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An Overview of Cement production: How "green" and sustainable is the industry?

Johannes H. Potgieter

School of Chemical & Metallurgical Engineering

University of the Witwatersrand

Private Bag X3, Wits, 2050

Johannesburg, South Africa

E-mail: johannes.potgieter@wits.ac.za

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Abstract

Problem statement: This paper tries to answer the question: Is cement production still a sustainable industry in the 21st century? *Approach*: It starts off by considering the current status quo and potential alternatives for the production process, right from the raw meal composition stage through to the final application of cement in concrete. *Results*: In the process alternative raw meal components and energy sources are reviewed in detail. The changes that could and should be made to cement plants and equipment to produce cement more sustainably, as well as different types of other binders that can be used for construction, are discussed. The suitability of the cement production process to destroy wastes and utilize byproducts from other industrial processes, are highlighted and analysed. Alternative methods and equipment to manufacture cement, are summarized and ways to get rid off or convert the released carbon dioxide from the cement manufacturing, are discussed. *Conclusions*: In the final instance the conclusion is reached that the cement industry, despite proven new technology, equipment and concepts, can do more to respond fast enough and to a sufficient extent to improve the sustainability of their operations substantially and to an acceptable level for the 21st century.

Keywords: Carbon dioxide, sustainable, building industry, cement production, waste materials, recycle

1. Introduction

Climate change is a topic that is almost daily in the news. It is well established and widely believed in society that the major contributor to climate change is the increase in greenhouse gases, which cause an increase in the temperature of planet earth. It is equally well established from many scientific investigations that one of the prime culprits is carbon dioxide, and recent years have seen increasing legislation to try and limit carbon dioxide emissions. Protesters often confront car makers, oil companies, power companies, shipping firms and the airline industry for their contribution to emissions, but one low-profile business which contributes a sizeable portion of 5% to greenhouse gas emissions has so far escaped attention. That is the cement industry, and as the demand for infrastructure such as houses, schools, roads, dams, sewers, hospitals and a myriad other structures keeps on growing, so will cement production, because it is the key ingredient of concrete used in construction. It is estimated that by 2050 cement plants worldwide will produce in the region of 5 billion tonnes of carbon dioxide, 20 times as much as government has pledged the entire UK will produce by that time [Adam, 2007]. Furthermore, cement production will always release carbon dioxide, because one cannot change the chemistry of the process. So the question arises, how sustainable can cement production be? What are the current technologies available to improve the industry's sustainability, and what needs to be done in future to improve it?

Modern life without cement is impossible to conceive. This inorganic binder acts as the glue for concrete to construct buildings, roads, dams, bridges, and makes modern infrastructure not just possible, but affordable. Furthermore, cement production and the concrete industry where it is ultimately applied and consumed, are important and dynamic sectors of the world economy and in every country. It is responsible for job creation and multiple cascading economic benefits in secondary associated industries and a major contributor to the improvement of living standards all over the world. Concrete is second only to water in terms of its use by mankind [Hanson, 1995]. Its production exceeds that of its closest industrial material rival, steel, by 30 times in terms of volume and 10 times in terms of mass [Hanson, 1995].

Cement-based materials, such as concrete (cement, water and aggregates) and mortars (cement and fine aggregates), are used in incredibly large amounts. This overview will be restricted to Ordinary Portland Cement (OPC) production, unless specifically stated otherwise. It is estimated that in 2009 the concrete production worldwide exceeded 10 billion tons [Meyer, 2009]. Apart from being abundant and relatively inexpensive compared to other materials, cement and concrete works well at room temperature, do not require sophisticated equipment to mix or apply, can be easily shaped and set to a hard and useful form within a few hours.

Despite its popularity and profitability, the cement industry faces many challenges due to environmental concerns and sustainability issues. It is fundamentally an energy intensive operation and not at all environmentally friendly by nature. Furthermore, it consumes large amounts of non-renewable raw materials and generates substantial amounts of carbon dioxide and environmental particulate matter in the process. It is estimated that 5-6% of all carbon dioxide greenhouse gases generated by human activities originates from cement production [Rodrigues & Joekes, 2010].

In order to minimize the impact of all of the abovementioned issues, it is clear that the cement and construction industry will have to adapt to remain sustainable and in the process adopt a number of innovative and new practices. It should be fairly obvious that a holistic approach is being called for to ensure survival and prosperity for the cement industry in future, and that it is unlikely that simply addressing one or a few of the challenges ahead will accomplish long term sustainability. This paper will give an overview of a number of areas where improvements have already been accomplished and which, if considered and applied collectively, can contribute substantially to long term sustainability in the cement industry. In the discussion to follow new manufacturing technology, combinations thereof, alternative raw materials and energy sources, alternative binders, as well as ways to deal with emissions, will all be discussed and "best practice" applications highlighted. This paper will contribute to the field by highlighting new developments in process modification for pollution prevention, reviewing the production and employment of alternative binders, raw materials and waste fuel usages, and comparing ways to reduce green house gas emissions. While sustainability incorporates a number of aspects and is certainly not limited to greenhouse gas emissions only, this paper will in the final instance attempt to answer the question: Is cement and concrete production sustainable on a long term basis in terms of carbon dioxide emissions, and are cement producers doing enough to pursue sustainability with reference to reducing, re-using and recycling to ensure the lowest possible emissions of particularly carbon dioxide?

