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Original Article

Properies of binder systems containing cement, fly ash, and limestone powder

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Abstract

Fly ash and limestone powder are two major widely available cement replacing materials in Thailand. However, the current utilization of these materials is still not optimized due to limited information on properties of multi-binder systems. This paper reports on the mechanical and durability properties of mixtures containing cement, fly ash, and limestone powder as single, binary, and ternary binder systems. The results showed that a single binder system consisting of only cement gave the best carbonation resistance. A binary binder system with fly ash exhibited superior performances in long-term compressive strength and many durability properties except carbonation and magnesium sulfate resistances, while early compressive strength of a binary binder system with limestone powder was excellent. The ternary binder system, taking the most benefit of selective cement replacing materials, yielded, though not the best, satisfactory performances in almost all properties. Thus, the optimization of binders can be achieved through a multi-binder system.

Keywords: cement replacing materials, multi-binder, fly ash, limestone powder, durability, mechanical properties

1. Introduction

The cement industry was reported to produce 5% of global man-made CO_2 emissions, of which 50% are from chemical processes and 40% from burning fuel (World Business Council for Sustainable Development, 2002). In addition, it is commonly known that the manufacturing of conventional cement is extremely CO_2 intensive; production of one ton of cement clinker results in approximately one ton of CO_2 released into the Earth's atmosphere. The concrete industry worldwide has realized this matter and has been seeking new solutions. Pozzolans, natural or industrial by-products, have been used extensively as cement replacing materials in the past decades. Cement replacing materials help reducing the proportion of cement in concrete, and at the same time they also can improve the properties of concrete in several ways. Besides pozzolans, finely ground inert material known as filler is also used widely. Recently, the use of more than one type of cement replacing materials in concrete, called ternary, quaternary, or multi binder concrete, has globally grown because they present some advantages over the binary binder concrete (Tahir and Önder, 2008; Mehmet *et al.*, 2009; Bassuoni and Nehdi, 2009; Bun *et al.*, 2010).

In Thailand, fly ash is one of the most popular pozzolans. Fly ash concrete has become practically common. Limestone powder is another material that has a bright future in the concrete industry in Thailand due to its main benefits, especially early strength. The global trend of ternary binder concrete is gaining popularity in Thailand since it is one of the optimized ways of cement replacing material usage. This paper focuses mainly on compressive strength, slump and slump loss, and durability properties of mixtures composed of cement, fly ash, and limestone powder as single, binary, and ternary binder systems.

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2. Experiment

2.1 Materials

Three particle sizes of limestone powder were used in this research. Limestone powder with average particle diameter (d_{50}) of 2, 4, and 11 μm are referred hereafter as LP#02, LP#04, and LP#11, respectively. Ordinary Portland cements type I, type V, and fly ash from the Mae Moh Power Plant in Northern Thailand were used. The chemical compositions and physical properties of ordinary Portland cement type I, ordinary Portland cement type V, Mae Moh fly ash, and limestone powder are shown in Table 1. Figure 1 illustrates the particle size distribution of the ordinary Portland cement type I, Mae Moh fly ash, and limestone powders. River sand complying with ASTM C33-92a and crushed limestone with a maximum size of 20 mm were used as the fine and coarse aggregates, respectively. Specific gravity of the river sand was 2.60 and that of the crushed limestone was 2.70.

2.2 Experimental programs

2.2.1 Compressive strength and slump

The mix proportions were designed to capture the effect of binder content and size of limestone powder on different binder system concrete. Binder contents of 258 kg/m^3 and 354 kg/m^3 were selected since they represent ranges of widely used concrete mix proportions in Thailand. Two different sizes of limestone powder, namely LP#02 and LP#11 were used. The replacement percentages were 30% of total binder weight for binary binder concrete with fly ash and 10% of total binder weight for binary binder concrete with limestone powder. In the case of ternary binder concrete, the contents of cement, fly ash, and limestone powder were 70%, 20%, and 10% by weight of total binders, respectively.

