

Alternative Fuels in Cement Manufacturing

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1. Introduction

Fossil fuels such as coal, petroleum and natural gas provide most of the energy needs of the world today. Coal and natural gas are used in their natural forms, but petroleum and other fossil fuels such as shale and bituminous sands require distillation and refinement to give usable fuels. These fuels exist in any of the following forms: solid, liquid and gas. The finite nature of global fossil fuel resources, high prices and most importantly, their damaging effect on the environment underscore the need to develop alternative fuels¹ for many industrial systems that rely on fossil fuels. Increased use of renewable and alternative fuels can extend fossil fuel supplies and help resolve air pollution problems associated with the use of conventional fuels.

This chapter reviews in detail some of the main alternative fuels used in cement production. It focuses on types of alternative fuels used, the environmental and socio-economic benefits of using alternative fuels, challenges associated with switching from conventional to alternative fuels, combustion characteristics of the alternative fuels concerned, and their effect on cement production and quality. The aim of this chapter is to provide empirical evaluation of alternative fuels. It offers an invaluable source of information for cement manufacturers that are interested in using alternative fuels. Researchers and students would also find this information valuable for their professional and academic development.

Cement is considered one of the most important building materials around the world. Cement production is an energy-intensive process consuming thermal energy of the order of 3.3 GJ/tonne of clinker produced. Electrical energy consumption is about 90 – 120 kWh/tonne of cement (Giddings, et al, 2000; European Commission [EC] 2001). Historically, the primary fuel used in cement industry is coal. A wide range of other fuels such as gas, oil, liquid waste materials, solid waste materials and petroleum coke have all been successfully used as sources of energy for firing cement-making kilns, either on their own or in various combinations.

The cement manufacturing industry is also under increasing pressure to reduce emissions. Cement manufacturing releases a lot of emissions such as carbon dioxide (CO₂) and nitrogen oxide (NO_x). It is estimated that 5 percent of global carbon dioxide emissions originate from cement production (Hendriks, et al, 1998). The use of alternative fuels in cement manufacturing, therefore do not only afford considerable energy cost reduction, but they also have significant ecological benefits of conserving non-renewable resources, the

¹ Alternative fuels here refer to fuels that can be used instead of conventional fuels such as coal, oil and natural gas.

reduction of waste disposal requirements and reduction of emissions. Use of low-grade alternative fuels in some kiln systems reduces NO_x emissions due to reburn reactions. There is an increased net global reduction in CO_2 emissions when waste is combusted in the cement kiln systems as opposed to dedicated incinerators.

1.1 Overview of alternative fuels

Alternative fuels and alternative sources of energy usually fall under eight broad headings: biofuels; natural gas; waste-derived fuels; wind energy; hydroelectric power; solar energy; hydrogen; and nuclear energy. Alternative fuels discussed in this chapter are predominantly agricultural biomass, non-agricultural biomass (e.g. animal waste and by-products), chemical and hazardous waste, and petroleum-based fuels.

Biofuels are from organic origin (plants or animals based) including organic waste, residues from agriculture and energy crops, meat and bone-meal, methane from animal excrement or as a result of bacterial action, ethanol and biodiesel from plant materials, as well as the organic part of waste.

Solid biofuels (generally called biomass) include plant tissues such as wood, charcoal and yarns; farm wastes such as coffee husks, straw, sugarcane leaves, sugarcane bagasse, rapeseed stems, palm nut shells, rice husks, etc.; and non-agricultural biomass such as animal fat, dung, meats and bones; and household or industrial biological degradable wastes. These materials are primarily composed of carbon-based organic matter, which releases energy when it reacts or combusts with oxygen (Seboka et al., 2009).

Solid biofuels should be distinguished from solid fossil fuels which are of biological origin but which are non-renewable. Similarly, liquid biofuels should be distinguished from fossil liquid fuels which are also of biological origin but which are non-renewable. Liquid biofuels are transport fuels, primarily biodiesel and ethanol. Another form of biofuel is biogas. Biogas is the product of organic material decomposition, composed mainly of methane and carbon dioxide.

Candidate materials for the hazardous waste fuel/waste derived fuels are too many to list. They include almost every residue from industrial or commercial painting operations from spent solvents to paint solids including all of the wash solvents and pot cleaners, metal cleaning fluids, machining lubricants, coolants, cutting fluids, electronic industry solvents (chlorinated/fluorocarbon solvents), oils, resins and many more. The list of candidate materials for use as alternative waste fuels continues to expand. Regulatory pressures, economic considerations, shrinking traditional solid waste disposal capabilities, and a host of similar factors are reflected in the constant change of the candidate waste fuel universe (Gabbard, 1990).

2. Alternative fuel options for the cement industry

Coal is the primary fuel burned in cement kilns, however, the use alternative fuels in cement kilns is now common and increasing. The range of alternative fuels is extremely wide. They are usually available as gas, liquid and solid as shown in Table 1.

Before proceeding to a consideration of some of these fuels and their properties it is necessary to consider briefly the cement production process.

2.1 Cement production process

Cement is considered one of the most important building materials around the world. In 1995 the world production of cement was about 1420 million tonnes (Cembureau, 1997).

Cement production is an energy-intensive process consuming thermal energy of the order of 3.3 GJ/tonne of clinker produced, which accounts for 30 - 40 percent of production costs (Giddings et al., 2000; EC, 2001). Worldwide, coal is the predominant fuel burned in cement kilns. Cement production consumes approximately 120 kg of coal per tonne of cement. In the European Union about 25 million tonnes of coal is required annually by the Cembureau² members to service the demand of cement in Europe. In 2005, the global cement industry consumed about 9 exajoules (EJ) of fuels and electricity for cement production (IEA 2007, as cited in Murray & Price, 2008).

Category	Fuels
Gaseous fuels	Refinery waste gas, landfill gas, pyrolysis gas, natural gas
Liquid fuels	Tar, chemical wastes, distillation residues, waste solvents, used oils, wax suspensions, petrochemical waste, asphalt slurry, paint waste, oil sludge
Solid fuels	Petroleum coke (petcoke), paper waste, rubber residues, pulp sludge, sewage sludge, used tyres, battery cases, plastics residues, wood waste, domestic refuse, rice husks, refuse derived fuel, nut shells, oil-bearing soils, diapers, etc.

Table 1. Alternative fuel options for the cement industry

Cement production involves the heating, calcining and sintering of blended and ground raw materials, typically limestone (CaCO_3) and other materials containing calcium, silicon oxides, aluminium and iron oxides to form clinker. Clinker production takes place at material temperatures of about 1450°C in either rotary or shaft kilns. Carbon dioxide is released during the production of clinker. Specifically, CO_2 is released as a by-product during calcination, which occurs in the upper, cooler end of the kiln, or a precalciner, at temperatures of 600-900°C, and results in the conversion of carbonates to oxides. Most modern cement kiln systems³ have a special combustion chamber called a 'precalciner' as part of the preheating tower, as shown in Fig. 1. The limestone (calcium carbonate) decomposition process known as 'calcination' ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$) is virtually completed (approximately 95 percent) in the precalciner if 50 - 60 percent of the total fuel required for clinker production is added to this chamber (Taylor, 1990).

The clinker is then removed from the kiln to cool, ground to a fine powder, and mixed with a small fraction (about five percent) of gypsum to create the most common form of cement known as Portland cement.

2.2 Benefits of using alternative fuels in cement production

Cement producers worldwide are striving to lower their production costs. One effective method of achieving this end is the use of alternative fuels. Use of low-grade alternative fuels such as waste coal, tyres, sewage sludge, and biomass fuels (such as wood products, agricultural wastes, etc.) in precalciners is a viable option because combustion in a

² CEMBUREAU - The European Cement Association.

³ The kiln system comprises a tower of pre-heater cyclones, precalciner and the rotary kiln.

precalciner vessel takes place at a lower temperature. In precalciners where kiln exhaust gases pass through, the NO_x emissions are much reduced due to reburn reactions. There is an increased net global reduction in CO_2 emissions when waste is combusted in the cement kiln systems as opposed to dedicated incinerators, resulting in reduction in the CO_2 penalties. Since alternative fuels are often deemed cheaper than conventional fossil fuels, the possibility of a competitive edge is generated.

