

SUNIL HERAT\*

## PROTECTING THE ENVIRONMENT FROM WASTE DISPOSAL: THE CEMENT KILN OPTION

Burning of wastes in cement kilns is gaining favour around the world as an important waste management option. High temperature ( $> 1500\text{ }^{\circ}\text{C}$ ), long gas residence times (6-10 secs) and high turbulence in the cement kiln ensure complete destruction of a variety of wastes. Tests have demonstrated 99.9999% destruction of these wastes. The alkaline environment inside the kiln absorbs 95-99% of hydrogen chloride formed during combustion of chlorinated wastes. Over 99% of lead metal entering the kiln is retained by process solids. The quality of cement is not affected up to a chlorine input of 0.7% of clinker production.

### 1. CEMENT KILN TECHNOLOGY

#### 1.1. RAW MATERIALS USED FOR CEMENT PRODUCTION

The principal chemical components required for the production of cement are calcium, silicon, aluminium and iron. Calcium is provided by limestone, which is usually quarried near the cement plant site. Silicon and aluminium are provided by an appropriate mixture of clay, shale or sand. Iron is provided by iron ore or steel mill scale. These raw materials contain approximately 75% of calcium carbonate, 15% of silicon dioxide, 3% of aluminium oxide, 2% of ferric oxide and 5% of other minerals.

#### 1.2. CEMENT PRODUCTION PROCESS

The production of cement usually consists of the following major steps:  
acquisition and transportation of raw materials,  
preparation of raw materials,

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pyroprocessing (high temperature reacting) of raw materials to form cement clinker,  
grinding clinker into cement.

The raw materials are selected, crushed, ground and proportioned so that the resulting mixture has the desired fineness and chemical composition for the pyroprocessing system. The pyroprocessing takes place in a cylindrical rotary kiln which is an elongated steel cylinder ranging in size up to 250 m in length and 8 m in diameter lined with refractory brick and inclined at an angle of 3–6 degrees. The kiln rotates at about 70 revolutions per hour in older generation plants and about 180 revolutions per hour in newer plants. The raw material feed is introduced at the elevated end and is moved slowly by the rotation of the kiln down towards the firing end where heat is applied with a coal, gas or oil flame.

There are three distinct thermal zones within an operating cement kiln, as described below:

- a) drying and preheating zone,
- b) calcining zone,
- c) burning zone (clinkering zone).

The material in the drying and preheating zone reaches a temperature of about 800 °C. In this zone, all water in the feed is evaporated. The preheating zone is followed by the calcining zone where carbon dioxide is driven off from the limestone material, thus forming calcium oxide. The feed temperatures in this zone reach 1000 °C. Following calcination is the burning or clinkering zone where, at a temperature of 1500 °C, the chemical reactions leading to the formation of clinker occur. The material, in a semi-liquid state at this stage, when cooled in the clinker cooler, is referred to as cement clinker. The clinker is then finely ground with addition of about 5% gypsum (calcium silicate) to give the final cement product.

During the cement manufacturing process, it is essential that the temperature in the feed material reaches 1500 °C in order to form the clinker. To achieve this clinkering temperature, combustion gas temperature in the burning zone of the kiln must generally exceed 1700 °C. In addition, combustion gas residence time in the burning zone of the kiln ranges from 2–5 seconds, depending on the size of the kiln, and the overall gas residence times during the process can reach 10 seconds.

Cement kilns operate in a countercurrent manner. The combustion gases and waste dust flow counter to the material, exiting at the elevated end of the kiln. Exhaust gases consist primarily of nitrogen, carbon dioxide, water, sulphur and nitrogen oxides together with the fine particles of the feed and clinker material. These particles are entrained in the gases flowing through the kiln and are removed by electrostatic precipitators or baghouse filters fitted at the end of kiln and returned back to the kiln as feed material or sold as a cement by-product for other industrial uses. The alkaline nature of the feed material in the kiln acts as a trap for sulphur dioxide. Thus, after passing through the pollution control devices, the combustible gases primarily contain carbon dioxide and water vapour and are discharged to the atmosphere through a stack.

## 2. TECHNOLOGY OF MANAGING WASTES IN CEMENT KILNS

The cement industry is an energy intensive as very high temperatures are required in order for the proper chemical reactions to occur in the kiln. The energy sources used by the cement industry includes coal, petroleum, coke, fuel oil and natural gas and also a wide range of materials having a calorific value such as used oils, waste tyres and organic solvents. The use of secondary fuels reduces the industry's consumption of primary fossil fuels and, therefore, contributes to the principles of energy saving and sustainable development.

