Green Chemistry: A Sustainable Solution In The Cement Production

Lamphai Trakoonsanti[1] Yaifa Trakoonsanti[2]

[1]Department of Air Cargo Management, College of Logistics and Supply Chain,
Suan Sunandha Rajabhat University, Bangkok, 10300
*Email: lamphai.tr@ssru.ac.th
[2]Department of Technology, Faculty of Industrial Technology, Nakhon Si Thammarat
Rajabhat University, Nakhon Si Thammarat, 80280
*Email: yaifa_tra@hotmail.com

Abstract

The purpose of this paper is to demonstrate the characteristics of green chemistry to improve the sustainability in the cement production and to investigate how alternative cements have significant potential for reducing carbon dioxide emission from cement making. To achieve the aims, alternative cements will be reviewed and compared to Portland cement in terms of their chemistries and properties as well as unit operation. Furthermore, the outcome of this paper is to improve the future of industrial science in several significant ways by adopting green chemistry. With the significantly increase of CO_2 emissions, alternative raw materials are highly considerable solution to replace OPC and can be emission mitigation option to reduce CO_2 emission from cement making. This paper can be high-quality guidance for global cement industries to realize about the significant potential of green chemistry and importantly may encourage cement manufacture to use alternative raw materials and alternative fuel in their productions, which lead to reduction of CO_2, cost and residue free combustion. Another significant is to support alternative raw materials become the selection of cement in the cement market instead of conventional OPC.

Keywords: Green Chemistry, Sustainability, Cement Production

Introduction

The treat of climate change is now considered as the major environment problem facing the globe. Carbon dioxide (CO_2) is the primary greenhouse gases that emits through human activities. The main anthropogenic sources of CO_2 are the combustion of fossil fuel such as coal, natural gas and oil for energy and transportation, deforestation, unstainablecombustion of biomass, and the emission of mineral sources of CO_2 (Worell, Price, Martin, Hendriks and Meida, 2001). Construction industry is a significant part in the world economy which is responsible for the creation of job and the modernization of infrastructure (Rodrigues and Joekes, 2011). Cement is one of the most important construction ingredients which are mainly used for the production of concrete. Because of inexpensive, abundant of raw materials and high density, cement consumption and production is generated in practically all countries (Worell, Price, Martin, Hendriks and Meida, 2001).

However, the production of cement is not an environmental friendly process due to the fact that it requires very high temperatures and the consumption of huge amounts of non-renewable raw materials (Rodrigues and Joekes, 2011).It is an important source of CO_2 emission that releases about 5% to global anthropogenic. It can contribute large amounts of persistent organic pollutants such as dioxins and heavy metals (Rodrigues and Joekes, 2011). In addition, the production of cement releases to the emission of CO_2 through the calcinations process of limestone, combustion of fuels in the kiln and power generation (Worell, Price, Martin, Hendriks and Meida, 2001).

In order to overcome these environmental issues, there are many alternative materials that are able to use to minimize the carbon dioxide production and reduce energy consumption (Rodrigues and Joekes, 2011).Green chemistry is considered to be one of the solution to improve the sustainability of cement industry. It is "the design of chemical products and processes that reduce and eliminate the use and generation of hazardous substance" (Beach, Cui and Anastas, 2009).Therefore, the use of alternative cement materials will be reviewed and compared to Portland cement in terms of chemical reaction and unit operations. It is clear that alternative cements have consideration potential for reducing carbon dioxide emission from cement production.

Objectives

This research consisted of two objectives:

2.1 To demonstrate the characteristic of green chemistry to improve the sustainability in cement production.

2.2 To investigate that alternative cements have significant potential for reducing carbon dioxide emissions from cement making.

Methodology

The methodology that presented in this paper was analysed main concepts of green chemistry which can be implemented for improving sustainability in cement production. As a consequence, the three alternative cements including alkali-activated cements, blend OPC- based cement and sulfoaluminate cement will be examined to replace OPC cement. In order to investigate this hypothesis, alternative cements will be reviewed and compared with OPC in term of their chemistry and properties as well as unit operation.

Data Analysis

Basis Chemistry of Portland Cement

This reaction are represented the result of ordinary Portland cement from the calcinations of limestone and silica.