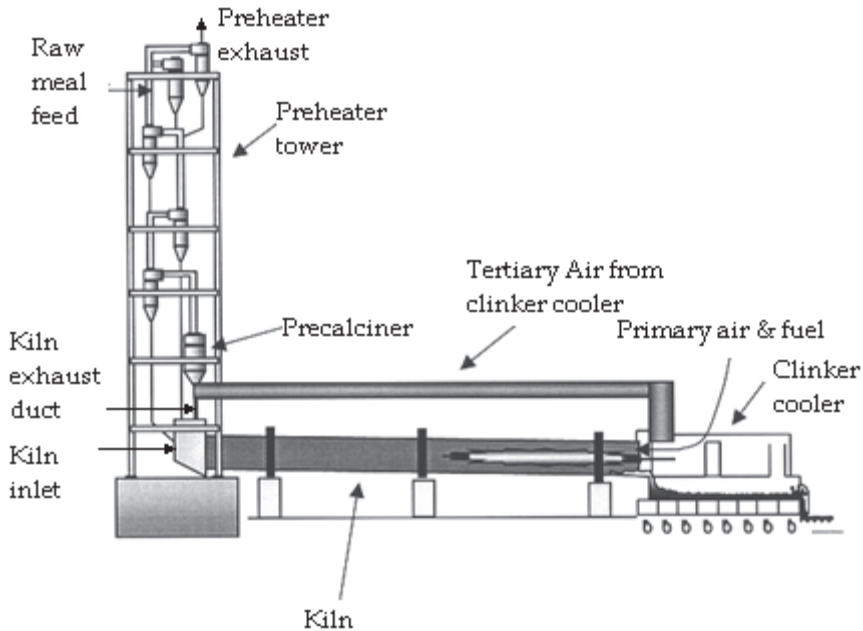


Fig. 1. The kiln system

The use of alternative fuels in cement manufacture is also ecologically beneficial, for two reasons: the conservation of non-renewable resources, and the reduction of waste disposal requirements. The use of alternative fuels in European cement kilns saves fossil fuels equivalent to 2.5 million tonnes of coal per year (Cembureau, 1999). The proportion of alternative fuels used in cement kiln systems between 1990 and 1998 in some European countries are as follows in order of importance: France 52.4 percent; Switzerland 25 percent; Great Britain 20 percent; Belgium 18 percent; Germany 15 percent; Czech Republic 9.7 percent, Italy 4.1 percent; Sweden 2 percent; Poland 1.4 percent; Portugal 1.3 percent and Spain 1 percent (Mokrzycki et al., 2003).

The process of clinker production in kiln systems creates favourable conditions for use of alternative fuels. These include: high temperatures, long residence times, an oxidising atmosphere, alkaline environment, ash retention in clinker, and high thermal inertia. These conditions ensure that the fuel's organic part is destroyed and the inorganic part, including heavy metals is trapped and combined in the product.

The wastes used as alternative fuels in cement kilns would alternatively either have been landfilled or destroyed in dedicated incinerators with additional emissions as a

consequence. Their use in cement kilns replaces fossil fuels and maximises the recovery of energy. Employing alternative fuels in cement plants is an important element of a sound waste management policy. This practice promotes a vigorous and thriving materials recovery and recycling industry (Cembureau, 1999).

2.3 Key considerations for co-processing alternative fuels

The potential benefits of burning alternative fuels at cement plants are numerous. However, the contrary is possible, where poor planning results in projects where cement kilns have higher emissions, or where alternative fuels are not put to their highest value use. Five guiding principles outlined by the German development agency, GTZ, and Holcim Group Support Ltd., reproduced in Table 2, provide a comprehensive yet concise summary of the key considerations for co-incineration project planners and stakeholders (GTZ and Holcim, 2006 as cited in Murray & Price, 2008).

Principle	Description
Co-processing respects the waste hierarchy	<ul style="list-style-type: none"> - Waste should be used in cement kilns if and only if there are not more ecologically and economically better ways of recovery. - Co-processing should be considered an integrated part of waste management. - Co-processing is in line with international environmental agreements, Basel and Stockholm Conventions.
Additional emissions and negative impacts on human health must be avoided	<ul style="list-style-type: none"> - Negative effects of pollution on the environment and human health must be prevented or kept at a minimum. - Air emissions from cement kilns burning alternative fuels cannot be statistically higher than those of cement kilns burning traditional fuels.
The quality of the cement must remain unchanged	<ul style="list-style-type: none"> - The product (clinker, cement, concrete) must not be used as a sink for heavy metals. - The product must not have any negative impacts on the environment (e.g., leaching). - The quality of the product must allow for end-of-life recovery.
Companies that co-process must be qualified	<ul style="list-style-type: none"> - Have good environmental and safety compliance records. - Have personnel, processes, and systems in place committed to protecting the environment, health, and safety. - Assure compliance with all laws and regulations. - Be capable of controlling inputs to the production process. - Maintain good relations with public and other actors in local, national and international waste management schemes.
Implementation of co-processing must consider national circumstances	<ul style="list-style-type: none"> - Country specific requirements must be reflected in regulations. - Stepwise implementation allows for build-up of necessary management and handling capacity. - Co-processing should be accompanied with other changes in waste management processes in the country.

Table 2. Guiding principles for co-processing alternative fuels in cement kilns

2.4 Challenges of using alternative fuels in cement production

Alternative fuels used in cement manufacturing have different characteristics compared to the conventional fuels. Switching from conventional fuels to alternative fuels presents several challenges that must be addressed in order to achieve successful application. Poor heat distribution, unstable precalciner operation, blockages in the preheater cyclones, build-ups in the kiln riser ducts, higher SO_2 , NO_x , and CO emissions, and dusty kilns are some of the major challenges (Roy, 2002; F.L. Smidth & Co., 2000).

The cement industry, like other industrial sectors, is strictly regulated by the national and international legislation as well as internal regulatory procedures regarding environmental protection, health and safety, and quality of products. Strict regulations are applied and plants are operated on the basis of permits from national authorities. Emissions are regularly checked by the authorities. Special approval from relevant authorities is therefore required to burn alternative fuels in many countries on account of potential environmental hazards (Hewlett, 2004).

The operation of cement kiln system is not only affected by the chemical composition of the main components of the raw meal but also the combustion and consequently the fuel used. The type of fuel used can introduce some material components which can interfere with the chemistry of the cement materials as well as affect the operation of the system. The use of a type of fuel is therefore subject to the constraints imposed by any deleterious effect on cement quality, refractory life, gas and material flow or potential emissions to the atmosphere (Bye, 1999).

In most kiln systems the fuel ash is incorporated into the clinker thereby changing the compound composition of the product. The main constituents of fuel ash are silica and alumina compounds which combine with the raw materials to become part of the clinker. The composition of fuel ash tend to limit the level of replacement of more conventional fuels, for instance rice husks have been used to replace 5 – 7 percent of traditional fuels since the ash contains 78 – 90 percent silica. Fuel ash with high content silica can on the other hand provide a very satisfactory means of increasing the silica modulus of the clinker, thus making it possible to reduce the amount of ground sand incorporated into the feedstock (Hewlett, 2004).

Approximately 95 percent of clinker consists of oxides of CaO , SiO_2 , Al_2O_3 , and Fe_2O_3 and the remainder consists of the so-called minor constituents. In cement manufacturing care is taken to avoid constituents which, even when present in small amounts (< 1percent), may have adverse effect upon the performance of the product and/or the production process. The most important of these are probably the oxides of potassium and sodium (K_2O and Na_2O) commonly known as alkalis. High levels of alkalis in cement can, in the presence of moisture, give rise to reactions with certain types of aggregates to produce a gel which expands and gives rise to cracking in concretes and mortars.

The alkali metals Na_2O and K_2O have a very strong affinity for SO_3 and where there is sufficient sulphate present in the clinker, the alkalis are normally present as compounds of sulphates such as K_2SO_4 , Na_2SO_4 , aphthalalite $\text{Na}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$ and langbeinite $2\text{CaSO}_4 \cdot \text{K}_2\text{SO}_4$ (Hewlett, 2004; Newman, et al., 2003). Higher levels of alkali sulphates in cements affect the reactivity of the cement, thus leading to possible setting problems (Hewlett, 2004). From kiln operational point of view, it is desirable that as much as possible the alkalis (and sulphates) get discharged from the system with the clinker. If this does not take place, the presence of these alkalis (and sulphates) can have an extremely disruptive effect upon production especially in kiln systems with high efficient heat exchangers such as the cyclones.

It is reported that in kiln systems equipped with high efficient pre-heaters, volatilized recirculation loads of 150 - 200 percent (of the total input) for K_2O , 100 - 150 percent for Na_2O and 350 - 400 percent for alkali sulphate exist because volatilized alkalis, chlorine and some heavy metal condense on the raw meal grains in the suspension preheater. With the raw meal they return to the kiln where they are volatilized again thereby increasing the recirculation load (Hewlett, 2004; Ghosh, 1991; Taylor, 1990). Some of the alkalis volatilized in the high temperature part of the system (kiln) condense in the cooler parts, causing build-up and blockages in the heat-exchange systems. The sticky deposits attract dust and bind it together to form build-up, which in an extreme case can completely throttle the flow of gas and/or cement solid materials. There are mainly two ways of maintaining the alkalis at a required level, firstly through the careful selection of materials and secondly by bleeding high-alkali dusts from the kiln system (Hewlett, 2004; Taylor, 1990).

