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Risk of Environmental Contamination Arising from Concrete Structures, Part I: CO_2 Emission

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Abstract

The present study concerns the CO_2 emission in the process of cement manufacture. Information on raw materials, energy source and oxide composition was achieved from Korean major six manufacturers. As a result, it was found that the energy efficiency for kilning and control for a loss of CaO in cement manufacture are key factors to emission of CO_2. The variation in the amount of coal in the process of kilning accounted for about 30 kg for one tonne of cement, as being equivalent to 70 kg CO_2/tonne-cem. Simultaneously, the loss of CaO in refinement of raw materials is crucial in reducing the CO_2 emission. The loss of CaO in the cement production was in the range of 9-24 kg for one tonne of cement, which may impose unnecessary energy of coal in kilning and a further decomposition of $CaCO_3$ to CaO and CO_2. Substantially, it can be said that energy control for high efficiency of coal in the kilning process and control for a loss of CaO may reduce several hundreds kg CO_2/tonne-cem, compared to 729-911 kg CO_2/tonne-cem in the cement production. Alternatively, the use of pozzolanic material for Portland cement can reduce the CO_2 emission. 30% PFA and 60% GGBS in a concrete mix reduced CO_2 emitted for a given mix about 28.9 and 49.6% respectively, compared to Portland cement.

Keywords: *cement, CO_2 emission, CaO, fossil fuel, pozzolanic material*

1. Introduction

The possibility of environmental contamination of constructing a concrete structure has been intuitively supported by some environmental disaster in aquatic conditions, skin disease in handling of fresh concrete and leaching of high alkaline concrete solution. When it comes to the CO_2 emission, the process of cement production needs fossil fuel in a large number, thereby emitting hazardous gases including CO_2. Moreover, a constructed concrete structure exposed to an aquatic environment is believed to be always risky of leaching of aggressive ions, which may lead to a further contamination of the exposure environment, together with a reduction of structural properties. For example, the leaching of high alkaline ions from concrete could break the ecological balance in the aquatic environment, presumably leading to a catastrophic ecological failure. Notwithstanding, the risk of environmental contamination arising from concretes structure was rarely assessed in a quantitative technique, due to the complexity of mutual chemical reaction between concrete structures and natural environment. In the present study, the CO_2 gaseous emission and leaching of toxic substances to an aquatic environment were taken as the usual suspects of environmental contamination of a concrete structure, then to evaluate their risk to the environment in a series consisting of (1) the CO_2 emission, (2) toxic metallic ions and (3) alkali leaching. As the Part I, this work is concerned with the CO_2 emission and its causes.

The CO_2 emission is a global issue due to an increasing intention on the environmental loading, in particular, after the Kyoto protocol dealing with the limitation of contaminant evaporation. In fact, about 8% of CO_2 gas emission in all industries is originated from cement industry (GreenBiz, 2009). Thus, every effort to reduce the CO_2 emission in cement production has been made in most countries. However, the amount of CO_2 emission in cement production is in a large variation depending on the production technique, process, energy efficiency etc. For example, it was reported that cement production in India emitted the largest number of CO_2, accounting for 930 kg CO_2/tonne-cem, while 890 in the US, 880 in China and 820 kg CO_2/tonne-cem in Korea, respectively (Hendriks *et al.*, 2004). To date, there have been advised methods to reduce the CO_2 emission in the majority of previous studies including (1) enhancement of energy and raw material efficiency and (2) a replacement with non-CO_2 emitting materials.

To enhance the efficiency of raw materials, lime saturation factor has been emphasized due to its influence on the CaO content in

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cement, which is a key factor to the strength of concrete and the content of CO_2 emission (Roskovic and Bjegovic, 2005). Alternatively, the higher energy efficiency in the burning process was recommended: the optimised energy sources (eg. natural gas, coal, BC oil and electricity) would increase heat energy generation, while in turn the CO_2 emission be reduced (Sheinbaum and Ozawa, 1998). However, no guideline for the energy efficiency has been provided, considering the economic expense, and moreover the portion of the CO_2 emission arising from fossil fuels is about 30-40%, while the decomposition of calcium carbonate to CO_2 occupies about 60-65%.