2. Raw Materials

Cement is basically produced from burning a mixture of calcerous and silicious material with smaller amounts of alumina (Al_2O_3) and iron oxide (Fe_2O_3) (combined as the raw meal) together at high temperature [Potgieter, 1997]. Table 1 gives a summary of the top ten cement producing countries in the world. Not surprisingly, and as is so often the case nowadays, China dominates the picture and produces almost half of the world's cement, with India second. This is in large part due to the urbanization and growth of cities in these Far East countries [Shen et al., 2005].

Table 1. Cement production for major countries in the world in the period 2004-2007 (thousand metric tons) (Rodrigues and Joekes, 2010)

Country	2004	2005	2006	2007
China	934 000	1 040 000	1 200 000	1 350 000
India(estimated)	125 000	145 000	155 000	170 000
USA	99 000	101 000	99 700	96 500
Japan	67 400	69 600	69 900	67 700
Russia	43 000	48 700	54 700	59 900
Korea	53 900	51 400	55 000	57 000
Spain	46 800	50 300	54 000	54 500
Turkey	38 000	42 800	47 500	49 500
Italy	38 000	46 400	43 200	47 500
Brazil	38 000	36 700	39 500	46 400
World (rest)(estimated)	2 130 000	2 310 000	2 550 000	2 770 000

Therefore, in view of the abovementioned figures, it is obvious that alternative raw material sources, innovative quarrying methods and less energy intensive milling/mixing of the raw meal ingredients could all play a part in conserving raw material reserves and energy.

2.1 Alternative Raw Material Sources

One possible way to increase sustainability in cement production, is to use alternative raw materials from those currently employed. One such candidate is fly ash, which has reportedly been tried as a source of silica and alumina needed in the cement manufacturing process [Canpolat et al., 2004; Sahu and Majling, 1994]. Another option is to revisit a previously proven German concept of using gypsum, especially some of the industrial byproduct gypsums, as starting material to simultaneously manufacture sulphuric acid and cement [Anonymous, 1996]. It seems theoretically possible to combine this process with the concept of using fly ash as the other ingredient required and make two useful industrial products from industrial byproducts.

The use of fluxes to lower melting temperature is a well known concept in pyrometallurgy. It has also previously been applied in cement making, and the use of calcium sulphate (gypsum), feldspar and a combination of the these have been reported in literature [El-Didamony et al., 2010; Kwon et al., 2006; Helmy, 2003; Darweesh, 2001; Wirsching, 1978] as a means to reduce the production temperature of OPC (ordinary Portland Cement) by between 150-200 ^{o}C. This practice has the potential to significantly contribute to lower energy consumption and improved sustainability in OPC production. Sadly, it seems not to be practiced very widely in the cement industry.

- ### *2.2 New/Different Quarrying Methods*

All cement plants rely on quarries supplying their basic raw ingredients for cement production. More effective explosives and new quarrying methods can therefore, at least theoretically, contribute to increased sustainability in the process of making OPC.

2.3 Better /Newer /Different Mills

While electrical energy is but one (and a smaller) part of the total energy consumption on a cement plant, the data in Table 2 indicate that the milling of raw meal components and final grinding of clinker and gypsum in the finishing mill, can account for more than 50% of a cement plant's electricity consumption [Thiesen, 1993; Kohlhaas & Laban, 1983]. The most commonly used mills are ball mills, but fortunately a newer generation in the form of high grinding efficiency roller mills and HORO mills (pressure mills) are available nowadays that can increase grinding efficiency and lower energy consumption.

Table 2. Electrical energy consumption processes within a cement plant (Stoiber, 2003)

CONSUMER	ENERGY DEMAND (kWh/t)	%
Extraction & Blending	5.5	5
Raw material grinding	26.4	24
Raw meal homogenization	6.6	6
Clinker production	24.2	22
Cement grinding	41.8	38
Conveying, packing & etc	5.5	5
TOTAL	110	100

Generally, the specific power consumption in ball mills is 25-35 kWh/t when grinding the cement to a fineness of 3500g/cm^2. According to Alsop et al. (2001), specific power consumption for clinker grinding can be reduced by 20% if pre-grinding of material can be done first. This usually takes place in a roller press mill. The combination of these grinding techniques has the advantage of avoiding two adverse effects, namely an increase in the water demand of the cement and the possibility of an unacceptable reduction in the initial setting time (Bye, 1999). The energy demand in the ball mills can also be reduced if they are equipped with a high efficiency classifier (Stoiber, 2003).

