



pH-Assisted Strength Gain Projection for Green Cement Mortar Composite Containing Marble Powder By-Product: Substitution and Intergrinding Methods

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Abstract

This manuscript reports the effects of substitution and interground of MP on the pH of cement and bending and compressive strengths of mortar composite as well as strength projection of green mortar composite from pH of green cement. It also presents the relationships between pH of cement and strength of mortar composite to compute strength gain from pH of cement. The feature of sample made with MP-cement is examined and compared to those made with pure Portland cement– including bending and compressive strengths at 7d, 28d, and 90d, and pHs of cement. Projection of strength gain from pHs of cement is also discussed, and the numeric equations, the coefficients, and the r squares, which are essential elements of the strength projection, are given in the experimental study proficiently. Regularly, this study results indicate that the projection for strength gains of green mortar composite could be computed from pHs of green cement properly.

Keywords: A.Recycling; B.Mechanical properties; B.Physical properties; pH; Bending strength; Compressive strength; Cement; Marble by-product; Mortar composite; Corrosion

1. Introduction & Objective

Since compressive strength is a significant primary characteristic for cement based non-resilience construction materials, plenty of much research suggests some equations to compute compressive strength from bending strength for reducing some workloads such as preparations of prism mortar and carrying out bending strength test (Popovics 1998). As these aforementioned equations need to measure the bending strength, they do reduce no the workloads for laboratory research and in-situ construction application. There is a need for comprehensive study so that these workloads are reduced. Since this research uses hydraulic cement's pH to predict compressive strength gains of hydraulic cements, it also reduces these workloads and recommends a novel method for scientists studying on quality controls for cements containing by-products: i.e., marble powder. On the other hand, the corrosion that consists of chemical process including the flows of electron and ion is another significant characteristic for cement based bearing materials. At active site on the metal, called anodes, iron atom loses electrons and surrounds cement based material as ferrous ions. This process is called a half-cell oxidation reaction. The electron remains in the metal and slides to site called cathode zone, where they combine with water and oxygen in the cement based material. The reaction is called a reduction reaction at the cathode zone. To maintain electrical neutrality, the ferrous ion migrates through the pore water to the cathode site where they combine to form iron hydroxides and/or rust. This initial precipitated hydroxide tends to react further with oxygen to form higher oxide. Increases the rust volume reacts further with dissolved oxygen leads to internal stress within the cement based bearing material that may be sufficient to cause cracking and spalling in bonds between cement paste and construction steel (Clear and Hay 1973; Clear

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1976). Corrosion of inset metal can be greatly reduced by placing crack-free with low permeability and sufficient cover in cement based material. Decreasing water to cement ratio and use of by-product could provide low-permeability for cement based construction material. By-product also increases the resistivity of cement based material due to reducing the corrosion rate even after it initiates.

However, pH of cement is a key factor for bearing construction material so that corrosion does not effect steel negatively. 12–13 alkalinity level (pH) saves the steel covering like a protective film layer in cement paste. Researches on cement containing by product need to measure the pHs of cement and by product in order to overcome negative corrosion effect aforementioned (ACI 222R–01 2001; ACI 318–11 2008; FM 5–578 2004; Hooton 2001). Marble particle is by-product from productions of marble which is essential material for construction industry. The particle is attractive cementitious material due to their significant chemical compound, but disposal of them is associated with environmental and ecological problem. Table1 states the chemical compound. In untreated condition, this MP volume generated is about 2 592 000 tons annually (Kırgız 2007). The particle finds no application in construction industry. An alternative way is to use marble particle employed in many European countries and Canada and USA as intergrinding and/or substitution material for Portland cement. However, because of the concerns on reduction the cement alkalinity, researches have not preferred this alternative way as the best option. Since MP particle does reduce no this alkalinity, this exacting non-budget research is carried out to more effective explain relationships between pH and strength gain of cement. As explained in this study, the article also presents some important relationships between pHs of cement and compressive strength and bending strength of cement.

Objective of this current experimental study is to present the projection for bending and compressive strength by assisting of cement's pH. Conventional testing methods are the uniaxial bending and compression tests to determine strength gain of cement. Although these kind of destructive testing methods give real results, they are both time-consuming and costly. There is also possible to analyze the cement alkalinity by pH testing method. This pH testing method is not developed for replacing the destructive strength methods entirely, but it can become an alternative method for these destructive strength method as more practical, faster, and inexpensive method. Plus, this study responds some primary questions i.e., which method is more beneficial for research related to cement containing by-product by way of substitution and/or intergrinding? How does the substitution method of MP for cement effect positively pH of cement and strength of cement mortar? How does the intergrinding method of MP with cement clinker effect positively pHs of cement and strength of cement mortar? Are the ratios of substitution and/or intergrinding significant in view of the protection for steel bar from corrosion in in-situ application? If so, how does by-product effect pHs of cement and strength of cement mortar? Do some relationships establish between the pHs of cement and strength of cement mortar? If so, are these relationships meaningful?

2. Experimental Procedure

2.1 Materials

In-situ studies use four different types of mortar. First is an ordinary lime based mortar made of a mixture of standard sand, water and quicklime, either in the form of hydraulic lime or non-hydraulic lime (Mulligan 1942; Mortar Industry Association 2004; McKay 1947). Second is cement based mortar is known following the invention of hydraulic Portland cement. Cement mortar composite displays a

faster setting time and is known to have a high mechanical strength and low level of porosity in comparison to lime mortar (Mulligan 1942; McKay 1947; Palomo et al. 2004). Third is cement-lime mortar composite is made of a proportioned mixture of lime, Portland cement, standard sand and water. Cement-lime mortar composite has such some benefits as the workability, deformation capacity and autogenous healing ability of a lime mortar, and also having the bond quality and compressive strength of a hydraulic cement mortar (McKay 1947; Tate 2005). ASTM presents the rigid categorizations for cement-lime mortars into five different groups according to their mix proportions by volume (ASTM C 270–08a 2008). Last one is lime-pozzolan mortar composite made of a lime mortar that also contains pozzolanic materials. Some reactions between pozzolanic material and lime enhance the mechanical strengths of the mortar, and therefore lime-pozzolan mortar generally exhibits a higher mechanical strength than that of a pure lime mortar. (Palomo et al. 2004; Martinez-Ramirez and Thompson 1999; Papayianni and Stefanidou 2006). *Difference of this non-budget research from the abovementioned types of mortar composite is that it uses novel cement-by-product mortar composite and by-product-cement that also contain marble powder as latent hydraulic additive in order to explain effectiveness of MP on strength gains of hydraulic mortar composite and pHs of cement. Table1 gives the chemical compositions of MP, CEM I 42.5N cement, and CEM I 42.5 clinker (Kırgız 2007).*