A replacement with waste materials after an appropriate refinement is much encouraged to reduce the CO_2 emission. In particular, Pulverised Fuel As (PFA) and Ground Granulated Blast Furnace Slag (GGBS) are representative CO_2-reducing materials: these materials partially replaced for Portland cement could save the CO_2 emission about 15-25%, compared to a concrete mix containing only Portland cement (Flower and Sanjayan, 2007; Nowak, 2008). Additionally, reuse of other waste materials such as rice husk ash (Zhang *et al*., 1996) and palm oil ash (Ismail *et al*., 2011) may benefit in reducing the CO_2 emission. Except for these pozzolanic replacements, a further investigation is being made currently to develop non-limestone type replacement, as being ineffective to date (Gartner, 2004; Research Council of Norway, 2010). Likewise, the use of waste materials for Portland cement is strongly advised, but the amount annual cement production is being increasing. Moreover, the refinement of waste materials is mainly associated with the burning process, which may emit unnecessary CO_2 gas.

To assess the sources of the CO_2 emission in cement production, raw materials, energy sources and efficiency in the process of cement manufacture were investigated in this study. In particular, the influence of fossil fuel and CaO content in cement on the CO_2 emission was extensively determined. Additionally, the benefits of pozzolanic materials including PFA and GGBS in reducing the CO_2 emission and concrete strength were quantitatively confirmed.

2. Cement Manufacture

2.1 Dependence of Raw Materials

In this study, it was investigated about the CO_2 emission in cement industry of Korea, using information on cement manufacture in six major cement companies, encompassing the production process, raw materials, energy use and price, as given in Table 1. These six major cement companies occupy about 95% of the cement market in Korea, of which production accounts annually for 47 million tonnes. Only the ordinary Portland cement has been dealt with in this study, while other cements such as calcium aluminate cement and white Portland cement were of no necessarily concern. The raw materials for Portland cement were limited in limestone, and energy sources in electricity and fossil fuels (i.e., coal and BC oil). This information was subsequently used to calculate the emission of CO_2, a development of the strength, and economic benefit. All information on raw materials, energy sources and price was converted to unit values to one tonne of Portland cement produced in each company. For example, the amount of limestone to produce one tonne of cement ranged from 1.19 to 1.47 tonne, while the fossil fuel from 68.1 to 97.3 kg. The use of electricity was also dependent on manufacturers, ranging from 96.3 to 119.6 kwh to produce one tonne of Portland cement.

It can be said that the oxide composition, CO_2 emission, strength development and price are varied with cement manufacturers. As seen in Fig. 1, for example, the amount of CO_2 emission in the process of cement manufacture was in a large range, accounting

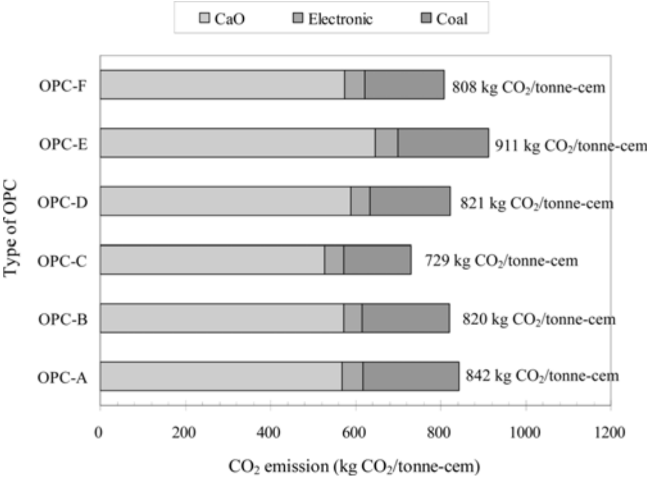

Fig. 1. CO_2 Emission Arising from CaO Formation and Energy Use Depending on Manufacturers

Table 1. Details for Cement Production of Korean Six Manufacturers including Materials and Energy Sources (Korean Cement Association, 2009)

