Third International Conference on Sustainable Construction Materials and Technologies http://www.claisse.info/Proceedings.htm

Study of Environmentally Friendly Concrete Using Limestone Powder as an Admixture

Shohei Kimura, Toyokazu Nishida, Hideaki Nakayama, and Noboru Takao

Mitsubishi Materials Corporation, Japan

[*]2270 Yokoze, Yokoze-machi, Chichibu-gun, Saitama, 368-8504, JAPAN

shkimura@mmc.co.jp, t-nisida@mmc.co.jp, h-naka@mmc.co.jp, takao@mmc.co.jp

ABSTRACT

Using limestone powder to replace cement binder is considered an effective method to reduce carbon dioxide emissions from cement production. This study focuses on the relationship between replacement levels of limestone powder for ordinary portland cement or the base cement of slag cement and carbon dioxide reduction. Using limestone powder as an admixture decreases compressive strength; thus, the water-binder ratio should be decreased in order to obtain the equivalent strength of plain cement. However, strength development of the ordinary portland cement-blast furnace slag-limestone powder ternary system is higher than that of the portland cement-limestone powder binary system. Therefore, the advantage of reduced carbon dioxide emission for the ternary system is higher than for the binary system. The maximum reduction ratios of carbon dioxide were 5.9% for the binary system and 16.7% for the ternary system.

Keywords: Environmentally friendly concrete, Limestone powder, Portland cement, Blast furnace slag, Compressive strength

INTRODUCTION

Carbon dioxide gas emission from cement production is the result of the burning process and decarbonation of limestone, a cement material. Reducing carbon dioxide is a global challenge, and cement industries as well as other industries are required to reduce carbon dioxide emission. However, the energy efficiency of cement industries in Japan is the top-level in the world (JCA, 2012), so it is difficult to improve their energy efficiency. Thus, it seems that carbon dioxide capture and storage technology, low-temperature burning technology, and increased admixture content of cement are effective methods of reducing carbon dioxide. In particular, increasing the admixture content of cement is an immediately effective method because it decreases clinker. Limestone powder (LS) is an admixture that is obtained simply by grinding limestone. Therefore, producing LS does not require as much energy as for producing cement, and using LS would effectively reduce carbon dioxide. Increasing the replacement level of LS for cement may decrease carbon dioxide. However, studies focusing on the relationship between reduced carbon dioxide and LS content under equal compressive strength are lacking. In this study, the influence of reduction carbon dioxide on replacing LS to binder was estimated under equivalent compressive strength concrete. First, the relationship between compressive strength and replacement level of LS was investigated to clarify the potential carbon dioxide reduction. In concrete tests, the reduction of carbon dioxide was calculated in concrete with equivalent compressive strength using LS -blended cement.

MORTAR TEST

First, the relationship between the replacement level of LS and compressive strength was investigated on mortar test.

Materials Used. Table 1 indicates the materials used, and Table 2 presents the chemical analysis of ordinary Portland cement (OPC) and blast furnace slag (GGBFS). This study investigated binary OPC-LS (OPC-LS series) and ternary OPC-GGBFS-LS (BFS-LS series) blended cement, and plain OPC and binary OPC-GGBFS were investigated as references. The OPC was a commercial product. Replacement levels of LS were 0, 10, 20, and 30% of OPC in binder. The replacement level of the BFS-LS series was 44%. Blended binders were blended using a V mixer. The SO_3 content in binders was adjusted to 2.3% for the OPC-LS series and to 1.4% for the BFS-LS series using a test reagent of gypsum. The sand used was natural silica (JIS R 5209).