Limestone + silica (1450) = Portland cement + carbon dioxide

$$5CaCO_3 + 2SiO_2 \longrightarrow (3CaO, SiO_2)\ (2CaO, SiO_2) + 5CO_2 \qquad (1)$$

In a reaction that takes place at 1450 , the production of 1 tonne of cement produces 0.55 tonnes of chemical CO_2 (McLeod, 2005). In addition, chemical components in Portland cement will be combined to form different potential compounds. The amounts of these compounds are responsible for physical properties of Portland cement (Ali, Khan, & Hossain, 2008). Four main components in Portland cement include C_2S, C_3S,C_3A and C_4AF which are shown in Table1. The most important compound which are responsible for the strength of the cement are C_3S and C_2S.The presence of C_3S causes undesirable heat and quick reacting properties that can be presented by adding $CaSO_4$ to the final product. Also, C_4AF present in cement in small quantities when compared with the other three it does not affect the behavior of the cement (Anonymous 2, 2012).

Table1 Major mineral constituents of Portland cement

Compound*	Abbreviation	Chemical formula	Typical concentration/%
Tricalcium silicate	C_3S	$3CaO^{*}SiO_2$	60-70
Dicalcium silicate	C_2S	$2CaO^{*}SiO_2$	10-20%
Tricalcium aluminate	C_3A	$3CaO^{*}Al_2O_3$	5-10%
Tetracalcium alumino-ferrate	C_4AF	$4CaO^{*}Al_2O_3{}^{*}Fe_2O_3$	3-8%

Table1 Major mineral constituents of Portland cement

Furthermore, both C_3S and C_2S combine with water to form a very poorly crystalline calcium silicate hydrate known as C-H-S, the colloidal gel that represents the primary binding phase in Portland cement and controls the strength development of the paste (Lecomte, et al., 2006). This can be represented by a reaction for the formation of tobermorite.

$$2C_3S + 6H \text{ (water)} \longrightarrow C_3S_2H_3 \text{ (tobermorite)} + 3CH$$

Environmental problems

Main environmental impacts related with Portland cement consist of the energy required for production and transportation of clinker and the emission of greenhouse gases either directly or indirectly during manufacture (Phair, 2006). Environmental issues rank from local, site specific issues related with processing of raw materials, to regional and finally global scales. The most serious environmental issues are global as they are the most difficult to battle. It is expected that cement use in developing countries will grow dramatically over the next 50 years, with growing world population. Moreover, the probability of infrastructure damage will also increase, since climate change is forecast to increase in the future with weather patterns becoming more extreme (Phair, 2006)

The comparison between alternative raw materials and OPC

Alkali activated

Alkali-activated cements consist of a big family of cement characterized by an important content of aluminosilcate bonding phase. Alkali activation is the process by which cement particles are begun to react after the addition of alkali in the early mixing stages. This intrinsically activates the liberate of certain chemical constituents that form the new binding phase and preparing surface for bonding (Phair, 2006). In addition, alkali- activated cements can be classified into five categories based on slight compositional differences which include alkali-activated slag-base cement, alkali-activated pozzolancements,alkali-activated lime-pozzolan/slag cements, alkali –activated calcium aluminate blended cements and alkali –activated Portland blended cements (hybrid cements) (Shi, 2011).

The mechanism of alkali-activation is comprised of combined reaction of destruction-condensation that consists of the destruction of the prime material into low stable structural units. The first steps include breakdown of the covalent bonds Si–O–Si and Al–O–S which occurs when the pH of the alkaline solution increases. Therefore, those groups are transformed into a colloid phase. After that an accumulation of the destroyed product happened which interacts among them in order to form a coagulated structure (Pacheco-Torgal, Castro-Gomes and Jalali, 2007).

Carbon dioxide emissions

The production of one tone of OPC emits 0.55 tons of chemical CO_2 and requires an additional 0.39 tonnes of CO_2 in fuel emissions in order to bake and grind, account for a total of 0.94 tons of CO_2 (Torgal-Pacheco, 2012).In contrast, the carbon dioxide generates from alkali-activated cements binders just 0.184 tons of CO_2 per ton of binder. The production of alkali-activated binders is related to a level of carbon dioxide emissions lower than the emissions generated in the production of OPC although the CO_2 emissions generated during the production of Na_2O are very high. A 40% to 64% decline in greenhouse gas emissions of alkali-activated binders when is compared to OPC. Additionally, life cycle assessment methodology can confirm that alkali-activated binders have a lower impact on global warming than OPC (Pacheco-Torgal, Castro-Gomes and Jalali, 2007).