Manufacturers		OPC-A	OPC-B	OPC-C	OPC-D	OPC-E	OPC-F
Total production	Cement (tonne)	7,608,961	3,100,796	6,935,274	4,948,551	11,996,807	6,216,866
	Limestone (tonne)	9839233	4,040,163	8,307,208	6,612,872	17,642,988	8112824
	Electricity (Mwh)	833,148	298,742	709,417	520,508	1,434,611	654,741
	Coal (tonne)	740,216	274,331	472,179	401,154	1,099,682	505,179
	BC oil (k*l*)	842	1257	2632	2957	5670	4337
1 tonne of cement	Limestone (tonne)	1.293	1.303	1.198	1.336	1.471	1.305
	Electricity (Kwh)	109.50	96.34	102.29	105.18	119.58	105.32
	Coal (kg)	97.28	88.47	68.08	81.06	91.66	81.26
	BC oil (*l*)	0.11	0.41	0.38	0.60	0.47	0.70

Table 2. Oxide Composition of Portland Cements Produced by the Six Manufacturers

Type	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3
OPC-A	60.2	21.2	4.93	3.24	1.93
OPC-B	61.1	21.8	5.57	3.47	1.62
COP-C	61.3	19.6	4.35	2.95	2.93
OPC-D	62.3	21.2	4.58	2.84	2.21
OPC-E	63.1	16.9	4.57	3.29	2.15
OPC-F	61.8	21.0	4.50	3.26	2.86

for 730-912 kg/tonne-cem, presumably due to the variation in the energy efficiency and ratio of raw materials. The decomposition of limestone (i.e., calcium carbonate; $CaCO_3$) and fossil fuel are mainly responsible for the CO_2 emission, whilst the electricity has a marginal impact on the CO_2 emission. The decomposition of $CaCO_3$ is allocated to about 70% and the fossil fuel in the burning process to 24% of the CO_2 emission in the process of cement manufacture. As seen in Table 2, the composition of cement has some differences with each manufacturer. In particular, the ratio of CaO in cement ranged from 60.2 to 63.1%, which may affect a development of the concrete strength and a key parametric value in evaluating the CO_2 emission.

2.2 Strength Development

Although Portland cements have the mostly identical oxide composition, their influence on the concrete quality in terms of a strength development can be different. In this study, the six Portland cements were tested for the strength to assess the influence of CaO content in cements. To minimise the affect of aggregate, mortar specimens were cast in a cubic mould (50 × 50 × 50 mm), rather than concrete. The ratio for mortar of cement: water: sand is 1.00: 0.40: 2.65. After demoulding, the specimens were cured in a damp chamber at 20 ± 2°C for 7, 28 and 56 days. Fig. 2 gives the strength development depending on type of Portland cements. It is seen that an increase in the content of CaO in cement resulted in a slight increase in the strength at all ages, but the benefits of CaO in enhancing the strength seemed marginal. It seemed that a reduction of the strength arising from a lower CaO in cement could be compensated to a certain range by a number of ways, including a lower W/C, refinement of aggregate and additional chemical admixtures. However, a dramatic reduction of CaO in cement may affect the concrete quality, implying that a further reduction of CaO in cement might induce unexpected defects such as a delay of hydration and high porosity in the cement matrix.