If chloride is introduced into the system either through the raw meal or the fuel, the melting point of the sulphates is reduced and sulphate-spurrite ($C_2S-CaSO_4$), which is stable within the temperature range 900–1200°C can also be formed. Sulphate-spurrite is considered to be associated with the formation of rings in cement kilns. It is recommended that chloride content must be kept low to avoid formation of kiln rings and preheater deposits (Taylor, 1990). Contents below 0.02 percent are preferred, though higher ones can be acceptable if a sufficient proportion of the kiln gases is bypassed or in less energy-efficient (e.g. wet process) plants. Ring formation is known to increase with an increase in the amount of excess sulphur over that which combines with alkalis (Hewlett, 2004).

Since sulphur is introduced into the system through the fuel and also with the raw materials, the sulphur content of the fuel can become an important factor in kiln system operation. It is however, important to distinguish between the sulphur in the raw meal that enters the kiln system in the form of sulphates (such as calcium sulphates) and that which enters as sulphides (such as pyrite, marcasite and organic sulphides). The latter can oxidize through an exothermic reaction at 400 - 600°C in sections of the system (for example cyclones) where there is less calcium oxide available. Consequently, the SO_2 released is emitted and treated. On the other hand, the calcium sulphates present do not decompose until 900 - 1000°C. This gives the oxides of sulphur an opportunity to react with the alkalis which have been volatilized and also with CaO that has already formed thereby increasing the chance of alkalis and sulphate being removed from the kiln system in the clinker. This is why it is generally possible to use fuels with high sulphur content in the cement industry without significant harmful consequences to the environment (Ghosh, 1991). As already mentioned, if significant amounts of the low melting point mixtures of calcium and alkali sulphates form in and around the preheater sections can lead to blockages.

Some of the waste materials used as alternative fuels in cement kiln systems such as polyvinylchloride (PVC), chlorinated hydrocarbons, sewage sludge, and meat and bone meal can increase the amount of chlorine (Cl) introduced into the system (Saint-Jean et al, 2005). Fuels containing high (> 0.7 percent Cl) can adversely affect the performance of some types of electrostatic precipitators on wet process kilns. It is also reported that in kilns with cyclone pre-heaters, only about 20 percent of the chlorine input is retained in the clinker, with the result that a recirculation chloride load of some 400 - 500 percent develops in the kiln/preheater system (Hewlett, 2004). Clogging may occur in the cyclone pre-warmer if chlorine content of fuel is more than 0.2 - 0.5 percent (Werther et al., 1997). Chlorine content is also known to affect the quality of the product. High Cl content increases the corrosion of reinforcement in concrete. From quality point of view most standards for Portland cements

restrict the amount of chloride present to 0.10 percent of the raw meal feedstock. However, in preheater kiln systems operational problems normally manifest themselves long before this quality point is reached (Hewlett, 2004).

The effect of other trace elements such as fluorine, barium, chromium, lead, manganese, thallium, titanium, vanadium and zinc on quality of cement range from very small to negligible. However, it is important to note the exceptions of fluorine and zinc from this list. There are indications that the use of fluorine as a mineraliser⁴ may give rise to the build-up of excessive coating in the kiln and that this may be due to the formation of additional spurrite. CaF_2 acts both as a mineraliser and as a flux in promoting the formation of alite⁵ (Taylor, 1990; Newman et al., 2003). Small amounts of zinc (0.01 – 0.2 percent) have been reported to increase the reactivity of C_3A ⁶ and in consequence lead to possible setting time problems. However, the presence of up to 0.5 percent of ZnO does not appear to have a profound effect upon other hydraulic properties (Hewlett, 2004). The zinc content in tyres is, from cement quality point of view, the main constraint in the use of scrap tyre as a fuel. Type ash contains about 20 percent Zn (Al-Akhras et al., 2002).

The incomplete combustion, poor heat distribution and unstable precalciner operation are problems associated with switching from conventional fuel to alternative fuels (Roy, 2002). The arrangement of combustion in such a manner as to create a reducing condition in some zones of the precalciner is useful for the diminution of NO_x emissions. On the other hand, it is important to note that low combustion efficiency at the precalciner stage can create reducing zones in deposited material at the kiln inlet, significantly increasing the volatilization rate of sulphur (Ghosh, 1991). Desmidt, 1987, observed a 78 percent volatilization of SO_3 at 93 percent combustion and 0.2 percent CO at kiln inlet, and a 42 percent volatilization of SO_3 at 98 percent combustion and 0.06 percent CO at kiln inlet. Incomplete combustion also gives rise in the carbon content in the product. This is undesirable for the following reasons. First, high carbon content accelerates corrosion of steel in concretes. Secondly, the carbon absorbs water reducing the quantity available for hydration reaction. Thirdly, the alkalinity of the cement is affected. Finally, high carbon content ash darkens the concrete reducing its aesthetic appeal and leading to inaccurate prejudgements of the concrete quality (Ha et al., 2005; Freeman et al., 1997; CIF, 2000).

2.5 Main alternative fuels used in the cement industry

Well-established technology, on the one hand, allows the rotary kiln of any cement plant to be fired with low-volatile fuels such as petcoke, low-volatile bituminous coal, and anthracite, without problem (Nielsen et al., 1986). On the other hand, high volatile-low calorific value alternative fuels have limited use in the kiln primary firing system due to their relatively low combustion temperatures. They are utilised more in the precalciner firing than in the kiln unless their calorific value exceeds about 16.8 MJ/kg (Hochdahl, 1986). Experience has shown that it is difficult to obtain complete combustion of low-volatile fuels in precalciners. The use of low-volatile fuels in precalciners, often requires design and operational modifications of the precalciner, or specially designed precalciners (Roy, 2002; Nielsen & Hundebol, 1986).

⁴ A mineraliser is an agent that promotes the formation of a particular solid phase by affecting the equilibria through incorporation in one or more of the solid phases (Taylor1990).

⁵ Alite is a cement phase $2\text{CaO}\cdot\text{SiO}_2$ or C_2S .

⁶ C_3A is another cement phase $3\text{CaO}\cdot\text{Al}_2\text{O}_3$.

Switching from conventional fuels to alternative fuels therefore presents several challenges that must be addressed. Poor heat distribution, unstable precalciner operation, blockages in the preheater cyclones, build-ups in the riser ducts, higher SO₂, NO_x, and CO emissions, and formation of rings in kilns are some of the major challenges (Roy, 1986; Pipilikaki et al., 2005; F.L Smidth, 2000).

The quality, type and quantity of fuel exert a profound effect on the quality of clinker produced. Consequently, selection of the proper type of fuel is vital for optimum efficiency. Waste derived fuels have different characteristics compared to conventional fuels such as coal and to be able to use them in cement manufacturing, knowledge of their composition is important. The energy and ash content as well as the moisture and volatile contents are all important limiting factors. A comparison of coal with some of the most common alternative fuels used in cement kiln systems is presented in Table 3. Ultimately, cost and availability of the alternative fuels remain the main influencing factors for their choice.

2.5.1 Petroleum coke

Petroleum coke (petcoke) is the solid residue that remains after extraction of all valuable liquid and gaseous components from crude oil. The world production of petcoke grew by 50 percent from 1997 to 1998. It reached 50 million tonnes in 1999 and was expected to reach 100 million tonnes by 2010 (International Energy Agency [IEA], 2001). Petcoke is a low-volatile fuel whose volatile content range is typically 5 - 15 percent, depending on the coking process (Roy, 2002). There are three processes of coking: delayed, fluid and flexi-coking with delayed coking producing over 90 percent of total production (IEA, 2001). Petcoke is composed mainly of carbon and it also contains high levels of sulphur and heavy metals such as vanadium and nickel (IEA, 2001; Bryers, 1995). The fixed carbon varies from 80 - 92 percent (Bryers, 1995). Irrespective of the coking process, petcoke has higher calorific value than coal, typically LHV of about 32.5-35 MJ/kg (Commandre & Salvador, 2005). The use of petcoke as fuel presents several challenges due to its high sulphur content, poor ignition and burnout characteristics because of its low volatile content. Low-volatile fuels are generally fired in an arch-type furnace to induce ignition and ensure flame stability (Bryers, 1995).

Petcoke is widely used in cement kilns worldwide. However, owing to the challenges associated with its burning, it is not possible to fire 100 percent petcoke in the kiln and precalciner in many existing cement kiln systems without co-firing with a high-volatile fuel or special design considerations (IEA, 2001; Roy, 2002; Nielsen et al., 1986; Tiggesbäumker & Beckum 1986). New plants specifically designed to enable 100 percent petcoke firing are coming on the market while the many classical precalciners are retrofitted to enable petcoke firing. One traditional solution to using petcoke is to grind the coke to a much finer residue than standard coal, up to 0.5 - 1 percent retained on 90 μm (Roy, 2002; Bryers, 1995). The burning rate of an individual char particle depends primarily on its particle size, the amount of oxygen present in the local atmosphere and the local temperature.