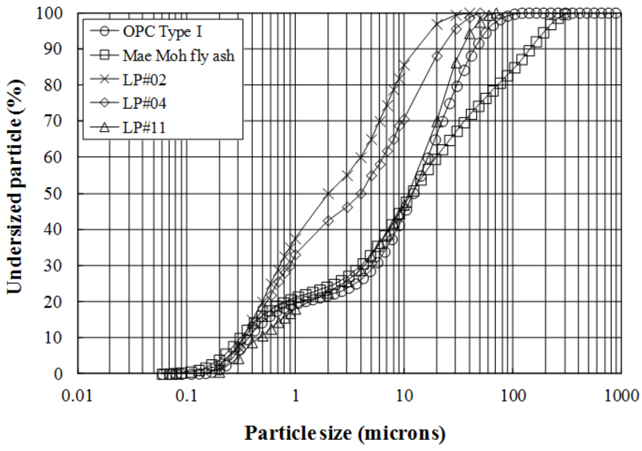

Figure 1. Particle size distribution of ordinary Portland cement type I, Mae Moh fly ash, and limestone powders.

For slump tests, concrete with binder content of 300 kg/m^3 was studied. The contents of LP#11 were 5% and 10% by weight of total binders in both binary binder concrete with limestone powder and ternary binder concrete, whereas binary binder concrete with fly ash contained fly ash content of 30% by weight of total binders. Mix proportions of

Table 1. Chemical compositions and physical properties of ordinary Portland cement type I, ordinary Portland cement type V, Mae Moh fly ash, and limestone powder.

Properties	Ordinary Portland Cement type I	Ordinary Portland Cement type V	Mae Moh Fly Ash	Limestone Powder
Chemical compositions (%)				
SiO_2	20.20	20.97	36.1	0.06
Al_2O_3	4.70	3.49	19.4	0.09
Fe_2O_3	3.73	4.34	15.1	0.04
CaO	63.40	62.86	17.4	54.80
MgO	1.37	3.33	2.97	0.57
SO_3	1.22	2.12	0.77	-
Na_2O	-	0.12	0.55	-
K_2O	0.28	0.47	2.17	-
LOI	2.72	1.21	2.81	43.80
Physical properties				
Specific gravity	3.11	3.18	2.44	2.70
Blaine fineness (cm^2/g)	3430	3727	2460	LP#02, 9260 LP#04, 8530 LP#11, 3320
d_{50} (mm)	11	n.a.	11	LP#02, 2 LP#04, 4 LP#11, 11

concrete mixtures for compressive strength and slump tests are shown in Table 2 and 3, respectively.

2.2.2 Durability properties

This part focused on durability properties of mixtures with cement, fly ash, and limestone powder as different types of binder systems, i.e. single, binary, and ternary. The properties in terms of autogenous and drying shrinkages, carbonation depth, chloride resistance, sulfate resistance were studied. Three different sizes of limestone powder, namely LP#02, LP#04, and LP#11 were used. The proportion of fly ash in binary binder system was 30% of total binder weight for all tests except for sulfate resistance tests which was 40% of total binder weight. The proportion of limestone powder was 10% by weight of total binders, both in cases of binary and ternary binder systems for all tests with the exception in chloride resistance test, which was reduced to 5% by weight of total binders.

Both autogenous and drying shrinkage tests were conducted on pastes with water to binder ratio of 0.30 and the tested specimens were bars with the dimensions of 2.5x 2.5x28.5 cm. Autogenous shrinkage specimens were demolded after final setting time, sealed all sides by aluminum foil and plastic sheet and then kept in a chamber with control temperature of 28±2°C and relative humidity of 50±5% while drying shrinkage specimens were cured in water for 7 days and subjected to drying conditions at a temperature of 28± 2°C and relative humidity of 50±5%. The length change of the bars was continuously monitored.

Table 2. Mix proportions of concrete for compressive strength test.