Table 1. Materials Used

<table>
<tr><th>Type</th><th>Name</th><th>Symbol</th><th colspan="2">Note</th></tr>
<tr><td rowspan="8">Cement</td><td>Ordinary Portland Cement</td><td>OPC-LS0%</td><td colspan="2">Density: 3.16/cm^3</td></tr>
<tr><td rowspan="3">Limestone Powder-Blended Cement</td><td>OPC-LS10%</td><td colspan="2">Replaced 10% of OPC with LS</td></tr>
<tr><td>OPC-LS20%</td><td colspan="2">Replaced 20% of OPC with LS</td></tr>
<tr><td>OPC-LS30%</td><td colspan="2">Replaced 30% of OPC with LS</td></tr>
<tr><td>Slag Cement</td><td>BFS-LS0%</td><td>OPC56%</td><td rowspan="4">GGBFS44%</td></tr>
<tr><td rowspan="3">Limestone Powder-Blended Slag Cement</td><td>BFS-LS10%</td><td>Replaced 10% of OPC with LS</td></tr>
<tr><td>BFS-LS20%</td><td>Replaced 20% of OPC with LS</td></tr>
<tr><td>BFS-LS30%</td><td>Replaced 30% of OPC with LS</td></tr>
<tr><td colspan="2">Ground Granulated Blast-Furnace Slag</td><td>GGBFS</td><td colspan="2">Blaine Surface Area: 3900cm^2/g</td></tr>
<tr><td colspan="2">Limestone Powder</td><td>LS</td><td colspan="2">Blaine Surface Area: 5000cm^2/g</td></tr>
<tr><td>Fine Aggregate</td><td>Natural Silica Sand</td><td>S</td><td colspan="2">JIS R 5209</td></tr>
<tr><td>Chemical Admixture</td><td>Air Entraining and Water Reducing Agent</td><td>Ad</td><td colspan="2">Complex of lignin sulfonic acid and polyol</td></tr>
</table>

Test Procedure. The test items are presented in Table 3. Regarding the mixture design of mortar, quantity of chemical admixture was 0.25% of weight of powder. The target value of mortar flow was 235±10mm and air content was 4.5±1.0%

Results and Discussion. The relationship between powder-water ratio and compressive strength is presented in Fig. 1. In mortar test, target compressive strength was 50N/mm^2 .In order to obtain the target compressive strength of 50N/mm^2, the water-cement ratio should be 55% for OPC-LS0% and 52% for BFS-LS0%. The mixture design by weight ratio for equal mortar flow and compressive strength is presented in Tables 4 and 5. Replacing OPC with LS decreases compressive strength, and it is necessary to decrease the water-cement ratio to obtain equal strength for OPC-LS0% or BFS-LS0% control mortar. Replacing LS in cement decreases compressive strength by the dilution effect (P. Thongsanitgam, 2011). However, the water-powder ratio to obtain equal strength for the BFS-LS series was higher than for the OPC-LS series at all LS replacement levels. Regarding the ternary OPC-GGBFS-LS system, aluminate hydrates produced by the reaction of GGBFS and LS fill the pores of matrix and increase strength (S. Hoshino, 2006). This study assumes that a similar effect increases compressive strength in the BFS-LS series.

Table 2. Chemical Analysis of Cement and Slag

Symbol	Chemical Analysis (%)													
	ig.loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	S^{2-}	Na_2O	K_2O	TiO_2	MnO	P_2O_5	Total
OPC	3.92	18.59	5.15	2.84	63.47	0.99	2.30	-	0.21	0.32	0.27	0.08	0.12	98.24
GGBFS	-	33.64	15.07	0.35	41.84	5.80	-	0.97	0.15	0.25	0.58	0.22	0.01	98.78

Table 3. Test Items (Mortar Test)

Test	Method
Mortar Flow	JIS R 5201:1997
Air Content	Calculate from unit weight
Compressive Strength	JIS A 1108:2006