Energy utilization during the grinding process of clinker and gypsum can also be improved by adding polar organic compounds to the charge in the mill. Because of their highly polar nature, grinding aid compounds preferentially adsorb on surface of ground materials and neutralize forces, which cause agglomeration of the newly produced cement particles. The resultant dry dispersion of cement increases fluidity and reduces mill retention time (Jeknavorian et al. 1998). Furthermore, one of the popular grinding aids, i.e. triethanolamine, is also known to increase the strength of the concrete in which the cement is used. With the consumption of electric energy per unit time held constant during the application of grinding aids, the capacity of the mill is increased, resulting in more efficient consumption of energy, reduced grinding costs and less energy consumption. This practice is nowadays widely employed by cement manufacturers.

3. Use of Industrial Byproducts and Wastes

Probably the most lucrative financial practice and source of improved sustainability of the cement and concrete industry, is the practice to use industrial byproducts and wastes in the production process. Not only does it lower costs, but it contributes substantially to lower carbon dioxide emissions per ton of cement produced. The unique fact that the cement production process is a high temperature process that can destroy certain types of waste, while in some cases encapsulating the resultant non-destructable portion safely in the final product, has lead to a variety of ways in which several wastes and industrial byproducts can be used as part of the final cement product or production process.

3.1 Wastes

The high temperature and oxidative environment in a clinker kiln is ideally suited to destroy a variety of organic wastes. These can range from solid polymer (plastic) type wastes or tyres, to municipal solid or industrial solid wastes and waste solvents or oils, in some cases even CFCs (chlorofluorocarbons) [Tamas, 1992(21); Auber, 1981(22); Weitzman, 1983(23); Mourninghan et al., 1985(24); Sutho et al., 1996(25); Uchikawa & Obana, 1995(26); Mullick, 1992(27); Potgieter et al., 2002(28)]. It is becoming increasingly important worldwide to destroy old or no longer useful tyres in cement kilns, were they can provide an additional source of energy to replace conventional coal, oil or gas. In the process zinc and vanadium gets incorporated into the resultant clinker [Tamas, 1992]. Provided that the process is properly controlled, the performance of the resultant clinker is not compromised at all [Bolio-Arceo & Glasser, 1998; Murat & Sorrentino, 1996].

Solid consumer polymer wastes (non-biodegradable plastic) are another popular source of alternative fuel in cement plants. While there is a danger that dioxins might occur if the destruction is incomplete, especially with chlorinated plastics [Shibamoto et al., 2007], the complete oxidation of such organic wastes leaves just water and carbon dioxide as combustion residues. In such cases careful monitoring of stack outlets are of crucial importance to ensure that no environmental damage is caused by the emissions from the process.

Municipal solid wastes are being increasingly used in the cement production process [Stavraki et al., 2005]. This is not only a good way of getting rid of it, they can also provide some energy to the kiln during the burning thereof. The major concern in the use of municipal solid wastes in the process, is potential release of heavy metals that can get volatilized. Once again the importance of careful monitoring cannot be overemphasized. In addition, certain changes to the design of off-gas handling equipment might be necessary, e.g. baghouses or additional filters before outlet gases are released into the stack [Stavraki et al., 2005]. Not all the heavy metals are necessarily volatilized, some simply get incorporated and encapsulated in the raw meal and resulting clinker. The volume is so small however, that the resulting cement's performance is not compromised compared to that of normal OPC [Murat & Sorrentino, 1996; Shirasaka et al., 1996; Kakali et al., 1998].

By far the easiest waste to handle as an additional fuel source, are waste solvents and oils. Cement companies usually erect blending facilities [Flowers & Linderman, 2003] to ensure that a reasonably homogenous mixture is being pumped into the kiln burners where it can be fully oxidized to carbon dioxide and water. Chlorinated solvents pose the same danger as chlorinated plastics, so it is essential that complete oxidation must take place.

3.2 Industrial Byproducts

(a) Phosphogypsum and other waste gypsums

Gypsum fulfils two functions in the cement manufacturing process. Firstly, it acts as a set controller by reacting with the C_3A (tricalcium aluminate) phase in the clinker, and secondly a correct dosage of gypsum ensures optimum strength development in cement [Taylor, 1997]. Usually natural gypsum is preferred for use in the cement industry, but a number of cement companies are also using industrially produced gypsum. A number of industrial processes produce gypsum as a waste product, e.g. titanium dioxide production [Potgieter et al., 2002], fertilizer production [Wisching, 1978] and citric / boric acid manufacturing [Bensted, 1980]. Of all these industrial gypsum wastes, phosphogypsum is the most well-known one and also the one being produced in the largest amounts.