### 2.1. CHARACTERISTICS OF A CEMENT KILN

The characteristics of a cement kiln that makes it an appropriate device for managing solid and hazardous wastes can be summarised as follows:

**1. High temperature and long residence times.** Combustion gas temperatures and residence times in cement kilns are much greater than those generally available in commercial incinerators. To produce the cement clinker, the material inside the kiln must reach a temperature of 1500 °C, while the combustion gas temperatures reach 1700 °C. These sustaining high combustion gas temperatures and long gas residence times (6–10 seconds) combined with intense turbulence inside the kiln ensure efficient destruction of even the most stable organic compounds. It is generally recognised that all organic compounds are adequately destroyed if exposed to a temperature of 1200 °C for a residence time of 2 seconds under oxidising conditions. The conditions in the burning zone of the cement kiln exceed these requirements by a wide margin.

**2. High thermal capacity.** The large size and amount of heated material in the cement kiln ensure that significant temperature oscillations in kiln temperature are not possible. Thus, in the case of an emergency shutdown due to operational problems, the flow of any organic waste can be halted before the temperatures fall below critical values.

**3. Alkaline environment.** The contents inside the kiln are alkaline. Therefore, virtually all of the chlorine entering the kiln and hydrogen chloride formed during the combustion of chlorinated wastes are neutralised to form calcium chloride, sodium chloride and potassium chloride, relatively non-toxic compounds. Thus, emissions of hydrogen chloride are significantly lower than emissions from commercial incinerators. Most of the sulphur oxides are similarly trapped as calcium sulphate.

**4. Minimum amount of waste generated.** The combustion of wastes in commercial incinerators generates ash which needs to be disposed of. In contrast, there is no ash equivalent in the cement production process. The only by-product of the process is cement kiln dust, which is recycled back to the kiln or recycled in other processes. Any incombustible material such as metals in the waste becomes incorporated in the cement clinker, eliminating disposal problems.

## 2.2. BENEFITS OF MANAGING WASTES IN CEMENT KILNS

The benefits associated with the management of solid and hazardous wastes in cement kilns can be summarised as follows:

**1. Energy recovery.** Burning solid and hazardous waste as supplementary fuel allows for the recovery of significant amounts of energy from these waste materials. This source of energy is one of the primary reasons for the cement industry's interest in burning solid and hazardous wastes as fuel.

**2. Conservation of non-renewable resources.** One of the most significant advantages of using solid and hazardous wastes as a supplemental fuel in the cement kiln is the conservation of non-renewable fossil fuels such as coal, gas and oil. It is possible to replace between 25–50% of the energy supplied by coal using hazardous wastes as fuel. For example, if only 25% of the energy used in the production of cement in the United States were replaced by hazardous waste, then 3.8 million tonnes of domestic coal or 14.4 million barrels of domestic crude oil could be saved each year [1].

**3. Reduction in cement production costs.** The production of cement is an energy intensive process. The energy costs generally account for about 40% of the cost of clinker production. Thus, by using the cheaper hazardous waste as a fuel, the industry can significantly reduce their manufacturing costs. The waste fuels typically have a heat value of 24 gigajoules/tonne, which is somewhat less than coal, but are available at a fraction of the cost [2].

**4. Facilities already existing.** One of the key advantages of using cement kilns is that the technology and facilities are already in place. Thus, there will be a significant reduction of capital expenditures required to site new disposal centres. A small capital investment of up to \$ 5–10 million is required to adapt a cement kiln to manage solid and hazardous wastes, whereas building a new incinerator facility could cost around \$ 50 million [3]. In addition, use of a cement kiln, as opposed to the construction of a new facility, does not result in the creation of a new source of emissions. Therefore, cement kilns provide an attractive option for the burning of large volumes of wastes.

**5. Reduction in waste transportation costs.** The use of cement kilns to manage solid and hazardous wastes reduces the amount of waste transportation and transportation costs by having many cement plants sites close to waste generators rather than one central facility.

## 2.3. TYPES OF WASTES MOST SUITABLE FOR CEMENT KILNS

Cement kilns offer excellent alternatives for the management of a wide variety of energy bearing solid and hazardous wastes. There are three main areas in the cement manufacturing process where an opportunity exists for the utilisation of such wastes as described below:

kiln burning stage,  
raw materials stage,  
clinker grinding stage.

