

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

The following relevant theories, concepts and data are provided in this literature review:

- 2.1 The cement manufacturing process
- 2.2 The chemical compositions of cement
- 2.3 The hydration of cement
- 2.4 Waste management
- 2.5 Chromium, Nickel, Zinc, and Lead
- 2.6 The effects of heavy metals in Portland cement
- 2.7 Leaching tests

2.1 The cement manufacturing process

Cement manufacturing consists of raw meal grinding, blending, pre-calcining, clinker burning, and cement grinding. Figure 2.1 illustrates the cement production process. The main chemical components of cement are calcium, silica, alumina, and iron. Calcium is derived from limestone, alumina, iron, white silica, chalk from the sand, clays, and iron ore. Other materials may include shells, shale, and wastes which can be used as alternative fuels and raw materials (AFR). All of the components are broken and milled into a raw meal. This raw meal is blended and is then heated in the pre-heating system to start the dissociation of carbonate to calcium oxide and carbon dioxide. A secondary fuel is fed into the preheating system to keep the temperature sufficiently high. The meal then continues to the kiln for heating that causes a reaction between calcium oxide and other elements to form calcium silicates and aluminates at a high temperature ranging from 1,450 °C to 1,600 °C. A primary fuel is used to keep the temperature high enough in the burning zone for the chemical reactions to take place. As the raw meal moves down the kiln, it progresses through

four stages of transformation. Initially, any free water in the powder is lost through evaporation. Next, decomposition occurs from the loss of bound water and carbon oxide; it is called calcinations. The third stage is called clinkering. During this stage, the calcium silicates are formed. The final stage is the cooling stage. The reaction products leave the kiln as marble-sized pieces called clinkers.

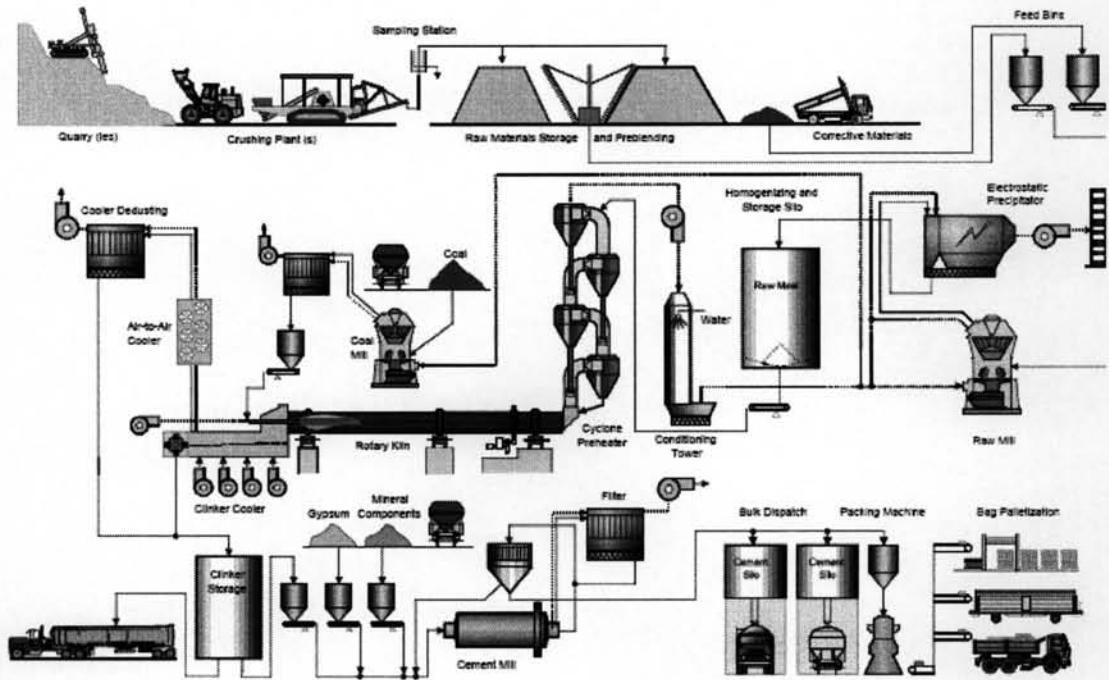


Figure 2.1 Cement Production Process (Holcim, 2006)

2.2 The chemical compositions of cement

The chemical reactions that occur in the kiln provide a basic understanding of cement, how and why it behaves as it does. The temperature is increased when going from the meal feed to the rotary kiln. The most important oxides that participate in the reactions are CaO , SiO_2 , Al_2O_3 and Fe_2O_3 . The four compounds are regarded as the major constituents of cement; they are listed in Table 2.1 together with their abbreviated symbols. From this table, it can be noted that the quantities do not add up to a total of 100%; consequently, the missing percentages are accounted for in the impurities. Each oxide formula is abbreviated with a single capital letter, with the number of the oxide formula in the compound designated by a subscript placed after

the letter. The shortened notations are $\text{CaO} = \text{C}$; $\text{SiO}_2 = \text{S}$; $\text{Al}_2\text{O}_3 = \text{A}$ and $\text{Fe}_2\text{O}_3 = \text{F}$. Likewise, H_2O in hydrated cement is denoted by H (Taylor, 1992; Neville and Brooks, 1994; Neville, 2003 and Mindess et al, 2003). These chemicals combine to form many chemical molecules. Important data on these molecules is summarized as follows:

1. Tricalcium silicate (C_3S) – Alite

C_3S makes up 50-60 percent of Portland cement. It is formed at a high temperature above $1,250^\circ\text{C}$ by the reaction of C_2S and C, which can be metastably obtained by the rapid cooling of the mixture. The other chemicals that highly influence the formation of C_3S and its polymorphs such as high SO_3 can retard the alite formation. C_3S is usually slow in the pseudohexagonal unit cell and can be identified in the clinker. A stabilization of polymorphs can be obtained by the incorporation of foreign ions in the alite-lattice. According to foreign ions and the stabilization of C_2S , only small amounts of alkalies are incorporated in C_3S which is more than what is in C_2S . The crystal structure of C_3S is composed of SiO_4 tetrahedrals that are linked with the calcium ions. Calcium is coordinated by eight oxygens.

2. Dicalcium silicate (C_2S) – Belite

C_2S makes up 10-40 percent of Portland cement. It can vary in range during transformation in temperatures from $\gamma\text{-C}_2\text{S}$ and $\beta\text{-C}_2\text{S}$. Belite can incorporate a large amount of foreign ions, more so than alite can. It can occur from many sources. For example, primary belite is formed by reactions of lime and silicon sources. Secondary belite is formed by the decomposition reaction of alite according to the changing of C_3S to C_2S and C, forming small crystals on the rims of the alite crystals. Finally, tertiary belite results from the recrystallization of the interstitial phase coming from the decomposition and decreased solution of SiO_2 in the C_3S phase.

3. Tricalcium aluminate (C_3A)

C_3A is the most abundant Al-containing phase in Portland cement. According to the Ca/Al ratio, the foreign ions can be replaced in the C_3A system. The C_3A

crystal structure contains the $(\text{AlO}_4)^{5-}$ - tetrahedral linked to the $(\text{Al}_6\text{O}_8)^{18-}$ ring which are connected by the Ca^{+2} -ions. The foreign ions take the place of the Ca and the second is located in the centre of the $(\text{Al}_6\text{O}_8)^{18-}$ ring. The solid solution of C_3A can transform into tetragonal polymorphs at high temperatures.

4. Tetracalcium aluminoferrite (C_4AF)

Iron is commonly fixed under oxidizing conditions in calcium aluminum ferrite. The composite of the ferrite phase can be explained by a limited solution between C_2F and $\text{C}_6\text{A}_2\text{F}$, whereas, the crystal structure of C_4AF is contained in the layers of the $(\text{Al,Fe})\text{-O}_6$ -octahedral and the $(\text{Al,Fe})\text{O}_4$ -tetrahedra is linked along the joint edges. It can be called "Brownmillerite."