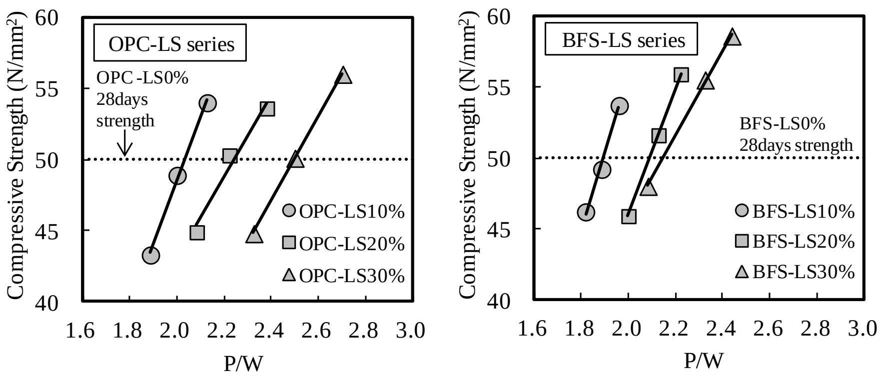

Fig. 1. Relationship between Compressive Strength and Powder-Water Ratio

Table 4. Mortar Proportions to Obtain Equal Flow and Strength (OPC-LS series)

Symbol	W/P (%)	Weight Ratio			
		OPC	LS	W	S
OPC-LS0%	55	1.82	-	1.00	5.45
OPC-LS10%	49	1.84	0.21	1.00	5.72
OPC-LS20%	45	1.77	0.44	1.00	5.55
OPC-LS30%	40	1.75	0.75	1.00	5.00

Table 5. Mortar Proportions to Obtain Equal Flow and Strength (BFS-LS series)

Symbol	W/P (%)	Weight Ratio				
		OPC	LS	GGBFS	W	S
BFS-LS0%	52	1.08	-	0.84	1.00	5.57
BFS-LS10%	50	1.01	0.11	0.88	1.00	6.00
BFS-LS20%	48	0.93	0.23	0.92	1.00	5.62
BFS-LS30%	47	0.84	0.36	0.94	1.00	5.53

CARBON DIOXIDE EMISSION OF MORTAR

Specific Carbon Dioxide Consumption. In order to clarify the effect of reduced carbon dioxide, the specific carbon dioxide consumption of mortar using LS-blended cement was calculated. The specific carbon dioxide consumption from producing OPC and milling LS was calculated. The carbon dioxide from GGBFS was not considered.

$$CO_{2total} = X\ CO_{2OPC} + Y\ CO_{2LS} \quad (1)$$

CO_{2total} Specific CO_2 consumption from binder (kg/ton)

CO_{2OCP} Specific CO_2 consumption from producing OPC (kg/ton)

CO_{2LS} Specific CO_2 consumption from grinding LS (kg/ton)

X Replacement ratio of OPC in binder (%)

Y Replacement ratio of LS in binder (%)

The specific carbon dioxide consumption of producing OPC adduced Life Cycle Inventory of OPC was quoted from the report of Japan Cement Association(JCA, 2012). The specific carbon dioxide consumption from grinding LS was calculated from the proportional relationship between the energy and grinding work index and the Blaine surface area. Carbon dioxide consumption from grinding OPC clinker (k) was determined to be 18 by

Table 6. Life-Cycle Inventory of Ordinary Portland Cement

Origin	CO_2 Emission (kg/ton)
Decarboxylation of limestone	467.7
Burning of fossil fuel	298.2
Total	765.9

reference to the previous study of Morioka (M. Morioka, 2002). The grinding work index was decided from typical values ($W.I._{LS}$ = 12.74, $W.I._{OPC}$ = 13.45) because grinding work indices differ by locality and grinding plant.

$$CO_{2LS} = k(W.I._{LS}/W.E._{OPC}) \times (BL_{LS}/BL_{OPC})^{1.3} \quad (2)$$

CO_{2LS}	Specific CO_2 consumption from grinding LS (kg/ton)
K	Specific CO_2 consumption from grinding clinker of OPC (kg/ton)
$W.I._{LS}$	Work index of grinding LS (kWh/ton)
$W.I._{OPC}$	Work index of grinding clinker of OPC (kWh/ton)
BL_{LS}	Blaine surface area of LS ($5000cm_2/g$)
BL_{OPC}	Blaine surface area of OPC ($3680cm_2/g$)

Carbon dioxide consumptions of LS-blended cement are presented in Tables 7 and 8. Blending with LS decreases carbon dioxide consumption by reducing clinker content.

