gases may require some degree of cooling in order for proper functioning of the clinker cooler. The use of pure oxygen allows for greater control over burning zone conditions, including temperature and kiln gas volumes, and introduces another plant to the site. Taking advantage of these differences and additions will allow the REO Kiln design to move beyond a CO_2 capture technology to an advanced form of cement manufacturing.

Electricity Production

The practice of returning the exhaust gases, now dominated by CO_2, back to the cooler via a recycle loop necessitates cooling the gases to a certain degree. The final amount of cooling will be determined by the optimum operating conditions in the clinker cooler. As shown in Figure 9, gaseous CO_2 absorbs more heat per unit temperature rise than N_2. The difference provides some flexibility with the cooler inlet temperature, as hotter CO_2 can produce the same amount of clinker cooling as ambient air owing to the higher specific heat capacity. Electricity generation would use heat recovered from the recycle loop to run a conventional Rankine cycle.

The objective of electricity generation would be to produce sufficient electricity for the plant needs with any extra being sold to the market. The advantage with cement plants is that electricity is not the main product and would therefore have a lower marginal cost for production as the fuel cost is already charged to cement production. The disadvantage is that electricity generation would be tied to cement production and stop with any shutdowns. The study referenced earlier used an availability of 84% (306/365), which may be sufficient to be considered a “base load” electricity producer.

The decision to produce electricity from the recycle loop will depend, in part, on whether the demand of the plant can be met. If there is insufficient capacity and the plant depends on the grid for a portion of the power, then the benefits of independent operation cannot be realized. The electrical demand of a REO kiln is 207 kWh per tonne of clinker compared to 90 kWh per tonne for a conventional cement plant. The electricity generation potential can be estimated by considering the temperature and mass of the exhaust CO_2 stream and the electrical conversion efficiency of the power plant. An initial estimate of the electricity production capacity is presented in Figure 11. The amount generated is the product of the heat recovered from cooling the CO_2 from the exhaust temperature (x axis) to $100^{o}C$ and the electrical conversion efficiency. The exhaust gas stream has been simplified to consist solely of exhaust CO_2 with no heat recovery from the cooler vent air. The total CO_2 is 1.63 kg per kg clinker consisting of 0.53 kg of calcination, 0.35 kg of combustion and 0.75 kg of ballast CO_2.

