THE EFFECT OF ZEOLITE ON MICROSTRUCTURE OF BLENDED CEMENT PASTE

CHUWIT NAPIA[1], THEERAWAT SINSIRI[1], PRINYA CHINDAPRASIRT[2]

ABSTRACT : This paper presents the effect of zeolite on microstructure of hardened blended cement pastes. Synthesise zeolite was used to partially replace Portland cement type I at the rate of 0, 20, and 40% by weight of binder. The water to binder ratio (W/B) of 0.35 was used for all the blended cement paste mixtures. XRD and DTA were used to investigate the pozzolanic reaction of blended cement paste and fractured surface of blended cement paste was studied by SEM. The pore size distribution of blended cement paste was studied by MIP.

Test results indicated that the pozzolanic reaction of blended cement paste was significantly affected by the replacement of zeolite. The $Ca(OH)_2$ of blended cement paste decreased with an increase in zeolite content at the longer curing. SEM results revealed that the pastes with zeolite became denser. The porosity and pore size of blended cement paste was significantly affected by the replacement of zeolite. The replacement of Portland cement by zeolite increased the total porosity but decreased the average pore size of the paste. The large capillary porosity trended to decreased and medium capillary porosity increased as a result of the addition of zeolite.

KEYWORDS: Zeolite, Microstructure (XRD, TGA, SEM,), Porosity (MIP), Blend cement paste

1. INTRODUCTION

Zeolite are crystalline alumimun-silicates, their structure is made up of a framework of SiO_4 and AlO_4 tetrahedra linked to each other at the corners by sharing their oxygens. The tetrahedra make up a tree-dimensional network, whith lots of voids and open spaces. It is these voids that define the many special properties of zeolites, such as the adsorption of molecules in the huge internal channels. Zeolite has a small size about 2-30 A°, which make this zeolite an interesting molecular sieve and a high-cation exchange material. Nowadays, zeolites to use is the components of detergent and use in problem adaptation about way environment contamination, such as be formed absorb the air pollution , and use in dirty water cure , etc.

Besides , have the lead zeolite come to apply in the work of the concrete increases. Natural zeolite has also been applied as mineral admixture for concrete production in China. It can prevent bleeding, segregation and delaminate of fresh concrete so as to make pumping process easier decrease permeability of hardened concrete, enhance durability especially the resistance to alkali-aggregate reaction , increase concrete strength , pozzolanic materials, etc. [1, 2, 3, 4]

[1] *Graduate Student, Department of Civil Engineering, Suranaree University of Technology, Nakorn Ratchasima 30000, Thailand.*
[1] *Lecturer, Department of Civil Engineering, Suranaree University of Technology, Nakorn Ratchasima 30000, Thailand.*
[2] *Professor, Department of Civil Engineering, Khon Kaen University, Khon Kaen 40002, Thailand.*

The researcher has studied the base property of the cement paste has mixed synthesized zeolite. There is the possibility will to use zeolite are pozzolanic mterials for use replace some part cement in concrete work [5]. Thus in this present paper then have the education adds by present the effect of zeolite on microstructure of hardened blended cement pastes, such as capacity porosity and pozzolanic reaction. For insist that , zeolite have the be pozzolan has can to apply in concrete product.

2. THE EXPERIMENTAL INVESTIGATION

2.1 Materials

Materials used in this experiment consist of :
Portland cement : ordinary Portland cement type I was used ASTM C150
Zeolite : synthesized zeolite form Chonburee (use Ze)
Mixing water : tap water was used.

2.2 Mix ratio

Synthesized zeolite was used to partially replace Portland cement type I at the rate of 0, 20, and 40 % by weight of binder. A constant water to binder ratio (w/b) of 0.35 was used to control the workability of pastes. The pastes were mixed in a mechanical mixer and the specimens were cast in 50 mm cube moulds. The fresh samples wee covered with plastic sheet to prevent water evaporation. After casting 24 hours, the sample were removed form the mould and cured in saturated lime water. The samples were tested at the ages of 28 day.

3. TEST PROGRAMS

3.1 The properties of cement and zeolite test.

3.1.1 Specific Gravity of Portland cement and zeolite by Le Chatelier Flask (ASTM C188).
3.1.2 Take photographs of Portland cement and zeolite by using a scanning electron microscope (SEM).
3.1.3 Chemical composition of Portland cement and zeolite by using X- Ray fluorescence.
3.1.4 Particle size analysis of Portland cement and zeolite by using Mastersizer.