Table 7. Specific CO_2 Consumption of Binder (OPC-LS series)

Symbol	Replacement Ratio of LS (%)	Specific CO_2 consumption (kg/ton-cem)			Decreasing Ratio (%)
		CO_{2OPC}	CO_{2LS}	CO_{2total}	
OPC-LS0%	-	776.6	0	776.6	-
OPC-LS10%	10	718.3	2.9	721.2	9.3
OPC-LS20%	20	638.5	5.9	644.4	17.1
OPC-LS30%	30	558.7	8.8	567.5	27.0

Table 8. Specific CO_2 Consumption of Binder (BFS-LS series)

Symbol	Replacement Ratio of LS (%)	Specific CO_2 consumption (kg/ton-cem)			Decreasing Ratio (%)
		CO_{2OPC}	CO_{2LS}	CO_{2total}	
BFS-LS0%	-	465.9	0	465.9	-
BFS-LS10%	10	431.0	1.8	432.7	7.2
BFS-LS20%	20	383.1	3.5	386.6	17.1
BFS-LS30%	30	335.2	5.3	340.5	27.0

Carbon Dioxide Emission of Mortar. The carbon dioxide emissions from producing $1m^3$ mortar with equal compressive strength ($50N/mm^2$) using several binders are presented in Fig. 2. The carbon dioxide emissions were calculated from Tables 4, 5 and Tables 7, 8. For the OPC-LS series, carbon dioxide emission decreased with increased LS replacement levels up to 20%. However, the carbon dioxide emission of OPC-LS30% exceeded that of OPC-LS20%. The unit powder content of OPC-LS30% increased because the water-cement ratio to obtain strength equal to that of the control decreased. Thus, the carbon dioxide emission of OPC-LS30% exceeded that of OPC-LS20%. However, the BFS-LS series decreased carbon dioxide emission with increased LS replacement at all replacement levels of LS because the strength developed in the BFS-LS series exceeded that of the OPC-LS series.

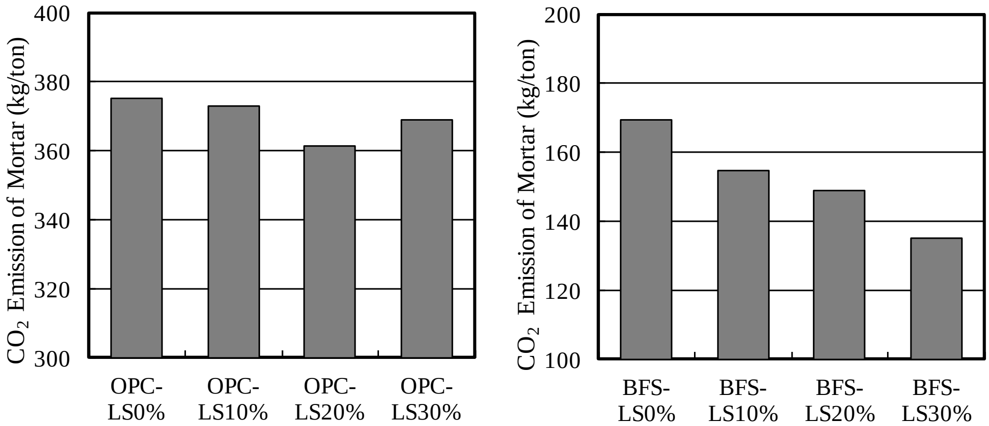

Fig. 2. CO_2 Emission of Mortar

CONCRETE TEST

The concrete properties using LS-blended binder were investigated. First, the relationship between powder-water ratio and compressive strength of concrete using LS-blended binder was investigated, and the water-powder ratio to obtain 28-day compressive strength equal to that of using plain binder (LS0%) was selected. The reduction of carbon dioxide emission was estimated for concretes of equal compressive strength. For the OPC-LS series, OPC-LS10% and OPC-LS20% were investigated because the advantage of carbon dioxide emission of OPC-LS30% was less than that of OPC-LS20% in the mortar test results. For the BFS-LS series, BFS-LS20% and BFS-LS30% were investigated because of the increased advantage of carbon dioxide emission with increased LS replacement levels.