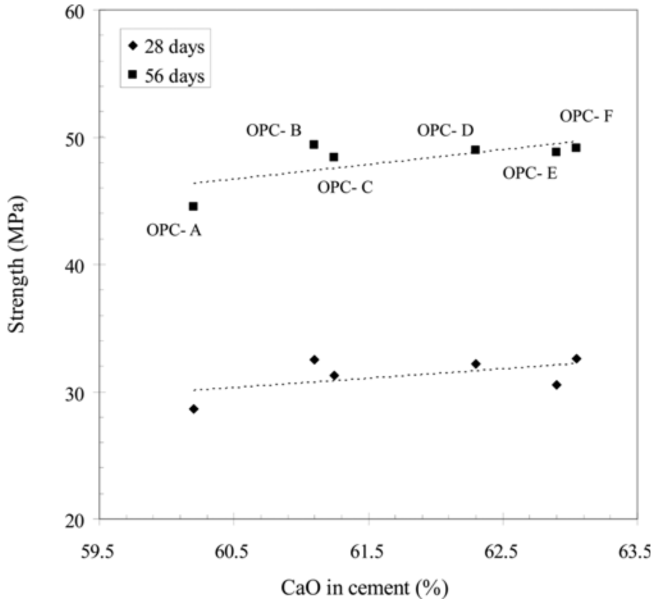

Fig. 2. Development of Strength with the Content of CaO in Cement

3. Emission of CO_2

3.1 Influence of Fossil Fuel

One of the main sources of the CO_2 emission in cement manufacture is the use of fossil fuel. The electricity is even less used due to its price, and the environmental loading is negligible, compared to fossil fuel, which is usually used in the burning process in the kiln. The amount of fossil fuel to produce cement can be dependent on the energy efficiency, production type (i.e. wet or dry process) and other facilitations. In this study, the raw material and energy consumed in Korean major cement companies were investigated. As a result, it was found that the amount of coal, in particular, ranged from 68.1 to 97.3 kg to produce one

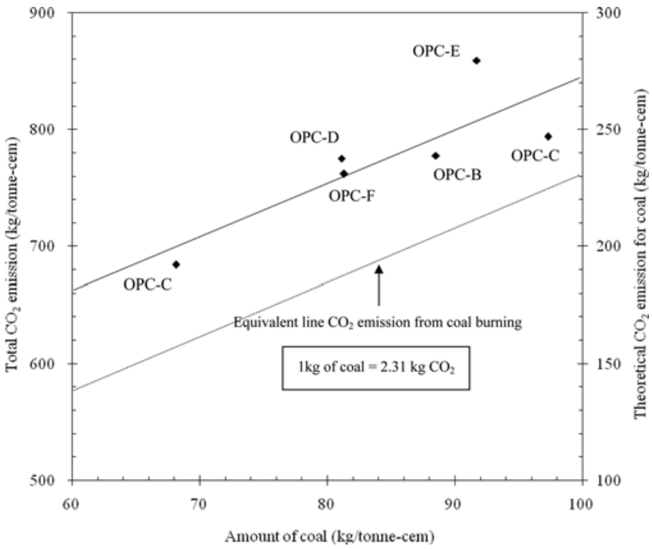

Fig. 3. Influence of the Use of Fossil Fuel (coal) on the CO_2 Emission

tonne of cement. Then, the relation between the use of coal and the total CO_2 emission was determined, assuming that coal is fully burned then to produce no other impurities except for CO_2 and ashes. Fig. 3 gives the influence of the use of coal in cement industry on the CO_2 emission. It is evident that an increase in the coal in cement production resulted in a significant increase in the CO_2 emission. As the burning of coal produces 2.31 kg CO_2/kg-coal, the margin of the CO_2 emission arising from the use of coal should be about within 68 kg CO_2/tonne-cem, considering the different amount of coal in use in each company. However, in fact, the difference in the total emission of CO_2 accounted for 180 kg CO_2/tonne-cem. This disaccord may arise from the other source of CO_2, such as CaO formation in cement. Notwithstanding, it must be remembered that the CO_2 emitted from the use of coal ranged from 157.2 to 224.4 kg CO_2/tonne-cem.

3.2 Decomposition of Calcium Carbonate

Decomposition of $CaCO_3$ in the burning process, as mentioned above, is the most dominant in emitting CO_2 gas. To secure the quality of cement, the content of CaO must be in the range of 60-65% in cement (Neville, 1996), and thus the CO_2 emission arising from CaO formation is inevitable. One tonne of $CaCO_3$ produces 440 kg of CO_2 and 560 kg of CaO, implying that 1.071 tonne of $CaCO_3$ at least is required to produce one tonne of cement containing 63% of CaO in the cement and the CO_2 gas simultaneously emits 495 CO_2/tonne-cem. Fig. 4 gives the CO_2 emission with the CaO content in cement manufactured by the six different companies. The CO_2 emission was even higher than the calculated value in a theoretical way, accounting for 730-912 kg/tonne-cem. In fact, the calculated CO_2 emission, when considering the CO_2 emission from the use of coal, ranged from 652.2 to 719.4 kg/tonne-cem, which is lower than real values by about 10.6-260 kg/tonne-cem, as being equivalent to 40% approximately of further emission at maximum. Moreover, no clear relation between the CO_2 emission and the CaO content in cement was observed. It may mean that another source of the CO_2 emission would be crucial rather than decomposition of $CaCO_3$ and fossil fuel, such as efficiency of raw material in terms of waste ratio of $CaCO_3$.