Table 2.1 The main compounds found in ordinary Portland cement

Name of compound	Oxide composition	Abbreviation	Weight percent
Tricalcium silicate	$3\text{CaO}\cdot\text{SiO}_2$	C_3S	55
Dicalcium silicate	$2\text{CaO}\cdot\text{SiO}_2$	C_2S	18
Tricalcium aluminate	$3\text{CaO}\cdot\text{Al}_2\text{O}_3$	C_3A	10
Tetracalcium aluminoferrite	$4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$	C_4AF	8
Calcium sulfate dehydrate	$\text{CaSO}_4\cdot 2\text{H}_2\text{O}$	CSH_2	6

Source: Mindess, Young, and Darwin, 2003

In addition to the main compounds listed in Table 2.1, there are also minor compounds such as MgO , TiO_2 , Mn_2O_3 , K_2O , and Na_2O . A general idea of the composition of cement can be obtained from Table 2.2, which gives the oxide composition limits of Portland cements (Taylor, 1992; Neville and Brooks, 1994; Neville, 2003 and Mindess et al., 2003).

When inorganic or organic waste is to be used as cement raw mix replacement, several previous studies have pointed out that the chemical composition of the raw mix is important. Therefore, the Bogue equations (Equations from 2.1 to 2.4) are usually employed to describe the chemical composition of the raw mix as well as the mineral composition, and the Modulus equations of the obtained clinker are typically applied to explain the composition parameters of the modern cement

clinker. A set of compositional parameters in cement chemistry, listed as follows (Equations from 2.5 to 2.8), are controlled at a silica ratio value (SR) of around 2.0 to 3.0, an alumina ratio (AR) value of around 1.0 to 4.0, a lime saturation factor (LSF) value of around 0.92 to 0.98, and a hydration modulus (HM) value of around 2.1 to 2.4. The clinker composition is estimated using the ASTM C150 and checked by the Bogue and Modulus equations.

Bogue equations

$$C_3S = 4.071CaO - 7.60SiO_2 - 4.479 Al_2O_3 - 2.859 Fe_2O_3 \quad (2.1)$$

$$C_2S = 2.867SiO_2 - 0.7544C_3S \quad (2.2)$$

$$C_3A = 2.65Al_2O_3 - 1.692Fe_2O_3 \quad (2.3)$$

$$C_4AF = 3.043Fe_2O_3 \quad (2.4)$$

Modulus equations

$$\text{Lime saturation factor (LSF)} = CaO / (2.8SiO_2 + 1.2Al_2O_3 + 0.65Fe_2O_3) \quad (2.5)$$

$$\text{Silica ratio (SR)} = SiO_2 / (Al_2O_3 + Fe_2O_3) \quad (2.6)$$

$$\text{Alumina-iron ratio (AR)} = Al_2O_3 / Fe_2O_3 \quad (2.7)$$

$$\text{Hydration modulus (HM)} = CaO / (SiO_2 + Al_2O_3 + Fe_2O_3) \quad (2.8)$$

The silica ratio represents the combustibility of a raw mix. The combustibility impacts how much energy is put into the system. As the ratio of silica to alumina plus iron increases, it becomes harder to burn and harder to combine the raw materials into the necessary phases. As the ratio decreases, the tendency for fluxing (the ability of the solid materials to become liquid) increases, and the combining reactions become easier. Another consideration is that silica presented as quartz is generally more difficult to combine than silica presented as silicates. The alumina-to-iron ratio is important because it controls the potential C_3A/C_4AF ratio in the finished cement, which is important because of sulfate resistance, heat generation, and the admixture compatibility issue. The lime saturation factor controls the potential C_3S to C_2S ratio in the finished cement. C_3S governs the early age strength development while C_2S governs the later age strength.

Table 2.2 Approximate composition of Portland cement

Element	Content (percent)
CaO	60-67
SiO ₂	17-25
Al ₂ O ₃	3.0-8.0
Fe ₂ O ₃	0.5-6.0
MgO	0.1-4.0
Alkalis (Na ₂ O and K ₂ O)	0.2-1.3
SO ₃	1.0-3.0

Source: Neville and Brooks, 1994

2.3 The hydration of cement

When cement is mixed with water its chemical compound constituents provide a series of chemical reactions that cause it to harden. These chemical reactions all rely on the addition of water to their basic chemical compounds. This chemical reaction with water is called "hydration." Reactions with water are designated as hydration and the new solids formed are collectively referred to as hydration products. In the presence of water, the silicates and aluminates of Portland cement form products of hydration of hydrates, which in time produce a firm and hard mass--the hardened cement paste. Each one of these reactions occurs at a different time and rate. The hydration characteristics of the cement compounds are summarized in Table 2.3. Thus, the results of these reactions determine how cement hardens and gains strength. As stated earlier, the two calcium silicates (C₃S and C₂S) are the main cementitious compounds in cement, the former hydrating is much more rapid than the latter. The product of hydration of C₃S is the microcrystalline hydrate C₃S₂H₃ with some lime separating out as crystalline Ca(OH)₂·C₂S, which behaves similarly but clearly requires less time chemistry for hydration. It is ascribed that the interaction between hydrating compounds affects the mix in Portland cement. The rate of hydration is in the order of C₃A>C₃S>C₄AF>C₂S and the approximate hydration reactions are shown in Equations 2.9, 2.10, and 2.11.

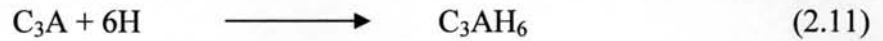
1. Tricalcium silicate (C_3S). Hydrates and hardens rapidly and is largely responsible for the initial setting and early strength. Cements with higher percentages of C_3S will exhibit higher early strength.



2. Dicalcium silicate (C_2S). Hydrates and hardens slowly and is largely responsible for strength increases which occur beyond one week.



3. Tricalcium aluminate (C_3A). Hydrates and hardens the quickest. Liberates a large amount of heat almost immediately and contributes somewhat to early strength. Gypsum is added to the cement to retard C_3A hydration. Without gypsum, C_3A hydration would cause the cement to set almost immediately after adding water.



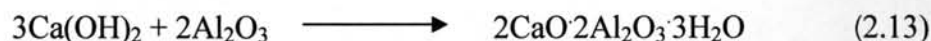
4. Tetracalcium aluminoferrite (C_4AF). Hydrates rapidly but contributes very little to strength. Most of the cement color effects are due to C_4AF .

Table 2.3 Hydration characteristics of the cement compounds

Compounds	Reaction rate	Amount of heat liberated	Contribution to cement	
			Strength	Heat liberation
C_3S	moderate	moderate	high	high
C_2S	slow	slow	low (initially), high (later)	low
C_3A+CSH_2	fast	very high	low	very high
$C_4AF+CSH_2$	moderate	moderate	low	moderate

Source: Mindess et al., 2003

The second step continuing from the hydration reaction is the pozzolanic reaction. In this step, calcium hydroxide ($Ca(OH)_2$) developed from the hydration reaction, reacts with silica (SiO_2) and alumina (Al_2O_3) from the pozzolanic material. The chemical equations (Taylor, 1990) are provided as follows:



C-S-H is the largest component of cement paste (50-70%), and it is the most important component in the hydration process. The amount of C-S-H coating on a C_3S grain is very small during hydration and increases rapidly during the acceleration period. The spines of C-S-H radiate outward from each grain with the bulk of the material below the spines. As the C-S-H hydrates further, the coating thickens, forcing the outward spines of adjacent particles to interlock to form solid bonds. As hydration continues, the intermeshed spines contribute to the increase in the undercoating of C-S-H growth. The resulting effect is a bonding of the cement grains together by the C-S-H coating.