Table 1. Chemical compositions of MP, CEM I 42.5N cement, and CEM I 42.5 clinker

Chemical compositions (%)	MP	CEM I 42.5N Cement	CEM I 42.5 Clinker
CaO	53.7	63,5	65,09
SiO ₂	0.3	19,9	21,01
Al ₂ O ₃	0.1	5,2	5,6
Fe ₂ O ₃	0.04	3,4	3,5
MgO	0.7	1,7	1,5
SO ₃	0.05	2,8	0,8
K ₂ O	0.01	0,7	0,8
Na ₂ O	0.3	0,8	0,8
LOI	44.1	0,015	0,3
pH	12.01	12,7	–

2.1.1 Preparations of cement and mortar composite

Preparations of cement and mortar composite consist of three stages. First stage is the preparation of MP in order to specify their characteristic properties. Laboratory type ball mill grinds this mineral waste of marble separately at thirty minutes to form fine particle. Second stage is the mixture proportion designs of cement. Group1 substitutes marble powder for pure Portland cement at the weight percentages of 6-20-21 and 35 and the substituted marble powder-cement (SMP-C) are named as CEMI42.5MP6, CEMI42.5MP20, CEMI42.5MP21 and CEMI42.5MP35. Group2 uses pure CEMI42.5N cement as reference cement. Moreover, Group3 intergrinds marble powder, pure Portland cement clinker, and plaster at the percentages of 6+89+5, 20+75+5, 21+74+5 and 35+60+5 and the interground marble powder-cement (IMP-C) are named as CCEMI42.5MP6, CCEMI42.5MP20, CCEMI42.5MP21, and CCEMI42.5MP35 (Kırgız 2007). TS EN 196–1 specifies the change ratios of ground MP for pure Portland cement in order to make appropriate cement proportion (TS EN 196–1 2009). Table2 presents groups and cements, percentages of by-product, pure CEMI42.5N cement, and CEM I 42.5 clinker (Kırgız 2007).

Table 2. Groups and types of cement, proportions of by-product, pure CEMI42.5N cement, CEM I 42.5 clinker, and intergrinding time

Cements		Proportions of By-products, Cements, Clinkers, and Gypsums				Intergrinding Time (s)
Groups	Codes	MP	CEM I 42.5N	CEM I 42.5 Clinker	Gypsum	
Group 1	CEM I 42.5 MP6	6	94	0	0	0
	CEM I 42.5 MP20	20	80	0	0	0
	CEM I 42.5 MP21	21	79	0	0	0
	CEM I 42.5 MP35	35	65	0	0	0
Group 2	CEMI42.5	0	100	0	0	0
Group 3	CCEM I 42.5 MP6	6	0	89	5	30
	CCEM I 42.5 MP20	20	0	75	5	30
	CCEM I 42.5 MP21	21	0	74	5	30
	CCEM I 42.5 MP35	35	0	60	5	30

Last stage deals with preparations of mortar composite containing SMP-C, IMP-C, and reference cement for monitoring strength gain at 7d, 28d, and 90d. In preparation of mortar composite, following procedure uses a medium planetary mixer for 4 (min): (1) add water and SMP-C and/or IMP-C, and/or reference cement into bowl; (2) mix them for 30 (s) at low speed; (3) add CEN standard sand at 30 (s); (4) mix them for 30 (s) at high speed; (5) stop the mixer for 15 (s) to scrape bowl; (6) mix for 60 (s) at high speed; (7) cast each mortar mixes in prism mould (40x40x160 mm) as three layers; (8) collapse each layer 60 times (Kırgız 2007; TS EN 196-1 2009). Mortar composite is mixed with water:cement:sand ratio of 1:2:6. Table3 presents types of substituted-cement mortar (SCM) composite, reference cement mortar (RCM) composite, interground-cement mortar (ICM) composite, and mixture proportions of the mortar composite for 0.000768 m³ (Kırgız 2007).

Table 3. Types of substituted-cement mortars (SCM), reference cement mortars (RCM), interground-cement mortars (ICM), and mixture proportions of these mortars for one standard 3-gang mould

Types of Mortar		Mixture proportions of cement mortar					
		Substituted-Cements		Interground-Cements* (g)	Tap water (mL)	Sand (g)	Water-to-binder ratio
		MP (g)	CEM I 42.5N (g)				
SCM	SC-MP6M	27	423	0	225	1350	0.5
	SC-MP20M	90	360	0	225	1350	0.5
	SC-MP21M	94.5	355.5	0	225	1350	0.5
	SC-MP35M	157.5	292.5	0	225	1350	0.5
RCM	CEMI42.5M	0	450	0	225	1350	0.5
ICM	IC-MP6M	0	0	450	225	1350	0.5
	IC-MP20M	0	0	450	225	1350	0.5
	IC-MP21M	0	0	450	225	1350	0.5
	IC-MP35M	0	0	450	225	1350	0.5

2.2 Methods

This research divides methods into two experimental parts and a numerical calculation to explain how the MP effects for strength-related properties of hydraulic mortar composite and pHs of cement.

These three stages include:

- Chemical experiments are carried out for pHs of cement in order to monitor how MP effects the alkaline levels of the cement.
- This study measures some strength gain of mortar containing the aforementioned cement in order for better explaining how MP effects the target strength levels of the cement.
- This article suggests some equations for the projections of strength from pH results.

2.2.1 pH experiments of cement

TS 12072 standard method measures the pHs of cement (Table 2) by a pH meter having specifications in the TS 5133 standard (TS EN 196–2 2012; TS 12072 1996; TS 5133/T1 1990). Following procedure uses automatic pH meter for measuring pHs of cement: (1) add 10 mL deionized water and 1 (g) cement into beaker; (2) mix the suspension on magnetic stirrer; (3) wait until cement precipitates; (4) wash electrode of pH meter with deionized water; (5) put electrode of pH meter in suspension; (6) record pH of cement based suspension. For each mix, pH meter tests three suspensions. The article presents average values of pH as the descriptive pH of cement. Image of pH meter for measuring of cement alkalinity is seen in Figure 1.



Figure 1. Image of pH meter for measuring of cement alkalinity

2.2.2 Bending strength experiments of mortar composite

Standard method examines the bending strengths of prism mortar 40x40x160 (mm) at 7d, 28d and 90d (Table 3). This study demolds and cures the prism mortar into water in closet at $22 \pm 3^\circ\text{C}$ and 98% relative humidity until testing. To maintain mortar immersed into curing water, fresh water is added when necessary. For each mix at each age, hydraulic bending machine tests six samples. The article presents average values of sample as the descriptive bending strength for hydraulic mortar composite containing MP (TS EN 196–1 2009). Equipment for mortar composite preparation is seen in Figure 2, left to right, the automatic-minute-controlled mixer, the bending moment testing machine, computer controlled water curing cabinet, bending moment testing of mortar composite containing MP.