In precalciner application where temperature is lower than in kilns, besides the particle size, considerable retention time is required to complete the combustion. In precalciners designed for coal firing where the gas retention time is less than 3 s, often petcoke is introduced directly into the tertiary air where oxygen is highest before mixing with kiln exhaust gases. In some of new precalciner designs the gas retention time is increased significantly to about 7 s by injecting petcoke in a long loop duct before joining the main calciner (Roy, 2002). The

combustion of petcoke in a relatively raw meal free hot-zone in the precalciner away from the walls is an important aspect in new precalciner designs and retrofits to achieve high burning rate and avoid build-ups.

The sulphur content of petcoke is several times higher than that of coal. It is therefore expected that combustion of petcoke will lead to higher emissions of SO₂. SO₂ emissions in pulverized fuel firings as mentioned earlier, normally correlate strongly with the sulphur content of the fuel and generally almost all the sulphur in the fuel is released as SO₂ (Commandre, 2005; Werther & Ogada, 1997; Spliethoff & Hein, 1998).

Petcoke has low ash content which easily fuses in the cement clinker. Table 4 shows typical ash analyses of various types of petcoke. Vanadium pentoxide (V₂O₅) is by far the highest except in a type of coke where iron oxide was highest. Molten V₂O₅ (melting temperature 675-690°C) is known to dissolve most refractory and metal oxides which could expose virgin metal surfaces to oxidising environment (Bryers, 1995; Hewlett, 2004). Vanadium, if present in clinker, tends to be found in the alite, the crystal size of which increases with additions of up to 0.4 percent (Hewlett, 2004). A 0.2 percent addition is reported to lead to a 10 percent reduction in 28-day strength of cement. However, due to low ash content of petcoke such high contents of vanadium in cement are unlikely.

	Coal	Petcoke, (Kääntee et al., 2004)	Predried Sewage sludge (Winter et al., 1997)	Meat and bone- meal (Kääntee et al., 2004)	Tyre
Proximate analysis (wt. percent)			As received (wt. percent)		
Moisture (wt. percent)	9.20	1.50	7.00	8.09	0.6
Ash (db)	8.85	0.90	26.70	28.30	19.1
Volatiles (daf)	36.22	11.80	60.60	56.41	56.6
C - fixed	45.63	85.80	5.70	7.20	23.7
Ultimate analysis (wt. percent daf)			As received (wt. percent)		
C	68.6	89.50	37.20	42.10	71.85
H	3.05	3.08	4.29	5.83	6.07
N	1.3	1.71	4.18	7.52	0.20
S	0.49	4.00	0.53	0.38	1.06
O	8.51 ⁷	1.11	20.10	15.30	1.12
Ash	7.0	0.90	26.70	28.30	19.1
LHV (MJ/kg)	27.89	33.7	14.8	16.2	31
Density (kg/m ³)	1300	2023	1140	720	1179

Table 3. Analyses of some common fuels used in cement manufacturing

⁷ By difference

Composition (wt. percent)	Delayed coke	Short coke	Fluid coke	Flexicoke
SiO ₂	10.1	13.8	23.6	1.6
Al ₂ O ₃	6.9	5.9	9.4	0.5
TiO ₂	0.2	0.3	0.4	0.1
Fe ₂ O ₃	5.3	4.5	31.6	2.5
CaO	2.2	3.6	8.9	2.4
MgO	0.3	0.6	0.4	0.2
Na ₂ O	1.8	0.4	0.1	0.3
K ₂ O	0.3	0.3	1.2	0.3
SO ₃	0.8	1.6	2.0	3.0
NiO	12.0	10.2	2.9	11.4
V ₂ O ₅	58.2	57.0	19.7	74.5

Table 4. Typical ash analysis of various types of cokes (Bryers, 1995)

2.5.2 Sewage sludge

A large amount of sewage sludge is produced worldwide. Sludge is formed during wastewater treatment. Wastewater is a combination of the liquid- or water-carried wastes removed from residential, institutional, commercial and industrial establishments (Werther & Ogada, 1997). Landfill, dumping in the sea and use in agriculture as organic fertiliser and soil conditioner are the main conventional methods of disposal. There are however, economical and ecological constraints to these methods. The increasing costs of land for landfill coupled with increasing stringent environmental standards are making landfill a less attractive option. The use of sewage sludge in agriculture poses human health and environmental risks. Uncontrolled addition of sludge to the agricultural land may increase the concentration of heavy metals in farmland. These factors are making the thermal utilisation of sewage sludge an attractive means of its management.

The thermal utilisation of sewage sludge is deemed feasible when its secondary environmental impacts are minimised. The most common sewage sludge disposal alternative is to incinerate it and deposit the ash in controlled landfill. Incineration accounts for 24 percent of the sludge produced in Denmark, 20 percent in France, 15 percent in Belgium and 14 percent in Germany (Hall & Dalimier, 1994). In the USA and Japan, 25 and 55 percent of the sludge produced, respectively, is incinerated (Werther & Ogada, 1997). Incineration ash of municipal solid waste accounts for a great portion of the matter in landfills. A total annual incineration of municipal waste of 26 million tonnes was estimated in the EU in 1997 (Kikuchi, 2001).

The formation of poisonous solid and gaseous by-products during sludge incineration is, however, noted to be a source of public concern. These include the release of heavy metals and the emission of substances such as NO_x, N₂O, SO₂, HCl, HF and C_xH_y (Ogada & Werther, 1996). SO₂ emissions in pulverized fuel fired systems normally correlate strongly with the sulphur content of the fuel and generally almost all the sulphur in the fuel is released as SO₂ (Spliethoff & Hein, 1998; Werther & Ogada, 1997). The sulphur content of the sludge is comparable with that of coal.

Other various processes have been proposed for the thermal utilisation of sewage sludge, including the co-briquetting with coal, the co-combustion with coal (Åmand et al., 2004; Folgueras et al., 2003; Lopes et al., 2003); the use of sewage sludge pyrolysis volatiles as a

reburn fuel in the air-staged combustion of coal (Boocock et al., 1992a, 1992b; Konar et al., 1994); incineration/combustion of sewage sludge alone (Sanger et al., 2001; Arai et al., 1989) as well as co-combustion with other fuels (Amand & Leckner, 2004).

In countries like Japan, USA, Denmark, Netherlands, Switzerland and Belgium sewage sludge is used in cement production. In cement production, sludge is usually co-fired with coal in predried form. Predried sludge is easier to store, transport and feed (Werther & Ogada, 1997). The sewage sludge for co-combustion is dried, pulverised and pneumatically fed to the burners. Either the sludge is preblended with coal and fed together, or the two fuels can be fed separately if multi-fuel burners are used. The environmental concerns associated with sewage incineration are significantly reduced when sewage sludge is used as fuel in cement kilns. The organic part is destroyed and the inorganic part, including heavy metals, is trapped and combined in the product (CEMBUREAU, 1997).

Combustion of sewage sludge is expected to lead to higher emissions of SO₂. In cement production this might not affect the SO₂ emissions significantly, since about 60 to 80 percent of the sulphur is captured by the calcium oxide in the kiln system (Manning et al., 2003; Cement Industry Federation [CIF], 2000). However, as discussed earlier on, in cement kilns sulphur is known to cause hard build-ups due to formation of sulphate compounds. The higher nitrogen content of the sewage sludge does not translate into a proportionate increase in NO_x emissions in precalciners. This is due to lower combustion temperatures, well below 1200°C, that suppresses thermal NO_x formation. The in-line precalciner in particular combines the merits of both the air staging and fuel staging technologies. In this arrangement, the fuel fired in the precalciner is used in reburn reactions.

Sewage sludge ash, however, has a high content of SiO₂, Al₂O₃ and Fe₂O₃ which could affect the quality of cement if excess amounts of sewage sludge are used. Table 5 shows the comparison of the composition of sewage sludge ashes with those of cements. A chlorine content of the sludge of more than 0.2 - 0.5 percent may cause clogging in the cyclone preheaters. To keep the levels of the oxides within limit (Werther et al., 1997) suggested the maximum sewage sludge feed rate to be no more than 5 percent of the clinker production capacity of the cement plant unless the sludge is conditioned and stabilised by lime, normally 0.3 - 0.5 kg CaO/kg dry sludge.

	Cement (Bye, 1999)	Sewage sludge ash (Werther & Ogada, 1997)
CaO	63 - 67	9 - 22
SiO ₂	19 - 23	30 - 49
Al ₂ O ₃	3 - 7	8 - 15
Fe ₂ O ₃	1.5 - 4.5	5 - 23
MgO	0.5 - 2.5	1 - 2
K ₂ O	0.1 - 1.2	
Na ₂ O	0.07 - 0.4	
SO ₃	2.5 - 3.5	

Table 5. Comparison of the compositions of sludge ash with those of cements

Sewage sludge has significantly higher contents of nitrogen, volatile matter and ash, and very low fixed carbon than typical coals. Up to 80 percent of the sludge carbon is volatile

carbon and sludge combustion is characterised by the gas-phase combustion of volatiles (Werther & Ogada, 1997). Published calorific values (HHV) of sludge typically range between 8 – 17 J/kg. The cause of this variation in HHVs is attributed to the treatment of producing the sludge and the heterogeneous nature of sludge (Vesilind & Ramsey, 1996).

