INVESTIGATION INTO LOWERING CEMENT CLINKER CONTENT USING AVAILABLE MATERIALS

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ABSTRACT

Reducing cement clinker with mineral addition has been considered an efficient way of saving energy, lowering CO_2 footprint of cement and concrete industries. The trend of using limestone as mineral addition in cement production started in 1992s. Cement containing limestone additions up 35% have been used in European countries adopting the European Standard EN 197. Similar standards have been developed, such as Canadian Standard, CSA A3000, which has approved the limestone addition from 5% up to 15% by mass. In U.S., ASTM standard C595 for Portland blended cement needs to be changed to have a significant impact on sustainability.

This research tested concrete fresh properties, strength development and durability properties made using different types of blended cement, a series of limestone addition rates, which changed from 5% to 18% by mass, and a series of ternary mixtures with limestone and fly ash combination at 20% replacement rate. Concrete mixtures using a type I/II cement was used as a baseline for comparison.

Results showed that limestone addition decreased concrete workability while fly ash addition in ternary mixtures improved workability. Concrete made using cement with limestone addition showed improved early age strength. Fly ash addition in ternary mixtures showed lower early age strengths. Mortars with limestone addition to 18% and ternary mixtures showed no statistically significant difference on volume stability comparing to the control group which were prepared using ordinary Portland cement. Blended cement with limestone addition has less length changes when exposed to sulfates. Limestone additions up to 18% by mass showed improvement for sulfate resistance. The ternary mixtures also showed sulfate resistance improvement. Concrete permeability increased with increasing limestone addition. Fly ash showed significant decrease in permeability. Concrete freeze-thaw resistance is strongly related with air content. Limestone addition rates up to 18% had freeze-thaw resistance decreased.

Results showed that the properties of blended cement such as particle size distribution, the quality and quantity of mineral addition can affect concrete fresh properties, harden properties and durability. Blend cement with limestone addition rate up to 18% have no significant negative effect on concrete performance.

APPROVAL PAGE

The faculty listed, appointed by the Dean of the School of Computing and Engineering, have examined a thesis titled “Investigation into lowering cement clinker content using available materials,” presented by Qiwei Cao, candidate for the Master of Science Degree, and certify in their opinion it is worthy of acceptance.

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CHAPTER 1

INTRODUCTION

1.1 Background

Concrete is the most used construction material in the world, and is employed for most of the infrastructure, buildings, industry and transportation in our society. Cement is the main ingredient in concrete; it acts as a hydraulic binder in concrete. Cement industry is well known to be energy intensive; manufacturing of one ton of the Ordinary Portland Cement clinker (OPC) generates 900 kg of CO_2. The total volume of cement production per year is approximately 5% of global anthropogenic CO_2 production (Damtoft, Lukasik, and Herfort, 2008).

Under great pressure to reduce CO_2 emissions and for energy savings, the cement industry has adopted three main approaches. First, alternative fuels and raw materials are selected at the starting point, by replacing conventional carbon based fuels with alternative low carbon based fuels such as bio-fuels, and then raw materials can be partly alternated by waste industry ashes, such as bottom ash from filter clays, coal fired power plants and fly ash (Damtoft, Lukasik, and Herfort, 2008). Another advantage of burning waste materials in cement kilns is that no residues are generated, because the ash is completely incorporated in the clinker.

Secondly, improving the process of clinker production reduces CO_2 emission and energy consumption. It is much easier for modern cement plants to deal with CO_2 emission reduction requirement, since modern kiln system have higher thermal efficiencies (Gartner, 2004). The other part of the second approach is reducing the amount of CaO in the clinker by changing the chemistry of clinker. Extensive study was done by producing clinkers that are high in belite and low in alite (Popescu, Muntean, 2003). But, belite is much less reactive than alite, therefore belite rich cement will sacrifice high percentage of early age properties, such as setting time, harden rate comparing to OPC, which it is the reason that belite rich cement has not been popular in the industry.

Thirdly, reducing clinker contents by mineral addition in cement is the best way to significantly reduce CO_2 emission. Mineral addition have been researched for several decades, minerals like fly ash, granulated blast-furnace slag, limestone, silica fume and natural pozzolans have been used where they are available. Limestone addition has been historically the most available materials and was therefore commonly used in cement industry. At the beginning, limestone replacement was considered an inert filler only, diluting cement clinker content. More recently research has shown that limestone filler does not only physically participate in the hydration process by providing additional surface area for nucleation and growth of hydration products, limestone filler also has chemically reactivity (Voglis, Kakali, 2005). European countries started to increase limestone addition in cement since 1992. Current European standard EN 197-1 allows limestone replacement of clinker up to 35% by mass of Portland cement (EN 197-1:2000). The Canadian standards Association (CSA) as of 2008 allows the use of Portland limestone cement (PLC) with up to 15% limestone replacement, except in application where there are sulfate concerns. In US, current standard ASTM C150-04 for blended cement allow up to 5% replacement of Portland cement (CSA A3000-98).

1.2 Project Overview and Research Scope

Testing had been undertaken in this thesis which covers the fresh properties, strength development and durability of concrete produced with cement different level of limestone additions. This study includes two series of mixtures. The first series consists of mixtures prepared with cement containing up to 18% limestone by mass of cement. The second series contains ternary mixtures produced with cement containing limestone and fly ash. The cement used in ternary mixtures had 20% by mass of cement replacement with fly ash and limestone. Control mixtures were prepared using Type I/II cement.

The scope of this research is to show that cement with reduced clinker content can have a similar performance as Type I/II cement. The clinker reduction can be obtained by replacing a part of clinker with ground limestone or with a mixture of limestone and fly ash. If this new cement with lower clinker content, it could be widely used by the industry, which would reduce CO_2 emission and save energy.

CHAPTER 2

LITERATURE REVIEW

2.1 General Aspect of Limestone Addition

Limestone is often considered an inert particle filler which dilutes cement clinker content, however limestone does not act completely inert and has positive effects on concrete microstructure (Popescu, Muntean, and Sharp, 2003). Limestone addition could be added with clinker and interground at the same time or can be dry blended (Gartner, 2004). Either way of replacement affects the particle size distributions which affect the fresh properties such as water demand, and harden properties such as strength development (Jackson, 1993). In a 1993 Building Research Establishment (BRE) study, the average specific surface of the cements increased from 300 to 350 m^2/kg and the 45 μm residue from 13.8% to 15.8% when 5% limestone was interground with the clinker (Jackson, 1993). When cements were dry blended with 5% limestone, the specific surface increased from 395 to 486 m^2/kg and the 45 μm residue decreased from 12.0% to 10.8% (Schmidt, 2004). Particle size distribution (PSD) of cementitious materials can influence the properties of concrete and paste, such as rheology, volume of voids and water demand. Therefore, optimizing the particle size distribution and particle packing would control water demanding in a reasonable range. Ready mixed concrete plants have already added limestone power into concrete mix as filler. The aspect of concrete strength and durability with using interground limestone cement needs to be studied.

The fine limestone particles act as nucleation sites, increasing the rate of hydration of the cement component, such as tricalcium aluminate (C_3A) and tricalcium silicate (C_3S).This then changes in calcium-silicate-hydrate (C-S-H) gel and microstructures in consequence (Schiller, 1992).

Schiller and Ellerbrock found that the particle size distribution of any one constituent is greatly influence by the grindabilities of the others. When cement clinker and limestone are interground, the limestone is normally easier to ground, and become the majority of smaller particles, shown as Figue.1 (Schiller, 1992).

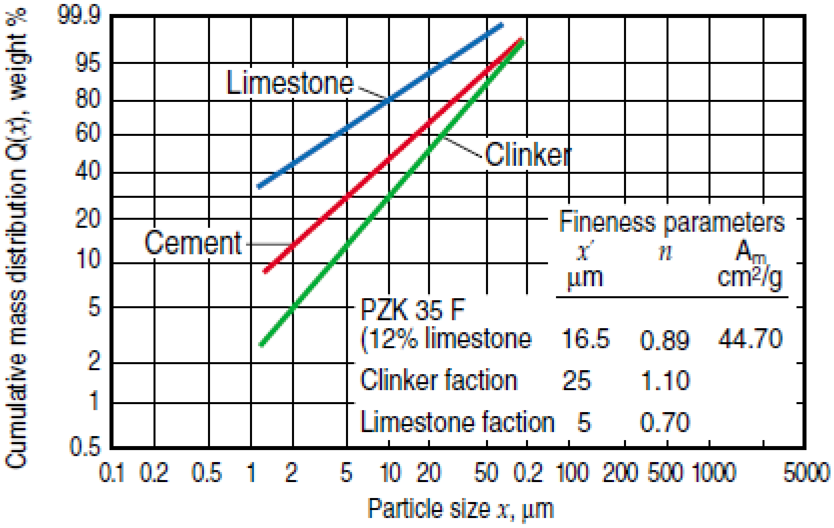

Figure.1 Cumulative mass distribution of a Portland limestone cement with a limestone content of 12 % by mass, as well as of the two individual constituent materials after intergrinding in an industrial ball mill (Schiller, Ellerbrock,1992)

2.2 Fresh Properties

Some research have been done to determine the effect of limestone addition on fresh properties of concrete such as workability, setting time, water demand, bleeding. Particle size distribution strongly influence workability and water demand of concrete. Since softer limestone usually has a wide particle size distribution with higher fines content, it helps to fill the gap between cement particles, reducing water demand. One way to depict the particle size distribution of granular materials is to use Rosin-Rammler-Sperling-Bennett (RRSB) diagram, which expresses the equation as: $R(d)=100 \times \exp(-d/d')^{n}$, where R(d) is the percentage by mass of particles with diameters larger than d. According to Detwiler, narrow particle size distribution of cement with RRSB gradients (n) greater than 1 generally results in high water demand, and wide particle size distribution has reduced water demand (Detwiler, 1995).

The relationship between particle size distribution, water demand, and strength is well documented. Schiller and Ellerbrock concluded that Portland cement which has the same specific surface area as PLC (Portland limestone cement) harden faster, but have higher water demands. Schiller and Ellerbrock studied both intergrounding and blending limestone addition cement. When addition up to 10%, using limestone with narrow or wide particle size distribution would both decrease the water demand. With larger quantities addition, the limestone with wider particle size distribution would continue decrease the water demand, while with narrower particle size distribution starts to increase water demand.

The effect of limestone for improving concrete rheology property is commonly related to the particle size distribution. The fine particles of limestone act as an internal lubricant to displace water from the voids. Sprung and Siebel showed that concrete with the same mixture proportion; the group using Portland limestone cement was less stiff than those made with Portland cement (Siebel, Eberhard, and Sprung, 1991). For ternary blends of either OPC or sulfate resistant cement, fly ash, and limestone, with fly ash and limestone was kept constant at 20%, but the individual materials varied from 0 to 20%; Heikal found increased water is needed to maintain consistency of cement paste as limestone content increase (Heikal, Helmy, and El-Didamony, 2004).

The fineness of limestone is a factor that influences cement paste setting time. Different level of limestone addition have different effect on setting time, which showed by several studies as below.

Hawkins (1986) conducted two test groups. In the first, clinker and gypsum were ground in a laboratory ball mill with 0%, 3%, 5.5%, and 8% limestone to a more or less constant Blaine fineness. The use of limestone appears to have little effect on the setting time. In the second series, the procedure was repeated with 0%, 2%, 5%, and 8% limestone, except that the #325 mesh value was kept more or less constant. This series indicates a reduction in setting time with the use of limestone (Hawkins, 2003).

El-Didamony showed increasing limestone additions decreased the setting time of cement paste (Figure.2) (El-Didamony, Salem, 1995).

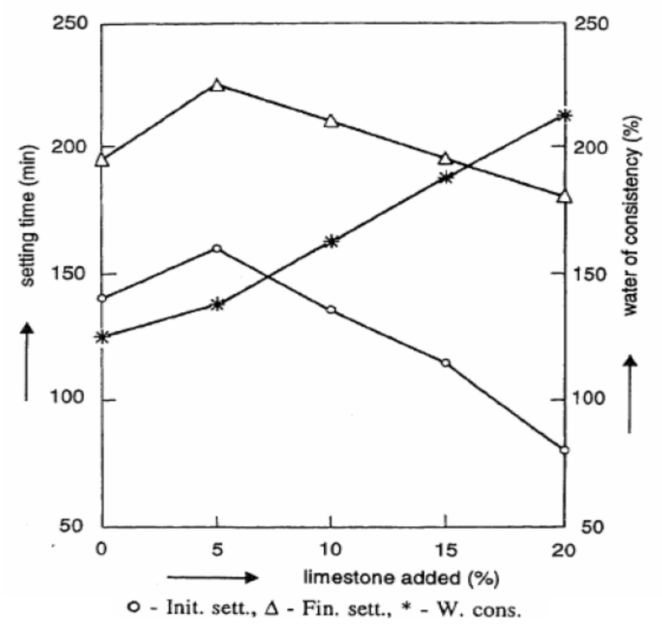

Figure.2 Water demand and setting time of limestone cement paste (El-Diamony et al, 1995)

2.3 Strength Development

According to Powers' model, hydration of cement in low water to cement ratio is a spacing limitation issue (Bentz, Irassar, Bucher, and Weiss, 2009). In a sealed condition, when water to cement ratio is lower than 0.36-0.38, the cement hydration product will not fill the originally water filled space. Hence, there are parts of cement stay unhydrated. When extra water is providing during curing, the least water to cement ratio remain unhydrated will increase to 0.42. This is the idea that brings relatively inert filler limestone into cement system started, which would dilute cement clinker content and cut the cost down.

Known that limestone acts as nucleation sites for hydration products, so introducing limestone into system could increase the rate of hydration and further affect early age strength. Bonavetti showed that 10%-20% limestone replacement at various water to cement ratio (0.25- 0.50), the degree of cement paste hydration was highly more rapid during the first 7 days in the higher W/C ratio with limestone addition. At a lower level of W/C (less than 0.30), the differences were not as noticeable (Bonavetti, Donza, and Rahhal, 2000). For the ternary blends of cement, fly ash and limestone, Heikal found that chemically combined water increases with limestone content increasing (Heikal, Helmy, and El-Didamony, 2004)

Concrete strength with limestone addition is effect by the quality of limestone are used, the way that added, and the final particle size distribution. Limestone is softer than cement clinker, for the same surface area (Blaine); the clinker particles in PLC will be coarser than clinker in PC. Hence, PLC is needed to ground finer. Research performed by Sprung and Siebel showed that limestone content up to 5% could increase early age strength because of better particles packing, and increased rate of hydration (Siebel, Eberhard, and Sprung, 1991).

At higher level of replacement, compressive strength would start to loss by dilute clinker content, but compensation can be made by grounding finer. Matthew showed that concrete strength is reduced significantly when high level of ground limestones are blended with Portland cement (Matthews, 1994). Tsivilis had the similar conclusion, for cement with limestone replacement up to 15%, Portland limestone cement could perform well with appropriate combination of clinker quality, limestone quality, limestone content and particles fineness (Tsivilis, Chaniotakis, and Badogiannis, 1999).

2.4 Shrinkage

Shrinkage is an indicator of concrete volume stability. Research performed by Adams and Race, showed a slight increase of blended limestone on drying shrinkage of Type I and Type II cements following ASTM C596. Adams and Race also concluded that optimization of sulfate content could offset the increased shrinkage (Adams, Lawrence, 1990).

2.5 Durability

2.5.1 Chloride Permeability

Concrete' permeability controls concrete durability, since concrete is porous by nature. A series of deteriorations in concrete are related to ingress of water, gas such as oxygen and carbon dioxide, and harmful ions such as chloride and sulfate ion. Permeability is related to pore structure, especially with the connectivity of pore system. Limestone addition improves the particle packing, and provides nucleation of clinker hydration. The effect of limestone addition on permeability is improving pore structure by reducing connectivity.