3.2 The properties of pastes

The paste cube at the specified ages 28 days were broken into small fragments (about 10 x 10 mm). The samples were cured in Acetone for 7 days to half hydration reaction. After that, the sample were dried by oven at 80-100 ^{o}C for 30 minutes. The dried sample pastes were ground in a ball mill at speed of 950 round/minute for 2 minute and sieved through 100 mesh (150 m). The samples was testing by XRD and TGA, DTA for analyze of $Ca(OH)_2$. The representative sample of 2x2 mm^2 were obtained to characterize the distribution of pore size by MIP test and the samples were broken into 1x1x0.5 cm^3 for SEM.

3.3 The symbol use the education

PC = Portland cement type I
ZE = Zeolite
PC100 = Portland cement type I paste
PZE20 = Paste are replacement of zeolite at 20 % by weight of total binder
PZE40 = Paste are replacement of zeolite at 40 % by weight of total binder

4. RESULTS AND DISCUSSION

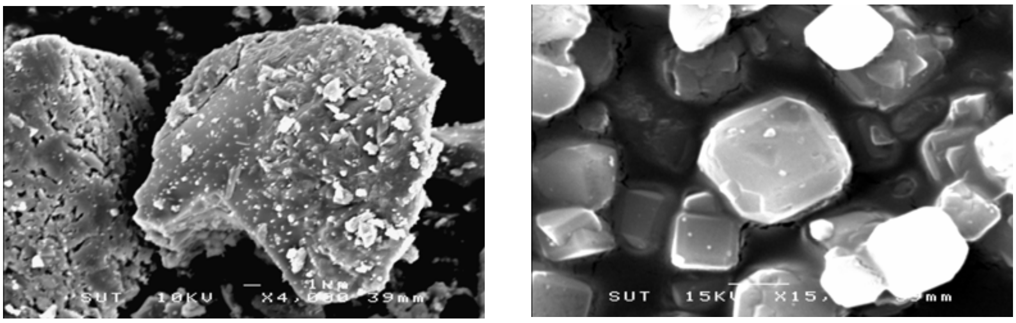
4.1 Properties of Materials

4.1.1 physical result of Portland cement type I and zeolite

Table 1 shows specific gravity and median particle size of Portland cement type I and zeolite. The particle shape of Portland cement type I is solid and angular (Figure 1a) whereas that zeolite surface is smooth and has the character is hexagon (Figure 1b). The median particle size of zeolite and Portland cement type I were 2.34 and 13.60 microns, respectively. The particle size distributions of Portland cement type I and zeolite by Mastersizer are shown in Figure 2.

Table 1. specific gravity and median particle size of Portland cement type I and zeolite

Sample	Specific Gravity	Mean Particle Size d_{50} (micron)
PC	3.15	13.60
Ze	1.87	2.34



(a) (b)

Figure 1. SEM :(a) Portland cement type I at 4,000 time, (b) zeolite at 15,000 time