CH constitutes 20-25% of the cement volume. In the acceleration stage, CH grows in the capillary pore space. CH will only grow in free space; on encountering another CH crystal, it will grow in another direction; also it will grow completely around a hydrating cement grain. The latter effect gives the CH a larger apparent volume in cement pastes than it would have as a pure crystal.

Calcium sulfoaluminate is a small component of cement paste (10-15%), having little effect on the microstructure. Young, spiny ettringite crystals might convert to flat monosulfoaluminate crystals.

2.4 Waste management

Waste management involves the correct and efficient handling of industrial waste. Many methods are available, such as stabilization, neutralization, solidification, and reutilization, which are methods that can decrease the quantity of industrial waste for treatment. A viable waste management option is co-processing in the cement industry. Waste shall be co-processed only if there is no better financial and ecological way of waste avoidance or recycling. The integration of co-processing

into the waste hierarchy is shown in Figure 2.2. The waste management hierarchy is defined as follows:

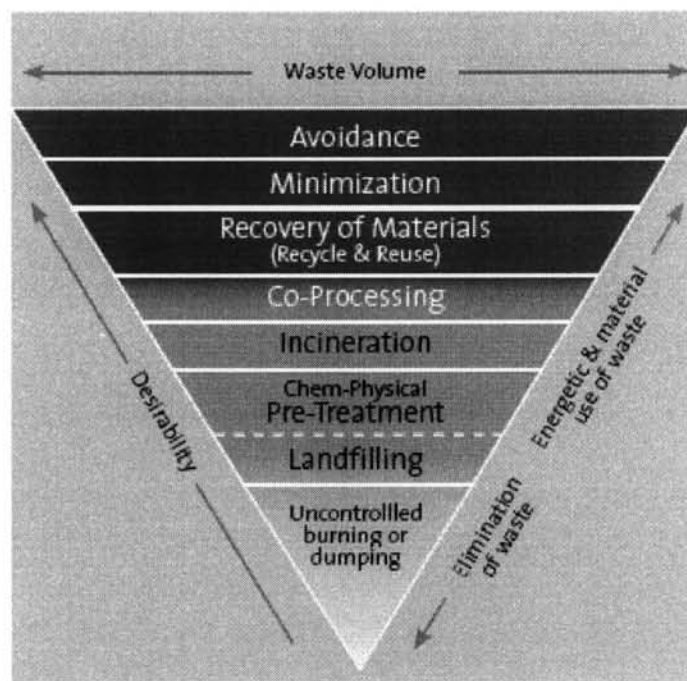


Figure 2.2 The waste management hierarchy (Holcim, 2006)

- Avoidance or prevention of waste is the ideal solution. This can be achieved only through a strict product policy that ensures that certain materials do not appear as residues at all.

- Recovery of waste material includes means of direct recycling and reuse of primary materials (e.g. metal to metal or paper to paper). It also includes other technologies like composting or anaerobic digestion.

- Co-processing involves the recovery of energy and materials from waste to be used as a substitute for fossil energy and virgin raw materials. The use of waste or by-products from one industrial process or municipal solid waste can be used as fuel or raw material substitutes in other processes; thus, they are referred to as alternative fuels and raw materials or AFR (Figure 2.3). Industries where co-processing is applicable include: cement manufacturing, thermo power plants, the steel industry,

lime production, ceramic, brick, glass, the chemical industry and the petroleum industry.

Principles of Industrial Ecology

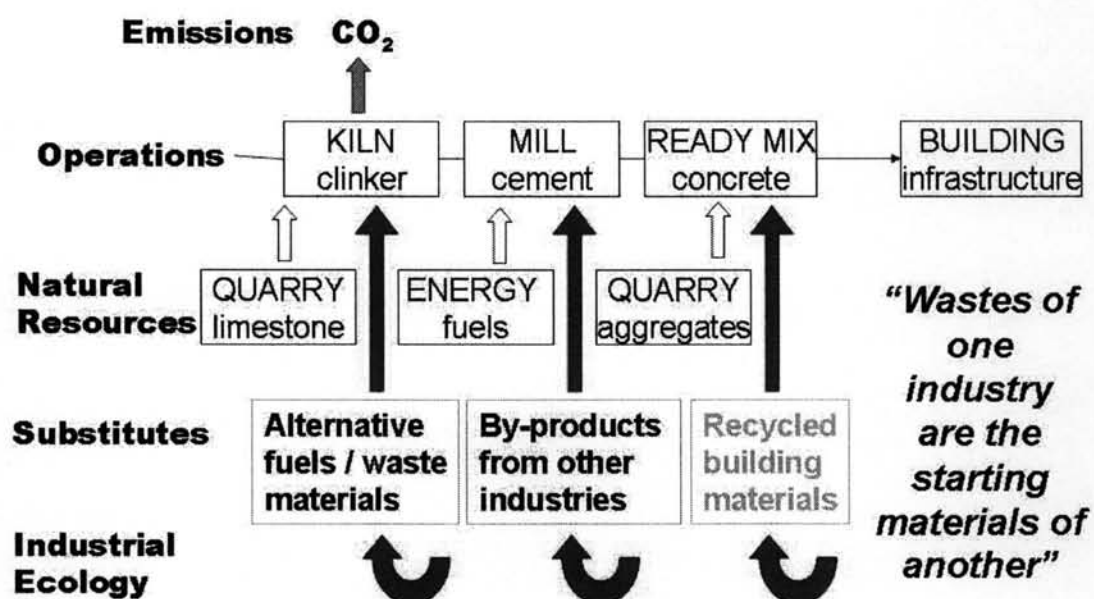


Figure 2.3 How waste can be used as alternative fuels in a cement kiln (Holcim, 2006)

- Incineration is primarily a disposal technology to reduce waste volumes, to reduce the potential negative impact of the waste material and to a certain extent recover the energy.

- Chemical-physical pre-treatment is a procedure to stabilize waste materials before final disposal.

- Controlled landfills are a common method for the final disposal of non-recyclable waste.

- Uncontrolled burning and dumping, often accompanied by open burning, is still the most common method of waste disposal in developing countries, where these pose a major threat to natural resources and human health. This form of waste disposal should be avoided.

The waste hierarchy has to be respected for any waste disposal option, including co-processing. Co-processing should be considered as a treatment alternative within an integrated waste management concept. Whenever possible, waste should be avoided or used for energy and material recovery, as seen from an ecological and economical point of view, this is the most appropriate solution for any country. However, it may take time to fully implement this approach in developing countries.

2.4.1 CO₂ challenges for the cement industry

The world-wide cement industry produces some 1.5 Gt of cement and contributes therefore roughly 1.2 Gt CO₂ per year (MT CO₂/MT Cement 0.81) to the total manmade CO₂-production of around 25 Gt, which corresponds to about 5 %. It is doubtless that the cement industry is a big fossil energy consumer and - due to the mandatory decarbonation process - an even over proportional CO₂ emitter.