From the literature, chlorides permeability of concrete can either use concentration gradient of ionic movement or measuring properties such as electrical conductivity or resistivity. Matthew tested reinforced concrete prisms which were exposed in chlorides for 5 years. Results showed that concrete with PLC (Portland limestone cement) with 5% limestone have slightly improved resistance than Portland Cement (OPC) group; PLC with 25% limestone showed slightly reduced resistance (Matthews, 1994). It was concluded that limestone has less effect on chloride resistance than fly ash.

A study conducted by Tsivilis showed that concrete with limestone addition from 0-35% and tested with "Rapid Chloride Permeability" followed by ASTM C 1202, slightly effected limestone addition increasing from 15%-20%, but when addition increased by 35%, even with lower w/cm to start with, a higher RCP was expected (Tsivilis, Batis, Chaniotakis, 2000). Table.1 shows the detail about the testing results.

Table.1 Effect of Limestone Addition on the "Chloride Permeability" of Concrete (Tsivilis et al.2000)

Limestone, %	0	10	15	20	35
Fineness, m²/kg	260	340	366	470	530
Mortar: strength at 28 days (MPa)	51.1	47.9	48.5	48.1	32.9
Concrete: w/cm	0.70				0.62
Concrete: strength at 28 days (MPa)	31.9	27.4	27.3	28.0	26.6
Concrete: RCPT (Coulombs)	6100	5800	6000	6400	6600

Study taken by Tezuka showed that chloride diffusion coefficient of cement paste with 35% limestone addition has similar with ordinary Portland cement (Tezuka, Gomes, and Martins, 1992). Field trials in Canada showed that there were no significant difference of concrete RCP results between produced by Portland cement with SCMs and produced with Portland limestone cement (Thomas, Hooton, and Cail, 2010). Curing condition could effect on chloride resistance differently between concrete produced with PLC and PC. Bonavetti tested concrete with PLC which had more chloride penetration than with PC curing in water, but the opposite effect for air-stored concrete (Bonavetti, Donza, and Rahhal, 2000).

2.5.2 Sulfate Resistance

Adding limestone into cement systems dilutes the C_3A content and other active aluminates by producing calcium-aluminates which reduce available alumina to participate in further sulfate reactions. However, beyond a certain amount of replacement, concrete strength and permeability becomes jeopardized. Hence, standards like ASTM C150 specify no deleterious effect of up to 5% limestone in cement. A major concern about increasing finely grounded limestone addition is the potential of thaumasite sulfate attack (TSA).

2.5.2.1Effect of Limestone Addition on Ettringite Type Sulfate Attack

Matthews showed concrete with cement containing C_3A contents of 7.1%, 5.3% and 8.6% performed well. For OPC there was a clear relationship between C_3A content and sulfate resistance (Matthews, 1994). With 25% limestone replacement, PLC has no difference with OPC. Using 25% limestone replacement and a wider range of C_3A content showed that the properties of OPC with lowest C_3A content is improved, the rate of deterioration of the highest C_3A content OPC being increased.

Study carried out by González and Irasser on both Type II and Type V cement with 10% and 20% limestone replacement showed that 10% limestone group has no effect on expansion or mass loss, on the other hand, 20% limestone group showed lower sulfate resistance. All the sulfate phase was confirmed by XRD were gypsum and ettringite (González, Irassar, 1998).

2.5.2.2 Effect of Limestone Addition on Thaumasite Sulfate Attack

There are two mechanisms of thaumasite formation in mortar and concrete. First, it can be derived from the evolution of ettringite when it incorporates Si_4^+ into its structure, substituting the Al^{3+} and interstitial replacement of $[(SO_4^{2-})_3(H_2O)_2]$ by $[(SO_4^{2-})_2(CO_3^{2-})_2]$.

Secondly, the thaumasite is the result of the interaction between sulfate and carbonate ions and the C-S-H gel (Irasser, Bonavetti, and Trezza, 2005). With limestone replacement increasingly used in cement system, more research has been done on thaumasite formation.

Thaumasite sulfate attack has only been found in historical structures and at the last stage of deterioration in marine locations. Evidences have been found that TSA can occur especially in wet and cold conditions on concrete with fine $CaCO_3$ content, which is normally considered sulfate resistant. Matthew found that TSA formation was not an obvious dependence on the level of limestone content in cement, and it being detected the same amount in the 5% and 25% limestone cement (Matthews, 1994). Barker and Hobbs studied that mortars with w/c 0.5 and 0.75, which stored in both sodium and magnesium sulfate solutions at 5^oC.Results showed reduced expansion of the 15% limestone cement in both solutions and little difference visual performance of mortar bar produced with high C_3A content with and without 15% limestone content (Barker, Hobbs, 1999). Borsoi found that the amount of limestone replacement within range 10% to 20% can change the dominant reaction product from ettringite to thaumasite.

2.5.2.3 Effect of Using Supplementary Cementitious Materials on Sulfate Resistance Limestone Cement

Research performed by Higgins and Crammond showed that 70% ground granulated blast- furnace slag has a positive effect on preventing the formation of TSA in concrete without limestone fillers (Higgins, Crammond, 2002). It is likely that usage of slag may improve the performance of limestone cements. Tsivilis also concluded that metakaolin appear to significantly reduce TSA expansions and damage, slower reacting pozzolans like fly ash appear to retard the damage but not prevent it (Tsivilis, Kakali, and Skaropoulou, 2003).

2.5.3 Freeze-thaw Resistance

Concrete freeze-thaw resistance has strong relationship with air content of concrete. From literature review, different concrete ingredients have different effect on air content, shown as Table. 2. Different cement properties such as alkali content, fineness, and fly ash addition could change the air content of concrete. Also production and construction methods would effect on air content of concrete. There are effects of limestone addition as another ingredient in cement on concrete freeze-thaw resistance.

Table.2 Effect of Concrete Ingredients on Air Content (Concrete Technology Today, PCA, Volume 19/Number 1 Apr, 1998)

Material	Effects	Guidance
Cement		
Alkali Content	Air content increases with increase in cement alkali level	Changes in alkali content require that air-entraining agent dosage be adjusted. Adjust agent if cement source or fineness changes. Increase air-entraining admixture dosage rate.
Fineness	Decrease in air content with increased fineness of cement	
Cement Content	Decrease in air content with increase in cement content	
Fly Ash	Air content decreases with increase in L.O.I. (carbon content)	Changes in L.O.I or fly ash source require that air-entraining agent dosage be adjusted.
Water Reducers	Air content increases with increase in dosage of lignin-based materials	Reduce dosage of air-entraining agent.
Aggregate	Air content increases with increased sand content	Decrease air-entraining agent dosage.

Research in Europe has suggested that limestone content higher than ASTM C150 and lower than 20% by mass can still be as freeze thaw resistance as with Portland cement.

The addition limestone has to be within specification European standard (EN 197-1), since freeze thaw resistance of limestone addition have strong relationship with the quality of the limestone, high clay content have high potential frost expanse (Schmidt, Michael, Harr, Klaus, and Boeing, 1993).

Study by Matthews showed that in non-air-entrained concrete, freeze-thaw resistance of PLC concrete is reduced compare to PC concrete, results shows opposite in air-entrained concrete system (Matthews, 1994), illustrated as Figure.3.

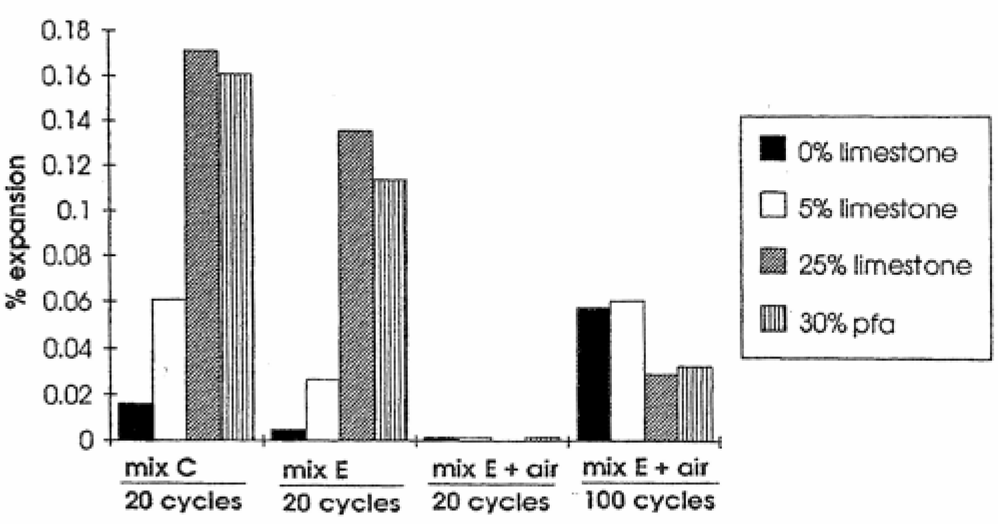

Figure.3 Effect of Air Entrainment on Freeze-Thaw Resistance of PC and PLC Concrete (Mathews, 1994)

Schmidt found that concrete with same strength class (32.5Mpa) using Portland limestone cement with limestone addition from 13-17% has no significant difference with concrete using Portland cement. Figure.4 shows exception, group F1 did not conform to the requirement of EN197 (Schmidt, Michael, Harr, Klaus, and Boeing, 1993).

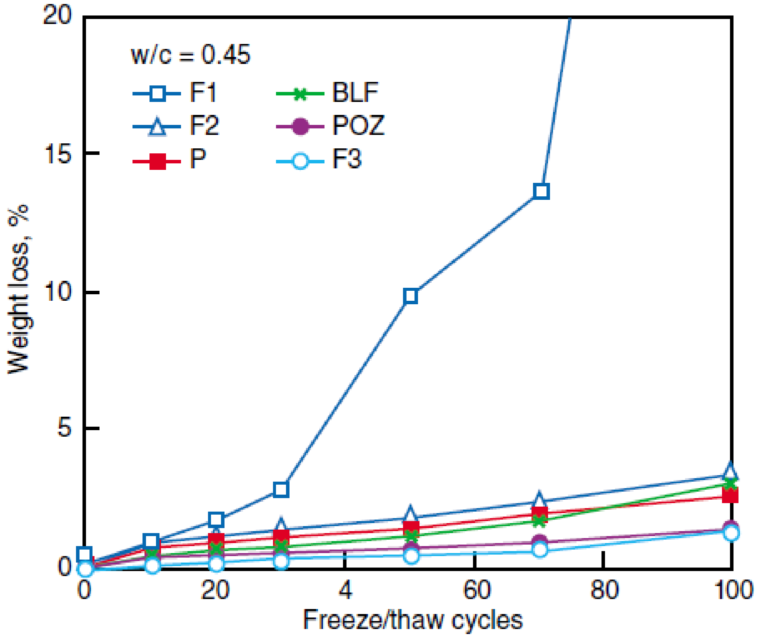

Figure.4 Effect of type of limestone on freeze-thaw resistance of concrete. Portland limestone cements of class 32.5 were produced from the same clinker, but with different types of limestone from 13-17%. In most cases the freeze-thaw resistance is comparable to that of the Portland cement (Schmidt et al. 1993)

2.6 Important Findings from the Literature Reviews

There are many important reasons to produce cement containing limestone as a mineral addition.

- Using Portland limestone cements can reduce CO_2 emission by reducing clinker content.
- Using Portland limestone cement can improve workability.
- Strength level can be achieved by optimizing fineness of limestone particles.
- Limestone is not only an inert filler, limestone addition can involve sulfate deterioration in certain environment.
- The particle packing effect of addition limestone into system could improve clinker hydration by providing nucleation sites.
- Strength of concrete and mortar produced by Portland limestone cement has a wide range of result. But an optimum amount of limestone addition could achieve certain level of strength.
- Permeability can be reduced by using limestone.
- Freeze-thaw resistance is more controlled by the air-entrained system.
- Limestone addition may increase thaumasite form of sulfate attack susceptibility.

CHAPTER 3

MATERIALS AND MIXTURE DESIGNS

3.1.1 Cement Properties

Three types of cement were used in this research, LaFarge Type I/II cement, LaFarge High-limestone content cement which has Type I/II cement with 18% limestone interground, LaFarge Fly ash Blended cement. Table.3 shows the different chemical composition and physical characteristics of all three types of cement.

Table.3 Different Chemical Composition and Physical Characteristics of OPC, PLC18, PFA25

Test	**OPC**	**PLC18**	**PFA25**
Silicon dioxide, SiO_2 (%)	19.7	17.3	28.9
Aluminum oxide, Al_2O_3 (%)	4.9	4.1	8.3
Ferric oxide, Fe_2O_3 (%)	3.1	2.6	4.2
Calcium oxide, CaO (%)	63.3	61.3	50.7
Magnesium oxide, (%)	1.6	1.6	1.9
Loss on Ignition, LOI (%)	2.7	17.9	2.2
Limestone Content (%)	4.3	18.0	-
Setting Time (min) (ASTM C 191)	102	147	136
Fineness:			
Blaine surface (m^2/kg)	373	495	354
45µm Sieve, %passing	98	97	91.5

3.1.2 Aggregate

Coarse Aggregate

The information on the coarse aggregate is listed in Tables 4 and 5.

Table.4 Coarse Aggregate Information

Property	Value
Aggregate	¾ inch Limestone
Specification	ASTM C33
Source	Hunt Martin
Supplier	Fordice
Date Received	7/3/2009
Specific Gravity (OD)	2.47
Absorption (%)	2.87
Dry Rodded Unit Weight (pcf)	96.2

Table.5 Coarse Aggregate Gradation

Sieve Size	% Passing
1.5"	100
1"	100
3/4"	100
1/2"	66.5
3/8"	37.7
#4	5.8
#8	2.2
#16	1.9
#30	1.7
#50	1.6
#100	1.5
#200	1

Fine Aggregate

The information on the fine aggregate is contained in Table 6 and 7.

Table.6 Fine Aggregate Information

Property	Value
Aggregate	Fine Concrete Sand
Specification	ASTM C33
Source	Holiday
Supplier	Fordice
Date Received	7/3/2009
Specific Gravity (OD)	2.62
Absorption (%)	0.4

Table.7 Fine Aggregate Gradation

Sieve Size	% Passing
1.5"	100
1"	100
3/4"	100
1/2"	100
3/8"	100
#4	99
#8	87
#16	67
#30	41
#50	11
#100	1
#200	0.4

Graded Standard Sand

Mortar cubes, shrinkage beams and sulfate resistance beams are required to use graded standard sand, which is graded between No.30 and No.100 sieves, meets requirements for ASTM C 109 and ASTM C 778, as well as AASHTO T 106.

3.1.3 Chemical admixtures

MB- AE 90 air-entraining admixture was used as chemical admixtures in all concrete mixtures. It meets the requirement of ASTM C 260, AASHTO M 154.

3.2.1 Experimental matrix

Two groups of blended cement were tested which were only limestone addition groups, and limestone and fly ash blended addition groups. Details of blended cements composition are shown as Table.8.

Table.8 Experimental matrix

No.	Composition (% by mass)			Designation
	OPC	Limestone	Fly Ash	
M1	100	0	0	OPC
M2	95	5	0	PLC5
M3	90	10	0	PLC10
M4	85	15	0	PLC15
M5	82	18	0	PLC18
M6	75	0	25	PFA25
M7	80	5	15	PL5F15
M8	80	10	10	PL10F10
M9	80	15	5	PL15F5
M10	80	18	2	PL18F2

3.2.2 Mixture Proportion

All the concrete proportion used a standard 564 pcy cementitious concrete with 1:1 by mass coarse aggregate to fine aggregate blend. The water to cement ratio was 0.45. Air entrainment was dosed at 0.25 fl oz/100 lb.