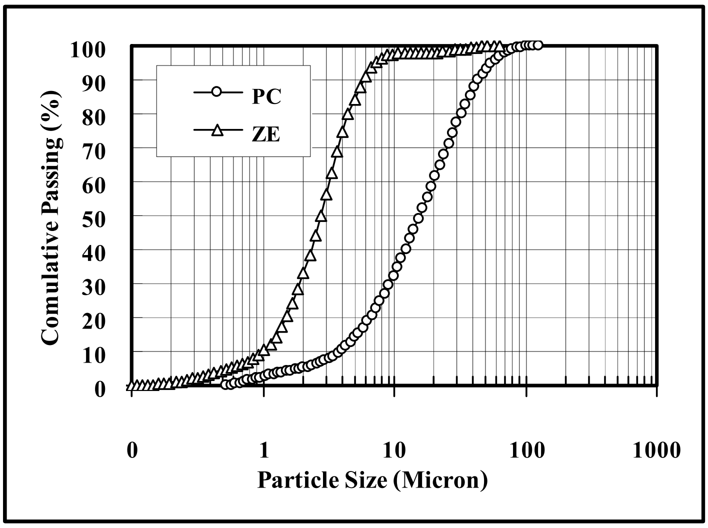


Figure 2. Particle size distribution of Portland cement type I and zeolite

4.1.2 Chemical composition of Portland cement type I and zeolite

Table 2 present the chemical composition of Portland cement type I and zeolite determined by XRF. The chemical composition of zeolite is SiO_2 and Al_2O_3 . Fgure 3 shown the XRD pattern of zeolite. The result show that the intensity peak of Sodium Aluminum Silicate ($Na_{96}Al_{96}Si_{96}O_{384}$) appeared at 2Ø or 0-60 degrees. The classified zeolite is type A known as Sodium Aluminum Silicate ($Na_{96}Al_{96}Si_{96}O_{38}$)

Table 2. Chemical composition of Portland cement type I and zeolite

Chemical Composition (%)	Portland Cement Type I (PC1)	Zeolite (Ze)
SiO_2	20.9	67.08
Al_2O_3	4.76	21.12
Fe_2O_3	3.41	0.03
CaO	65.41	0.18
MgO	1.25	0.08
K_2O	0.35	2.87
LOI	0.96	6.27

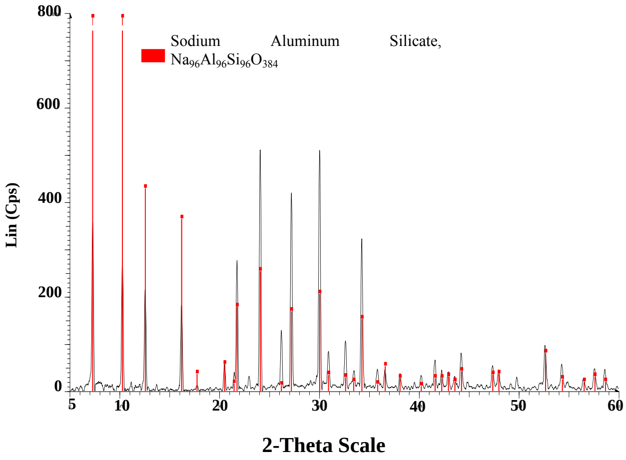
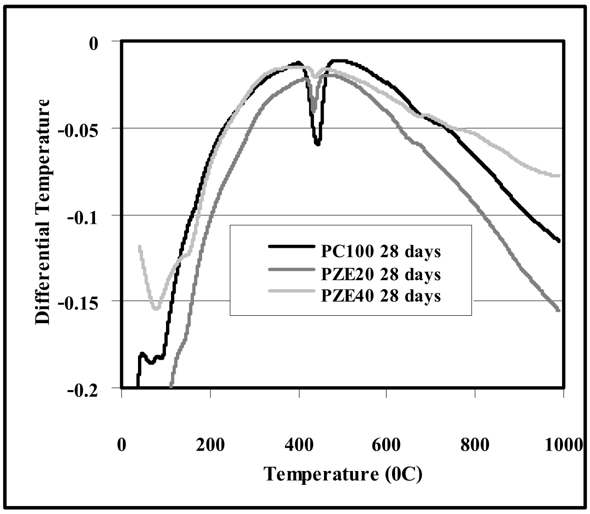


Figure 3. XRD pattern of zeolite

4.2 Properties of Pastes

4.2.1 Thermal Analysis in Pastes

Differential Thermal Analysis (DTA) involves heating or cooling a test sample and an inert reference under identical conditions, while recording any temperature difference between the sample and reference. This differential temperature is then plotted against time, or against temperature. Changes in the sample which lead to the absorption or evolution of heat can be detected relative to the inert reference, shows that in Figure 4.