Mix designation	w/b	Cement (kg/m^3)	Fly ash (kg/m^3)	Limestone powder (kg/m^3)		Water (kg/m^3)	Sand (kg/m^3)	Gravel (kg/m^3)
				LP#02	LP#11			
I-C100	0.72	258	0	0	0	185	808	1,111
I-C95LP#02 5	0.72	245	0	13	0	185	807	1,110
I-C90LP#02 10	0.72	232	0	26	0	185	806	1,110
I-C95LP#11 5	0.72	245	0	0	13	185	808	1,111
I-C90LP#11 10	0.72	232	0	0	26	185	807	1,110
I-C70FA30	0.72	181	77	0	0	185	806	1,110
I-C70FA25LP#02 5	0.72	181	65	13	0	185	799	1,100
I-C70FA20LP#02 10	0.72	181	52	26	0	185	799	1,100
I-C70FA25LP#11 5	0.72	181	65	0	13	185	800	1,102
I-C70FA20LP#11 10	0.72	181	52	0	26	185	799	1,100
II-C100	0.53	354	0	0	0	188	736	1,100
II-C95LP#02 5	0.53	336	0	18	0	188	735	1,098
II-C90LP#02 10	0.53	319	0	35	0	188	734	1,096
II-C95LP#11 5	0.53	336	0	0	18	188	736	1,100
II-C90LP#11 10	0.53	319	0	0	35	188	735	1,098
II-C70FA30	0.53	248	106	0	0	188	734	1,096
II-C70FA25LP#02 5	0.53	248	88	18	0	188	724	1,083
II-C70FA20LP#02 10	0.53	248	69	35	0	188	725	1,084
II-C70FA25LP#11 5	0.53	248	88	0	18	188	726	1,085
II-C70FA20LP#11 10	0.53	248	69	0	35	188	724	1,083

Table 3. Mix proportions of concrete for slump test.

Mix designation	w/b	Cement (kg/m^3)	Fly ash (kg/m^3)	Limestone powder LP#11 (kg/m^3)	Water (kg/m^3)	Sand (kg/m^3)	Gravel (kg/m^3)
S-C100	0.55	300	0	0	165	873	1,064
S-C95LP#11 5	0.55	285	0	15	165	872	1,063
S-C90LP#11 10	0.55	270	0	30	165	871	1,062
S-C70FA30	0.55	210	90	0	165	862	1,051
S-C70FA25LP#11 5	0.55	210	75	15	165	863	1,052
S-C70FA20LP#11 10	0.55	210	60	30	165	864	1,053

An accelerated carbonation test was selected in order to shorten the test period. The CO_2 subjection environment was controlled such that the CO_2 concentration, the temperature, and the relative humidity were 4% (40,000 ppm), 40±2°C, and 50±5%, respectively. The test was conducted on 5x5x5 cm mortar cube specimens. The sand to binder ratio was 2.75 and the water to binder ratio was 0.485 for all mixtures. The specimens were cured in water for seven days before subjecting to CO_2 environment. After being under CO_2 exposure for 28 days, the specimens were split into half, sprayed with 1% phenolphthalein solution and the carbonation depth was measured.

Chloride resistance was observed in terms of chloride permissibility according to ASTM C1202. The test was carried out on mortar with sand to binder ratio of 2.75 and water to binder ratio of 0.40. The charge passed was measured at 28 days and an interpretation of chloride permissibility was made.

In case of sulfate resistance, both performances in sodium sulfate (Na_2SO_4) and magnesium sulfate ($MgSO_4$) were studied. The test included measurement of expansion of 2.5x2.5x28.5 cm mortar bars in Na_2SO_4 solution and weight loss of 5x5x5 cm mortar cubes in $MgSO_4$ solution. The concentrations of Na_2SO_4 and $MgSO_4$ solutions are 5% (50 g/1 L). The specimens were cast with water to binder ratio of 0.55 and sand to binder ratio of 2.75. All specimens were cured in water for 28 days before being submerged in Na_2SO_4 and $MgSO_4$ solutions. The length change of specimens immersed in Na_2SO_4 solution and weight loss of specimens immersed in $MgSO_4$ solution were periodically recorded.

3. Results and Discussion

3.1 Compressive strength

Results of compressive strength of concrete with 258 and 354 kg/m^3 binder contents are expressed in Figure 2 and 3, respectively. Cement-only concrete exhibited the highest compressive strength at all tested ages in the case of concrete with 258 kg/m^3 binder content. In the case of concrete with 354 kg/m^3 binder content, concrete with fine limestone powder, both binary concrete with 10% of LP#02 and ternary concrete with 10% of LP#02, showed an outstanding improvement of compressive strength, especially at early age. At low binder content, limestone powder does not improve compressive strength due to inadequate cement content. However, fine limestone powder effectively increases the compressive strength especially at early age when binder content becomes greater. Limestone powder accelerates the hydration reaction, resulting in an early gain of strength, though it is a filler. The increase of strength is also partly due to the filling effect of binders in the system, especially when fine limestone powder is used.