Co-processing Reduces Global Warming

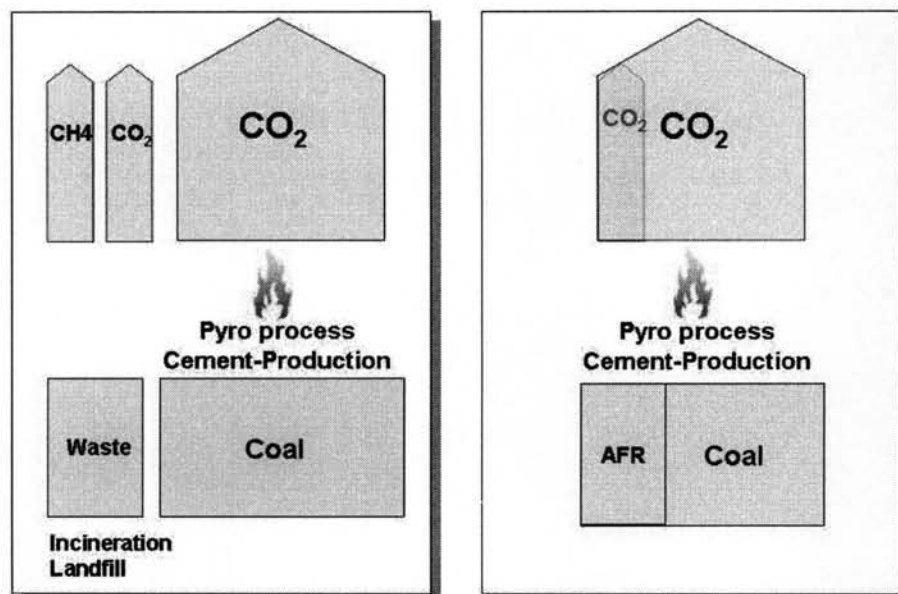


Figure 2.4 Waste/AFR contributes to global CO₂ emission reduction (Holcim, 2006)

Co-processing is a sustainable and efficient means of managing waste. By incorporating the energy potential and mineral components of wastes into the manufacture of an essential Portland cement, the wastes are totally destroyed. In this process, fossil fuels and raw materials are preserved and the waste materials are diverted from landfills or incinerators, less desirable disposal options for waste. Co-processing can reduce CO₂/Greenhouse gases, helping to reduce their impact on global warming (Figure 2.4).

- ◆ Biomass waste fuels can be considered close to 100 % CO₂/Greenhouse gas neutral, (i.e. sewage sludge, waste timber, dry agriculture residues).
- ◆ Fossil fuel based waste/alternative fuels (i.e. waste oils, solvents, plastic, rubber, etc.) are greenhouse gas neutral to the degree that the cement process is more fuel efficient than a competing disposal process (such as, incinerators, power stations, blast furnace kilns, etc.).
- ◆ Compared to landfills, the greenhouse gas efficiency of such alternative fuels is around 50 %.

2.4.2 The alternative fuels and raw materials (AFR) policy

The cement making process is energy and material intensive. Traditionally, fossil fuels and natural raw materials have been used to make the clinker, the main ingredient in cement. To operate its business in a more environmentally, economically and socially beneficial way, this cement plant is increasingly using non-traditional or “Alternative Fuels and Raw Materials” (AFR) for clinker production. AFR allows for the recovery of both energy and material from selected wastes, thus conserving non-renewable natural resources.

To achieve these benefits in a responsible way, this cement plant must follow the nine principles of the AFR policy (Holcim, 2006). Its purpose is to govern the cement industry’s behavior when using AFR. It also covers facilities at which selected waste streams are pre-treated for utilization in their kilns (Figure 2.5). The nine principles are as follows:

Principle 1 Act as a partner to society by offering waste management solutions

- a) Take the initiative, when appropriate, to cooperate with authorities to develop environmentally, economically and socially sound waste management solutions.
- b) When using wastes that do not contribute either energy or material, their disposal in our cement kilns must be the best locally available solution.
- c) Unabridged when considering international shipments of waste.

Principle 2 Keep the environment safe

- a) Contribute to the preservation of natural resources, or to the reduction of the global environmental impact.
- b) Ensure that the effluents do not degrade the water quality.
- c) Storage and handling of AFR will be done in a manner to avoid spillage and leaching and to limit fugitive emissions, odor and noise to reasonably acceptable levels.

Principle 3 Add value to our core business

- a) Use AFR to help realize our commitment to sustainable development.
- b) Use of AFR should either reduce costs through the substitution of more expensive fossil fuels and raw materials or generate revenues by providing a service to our customers.
- c) This policy will govern AFR-related business decisions.

Principle 4 Ensure occupational health & safety

- a) The employer will provide appropriate precautionary measures such as data sheets, equipment, training, controls, procedures, health monitoring, facility design, and emergency response planning to protect the health & safety of the employees.
- b) The employees have the duty to use the measures provided by the employer and are responsible for following their rules.
- c) The employer will provide relevant safety information to our sub-contractors and visitors to our premises.

Principle 5 Do not use the listed "banned wastes"

1. Electronic waste

E-waste is composed of computers and accessories, entertainment electronics, communication electronics, toys but also white goods such as kitchen devices or medical apparatus. These wastes contain on the one hand, substances harmful to health, but also to the environment, such as Cl, Br, P, Cd, Ni, Hg, and PCB.

2. Entire batteries

Batteries can be classified as automotive batteries, industrial batteries and portable (consumer) batteries. Automotive batteries are mainly lead-acid batteries; industrial batteries comprise both lead-acid batteries and nickel-cadmium batteries. The portable battery consists of general purpose batteries (mainly zinc, carbon and alkaline manganese batteries), button cells (mainly mercury, zinc air, silver oxide, manganese oxide, and lithium batteries), and rechargeable batteries (mainly nickel-cadmium, nickel-metal hydride, lithium ion, and sealed lead-acid batteries). Most of these substances are harmful to both health and the environment. Co-processing of batteries would lead to an undesirable concentration of pollutants in the cement and the air emissions.

3. Infectious and biologically active medical waste

Infectious, biologically active hospital wastes are generated in the human medical care, in veterinary care and in the research. Examples include blood transfusion bags, blood contaminated bandages, dialyzed filters, injection needles, and also parts of the body and organs. Biologically active hospital wastes include pharmaceuticals. The disposal requires special hygienic and work safety requirements on handling, packaging, and transportation. The conditions in the cement kiln would be appropriate to treat infectious and biologically active hospital wastes, but require special precautions on occupational health and safety in supply chain of this type of waste. As the problem persists and might become even more severe with a wider spread of infectious diseases (such as AIDS, SARS, Bird flu, Ebola etc.)

4. Mineral acids and corrosives

Mineral acids are derived from inorganic minerals. Examples are hydrochloric acid, nitric acid, phosphoric acid and sulphuric acid. The inorganic minerals such as S and Cl that are the main components of the acid have a negative impact on the clinker process and product quality and may lead to unwanted waste gas emissions. Acid may corrode and damage the production facilities.

5. Explosives

Explosives are any chemical compounds, mixtures or devices capable of producing an explosive-pyrotechnic effect, with substantial instantaneous release of heat and gas. A reason to exclude them from co-processing is for occupational safety due to the risk of uncontrolled explosions during pre-processing activities such as transportation, handling, shredding etc. Explosive reactions in the cement kiln would have a negative impact on process stability.

6. Asbestos

Asbestos is a name given to a group of minerals that occur naturally as masses of long silky fibers. Asbestos is widely used in construction and industry. Asbestos fibers are woven together or incorporated within other materials to create many products. People whose work brings them into contact with asbestos may inhale fibers. They are deposited and retained in the airways and tissues of the lungs and can cause cancer.

7. Radioactive waste

Radioactive waste is normally excluded from 'classical' waste management, and therefore specific regulations have to be applied according to international agreements. This means that radioactive waste can't be treated under the regulations of municipal and household waste and special licensing for its treatment is required. The procedure is normally stipulated in national nuclear laws. Cement plants are not suited to handle radioactive waste.

8. Unsorted municipal waste

Municipal waste is a heterogeneous material and consists in developing countries mainly of native organic, inert, and post-consumer fractions. Valuable recycling goods such as cardboard, plastic, glass or metal are often sorted out according to the information of a formal section. However, from an ecological, technical, and financial point of view, the co-processing of unsorted municipal waste is not recommended. Mixed municipal waste must be sorted in order to obtain defined waste streams from a known quality. For specified materials, co-processing should be regarded as an integrated part of municipal solid waste management.

Principle 6 Guarantee the quality of cement products

- a) Ensure that product quality remains within specifications.
- b) Apply the same quality assurance, control methods and standards as for products made without the use of AFR.