Table.9 Concrete Mixture Proportion

Component	US	SI
Cementitious Content	564 (lb/yd^3)	335 (kg/m^3)
Coarse Aggregate	1463 (lb/yd^3)	868 (kg/m^3)
Fine Aggregate	1463 (lb/yd^3)	868 (kg/m^3)
Water	253.8 (lb/yd^3)	151 (kg/m^3)
Air Entrainment	0.25 oz/cwt	17.5 ml/100 kg

According to ASTM C 1012, mortar for sulfate resistance use water to cement ratio 0.485 by mass since all cement blended are non-air entraining. Sand to cement ratio was 2.75 by mass. For shrinkage mortar beams, a water to cement ratio 0.38 by mass and a sand to cement ratio 2 by mass was used.

CHAPTER 4

TEST METHODS

4.1 Specimen Preparation

Concrete specimen preparation procedure followed ASTM C192 (Standard Test Method for Making and Curing Concrete Test Specimens in the Laboratory). A 3.0 cf rotating drum mixer was used to make concrete specimen for testing fresh properties, compressive strength development, rapid chloride permeability, and freeze-thaw resistance. Compressive strength development was determined at 7 days, 28 days, and 56 days. A total of nine 4 inch by 8 inch cylinders per mixture were produced, three for each time periods. Two 4 inch by 8 inch cylinders of specimen per mixture were produced for rapid chloride permeability test. Three 3 inch by 4 inch by 16 inch concrete beams were produced for freeze-thaw resistance test for each mixture.

Mortar beams were produced to test shrinkage and sulfate resistance. Six 1 inch by 1 inch by 11 1⁄4 inch beams were produced to for shrinkage, three for measuring total shrinkage and three for measuring autogenous shrinkage. Six 1 inch by 1 inch by 11 1⁄4 inch were produced to for sulfate resistance as well. Mortar mixtures were different for shrinkage and sulfate resistance, as described in Chapter 3.

4.2 Fresh Properties Tests

Fresh properties of concrete included air content with same amount air-entraining agent, slump, unit weight and setting time.

Air Content

Air content of freshly mixed concrete was tested using ASTM C231 (Standard Test Method for Air Content of Freshly Mixed Concrete by the Pressure Method). A Type B pressure meter was used in this test.

Slump

Workability of freshly mixed concrete was determined according to ASTM C143 (Standard Test Method for Slump of Hydraulic-Cement Concrete). Slump test is a common method for quality control on the field. In this thesis, different type of cement and air content affect the slump of freshly mixed concrete batch.

Unit weight

Unit weight (density) was tested according to ASTM C138 (Standard Test Method for Density (Unit Weight), Yield, and Air Content (Gravimetric) of Concrete), using the same steel cylindrical container as measuring the air content. Unit weight was measured before air content to make sure no extra water was introduced into the system. The same consolidation method was used for all mixtures.

Setting time

Setting time was measured right after concrete was mixed according to ASTM C 191 (Standard Test Method for Time of Setting of Hydraulic Cement by Vicat Needle). Paste was taken from freshly mixed concrete sieved through No.4 sieve. Allow the time of setting specimen to remain in the moist cabinet for 30 min after molding without being disturbed. Determine the penetration of the 1-mm needle at this time and every 15 min thereafter until a penetration of 25 mm or less is obtained.

4.3 Harden Properties Tests

4.3.1 Compressive Strength development

Compressive strength tests were performed according to ASTM C39 (Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens). Compressive strength with time was determined at age of 7 days, 28 days, and 56 days.

4.3.2 Shrinkage

For volume stability of concrete, creep and shrinkage over time are the two mainly concerned properties. In this thesis, unrestrained drying shrinkage and autogenous shrinkage of mortar were tested. The length of testing period was 28 days, according ASTM C 596 (Standard Test Method for Drying Shrinkage of Mortar Containing Hydraulic Cement). The length change measurement was conducted by ASTM C490 (Standard Practice for Use of Apparatus for the Determination of Length Change of Hardened Cement Paste, Mortar, and Concrete). The instrument set up is shown as Figure. 5.

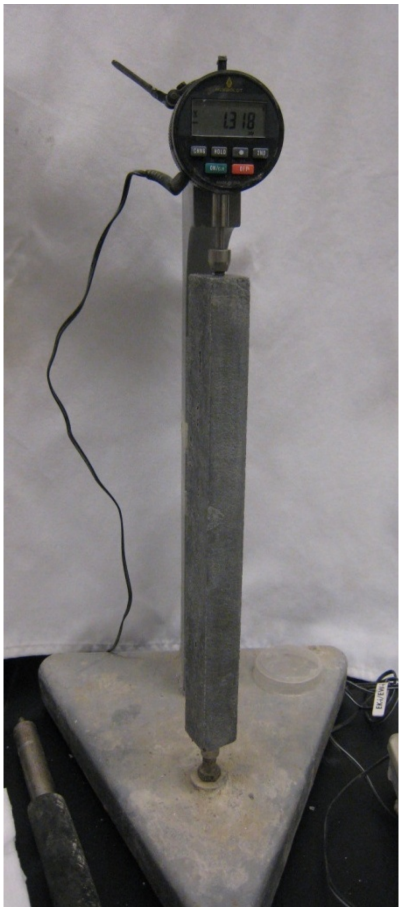

Figure.5 Apparatus Set Up for Measurement of Length Change

4.4 Durability Tests

Four parts of durability testing were performed including shrinkage, sulfate resistance, rapid chloride permeability and freeze-thaw resistance.

4.4.1 Sulfate resistance

Sulfate resistance of different mortar mixtures was tested according to ASTM C1012 (Standard Test Method for Length Change of Hydraulic-Cement Mortars Exposed to a Sulfate Solution). While producing mortar beams, 21 2 inch by 2 inch cubes were also produced for strength development. After demolding all specimens, transfer these specimens in the curing tank of saturated limewater at 23.0 °C. Two cubes were tested in compression every other day until the mean strength was achieved 20 MPa. Beams were then placed in a pre-prepared 50g/L sodium sulfate solution. Initial length was measured before storage in the solution. Length change were measured at the age of 1 week, 2 weeks, 3 weeks, 4 weeks, 8 weeks, 13 weeks, 15 weeks, 4 months, and 6 months. All the specimens were then stored at 5°C environment, shown as Figure.6, and measurements taken every three month.

Figure.6 All Specimen Storage at 5°C Freezer

The purpose of two environments was concerned about the performance of concrete exposed to sulfates at a lower temperature which may have thaumasite form of sulfate attack especially when concrete contains a source of carbonate ions (Irasser, Bonavetti, and Trezza, 2005).

4.4.2 Rapid chloride permeability

For determining permeability and chloride resistance of concrete, rapid chloride permeability (RCP) was performed according to ASTM C1202 (Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration).

4.4.3 Freeze-thaw resistance

Freeze-thaw resistance was performed according to ASTM C666—procedure A in which the samples were rapidly frozen and thawed in saturated condition (Figure. 7). The fundamental frequency and mass changes were measured every 30 cycles, according to ASTM C215 (Standard Test Method for Fundamental Transverse, Longitudinal, and Torsional Frequencies of Concrete Specimens).

Assessment testing is a nondestructive method for assessing the dynamic response of the specimen. ASTM C215 uses modal testing to assess damage to beams undergoing freeze-thaw testing. A natural frequency of vibration is a characteristic (dynamic property) of an elastic system. Assuming a homogeneous, isotropic, elastic material, the dynamic modulus of elasticity is related to the resonant frequency and density.

The calculation of relative dynamic modulus of elasticity is shown as below:

$$P_c = (n_1^2/n^2) \times 100 \qquad \text{Equation (1)}$$

Where,

P_c = relative dynamic modulus of elasticity, after c cycles of freezing and thawing, percent,

n = fundamental transverse frequency at 0 cycles of freezing and thawing,

n_1 = fundamental transverse frequency after c cycles of freezing and thawing.

The test was completed when the sample reached 300 cycles or 15% mass loss. Then according to ASTM C666, the caculation of durability facotr is shown as follow:

$$DF=PN/M \qquad \text{Equation (2)}$$

Where,

DF = durability factor of the test specimen,

P = relative dynamic modulus of elasticity at N cycles, %,

N = number of cycles at which P reaches the specified minimum value (60%) or the specified number of cycles at which the exposure is to be terminated (300 cycles), whichever is less,

M = specified number of cycles at which the exposure is to be terminated.

Figure.7 Saturated Freeze-Thaw Samples in the Tank

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Fresh Properties Results

The target air content was 6%, the air content of freshly mixed concrete were all below 6%, shown on Table.10.

Table.10 Summary of Fresh Properties of All Mixtures

Mixture	Air Content (%)	Slump, cm (in.)	Unit Weight, kg/m^3 (pcf)
OPC	4.0	20(8.0)	2330(146)
PLC5	4.5	22(8.5)	2300(144)
PLC10	4.0	19(7.5)	2310(144)
PLC15	3.5	15(6.0)	2340(146)
PLC18	2.5	5(2.0)	2380(149)
PFA25	1.8	23(9.0)	2380(149)
PL5F15	2.0	22(8.5)	2403(150)
PL10F10	2.5	20(8.0)	2355(147)
PL15F5	4.2	19(7.6)	2355(147)
PL18F2	4.0	13(5.1)	2370(148)

The rate of limestone addition related to slump, with limestone addition rate increases, slump decreases. At the level of 18% replacement rate, concrete was a very stiffer mix, with a slump of 2 inches. Fly ash addition improved concrete workability, by increasing slump. At the level of 25% fly ash replacement rate, the slump was 9 inches. For the ternary mixtures, the slump changes, but overall is higher than single limestone addition groups.

Unit weight was slightly influenced by different cement type; overall the single limestone addition groups have lower unit weight than ternary groups. However, different rate of replacement does not have strong relationship with unit weight.

5.2 Compressive Strength Profile

Compressive strength as a primary mechanical property of concrete is effected by quality and quantity of cement. In this study, the different blended cement effects on compressive strength development were compared.

5.2.1 Compressive Strength Development of All Mixtures

With different types of cement as the only variance of concrete mixtures, Figure 8 shows the overall compressive strength development of all concrete mixtures.

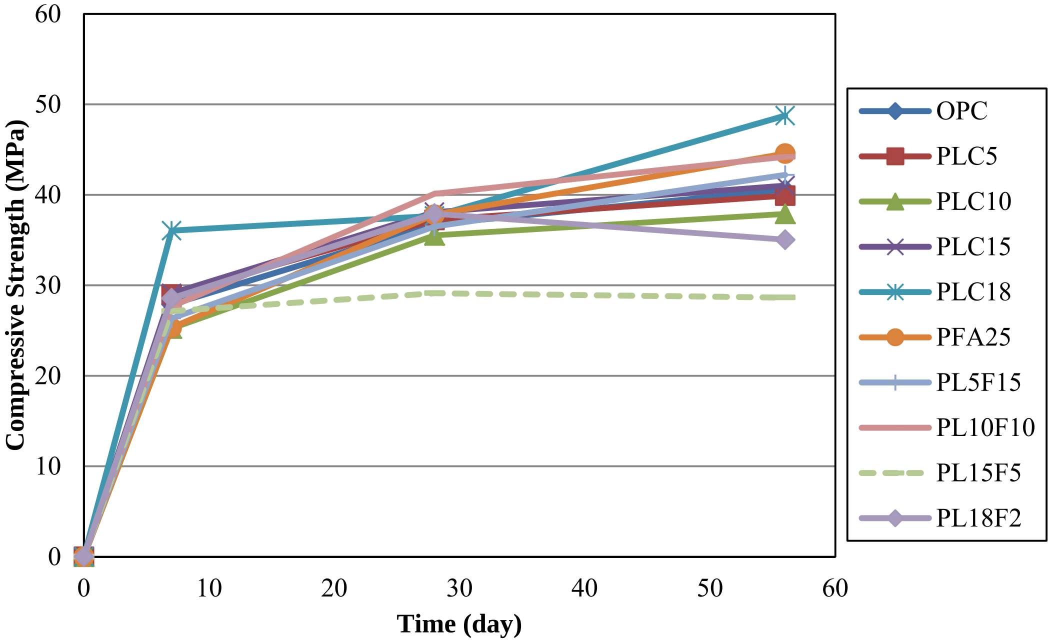

Figure.8 Compressive Strength Development of All Mixtures

From Figure.8, concrete produced with Portland limestone cement with 18% (PLC) had the best compressive strength performance. From a group of full-scale plant trials in Canada, it has been shown that equivalent strength can be achieved in concrete produced with PLC with up to 15% limestone intergrounding (Thomas et al. 2010a; 2010b; 2010c; 2010d). Generally, Blaine fineness of PLC has to get an increase between 100 m²/kg-120

m^2/kg to achieve the same 28 days compressive strength (Dhir et al. 2005). For PLC used in this research, intergrounding limestone is 18% replacement by mass with clinker, and has fineness of 495 m^2/kg. Comparing the fineness of OPC is 373 m^2/kg, increase is 122 m^2/kg which slightly higher than the recommendation, may explain the overall better compressive strength.

One of the ternary group, PL15F5 which has 15% limestone replacement and 5% class F fly ash replacement below the overall trends of other groups. The 28 days and 56 days compressive strength was low. Cementitious materials were batched by using Type I/II cement, 18% interground limestone PLC, and 25% blended class F fly ash cement. Blending process of all these three kinds of cement is not as evenly distributed as produced in the plant, and blain fineness is unknown.

The hydration rate was changed when limestone powder or fly ash or both were introduced into Portland cement system. The comparisons of compressive strength of different concrete mixture at different ages are shown as Figure. 9.

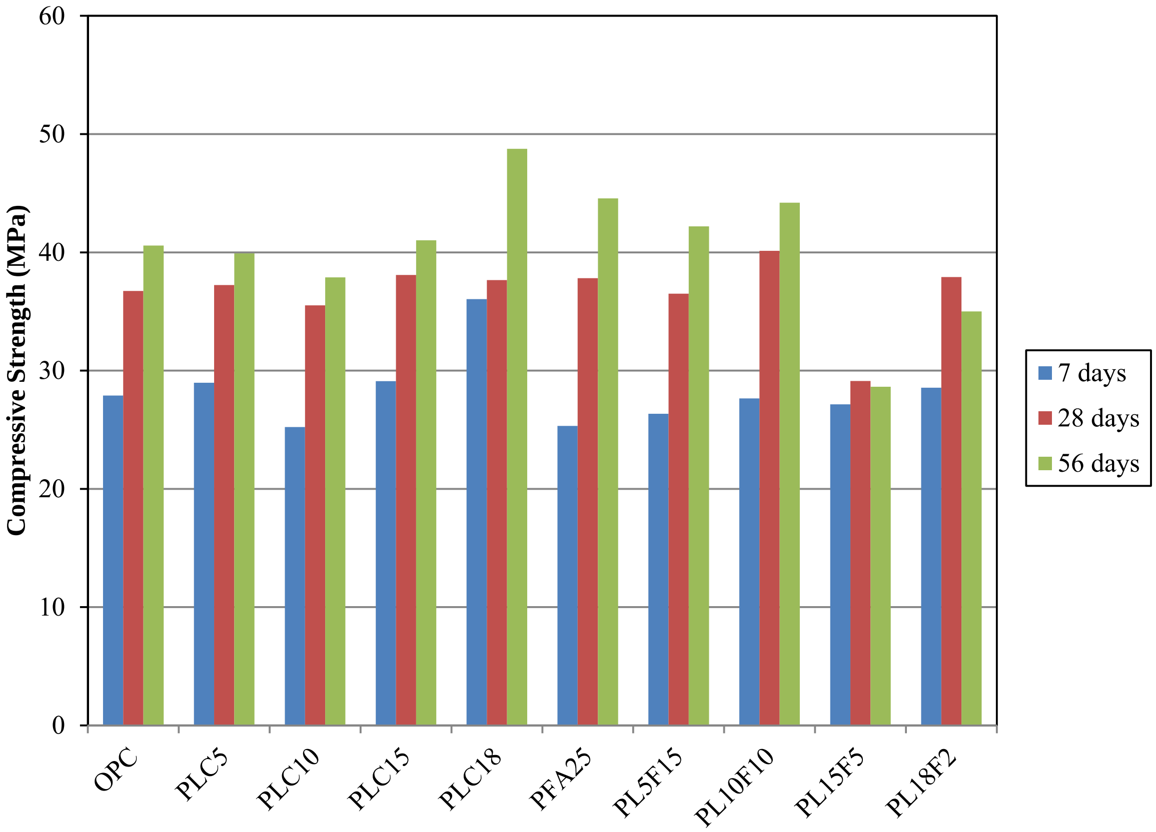

Figure.9 Comparison Compressive Strength of Different Concrete Mixture at Different Ages

From Figure 9, shows that at 7 days that PLC with 18% limestone content had the highest compressive strength which was 36 Mpa. All the limestone addtion groups had higher 7 days compressive strength results than OPC group, except PLC10 which had 10% limestone addition. Concrete produced with cement with 25% class F cement (PFA25) had the lowest 7 day compressive strength which due to its slow pozzolanic nature. Fly ash in blended cement could start hydration process until weeks after concrete was mixed, which also depend on the alkalinity in the pore water.