Solubility

The aluminosolicate binding phase which is extremely durable in an aggressive environment and mechanically strong is the greatest advantage of alkali activated cements (Phair, 2006). Table 2 presents a comparison of the relative solubilities of the typical phase found in an alkali –activated cement compared to those found in OPC, with the phases found in alkali-activated cements normally more insoluble (Phair, 2006). Geographic cements reported with lower porosity than Portland cement cause a microstructure that is more heat resistant, fire resistant and has more thermal expansion, cracking and swelling properties than Portland cement (Phair, 2006).

Table 2 Comparative solubility data for phases within alkali-activated slag cements and Portland cements (Chao, Henghu and Longtu, 2010)

Cement Type	Mineral Phase	Stoichiometric Formula	Solubility/kg m^{-3}
Alkali-activated Cement	CSH(B)	$5CaO\ SiO_2\ nH_2O$	0.05
	Xonotlite	$6CaO\ 6SiO_2\ nH_2O$	0.035
	Riversideite	$5CaO\ 6SiO_2\ 3H_2O$	0.05
	Plombierite	$5CaO\ 6SiO_2\ 10.5H_2O$	0.05
	Gyrolite	$2CaO\ 3SiO_2\ 2.5\ H_2O$	0.051
	Calcite	$CaCO_3$	0.014
	Hydrogarnet	$3\ CaO\ Al_2O_3\ 1.2SiO_2\ 3H_2O$	0.02
	Na–Ca hydrosilicate	$(Na,\ Ca)\ SiO_4\ nH_2O$	0.05
	Thomsonite	$(Na,\ Ca)\ SiO_4\ Al_2O_3\ 6H_2O$	0.05
	Hydronepheline	$Na_2O\ Al_2O_3\ 2SiO_2\ 2H_2O$	0.02
	Natrolite	$Na_2O\ Al_2O_3\ 3SiO_2\ 2H_2O$	0.02
	Analcime	$Na_2O\ Al_2O_3\ 4SiO_2\ 2H_2O$	0.02
Portland Cement	Calcium Hydroxide	$Ca(OH)_2$	1.3
	C_2SH_2	$2CaO\ SiO_2\ nH_2O$	1.4
	CSH(B)	$5CaO\ SiO_2\ nH_2O$	0.05
	Tetracalcium hydroaluminate	$4CaO\ Al_2O_3\ 13H_2O$	1.08
	Tricalcium hydroaluminate	$3CaO\ Al_2O_3\ 6H_2O$	0.56
	Hydrosulfoaluminate	$3CaO\ Al_2O_3\ 3CaSO_4\ 31H_2O$	high

Sulfoaminate cements

To form calcium sulfoaluminate clinker, limeston,bauxite and calcium sulfate are mixed and heat at 1250-1350 in rotary calcining kiln as equation follows.

$$\left.\begin{array}{l}\text{Limestone}\\ \text{Bauxite}\\ \text{Calcium sulphate}\end{array}\right. \xrightarrow{1250\text{-}1350} \text{calcium sulfolaluminate clinker}$$

Commercial sulfoaluminate clinkers include C_4A_3S (55-75%) and c_2s (15-25%) .The remaining phase presents are C_4A_7, C_4af and CaO,but C_2AS and CS are undesirable ,since they are considered deleterious. Belite (C_2S)-rich sulfoaluminate content are preferred to alite (C_3S) due to the fact that belite-based cement is able to formed at around 1200 ,as apposed to 1400 for alite cement. This associates to an energy savings of ~20% during manufacture (Phair, 2006).

Energy saving

According to table 3, the least amount of CO_2 per gram of raw material as by product of its reaction of formation were generated by the calcium sulfoluminate (C_4A_3S).Moreover, the calcining of raw materials for clinker production happens at temperature (1160-1200) much lower than those used for firing Portland cement clinker (Phair, 2006). Also, energy saving occur in the grinding of the clinker compared to OPC because the low firing temperatures result in clinker which is normally softer. Additionally, calcium sulfoaluminate cements can use gypsum in order to form hydration products which have not undergone any heat treatment in a kiln. Therefore, this causes a considerable energy saving (Phair, 2006).