Most of the industrial byproduct gypsums contain impurities that are detrimental to the cement being produced from it. Phosphogypsum in particular contains phosphorous and fluoride compounds that can interfere with and retard cement setting [Potgieter et al., 2003; Potgieter & Potgieter, 2000]. However, a number of suggested purifying processes have been reported in literature for these industrial byproduct gypsums to be treated and rendered safe for use in the cement production process without compromising the performance of the final product [Potgieter et al., 2003; Potgieter & Potgieter, 2000; Cotea et al., 1986; Singh et al., 1993; Singh et al., 1984].

Gypsum, in combination with or without feldspar, can also lower the clinkering temperature by acting as a flux in the process [Kacimi et al., 2006]. In this instance it is added to the front end of the process, as part of the raw meal mixture, and not in the final step of producing cement. Furthermore, as referred to elsewhere in this paper, gypsum can be used as one of the ingredients of calcium sulpho-aluminate cements (CSA) to produce a low temperature, alternative cement to OPC.

(b) Fly ash

Fly ash is a byproduct from coal combustion during the power generating process. It is an extremely fine ash formed from the inorganic components of the coal that remains after combustion of the carbonaceous part of the coal. It occurs as a silico-aluminate glass with a spherical appearance and average diameter smaller than 45 μm [Bakovic et al., 2006; Kruger, 1999]. It is estimated that worldwide nearly 600 million tons are produced annually [Wang et al., 2008, Yao et al., 2009].

Fly ash undergoes a pozzolanic reaction with alkali activators, e.g. the calcium hydroxide released in the hydration of cement to form cement-like compounds. Furthermore, its spherical nature improves the workability, as well as flowability, of concrete mixtures and decreases the permeability of the concrete produced from it. Fly ash additions to cement products are governed by the European Norm 197 [2000] and several other local standards in many countries around the world. Nowadays it is a standard component of most cements and concretes in varying quantities. Its addition to cement allows a reduction in the total carbon dioxide produced per ton of cementitious product produced.

Fly ash furthermore has the advantage that it can be used as a partial replacement for clay in the raw meal of cement [Canpolat et al., 2004], which further contributes to a reduction in the quarrying and use of natural resources. As referred to elsewhere in this paper, it also forms an important component of alternative cements and binders such as geopolymers, alkali-activated cements (AAC) and calciumsulphoaluminate cements. Bottom ash produced by power stations can be incorporated into raw meal as one of the silica-alumina components [Canpolat et al., 2004].

(c) GGBFS (granulated ground blast furnace slag)

GGBFS is a byproduct of the steel production industry. Contrary to fly ash, it is a latent hydraulic binder that can develop strength due to the formation of cement-like compounds as a result of its composition that contain compounds similar to those found in cement clinker. It can be further activated with alkali activators, especially calcium hydroxide. GGBFS is usually milled to a finer composition than OPC [Maeng, 1996], and as such it can have several beneficial effects if added to cement or concrete mixtures. Just like fly ash, it can form an ingredient in the raw mix for CSA cements, AACs and geopolymers [Kumar et al., 2010; Mozgwa & Deja, 2009; Komnitsas & Zaharaki, 2007]. The usually standards and EU norm 197 also governs the allowable additions of GGBFS to cement, and it can be as high as 70% [EU Norm 197, 2000].

(d) Silica fume

Silica fume is an extremely fine spherical residue from the silicon smelting industry [Toutanji et al., 2004]. Similar to fly ash, it is a pozzolan that can be activated with calcium hydroxide and other alkali activators to form cement-like hydrates that can contribute to the strength of concrete mixtures. As a waste product, its addition to concrete lowers the carbon dioxide equivalent tonnage of production compared to pure OPC alone in the mix. Silica fume displays a physical packing effect in addition to its chemical compound formation contribution in the strength development of concrete mixtures, and is therefore an essential component of high strength concretes. It is usually used in conjunction with a superplasticiser and is often a component of self-leveling concrete.

(e) Metakaolin

Kaolin is a clay, and is normally used for the production of chinaware. However, when it is heated to approximately 800 ^{o}C, it becomes activated and as metakaolin it possesses pozzolanic properties. Although it requires heat to produce, metakaolin additions to cement can increase its strength substantially [Curcio et al., 1998; De Silva and Glasser, 1992; Potgieter-Vermaak and Potgieter, 2006]. It has been reported in literature that up to 30% of OPC can be replaced by an equivalent amount of metakoalin produced at a much lower temperature and without any carbon dioxide release in the process, while at the same time achieving a substantial increase in the cementitious mixture’s strength.