The main products of sludge pyrolysis are gas (volatiles); char and oil; the quantities of which depend on factors such as pyrolysis temperature. Sewage sludge releases volatiles over a wide range temperature 250 – 850°C (Stolarek & Ledakowicz, 2001; Inguanzo et al., 2002). The percentage of the gaseous component increases whereas the amounts of oil and char decrease with increasing temperature (Rumphorst & Ringel, 1994; Inguanzo et al., 2002). The composition of pyrolysis gas from predried sludges depends upon on the type of sludge. However, in general the main gaseous components are CO, CO₂, H₂, O₂, N₂ and C_xH_y. CO and H₂ are reported to increase whereas CO₂ and C_xH_y decrease with increasing temperature (Inguanzo et al, 2002; Ogada & Werther, 1996).

2.5.3 Used tyres

Scrap motor tyres have been utilised as a supplementary energy source in Japan, Europe and USA since the 1970s (Gray, 1996) and represent a rapidly growing application in most developed countries where scrap tyres are an environmental nuisance. About 290 million tyres were discarded in the USA in 2003, and nearly 45 percent of these scrap tyres were used as tyre derived fuel (TDF). Approximately 58 percent of the TDF was used in the cement industry (Rubber Manufacturers Association [RMA], 2003). In the EU over 2.5 million tonnes of tyres are produced per year and almost 40 percent of these tyres are thrown away untreated (Diez et al., 2004).

Although the environmental acceptability of the use of tyres as fuel in kiln systems is dependent on individual plant performance, extensive environmental data has been generated for a variety of kiln configurations and fuel displacement. In general, the different test results have shown that TDF has no adverse effect upon the emissions; that is to say, the use of TDF has not caused a facility to exceed its operating limits (Gray, 1996; Environmental Agency, 1998; Blumethal, 1992a, 1992b). In comparison with coal, particulates, SO_x, NO_x and HCl emissions generally decline or remain constant with TDF use. Organic emissions, dioxins and furans are also observed to decline while changes in heavy metal concentrations are nominal (Gray, 1996; Scrap Tyre Management Council [STMC], 1992).

Table 6 shows an elemental ash analysis of tyres in comparison with coal. The use of TDF in cement kiln systems is technically sound as the rubber is destroyed and the inorganic part, including heavy metals, is trapped and combined in the product (CEMBUREAU, 1997).

An additional advantage of TDF use is its steel portion. The steel can substitute, in part, for the iron requirement in the raw meal recipe. The content of iron oxide in Portland cement is 1.5 - 4.5 percent on weight basis. On the other hand, although zinc oxide acts as a flux as well as mineraliser, it is known to have detrimental effect on the quality of cement if it is in excess. It strongly retards the setting time and strength of the cement if the total zinc content of all fuels exceeds 4000 parts per million (PPM) (STMC, 1992; Olmo et al., 2001; Murat & Sorrentino, 1996). Therefore, other than the problems of incomplete combustion, the zinc oxide content in tyres tend to limit its displacement of conventional fuels in cement production (STMC, 1992).

Combustion of whole tyres requires long residence times to obtain complete conversion. In some cement installations, tyres are fired whole, mostly in the rotary kiln. More commonly,

they are shredded in a slashing process, producing tyre chunks or chips, and co-fired with coal in the precalciner. They cannot, however, be finely comminuted economically. At best they can be shredded to pieces (chips) of about 25 mm, typically, their size ranges from 25 – 100 mm.

Element (oxide)	Coal	TDF with wire	TDF without wire
Aluminium	20.7	1.93	13.11
Calcium	3.3	0.56	3.8
Iron	18.89	0.35	2.37
Magnesium	0.79	0.10	0.68
Phosphorous	0.62	0.10	0.68
Potassium	2.06	0.14	0.95
Titanium	0.82	0.14	0.95
Silicone	47.98	5.16	35.05
Sodium	0.48	0.13	0.88
Sulphur	4.33	0.99	6.72
Zinc	0.02	5.14	34.81
Metal		85.26	
Total	100	100	100

Table 6. Elemental ash analysis of tyres in comparison with coal (Gray, 1996)

The majority of precalciners are basically entrained flow combustion vessels. Due to the relatively short residence time in the precalciners, circa 2 to 4s, firing tyre chips often results in incomplete combustion. Some of the tyre chips drop directly into the kiln back end or into the tertiary air duct, in an in-line precalciner arrangement before they are fully devolatilised. At the kiln back end there is very little oxygen in the kiln gas for the combustion of the tyre chips. Smaller chips and fragments of devolatilised chips levitate much more easily and are carried over before their combustion is complete in the precalciner. This means that a considerable fraction of tyre chips may also pass to the rotary kiln as carbon particles mixed with the calcined meal. Besides the under utilisation of the fuel energy, an increase in carbon content in ordinary Portland cement accelerates corrosion of the steel reinforcing in concretes, the alkalinity of the cements is affected and the cement loses its characteristic colour (Kääntee et al., 2004; Winter et al., 1997).

The problems of using scrap tyre as alternative fuel emanate from the lack of understanding of their devolatilisation and combustion behaviour. Tyres, like most of the alternative fuels suffer from insufficient characterisation. Tyres are a hydrocarbon-based material derived from oil, natural rubber and gas. Some inorganic materials, as shown in Table 7, are added to enhance reactions or performance properties. As such tyres are very non-homogeneous and exhibit major property variations. The non-homogeneity arises because of the cord reinforcing materials and steel beading used in their construction. The property variations arise due to applications dependence, extreme size and geometric differences as shown in the differences between passenger car and truck tyres in Table 8. The property variations could also arise due to variable degree of used tyre wear and country dependent construction. Table 8 presents comparisons of analyses of different tyres, and petcoke and bituminous coal. In addition to these variations there are also as received shredded chip size and shape distributions variations.

The thermal degradation of tyres is known to produce a wide variety of products in the liquid (oil) and gas phases in addition to the residual char. The main gases produced during

the pyrolysis of tyres are: CO₂, CO, H₂, CH₄, C₂H₆, C₃H₆, C₃H₈, and C₄H₆, with lower concentrations of other hydrocarbon gases (Williams et al., 2001; Conesa et al., 1997).

Composition	Approximate percent
Rubber (natural & synthetic)	38
Fillers (carbon black, zinc oxide, etc.)	30
Reinforcing materials (fibres, steel cords, bead wire)	16
Plasticizers (oils & resins)	10
Chemicals	5
Miscellaneous	1

Table 7. Typical tyre composition (Bhowmick et al., 1994)

Tyres					Conventional fuels	
	Passenger car (Chen et al., 2001)	Truck (Chen et al., 2001)	Samples used by Williams et al., (2001)	Samples used by Giddings et al., (2001)	Petcoke, (Giugliano et al., 1999)	Bituminous Coal (Kääntee et al., 2004)
Ultimate Analysis, (wt. percent)						
C	81.16	85.19	85.90	78.35	85-90	70.6
H	7.22	7.42	8.0	6.62	5-10	4.3
N	0.47	0.31	0.4	0.22	1.5-2	1.2
S	1.64	1.52	1.0	1.15	3-5	1.3
O	2.07	1.72	2.3	1.22		11.8
Ash	7.44	3.84	2.4	11.74		11.1
Proximate Analysis (wt. percent)						
Fixed Carbon			30.3	23.7	84-88	53.0
Volatile matter			66.5	56.6	11-13	35.9
Ash			2.4	10.8	0.3-0.5	11.1
Moisture			0.8	0.6	1-3	3.0
Wire				8.3		
Heating Value: High Heat Value, (HHV, MJ/kg); and Low Heat Value (LHV, MJ/kg)						
HHV:						
Wire free			40.0	34.8		28.4
With Wire				31.9		
LHV	32.8	31.6			34.5	27.4

Table 8. Comparative analysis between tyres and conventional fuels

The devolatilisation and combustion burnout times of tyre chips remain sources of controversy. Devolatilisation of an average tyre chip held in a precalciner at temperatures of between 1050 - 1150°C, at a gas speed of 22 m/s, was reported nearly complete in 30 seconds (Giuliano et al., 1999). Complete devolatilisation and total burnout times of tyre

chips held at about 900°C in a refractory-lined furnace as long as 2 minutes and 20 minutes respectively have been recorded (Giddings et al., 2002).