Waste/AFR Specification

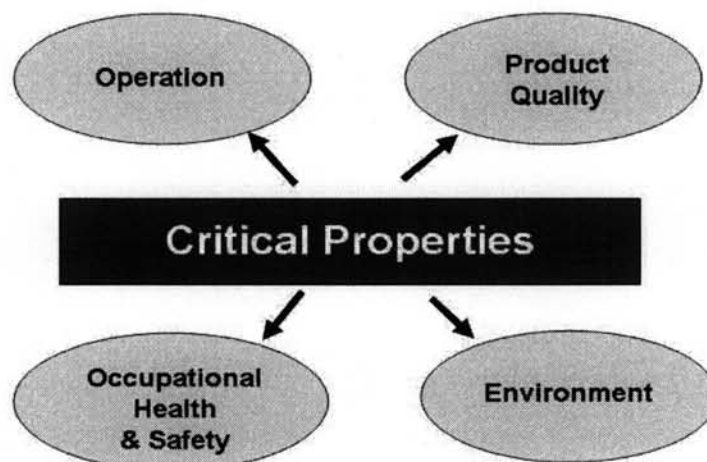


Figure 2.5 Waste/AFR Specification (Holcim, 2006).

Principle 7 Comply with the relevant regulations and promote the best practices

- a) Obtain permits and comply with their conditions.
- b) Promote the use of the best practices when local regulations do not exist.
- c) Assess health & safety and environmental risks prior to using AFR, even if it is not requested by the local regulations.

Principle 8 Monitor and control the inputs, process, products and emissions

- a) Accept wastes from parties whose practices are consistent with this policy.
- b) Understand the physical and chemical properties and health & safety aspects of the wastes accepted. Analyze the waste when necessary for this purpose.
- c) Control volatile and leachable heavy metals.
- d) Ensure the traceability of wastes from their reception up to the final treatment.
- e) AFR stocks will be limited to cover operational requirements.
- f) Measure and monitor the emissions according to the corporate standard: "Emission Monitoring & Reporting".

Principle 9 Communicate transparently

- a) Communicate in a transparent way.
- b) The message will be consistent to the different stakeholders and relevant to our relationships with them.
- c) Engage with and listen to the stakeholders, from the beginning, when developing AFR initiatives.
- d) Report on performance and progress on a regular basis.

2.4.3 Waste co-processing in a cement kiln

Co-processing refers to the use of waste materials in industrial processes, such as cement, lime, or steel production by power stations or any other large combustion plant. In a few cases this process is also called co-incineration, but co-processing is a preferred term as the main objective is not the final disposal of waste, but rather the substitution of primary fuel and raw material by waste. It is a recovery of energy and material from refuse. Different types of wastes have been successfully co-processed as alternative fuel and raw materials (AFR) in cement kilns

in Europe, Japan, the USA, Canada and Australia since the beginning of the 1970s. The use of AFR can decrease the environmental impacts of wastes, ensure safe disposal of hazardous wastes, decrease greenhouse gas emissions, decrease waste handling costs, and save money in the cement industry.

Developing and transitional countries are generating increasing amounts of waste, which is commonly buried or burned, channelled into sewers, or illegally dumped into poorly managed landfills. The uncontrolled disposal of waste is a problem in itself, but becomes particularly serious where hazardous industrial waste is involved. In developing countries, solid waste is generally managed without appropriate infrastructure for safe disposal, appropriate laws and/or enforcement and awareness of the damage caused and the high cost of remediation. As a consequence, soil, water, and air are contaminated, causing living conditions to deteriorate, threatening public health. The cement industry offers an alternative form of waste treatment known as co-processing: alternative fuels and raw materials are used in cement kilns in place of fossil fuels and primary raw materials. Alternative fuels are always fed into high-temperature combustion zones of the kiln system (shown in figure 2.6) during the main firing or secondary firing.

Waste co-processing in cement manufacturing with special high temperatures and for long time periods are suitable conditions for the burning of industrial waste. Ash from burning is mixed with the clinker. In co-processing, organic compounds are destroyed completely. Metals cannot burn or ignite, which means they may be found in some part of the cement kiln dust or combined with the cement clinker, as well as combined with the final production of cement (Trezza and Scian, 2000). During co-processing, waste materials are fed at a certain feed rate or amount into a rotary kiln. Since the wastes have a high heating value, the generated heat or energy adds up to the required temperature in the kiln. Hence, the amount of coal used to maintain the temperature in the kiln is greatly reduced. This results in significant savings in coal consumption. Materials like silica, aluminum, calcium, iron, and magnesium are present in the industrial wastes and these are calcined during co-processing and formed into the clinker. The clinker can now be used as a raw material and added to other components to produce cement. To insure the safety of

using such waste in cement manufacturing, the use of waste must be carried out under controlled conditions, and the gas emissions must comply with environmental laws and regulations.

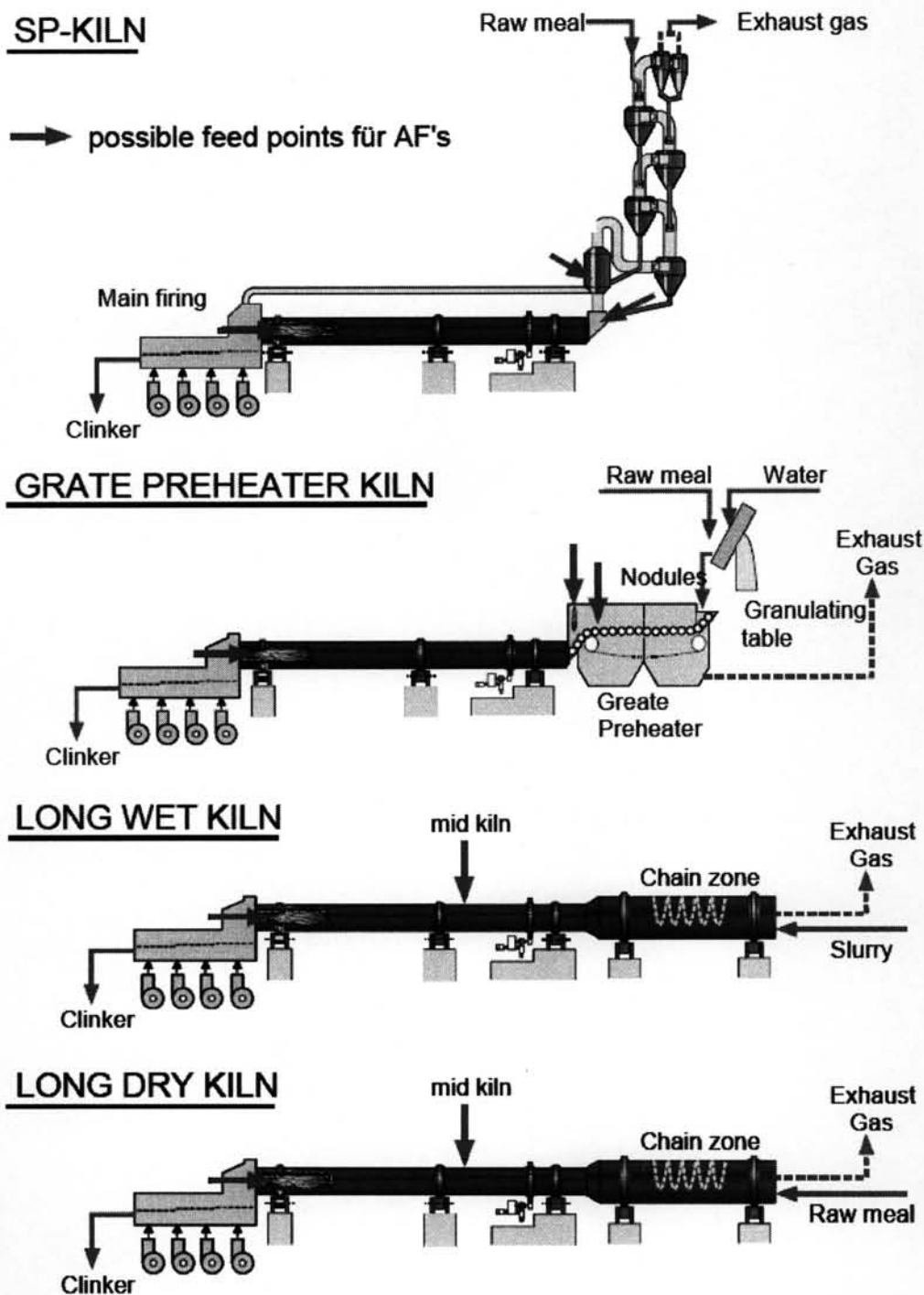


Figure 2.6 Possible feed points of various kiln type (Holcim, 2006)