Figure 2. Equipment for preparation and testing of mortar composite, left to right, the automatic-minute-controlled mixer, the bending moment testing machine, curing cabinet whose relative humidity and water temperature is controlled by computer, bending moment testing of mortar composite containing MP

2.2.3 Compressive strength experiments of mortar composite

Standard method specifies compressive strengths of cubic mortar 40x40x40 (mm) at 7d, 28d, and 90d (Table 3) (TS EN 196–1 2009). This non-budget research demolds and cures the cubic mortar into water in closet at $22 \pm 3^\circ\text{C}$ and 98% relative humidity until testing. To maintain mortar immersed into curing water, fresh water is added when necessary. For each mix at each age, hydraulic compression machine tests twelve samples. The article gives average values as the descriptive compressive strength for hydraulic mortar composite containing MP. Equipment for measurement of mortar composite compressive strength is seen in Figure 3.



Figure 3. Equipment for measurement of mortar composite compressive strength

3. Outcomes and Arguments

Table4 presents the pHs of cement, bending strengths of mortar composite and compressive strengths of mortar composite at 7d, 28d, and 90d. It also gives the names of cement and of mortar (Kırgız 2007). Table 4. The pHs of cement, compressive strengths of mortar, and bending strengths of mortar at 7d, 28d, and 90d, and the types of cement and of mortar

Types of Cement	Chemical Properties	Types of Mortars	Mechanical Properties					
			Bending Strengths (MPa)			Compressive Strengths (MPa)		
	pH		7th-d	28th-d	90th-d	7th-d	28th-d	90th-d
CEM I 42.5 MP6	12.51	SC-MP6M	6.44	6.87	6.2	39.63	45.09	39.31
CEM I 42.5 MP20	12.51	SC-MP20M	5.05	5.67	5.59	31.81	40.52	32.96
CEM I 42.5 MP21	12.49	SC-MP21M	4.7	5.2	4.32	28.78	33.36	30.15
CEM I 42.5 MP35	12.46	SC-MP35M	4.49	4.5	4.13	22.71	24.73	22.09
CEM I 42.5N	12.72	CEMI42.5M	5.37	6.25	5.39	34.29	43.06	44.15
CCEM I 42.5 MP6	12.73	IC-MP6M	5.4	6.26	6.37	31.76	40.72	42.61
CCEM I 42.5 MP20	12.71	IC-MP20M	4.84	5.43	5.3	26.99	37.82	32.31
CCEM I 42.5 MP21	12.77	IC-MP21M	4.66	5	5.13	24.61	32.52	30.26
CCEM I 42.5 MP35	12.58	IC-MP35M	4.1	4.12	3.88	21.89	22.55	22.04

3.1 pHs of cement

Although the natural tendency of construction steel is to undergo corrosion reaction, the alkaline structure of cement (pH of 12 to 13) provides a protective layer for construction steel. With the high pH level, there is a thin oxide layer on the steel. This layer prevents metal atoms from dissolving and stops no corrosion actually, it reduces the corrosion rate in a significant level. For steel in construction, the passive corrosion rate is typically 0.1 (μm) per year. Without the protective film layer, the corrosion of steel is 1000 times higher than steel having protective layer (ACI 222R-01 2001). Because of this inherent protection, reinforcing steel does not corrode in the majority of cement pastes and structures. However, corrosion can rapidly occur when the protective layer is destroyed. The destruction of protective layer occurs since the alkalinity of cement is reduced. Table4 states the pHs for cement containing marble powder (Kırgız 2007). Since this study replaces MP with pure Portland cement up to 35%, the cement displays no less pH ratio than 97% of pH of Portland cement. The highest reduction of pH is in CEM I 42.5 MP35 cement with decreasing ratio of 2.1% while the lowest reduction of pH is in CEM I 42.5 MP6 cement with decreasing ratio of 1%. Results imply that the substitution effect of MP leads to reducing for cement's pH without deteriorating its alkaline structure (Table 4). The interground-cement also exhibits same effect on pH of cement, similar to the substituted-cement. Since the 35%-MP is added to cement clinker for intergrinding, pH of the cement is no less than 99% of pH of Portland cement. The highest reduction of pH is in CEM I 42.5 MP35 cement with decreasing ratio of 1.2% while the equal pH is in CEM I 42.5 MP6 cement. Results also reveal that this intergrinding effect leads to no reduction for alkaline structure of cement since MP is added up to 6% (Table 4).

3.2 pH-assisted projection for bending strengths of mortar composite

Table4 presents the bending strengths at 7d, 28d, and 90d for mortar prepared with SMP-C, IMP-C, and reference cement (Kırgız 2007). Following figures illustrate some relationships between pHs of cements and bending strengths of mortars. They also present differences in equations specified for

substitution and intergrinding of by-product. Since cement-based construction material is accepted non-resilience material, author expresses results such as ups-and-downs on bending strengths of mortar. Therefore, effects of microstructure of cement hydration on bending strength gains will not be signified. Increasing of loss on ignition (LOI) and alkali in cement paste also causes the reduced strength gain in hydraulic cement mortar (Kırgız 2011; Kırgız 2014a; Kırgız 2015a; Kırgız 2015b). Figure4 specifies two relationships between pHs of cement and 7th-d bending strengths of mortar containing marble powder by way of substitution and intergrinding.

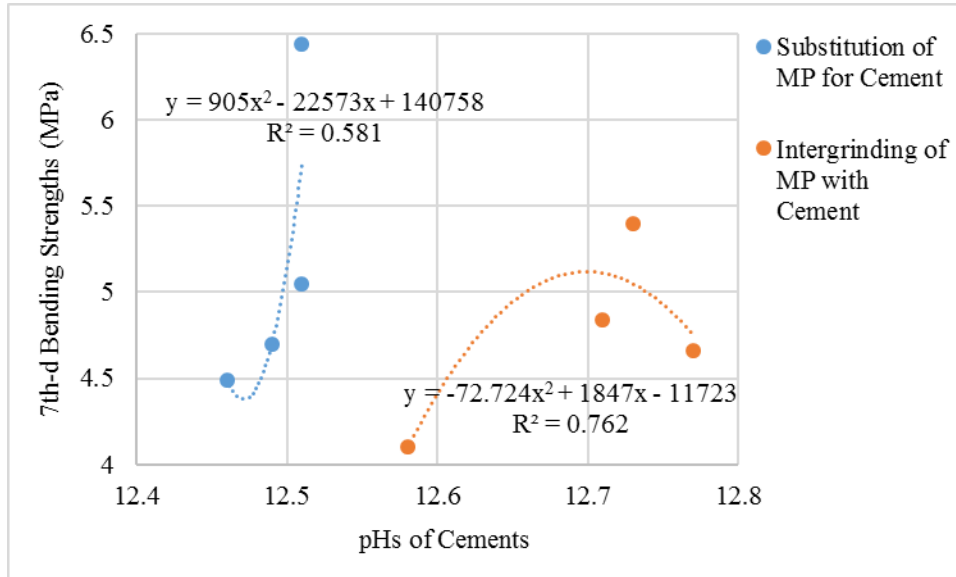


Figure 4. Relationships between pHs of cement and 7th-d bending strengths of mortar containing marble powder by way of substitution and intergrinding