(f) Red Mud

The accident at the alumina plant near Kolontár in Hungary in October 2010, when approximately one million cubic meters of red mud were accidentally released into the surrounding countryside, once again draw the attention to the problems associated with this and many other types of solid industrial waste products. Red mud is a by-product waste of the Bayer process, which is the main industrial means of refining bauxite in order to obtain alumina. This alumina is then used as raw material to produce aluminium through electrolysis of alumina by the Hall–Héroult process [Schmitz, 2006; Chandra, 1996]. Red mud consists of a mixture of solid and metallic oxide-bearing impurities, which includes oxidised iron(the source of the red colour), silica, unleached residual aluminium, and titanium oxide. One of the major disposal problems of red mud is the energy required to dry it. One possible solution is to use waste heat (e.g. from a cement kiln) to dry this waste. However, it can act as an ideal raw meal component in the cement making process if the handling problems can be overcome, as it contains many of the essential raw meal element required for clinker production. However, a necessary condition for the use of red mud is that the sodium hydroxide it contains should be removed to an acceptable level (<0.5%).

3.3 Concrete

Industrial wastes and byproducts are not only added to cement, but also to concrete mixes produced from it. Apart from the usual fly ash, blast furnace slag, metakaolin and silica fume already mentioned above, a number of other wastes can be utilized in concrete to lower the amount of either cement or aggregates use. Typical examples include the recycling of building and demolition debris as coarse aggregates in concrete [Marinkovic et al., 2010; Corinaldesi, 2010] and glass cullets [Rajabipour et al., 2010; Idir et al., 2010]. Organic admixtures in the form of water-reducers to reduce the amount of cement used in a concrete mixture [Li et al., 2005; Jolicoeur & Simard, 1998], superplasticers to increase pumpability and the design of self-leveling concrete [Djelal et al., 2002; Leeman & Winnefeld, 2007] to reduce the need for vibration of concrete in formwork are all examples of how energy usage associated with construction can be further reduced.

3.4 Energy Efficiency

The addition of industrial byproducts and wastes to cement in the manufacturing process or to concrete mixtures, essentially improves the overall energy balance and efficiency of the production process. However, it is not the only way in which energy efficiency can be improved. Over the decades the cement manufacturing process has changed from one using a slurry process to mix the raw meal ingredients, to a totally dry process in the modern plants. Furthermore, the addition of pre-heaters to the older, long kilns has increased heat recovery and caused an increase in production capacity. This all has lead to the decrease in the energy required for the production of cement from around 5 700kJ/kg in the old wet processes to 3 100 kJ/kg-3 600 kJ/kg in modern plants [Zur Strassen, 1957; Johansen & Kouznetsova, 1992; Popescu et al., 2003]. This in itself has made a huge contribution to the sustainability of cement production. Nowadays up to 6 pre-heaters and a pre-calciner are considered standard equipment in a modern cement plant.

Another modern development in improving energy efficacy, is the practice of heat recovery to generate electricity. Waste heat from cement kilns have traditionally being used to dry either coal and/or raw materials, but since the 1980's various boiler and heat exchanger combinations have been installed at cement plants worldwide to generate steam and subsequently electricity from it. This concept is of course not limited to cement kilns, but is equally widely employed in steel smelters and non-ferrous smelting plants that all have high temperature waste gases coming off at the back end of the process. Some companies advertising on the internet claim that up to 30% savings can be achieved in the electricity consumption of a cement plant if waste heat recovery systems are installed to generate on-site electricity.

4. Alternative Cements and Binders

4.1 Alkali Activated Cements (AAC)

Alkali activated cements typically consist of limestone, iron slag, coal fly ash or thermally activated clays, which are then activated by soda ash (alkali carbonate), NaOH, or alkali silicates (water glass). The binder material must contain a reasonable amount of a glassy or amorphous silica phase. AAC typically produce 95% less CO_2 emissions than a similar mass of OPC and is also beneficial from the point that it reduce the impact of other industrial by-products on the environment. Furthermore, these AAC can be cured at room temperature. A number of studies have been reported in literature on their use and production. [Zuda et al., 2010; Green, 2006 and references therein; Palomo et al., 1999; Roy, 1999].

4.2 Calciumsulphoaluminate (CSA) Cement

Typically low-grade limestone, bauxite fines, phosphogypsum, fly ash and blast furnace slag, in various proportions, can be utilized to manufacture CSA cement. CSA cements are expansive cements and can be produced at about 1 200 ^{o}C, which is 200-250 ^{o}C below OPC's production temperature. Furthermore, the fired clinker is relatively soft and friable and is easy to grind. Consequently the manufacturing of CSA cement consumes less energy than OPC [Beretka et al., 1992; Taylor, 1997]. Combinations of CSA cement and OPC can be interground and applied together in construction, as the expansive cement could counter the shrinkage of concrete and mortar on hardening. Care should be taken if any pozzolans are to be used, as the reduced level of calcium hydroxide production during the hydration of the OPC component of such mixtures might not be sufficient to activate the pozzolans.