In the kiln burning stage, most of the energy bearing solid and hazardous wastes can be managed as supplementary fuels. At present, a variety of waste fuels, both hazardous and non-hazardous, is being utilised in cement kilns. In the raw material stage, a variety of waste materials can be combined to produce the correct chemical composition for raw material feed. Finally in the cement grinding stage, gypsum can be replaced with some suitable waste materials.

#### 2.3.1. LIQUID WASTE FUELS

Paint thinners, degreasing solvents, solvent washes from ink and printing industries, chemical by-products from pharmaceutical and chemical manufacturing, waste oils and other flammable, readily pumpable waste materials can be used to prepare high quality liquid waste fuels for cement kilns [4]. Furthermore, metal cleaning fluids such as metal working and machining lubricants, coolants and cutting liquids and cleaning solvents from automotive aftermarket operations such as automobile shops, paint shops and service stations and liquid petroleum and petrochemical wastes can also be used as liquid waste fuels in the cement industry [5], [6]. Acid tar produced by several industries, which use concentrated sulphuric acid for the treatment of hydrocarbon materials, is also considered to be a useful waste fuel for the cement industry [7]. The other types of liquid waste fuels used by the cement industry include pesticides and insecticides [8] and [9], PCBs and PCB contaminated solvents and coal tars [10].

#### 2.3.2. SOLID WASTE FUELS

Municipal solid waste or its separated energetic fraction, commonly known as refuse derived fuel (RDF), has been used in cement industry since early 1970s [11]. Depending on the chlorine content of the waste, up to 30% of the total fuel consumption may be covered by RDF [12].

Waste tyres used as supplementary fuel in cement manufacture can be considered as one of most common fuel substitutes in the industry. Carbon and oxygen amount to 88% of a tyre, which accounts for its rapid combustion and relatively high heating value [13]. Tyres contain approximately 34900 kJ/kg and can be compared favourably to coal which, on the average, contains some 27900 kJ/kg. Subsequently, when substituting waste tyres for coal it is possible to reduce coal by 1.25 kg for every kg of tyres [14].

Cement kilns also offer the following advantages for the disposal of sewage sludge [15]:

- elimination of heavy metals in sewage sludge,
- making use of organic matter in sewage sludge as fuel,
- making use of inorganic matter in sewage sludge as raw materials,
- complete destruction of organic pollutants in sewage sludge.

The only reservation in using cement kilns for burning sewage sludge is mercury contamination in the sludge, which in the long term may be all emitted to atmosphere. However, the situation is the same even if the sludge is utilised in agriculture.

Another type of solid waste receiving attention by the cement industry is spent potlinings from aluminium industry. Spent potliner is a layer of carbon situated between the molten metal and refractory material inside the steel shell of an aluminium reduction cell. Generally the useful life of potliner is 3–7 years and the removal of spent potliner (SPL) is a lasting process. One of the advantages of using SPL in cement kilns is that the fluoride content of the SPL may speed up the clinkering reaction, resulting in lower operating temperatures. However, cement produced by some facilities using SPL has exhibited a relatively high alkali content due to sodium in SPL [16]. The process of incinerating SPL by fluidised bed combustion and offering the ash to cement industry is reported to be very attractive [17]. The by-product ash can lower the clinkering temperature.

A number of cement plants are testing and/or constructing pyrolysis systems to allow organically contaminated soils to be recycled for both fuel value as well as the silicon and aluminium present in most soils [5]. There is an increasing volume of soils being generated from underground storage tanks removal and industrial sites that are contaminated by petroleum products. From the accepted methods of treating the contaminated soils, thermal desorption and incineration appear to be the most suitable options, although these options are costly. The cement kiln offers an economic alternative to thermal desorption in incineration plants [18]. Furthermore, cement kilns with their large capacities are capable of handling large tonnages of soils contaminated either by organic or inorganic contaminant. However, this option has only been used to a limited extent due to public perception and industry concerns [19].

In addition to the above mentioned solid waste fuels, there are a number of other types which are presently used in the industry. These include coal wastes, low-grade lignite, charcoal fines, powdered graphite dust from electrode production, petroleum coke and battery casings [20]. Furthermore, wood chips and saw dust, rice hulls and coconut shells are also used to some extent [21].

### 2.3.3. GAS WASTE FUELS

The cement kilns are also capable of using waste gases to supplement the fuel requirements. The primary waste gas considered for fuel substitution is landfill gas. In the landfill, the organic components of the municipal solid waste decompose producing landfill gas which contains mainly methane and carbon dioxide. The methane content of this gas can be between 40–70% with the possibility of increasing up to 90% by gas separation systems. If the landfill is adjacent to the cement kiln this can be utilised easily as a fuel [12].