Since this comprehensive study substitutes MP with cement from 6% to 35% (over 5.5 times) in mortar, this substitution leads to the reduction of 4% bending strength at 7d, except SC-MP6M. These SC-MP6M has over 19% greater bending strength than that of CEMI42.5M at 7d. This growth explains the mechanism of MP substitution as initial bending strength activator. Plus, bending strengths of MP-SCM are located in a relatively wide range of 4.4–6.4 (MPa) at 7d. This wide range implies that high substitution ratio of MP for cement causes the reduction for 7th-d bending strengths of hydraulic cement mortar, nevertheless once again, *the 6%-MP substitution shows the most pronounced enhancing effect on bending strength gain at 7d* (Table 4). Although ball mill intergrinds marble powder and cement clinker together, the mortar prepared with the IMP-C displays over 5% lower bending strength than that of CEMI42.5M and SC-MPs at 7d, except IC-MP6M. These IC-MP6M also has approximately 0.5% higher bending strength than that of CEMI42.5M mortar at 7d. In view of these intergrinding of MP with cement clinker, the bending strength locates in a relatively narrow range of 4.1–5.4 (MPa) at 7d. This narrow range can explain the mechanism of MP intergrinding as stabilizer for hydraulic pure Portland cement system. This narrow range is also the lowest in the mortar containing marble powder by way of intergrinding. This high intergrinding of MP with cement clinker leads to the reduction for bending strength, nevertheless, *the 6%-MP blending shows the enhancing effect for 7th-d bending strength gain* (Table 4). *The substitution of MP for cement is more effective*

than the intergrinding of it with cement clinker in view of 7th-d bending strength. Moreover, Figure 4 also reveals relationships between pHs of cement and 7th-d bending strength for mortar containing marble powder by way of substitution and intergrinding. This figure gives polynomial equations to show these relationships. Figure 4 also presents the R-squared values show two significant relationships for projection of 7th-d bending strengths of mortar from pHs of cement. They show a good compatibility between two specified properties. As figure exhibits important relationships between pHs of cement and 7th-d bending strength, one may predict a specified strength by testing at least one of the pHs of cement (Figure 4). However, these results are in coherence with previous study (Kırgız 2011; Kırgız 2014a; Kırgız 2015a; Kırgız 2015b) when considering the changes of chemical composition at 7d and 28d and 90d. Effect of admixture containing high calcium oxide on strength gain deals with fluctuation of silicon oxide (SiO_2), sodium oxide (Na_2O), and alkali as well as increasing of LOI (Kırgız 2016b). This knowledge implies that more than 6% of admixture containing high calcium oxide has no positive effect on early bending strength gains of mortar (Kırgız 2011; Kırgız 2014a; Kırgız 2015a; Kırgız 2015b). Moreover, these results are in coherence with previous study when considering the changes of chemical composition at 7d and 28d and 90d. Blending of artificial pozzolan accelerates the tendency of strength gain at later ages because it reduces the LOI in the cement. Mortar containing up to 35% artificial pozzolan displays a greater 28th-d bending strength than that of 7d (Kırgız 2011; Kırgız 2014a; Kırgız 2015a; Kırgız 2015b). Figure 5 reveals relationships between pHs of cement and 28th-d bending strength for mortar containing marble powder by way of substitution and intergrinding.

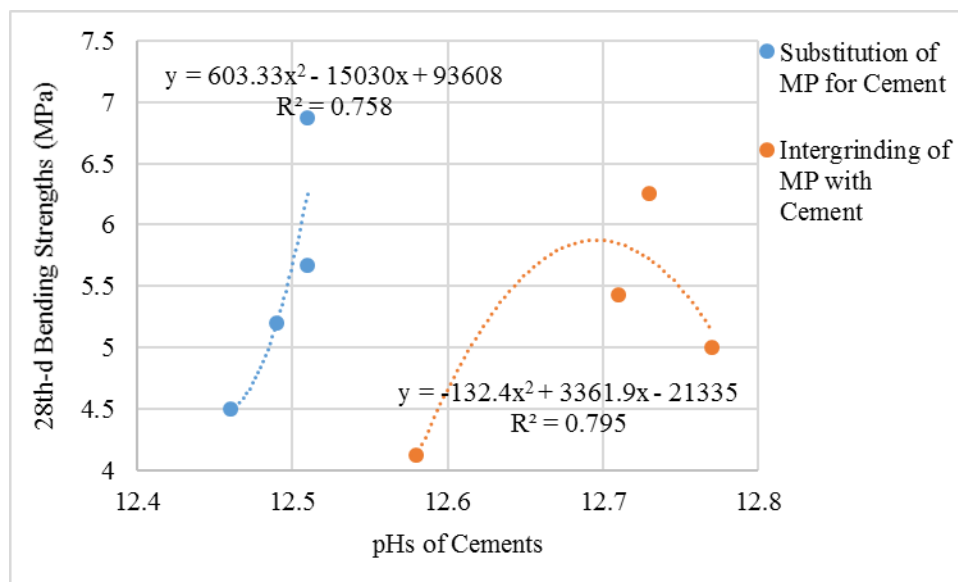


Figure 5. Relationships between pHs of cement and 28th-d bending strengths of mortar containing marble powder by way of substitution and intergrinding

Since this study substitutes MP with cement up to 35% (over 5.5 times) in mortar, this substitution leads to the reduction of 12% for bending strength at 28d, except SC–MP6M. The SC–MP6M has over 9% greater 28th-d bending strength than that of CEMI42.5M. Plus, bending strength of SMP–C mortar at 28d is located in a relatively wide range of 4.5–6.8 (MPa). Once again, this wide range indicates that high substitution ratio of MP for cement causes the reduction for 28th-d bending strength of hydraulic