Table 3 The quantities of CO_2 generated from the conversion of raw materials into OPC compared to alternative cement compounds (Henghu, Ravi, Kenedi and John, 2010)

Cement compound	Raw materials used	Quantity of CO_2 generated (g of raw material per g of CO_2)	Quantity of CO_2 generated (g of raw material per ml of CO_2)
M (magnesia, periclase)	Magnesite	1.092	3.91
C (calcia, quicklime)	Limestone	0.784	2.63
C_3S (alite)	Limestone + silica	0.578	1.80
β-C_2S (belite)	Limestone + silica	0.511	1.70
C_3A (tricalcium aluminate)	Limestone + alumina	0.489	1.50
C_4AF (calcium aluminoferrite)	As above + iron oxide	0.362	1.29
NS (sodium metasilicate)	Soda + silica	0.361	—
CA (monocalcium aluminate)	Limestone + alumina	0.279	0.83
$C_4A_3\bar{S}$ (calcium sulfoaluminate)	As above + anhydrite	0.216	0.56

Carbon dioxide emissions

The table below is shown the comparison of carbon dioxide emission between Portland cement clinker and Sulfoaluminate clinker in term of CO_2 emitted per ton clinker produced, specific heat consumption during clinkering and energy cost of crushing *(Henghu, Ravi, Kenedi and John, 2010)*.

	Portland clinker	Sulfoaluminate clinker
CO_2 emitted per ton of clinker produced	535 kg/t	305 kg/t
Specific heat consumption during clinkering (Popescu et al, 2002)	3.845 GJ/t	3.305 GJ/t *
Energetic cost of crushing (Janotka I. and Krajci L., 1999)	45 to 50 kWh	20 to 30 kWh

Blended OPC-based cement

Reaction mechanism

Blened Portland cements or pozzolanic cements refer to hydraulic cement that includes a homogeneous mixture of a Portland cement and replacement material. Blended cement are normally produced by grinding the replacement material in the occurrence of Portland cement clinker, by blending the substitution material and Portland cement during mix proportioning (Phair, 2006).To replace pozzolan material can be either naturally derived or waste material (silica- or alumino- silicate-rich) that reacts with calcium hydroxide in order to form calcium silicate hydrate. Popular pozzolans which is used in nowadays consist of reactive silicates and aluminosilicates such as fly ash,slag, silica fume and metekaolin of either a crystalline or amorphose structure as shown bellows (Phair, 2006).

$$CH + S + H \longrightarrow C\text{-}H\text{-}S$$

$$A_xS_y + CH + H \longrightarrow C\text{-}H\text{-}S + C\text{-}A\text{-}H$$

The definite composition of the final product of these reactions is depend on the nature of the pozzolans, reaction condition and other contaminants occurrence (Phair, 2006).

Carbon dioxide emissions

A achievement of blended cement is because of improved properties that can be achieved when compared with plain Portland cement concretes under some particular conditions. These consist of a lower heat of hydration that minimizes the risk of thermal contraction cracking, providing the concrete is insulated for minimizing temperature differentials between surface temperature and the core at early ages (Stanley, 2010).In addition, the utilization of blended cement may improve the in the workability of fresh paste and the capability of the substitution material to chemically join with lime and alkalis liberated from the Portland cement during the hardening period. As a consequence, blended concrete may frequently be more resistant to chemical effect related with the alkiali-agrregate reaction (Phair, 2006). Additionally, the LCA study concludes that blended cement production has lower CO_2 emission than OPC as can be proven by the total environment points in the table below. Thus, blended cement has a lower environment impact when compared to OPC (WWF, 2012)

Table 4 The difference between climate change impacts between OPC and blended cement

Type	Total burden	Climate change impact
Portland		
Average	6355.5	1858.5 (29.2%)
Highest	7559.2	2163.6 (28.6%)
Lowest	1274.975	375.61 (29.5%)
Blended		
Average	4853.4	1419.2 (29.24%)
Highest	5983.9	1712.7 (28.84%)
Lowest	937.46	275.96 (28.16%)

The cement manufacturing process and carbon dioxide emissions

A major raw material used in the production of cement is limestone. It is burnt at approximately 1450 in order to make clinker, and is blended with additives. Then, the finish product is finely grounded to create various type of cement. Emissions are produced mostly by de-carbonation of limestone and the utilize of carbon based fuels for heating. Fig 2 summarizes the cement production process and associated CO_2 emissions at different sections of a cement manufacturing process (Ali, Saidur, & Hossian, 2011)