Ternary combination of fly ash and limestone were expected to interact in the hydration process and futher effect compressive strength. Up to 7 days, the group of PLC with fly ash were all sligthly lower than the control group OPC and the PLCs groups. At early age, particle packing had a higher influence on strength gain than the synsitic reaction that happen between clinker, fly ash and limestone powder.

At 28 days, as hydration process keeps going on, compressive strength of all groups continued to increase. PL15F5 did not show as much strength gain as others. PFA25 with 25% fly ash group started to gain strength signifantly, higher than the control group OPC. PLC18 with 18% intergrounding limestone groups continued slightly gain strength, had the relativly the same compressive strength as PLC15 which had 15% limestone interground, and PFA25. PLC5 which was 5% limestone interground still had higher stregnth at this age.

For the ternary groups, hydration reaction between clinker and fly ash and limestone started to become more obvious. PL10F10 had significant strength gain at 28 days age, PL18F2 had strength gain but not as much as PL10F10. Fly ash addition would introduce aluminate into system and impact on SO_3/Al_2O_3 ratio, further effect on hydration process and strength gain.

At the age of 56 days, trends of compressive strength comparison obtain from all mixture are different, showed on Figure 9. Compressive strength of PLCs groups were slightly higher than control group OPC, except PLC10 with 10% limestone addition which had not showed strength gain benefit along all the ages. PFA25 started to gain more strength than control group OPC, fly ash's pozzolanic reaction kept processing with time. Fly ash affected the hydration of cement clinker minerals, during long-term hydration, alite was accelerated, and belite and C_4AF were retarded (Etsuo Sakai, 2005). Introducing additional fly ash into system, result in low CaO/SiO_2 ratio of C–S–H in hardened hydration products. With PFA25, compressive strength continually grown over time, at the age of 28 days, PFA25 achieved the same strength as OPC, at the age of 56 days, and PFA25 had higher strength than OPC.

5.2.2 The Effect of Increasing Limestone Addition on Strength Development

Comparision of 7 days, 28 days, 56 days strengths, with limestone addtion increase, are shown by Figure.10. Overall compressive strength gains during 7 days to 28 days much more than during 28 days to 56 days. With interground limestone addition of 18%, the later age strength gain are significant, which can be contributed to delayed ettringite transformation into monosulfate.

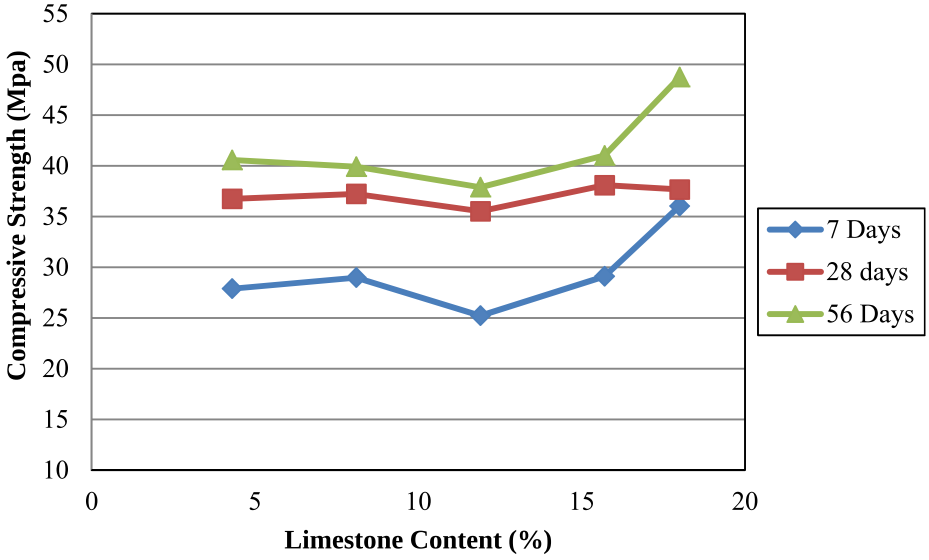

Figure.10 Comparison of Compressive Strength Concrete with Increasing Limestone Content at Different Ages

5.2.3 The Effect of Increasing Limestone Addition on Strength Development of Ternary Mixtures

Ternary mixtures keep the blended materials at 20% level of replacement with Portland cement, increasing limestone addition and decresing fly ash addition. The effect of ternary blended cement concrete on compressive strength at different age is comparied at Figure.11.

Despite of Group PL15F5, all other ternary groups later strength gain are not significantly.

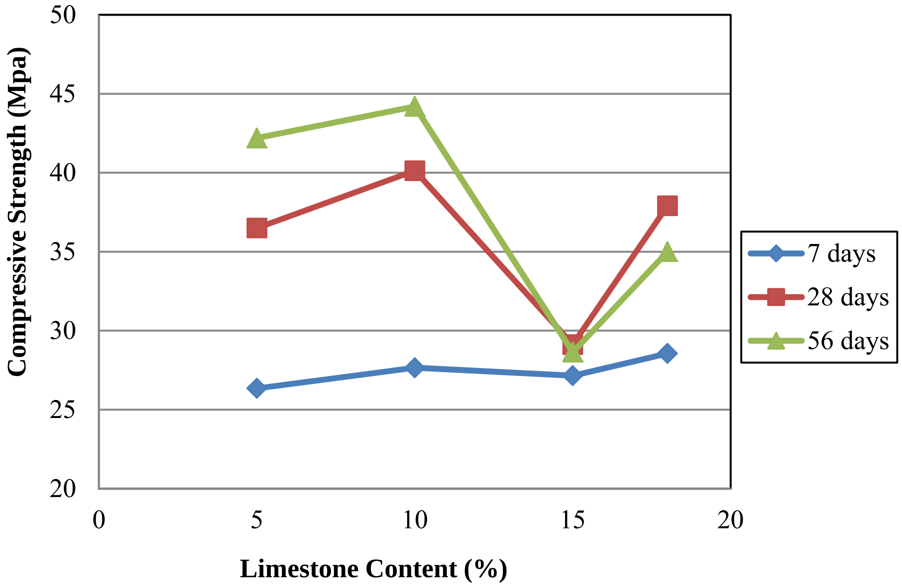

Figure.11 Comparison Compressive Strength of Concrete Produced with Ternary Cement

At different limestone replacement rates, the effect of with and without fly ash addition on compressive strength development is shown as Figure.12. At the level of 5% limestone addition rate, adding fly ash lowered the compressive strength at early age (7 days and 28 days). Because the nature of fly ash's pozzolanic reaction, fly ash hydration process happened later than Portland cement. At the level of 10% limestone addition rate, the ternary blended groups shows increasing compressive strength at all ages. At the level of 15%, without fly ash blended group have higher compressive strenght than ternary groups at any ages, so as the level 18% replacement rate.

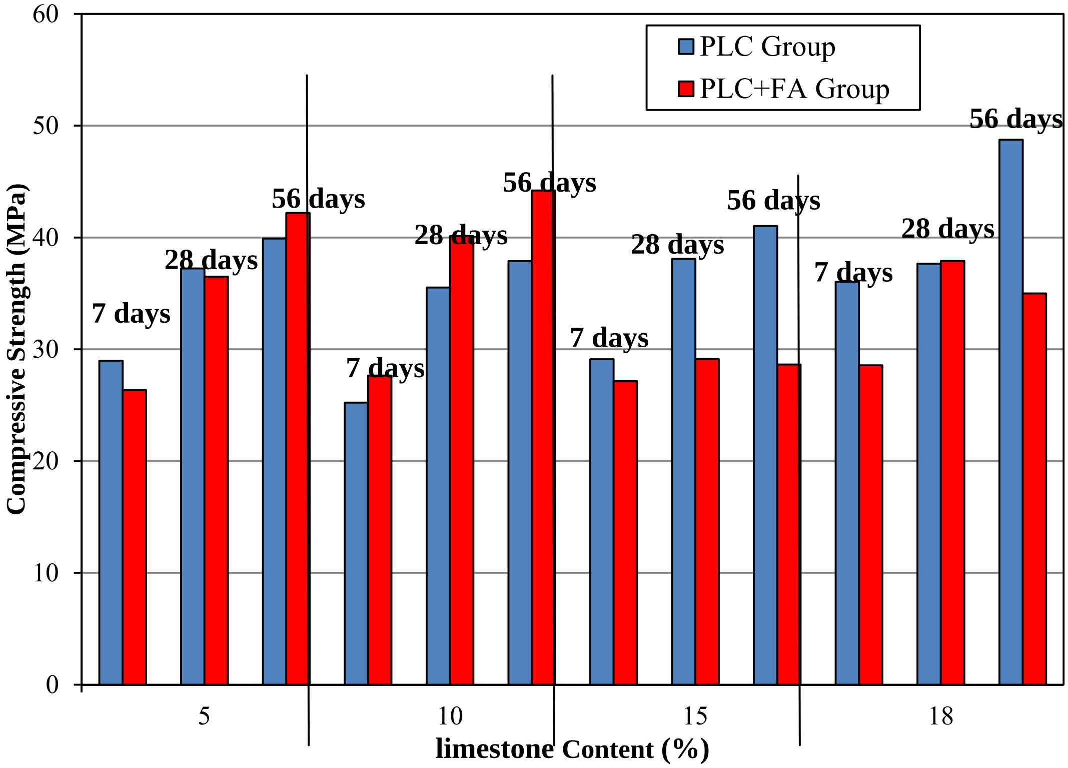

Figure.12 Comparison Compressive Strength of PLC Groups and PLC+FA Groups with Limestone Content Increased

5.3 Shrinkage Profile

The effect of limestone addition and the rate of limestone addition on shrinkage properties were compared. The effect of different type of ternary blended cement on shrinkage properties was compared as well.

5.3.1 Overall drying shrinkage and autogenous shrinkage of all mixtures

Total shrinkage, drying shrinkage, autogenous shrinkage of all mixtures was compared in this section.

Total unrestrained total shrinkage of all mixtures is shown in Figure.13. Portland cement with 25% class F fly ash had the lowest volume change, both in early age and latter age, followed by Portland cement with 10% limestone addition, and then followed by PLC 15 and PLC 5 which were similar. PLC with 18% limestone addition has the greatest volume changes.

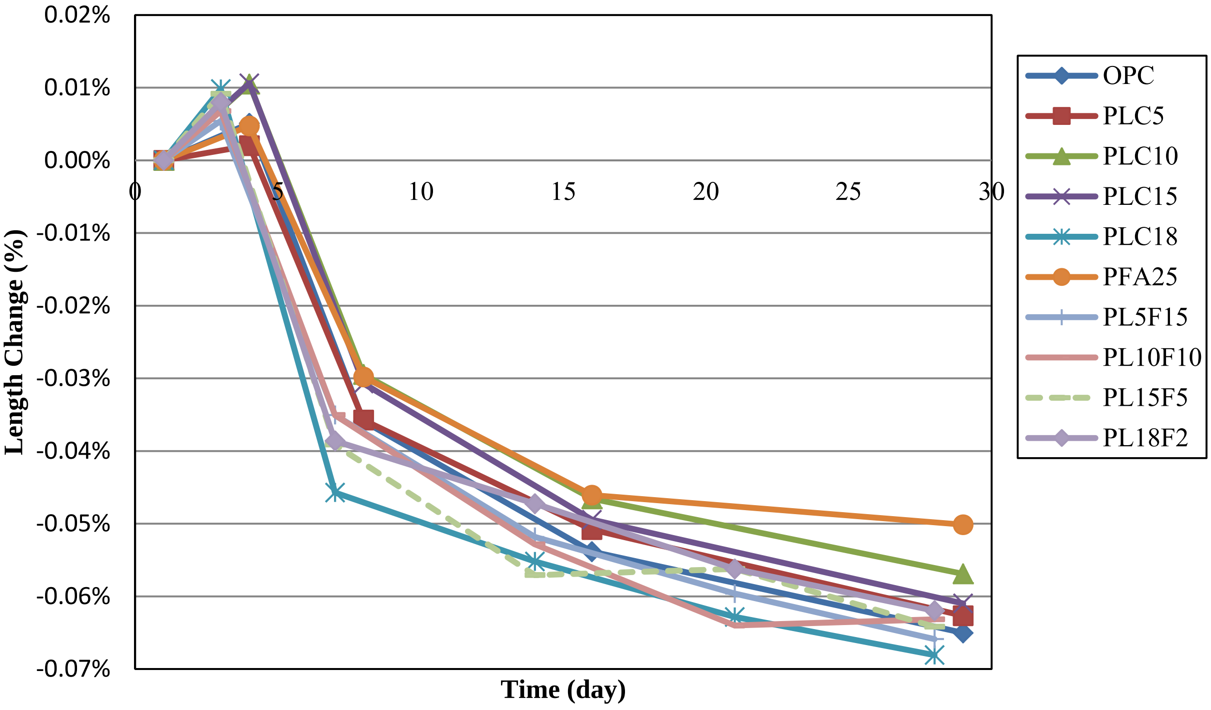

Figure.13 Total Shrinkage of All Mixtures

Unrestrained drying shrinkage of all mixtures was compared in Figure 14. The values of unrestrained drying shrinkage were obtained from the difference between total shrinkage and autogenous shrinkage. At early ages, mortar with higher limestone addition rate cement with or without fly ash addition (PLC15, PL15F5, PLC18, and PLC18F2) showed larger length change than OPC control group. At later ages, all blended cement mortar showed smaller length change than OPC control group. The groups with limestone addition rate at 18% (PLC 18, PLC18F2) showed lest length change at the age of 28 days.