cement mortar. These results also reveal that the 6%-MP substitution shows a pronounced enhancing effect on bending strength gain at 28d (Table 4). Although marble powder and cement clinker are interground, the mortar prepared with the IMP-C displays over 20% lower 28th-d bending strength than that of CEMI42.5M, except IC-MP6M. The IC-MP6M also has approximately 0.5% higher 28th-d bending strength than that of CEMI42.5M. In view of the intergrinding of marble powder with cement clinker, the bending strength is located in a relatively wide range of 4.1–6.2 (MPa) at 28d. This wide range implies that high substitution ratio of MP for cement causes the reduction for 28th-d bending strength of hydraulic cement mortar. The strength value is the lowest in the mortar containing marble powder. This high intergrinding of MP with cement clinker leads to the reduction for 28th-d bending strengths, nevertheless, the 6%-MP blending provides an enhancing effect for 28th-d bending strength gain (Table 4). *The substitution of MP for cement is more effective than the intergrinding of it with cement clinker in view of 28th-d bending strength.* Moreover, Figure5 shows two meaningful relationships for projection of 28th-d bending strength of mortar from pH of cement. Polynomial equations are placed on this figure to show these relationships. Figure5 also presents the R-squared values. They show a good compatibility between two specified properties. As figure exhibits influential relationships between pH of cement and 28th-d bending strength, one may predict a specified strength by testing at least one of the pH of cement (Figure 5). However, these results are in coherence with previous study (Kırgız 2011; Kırgız 2014a; Kırgız 2015a; Kırgız 2015b) when considering the chemical composition change at 7d and 28d and 90d. Chemical composition change of cement paste explains the mechanism of admixture containing high calcium oxide. Blending of high calcium oxide based admixture provides to continue the strength gain in mortar after 28d since it activates hydrations of calcium based compounds in cement pastes (Kırgız 2011; Kırgız 2014a; Kırgız 2015a; Kırgız 2015b). Moreover, Data obtained from current research on mortar containing fly ash (Kırgız 2014b; Kırgız 2015a) reveals that there are at least two mechanisms on early strength gain of Portland pulverized fly ash cement (PPFA-C) containing nano graphite particle (nG). First, the nG could open between cement particles to provide proper dispersion of fly ash for the nucleation and growth of hydration product of the calcium carbon hydroxide (C-C-H). In this case, well-dispersed nG particle accelerates the initial strength gains for PPFA-C (Kırgız 2014b; Kırgız 2015a). Following paragraphs will explain the second mechanism. Figure6 reveals relationships between pH of cement and 90th-d bending strength of mortar containing marble powder by way of substitution and intergrinding.

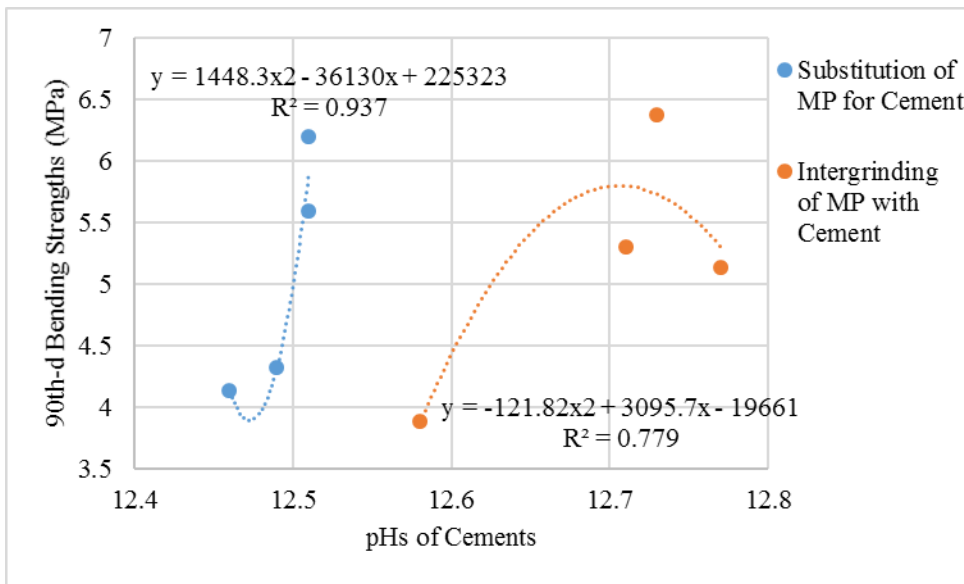


Figure 6. Relationships between pHs of cement and 90th-d bending strengths of mortar containing marble powder by way of substitution and intergrinding

Since MP is substituted for cement from 6% to 35% (over 5.5 times) in mortar, this substitution leads to the reduction of 6% for bending strength at 90d, except SC-MP6M. This SC-MP6M has over 15% greater 28th-d bending strength than that of CEMI42.5M. Plus, 90th-d bending strength of SMP-C mortar is located in a relatively wide range of 4.1–6.2 (MPa). This wide range points that the low substitution of MP provides strength gain for hydraulic cement at later age. These results also imply that high substitution ratio of MP for cement causes the reduction for 90th-d bending strength of SMP-C mortar, nevertheless once again, the 6%-MP substitution shows a pronounced enhancing effect on bending strength gains at 90d (Table 4). Although marble powder and cement clinker are interground, the mortar prepared with the IMP-C displays over 4% lower bending strength than that of CEMI42.5M at 90d, except IC-MP6M. The IC-MP6M also has over 18% higher bending strength than that of CEMI42.5M at 90d. In view of the intergrinding of marble powder with cement clinker, the bending strength is located in a relatively wide range of 3.8–6.3 (MPa) at 90d. This wide range points that the low intergrinding of MP provides strength gain for hydraulic cement at later age. This high intergrinding of MP with cement clinker also leads to the reduction for bending strength, nevertheless once again, the 6%-MP blending shows an enhancing effect for 90th-d bending strength gains (Table 4). *The substitution effect of MP for cement is similar to the intergrinding effect of MP with cement clinker in view of 90th-d bending strength.* Moreover, Figure6 shows two relationships for projection of 90th-d bending strength of mortar from pH of cement. Polynomial equations are placed on this figure to show these relationships. Figure6 presents the R-squared values. They show a good compatibility between two specified properties. As figure exhibits significant relationships between pH of cement and 90th-d bending strength, one may predict a specified strength by testing at least one of the pH of cement (Figure 6). In addition to the first mechanism aforementioned, the nG particle could potentially provide an additional source of carbon for activation of calcium oxide in cement hydration. Since cement consists of 65% calcium oxide (CaO) content, the rest of 35% cement oxides is not enough to saturate this CaO content, during cement hydration for gaining of hardness and strength. Therefore, the nG

particle may produce the calcium carbon oxide (CaCO) as the nG particle can combine with free 30%-CaO content in cement (Kırgız 2014b; Kırgız 2015a; Kırgız 2016a).