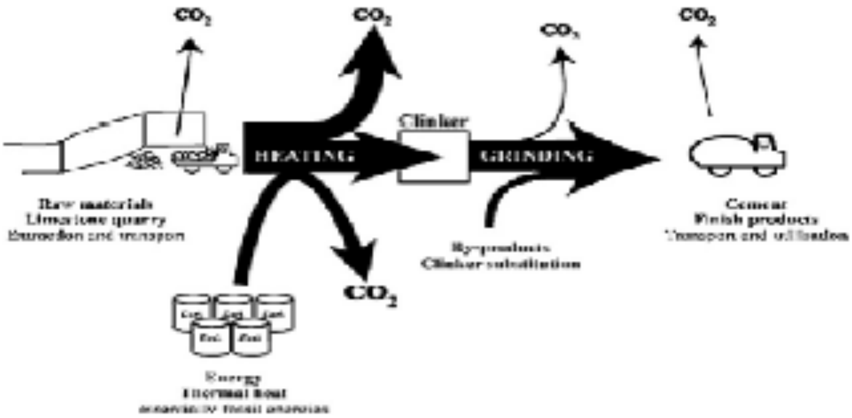

Figure 1 Simplified cement fabrication, with a specific interest in the CO_2 emissions.

Process description of cement making

Cement production is a highly energy consuming process and has a negative impact on the environment (Bignozzia, 2011).The making of cement include three major process steps : raw material preparation , clinker making in the kiln, and cement making as shown in Fig 2.

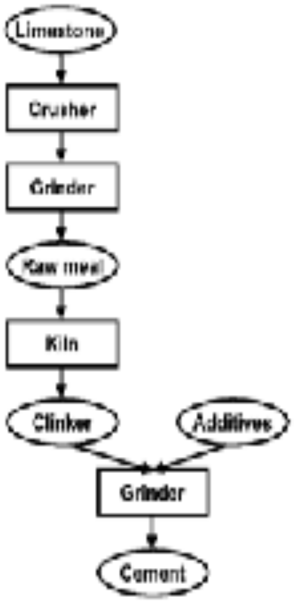

Figure 2 The process of cement making

The main electricity –consuming process are raw material preparation and cement making, whereas almost all the fuel in a typical cement plan is used by the clinker kiln (Worrell, Price, Martin, Hendriks, & Meida, 2001).Clinker production is the main component of most used cement ,since its production can cause a huge consume of natural raw materials(calcium carbonate (70-80 wt%) and clay (20-25%)), high temperature process (~ 1500, a huge consume of natural solid fuels and a massive production of CO_2 emissions in atmosphere (Bignozzia, 2011).Also, clinker production is the most energy –intensive production step which response about 70-80% of the total energy consumed. (Worrell, Price, Martin, Hendriks, & Meida, 2001).

Carbon dioxide emissions from cement production

Carbon dioxide emission in cement production come from combustion of fossil fuels and from calcining the limestone in the raw mix (WBCSD, 2012).Other indirect sources of CO_2 is from consumption of electricity which is generated by burning fossil fuels. Approximately half of the emitted CO_2 originate from the conversion of raw material and half of them originate from combustion of the fuel (WBCSD, 2012).

Total CO_2 emissions emitted from a cement industry could be considered as the sum of emissions released from the consumption of thermal energy and generation of electric energy required for the industry. The following equation can estimate total CO_2 emissions (Ali, Saidur, & Hossian, 2011).

Total CO_2 emissions = CO_2 emission $_{\text{clinker use}}$+CO_2 emission electric $_{\text{energy use}}$
+ CO2 emission $_{\text{thermal energy use}}$

Reduction of CO_2 emissions in cement production

Blended cements

The most energy-intensive step in the cement manufacturing process and cause large process emissions of CO_2 is the production of clinker (Worrell, Price, Martin, Hendriks, & Meida, 2001). Decreasing the amount of clinker in blended cement could be considered as one of the most efficient way to reduce CO_2 emission (Ali, Saidur, & Hossian, 2011).Blended cements include additional cementitious materials that substitute a portion of the clinker used to make Portland cement (Envirionmental Protection Agency, 2010).

In blended cement, a portion of the clinker is substituted with industrial by-products, such as coal fly ash, blast furnace slag, or other pozzolanic materials. Then, these products are mixed with the ground clinker for producing a blended cement product, which has different properties than Portland cement. (Worrell, Price, Martin, Hendriks, & Meida, 2001).The global potential for CO_2 emission reductions through the blended cement is approximated to be at least 5% of total CO_2 emission from cement production (56Mt of CO_2, yet may be as high as 20%) (Ali, Saidur, & Hossian, 2011).