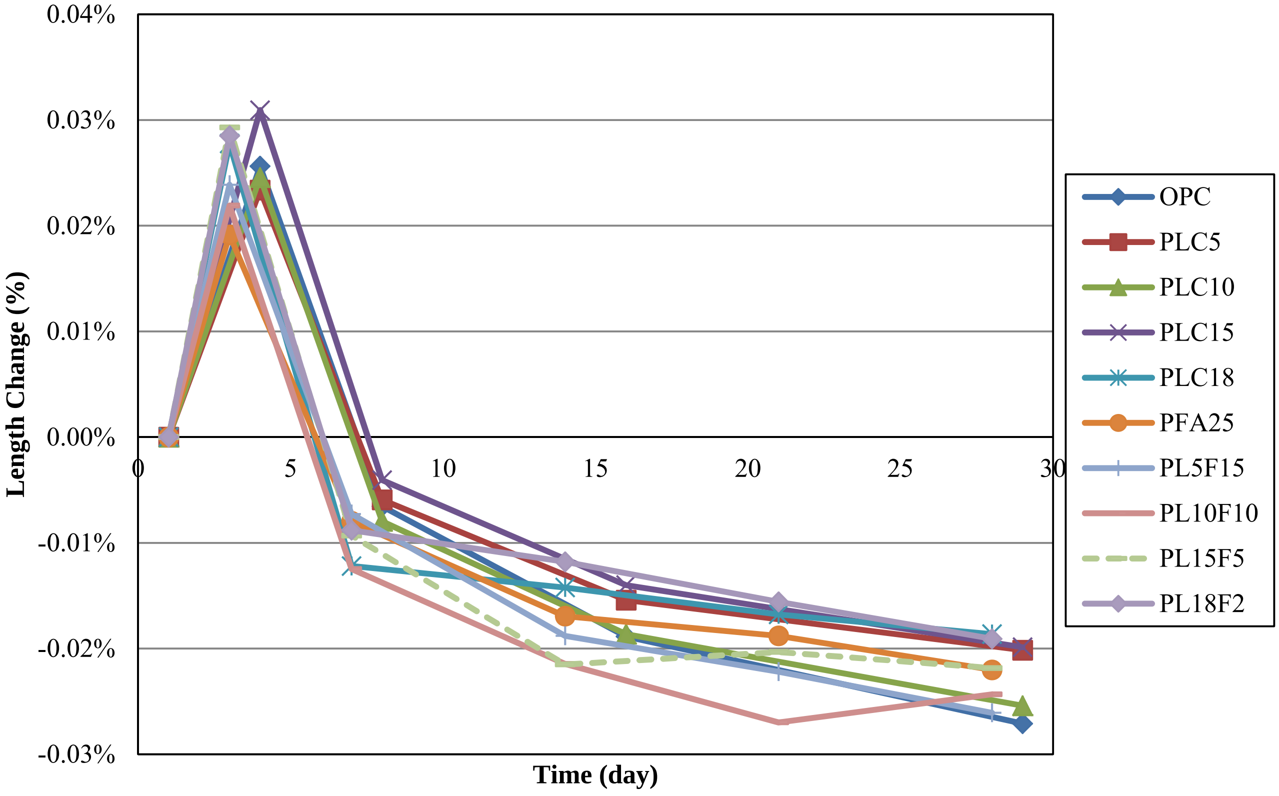

Figure.14 Drying Shrinkage of All Mixtures

Drying shrinkage refers to the reduction in concrete volume by losing water from concrete. As water is lost, concrete will shrink. The drying shrinkage is main concern, since drying shrinkage is related to early age cracking (Mindess, Young, 1981). The drying shrinkage mechanism is dependent on the internal pore space. At the early age of hydration process, mortar with higher limestone addition showed larger expansion by providing nucleation sites, increasing the rate of hydration. At the later ages, because of more hydration product had been produced to fill up the pores caused by vapor water, all blended cement mortars showed less length change comparing to OPC control group.

Autogenous shrinkage of cement paste and concrete is defined as the macroscopic volume change occurring with no moisture transferred to the exterior surrounding environment. It is the result of chemical shrinkage affiliated with the hydration of cement particles (Japan, 1999).

Autogenous shrinkage occurs over three different stages, within the first day after mixing: liquid, skeleton formation, and hardening (Baroghel-Bouny, 2006). Hardening stage happen over age of 1 day, when chemical shrinkage is no longer involved. At this stage is a competition between autogenous shrinkage due to self-desiccation and autogenous expansion due to cement hydration reaction products at early age, for example: ettringite formation, the growth of calcium hydroxide crystals, and/or the imbibition of water by the gel hydration products (Baroghel-Bouny, 2006). Powers theory showed that autogenous shrinkage due to self-desiccation occurs when the water/cement ratio is below 0.42 (Powers, Brownyard, 1948). In this study, a w/c of 0.385 was used.

Autogenous shrinkage of all mixtures is shown at Figure 15. Limestone addition with 10% rate (PLC10) showed the minimum length change of all groups, followed by fly ash 25% replacement group (PFA25). Then OPC control group has moderate length change. The highest length changes are groups with 18% limestone addition rate, with and without fly ash addition.

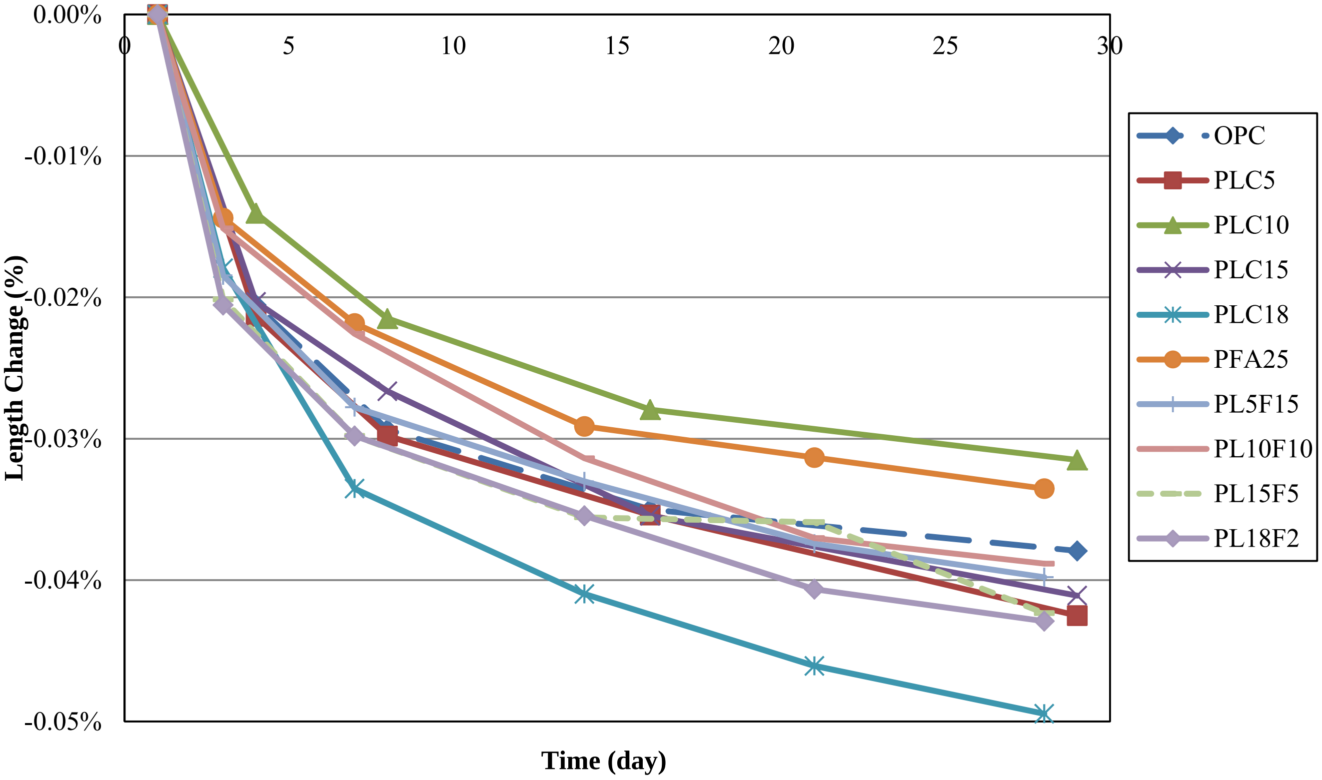

Figure.15 Autogenous Shrinkage of All Mixtures

Autogenous shrinkage can be improved by modify the particles distribution of the cement paste, balancing cement paste self-desiccation and the rate of hydration production. Bentz studied a modification focus on modifying the surface area and interparticle spacing of the particles comprising the cementitious matrix component could reduce the potential of early cracking caused by autogenous cracking (Bentz, Peltz, 2008). Autogenous deformation of the mortars made with fine cement, fine cement with coarse limestone replacement, and fine cement with fine limestone replacement was compared.

Comparison the total length change of all the mixture at 28 days during drying process, Figure.16 are more clearly showed that for PLC group, limestone addition with 10% are almost as less length change as Portland cement with 25% fly ash. Limestone addition less than 15% have less length change than OPC. Ternary are not much difference compared to OPC.

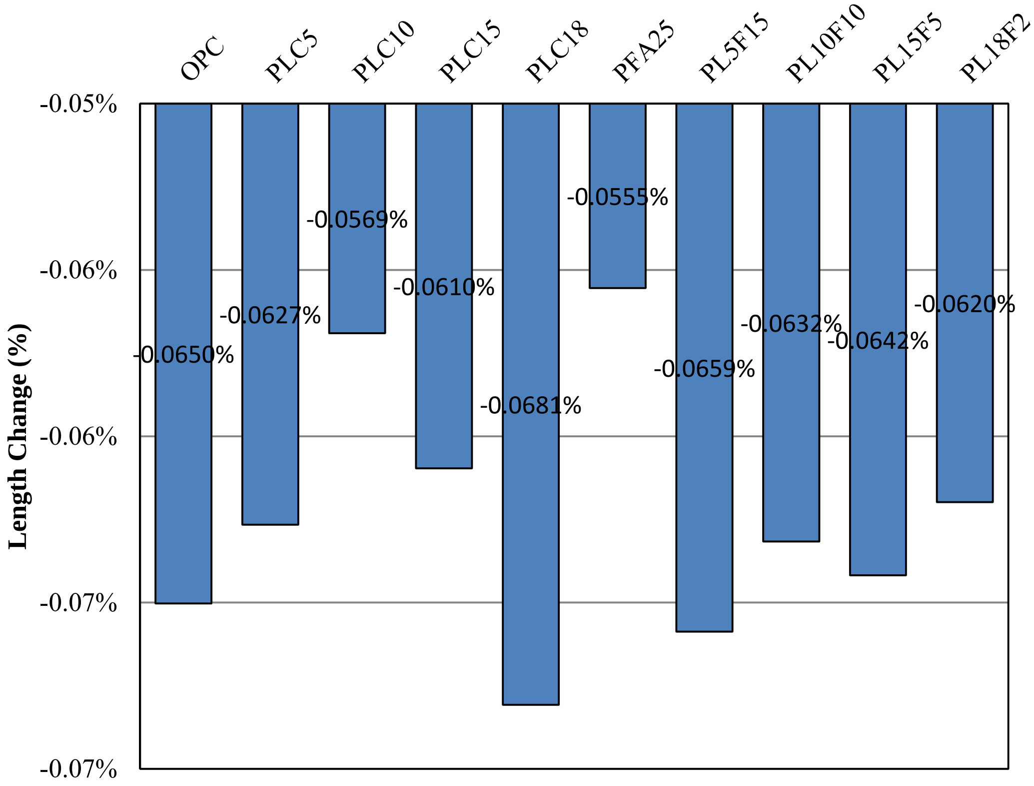

Figure.16 Total shrinkage of all mixtures at 28 days

Figure.17 shows autogenous shrinkage of all mixtures over 28 days. For autogenous shrinkage PLC10 has the minimum length change, and then followed by PFA25. Portland cement with 18% limestone addition (PLC18) has the biggest length change. All the other mixtures are in the middle range, the length change differences have no statistical significant. Compare other level of limestone addition, the length change are larger than OPC. Comparing PL18F2 and PLC18, 2% fly ash addition are effectively mitigate the length change.

Ternary groups have slightly larger length change comparing to OPC, so as PLC5 and PLC 15.

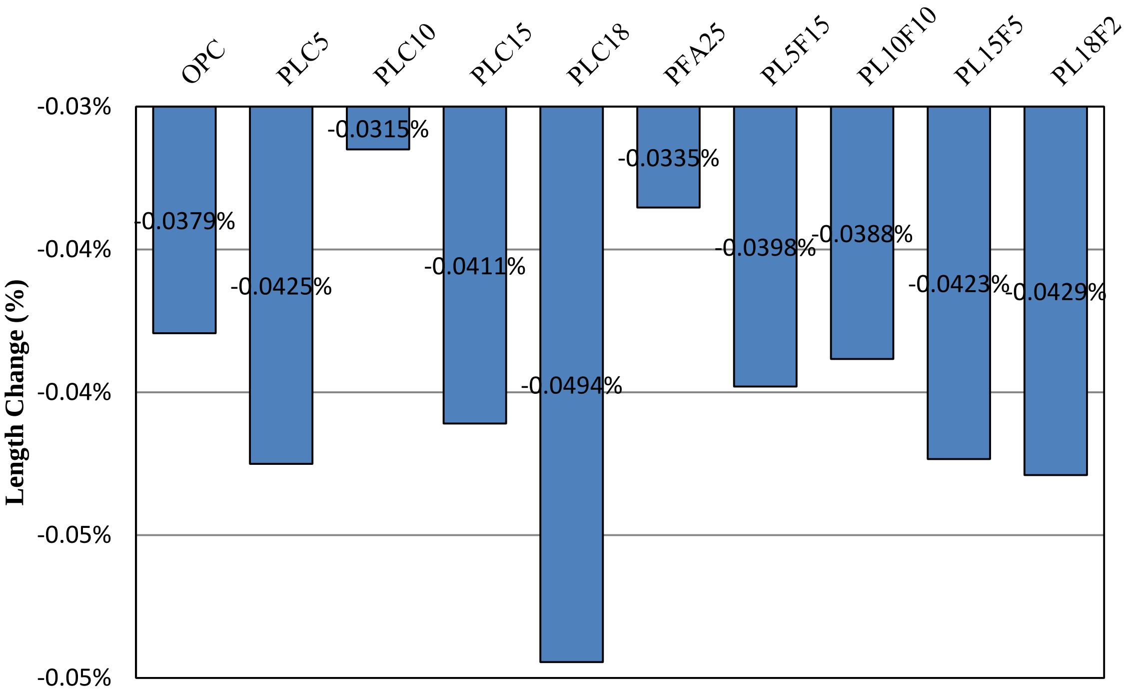

Figure.17 Autogenous Shrinkage of All Mixtures at 28 Days

After performing a statistical analysis between OPC and other blended group, Table. 11 shows there are no significant difference length change of drying shrinkage and autogenous shrinkage.

Table.11 the Analyses of Variance (ANOVA) for Total and Autogenous Shrinkage at 28 Days

Comparison Group		Total shrinkage		Auto shrinkage	
		Prob>F	Significant	Prob>F	Significant
OPC	PLC5	0.184492557	NS	0.953085897	NS
OPC	PLC10	0.163178842	NS	0.094414576	NS
OPC	PLC15	0.156035946	NS	0.860888557	NS
OPC	PLC18	0.206821565	NS	0.233054897	NS
OPC	PFA25	0.265303426	NS	0.131377987	NS
OPC	PL5F15	0.197443907	NS	0.650097151	NS
OPC	PL10F10	0.186447033	NS	0.454637923	NS
OPC	PL15F5	0.190511756	NS	0.973589803	NS
OPC	PL18F2	0.181947618	NS	0.567313532	NS

It should be noted that Portland cement with certain amount interground limestone (around 10%) will benefit drying shrinkage and autogenous shrinkage to further reduce in the cracking potential. In regarding volume change, PLC10 performed as well as Portland cement with 25% cement (PFA25), which is commercially used cement in the industry. Research conducted at Purdue University by Bucher (Bucher, Radlinska, 2008) showed similar results.