3.2 Slump

The initial slump of binary concrete with fly ash was the highest as can be seen from Figure 4. It is generally known that the spherical shape of fly ash results in a higher slump. In the case of binary binder concrete with limestone powder, the initial slump was slightly improved when compared with that of cement-only concrete, and the increase of slump was more obvious at 10% limestone powder. Ternary binder concrete exhibited smaller initial slump than binary binder concrete with fly ash, but was still higher than that of the cement-only concrete. Since the particle shape of limestone powder is irregular, replacing fly ash with limestone powder causes reduction of initial slump in ternary binder concrete.

Concrete with limestone powder, both in binary and ternary binder concrete, lost their slump slightly faster than cement-only concrete and binary binder concrete with fly ash. Mixtures with 10% of limestone powder led to a higher rate of slump loss than mixtures with 5% of limestone powder.

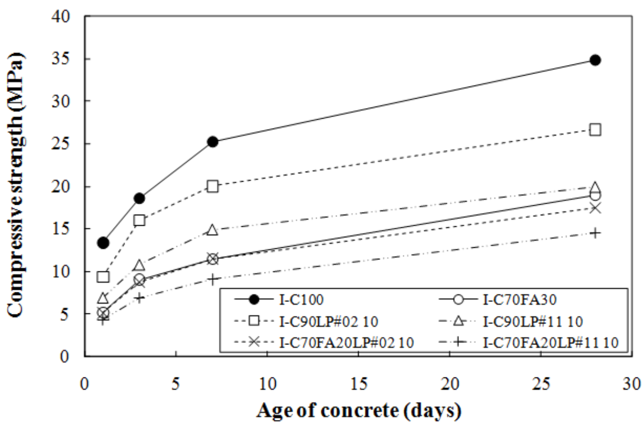

Figure 2 Compressive strength of concrete with binder content = 258 kg/m^3 and w/b = 0.72.

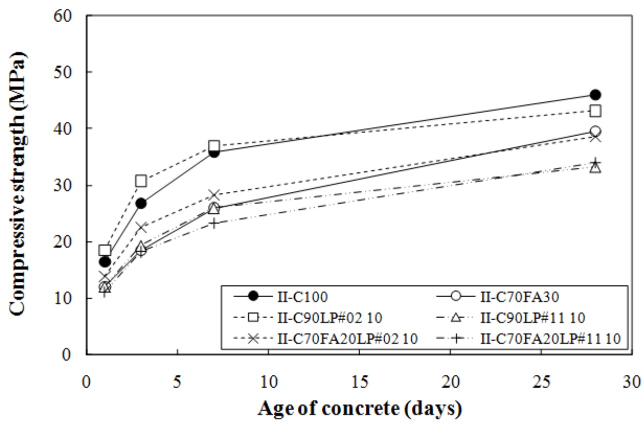

Figure 3. Compressive strength of concrete with binder content = 354 kg/m^3 and w/b = 0.53.

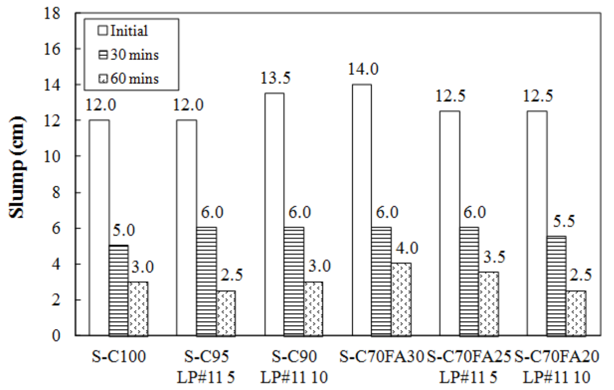

Figure 4. Slump of concrete with binder content = 300 kg/m^3 and w/b = 0.55.