Materials Used. The materials used are presented in Table 9.

Test Procedure. Table 10 lists test items. The target slump was 18±1.0cm for the OPC-LS series and 12±1.0cm for the BFS-LS series. The target air content was 4.5±1.0%.

Results and Discussion. The relationships between powder-water ratio and 28-day compressive strength of concrete are presented in Figs. 3 and 4. Blending with LS decreased the powder-water ratio to obtain 28-day compressive strength equal to that of LS0%. The mixture design of concrete to obtain 28-day compressive strength equal to that of LS0% is presented in Table 11. Fresh properties and compressive strength until 91 days are presented in Figs. 5 and 6. The strength development up to 56 days was similar for the two series. However, 91-day compressive strength for BFS-LS30% decreased compared to that for other BFS-LS series. GGBFS increased 90-day compressive strength, whereas LS decreased it (M. F. Carraso, 2005). These results indicate that replacing 30% of the base cement of the OPC-GGBFS system with LS decreases 91-day compressive strength even though the 28-day compressive strengths were equivalent.

Table 9. Materials Used

Type	Name	Symbol	Note	
Cement	Ordinary Portland Cement	OPC-LS0%	Density: 3.16/cm^3	
	Limestone Powder-Blended Cement	OPC-LS10%	Replaced 10% of OPC with LS	
		OPC-LS20%	Replaced 20% of OPC with LS	
	Slag Cement	BFS-LS0%	OPC 56%	GGBFS 44%
	Limestone Powder-Blended Slag Cement	BFS-LS20%	Replaced 20% of OPC with LS	
		BFS-LS30%	Replaced 30% of OPC with LS	
Ground Granulated Blast-Furnace Slag		GGBFS	Blaine Surface Area: 3900cm^2/g	
Limestone Powder		LS	Blaine Surface Area: 5000cm^2/g	
Fine Aggregate	Pit Sand	S	SSD Density: 2.64g/cm^3, Absorption: 1.38%	
Coarse Aggregate	Crushed Stone	G1	SSD Density: 2.72g/cm^3, Absorption: 0.51%	
	Crushed Stone	G2	SSD Density: 2.72g/cm^3, Absorption: 0.70%	
Chemical Admixture	Air Entraining and Water Reducing Agent	Ad	Complex of lignin sulfonic acid and polyol	

Table 10. Test Items (Concrete Test)

Test	Method	Measuring Ages
Slump	JIS A 1101:2005	-
Air Content	JIS A 1128:2005	
Concrete Temperature	JIS A 1156:2006	
Compressive Strength	JIS A 1147:2006	Test ages: 7, 28, 56, and 91days

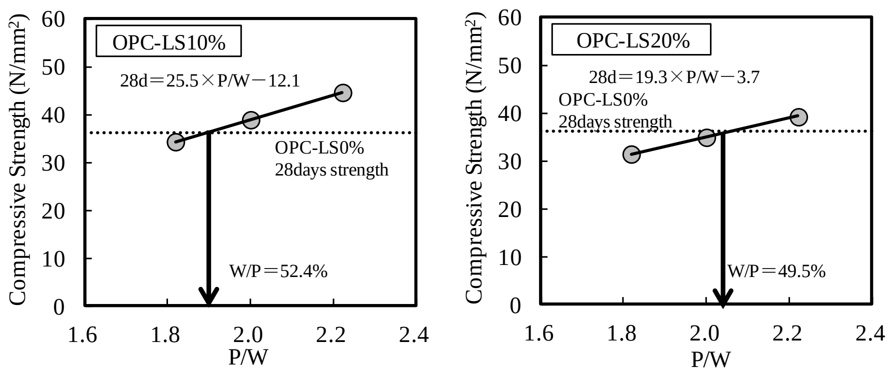

Fig. 3. Relationship between Strength and Powder- Water Ratio (OPC-LS series)