2.4.4 The alternative fuels and raw materials (AFR) utilization in the cement industry

Typically, a cement kiln is fired with coal, petroleum coke, oil or natural gas. However, some cement production facilities have used hazardous waste to replace a portion of their conventional fuel and raw materials. Burning hazardous waste in the cement production process does not only dispose of hazardous waste, but it also recovers energy from the waste. Hazardous waste does not have an energy value and its composition is similar to the raw material of cement such as SiO_2 , Al_2O_3 , and Fe_2O_3 . For waste to serve as a suitable supplemental fuel, it should be combustible and have significant energy content. The advantages of the use of hazardous waste as an alternative fuel or alternative raw materials are as follows:

- 1) Provides a permanent solution to waste management problems with lesser need for dedicated incineration and landfills. Co-processing is the utilization/use of excellent temperature conditions in the cement manufacturing process (approximately 1450°C) to destroy several kind of industrial waste in a safe way and according to the national and international standards. This procedure is largely utilized in Europe, the USA and day by day it has been used more in Brazil.
- 2) Saves on the use of non-renewable, natural resources
- 3) Reduces dependence on fuel imports
- 4) Offers a green contribution to waste management: lower overall CO_2 and CH_4 emissions, complete destruction of organic compounds, no residual ash, no waste water
- 5) Reduces energy costs to the company/ improves competitiveness

People think that industrial waste has no utility, but in fact many kinds of industrial wastes have both chemical and physical properties, which allow them to be used as alternative materials. The strategy of co-processing hazardous wastes in cement production has been utilized for more than 20 years (Achterbosch et al., 2003). Waste utilization is an appropriate alternative to managing these residues in order to reduce landfill disposals and to decrease landfill operation problems, i.e.

leachate containing heavy metals. In other words, the utilization of these residues would be their actual final disposal.

The range of fuels is extremely wide. Traditional kiln fuels are gas, oil or coal. Materials like waste oils, plastics, auto shredded residues, waste tyres and sewage sludge (SS) are often proposed as alternative fuels for the cement industry. Also, all kinds of slaughterhouse residues are offered as fuel nowadays (Kääntee et al., 2005). The utilization of hazardous and industrial waste as raw materials and fuels is possible due to the fact that many kinds of industrial wastes are composed of large amounts of silicates, calcium, and alumina, which are the basic constituents of cement. In fact, several kinds of hazardous and industrial waste have the potential to be applied as raw materials and fuels in Portland cement production. Table 2.4 shows alternative fuels classification for the cement industry. They are separated into five groups and Table 2.5 shows alternative raw materials classification for the cement industry. The utilization of hazardous and industrial wastes as alternative fuels and raw materials in cement production is positive as long as it does not impact public health, the worker or the environmental quality of the local community. Therefore, there should be suitable management and controls (Lerdshuwongsa, 2003). However, the management and employees must be trained in the handling and processing of AFR. Hazardous Operations training for new workers and subcontractors should be completed before starting with co-processing. Periodic re-certification should be done for employees and subcontractors and third parties. Understanding risks and how to mitigate them are keys to training. Training authorities is the basis for building credibility. Introducing AFR requires open communications with all stakeholders. Providing all the information stakeholders need to allow them understand the purposes of co-processing is obligatory. Risk can be minimized by properly locating plants in terms of environmental setting, proximity to populations and settlements, and the impact of logistics and transport. Plants will require good infrastructure in terms of technical solutions for vapors, odors, dust, infiltration into ground or surface waters, and fire protection. All aspects of using AFR must be well documented, as documentation and information are the basis for openness and transparency about health and safety measures, inside and outside the plant.

Table 2.4 Alternative fuels classification for the cement industry

Fuel Family	Examples
Liquid AF high grade > 21 MJ/kg	Solvents, waste oil
Liquid AF medium grade	Emulsions
Liquid AF low grade < 7 MJ/kg	Waste water
Whole tires	
Lump > 50 mm	Tire chips, toner cartridges or filter cakes
Solids < 50 mm	Residue from car shredding, tire chips
Solids < 5 mm	Saw dust or coarse animal meal
Solids < 1.5 mm	Saw dust or dried sewage sludge
Solids < 0.5 mm	Fly ash or ground AF
Gaseous fuels	Landfill gas, pyrolysis gas and natural gas

Source: Holcim, 2006

Table 2.5 Alternative raw materials classification for the cement industry

Fuel Family	Examples
Blast furnace slag	Huttensand, laine de laitier
Other slag	Copper slag, iron slag
Fly ash	Fly ash from thermal, power station
Bottom ash	Bottom ash from power plant

Source: Holcim, 2006

2.5 Chromium, Nickel, Zinc, and Lead

2.5.1 Chromium

Chromium is an element found naturally in rock, soil, and plants. It occurs in combination with other elements, such as chromium salts, some of which are soluble in water. The pure metallic form rarely occurs naturally. Chromium does not evaporate but it can be present in air as particles. In nature, it is found in three forms: metal ore, trivalent chromium (Cr III), and hexavalent chromium (Cr VI). The chemical properties of chromium are as follows (Vincoli, 1997):

Atomic Mass (amu): 51.996

Melting Point:	1,857 °C
Boiling Point:	2,672 °C
Density:	7.19 g/cm ³

In general, chromium (VI) is more toxic than chromium (III) because its oxidizing potential is high and it easily penetrates biological membranes. Chromium is a confirmed human carcinogen. It is a human poison by ingestion with gastrointestinal effects. It can also be toxic by inhalation. Exposure to the dust of chromites and ferrochrome alloys may cause lung diseases, including pulmonary fibrosis and pneumoconiosis.

In the cement industry, chromium is found in limestone, clay, char, and oil, which are the fuel sources in the production process (Sprung, 1985), including hazardous waste co-processing in cement kilns which uses waste as a fuel or as raw materials in partial substitution for natural materials. The effect of chromium on the cement product is that it reduces the viscosity of the clinker melt and can decrease the C₃S formation temperature (Achterbosch et al., 2003).

2.5.2 Nickel

Nickel is an abundant natural element. Pure nickel is a hard, silvery-white metal. Nickel can be combined with other metals, such as iron, copper, chromium, and zinc, to form alloys. Nickel is found in all soil and is emitted from volcanoes. Nickel is also found in meteorites and on the ocean floor. Nickel and its compounds have no characteristic odor or taste. The chemical properties of nickel are as follows (Vincoli, 1997):

Atomic Mass (amu):	58.71
Melting Point:	1,455 °C
Boiling Point:	2,730 °C
Density:	8.9 g/cm ³ at 25 °C

Nickel is a severe human poison by ingestion and inhalation of its finely divided powders and dusts. Skin contact with the dusts of nickel may result in

scratching and scarring. Nickel is a confirmed carcinogen in animals causing lung and nasal tumors. Its carcinogenic potential in humans is considered highly suspect. Inhalation of nickel dusts or fumes can cause severe inflammation and irritation of the upper respiratory tract with cough, rapid breathing and tightness in the chest.

In cement industries, the main sources of nickel in the production of Portland cement are limestone, clay, coal, oil, and coke (Sprung, 1985). Waste as galvanic sludge and electroplating sludge are disposed of in the cement process. These wastes are one of the main sources of nickel (Ract et al., 2003).