4.3 Belite Cement

One approach to the reduction in energy consumption in the production of cements is to reduce the lime saturation factor (LSF) of the raw feed. The LSF is an indication of how much lime (from the calcined limestone) is consumed in the clinker production through the formation of calcium silicate and calcium aluminate phases. A high quality lime is required to obtain the,typical LSF of between 92-98% that is usually employed in normal OPC production (Potgieter & Love, 2010). The substitution by a low lime cement leads to energy saving and also to a reduction of CO_2 emission from the decarbonation of the limestone. A reduction in LSF increases the belite content (C_2S) and decreases the alite content (C_3S) in the clinker produced [Popescu et al., 2003; Sharp et al., 1999; Lawrence, 1998]. This has the advantage that formation of C_2S (65.1% CaO) occurs at lower temperature than the formation of C_3S (73.7% CaO). When the LSF is reduced to 75%, a virtually alite free clinker is formed. This kind of cement has low aluminium content and its main mineral phase is dicalcium silicate (belite). The reduction of the $CaCO_3$ content reduces the energy demand by 15–20% for a Lime Saturation Factor of 80–85% and allows satisfactory clinker formation at 100–150 ^{o}C lower than for OPC production [Popescu et al., 2003]. Further substitution of some natural raw materials by suitable waste materials also leads to a decrease in the energy demand. To produce low energy cement with adequate strength development and LSF below 85%, belite of sufficient reactivity must be produced [Sharp et al., 1999, Lawrence, 1998]. Active forms of dicalcium silicate (a' and β-C_2S) in belite clinkers can be achieved by very quick cooling at a rate of at least 500 ^{o}C/min in the range of 1300–700 ^{o}C, or by inclusion of an appropriate mineraliser [Popescu et al., 2003].

4.4 Geopolymers

Geopolymers are inorganic polymers consisting of repetitive and alternating SiO_2 and Al_2O_3 units in an amorphous mass [Davidovits, 1989]. Geopolymers are typically made from a silica-alumina source, such as fly ash, metakaolin, blast furnace slag and a strong alkali activator, such as sodium hydroxide, water glass, potassium hydroxide, sodium sulphate, lime or combinations thereof. It has excellent strength and is often applied for waste stabilization purposes, encapsulation of heavy metals and for refractory purposes [Berger et al., 2009; Duxson et al., 2007 and references therein; Provis et al., 2009; Zhang et al., 2008].

4.5 MDF Cement

An interesting composite made from Portland cement is so-called MDF, or macro-defect free cement [Kendall et al., 1983]. MDF can be processed like polymers, and combines cement properties with that of water-soluble polymers, e.g. polyvinyl alcohol (PVC) or poly-acryl amide. When compared to traditional cement-based materials, the properties of MDFs are superior [Santos et al., 1999]. However, when exposed to water, their mechanical properties are severely damaged, and this, among other things, limits their use.

4.6 Novacem

A British company, Novacem, has recently come up with a new cement based on the use of magnesium silicates, a group of compounds which mean the cement absorbs atmospheric CO_2 during the hardening process. The cement production is based on magnesium oxide (MgO) and hydrated magnesium carbonates. During the production process accelerated carbonation of magnesium silicates takes place under elevated temperature and pressure (i.e. 180 ^{o}C/150 bar) levels. The material produced is then heated at low temperatures (700^{o}C) to produce MgO, with the CO_2 generated being recycled back in the process. The use of magnesium silicates eliminates the CO_2 emissions from raw materials processing. In addition, the low temperatures required allow the use of low energy fuels which further reduce carbon emissions. Overall, the production process to make 1 ton of Novacem cement absorbs up to 100 kg more CO_2 than it emits, making it a carbon negative product. [http:///novacem.com, 2010]

4.7 Hydraulic Lime

The hydraulic behavior of this material is related to the clay content of the limestone from which the lime was made, and it has been used since Roman times in building applications [Black et al., 2010]. One of the best examples of the application of hydraulic lime is in the construction of the Eddystone Lighthouse in the UK by Smeaton. Nowadays this material is very popular in the heritage sector, and it is often combined with ground glass cullet and other waste materials in which the lime can induce a pozzolanic reaction to result in C-S-H binding phase. Artificial hydraulic lime can also be synthetically made from a low silica limestone blended with waste materials such as fly ash, burnt shale and glass cullet [Zawawi & Banfill, 2006].

4.8 Plaster of Paris

Plaster of Paris is a building material in the form of a dry powder that, when mixed with water to form a paste, liberates heat and then hardens, similar to mortar or cement [Wischung, 1978]. However, unlike mortar and cement, plaster remains quite soft after setting, and can be easily manipulated with metal tools or even sandpaper. It is based on calcium sulphate hemihydrate, or bassinite, with the chemical formula composition of $CaSO_4 \cdot 1/2H_2O$. It is derived from gypsum by heating it to about 150 - 180 °C:

$$2\ CaSO_4 \cdot 2H_2O \rightarrow 2\ CaSO_4 \cdot 0.5H_2O + 3\ H_2O \text{ (released as steam).}$$

It is particularly popular for use in the heritage industry for repair work.