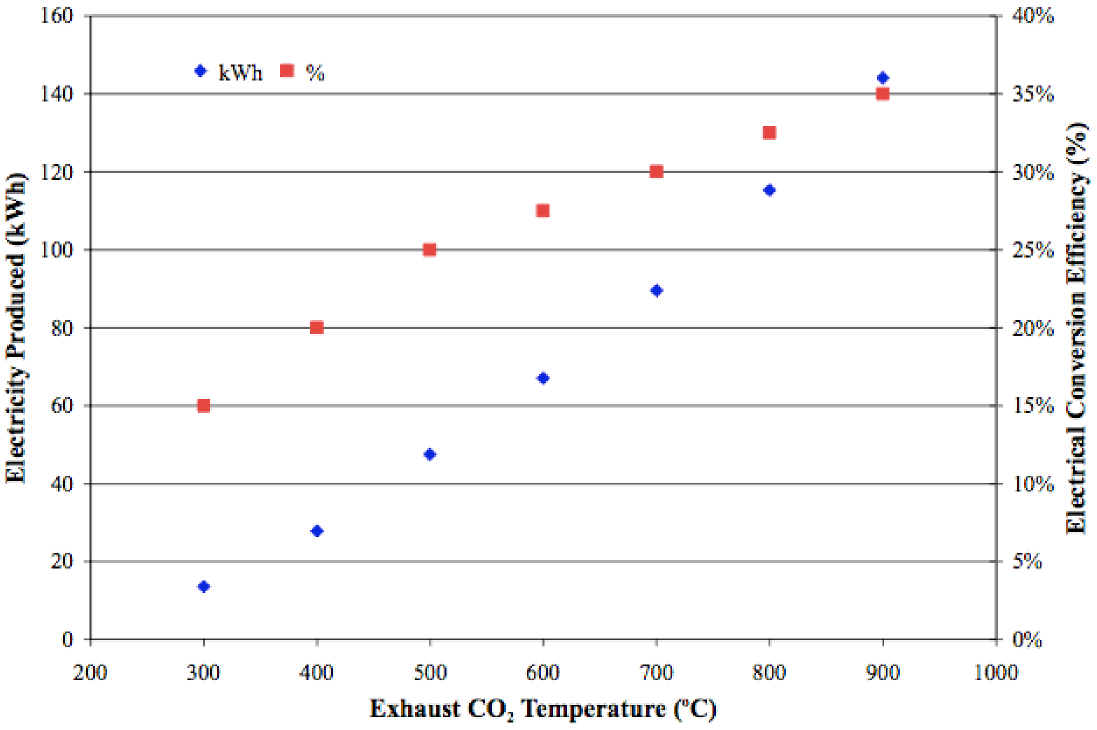

Figure 11: Electricity Production from Cooling Kiln Exhaust per tonne of clinker

Figure 11 suggests that the heat recovered from exhaust gases will be insufficient to meet plant needs. The result is similar to analysis performed by other researchers using conventional kilns (Khurana et al. 2002). It is worth noting that at temperatures above 700^{o}C, 50% of the electrical demand can be met. The savings would depend on the price of electricity but could amount to more than $5 per tonne of clinker assuming $0.05 per kWh. Rankine cycles based on working fluids other than steam, e.g. pentane, can also be investigated (Claus & Kolbe 2002). Any electricity generated at the plant would also have a reduced carbon emissions profile if CCS has been implemented. We assume, however, that emissions reductions efforts will be occurring across all industries.

Therefore, indirect greenhouse gas emissions due to electricity consumption would be lower, per unit electricity, than current levels.

Fuel Pre-processing

The heat recovered from the recycled CO_2 can be used for purposes other than electricity generation in the cement plant. It can be used to drive endothermic gasification reactions as a form of pre-processing for fuel destined for the kiln. In combination with auto thermal reforming using the pure oxygen, the cement operators can achieve a chemically stable fuel supply to the kiln despite using a variety fuels, which is expected to reduce operational variability. The potential also exists to extract the energy content of the fuel while avoiding some of the trace compounds contained in the fuel that may be detrimental to kiln operation and emissions targets.

The addition of a dedicated oxygen production facility and a recycle loop returning hot CO_2 provide important components for a gasification system. The use of CO_2 as the carrier fluid further alters operations as the oxygen content of each fluid stream can be controlled. A REO Kiln design has the potential to harness heat, steam and oxygen for fuel gasification purposes. In addition to the carbon gasification reaction, shown in equation 2, steam gasification proceeds according to reaction 5.

$$C + H_2O_{(g)} \leftrightarrow CO_{(g)} + H_{2(g)} \quad \Delta H^o = +136 \text{ kJ/mol}, T=650^0C \qquad (5)$$

The steam gasification reaction consumes less heat as it occurs at a slightly lower temperature than the Boudouard reaction, which may favor the production of hydrogen. Additional energy may be required as both reactions occur at temperatures well above the outlet temperatures of conventional coal mills. In order to reach reaction temperatures, the fuel can be partially oxidized using some of the oxygen produced for the kiln. The endothermic gasification reactions act as a heat sink preventing excess combustion. If excessive heat is released, gasification commences effectively storing the heat in the form of carbon monoxide and hydrogen. All of the fuel carbon can be gasified if keeping the associated inert residue out of the kiln enhances operation.

Alternative Fuel Use

The substitution of alternative fuels for fossil fuels, such as waste oils and bone meal, in the cement industry is a trend that is likely to increase with time. The implementation of oxygen combustion with CCS will support this trend. The capture and storage of CO_2 generated from a "carbon neutral" energy source would result in a net reduction of CO_2 levels in the atmosphere. The storage of CO_2 breaks the biological cycle. A cement plant that uses alternative fuels will effectively capture more CO_2 than is generated at the facility. As a result, a plant operating in this manner can reduce emissions from another plant where CCS technologies are less cost effective.

