The Zero Emission Kiln

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The global consensus on climate change, its anthropogenic source, and the need for a regulatory framework, typified by the Kyoto Accord, is strengthening. Whether the Kyoto accord or similar national frameworks come into force, the pressure on all carbon dioxide (CO_2) producers to reduce emissions is likely to increase. Furthermore, the Intergovernmental Panel on Climate Change (IPCC) Special Report on Carbon Capture and Storage (CCS) has identified the cement industry as an early candidate for emission reductions[1]. Regulatory mechanisms, such as emissions trading, provide a financial incentive by allowing industries that can exceed their target reduction to sell the excess for profit. The cement industry, because of its large size and the production of a highly concentrated stream of CO_2, is well positioned to take advantage of these trading mechanisms.

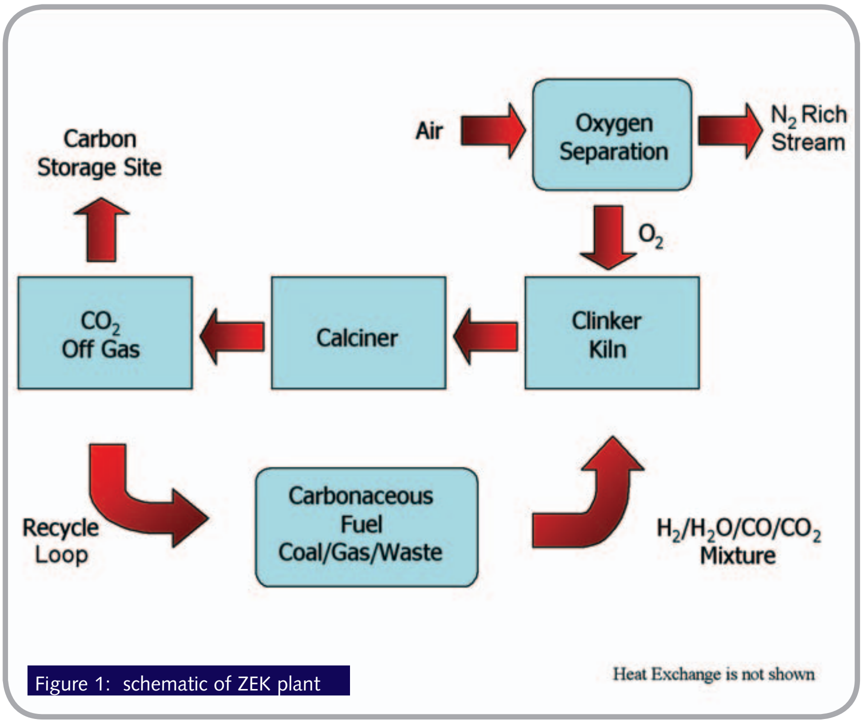

Figure 1: schematic of ZEK plant

Concrete is consumed throughout the world and is second only to water in terms of per capita consumption[2]. The production of cement, the critical ingredient in concrete, is an energy intensive process that produces ~four per cent of the carbon dioxide emitted globally[3]. The process of cement manufacturing involves the release of chemically bound CO_2, through the decomposition of limestone[4, 5], and CO_2 resulting from the combustion of fossil fuels. A summary of the CO_2 emissions from a cement kiln shows that 40 per cent is from the fuel combustion and 50 per cent is from the chemical reaction with the remainder derived from electricity consumption and transportation[6]. The large proportion of chemically bound CO_2 limits the effectiveness of fuel switching as a strategy for CO_2 reductions. The large mass of the end product inhibits relocation to countries without emission regulations as an alternative strategy. This suggests a novel approach is needed to reduce CO_2 levels.

A successful re-design of the cement kiln could encompass modifications to fuel systems and plant layout with potential for other improvements in electricity generation and feed preparation. Ideally, strategies should maintain the ability to retrofit existing facilities. However, the most efficient designs are likely to aim at new plants. Furthermore, any changes would have to consider the important role of alternative fuels in the cement industry. Cement companies provide an important service by consuming waste materials as alternative fuels. These range from spent solvents and paint residues to sewage sludge. Developing the ability to manage all of the emissions and maintain fuel flexibility would provide economic certainty in a carbon constrained marketplace.

The technology

The start-point is to propose combining oxygen combustion, flue gas recycling and fuel preprocessing to create the Zero Emission Kiln (ZEK). These technologies will be optimised to improve the efficiency of cement production, which reached a plateau for new plants in the early 1990s[7]. The efficiency improves as the actual amount of energy used per unit product approaches the thermodynamic requirement. Newer plants consume ~3.7MJ of primary energy/kg of clinker, which is twice the thermodynamic requirement of 1.75MJ/kg.

An overview of the proposed design is shown in Figure 1. The general concept is similar to conventional plants in that the combustion energy is used to form clinker with the waste heat used for calcination. To avoid diluting the off-gas with nitrogen, the fuel is combusted in oxygen rather than air. An on-site cryogenic oxygen plant will deliver the oxygen required for combustion. The use of high purity oxygen allows for the recycling of the flue gas, now dominated by CO_2, back to the combustion zone. A portion of the flue gas must be removed from the system and sent to storage to maintain mass balance. The remainder, still at temperatures around 900°C, could be used for fuel preprocessing. The fuel and flue gas will be mixed prior to combustion to gasify and preheat the reactants. Gasification will homogenise the feed entering the kiln.