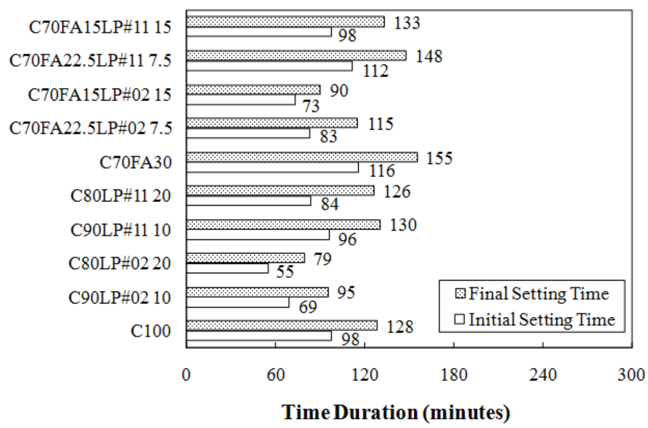

Figure 5. Initial and final setting times of pastes.

This can be explained from the fact that limestone powder accelerates the hydration reaction and accelerates setting of concrete. The higher content of limestone powder led to the faster reaction rate and settings as illustrated in Figure 5.

3.3 Autogenous shrinkage

It is clear from the results of autogenous shrinkage shown in Figure 6 that binary binder mixture with fly ash gave the lowest autogenous shrinkage. Binary binder mixture with limestone powder (both LP#02 and LP#11) had smaller autogeneous shrinkage when compared with cement-only mixture. Autogenous shrinkage has the potential to become greater when limestone powder is used to replace a portion of fly ash in ternary binder mixture. Both in binary and ternary binder system, mixtures with LP#11 had smaller autogeneous shrinkage than mixtures with LP#02. It can be explained from the fact that limestone powder is a non-reactive material and it does not change its volume with time. When it is used to replace a part of cement in a binary binder system, the products which change their volume with time are reduced, causing the reduction in autogeneous shrinkage. Fly ash helps reduce shrinkage by delaying the hydration and pozzolanic reactions and by the expansion of the SO_3 related products (Tangtermsirikul *et al.*, 1995). In the case of the ternary binder system in this study, limestone powder was used to replace a part of fly ash, thus, autogeneous shrinkage was increased when compared to that of the binary mixture with fly ash. The increase is also caused by the acceleration of hydration reaction when limestone powder is incorporated.

3.4 Drying shrinkage

The shrinkage of dried specimens was measured in terms of total shrinkage. From Figure 7, limestone powder helps to reduce total shrinkage, both in binary and ternary binder system. The total shrinkage is smaller when using coarser limestone powder. However, the reduction is not significant.

3.5 Carbonation

As shown in Figure 8, it can be observed that carbonation depth increases in mixtures with limestone powder content (both LP#02 and LP#11), in either binary or ternary binder systems. Coarser limestone powder tends to result in greater carbonation depth in case of ternary binder mixtures. However, binary mixtures with fine and coarse limestone powder yield much less carbonation depth than binary binder

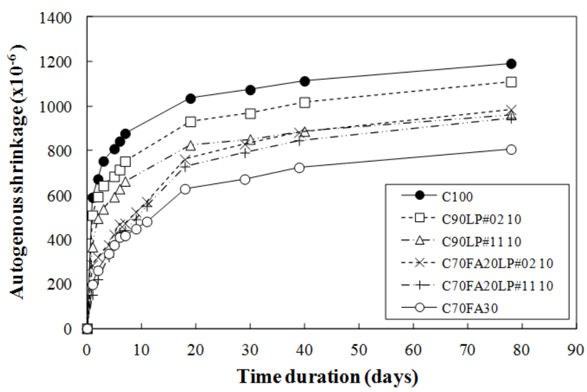

Figure 6. Autogenous shrinkage of pastes with w/b = 0.3.

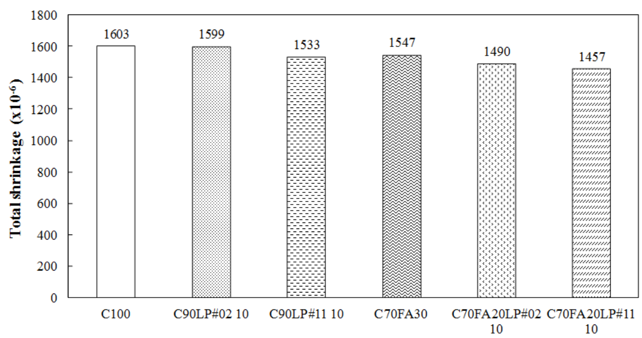

Figure 7. Total shrinkage of paste with w/b = 0.3 after 73 days of drying.