3.3 pH–assisted projections for compressive strengths of mortar composites

Table4 presents the compressive strengths at 7d, 28d, and 90d for mortar prepared with SMP–C, IMP–C, and reference cement. Following figures illustrate some important relationships between pH of cement and compressive strength for mortar containing marble powder by way of substitution and intergrinding. They also present differences in equations specified for substitution and intergrinding of by–product. Figure7 specifies relationships between pH of cement and 7th-d compressive strength of mortar containing marble powder by way of substitution and intergrinding

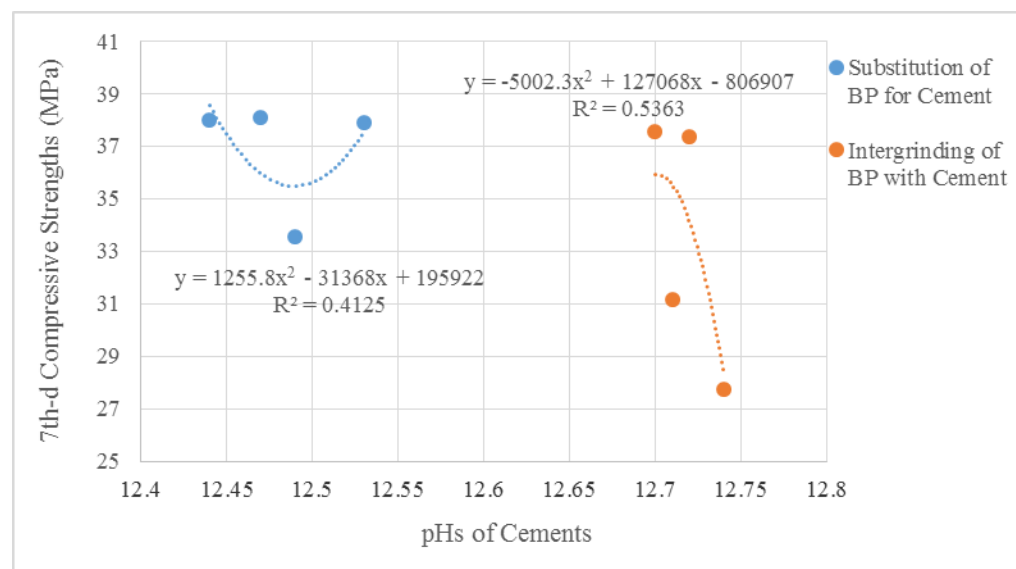


Figure 7. Relationships between pHs of cement and 7th-d compressive strengths of mortar containing marble powder by way of substitution and intergrinding

Since MP is substituted for cement from 6% to 35% (over 5.5 times) in mortar, this substitution leads to the reduction of 11% compressive strength at 7d, except SC–MP6M. The SC–MP6M also has over 15% greater compressive strengths than that of CEMI42.5M at 7d. Plus, compressive strength of SMP–C mortar is located in a relatively wide range of 22.7–39.6 (MPa) at 7d. This wide range implies that high substitution ratio of MP for cement causes the reduction for 7th-d compressive strength of hydraulic cement mortar, nevertheless, the 6%-MP substitution shows the most pronounced enhancing effect on compressive strength gain at 7d (Table 4). Although marble powder and cement clinker are interground, the mortar prepared with the IMP–C displays over 23% lower compressive strength than that of CEMI42.5M at 7d. In view of the intergrinding of marble powder with cement clinker, the compressive strength is located in a relatively narrow range of 21.8–31.7 (MPa) at 7d. This narrow range can explain the mechanism of MP intergrinding as stabilizer for hydraulic cement. This narrow range is the lowest in the mortar containing marble powder at 7d. This high intergrinding of MP with cement clinker leads to the reduction for compressive strength (Table 4). *The substitution of MP for cement is more effective than the intergrinding of it with cement clinker in view of 7th-d compressive strength.* Moreover, Figure7 also shows two relationships for projection of 7th-d compressive strength

of mortar from pH of cement. Polynomial equations are placed on this figure to show these relationships. Figure 7 also presents the R-squared values. They show a good compatibility between two specified properties. As figure exhibits prominent relationships between pH of cement and 7th-d compressive strength, one may predict a specified strength by testing at least one of the pH of cement (Figure 7). However, compressive strength of mortar containing high calcium oxide based admixture is notably lower than that of pure Portland cement based mortar. This can be explained by the increasing of calcium-to-silicon (Ca/Si) ratio from 1.76 up to 2.8 (Kırgız 2011; Kırgız 2014a; Kırgız 2015a; Kırgız 2015b; Kırgız 2015c; Kırgız 2016a). On the contrary to the aforementioned scientific fact, compressive strength is the greatest in the mortar containing artificial pozzolan. This can be explained by the increase of silicon-to-calcium (Si/Ca) ratio, from 0.53 up to 0.96 (Kırgız 2011; Kırgız 2014a; Kırgız 2015a; Kırgız 2015b; Kırgız 2015c). Figure 8 reveals relationships between pH of cement and 28th-d compressive strength for mortar containing marble powder by way of substitution and intergrinding.

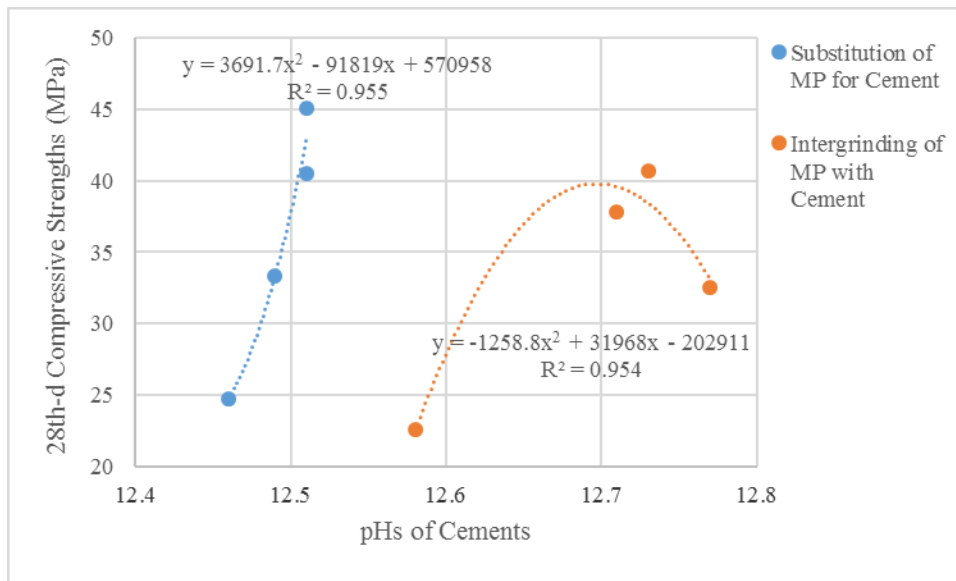


Figure 8. Relationships between pHs of cement and 28th-d compressive strengths of mortar containing marble powder by way of substitution and intergrinding