5. Alternative Production Methods

5.1 Microwaves

Microwave energy is new technology application to drying, calcining, curing and manufacturing processes requiring thermal processing. In a conventional gas or electric furnace, an object is warmed gradually by convection or radiation as heat penetrates from the outside inwards. Microwave energy, by contrast, is cold and heat is only produced when the microwave energy is absorbed by the sample. Since microwaves easily penetrate materials (with the exception of metals) they can be directed and uniformly absorbed throughout the entire volume of an object. This volumetric heating effect causes a material to heat up evenly and rapidly. The capabilities of microwave energy have opened up new opportunities in chemistry, materials science and other areas [Dagani, 1997]. In the building and construction industry these include drying of gypsum [Lindroth and Berglind, 1994], sample preparation for analyses [Figg, 1973; Strydom et al., 1999], curing of concrete [Xuequan et al., 1987] and syntheses of ceramics [Fang et al., 1996]. Very novel work done at the Materials Research Laboratory of Pennsylvania State University by various researchers illustrated the feasibility of manufacturing different types of cement using microwave technology [Fang et al., 1996; Li et al., 1998;1999;2001]. With the development of more and larger commercial microwave units, this approach might just in future become a reality on commercial scale.

5.2 Fluidised Bed

Although still at pilot plant scale, several commercial companies and designs for fluidized bed kilns have been developed to produce clinker in a different configuration from the usual rotary kiln. Fluidized-bed cement kiln systems can efficiently combust low-grade coal, significantly reduce NOx emissions, and increase the heat recovery efficiency between solids and gases discharged from the process. This is due to the advantages of the fluidized-bed process, such as increased combustion and heat transfer efficiencies. It contributes to energy conservation and improves sustainability [Yuko et al., 2000]. The clinker produced is also smaller in size than those from conventional rotary kilns and require less grinding. This is clearly the next generation technology to improve sustainability in the cement production industry

5.3 Sol-gel Technique

The sol-gel method is based on colloid chemistry in which solid raw materials are dissolved in selected solvents under specific conditions of temperature, pressure, etc. until a homogeneous solution is formed by a hydration process. The sol is a combination of monomers of solvent-soluble or water-soluble polymers along with a precipitator. Once formed, the sol can be transformed into a gel under similar controlled conditions of temperature, pressure, etc. The sol-gels are transformed into ceramics by heating at relatively low temperatures and have better chemical and structural homogeneity than ceramics obtained by conventional solid state sintering. Materials prepared by a sol-gel process are more reactive than materials of the same compositions prepared by other methods because of their very high surface areas. One of the best known experimental methods in this area is the Pechini process to prepare high surface area materials [Pöllmann, Martin Luther University, Halle]. Although this is still in the laboratory development phase, it is a technology with much potential for full scale plant application and something that can greatly contribute to sustainability in cement manufacturing.

6. Reduction and Elimination of Carbon Dioxide Emissions

Ultimately the cement industry also has to address their actual carbon dioxide emissions, and not just the dilution of cement products, use of alternative fuels or increased energy efficiency and alternative cements to remain sustainable in future. Fortunately, there is a welcome move to embrace many of the new and novel technologies to deal with the actual carbon dioxide still being generated in cement manufacturing.

6.1 Carbon Capture and Storage (CCS)

One of the latest developments worldwide to deal with any carbon dioxide emitted from industrial processes, is carbon capture and storage. Essentially it entails a capturing of the released carbon, liquefying it under pressure and then disposing of it deep in the ocean or in a deep storage repository like a mine. It can also be used to enhance oil recovery from oil wells in the sea or on land. Although this technology is still in its infancy, it looks like a promising way to deal with a part of the greenhouse gas emission problem worldwide.

6.2 Biodiesel Production from Algae

Any technology that simply captures released carbon dioxide and deposits it somewhere else, does not really address the issue of how to get rid of it. It merely reduces the size of the problem and displaces the disposal elsewhere. Lately much attention has been focused on the production of algae using carbon dioxide as a carbon source, and the subsequent production of biofuel from such algae [Extance, 2011]. An approach like this has obviously a lot of credibility to improve sustainability. In a recent announcement the company GEA NIRO claimed that it has developed a new process to convert carbon dioxide into fuel alcohol, proteins for animal feed and fertilizer for agricultural purposes by feeding the carbon dioxide to algae. The algae are then transformed to alcohol by fermentation and the residual biomatter to fertilizer. Exhausted yeast cells are then spray dried into protein powder for animal feed (Djernaes, 2011).