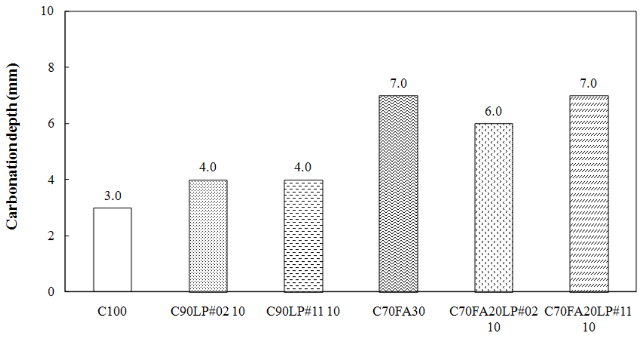

Figure 8. Carbonation depths of mortars after 28 days of being under CO_2 exposure.

mixture with fly ash. The increase of carbonation depth when limestone powder was used to partially replace cement could be due to the reduction of $Ca(OH)_2$ by the effect of cement replacing. Since limestone powder is a non-reactive material, it does not undergo hydration reaction and does not produce $Ca(OH)_2$. In binary binder mixture with limestone powder, the substitution of cement by limestone powder reduces $Ca(OH)_2$. The reduction of $Ca(OH)_2$ results in higher carbonation depth. In the case of a ternary binder mixture, limestone powder replaces a part of fly ash which consumes $Ca(OH)_2$ in the pozzolanic reaction. Therefore, $Ca(OH)_2$ reduction in the ternary binder mixture is less when compared with the binary binder mixture with fly ash.

3.6 Chloride resistance

The charge passed through a binary binder mixture with fly ash was less than that of cement-only mixture (see Figure 9), meaning better chloride penetration resistance. When a part of fly ash was replaced by limestone powder with an average particle size of 4 mm in a ternary binder mixture, the charge passed was slightly reduced which indicates even better chloride penetration resistance. The charge passed was increased in the case of a binary binder mixture with limestone powder when compared with the cement-only mixture, expressing poorer chloride penetration resistance. The higher chloride ion permissibility of the mortar containing limestone powder, as compared to that of cement-only mortar, can be attributed to the porous and connected paste aggregate interfacial transition zone (ITZ) associated with limestone powder (Ghrici *et al.*, 2007). The lower chloride ion permissibility of the mortar with fly ash may be related to the refined pore structure and its reduced electrical conductivity (Talbot *et al.*, 1995).

3.7 Sulfate resistance

3.7.1 Sodium sulfate resistance

The expansion of all mixtures immersed in sodium sulfate solution is plotted in Figure 10. As expected, binary binder mixture with fly ash shows low expansion, and so does the ternary binder mixture. Although binary binder mixture with limestone powder shows larger expansion than ordinary Portland cement type V mixture, the mixture had lower expansion than ordinary Portland cement type I mixture. The dilution effect due to cement replacing materials, either by the use of fly ash or limestone powder, reduces the amount of $Ca(OH)_2$ and ettringite, a hydrous calcium aluminum sulfate mineral ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$). With fly ash, the availability of $Ca(OH)_2$ for further sulfate-related reactions is reduced because it is consumed in the pozzolanic reaction. In the presence of limestone powder, the conversion of ettringite to monosulfoaluminate is suppressed or delayed because of the formation of monocarboaluminate (Ghrici *et al.*, 2007).

3.7.2 Magnesium sulfate resistance

From Figure 11, it can be seen that the weight loss of the binary binder mixture with limestone powder is drastically smaller than that of the binary binder mixture with fly ash. Slight differences in weight loss are found in a binary binder mixture with coarse limestone powder when compared with

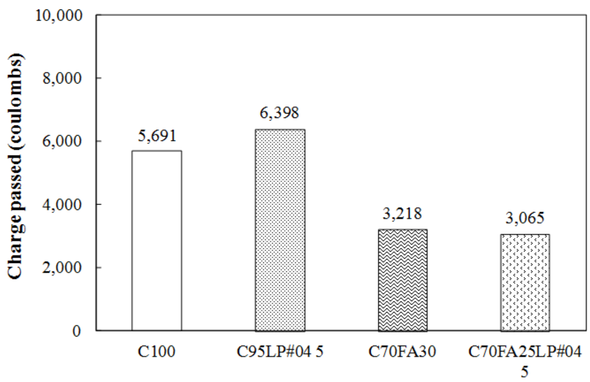

Figure 9. Chloride permissibility test by measuring charge passed at 28 days.