The list of viable alternative fuels can be expanded to include fuels not directly suitable for use in the kiln. For example, sulfur could be imported and converted to gypsum in a dedicated facility. Regulations stemming from acid rain concerns are resulting in more sulfur removal at the upstream end of oil and gas production (Rappold & Lackner 2008). An excess of sulfur is produced that requires eventual disposal. Cement plants could import sulfur, produce gypsum on-site according reaction 6 and transfer the heat to the manufacturing process.

$$S + 1.5O_{2(g)} + CaCO_3 \leftrightarrow CaSO_4 + CO_{2(g)} \qquad \Delta H^o = -630\ kJ/mol \qquad (6)$$

The production of gypsum at the cement plant can be expected to have several benefits. The heat released could partially displace fossil fuels in the kiln and the products would displace gypsum purchases. At current prices, the use of sulfur is a cost effective substitute for coal and gypsum use. This assumes a high degree of heat transfer from the gypsum production facility to the cement plant. Reaction 6 also releases an equivalent amount of heat per unit oxygen (400 kJ per mole O_2) as fossil fuels. The feasibility of such a system would depend on the market trends for sulfur and gypsum. This concept can also be applied to the pre-treatment of high sulfur petroleum coke.

Conclusion and Recommendations

The REO Kiln represents a paradigm shift in the manufacturing of cement clinker. At best, it isolates the burning zone from the environment removing variability associated with temperature, humidity and fuel choice. As a minimum, it may be a cost effective method for CO_2 capture from a cement plant. The design targets virtually all pollutants by reducing the stack freight, allowing for better gas clean up. With the environmental concerns minimized, the operator's focus can be directed towards the efficient production of high quality clinker. Oxygen combustion will integrate the separate components of a cement plant even further. This may pose operational challenges as shutdowns or "upsets" in parts of a cement plant can lead to a shutdown of the entire plant. The REO kiln would tighten these interconnects even further and outlets for kiln upset will likely have to be integrated into the final design. The implementation of such designs involves many direct and indirect steps.

The direct steps involve modifications and alternatives to the process components of an existing cement plant. Future work may show that a complete redesign of the cement manufacturing process is necessary. Indirect steps involve changes and processes external to the cement plant. These include transportation of the CO_2 to the disposal site, injection of the CO_2 and monitoring after injection. To this end, the Cement Sustainability Initiative may consider aligning "sources and sinks." The sources are the cement plant while the sinks consist of the appropriate storage sites. The ease of CO_2 transport and storage, including potential revenues, will be an important part of the feasibility of CCS.

The need to include deep reductions in greenhouse gas emissions from cement plants comes with the knowledge that it may not be implemented uniformly across the globe. Leakage will be a concern requiring international agreements. In some form, any disparities in CCS requirements must be reflected in the price of cement imports. Expanding the Cement CO_2 Protocol (CSI 2005) to include kiln types and transportation emissions will allow for the estimation of emissions from most cement imports. The end result could be a simple algorithm that uses the type of kiln, fuel, transportation method and distance to market to estimate the unit CO_2 emissions associated with the specific import.

Recognizing that restrictions to greenhouse gas emissions are coming, it is usually more beneficial to be proactive than reactive. Moving forward, we assume that any obligations under the Kyoto Protocol and its successors can be met through a combination of best available technology, alternative fuels and blending. Next generation technologies, such as the REO kiln, could be required for deployment around 2020. If such technologies are lacking the purchase of carbon offsets in a carbon trading scheme could prove expensive. A deliberate research effort promotes forward progress while highlighting new technologies, such as the kiln sheath, that may improve cement kiln performance even if applied today. The REO kiln, and other innovative technologies, will yield returns for the cement industry provided the appropriate level of investment is made in research and development.

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