Since MP is substituted for cement up to 35% (over 5.5 times) in mortars, this substitution leads to the reduction of 22% compressive strength at 28d, except SC-MP6M. The SC-MP6M has over 4% greater 28th-d compressive strength when compared to CEMI42.5M. Plus, compressive strength of SMP-C mortar is located in a relatively wide range of 24.7–45 (MPa) at 28d. This wide range reveals that by-products having high CaO content reduce compressive strength of hydraulic cement. These results also imply that high substitution ratio of MP for cement causes the reduction for 28th-d compressive strength gain of SMP-C mortar, nevertheless, the substitution of 6%-MP for cement shows the enhancing effect for 28th-d compressive strength gain (Table 4). Although marble powder and cement clinker are interground, the mortar prepared with these IMP-C displays over 30% lower 28th-d compressive strength than that of CEMI42.5M mortar at 28d. In view of the intergrinding of marble powder with cement clinker, the compressive strength is located in a relatively wide range of 22.5–40.7

(MPa) at 28d. This wide range explains the non-resilience structure of hydraulic cement. These strength values are the lowest in the mortar containing marble powder at 28d. This high intergrinding of MP with cement clinker leads to the reduction for 28th-d compressive strength (Table 4). *The substitution of MP for cement is more effective than the intergrinding of it with cement clinker in view of 28th-d compressive strength.* Moreover, Figure 8 shows two important relationships for projections of 28th-d compressive strength of mortar from pH of cement. Polynomial equations are placed on this figure to show these relationships. Figure 8 also presents the R-squared values. They show a good compatibility between two specified properties. As figure exhibits meaningful relationships between pH of cement and 28th-d compressive strength, one may predict a specified strength by testing at least one of the pH of cement (Figure 8). However, blending of artificial pozzolan accelerates the tendency of strength gain at later ages because it reduces the LOI in the cement paste. Up to 35% artificial pozzolan displays the greatest compressive strength and bending strength in the mortar (Kırgız 2011; Kırgız 2014a; Kırgız 2015a; Kırgız 2015b). Moreover, effects of artificial pozzolan on strength gain deals with increasing of SiO₂ in cement paste. Average of SiO₂ tends to increase in cement paste continuously. Strength gain in mortar containing artificial pozzolan acts similar to SiO₂ in the cement paste. Since mortar containing artificial pozzolan achieves nearly 52.5 (MPa) compressive strength at 90d, blending up to 35% artificial pozzolan has a positive effect on strength gain of cement mortar at later age (Kırgız 2011; Kırgız 2014a; Kırgız 2015a; Kırgız 2015b). Figure 9 reveals relationships between pH of cement and 90th-d compressive strength for mortar containing marble powder by way of substitution and intergrinding.

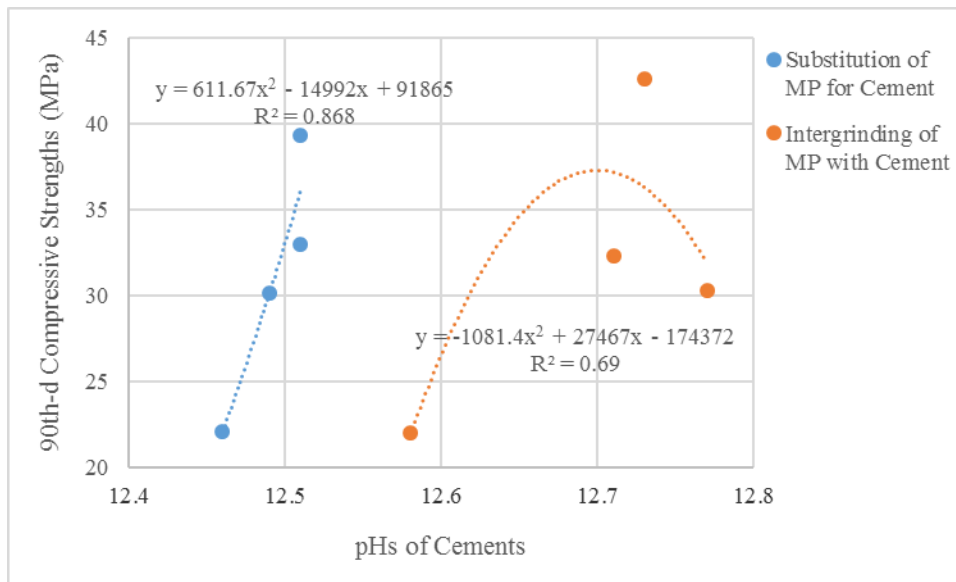


Figure 9. Relationships between pHs of cement and 90th-d compressive strengths of mortar containing marble powder by way of substitution and intergrinding

Since MP is substituted for cement up to 35% (over 5.5 times) in mortar, this substitution leads to the reduction of 42% compressive strength at 90d. Plus, compressive strength of SMP-C mortar is located in a relatively wide range of 22–39.3 (MPa) at 90d. As 90th-d compressive strength of SMP-C mortar is lower than that of 28th-d compressive strength of SMP-C mortar, these result reveals that by-product

having high CaO content reduces compressive strength of cement, more than over 50%. The results also imply that high substitution ratio of MP for cement causes the reduction for 90th-d compressive strength gain of SMP-C mortar and hence, the substitution of MP for cement shows the most pronounced enhancing effect on initial compressive strength gain (Table 4). Although marble powder and cement clinker are interground, the mortar prepared with these IMP-C displays over 38% lower compressive strength than that of CEMI42.5M mortar at 90d. In view of these intergrinding of marble powder with cement clinker, the compressive strength is located in a relatively wide range of 21.8–31.7 (MPa) at 90d. This wide range indicates that the MP as intergrinding constituent provides a non-resilience for compressive strength gain of hydraulic cement. The values are the lowest in the IMP-C mortar at 90d. This high intergrinding of MP with cement clinker also leads to the reduction for compressive strength (Table 4). *The substitution effect of MP for cement is similar to the intergrinding effect of it in view of 90th-d compressive strength.* Moreover, Figure9 shows two influential relationships for projection of 90th-d compressive strength of mortar from pH of cement. Polynomial equations are placed on this figure to show these relationships. Figure9 also presents the R-squared values. They show a good compatibility between two specified properties. As figure exhibits significant relationships between pH of cement and 90th-d compressive strength, one may predict a specified strength by testing at least one of the pH of cement (Figure 9). However, in the pure Portland cement, where the Ca(OH)_2 content is greatest when compared to all other cement combinations, the strength gain would depend on the formation of other hydration products, most probably ettringite and calcium-silicon-hydrates (C-S-H) and calcium-alumina-hydrates (C-A-H) and calcium hydrates (Ca(OH)_2) (Kırgız 2011; Kırgız 2014a; Kırgız 2015a; Kırgız 2015b; Kırgız 2015c). Moreover, the results are in coherence with previous study (Kırgız 2011; Kırgız 2014a; Kırgız 2015a; Kırgız 2015b; Kırgız 2015c) when considering the chemical composition change at 7d and 28d and 90d. The chemical composition change of cement paste explains mechanism of admixture containing artificial pozzolan on strength gain. Blending of it provides to continue the strength gain of mortar up to 90th-d since it activates hydrations of silica based compound in cement paste. Therefore, it tends to be activator for strength gain of mortar at later age. In high blending ratio of artificial pozzolan, the increasing ratios of strength gain are greater than that of strength gain of pure Portland cement mortar (Kırgız 2011; Kırgız 2014a; Kırgız 2015a; Kırgız 2015b).