The use of oxygen combustion has been previously suggested as a suitable technology for cement plants to capture CO_2[6]. This concept is more attractive than flue gas recovery based on amine sorbents. At the high CO_2 concentration of ~30 per cent, typical for a cement plant exhaust, the regeneration of the sorbent would consume a large amount of energy per unit product for a relatively small factor in enrichment. The flue gas also contains significant amounts of particulate matter, sulphur compounds and other impurities, which may hinder the use of amine based sorbents. In contrast to an air fired system, the oxygen fired system produces a flue gas stream completely dominated by carbon dioxide. The off-gas could thus be stored underground without having to be scrubbed of the remaining impurities, like NO_x and SO_x. Provided that the impurities can be safely handled and stored, oxygen fired systems could avoid all gas scrubbing equipment.

The most cost-effective method for producing oxygen is through cryogenic distillation[8] with large scale facilities achieving production costs below US$30/t of oxygen[9]. Assuming coal is the fuel, a conventional plant consuming 3.7MJ/kg clinker would see an oxygen cost of one cent/kg of clinker. There are other methods of oxygen production, still in the pilot stage, which may provide better alternatives. For example, Ion Transport Membranes (ITM) transfer oxygen through mixed oxide membranes at high temperatures[10]. These membranes offer several exciting synergies with cement production. The operating temperature is 900°C, which is similar to the calcination temperature in a CO_2 environment. In addition, ITM systems can also produce power and steam, both of which would be useful in the new plant design. Oxygen combustion itself has several benefits including flame temperatures well above 1500°C with minimal thermal NO_x production[11]. The flame temperature would be controlled by recycling exhaust CO_2 as a sweep gas. CO_2 is a logical choice as it eliminates the need for separation of the combustion products resulting in a flue gas ready for storage. Oxygen blown combustion could thus eliminate the need for a smoke stack at cement plants.

The recycled hot gases will reduce the amount of heat transfer required and increase overall efficiency. The hot gases could also be used in fuel pre-processing to gasify carbonaceous fuels via the Boudouard reaction[12]. This reaction generates carbon monoxide (CO) from CO_2 and carbon, which would stabilise the fuel mix entering the kiln and widen the options for alternative fuels. Gasification may also reduce the non-criterion compounds, such as dioxins and furans, generated in the kiln[13, 14]. The addition of a fuel pre-processing step further allows a segregation of fuels according to pretreatment required. The aim of the preprocessing is to provide a stable fuel composition regardless of the fuel source. This would improve kiln operation.

The goal

The previous discussion outlines the concepts to be investigated as part of a multi-year research programme assessing the feasibility of a zero emission kiln that produces a concentrated stream of pressurised carbon dioxide ready for disposal.

The feasibility study will first ascertain that clinker formation in a different atmosphere will still generate a useful product. Therefore, the initial focus of this investigation is a comparison between conventional clinker and that produced in a CO_2 environment. More specifically, the experiment will trial oxygen blown calcination and flue gas recycling. The objective is to demonstrate that the lime and clinker produced have similar material properties to those produced by conventional means. There is currently no concerted research into the field of oxygen calcination and clinker production or the quality of the lime/clinker produced. Although there is considerable interest in oxygen combustion for power generation, this information may not be directly applicable to cement manufacturing. With the successful conclusion of this phase, it is possible to design a cement plant that could operate as a zero emission kiln.

Improving the design of the cement kiln refers to taking advantage of the new features that come with oxy-fuel combustion. The initial design changes will incorporate the oxygen production and flue gas recycling into both an existing plant and new design. As stated earlier, the aim is to make the new plant more efficient and more consistent in its operation. A process model will be created to incorporate experimental data to simulate the effects on a new plant. The important questions will centre on the kinetics and characterisation of calcination and clinker production in an oxygen environment. The results of these experiments will form the basis for any redesign of the cement plant. In studying retrofit options, particular attention will focus on the cost of proposed changes to the existing facility.

One potentially important difference between air blown combustion and oxygen blown combustion is that it is far easier to reach high temperatures in the latter process. The higher temperatures available through oxygen combustion could improve heat transfer and shorten residence times. This may permit a substantial reduction in the size of the kiln. These higher temperatures would require more efficient heat management systems. As an example, one of the process necessities in clinker manufacturing is rapid cooling to 1200°C to avoid alite decomposition to belite. The quench rate would increase if higher temperatures are used and this must be incorporated into any redesign.

The main objective of the investigation is to improve the cement making process. It is hoped this will be achieved from an environmental and economic perspective. Through reduced emissions, less fossil fuel use, generation of carbon credits for sale, and improved access to alternative fuels, the cement manufacturer should be well positioned for future growth. In terms of carbon markets, the large volume of CO_2 produced by the cement industry would make it the dominant seller in any trading system.

By developing the right technology early, the industry can offset its own carbon costs by selling carbon credits to others, who create streams of CO_2 that are more difficult to manage.

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