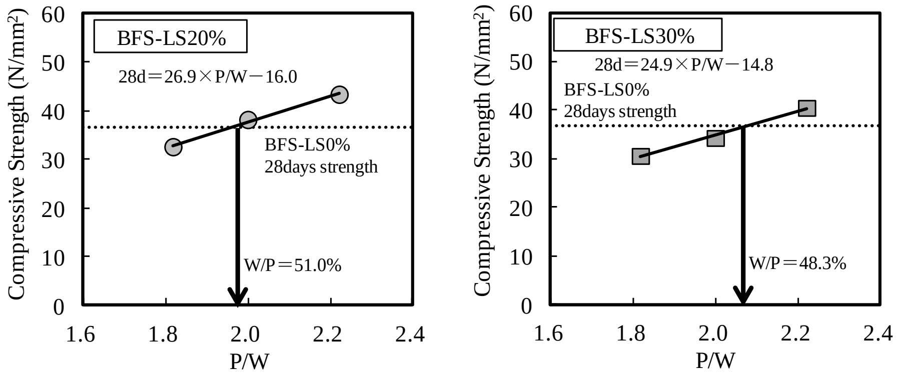

Fig. 4. Relationship between Strength and Powder-Water Ratio (BFS–LS series)

Table 11. Concrete Proportions to obtain equal Strength of OPC-LS0% and BFS-LS0%

Symbol	W/P (%)	s/a (%)	Unit Weight (kg/m^3)				Ad (P x %)
			OPC	GGBFS	LS	W	
OPC-LS0%	55.0	45.0	299	-	-	168	0.25
OPC-LS10%	52.4	44.0	289	-	32		
OPC-LS20%	49.5	42.0	271	-	68		
BFS-LS0%	55.0	45.0	158	124	-	155	0.25
BFS-LS20%	51.0	43.5	136	134	34		
BFS-LS30%	48.3	42.0	126	141	54		

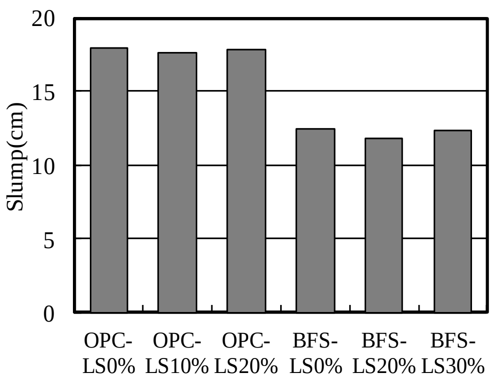

Fig. 5. Slump

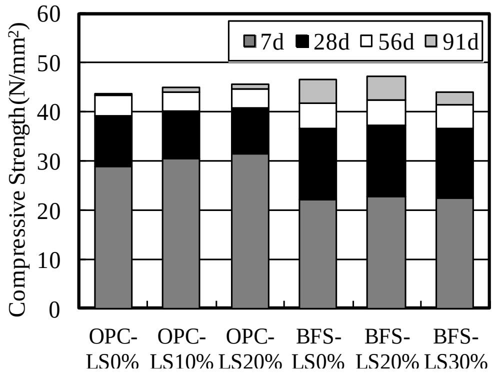

Fig. 6. Compressive Strength

CARBON DIOXIDE EMISSION OF CONCRETE

Carbon Dioxide Emission of Concrete. The carbon dioxide emissions from producing equal-strength concrete are presented in Fig. 7. The carbon dioxide emissions were calculated by specific CO_2 consumption of binder in Tables 7, 8 and unit weight of binder in Table 11. The percentages in Fig. 7 are decreasing ratios of carbon dioxide emission. The result indicates that the maximum decreasing ratio is 5.9% for the OPC-LS series and 16.7% for the BFS-LS series. Therefore, when the replacement level is the same (LS20%), the advantage of decreased carbon dioxide emission is higher for the BFS-LS series.