2.5.3 Zinc

Zinc is an element commonly found in the earth's crust. In nature, zinc occurs as a sulfide, oxide, or carbonate. In solution, it is divalent which can form hydrated Zn^{2+} cations in acid. Zinc ligands are soluble in neutral and acidic solution, so zinc is readily transported in most natural waters. Zinc oxide, the compound most commonly used in industry, has a low solubility in solvents. Zinc appears as a shining white metal with a bluish-white or gray luster. It is used in alloys, electroplating, metal spraying and auto parts. The chemical properties of zinc are as follows (Vincoli, 1997):

Atomic Mass (amu):	65.37
Melting Point:	419 °C
Boiling Point:	907 °C
Density:	7.14 g/cm ³

Zinc exhibits a relatively low toxicity but its compounds and salts are highly toxic. It is primarily toxic through the inhalation of its dusts. Zinc is poorly absorbed through the digestive tract. Therefore, ingestion is not considered a toxic exposure route. Skin contact may cause localized irritation. There is no data in the references regarding its carcinogenic or mutagenic properties. Inhalation of zinc dusts can lead to coughing, phlegm, sneezing and other indications of mechanical irritation.

In cement industries, zinc is present as a minor element in co-burning tires. It is extensively used as an alternative fuel in the cement industry worldwide. It is also found in electroplating sludge (Suwimol and Duangruedee, 2004). The effect of zinc on the cement product is that higher inputs can cause a shorter setting time and a higher water demand (Holcim, 2006).

2.5.4 Lead

Lead is an element commonly found in the earth's crust in low amounts. Lead is bluish white when freshly cut, but tarnishes to dull gray when exposed to air. Lead is a poisonous metal that can damage nervous connections (especially in young children) and cause blood and brain disorders. Long-term exposure to lead or its salts (especially soluble salts or the strong oxidant PbO_2) can cause nephropathy, and colic-like abdominal pains. Its chemical properties are as follows (Vincoli, 1997).

Atomic Mass (amu):	207.17
Melting Point:	327.4 °C
Boiling Point:	1,755 °C
Density:	11.35 g/cm ³

Lead is used in building construction, lead-acid batteries, bullets and shot, weights, and is a part of solder, pewter, and fusible alloys. Lead has the highest atomic number of all stable elements, although the next element, bismuth, has a half-life so long (longer than the estimated age of the universe) that it can be considered stable. Like mercury, another heavy metal, lead is a potent neurotoxin that accumulates in soft tissues and bone over time (ATSDR, 2005). The effect of lead on the cement product is that higher inputs can cause a shorter setting time and a higher water demand (Holcim, 2006).

2.6 The effect of heavy metals in Portland cement

Many kinds of hazardous waste have the potential to be used in cement production. But industrial wastes have many unwanted components, which may create problems. For example, hazardous wastes contain forms of chlorine such as carbon tetrachloride or trichlorobenzene, and when burned in a kiln they become hydrogen chloride which is an acidic gas. It can react with potassium oxide and sodium oxide in the kiln and produce alkaline salts. These volatile salts then condense and become distilled in the cooling part of the kiln, disrupting cement production. Some heavy metals do not form insoluble compounds, but they are retained in the structure by physical encapsulation. By adding sodium silicate into the mix, the interaction between the calcium in the cement and the added sodium silicate can add massive deposits of calcium-silicate gel reducing the porosity of the structure (Kulyakorn, 2002).

However, the presence of heavy metal in the cement paste can increase the porosity of the structure resulting in an adverse effect. Poon et al. (1985) studies the effect of heavy metals on porosity by using the Mercury Intrusion Porosimetry (MIP) test. They found that the addition of heavy metals significantly increased the porosity and shifted the pore size distribution toward a larger pore radius. Barros et al. (2004) investigated the effects of Cr_2O_3 and NiO additions on transformations during the production of the Portland cement clinker. The results showed that the Cr_2O_3 additions to cement raw meal inhibit C_2S formation, while NiO has very little effect on clinker reactions. Murat et al. (1996) examined the effects of large additions of Cd, Pb, Cr, and Zn to Portland cement raw meal on the composition and properties of the clinker. The results showed that a large amount of chromium (84%) was trapped and 53% of zinc was fixed in the Portland cement clinker. Also, a ZnO addition increased the size of the alite crystals.

2.7 Leaching tests

2.7.1 Definition

Leaching is the process in which inorganic or organic contaminants are released from the solid phase into the water phase under the influence of mineral dissolution, desorption, and complexation processes as affected by the pH, redox, dissolved organic matter, and (micro) biological activity.

When a waste is exposed to water, the rate of dissolution can be measured. This process is called leaching; the water which starts the process is called the leachant and the contaminated water which has passed through the waste is called the leachate. The capacity of the waste material to leach is called its leachability (Spence, 2000).

Leaching is a rate phenomenon in which hazardous or other undesirable constituents are removed from the waste and spread into the environment via the leachate. This rate is usually measured and expressed in terms of the concentration of the constituent in the leachate. This is because the concentration determines the constituent's effects on living organisms, especially humans (U.S. EPA, 1989).

2.7.2 Factors affecting leachability

There are two sets of factors which affect the leachability of a treated waste: (1) those which originate with material itself and (2) those which are a function of the leaching test or the disposal environment. The combination of the two sets determines the leachability of the material. They include the surface area of the waste, the nature of the extraction vessel, the agitation technique, the nature of the leachant, the ratio of leachant to waste, the number of elution used, the time of contact, temperature, pH of the leachant, and the method used to separate the extract from the solid (Spence, 2000).

2.7.3 Leaching methods

The leaching methods are separated into three types: (1) the regulatory methods approved by a regulatory agency to generate specific information for submission in a legal context (i.e. Toxicity Characteristic Leaching Procedure (TCLP), Multiple Extraction Procedure (MEP), etc.); (2) the standardized methods adopted by a standard organization (ASTM or ISO) for a specific set of conditions and sometimes for specific materials (i.e. Standardized Test for a Single Batch Extraction Method for Wastes (ASTM method D-5233), Availability Leaching test (NEN 7341), etc.); and (3) the research methods developed for a particular objective. Regulatory and standardized methods are frequently used in research projects. The leaching testing techniques that are widely used to evaluate the leaching amount of heavy metals from the cement include the TCLP, pH static leach test, and Notification of the Ministry of Industry No.6 B.E. 2540 (1997).

Leaching methods can be divided into two general categories: static extraction tests and dynamic extraction tests. In static extraction protocols, leaching takes place with a single, specified volume of leaching fluid. In dynamic extraction protocols, the leaching fluid is renewed throughout the test. In the static extraction protocols, a specific amount of leaching fluid is placed in contact with a specific amount of waste for a specified length of time. The leachate from the test is moved at specified times, usually the end of the test, for analysis. Types of static extraction tests include: agitated and non-agitated extraction test, sequential chemical extraction tests, and concentration buildup tests. In agitated extraction tests, the waste and leachant are co-mingled and agitated, so the test reaches steady-state conditions as quickly as possible. Agitated extraction tests measure the chemical properties of a waste/leachant system rather than the physical, rate-limiting mechanisms. Because of this, this type of test may over-estimate the short-term release of constituents. Examples of agitated extraction tests include the TCLP, WET, and SPLP.

The leaching test techniques that are widely used to evaluate the leached amount of heavy metals from the cement include the TCLP, WET and Availability Test (NEN 7341). Leaching tests for this research were used to predict the distribution of heavy metals in cement when the application of cement from co-

processing using industrial sludge containing petroleum and heavy metals as alternative fuel was dumped into a landfill for example with the U.S. EPA SW 846 method 1311 Toxicity Characteristic Leaching Procedure (TCLP). The TCLP determines the mobility of both organic and inorganic analytes present in liquid, solid and multiphase wastes for demonstration in the landfill condition and The Notification of the Ministry of Industry B.E. 2548 (2005) by the Waste Extraction Test (WET) evaluates classification of the hazardous waste before dumping it into the landfill. Many previous researchers have studied the use of the leaching test on cement-based products, cement-base stabilized, and other materials.