When tyre chips are inserted into the furnace, they burn with a vigorous flame after ignition. The ignition time is clearly temperature dependent. At 900°C an average time to ignition of 3 s was observed (Chinyama et al., 2007). The vigorous flame is evidence of intense devolatilisation of the tyre chip (Giddings et al., 2002, Atal & Levendis, 1995). Upon burnout of the volatiles, a low-intensity flame follows and burns to extinction - characterising the burning of char. Tyre char originates from the reinforcing carbon black used as fillers in tyre production. Tyre char also contains almost all the inorganic compounds present in tyres (Helleur et al., 2001).

2.5.4 Meat and bone meal

Meat and bone meal (MBM) is produced in rendering plants where animal offal and bones are mixed, crushed and cooked. Tallow is extracted during the cooking process, and the remaining material is then dried and crushed. Feeding MBM to cattle, sheep or other animals was banned within the EU in 1994 and disposal to landfill is not an option since this does not destroy any potential bovine spongiform encephalopathy (BSE) pathogens (Gulyurtlu et al., 2005). This change in legislation increased the interest in using MBM as fuel to ensure that any living organism is thermally destroyed totally and its energy potential is utilised.

Co-incineration in cement kiln systems is the most common way for MBM destruction (Deydier et al., 2005; Conesa et al., 2005). Compared with coal, MBM has lower fixed carbon and high ash content and chlorine. Most of the chloride in MBM is present as common salt (NaCl) (Conesa et al., 2005). Proximate and ultimate analyses of typical MBM samples and coal are presented in Table 3. The sulphur content of MBM is slightly lower than coal. However, on the basis of calorific value, the sulphur content of MBM could be about same as coal. MBM has calorific value (HHV) of approximately 14 -17 (MJ/kg), this is about half that of coal (Deydier et al., 2005; Gulyurtlu et al., 2005). The high content of calcium in MBM could be an advantage as it could act to retain most of SO₂ formed during MBM combustion. Using MBM in cement production further reduces the possibility of increase in SO₂ emissions.

In France where about 850,000 tonnes of MBM are produced per year, about 45 percent is burnt in cement plants. The remaining 55 percent is usually stored waiting for further destruction or valorisation (Deydier et al., 2005). Apart from use in cement plants, in other countries, for example England, dedicated MBM incinerators are used. The feeding rates of MBM in cement kilns vary from country to country, in Spain the limit is 15 percent of the energy needed in the kilns (Conesa et al., 2005). However, the limit in the feed rate of MBM is due to the effects of chlorides. Chlorides readily volatilise in the burning zone of the kiln and condense in the heat exchangers to combine with alkalis and sulphates to form low melting point mixtures. This leads to build-up and blockages in preheater units. Their effect upon the operation of kilns with cyclone preheaters and gate preheaters is so serious that for the former it is normal practice to limit the total amount of chloride introduced into the process to a maximum of 0.015 percent of the raw meal feed (Hewlett, 2004).

As the nitrogen content in the MBM is about 7-8 times higher than that in coal, it could be expected that NO_x emissions would increase with an increase of MBM in co-combustion. However, the fuel-N conversion to both NO_x and N₂O was observed to decrease with increasing MBM content in coal-MBM blend (Gulyurtlu et al, 2005). A 20 percent (wt.) MBM addition to the fuel gave rise to a reduction in the NO_x concentration of about 25 percent compared to the combustion of coal alone, although the N input was almost double. This

was attributed to a significant part of the fuel-N being released as NH_3 during devolatilisation which reduces NO_x to N_2 through the known De NO_x mechanism (Wenli et al., 1990). The minimisation of the emission of nitrogen compounds in MBM co-combustion was also observed by Goeran et al., (2002).

As MBM ash mainly arises from bone combustion, it contains a high amount of phosphate (56.3 percent) and calcium (30.7 percent), the two major constituents of bone. It also has significant levels of sodium (2.7 percent), potassium (2.5 percent) and magnesium (0.8 percent) (Deydier et al., 2005; Gulyurtlu et al., 2005). Whereas the high content of calcium in MBM is an advantage in cement, high levels of phosphate, sodium, potassium and magnesium can have harmful effects on the production process and/ or cement quality. Phosphate is a compound of phosphorus. The normal range of P_2O_5 contents in Portland cement clinker are from 0.03 to 0.22 percent. When higher amounts of P_2O_5 are present, the dicalcium silicate (C_2S)⁸ is stabilised to an extent that the conversion to tricalcium silicate (C_3S) is inhibited. When the amount of P_2O_5 present exceeds 1 percent, it has been reported that 10 percent of C_3S is lost for each additional 1 percent of P_2O_5 (Hewlett, 2004; Taylor, 1990). Potassium and sodium are alkalis and in cement, high alkali levels can, in the presence of moisture give rise to reactions with certain types of aggregates to produce a gel which expands resulting in cracking in concretes and mortars. Where there is sufficient sulphate present in the clinker, the alkalis are normally present as sulphates. Higher alkali levels in cements (over ≈ 0.8 percent $(\text{Na}_2\text{O})_e$)⁹ when present as alkali sulphates have the effect of increasing the early strength (≈ 10 percent) of cements at the expense of their 28 day strength (Hewlett, 2004; Taylor, 1990). The presence of alkalis (and sulphates) also causes blockages in preheater units. Excessive amounts of magnesia (MgO) (usually considered to be over 5 percent of the clinker as a whole), can crystallise out from the flux as a periclase¹⁰, the presence of which has been associated with long term unsoundness¹¹ (Boynton, 1980; Hewlett, 2004).

Use of MBM in cement production can therefore be limited by the constituents of the ash produced.

2.5.5 Agricultural biomass

Biomass and biomass residues, if sourced in an environmentally and socially sustainable fashion, represent a vast – and largely untapped – renewable energy source. Crop and agro-industrial residues have low bulk and energy density, and for these reasons cannot be transported far from production sites without some form of processing. Residues from large commercial farms and agro-industries can be converted to relatively high-quality and high-energy density fuels for use in the domestic, commercial and industrial sectors through a number of physical, biological and thermo-chemical conversion processes (Seboka et al., 2009). The use of agricultural biomass residues in cement manufacturing is less common in industrialized countries and appears to be concentrated in more rural developing regions such as India, Thailand, and Malaysia. The type of biomass utilized by cement plants is highly variable, and is based on the crops that are locally grown. For example rice husk, corn stover, hazelnut shells, coconut husks, coffee pods, and palm nut shells are among the many varieties of biomass currently being burned in cement kilns (Murray & Price, 2008).

⁸ C_2S and C_3S are cement clinker phases.

⁹ $(\text{Na}_2\text{O})_e$ is sodium oxide equivalent given as $0.658 (\text{K}_2\text{O}) + \text{percent Na}_2\text{O}$

¹⁰ Periclase – MgO becomes sintered into a dense, stable form.

¹¹ A cement is said to be unsound if the hydration of a hardened paste of it is eventually accompanied by excessive expansion, causing cracking and reduction in strength.

Biomass fuels are considered carbon neutral because the carbon released during combustion is taken out of the atmosphere by the species during the growth phase (Intergovernmental Panel on Climate Change [IPCC] 2006). Because the growth of biomass and its usage as fuel occurs on a very short time-scale, the entire cycle is said to have zero net impact on atmospheric carbon emissions. An important caveat to this assumption is that growing biomass and transporting it to the point of use requires inputs like fuel and fertilizer that contribute to the carbon footprint of biomass. When biomass is grown specifically for fuel, the upstream GHGs that are typically attributed to the biomass are those associated with fertilizer, collection, and transportation to the facility. When biomass residues are used, fertilizer is only considered part of the carbon footprint if residues that would normally stay in the fields to enrich the soil are collected (Murray & Price, 2008).

In addition to serving as an offset for non-renewable fuel demand, the use of biomass residues has the added benefit of reducing a cement kiln's nitrogen oxide (NO_x) emissions. Empirical evidence suggests that the reductions in NO_x are due to the fact that most of the nitrogen (N) in biomass is released as ammonia (NH_3) which acts as a reducing agent with NO_x to form nitrogen (N_2) (McIlveen-Wright 2007 as cited by Murray & Price, 2008). Interestingly, there does not seem to be a strong relationship between the N content in the biomass and the subsequent NO_x emissions reductions (McIlveen-Wright 2007 as cited by Murray & Price, 2008).

There is a wide range in the calorific values reported in the literature for agricultural biomass categorically, as well as for individual types. The range in lower heating values¹² (LHV) of agricultural biomass is from 9.2 - 19.4 GJ/dry ton. The quantity of agricultural biomass residues that are necessary to replace one tonne of coal depends on the fuel's energy value and water content. As a rule of thumb, a 20 percent substitution rate of agricultural biomass residues for fossil fuel (on a thermal energy basis¹³) is quite feasible in cement kilns without the need for major capital investment (Seboka et al., 2009; Demirbas 2003 as cited by Murray & Price, 2008).