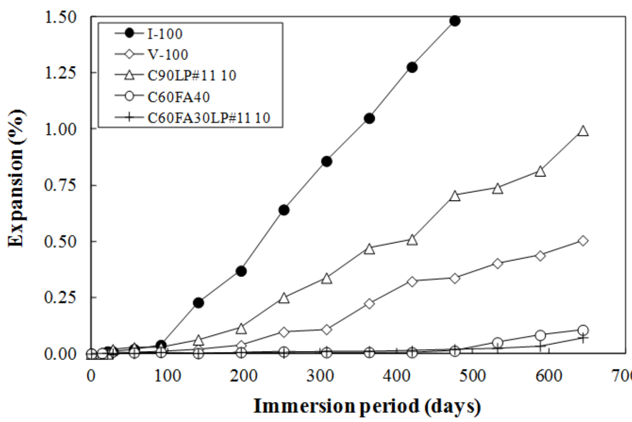

Figure 10. Expansion of mortar bars submerged in sodium sulfate solution.

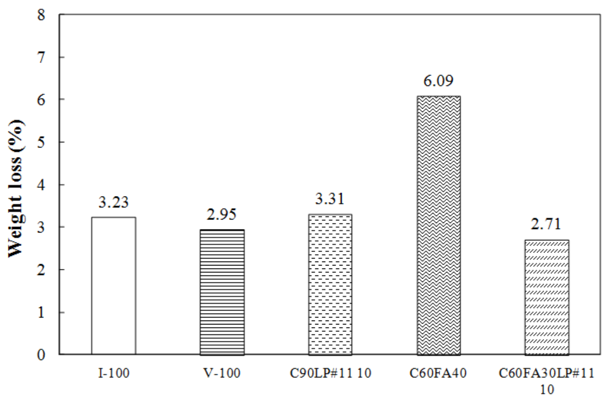

Figure 11. Weight loss of 5x5x5 cm cubic specimens submerged in magnesium sulfate solution for 92 weeks.

a mixture with ordinary Portland cement type I. Replacing a portion of fly ash by limestone powder in a ternary binder mixture greatly reduces the weight loss. The relative performances of each binder system are compared and summarized in Table 4.

4. Conclusions

The fresh, mechanical and durability properties of mixtures containing cement, fly ash, and limestone powder as single, binary, and ternary binder system were studied. The uses of fly ash and limestone powder as binary binder systems show distinct enhancement on certain properties. Incorporating fly ash in a mixture improves workability, chloride and sodium sulfate resistances, as well as reduces shrinkages. The early gain of compressive strength is noticeable when 10% of limestone powder having an average particle diameter (d_{50}) of 2 mm is used to replace cement in concrete with binder content of 354 kg/m^3. In addition, the combination of fly and limestone powder in a ternary binder system exhibits performances in an acceptable level and is better than a single binder system having only cement. The use of more than one type of cement replacing materials in concrete is gaining attraction in Thailand because it is the best way to fully utilize the advantages of each type of cement replacing materials.

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Table 4. Summary of performances of mixtures with various binder systems.

Binder systems / Properties	Single		Binary		Ternary
	Type I	Type V	C+LP	C+FA	C+FA+LP
Compressive strength					
- Early age strength	●●●	-	●●●●	●	●●●
- Long-term strength	●●●	-	●	●●●●	●●●
Slump	●●	-	●	●●●●●	●●●
Autogenous shrinkage	●	-	●●	●●●●	●●●
Drying shrinkage	●	-	●●	●●●●	●●●●
Carbonation	●●●●	-	●●●	●	●●
Chloride resistance	●●	-	●	●●●●	●●●
Sulfate resistance					
- Sodium sulfate	●	●●●	●●	●●●●	●●●●
- Magnesium sulfate	●●●	●●●●	●●●	●	●●●●

Remarks: ●●●●● = best performance to ● = worst performance; FA content $\geq$ 30%, LP content $\leq$ 10%, LP size (d_{50}) ranges from 2–11 μm.

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