## 2.3.4. SOLID WASTES AS RAW MATERIAL SUBSTITUTES

One of the main growing trends to use cement kilns to properly and safely manage wastes, which is not related to fuel substitution, is the raw material substitution. By substituting original raw materials for waste materials it is possible to conserve the raw materials as well as to reduce the expensive mining operation costs. Some sources of raw material substitution that have been demonstrated to be effective in cement making include fly ash from utilities/power plants, petroleum contaminated soils, sludge waste from paper mills, mill scale from steel production and foundry sand [22]. The other types of waste materials that can be used for raw material substitution include aluminium processing residues, contaminated soils, glass and ceramic residues, lime sludges and slags [23], [24]. Roasted pyrite, a residue in the production of sulphuric acid, is also used in the raw meal to supplement iron content [25].

In addition to the solid wastes mentioned above for raw material substitution, large quantities of aqueous hazardous waste are currently being managed through deep well injection. Many of these wastes can effectively be managed in wet process cement kilns by substituting a percentage of water used for slurry making [4].

### 3. DESCRIPTION OF STUDIES CONDUCTED IN CEMENT KILNS

The waste materials used by the cement industry contain organic materials as well as various amounts of metal components. In order to determine whether the cement kilns can manage these wastes effectively without any adverse effects, specially to the environment, the fate of both organic and metal constituents must be determined. This task is achieved by conducting a study, commonly known as a test burn, in a cement kiln with various operating conditions and different types of wastes. A summary of test burns conducted in cement kilns is given by [26].

#### 3.1. FATE OF ORGANIC CONSTITUENTS IN THE WASTE

The combustion of organic compounds results in various end products depending on the original composition of the compound. If the organic compound is composed only of carbon and hydrogen, combustion produces carbon dioxide and water; in addition, if the compound is composed of chlorine then the combustion produces hydrogen chloride or chlorine as well. Further if the compound is composed of nitrogen or sulphur, combustion produces nitrogen oxides and sulphur dioxide. An organic compound is considered to be totally destroyed if the end products mentioned above are the only ones formed during the combustion process. The values of destruction and removal efficiency (DRE) reveal the degree of destruction of organic compounds.

DRE test results reported to date indicate that cement kilns, when properly operated, can achieve DREs similar to, in some cases better than, those achieved by well designed and well operated commercial waste incinerators burning hazardous wastes. Four nines (99.99%) removal was reached in most of the cases even for the most difficult to incinerate organic substances and some test burns even achieved DREs approaching six nines (99.9999%).

### 3.2. EMISSIONS OF PARTICULATE MATTER

The effect of waste combustion on particulate matter emissions has been of interest because the earlier cement kiln test indicated that burning chlorinated wastes increased particulate emissions. The kilns equipped with electrostatic precipitators (ESPs) encountered increased particulate emissions when high amounts of chlorine was fed and especially if ESP hopper dust was recirculated to the kiln. Recirculation allows the chloride content in the dust to build up to much higher levels and eventually the resistivity of dust changes such that the ESP will cease to function properly. However, the particulate emissions from chlorinated waste combustion can be controlled by properly operating the control device and limiting the chloride loading. Adjustments may be required to optimise the ESP performance to compensate for the change in dust's resistivity [27]. These adjustments have resulted in reduced particulate emissions in most of the recent test burns. However, the kilns equipped with baghouse type dust control are not affected by the chlorine contents in the waste. The collection efficiencies were found to be stable for a wide range of chlorine feed rates.

### 3.3. EMISSIONS AND EFFECTS OF CHLORINE

When the chlorinated wastes are incinerated in a cement kiln, the temperatures in the kiln favour the complete conversion of chlorine in the waste to hydrogen chloride (HCl), which is absorbed by the calcium, potassium and sodium oxides in the kiln's solids and converted to their respective chlorides. These chlorides are vapourised at the hot end of the kiln and begin to condense on cooler surfaces or in the gas when they travel down the length of the kiln. The condensed chloride particles, which are entrained in the gases, are finally removed by the dust collection system. It is a routine practice to recycle a major portion of this collected dust back to the kiln effecting the dust particles to pass thorough the same cycle again. This is referred to as the "chloride cycle". The portion of dust, which is not recycled, is discarded. Thus by increasing the amount of waste dust, the chloride loading on the gas cleaning devices can be effectively decreased. Therefore, disposal of a portion of the waste dust is a common practice adopted by kiln operators and several kilns burning chlorinated wastes increase their dust disposal rates to control the chloride cycle.