Major challenges of using agricultural biomass residues include the relatively low calorific value which can cause flame instability, and availability since most of the agricultural residues are seasonal (not available all year round). The flame instability problems could be overcome with lower substitution rates and ability to adjust air flow and flame shape. Collection and storage of residues during the months of availability or alternatively, sourcing different residues at different times of the year could overcome the availability problem. Another challenge is that biomass is prone to change with time, thus care must be taken to use the material before it begins to breakdown. Importantly, new biomass should be rotated into the bottom of storage facilities such that the oldest material is injected into the kiln first. Related to biomass conveyance, the flow behaviour of different materials is quite variable, therefore, cement kiln operators must choose the method for injecting fuel into the kiln that will facilitate a constant and appropriate heat value.

As discussed in section 2.3, the presence of halogens (e.g., chlorine) found in biomass such as wheat straw and rice husks may be a concern for slagging and corrosion in the kiln;

¹² The energy content of fuels can be reported in terms of the lower heating value (LHV) or the higher heating value (HHV), alternatively referred to as net and gross calorific value, respectively. The LHV assumes that the latent heat of vaporization of water in the material is not recovered, whereas the HHV includes the heat of condensation of water.

¹³ Biomass can replace up to 20 percent of the total energy demand. Substitution rates on a mass basis are relative to the heat content of the alternative fuel in comparison to coal.

however studies have shown that co-firing biomass with sulphur containing fuels (such as coal) prevents the formation of alkaline and chlorine compounds on the furnaces (Demirbas 2003; McIlveen-Wright 2007 as cited in Murray & Price, 2008). However, ash deposits may decrease heat transfer in the kiln.

Biomass can be used in cement plants through two major modes, namely direct combustion and transformation into producer gas. Direct combustion of biomass in pre-heaters / pre-calciners and in the kiln by part-replacing the fossil fuel used in raising the temperature of the raw meal. This can happen in two ways: first, by mixing crushed and pulverized biomass with coal or petcoke for use in the kiln, and secondly, by direct feeding of biomass in solid lump form (such as pellets and briquettes) into the rotary kiln and / or pre-heater/pre-calciner combustion chamber. The biomass can also be transformed into producer gas (also known as 'synthesis gas' or 'syngas') and co-firing it in the kilns using a gas burner (Seboka et al., 2009).

3. Conclusions

This chapter presents the current fuel alternatives to fuel of fossil origin for cement manufacturing. The chapter introduces different potential alternative fuels that can be used in the cement manufacturing industry and how these fuels are to be considered in order to avoid negative effects on the final product. The type of fuel used in cement production is subject to the constraints imposed by any deleterious effect on cement quality, refractory life and emissions released to the atmosphere. The benefits of using alternative fuels are highlighted, showing that good planning is needed before the alternative fuel to be used is chosen. The chapter has included detailed study of the main alternative fuels used in the cement industry including petcoke, sewage sludge, used tyres, meat and bone meal, and agricultural biomass.

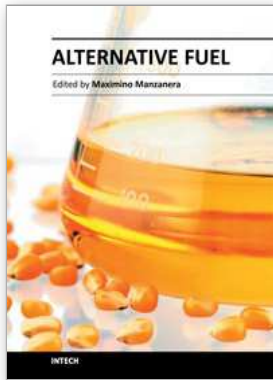
4. References

- Al-Akhras, N.M, & Smadi, M.M. (2004). Properties of tyre rubber ash mortar. *Cement & Concrete Composites*, 26: 821 - 826.
- Åmand, L.E, & Leckner, B. (2004). Metal emissions from co-combustion of sewage sludge and coal/wood in fluidized bed. *Fuel* 83: 1803 - 1821.
- Arai, N, Hasatani, M, & Nakai, Y. (1989). In-furnace reduction of NO_x during the parallel-flow moving-bed combustion of surplus activated sludge char by an active use of self-evolved ammonia. *Fuel*. 68: 591 - 595.
- Atal, A., and Levendis, Y.A. (1995). Comparison of the Combustion Behaviour of Pulverized Waste Tyres and Coal. *Fuel*; Vol. 74, No. 11: 1570 - 1581.
- Bhowmick, A.K., Hall, M.M, & Benarey, H.A. (1994). *Rubber Products Manufacturing Technology*. Marcel Dekker, Inc. New York.
- Blumenthal, M.H. (1992a). *A report on An Emission Study on the Use of Scrap Tyres in Cement Kilns*. Scrap Tyre Management Council, Washington, DC.
- Blumenthal, M.H. (1992b). The Use of Scrap Tyres in the US Cement Industry. *World Cement*.
- Boocock, D.G.B., Konar, S.K., Leung, A, & Ly, L.D. (1992a). Fuels and chemicals from sewage sludge: 1. The solvent extraction and composition of a lipid from a raw sewage sludge. *Fuel*. 71: 1283 - 1289.
- Boocock, D.G.B., Konar, S.K., Mackay, A, Cheung, P.T.C, & Liu, J.N. (1992b). Fuels and chemicals from sewage sludge: 2. The production alkenes by the pyrolysis of triglycerides over activated alumina. *Fuel*. 71: 1291 - 1297.

- Boynton, R. S. (1980). *Chemistry and Technology of Lime and Limestone*. (2nd edition). John Wiley & Sons. Inc., New York.
- Bryers, R.W. (1995). Utilisation of petroleum coke and petroleum coke/coal blends as a means of steam raising. *Fuel Processing Technology*, 44: 121 – 141.
- Bye, G.C. (1999). *Portland Cement*. (2nd edition). Thomas Telford Publishing, London E14 4JD.
- CEMBUREAU. (1997). *Alternative Fuels in Cement Manufacturing: Technical and Environmental Review*. Brussels, The European Cement Association: 24.
- CEMBUREAU. (1999). *Environmental Benefits of Using Alternative Fuels in Cement Production*. Brussels, The European Cement Association: 25.
- Cement Industry Federation (CIF). (2000). *Applied Energy*, 74: 101-111.
- Chen, J.H., Chen, K.S., and Tong, L.Y. (2001). On the Pyrolysis of Scrap Automotive Tires. *Journal of Hazardous Materials*; B84: 43 – 55.
- Chinyama, M. P. M, and Lockwood, F. C. (2007). Devolatilisation behaviour of shredded tyre chips in combusting environment. *Journal of the Energy Institute*, Vol. 80, no. 3: 162 – 167.
- Cement Industry Federation (CIF). (2002). Australian Cement Industry.
- Commandre, J.M, & Salvador, S. (2005). Lack of correlation between the properties of petroleum coke and its behaviour during combustion. *Fuel Processing Technology*, 86, pp. 795 – 808.
- Conesa, J.A., Font, R, & Fullana, A. (2005). Kinetic Model for the combustion of tyre wastes. *Chemosphere*. 59: 85 – 90.
- Conesa, J.A., Font, R, & Marcilla, A. (1997). Mass Spectrometry Validation of Kinetic Model for the Thermal Decomposition of Tyre Wastes. *Journal of Analytical and Applied Pyrolysis*; 43, pp. 83 – 96.
- Desmidt, F, 1987. *World Cement*, 18: 404.
- Deydier, E., Guilet, R., Sarda, S, & Sharrock, P. (2005). Physical and chemical characteristics of crude meat and bone meal combustion residue: “waste or raw material?” *Journal of Hazardous Materials* B121: 141 – 148.
- Diez, C., Martinez, O., Calvo, L.F, & Cara, J. (2004). Pyrolysis of tyres. Influence of the final temperature of the process on emissions and the calorific value of the products recovered. *Waste Management*. 24: 463 – 469.
- Environmental Agency (Bristol) (1998). Tyres in the Environment.
- European Commission (EC) (2001). Integrated Pollution Prevention and Control. Reference Document on Best Available Techniques in the Cement and Lime Manufacturing Industries.
- F.L Smidth & Co. (2000). Dry process kiln systems, technical brochure.
- Freeman, E., Gao, Y., Hurt, R, & Suuberg, E. (1997). Interactions of Carbon-Containing Fly Ash with Commercial Air - Entraining Admixtures for Concrete. *Fuel*; Vol. 76, No. 8: 761 – 765.
- Gabbard, W. D, & Gossman, D. (1990). Hazardous waste fuels and the cement kilns – The Incineration Alternative. *ASTM Standardization News*, September 1990, 10th March 2011, <http://gcisolutions.com/HWF&CKS.htm>
- Ghosh, S.N. (1991). *Cement and Concrete Science & Technology*. (Vol. 1, Part 1), ABI Books Private Limited.
- Giugliano, M., Cernuschi, S., Ghezzi, U, & Grosso, M. (1999). Experimental Evaluation of Waste Tires Utilization in Cement Kilns. *J. Air & Waste Manage. Assoc.* 49: 1405 –1414.
- Giddings, D., Eastwick, C.N., Pickering, S.J, & Simmons, K. (2000). Computational fluid dynamics applied to a cement precalciner. *Proc. Instn. Mech. Engrs. Vol. 214 Part A*.