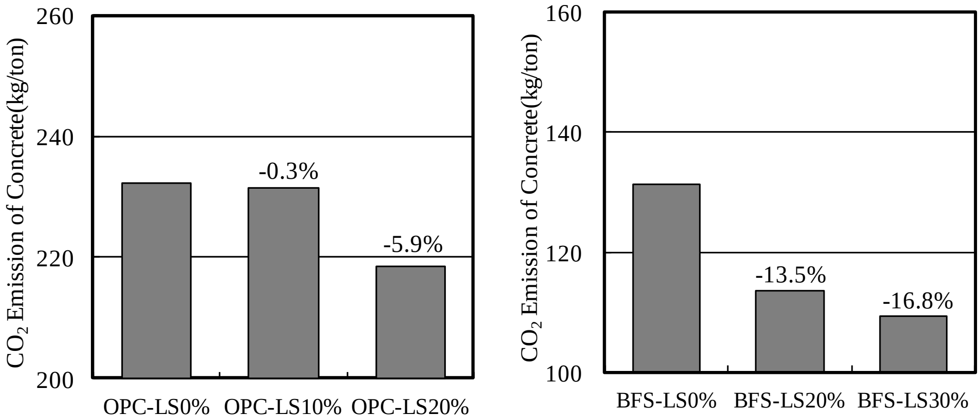

Fig. 7. CO_2 Emission of Concrete

CONCLUSIONS

This study reports the advantage of reduced carbon dioxide emission using OPC blended with blast furnace slag and limestone powder. The following conclusions can be drawn from the obtained experiment data.

(1) For the OPC-LS binary system, compressive strength is decreased by the dilution of clinker, and the water-powder ratio should be decreased to obtain equal-strength concretes. Thus, reduction of carbon dioxide emission is confirmed for replacement levels up to 20%. For a limestone powder replacement level of 30%, the advantage of carbon dioxide emission reduction is less than 20%.

(2) For the OPC-GGBFS-LS ternary system, compressive strength is decreased by the dilution of clinker. However, the water-powder ratio to obtain equal-compressive strength concrete is higher than for the OPC-LS binary system. Thus, the advantage of reduced carbon dioxide emission increases with increased replacement levels of limestone powder up to 30%.

(3) The maximum reduction ratios of carbon dioxide emission of concrete using LS-blended cement are 5.9% for the OPC-LS binary system and 16.7% for the OPC-GGBFS-LS ternary system. Thus, the replacement of cement with limestone effectively reduces carbon dioxide emission from concrete, and the advantage of reduced carbon dioxide emissions is higher for the OPC-GGBFS-LS ternary system than for the OPC-LS binary system.

REFERENCES

Japan Cement Association (2012). "Carbon Dioxide Emission and Energy Efficiency of Cement Industries in the World." *http://www.jcassoc.or.jp/cement/1jpn/jg1f.html*.

Japan Cement Association (2012). "Brief of Life-Cycle Inventory Data of Cement ." *http://www.jcassoc.or.jp/cement/4pdf/jg1i_01.pdf*.

M.Morioka, T.Higuchi, M.Takahashi and E.Sakai. (2002). " Charactarictics and ecological evaluation of 32.5N/mm2 grade cement using slowly cooled blast furnace slag powder "*Cement Science and Concrete Technology*, 56,79-84. (in Japanese)

M.F.Carrasco, G.Menendez, V.Bonavetti and E.F. Irassar (2005). "Strength optimization of “tailor-made cement” with limestone powder and blast furnace slag" Cement and Concrete Research, 35,1324-1331

P.Thongsanitgarn, W.Wongkeo, S.Sinthupinyo and A.Chaipanich (2011). "Effect of Limestone Fillers on Compressive Strength and Setting Time of Portland-Limestone Cement Pastes." *TIChE International Conference 2011*.

S.Hoshino, K.Yamada and H. Hirao (2006). "XRD/Reitveld Analysis of the Hydration and Strength Development of Slag and Limestone Blended Cement."*Journal of Advanced Concrete Technology*, 4,357-367.