Different composition and fineness of cements have distinctive effect on volumetric change. By adding certain among of coarser filler can improve shrinkage (10% limestone addition in this research).

5.3.2 The Effect of Fly Ash

Figure.18 shows the drying shrinkage of different level of Portland cement with limestone addition comparing with the same level of limestone addition with decreasing amount of fly ash addition. Ternary groups have larger length change overall comparing to PLC groups. Also ternary groups keep total replacement rate at 20% of Portland cement.

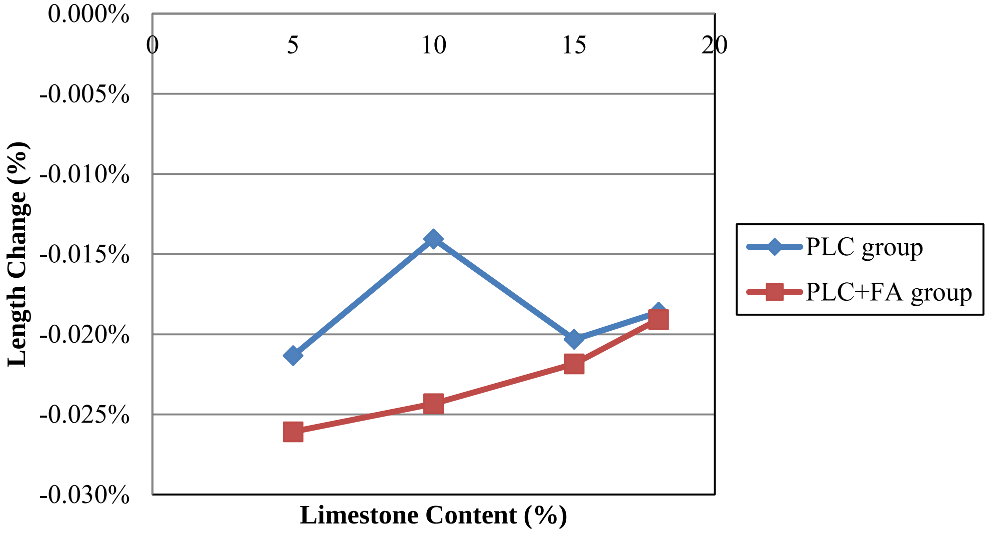

Figure.18 Comparison 28 Days Drying Shrinkage between PLC Group and PLC with Fly Ash Group

Despite of PLC10 outstanding performance on both drying shrinkage and autogenous shrinkage which was discussed previously, with fly ash replacement rate decrease, the length changes decrease too. The reason of fly ash groups have higher length change maybe relate to the large surface area of fly ash. The internal water loss causes cement paste drying shrinkage. From Figure 19 shows that when evaporating water (W) exceeds the bleed water moving to the surface from within the concrete, capillary pressure developed. When fly ash introduced into the system, as the particle size decreases, the meniscus radius decreases, then the capillary pressure increases. Therefore, more internal water is lost, with a consequence of increasing drying shrinkage.

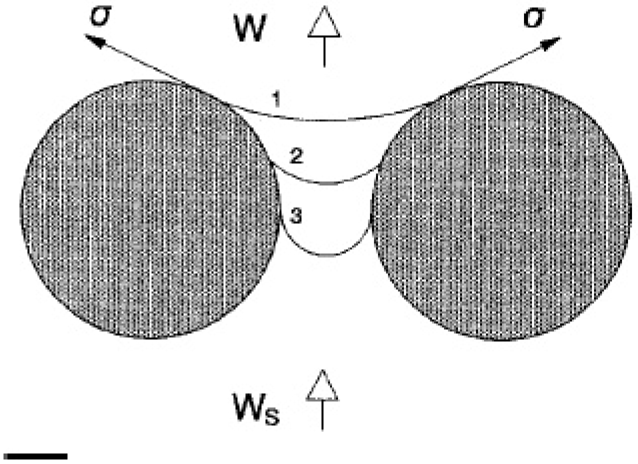

Figure.19 Stress Pulling the Water Meniscus between Two Cement Particles Due To Moisture Transfer and Capillary Pressure Development (Radocea, 1992)

Autogenous shrinkage is more about interparticle spacing of the particles and surface area. Introducing fly ash into the system does not significant effect length change of autogenous shrinkage in Figure.20. Autogenous shrinkage of ternary systems with different limestone and fly ash combination are not affected. On the other hand, PLCs group has a peak when limestone replacement reaches to 10% which has the smallest length change.

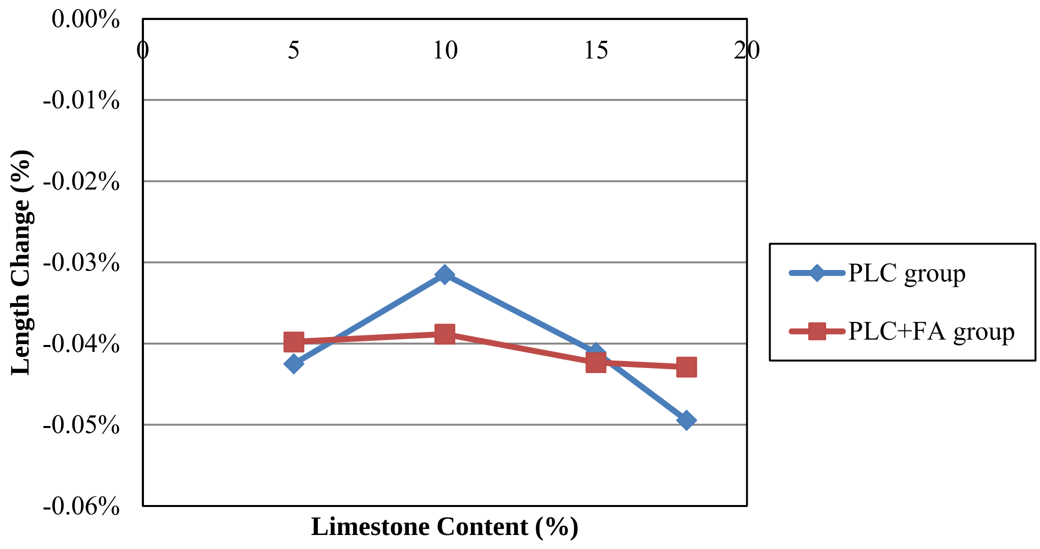

Figure.20 Comparison 28 Days Autogenous Shrinkage between PLC Group and PLC with Fly Ash Group

5.3.3 Early age of volume stability

At the early age, all mixtures experience expansions for drying shrinkage, contraction for autogenous shrinkage. The magnitude of overall length changes at early ages, the group with 25% fly ash replacement showed the lowest length change, shown as Figure.21. Then, the level of 10% limestone replacement, with and without fly ash addition showed less length change.

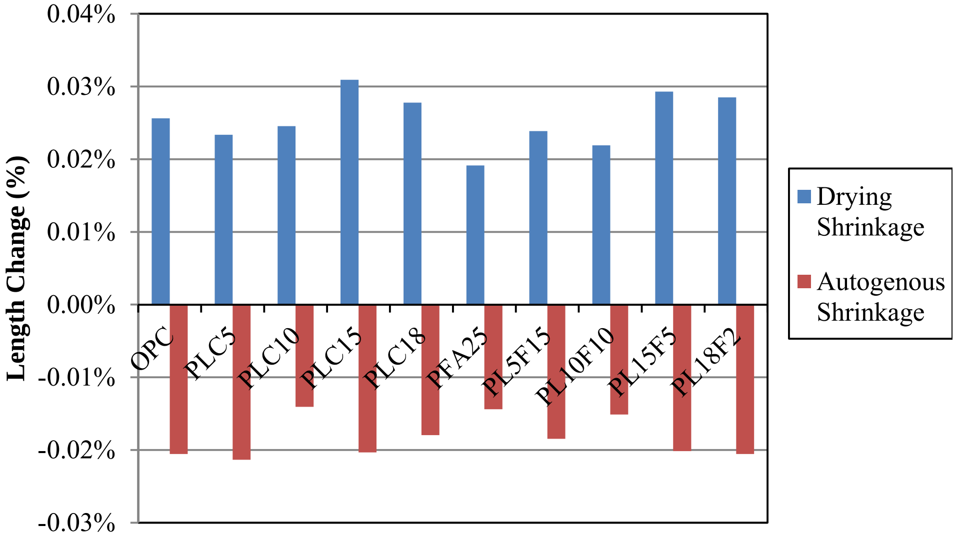

Figure.21 Volume Changes of All Mixtures at Age of 4 Days

5.4 Sulfate Resistance Profile

Sulfate resistance tests were conducted with the respect of length change. Different types of blended cement with different rate of replacement were compared as below. Figure. 22 showed that the effect of limestone addition on sulfate resistance, the different rates of replacement effect on sulfate resistance as well.

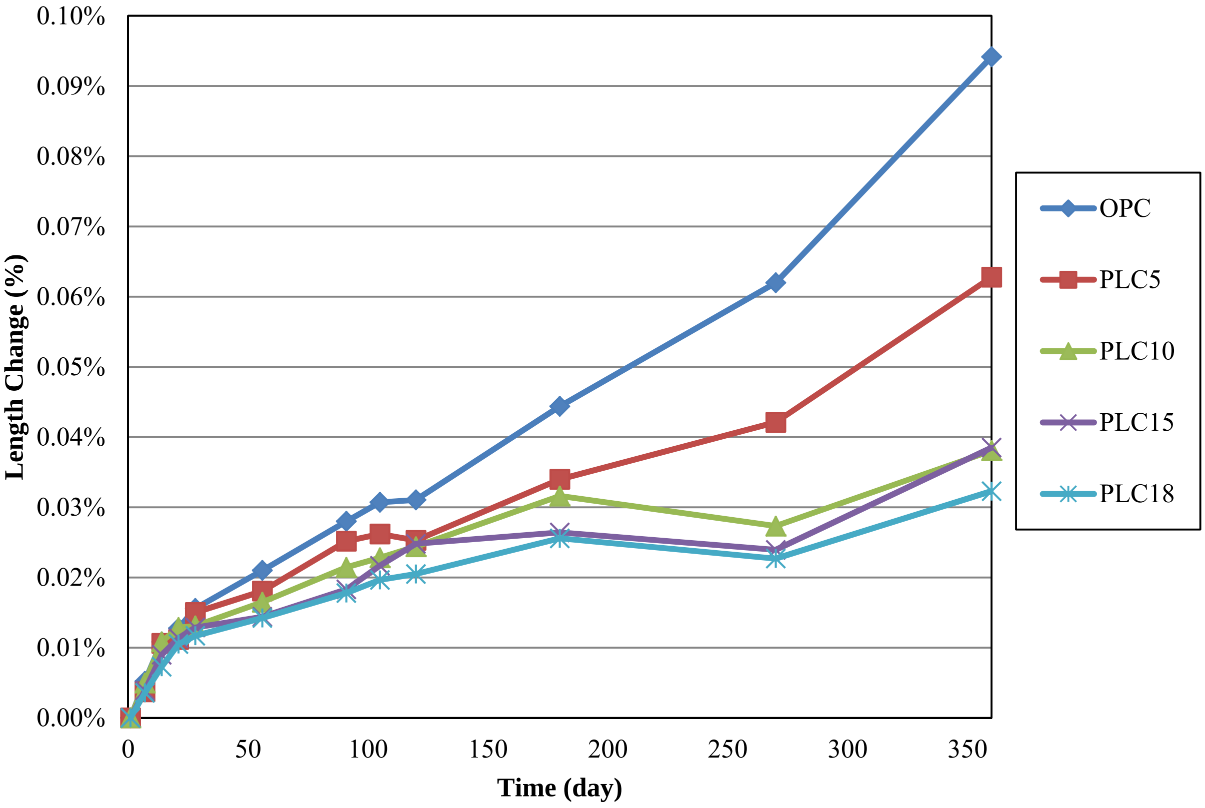

Figure.22 Comparison of Length Change of Limestone Addition Groups and Control Group (OPC) over 360 days

Limestone addition showed decreased in length change from the early age until a year later. With limestone addition rate increase, the length reduction increased as well. PLC18 shows the lowest length change overall. After moving from 23 °C to 5°C environment, groups with over 10% limestone addition rate (PLC10, PLC15, and PLC18) showed the length increasing rate decrease, by comparing the slopes in the Figure 22.

The fly ash additions had significant effect on decreasing expansion, shown as Figure.23. The overall fly ash addition groups have the length expansion under 0.03%, by comparing to the control group (OPC) with under 0.1% expansion. PL5F15 have the least length changes, and then PFA25 have higher length changes, the rest ternary blended groups are close together, with slight differences.

After moving from 23 °C to 5°C environment, the length changes rate decrease overall.

The effect of different ternary blended ratio of limestone and fly ash, on length change was different. It maybe relate to the particle size distribution. By comparing, PLC5 in Figure 22 and PL5F15 in Figure 23, PLC5 with only 5% limestone addition had length change of 0.06%; however, PL5F15 with 5% limestone addition and 15% fly ash addition has the lowest length change 0.015%. When the fly ash addition ratio decreased to 2%, comparing PLC18 and PL18F2, the length changes were around 0.03%, PL18F2 still had lower length change than PLC18, but not as significant as the group with 15% fly ash addition.

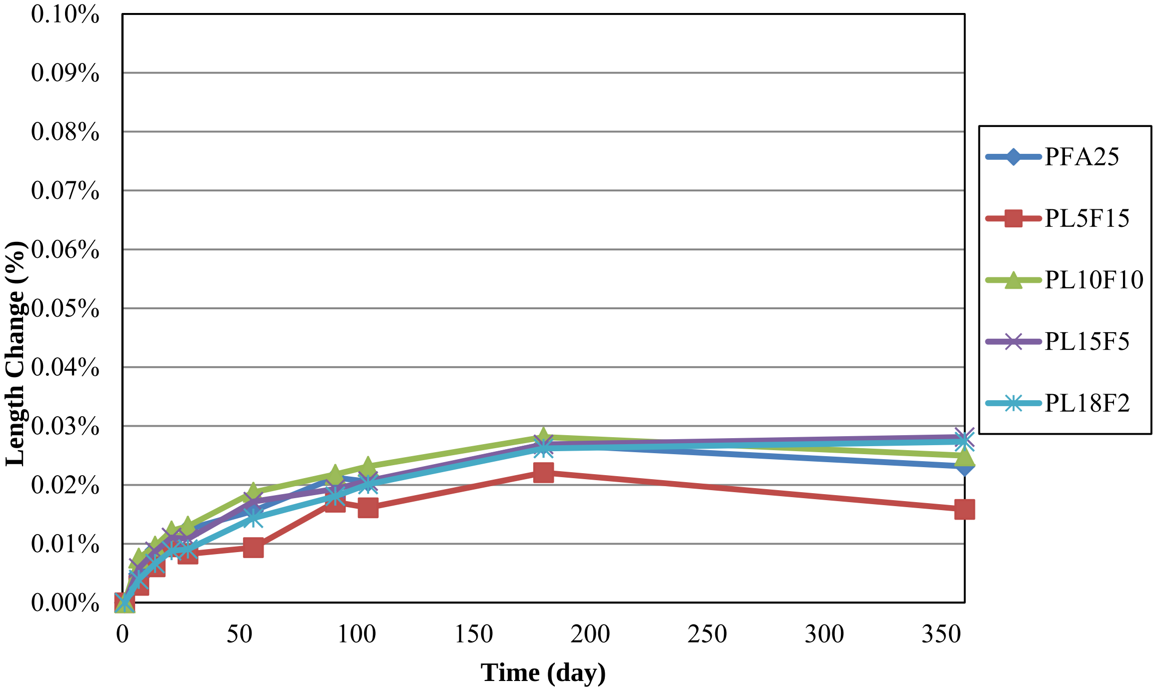

Figure.23 Comparison of Length Change of Ternary Groups over 360 days

After specimen had been removed to 5°C from 23 °C, the rate of length change showed similar to the PLCs groups.