- Giddings, D., Eastwick, C.N., Pickering, S.J, & Simmons, K. (2002). Combustion and aerodynamic behaviour of car tyre chips in a cement works precalciner. *Journal of the Institute of Energy*. 75: 91 - 99.
- Goeran, O., Wang, W., Ye, Z., Bjerle, I, & Anderson, A. (2002). Repressing NO_x and N₂O emissions in fluidized bed biomass combustor. *Energy Fuels*. 16 (4): 915 - 919.
- Gray, T.A. (1996). *Tyre derived fuel: an environmentally friendly resource*. Texas Natural Resource Seminar.
- Gulyurtlu, I., Boavida, D., Abelha, P., Lopes, M.H, & Cabrita, I. (2005). Co-combustion of coal and meat and bonemeal. *Fuel*. 84: 2137 - 2148.
- Ha, T., Muralidharan, S., Bae, J., Ha, Y., Lee, H., Park, K.W. & Kim, D. (2005). Effect of Unburnt Carbon on the Corrosion Performance of Fly Ash Cement Mortar. *Construction and Building Materials*; 19: 509-515.
- Hall, J.E, & Dalimier, F. (1994). Waste management - sewage sludge: survey of sludge production, treatment, quality and disposal in the EC. EC Reference No: B4-3040/014156/92, Report N: 3646.
- Helleur, R., Popovic, N., Ikura, M. & Stanciulescu. (2001). Characterisation and potential applications of pyrolytic char from ablative pyrolysis of used tyres. *Journal of Analytical and Applied Pyrolysis*. 58-59: 813-824.
- Hendriks, C.A., Worrell, E., de Jager, D., Block, K., & Riemer, P. (1998). Reduction of Greenhouse Gases from the Cement Industry. IEA GHG Paper presented at GHGT-4 Interlaken, Switzerland.
- Hewlett, P.C. (2004). *LEA's Chemistry of Cement and Concrete*. (Fourth Edition). Elsevier Butterworth-Heinemann.
- Hochdahl, O. (1986). Fuels and heat economy. *Zement-Kall-Gips*, No. 4: 90 - 96.
- Inguanzo, M., Dominguez, A., Menendez, J.A., Blanco, C.G, & Pis, J.J. (2002). On the pyrolysis of sewage sludge: the influence of pyrolysis conditions on solid, liquid and gas fractions. *Journal of Analytical and Applied Pyrolysis*. 63: 209 - 222.
- International Energy Agency (IEA) (2001). Coal Research. *The use of petroleum coke in coal-fired plant*.
- Intergovernmental Panel on Climate Change (IPCC) (2006). Guidelines for National Greenhouse Gas Inventories, Vol. 5 Waste.
- Kääntee, U., Zevenhoven, R., Backman, R, & Hupa, M. (2004). Cement Manufacturing Using Alternative Fuels and the Advantages of Process Modelling. *Fuel Processing Technology*; 85: 293 - 301.
- Kikuchi, R. (2001). Recycling of municipal solid waste for cement production: pilot scale test for transforming incineration ash of solid waste into cement clinker. *Resources, Conservation & Recycling*. 31: 137-147.
- Konar, S.K., Boocock, D.G.B., Mao, V, & Liu, J.N. (1994). Fuels and chemicals from sewage sludge: 3. Hydrocarbon liquids from the catalytic pyrolysis of sewage sludge lipids over activated alumina. *Fuel*. 73: 642 - 646.
- Manning, R., Cooper, S, and Macfadyen, J. (2003). Petcoke firing in lime recovery kilns becomes option as energy cost rise. *Pulp & Paper*, Vol. 77, No. 12.
- Mokrzycki, E, Uliasz-Bohenczyk, A, & Sarna, M. (2003). Use of Alternative Fuels in the Polish Cement Industry. *Applied Energy*, 74: 101 - 111.
- Murray, A, & Price, L. (2008). Use of Alternative Fuels in Cement Manufacture: Analysis of Fuel Characteristics and Feasibility for Use in the Chinese Cement Sector, *Ernest Orlando Lawrence Berkeley National Laboratory*, 10 March 2011, <http://ies.lbl.gov/iespubs/LBNL-525E.pdf>

- Murat, M, & Sorrentino, F. (1996). Effects of large additions of Cd, Pb, Cr, Zn to cement raw meal on composition and properties of clinker and the cement. *Cement and Concrete Research*. 26 (3): 377 – 385.
- Newman, J, & Choo, B.S. (2003). Advanced Concrete technology; Constituent Materials. Elsevier Butterworth Heinemann.
- Nielsen, P.B, & Hundebol, S. (1986). Precalcing with low-volatile solid fuels. *Zement-Kall-Gips*, No. 4: 99 – 100.
- Ogada, T, & Werther, J. (1996). Combustion characteristics of wet sludge in a fluidized bed: Release and combustion of the volatiles. *Fuel*, Vol. 75. No. 5: 617 – 626.
- Olmo, I.F., Chacon, E, & Irabien, A. (2001). Influence of lead, zinc, iron (III) and chromium (III) oxides on the setting time and strength of Portland cement. *Cement and Concrete Research*. 31: 1213 – 1219.
- Pipilikaki, P., Katsioti, M., Papageorgiou, D., Fragoulis, D, & Chaniotakis, E. (2005). Use of tyre derived fuel in clinker burning. *Cement & Concrete Composites*. 27: 843-847.
- Rubber Manufacturers Association (RMA). (2003). *U.S Scrap tyre Markets 2002*.
- Roy, G.R. (2002). Petcoke combustion characteristics. *World Cement*.
- Rumphorst, M.P, & Ringel, H.D. (1994). Pyrolysis of sewage sludge and use of pyrolysis coke. *Journal of Analytical Applied Pyrolysis*. 28: 137- 155.
- Saint-Jean, S.M., Jons, E, Lundgaard, N, & Hansen, S. (2005). Chlorellestadite in the preheater system of cement kilns as an indicator of HCl formation. *Cement and Concrete Research*, 35: 431 – 437.
- Sänger, M, Werther, J, & Ogada, T. (2001). NO_x and N₂O emission characteristics from fluidized bed combustion of semi-dried municipal sewage sludge. *Fuel*. 80: 167 – 177.
- Seboka, Y. Getahun, M.A & Haile-Meskel, Y. (2009). Biomass Energy for Cement Production: Opportunities In Ethiopia. CDM Capacity Development in Eastern and Southern Africa. United Nations Development Programme.
- Splithoff, H, & Hein, K.R.G. (1998). Effects of combustion of biomass on emissions in pulverized fuel furnaces. *Fuel Processing Technology*, 54: 189 – 205.
- Scrap Tyre Management Council (STMC) (1992). The Use of Scrap Tyres in Cement Rotary Kilns.
- Stolarek, P, & Ledakowicz, S. (2001). Thermal processing of sewage sludge by drying, pyrolysis, gasification and combustion. *Water Science and Technology*, Vol. 44, No. 5: 333-339.
- Taylor, H.F.W. (1990). *Cement Chemistry*. Academic Press, London.
- Tiggsebäumker, P, & Beckum, K.M. (1986). Investigations on combustion of solid fuels in calciners. *Zemet-Kall-Gips*, No. 4, pp. 104 – 106.
- Vesilind, P.A, & Ramsey, T.B. (1996). Effect of drying temperature on the fuel value of wastewater sludge. *Waste Management & Research*. 14, pp. 189-196.
- Wenli, D., Dam-Johansen, K, & Ostergaard, K. (1990). Widening the temperature range of thermal DeNO_x process. An experimental investigation. *Proceedings of the 23rd International Symposium on Combustion*. Pittsburg, PA: The Combustion Institute, pp. 297 – 303.
- Werther, J, & Ogada, T. (1997). Sewage sludge combustion. *Progress in Energy and Combustion Science*, 25: 55 – 116.
- Williams, P.T., Cunliffe, A.M, & Brindle, A.J. (2001). Enhanced Pyrolysis Processing of Scrap Tyres. *Journal of the Institute of Energy*; 74: 100 – 112.
- Winter, F., Prah, M.E, & Hofbauer, H. (1997). Temperature in a fuel particle burning in a fluidized bed: The effects of drying, devolatilisation and char combustion. *Combustion and Flame*, 108: 302 – 314.



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Renewable energy sources such as biodiesel, bioethanol, biomethane, biomass from wastes or hydrogen are subject of great interest in the current energy scene. These fuels contribute to the reduction of prices and dependence on fossil fuels. In addition, energy sources such as these could partially replace the use of what is considered as the major factor responsible for global warming and the main source of local environmental pollution. For these reasons they are known as alternative fuels. There is an urgent need to find and optimise the use of alternative fuels to provide a net energy gain, to be economically competitive and to be producible in large quantities without compromising food resources.

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