2.7.3.1 The Sequential Extraction Test

Sequential extraction methods have often been used to study the speciation and possible associations between metals and soil, sediment components (Tessier et al., 1979). The chemical partitioning of metals is operationally defined according to the reagents used and the matrix of the samples. For cement-based S/S waste, this method can be useful to evaluate the metal distribution in the different phases of the S/S waste matrix, potential binding mechanisms, and leaching behaviors (Li and Poon, 1998). There may be some analytical limitations imposed by the interference, selectivity, and sensitivity of the sequential extraction methods, which could affect the differentiation of metals between various physicochemical forms in the stabilized/solidified materials. At present, a number of schemes have been proposed to fractionate metals on the basis of extractability in various chemical reagents either discretely or sequentially (Roy and Cartledge, 1997).

Sequential extraction procedures have been commonly applied to soils and sediments in environmental studies (Iwegbue et al., 2007) to evaluate the availability of metals to plants and/or metal distribution/mobilization in polluted soil (Quevauviller, 2002).

Keawkanya (2004) studied the physical and chemical properties of heavy metals in mortar from co-burning using copper slag as the alternative fuel.

The study result found that most of the heavy metals were likely to form bonds with iron and manganese oxide at step 3 of the sequential extraction.

Sammasut (2006) investigated the sequential extraction of heavy metals in cement from co-processing cement using copper slag and found that approximately 20% of heavy metals are distributed in Fraction 3 (bound to iron and manganese oxide) and a major concentration of the heavy metals (70%) are found in Fraction 5 (residual fraction). Ni is able to leach more easily to the environment than other metals.

2.7.3.2 The U.S. EPA SW-846 method 1311 Toxicity Characteristic Leaching Procedure (TCLP)

The TCLP test is one of the universal extraction test procedures issued by the U.S. EPA under the Hazardous and Solid Waste Amendments of 1984 (HSWA). The TCLP is designed to determine the mobility of both organic and inorganic analytsts present in liquid, solid and multiphase wastes.

Wang et al. (2000) investigated the leachability of chromium (VI) from the solidification of chromium (VI) with cement. The Toxicity Characteristic Leaching Procedure (TCLP) was used to observe the leachability of chromium (VI). The result concluded that the leachability of chromium (VI) during TCLP testing was dependent on the initial concentration and the time. They also concluded that the K_2CrO_4 /cement ratio should not be higher than 0.2% in order not to exceed the chromium concentration of 5 ppm established by the TCLP limit.

Asavapisit and Chotklang (2004) investigated the potential utilization of alkali-activated pulverized fuel ash as a solidification binder to treat electroplating sludge. Compressive strength and leachability of heavy metals from the solidified electroplating sludge were determined to assess the potential for utilization. Metals leaching from the solidified wastes were assessed using the Toxicity Characteristic Leaching Procedure (TCLP). The results showed that lead, cadmium

and copper were not found in the Toxicity Characteristic Leaching Procedure leachates. Chromium, zinc and ferric were detected. In some cases, chromium exceeded the U.S. EPA allowable limits.

Taweekijwanij (2004) investigated the leaching behavior of metals (Cr, Ni, Zn) from cement derived from the co-burning of hazardous waste using the Toxicity Characteristic Leaching Procedure (TCLP) and The Notification of the Ministry of Industry No. 6 B.E. 2540 (1997). The study results showed that when the raw material was doped with more than 0.1 wt. % of chromium, the cement was classified as hazardous waste. When the raw material was doped with nickel and zinc up to 2 wt. %, the cement was not classified as hazardous waste.

2.7.3.3 The Notification of the Ministry of Industry No. 6 B.E 2540 (1997)

According to the Notification of the Ministry of Industry No. 6 B.E 2540 (1997), the purpose of this experiment is to analyze the mobility of both organic and inorganic matter that is found in liquid, solid and multiphase wastes. The stabilized and solidified materials must be tested for the leachate characteristics by the leachate extraction procedure and the concentrations in extraction fluid must be determined. The extraction fluid composition (80% sulfuric acid and 20% nitric acid in deionized (DI) water at a pH of 5.0) was selected to mimic the conditions of acid rain.

In the Notification of the Ministry of Industry No. 6 B.E 2540 (1997), Thailand has developed its own leaching procedure. This leaching procedure is similar to the TCLP except for the fact that 80% of the extraction fluid is composed of sulfuric acid and the remaining 20% is nitric acid in deionized (DI) water at a pH of 5.00 (Podjane, 2002).

The leachate extraction procedure described in the Notification of the Ministry of Industry No. 6 B.E 2540 (1997) is used to determine the toxicity of leachate. This test does not determine the total elemental contents of the specimens,

but it indicates the leaching potential of eight elements: arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), lead (Pb), mercury (Hg), selenium (Se) and silver (Ag). The maximum permissible concentrations in the leachate from toxic wastes have been set at 100 times the drinking water standard. The leachate standard for lead and chromium is 5.0 mg/L for both (Peralta et al., 1992).

Ruangchuay (2005) studied the utilization of bagasse and bagasse fly ash (BFA) as adsorbents for the removal of lead and chromium and their subsequent utilization as construction materials. The results of the leaching test for the mortars that incorporated BFA-Pb and BFA-Cr showed that Pb and Cr concentrations in the leachates from the specimens were lower than 1.2 mg/L at all replacement ratios (10, 20, and 30%) and curing periods (3, 7, 14, and 28 days). This indicated that the concentrations of all cases were well below the limits established by the Notification of the Ministry of Industry No. 6 B.E 2540 (1997).

2.7.3.4 The Notification of the Ministry of Industry B.E 2548 (2005)

The Notification of the Ministry of Industry B.E 2548 (2005) has determined concentration limits for hazardous metals in extraction fluids (which demonstrate landfill conditions) that indicate whether wastes should be classified as hazardous waste or non-hazardous. The Waste Extraction Test (WET) is used for testing waste when the total concentration of heavy metals in the waste is less than the Total Threshold Limit Concentration (TTLC). After leaching test with the waste extraction test, if the heavy metals concentration is equal or higher than the Soluble Threshold Limit Concentration (STLC), waste should be classified as hazardous waste. However, if the heavy metals concentration is less than the Soluble Threshold Limit Concentration (STLC), waste should be labeled non-hazardous. Table 2.6 shows a comparison of the leaching test methods.

Keawkanya (2004) studied the physical and chemical properties of heavy metals in mortar from co-burning using copper slag as the alternative fuel.

Metal leaching was assessed using the TCLP. The study results showed that the leaching concentrations of heavy metals were lower than standard values of TCLP and The Notification of the Ministry of Industry B.E. 2548 (2005).

Table 2.6 Comparison of leaching tests

Types of leaching test	Leaching solution	Target	Objectives
Sequential Extraction Test	Each fraction uses different leaching solutions.	-To display chemical partitioning of heavy metals. -To determine the heavy metals distribution, potential incorporated mechanisms, and leaching behaviors.	-To study the speciation and possible associations between the metals and solid matrix.
EPA SW 846 Method 1311 Toxicity Characteristic Leaching Procedure (TCLP)	-0.1M HAc, -pH 2.88 (Extraction type 2)	-To demonstrate in landfill conditions.	-To determine the mobility of both organic and inorganic matter present in the liquid, solid and multiphase wastes.
The Notification of the Ministry of Industry No.6, B.E.2540 (1997)	-80:20 ratio of nitric acid to sulfuric acid -pH 5	-To demonstrate the acid rain condition.	(Similar to that of the TCLP)

Table 2.6 (cont.) Comparison of leaching tests

Types of leaching test	Leaching solution	Target	Objectives
The Notification of the Ministry of Industry B.E.2548 (2005)	-0.2M sodium citrate -pH 5.0±0.1	-To evaluate waste before dumping in a landfill.	-To classify hazardous waste.