3.3 Optimised Process

Although the CO_2 emission is mainly governed by the decomposition of $CaCO_3$ in the burning process and fossil fuel, unexpected sources of CO_2, as mentioned, increase the CO_2 emission. Thus, in the present study, the waste ratio of $CaCO_3$ in terms of the loss of CaO in cement production was investigated, being related with the CO_2 emission. The loss of CaO was calculated by subtracting the real content of CaO in cement from the theoretical content of CaO at a given amount of $CaCO_3$. As seen in Table 1, the amount of $CaCO_3$ was different with each company although the CaO content in cement was in a similar range, implying that the loss of CaO in the process of cement manufacture would take place at a different ratio. As a result, the loss of CaO ranged from 8.7 to 23.6%, presumably leading to a huge difference in the CO_2 emission.

Then, the relation between the loss of CaO in cement production and CO_2 emission was depicted in Fig. 5. It is evident that an increase in the loss of CaO resulted in a dramatic increase in the CO_2 emission for all cases of cement manufacture. This information has an important implication in assessing the CO_2 emission. The loss of CaO in the process of manufacture may impose further unnecessary burning process and decomposition of $CaCO_3$, leading to a further generation of the CO_2 emission. For example, 20% of the loss of CaO in producing one tonne of cement may impose 214 kg of further $CaCO_3$, as being equivalent to 16 kg of fossil fuel and 120 kg of CaO for the unnecessary process and effort. Thus, CO_2 gas would be additionally emitted about 39 kg for the fossil fuel, and 94 kg for the CaO formation, respectively. It implies that the loss of CaO in cement production produces

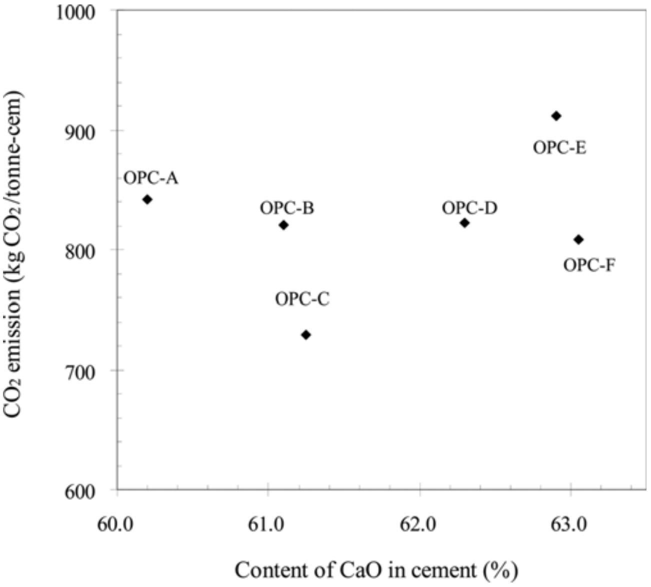

Fig. 4. Influence of the Content of CaO in Cement on the CO_2 Emission

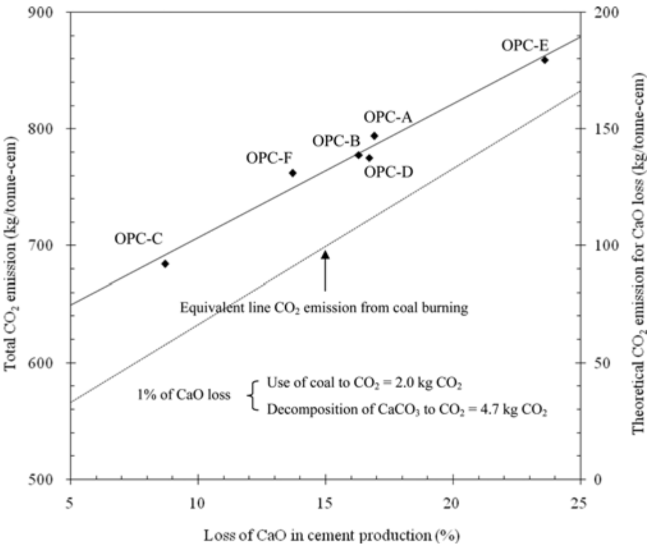

Fig. 5. Relation between the CO_2 Emission and the Loss of CaO in Cement Production