4. Inferences and Suggestions

This comprehensive non-budget research presents novel insight between pH of cement and strength gain of mortar in view of corrosion and strength gain projection. Chemical compound of MP such as oxide compounds, LOI, and pH, offers advantages for pure Portland cement. Furthermore, the use of MP as substitution and intergrinding constituent in pure Portland cement saves existing resources of natural raw materials. Economic and environmental benefit by reducing CO_2 emission is well established in literature.

However, the experimented properties confirm that the MP enhances the strength gain of mortar as well as pH of cement in specific cement mixture. Cement mixture prepared with MP, pure Portland cement, and/or cement clinker meets the required strength gain of standard mortar as well as pH of cement for saving the inset metal from corrosion. However, results present substantial relationships, equations, coefficients, and r squares between strength gain of mortar and pH of cement to project strength gain from pH of cement. Additionally, MP can be described as initial strength gain accelerator. In view of

inferences, this study could suggest to use MP particle by-product as prepared in this research method for the large scale productions of substituted–cement and intergrinding–cement.

5. References

1. ACI 222R-01: Protection of Metals in Concrete against Corrosion. American Concrete Institute, Farmington Hills, Michigan, USA (2001)
2. ACI 318-11: Building Code Requirements for Structural Concrete. American Concrete Institute, Farmington Hills, Michigan, USA, (2008)
3. ASTM C 270–08a: Standard Specification for Mortar for Unit Masonry. ASTM International West Conshohocken PA, USA (2008).
4. Clear, K.C., Hay, R.E.: Time-to-Corrosion of Reinforcing Steel in Concrete Slabe, V.1: Effect of Mix Design and Construction Parameters. FHWA-RD-73-32 Report, Federal Highway Administration, Washington, (1973).
5. Clear K.C.: Time-to-Corrosion of Reinforcing Steel in Concrete Slabs. PB 258 446 Report, Federal Highway Administration, Vol. 3, pp.43-67. Washington (1976)
6. FM 5-578: Florida Method of Test for Concrete Resistivity as an Electrical Indicator of its Permeability. Florida Department of Transportation Publication, USA, (2004)
7. Hooton, R.D.: Development of Standard Test Methods for Measuring Fluid Penetration and Ion Transport Rates. Materials Science of Concrete: Fluid and Ion Transport Rates in Concrete, American Ceramic Society, 1–12 (2001)
8. Kırgız, M.S.: The usage of the wastes of marble and brick industries in cement manufacturing as mineralogical additive. Ph.D. thesis, Gazi University Graduate School of Natural and Applied Sciences Institute, Ankara, Turkey (2007) (<https://tez.yok.gov.tr/UlusalTezMerkezi/> (for reading abstract of thesis, please write full name of author known Mehmet Serkan KIRGIZ to search engine above red webpage and then click “Bul” button)
9. Kırgız, M.S.: Chemical properties of blended cement pastes. Journal of Construction Engineering and Management, 137, 12, 1036–1042 (2011)
10. Kırgız, M.S.: Effects of blended–cement paste chemical composition changes on some strength gains of blended–mortars. The Scientific World Journal, 2014, 1, 1–8 (2014a)
11. Kırgız, M.S.: Advances in physical properties of C class fly ash cement systems blended nanographite– Part1. ZKG International, 12, 42–48 (2014b)
12. Kırgız, M.S.: Fresh and Hardened Properties of Green Binder Concrete Containing Marble Powder and Brick Powder. European Journal of Environmental and Civil Engineering, Issue Sup1: Supplement: Green Binder Materials for Civil Engineering and Architecture Applications, 20, 64–101, (2016a).
13. Kırgız, M.S.: Strength Gain Mechanism for Green Mortar Substituted Marble Powder and Brick Powder for Portland Cement. European Journal of Environmental and Civil Engineering, Issue Sup1: Supplement: Green Binder Materials for Civil Engineering and Architecture Applications, 20, 38–63 (2016b).
14. Kırgız, M.S.: Advance Treatment by Nanographite for Portland Pulverised Fly Ash Cement (The class F) Systems. Composites Part B, 82, 12, 59–71, (2015a)
15. Kırgız, M.S.: Strength gain mechanisms of blended–cements containing marble powder and brick powder. KSCE Journal of Civil Engineering, 19, 1, 165–172 (2015b)



16. Kirgiz, M.S.: Use of ultrafine marble and brick particles as raw materials in cement manufacturing. *Materials and Structures*, 48, 9, 2929–2941, (2015c)
17. McKay, W.B.: *Brickwork*. Longmans, Green and Co. Publication, London (1947)
18. Martinez-Ramirez, S., Thompson, G.E.: Degradation of lime-pozzolan mortar exposed to dry deposition of SO₂ pollutant gas: Influence of curing temperature. *Materials and Structures*, 32, 5, 377–382 (1999)
19. Mortar Industry Association: The use of lime in mortar. London. <http://www.mortar.org.uk/downloads/miadata18.pdf> (2004). Accessed 20 October 2014
20. Mulligan, J.A.: *Handbook of brick masonry construction*. McGraw-Hill Publication, New York (1942)
21. Palomo, A., Blanco-Varela, M.T., Martinez-Ramirez, S., Puertas F., Fortes, C.: *Historic Mortars: Characterization and Durability: New Tendencies for Research*. European Research on Cultural Heritage: State-of-the-Art Studies, Institute of Theoretical and Applied Mechanics Publication, Prague (2004)
22. Papayianni, I., Stefanidou M.: Strength-porosity relationships in lime-pozzolan mortars. *Construction and Building Materials*, 20, 9–10, 700–705 (2006)
23. Popovics, S.: *Strength and Related Properties of Concrete A Quantitative Approach*. John Wiley & Sons Inc. Publication, Toronto (1998)
24. Tate, M.: The Most Important Property of Cement Lime Mortar in Masonry Construction is. *Proceedings of International Building Lime Symposium*, Orlando, Florida (2005)
25. TS EN 196–1: Methods of testing cement—Part 1: Determination of strength. Turkish Standard Institute, Ankara (2009)
26. TS EN 196–2: Methods of testing cement—Part 2: Chemical analysis of cement. Turkish Standards Institute, Ankara (2012)
27. TS 12072: Solid waste—Determination of pH. Turkish Standards Institute, Ankara (1996)
28. TS 5133/T1: pH Meter—For laboratory use. Turkish Standards Institute, Ankara, (1990)