In most of the test burns, burning of chlorinated wastes generally increased HCl emissions rates. However, up to 95–99% of chlorine entering the kiln was retained by the process solids (clinker or dust), thus reducing any risk of HCl emissions to the atmosphere. The test results also indicated that high HCl removal efficiencies can be obtained by increasing the waste discard rates and optimising the chloride cycle. It was also revealed that the operation of the kiln showed no effects up to a chlorine input of 0.7% relative to clinker.

### 3.4. EMISSIONS OF METALS

Several studies in cement kilns have attempted to study the fate and distribution of metals found in the waste fuels. Although a metal compound is changed during the combustion process, a metal is not destroyed. Therefore, any metal present in the waste fuel, fossil fuel or raw feed will be present in either the kiln stack emissions, the cement kiln dust (CKD) or the clinker. Various test results have suggested that the cement kilns have a large potential for retaining metal elements entering with waste fuel. The tests have reported that over 99% of the metals in the waste fuel are retained in the process solids without any adverse effects to cement quality. When chlorinated wastes are burnt, studies have found that metals such as lead and cadmium tend to appear more in the waste dust. It is also important to note that lead emissions during all the tests were lower than 10 mg/s which is approximately comparable to the emission of lead from automobiles burning leaded fuel.

## 4. CONCLUSIONS

Test burns conducted to date demonstrate that properly operated cement kilns can achieve DREs equal to or better than DREs achieved by well designed and operated commercial hazardous waste incinerators. DREs exceeding 99.99% and reaching up to 99.9999% were reached in most of the test burns even for the most difficult to incinerate organic substances such as PCBs.

The test results for particulate matter indicate that particulate emissions from chlorinated waste combustion can be controlled by properly operating control devices and limiting the chloride loading. The kilns equipped with ESPs encountered increased particulate emissions when high amounts of chlorine were fed into the kiln and specially if ESP hopper dust was recirculated to kiln. It is possible to reduce the particulate emissions in these cases by discarding a portion of ESP hopper dust and also by adjusting the ESP to compensate for the change in dust's resistivity due to addition of chlorides. Apparently, the kilns equipped with baghouse type dust control are not affected by the chlorine content of the waste.

Burning chlorinated wastes generally increases HCl emissions. However, test burns indicate that up to 95–99% of chlorine entering the kiln is retained by the process solids (i.e. cement clinker and cement kiln dust) reducing any risk of HCl emissions to the atmosphere. As most of the additional chlorides is removed with waste dust, high HCl removal efficiencies can be obtained by increasing the waste dust discard rate and optimising the chloride cycle. Test results also indicate that chlorine can be added to the kiln up to 0.7% of clinker weight without causing any upsets to the kiln operation or cement quality.

Test results indicate that cement kilns have a large potential for retaining metals such as lead entering with the waste fuel. This is a definite advantage considering the fact that most hazardous waste fuels contain high concentration of lead. Tests indicate that over 99% of the lead in the waste fuel is retained in the process solids. Although the distribution of lead within the process solids is not clearly understood, it appears that more of the lead is removed by the waste dust.

Burning of solid and industrial wastes in cement kilns would benefit both the public and the cement industry. Public would benefit as society's solid and industrial wastes would be destroyed in an environmentally safe manner. Cement industry would benefit from utilising the fuel value of these waste materials.

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#### OCHRONA ŚRODOWISKA PRZED ODPADAMI – SPALANIE W PIECU CEMENTOWYM

Spalanie odpadów w piecach cementowych staje się coraz popularniejsze jako jedna z opcji gospodarki odpadami. Wysoka temperatura ( $> 1500\text{ }^{\circ}\text{C}$ ), długi średni czas przebywania w reaktorze (6–10 s) i duża turbulencja w tego typu piecach zapewniają całkowity rozpad wielu odpadów. Doświadczenia wykazały 99,9999% rozpad tych odpadów. Zasadowe środowisko pieców absorbuje 95–99% chlorowodoru, który powstaje podczas spalania chlorowanych odpadów. Ponad 99% ołowiu wprowadzonego do pieca zostaje zatrzymane przez powstające odpady stałe. Jakość cementu pozostaje stała aż do dawki chloru wynoszącej 0,7%.