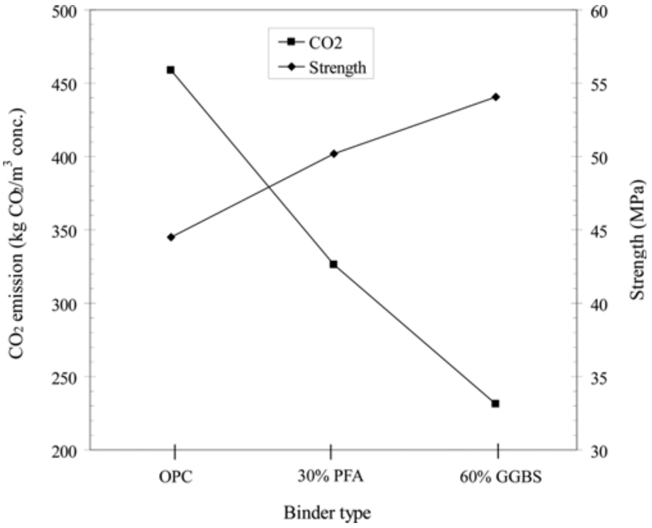

Fig. 6. CO_2 Emission and Strength Development in the Use of PFA and GGBSs

133 kg CO_2/tonne-cem. Therefore, it seems that a reduction of the loss of CaO would be the best option in lowering the CO_2 emission, as long as a replacement of non-CO_2 emission materials is applied.

4. Effect of Pozzolanic Materials

4.1 Production of Pozzolanic Materials

To mimic cementitious materials in construction of concrete structure, pozzolanic materials were used for Portland cement. For the concrete quality, Pulverised Fuel Ash (PFA) and Ground Granulated Blast Furnace Slag (GGBS) are well known about their competence against the aggressive environment. In particular, filling-up of pores, when PFA and GGBS are replaced for Portland cement, results in the denser pore structure, leading to a high durability against the penetration of external ions including sulfate and salt ions. Thus, these materials have already been used widely in concrete structures.

Moreover, these pozzolanic materials are produced by a refinement of waste byproducts. Thus the environmental loading would be significantly lower than Portland cement. As the production of PFA and GGBS simply consists of transportation and grinding to a certain level, the CO_2 emission is very low, compared to Portland cement. Table 3 gives the CO_2 emission and the economic expense to produce one tonne of binders in the Korean market. It is clear that the CO_2 emission for PFA and GGBS is even lower than for Portland cement: only 27 and 143 kg CO_2/tonne for PFA and GGBS are emitted by the grinding and refining process, whilst Portland cement generates 822 kg CO_2/tonne. The higher CO_2 emission and price for GGBS, compared to PFA, may be attributed to the grinding process, for which GGBS requires a finer grinding to meet the standard fineness modulus, accounting for about 4000 cm^2/g.

4.2 Reduction of CO_2 Emission

To ensure the benefits of pozzolanic materials in reducing the CO_2 emission together with concrete quality, in the present study, the CO_2 emission was calculated by testing a sample mortar, and the strength was measured at 56 days to ensure the hydration of pozzolanic materials. OPC-A was used for Portland cement. The replacement ratio for Portland cement was 30% with PFA and 60% with GGBS respectively. The transportation and manufacture of aggregate was removed from the calculation of the CO_2 emission in producing 1.0 m^3 of mortar/concrete.

Table 3. CO_2 Emission in Producing PFA and GGBS, together with their Economic Expense

	Portland cement	PFA	GGBS
CO_2 (kg CO_2/tonne)	822	27	143
Expense* (USD)	54.5	45.5	29.1

*The expense is the sale price in market.