Length change was not necessary related to limestone content effect on thaumasite formation or erttrigite formation. Limestone content could relate to strength loss or mass change. In this study, mass change were recorded which is shown as Figure.24 and Figure.25.

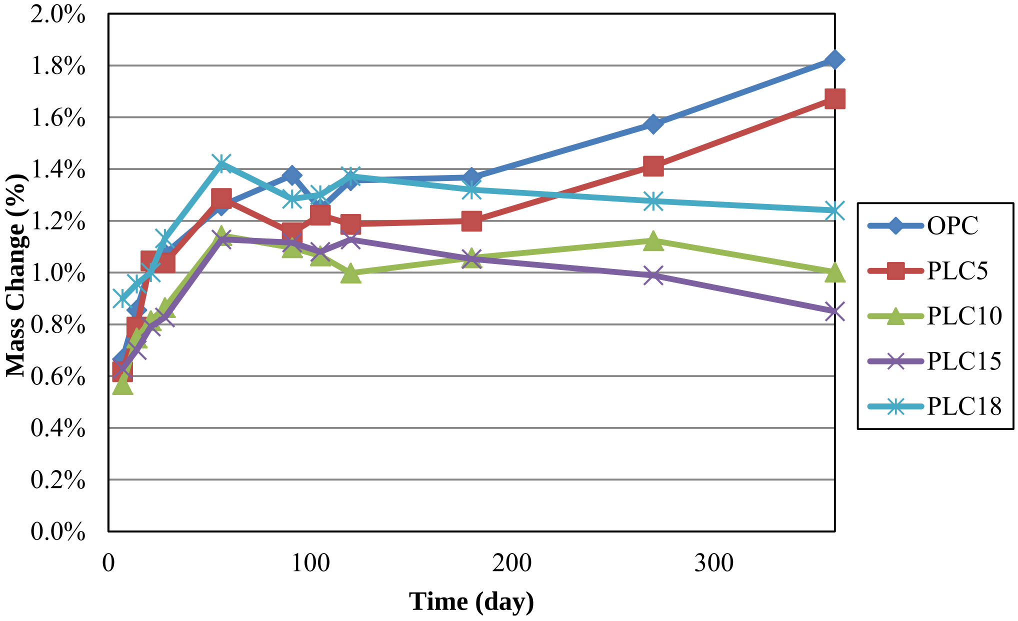

Figure.24 Comparison of Mass Change of Limestone Addition Groups and Control Group (OPC) over 360 days

Figure.24, shows that up until less than 100 days, the mass change was rapid, the rest time until moving to a lower temperature, the mass changes was not significant. After samples were removed to 5°C, the mass changes trends changed. The mass changes of OPC and PLC5 grew faster again, however, with higher limestone addition 10%, 15%, 18%, mess changes decreased. From visual observation, mortar samples started to dissolve. Figure.26 shows the corner and the edge of the mortar sample, starting to expanse and loses materials.

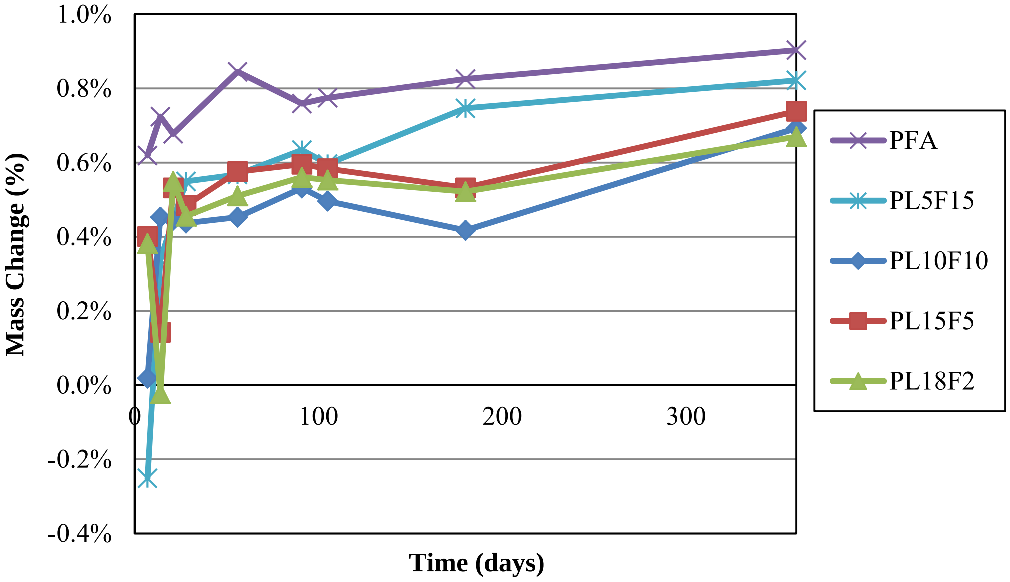

Figure.25 Comparison of Mass Change of Fly Ash Groups over 360 days

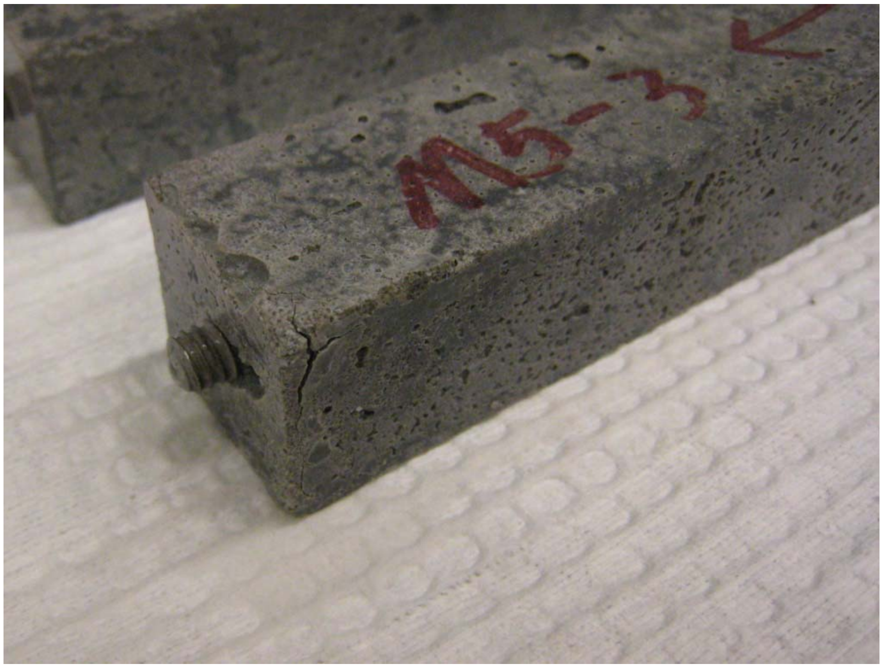

Figure.26 Specimen at 270 Days

From Figure.25, at the early ages, all the ternary groups with limestone and fly ash addition had mass loss, however, the groups with only fly ash addition PFA25 had mess grow the whole time, also has higher mass change then other groups. PL5F15 has the second mass changes, following by PL15F5 and PL18 F2, PL10F10 has the lowest mass change. After samples were removed to 5°C, all the groups on Figure.25 had mass gain, which is different from PLCx (PLC5, PLC10, PLC15, and PLC18) which were only with limestone addition.

A thaumasite formation can be identified by using scanning Electron Microscopy (SEM). Also the formation is a long time process in the field.

5.5 Rapid Chloride Permeability Profile

The permeability and chloride resistance of concrete mixtures with different type of blended cement were evaluated by conduced "rapid chloride permeability test" (RCPT). The overall results are shown as Figure.27.

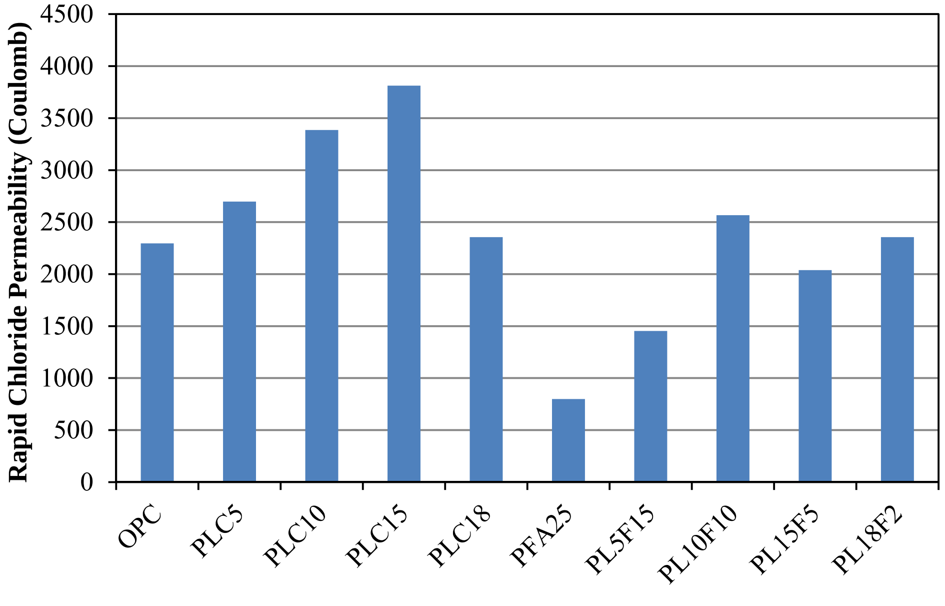

Figure.27 RCPT of All the Mixtures

Fly ash blended ternary groups have significantly improved chloride resistence and lower permeability comparing to control group (OPC) and only limestone addtion groups (PLCx). All the specimen were cured in lime-water until the age of 56 days, then removed to the testing. The hydration processing kept happening within 56 days. Due to the pozzolanic activity, fly ash chemically react with water and calcium hydroxide, forming much more hyration products to density concrete. Fly ash addition have much more effect on reducing concrete permability than limestone replacement of providing more nucleation sites to improve hydration processing. With fly ash addition decresed, the permeability of concrete increased.

The limestone addition groups showed the trend that with limestone addition increases, the permeability of concrete decreases until the 15% level of replacement. At the level of 18% replacement (PLC18), the RCPT result were similar to control group (OPC), slightly higher than OPC. The compressive strength of PLC18 at the age of 56 days was the highest among all the specimen. The comparision of RCPT results along 56 days compressive strength was presented at Table.12.

Table.12 Permeability Result of Concrete Produced by PLC group

No.	OPC	PLC5	PLC10	PLC15	PLC18
Limestone, %	4.7	5	10	15	18
Concrete: Strength at 56days (MPa)	40.57	39.91	37.89	41.02	48.75
Concrete: RCPT (Coulombs)	2295	2698	3386	3812	2355
Concrete: W/CM	0.45				

There is not strong relationship between strength and rapid chloride permeability test results.

The effect of fly ash replacement with limestone content increases was compared, shown on Figure.28. Fly ash has more effect on permeability of concrete. For ternary mixtures keep 20% total replacement, as limestone content increases, fly ash content decreases, and the RCPT results increase. The RCPT results and 56 days compressive strength is presented on Table.13.

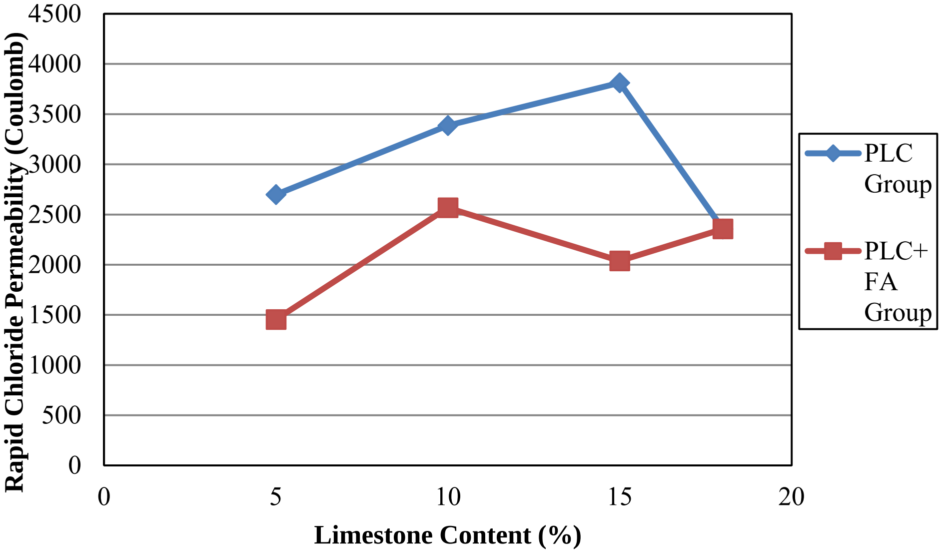

Figure.28 Comparison RCPT of PLC Group and PLC+FA Group with Limestone Content Increase

Table.13 Permeability Result of Concrete Produced by PLC+FA group

No.	PFA25	PL5F15	PL10F10	PL15F5	PL18F2
Limestone, %	0	5	10	15	18
Fly Ash, %	25	15	10	5	2
Concrete: Strength at 56days (MPa)	40.57	39.91	37.89	41.02	48.75
Concrete: RCPT (Coulombs)	2295	2698	3386	3812	2355
Concrete: W/CM	0.45				

There is not strong relationship between RCPT results and 56 days compressive strength. But overall results with up to 20% limestone replacement, the rapid chloride permeability test result showed moderate permeable level as the worst result. The others permeability tests such as gas permeability, water permeability could be further studied for a comprehensive recommendation about the effect of limestone addition on concrete permeability.

5.6 Freeze-Thaw Resistance Profile

Freeze-thaw resistance testing was conducted according to ASTM C666A, with saturated specimen freeze and saturated thaw. This test represents the most extreme case, therefore it cannot be determined the deterioration fact in the actual field.

The aggregate used in this study are frost-resistance, the freeze-thaw resistance of the cement paste determines the overall resistance of the concrete to freezing and thawing cycles.

5.6.1 Damage Assessment of All Mixture

Assessment testing is a nondestructive method for assessing the dynamic response of the specimen. ASTM C215 uses modal testing to assess damage to beams undergoing freeze-thaw testing.

Relative dynamic modulus of elasticity of all mixtures under freeze-thaw cycles is compared on Figure.29, shown as below. When the relative dynamic modulus of elasticity of any mixture under 60%, concrete group was considered failure.