6.3 Electrochemical Carbon Reduction (ECR)

One of the most promising technologies for improving sustainability in terms of greenhouse gas (GHG) emissions, is the development of a process to reduce carbon dioxide in the presence of water to formic acid. The ERC process, the "Electrochemical Reduction of Carbon Dioxide," combines captured carbon dioxide with water to produce high value materials, such as formic acid and formate salts, which are conventionally obtained from the thermochemical processing of Fossil Fuels. However, ERC has an advantage over the established thermochemical methods for converting carbon dioxide to green chemicals, new chemicals beyond formic acid, building products and liquid fuels.

While thermochemical reactions must be driven at relatively high temperatures that are normally obtained by burning fossil fuels, ERC operates at near ambient conditions and is driven by electric energy that can be taken from an electric power grid supplied by hydro, wind, solar or nuclear energy (forms of clean or renewable energy). Formic acid is a precursor of a number of other chemicals made in various processes, especially in the pharmaceutical industry [Basile & Ganjian, 2004; Fleischman et al., 2003].

An example of the implementation of this technology is the recently announced investment by Lafarge North America Inc. in a deal with Mantra Venture Group (Ltd) to build such a plant at one of the Lafarge group’s North American cement manufacturing sites (Worldcement.com, 2010)

6.4 Supercritical Carbon Dioxide Treatment of Concrete/Lime

Recent research [Fabbri et al., 2009; Rimelle et al., 2008; Garcia-Gonzalez et al., 2008 and references therein; Short et al., 2004] has indicated that it is possible to increase the strength of concrete by treating it with supercritical (SCF) carbon dioxide. The carbon dioxide penetrates the concrete mixture, and reacts with the calcium hydroxide formed by the hydrated cement binder, turning it into calcium carbonate. Not only does this increase the strength of the concrete, it also makes it less permeable and therefore more durable. This could be a very beneficial use of at least some carbon dioxide, also in cases where hydraulic lime has been used as a binder.

6.5 Other Emissions

Carbon dioxide is not the only environmentally harmful gas released by the cement industry. SO_X and NO_X compounds are also emitted and are also potentially very environmentally damaging, because they are known to cause acid rain and smog and can therefore have very damaging effects on local populations. New burner designs and lower firing temperatures are some of the methods used to curb NOx emissions. However, care should be taken to maintain the temperature high enough to destroy dioxins if any waste fuels are employed. Released SO_X compounds can be reduced by the same methods employed in the power generating industry, i.e. by absorption in a lime/limestone slurry to produce FDG (flue gas desulphurised gypsum) [Srivastava et al., 2001; Ogenga et al., 2010; Lee et al., 2008].

7. Conclusions

So, how would an ideal, environmentally sustainable cement plant look like with the technology that is currently available? Assuming that it will still produce mostly OPC, it should start off with a large proportion of waste materials such as red mud, bottom ash and fly ash as components of the raw meal, with purified industrial gypsum as a flux to lower the burning temperature. The kiln should have at least 4-5 pre-heaters to ensure the highest energy efficiency and if appropriate, a pre-calciner should be added into the process. A substantial portion of the energy used should be derived from waste fuels, e.g. tyres, used solvents and oils, and the waste heat from the process should be recovered to generate electricity to supplement the plant's electricity requirements. The latest mills should be used to do grinding of the final product with grinding aids, and purified industrial gypsum should be used exclusively as the set-retarder in the cement produced. A part of the final OPC produced should be substituted with an inorganic mineral admixture such as fly ash, slag or metakaolin or even combinations thereof. The carbon dioxide emissions should be converted through the ERC process to starting material for further chemicals manufacturing, or buried in a deep level repository with the aid of CCS equipment.

- All these technologies have been discussed and have been proven through research, some as long ago as 3-4 decades. In many plants all over the world parts of these solutions are already implemented. One can rightly ask if the cement industry is too slow to embrace new technology and make a wholesale shift to sustainability, or if instead it prefers incremental improvements in their environmental footprint? Is it going to increase cement prices if all the technologies referred to in here are adopted? Probably, yes. Is it worth it? This author thinks so. The cement industry has to place the sustainability of the planet and the welfare of future generations high on their agenda before profit making only, and step up to their environmental responsibility. It is simply too important an industrial sector for mankind to go without, and it is possible with current technology and will power to operate in both a sustainable as well as economically profitable way. So, to answer the question posed originally, namely: Is cement and concrete production sustainable on a long term basis, and are cement producers doing enough to pursue sustainability?, the evidence cited in this paper suggest that cement and concrete production can definitely be sustainable in the long run. Judging from the possibilities to improve sustainability by adapting the raw material supply, modifying the production process by substituting alternative fuels and raw materials, and finally diluting the final product and treating or converting the carbon dioxide emissions, it seems that the emphasis of most cement producers are still focused on selected parts of these different possibilities, especially the final dilution and substitution of cement by various mineral admixtures. It is therefore questionable if cement producers are adapting fast enough and to a sufficient degree to exploiting all the possible options to reduce their environmental footprint.

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