As a result, a replacement with PFA and GGBS reduced the CO_2 emission, while the strength was increased. The reduction of CO_2 emission for 30% PFA and 60% GGBS was 28.9 and 49.6% respectively, compared to Portland cement. The greater reduction of CO_2 in 60% GGBS is attributed to a larger replacement than PFA, despite the higher emission of CO_2 in the manufacture process. The strength for 30% PFA and 60% GGBS was also higher than for Portland cement by 12.7 and 21.5% respectively, compared to Portland cement. The price for the mortar/concrete can be calculated, using information in the Table 3. The economic saving for 30% PFA and 60% GGBS is expected about 10.0-13.9% against Portland cement. Consequently, these pozzolanic materials may have the benefit in both reducing the CO_2 emission and in securing the quality of concrete.

5. Conclusions

To evaluate the CO_2 emission in the cement industry, an investigation on cement raw materials, energy sources and strength was performed. All information was achieved from Korean six major manufacturers. Thus, the influence of decomposition of $CaCO_3$ and fossil fuel in use on the CO_2 emission was investigated. Simultaneously, the benefits of pozzolanic materials in reduction the CO_2 emission were assessed. The following is achieved conclusion.

1. The content of CaO in cement has a marginal influence on the strength development within the range of 60.2-63.1% an increase in the CaO content resulted in a slight increase in the strength. However, there was no relation of the CaO content in cement with the CO_2 emission, due to more significant factors to CO_2 generation.
2. The use of fossil fuel, in particular, the amount of coal was crucial to the emission of CO_2. An increase in the amount of fossil fuel for the burning process resulted in an increase in the CO_2 emission. This suggests that an effective energy control may reduce the emission of CO_2.
3. The most dominant factor to the CO_2 emission was the loss of CaO in the burning process for $CaCO_3$. An increase in the loss of CaO resulted in a dramatic increase in the CO_2 emission. For example, 20% of the loss of CaO may impose

about 133 kg CO_2/tonne-cem of the further emission, due to the unnecessary burning process and a further decomposition of $CaCO_3$ to CaO and CO_2.

4. The PFA and GGBS have benefits in reducing the CO_2 emission together with concrete quality. When 30% PFA and 60% GGBS is used as binder in a concrete mix, the CO_2 emission is reduced by about 28.9 and 49.6% respectively, compared to Portland cement, due to their simple, non-emitting manufacture processes. In fact refinement processes for the pozzolanic materials impose even lower emission of CO_2.

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References

Flower, D. J. M. and Sanjayan, J.G. (2007). “Greenhouse gas emission due to concrete manufacture.” *The International Journal of Life Cycle Assessment*, Vol. 12, No. 5, pp. 282-288.

Gartner, E. (2004). “Industrially interesting approaches to low CO_2 cements.” *Cement and Concrete Research*, Vol. 34, No. 9, pp. 1489-1498.

GreenBiz (2009). *World's largest cement firms slow CO_2 emissions despite production growth*, Green Biz.

Hendriks, C.A., Worrell, E., Jager, D., Blok, K., and Riemer, P. (2004). “Emission reduction of greenhouse gases from the cement industry.” *Greenhouse Gas Control Technologies Conference*, London, UK.

Ismail, M., Ismail, M.E., and Muhammad, B. (2011). “Influence of elevated temperatures on physical and compressive strength properties of concrete containing palm oil fuel ash.” *Construction and Building Materials*, Vol. 25, pp. 2358-2364.

Korean Cement Association (2009). *Cement statistics report*, Korea.

Neville, A. M. (1996). *Properties of concrete*, Wiley, New York.

Nowak, R. (2008). “Geopolymer concrete opens to reduce CO_2 emissions.” *The New Scientist*, Vol. 197, pp. 28-29.

Roskovic, R. and Bjegovic, D. (2005). “Role of mineral additions in reducing CO_2 emission.” *Cement and Concrete Research*, Vol. 35, No. 5, pp. 974-978.

Sheinbaum, C and Ozawa, L. (1998). “Energy use and CO_2 emission for Mexico's cement industry.” *Energy*, Vol. 23, No. 9, pp. 725-732.

The Research Council of Norway (2010). *Combustion residue lowers carbon dioxide emissions in concrete*, Norway.

Zhang, M. H., Lastra, R., and Malhotra, V. M. (1996). “Rice-husk ash paste and concrete: Some aspects of hydration and the microstructure of the interfacial zone between the aggregate and paste.” *Cement and Concrete Research*, Vol. 26, Issue 6, pp. 963-977.