Carbon dioxide emission reducing from combustion process

Alternative fuel

Cement kilns uses fuel sources to provide the energy required to produce the high temperatures requirement for the clinker formation. Fuel is fed into the rotary kiln mostly on the back end as well as raw material flows counter –current to a steam of hat gases. The energy generated by the fuel combustion, which will dissolve any water from the raw materials, calcine the limestone and lastly, form the clinker (Caruso, 2006).

Carbon dioxide emissions can be reduced by the use of alternative fuels, which can replace fossil fuels in the production of Portland cement clinker. Alternative fuels used in the cement production can be separated in to three groups as follows (Ali, Saidur, & Hossian, 2011)

- Gas (landfill gas, pyrolytic gas , biogas)
- Liquid (used oil, solvents)
- Solid (tires, wood waste , plastics)

In addition, some cement plant use alternative fuels and natural gas. The most normally used fuels and their energy content are demonstrated in Table 6.

Table 5 Typical Data on Energy Content and CO_2 Emission for Frequent Fuels. (Beach, Cuiand and Anastas, 2009).

Fuel	Energy content (MJ/kg)	CO_2 emission factor (kg/MJ)
Coal	32	0.103
Fuel oil	40	0.077
Natural gas	36	0.056
Petroleum coke	34	0.073 to 0.095

Additionally, the advantages of using alternative fuels in cement industry are following (Ali, Saidur, & Hossian, 2011).

1. Reduction of CO_2 emissions as shown in Fig 3.

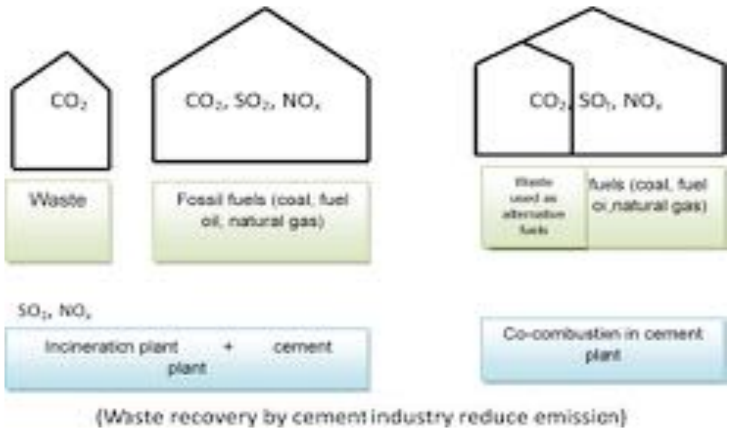

Figure 3 Benefits of co- combustion of alternative fuels in cement industry.

2. Cost reduction of clinker production because of using inexpensive fuel
3. No significant change of emissions
4. High thermal efficiency
5. High yielding ecological balance

Discussion

The research have been compared between alternative raw material, including alkali activated cement , sulfoaminate cements and blended OPC- basted cement to OPC. A 40% to 64% is decline in greenhouse gas emissions of alkali-activated binders when compared to OPC. Additionally, according to CO_2 emitted per ton of clinker, Sulfoluminate clinker is lower than Portland clinker, 535 kg/t to 305 kg/t respectively. In term of climate change impact, blended cement production has lower CO_2 production than OPC. Moreover, in case of unit operation, clinker production , The global potential for CO_2 emission reductions through the blended cement is approximated to be at least 5% of total CO_2 emission from cement production (56Mt of CO_2, yet may be as high as 20%).As a result, alternative raw material cements have significant potential to reduce CO_2 emission as compared to OPC .Also, the sustainability in cement production can be improved by them.

Conclusion

It has been found that the production of cement production is a significant source of CO_2 emission that releases about 5% total of anthropogenic. It can contribute large amounts of persistent organic pollutant s to the atmosphere. From these reasons, special attention is needed to on the cement manufacture to reduce CO_2 emissions. Consequently, green chemistry will be considered to be the solution for improving sustainability in cement industry by using alternative raw materials. This research has examined the relationship between the green chemistry and sustainable in cement production. It has highlighted the twelve principles of green chemistry in particular the efficient use of alternative cements. Also, alternative raw materials were investigated and compared to OPC. Further development and new technique may continue to be introduced into cement industry .Finally, alternative cements should provide a relatively simple and solution to replace OPC .

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