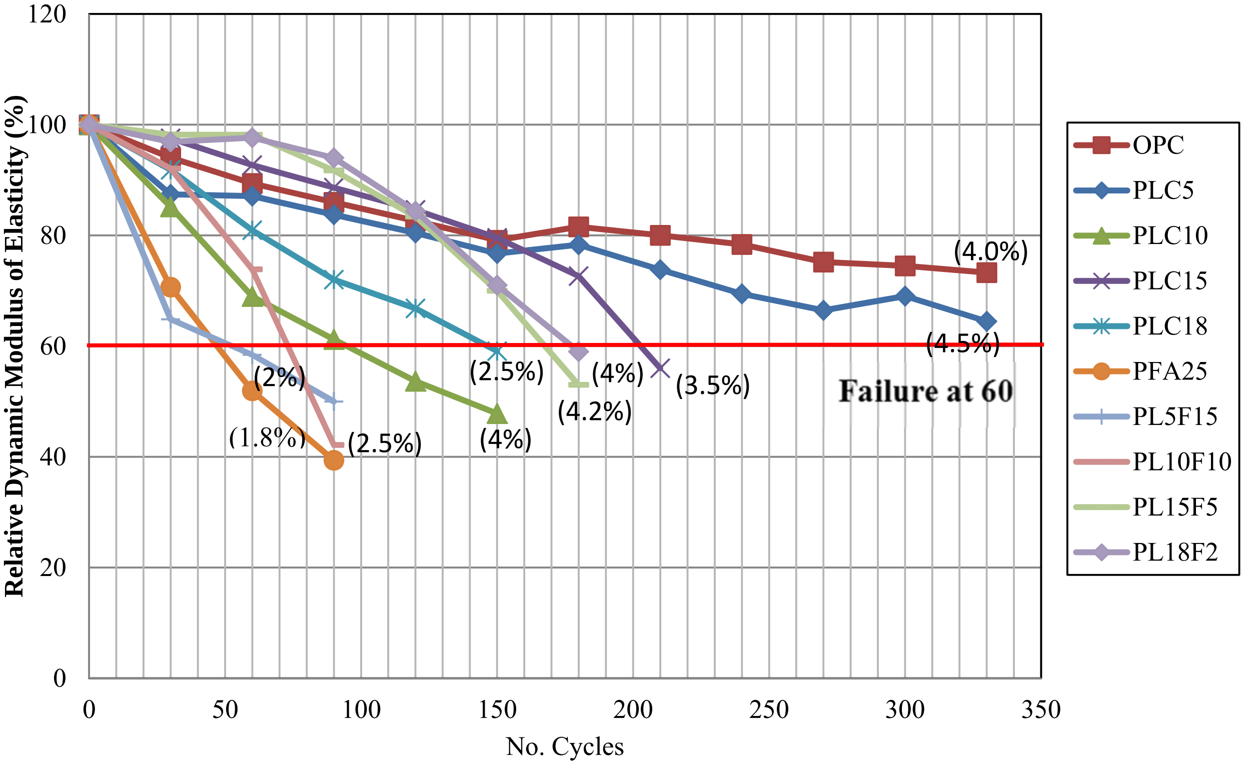

Figure.29 Relative Dynamic Modulus of Elasticity of All Mixtures Under Freeze-Thaw Cycles

Concrete freeze-thaw resistance has strong relationship with air content. PFA25 and PL5F15 with the lowest air content which are 1.8% and 2.0% failed the first. Control group (OPC), PLC5 and PL18F2 have the highest air content, 4%, 4.5% and 4% respectively. OPC has overall better performance during 300 cycles than PLC5, even with slightly lower air content. PL18F2 with relatively high air content, but failed at 210 cycles. Air void system is another factor that effect concrete freeze-thaw durability. Either limestone or fly ash has higher surface area, which could affect the spacing factor or specific surface of air void system, which could further affect freeze-thaw durability.

5.6.2 Comparison of Durability factor of All Mixtures

According to ASTM C666, the results of durability facotr of all mixtures is shown at Table.14.

Table.14 Durability Factor of All Mixtures

No.	Durability Factor (%)	No.	Durability Factor (%)
OPC	74	PFA25	10
PLC5	66	PL5F15	12
PLC10	24	PL10F10	13
PLC15	40	PL15F5	32
PLC18	30	PL18F2	35

Research about the relationship between air content and durability factor had been studied, which is shown as Figure.30 below.

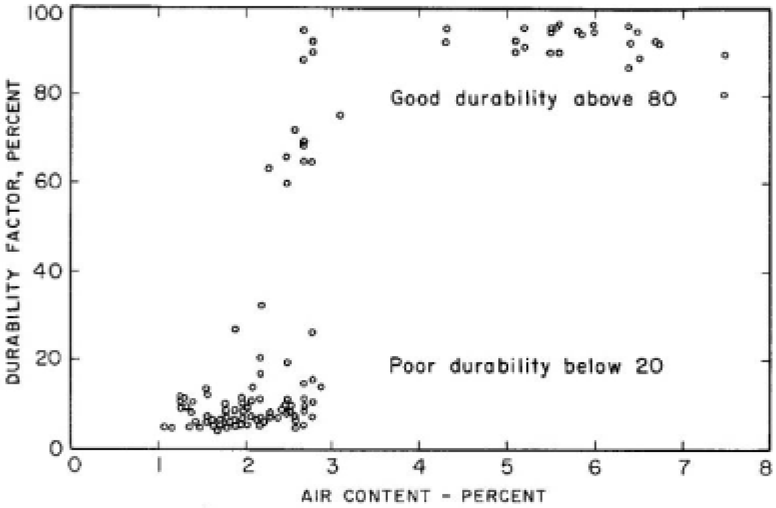

Figure.30 Freeze-thaw durability factor for different levels of total air contents (Cordon, 1963)

Concrete air content above 3% is practically considering good F-T durability, with a durability factor over 80%. All the durability factors of 10 mixtures with respective air content are listed on Figure. 31. The properties of cement paste have effect on concrete F-T durability as well; hence Figure.31 is not exactly like Figure. 30.

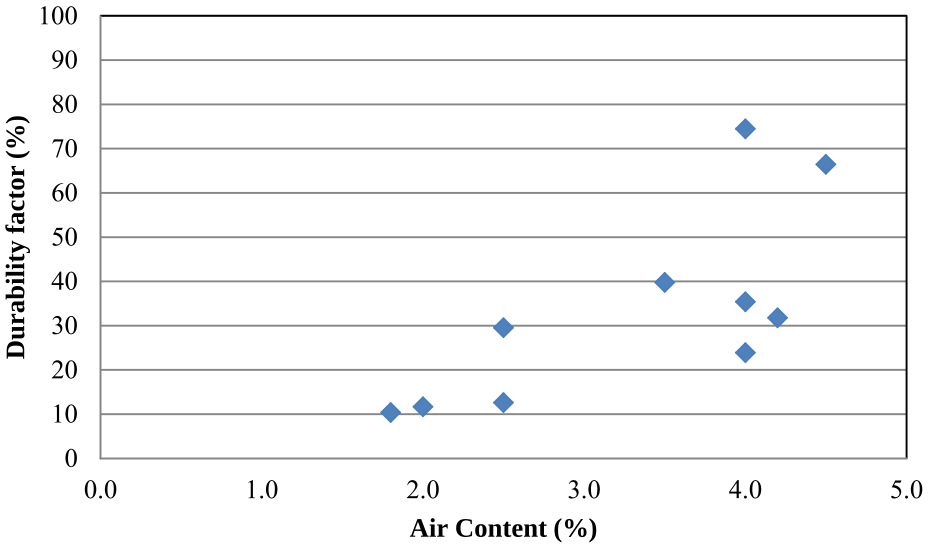

Figure.31 All the Mixtures' Durability Factor for Different Levels of Total Air Contents

5.6.4 Visual Comparison of Freeze-Thaw (F-T) Cycles Damage

The comparison of visual damage of all mixtures when the specimens failed freeze-thaw cycles are shown as follow, Figure 32-Figure.36.

After 300 FT cycles, the control group (OPC) had relative dynamic modulus of elasticity of 74.5%, specimen remained volume integrity, shown as Figure.32 on the left. After 300 FT cycles, mixture with 5% limestone replacement (PLC5) had relative dynamic modulus of elasticity of 69%, specimen remained volume integrity, shown as Figure.32 on the right.

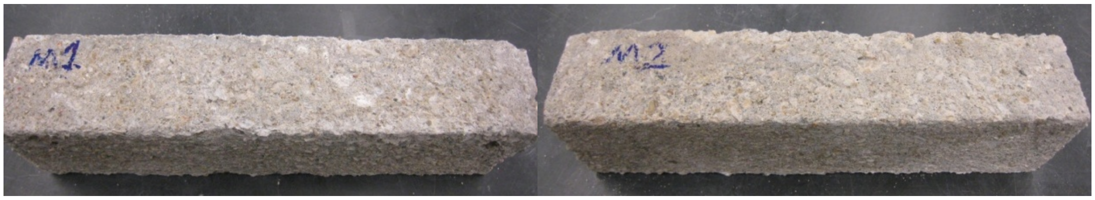

Figure.32 OPC (control group) on the left, PLC5 (5% limestone) on the right

Mixture with 10% limestone replacement (PLC10) failed after 120 FT cycles, with remaining relative dynamic modulus of elasticity of 53.7%, specimen surface with coarse aggregate exposure, no big pieces losing, shown as Figure.33 on the left. Mixture with 15% limestone replacement (PLC15) failed after 210 FT cycles, with remaining relative dynamic modulus of elasticity of 56%, specimen surface with coarse aggregate exposure, pieces lost on the corner, shown as Figure.33 on the right.

Figure.33 PLC10 (10% limestone) on the left, PLC15 (15% limestone) on the right

Mixture with 18% limestone replacement (PLC18) failed after 150 FT cycles, with remaining relative dynamic modulus of elasticity of 59.1%, specimen surface with coarse aggregate exposure, pieces lost on the corner and edges, shown as Figure.34 on the left. Mixture with 25% limestone replacement (PLC25) failed after 60 FT cycles, with remaining relative dynamic modulus of elasticity of 51.9%, specimen surface with coarse aggregate exposure, specimen was felt hallow, shown as Figure.34 on the right.

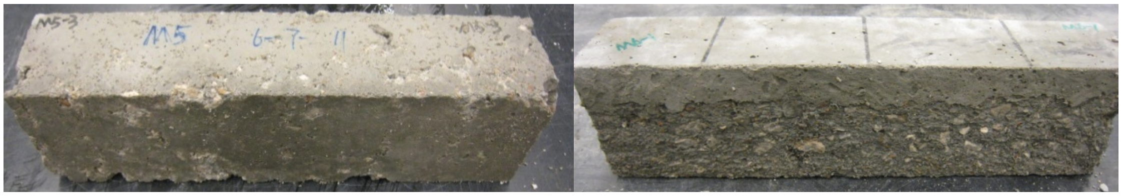

Figure.34 PLC18 (18% limestone) on the left, PFA25 (25% fly ash) on the right

Mixture with 5% limestone and 15% fly ash replacement (PL5F15) failed after 60 FT cycles, with remaining relative dynamic modulus of elasticity of 58%, specimen surface with coarse aggregate exposure, pieces lost on the corner, specimen was felt hallow, shown as

Figure.35 on the left. Mixture with 10% limestone and 10% fly ash replacement (PL10F10) failed after 90 FT cycles, with remaining relative dynamic modulus of elasticity of 42.1%, specimen surface with coarse aggregate exposure, pieces lost on the corners, shown as Figure.35 on the right.

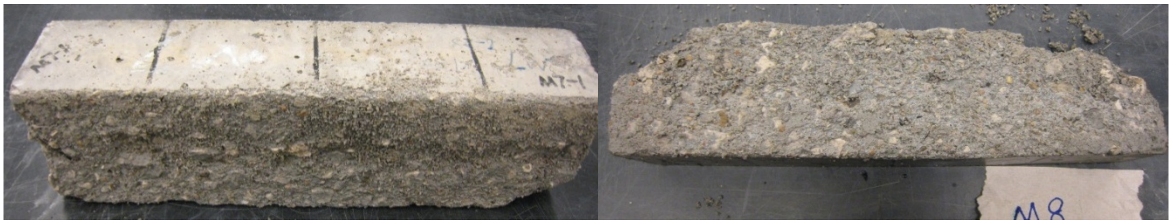

Figure.35 PL5F15 (5% limestone, 15% fly ash) on the left, PL10F10 (10% limestone, 10% fly ash) on the right

Mixture with 15% limestone and 5% fly ash replacement (PL15F5) failed after 180 FT cycles, with remaining relative dynamic modulus of elasticity of 53%, specimen surface with coarse aggregate exposure, shown as Figure.36 on the left. Mixture with 18% limestone and 2% fly ash replacement (PL18F2) failed after 180 FT cycles, with remaining relative dynamic modulus of elasticity of 59%, specimen surface with coarse aggregate exposure, pieces lost on the corners, shown as Figure.36 on the right.

Figure.36 PL15F5 (15% limestone, 5% fly ash) on the left, PL18F2 (18% limestone, 2% fly ash) on the right

CHAPTER 6

CONCLUSION

The fresh properties results showed that different ratio of limestone addition altered workability compared to standard Portland cement. As limestone addition ratio increases, concrete slump decreased. At 18% limestone addition, the concrete slump decreased to 2 inches. Fly ash addition has a positive influence on the workability of concrete. With 25% fly ash, concrete slump increased to 9 inch. The different ratio ternary additions of limestone and fly ash have changes on workability as well. Overall has a trend that concrete with a higher content of fly ash, has a better workability. Overall ternary systems have better workability than only limestone addition. The fineness of limestone has main factor on workability and water demand. Therefore, using limestone addition limestone cement can achieve the similar workability as using standard Portland cement by introducing a certain amount of fly ash. Trial mixing is required in the practice.

For the compressive strength development, the strength of concrete produced with limestone up to 18% addition cement has increased early-age strength compared to use standard Portland cement. The reason of the increases may relate to the improving particle packing and increased rate of cement hydration. With fly ash addition cement, the strength of concrete development slowed compared to standard Portland cement. The reason of the changes may relate to the pozzolanic nature of fly ash. The ternary system with higher limestone addition rate and lower fly ash rate had higher early age strength and 56 days compressive strength, modified the later strength development caused by limestone addition, and the early strength development caused by fly ash addition. With appropriate limestone addition, and mixture design, using limestone addition up to 18% could achieve the desired strength as using standard Portland cement.

For volume stability, cement mortar with higher limestone addition rate showed higher drying shrinkage than using standard Portland cement. With fly ash introducing into the system, the later ages drying shrinkage improved than only have limestone addition groups. For autogenous shrinkage, over than 10% limestone addition had negative effect on autogentous shrinkage. The limestone addition rate with 10% and fly ash addition rate with 25% showed the minimum autogenous shrinkage. But overall the different addition rate had no statistical differences on volume stability.

For sulfate resistance, cement mortar using limestone addition had a less length changes comparing to using standard Portland cement. With increasing limestone addition up to 18%, the length change kept decreasing. With introducing fly ash into the system, the ternary groups showed significant length change decreasing. PL5F15 showed the most minimum length change overall. For a more comprehensive understanding of the effect of limestone addition, limestone and fly ash addition on sulfate resistance, mass changing were recorded as well. Overall with limestone addition, cement mortar had less mass changes. Testing programs were designed two environments, at 23°C for 6 months and at 5 °C for 6 months. With literature review showed that thaumasite formation tend to happen at a lower temperature. The mass change after changing environmental temperature, limestone addition with over 10% groups, showed mass decrease. With only fly ash addition, mass changes were between 0.60% to 0.8% which was much lower than limestone addition groups. The ternary groups showed even less mass changes, PL10F10 had the least mass changes. Further thaumasite identification needs to using scanning electron microscope (SEM) to identify.

For concrete permeability, limestone addition groups showed increased concrete permeability by using rapid chloride permeability test. Even though limestone addition was used as improving the particle size distribution and make the micro-structure denser. But the RCPT results showed, concrete made with limestone addition cement, RCPT value increased. However, fly ash had a positive effect on reduced concrete permeability. The ternary groups had lower RCPT values than the groups only have limestone addition.

The freeze-thaw resistance of concrete has strong relationship with the air content of concrete. OPC and PLC5 had the highest air content, and the highest freeze-thaw durability. Among the groups with lower air content, concrete that produced with higher limestone content (PLC15, PL18F2, PL15F5 and PLC18) had better freeze-thaw resistance than other groups. The effect of a wide particle size distribution of cement can improve cement paste freeze-thaw durability.

The data showed cement with limestone addition has good properties with up to 18% addition rate. The ternary blended cement with limestone and fly ash addition, showed better properties. Cement with lower clinker had good performance and a better environmental impact as well, are recommended to use in industry.

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Vita

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