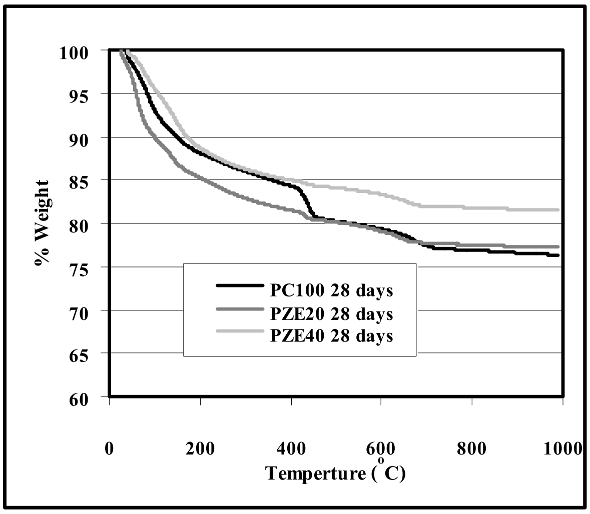


Figure 4. Differential temperature during the DTA of pastes

Figure 5. Weight loss during the TGA of pastes

Thermogravimetric Analysis (TGA) is a technique that measure the change in weight of pastes when subjected to a temperature program under controlled atmosphere. such as , the decomposition of materials , the evaporation of water in pastes, etc. TGA analysis of the samples was performed using thermal analyzer. Computer controlled graphics can calculate weight percent losses. The graph referring to the weight loss during each peak compared with the original weight of substances prior to the test, shows that in Figure 5.
Figure 4 and 5 shows Differential Thermal Analysis and Thermogravimetric of pastes at 28 days with rate of 0, 20, and 40% by weight of binder. When heating the cement paste at the temperature between 450-580 ^{o}C, [6, 7, 8] $Ca(OH)_2$ will be decomposed into calcium oxide (CaO) and water as in equation 1.

$$Ca(OH)_2 \longrightarrow CaO + H_2O \quad (1)$$

For Figure 4 and 5 the disintegration of $Ca(OH)_2$ decreased with an increase in the zeolite replacement level (PZE20, PZE40). The amount of $Ca(OH)_2$ of the blended cement paste with zeolite decreased with increasing replacement percentage of zeolite and were lower than that of PC paste. For PC paste the $Ca(OH)_2$ was produced by the hydration reaction. The $Ca(OH)_2$ of PZE20 and PZE40 pastes was produced by the hydration reaction and pozzolanic reaction of zeolite.

4.2.2 Effect of zeolite on pore volume of paste

Table 3 shows all pore volume, average pore diameter and total porosity of PC100, PZE20 and PZE40 at 28 days. Figure 6. show that the total porosity of PC100, PZE20 and PZE40 at 28 days. The results total porosity and total pore area increased with an increase in replacement by zeolite. Because the smaller hole particle or blended small pore size of zeolite resulting pore volume and pore area increase. The average pore diameter decreased with an increase in zeolite replacement level. This was because the small particle of zeolite (2.34 μm) at compare with the cement (13.60 μm). The small particle of zeolite dispersed in blended cement paste, then the pore size decreased but medium capillary (10,000-50 nm) an increase. The replacement of Portland cement by zeolite increased the small pore except the small particle of zeolite. This effect form pozzolanic reaction, but in the presents have no result to insist

Figure 7 shows the pore size and accumulation pore volume of PC100, PZE20 and PZE40 paste at 28 days. Figure 8 shows pore size and incremental pore volume of PC100, PZE20 and PZE40 paste at 28 days. From Figure 7, The replacement of Portland cement by zeolite spread pore size are powdery more than PC100. Correspond Figure 8, the replacement of Portland cement by zeolite decreased the capillary porosity compare with PC100 at 28 days. The peak of capillary pores of PZE20 and PZE40 pastes was 45.20 nm at the incremental pore volume of 0.0146 mL/g and 36.20 nm at incremental pore volume of 0.0264 mL/g, respectively. These values were lower than those of PC100 was 68.10 nm at the first peak, at incremental pore volume of 0.015 mL/g. The results also showed that the blended cement paste containing by hydration reaction more than pozzolanic reaction from zeolite. Then the replacement of Portland cement by zeolite with the quantity and the size that are appropriate decreased the capillary porosity.

Table 3. Pore volume, average pore diameter and total porosity of PC100, PZE20 and PZE40

	PC100	**PZE20**	**PZE40**
Air Void (%) (> 10,000 nm)	6.31	8.32	10.75
Large Capillary (%)(10,000-50 nm)	8.27	9.98	6.48
Medium Capillary (%) (5-10 nm)	5.24	11.26	23.03
Total Porosity (%)	19.83	29.56	40.26
Average Pore (nm)	47.90	44.00	40.25
Total Pore Area (m^2/g)	8.80	17.14	25.90

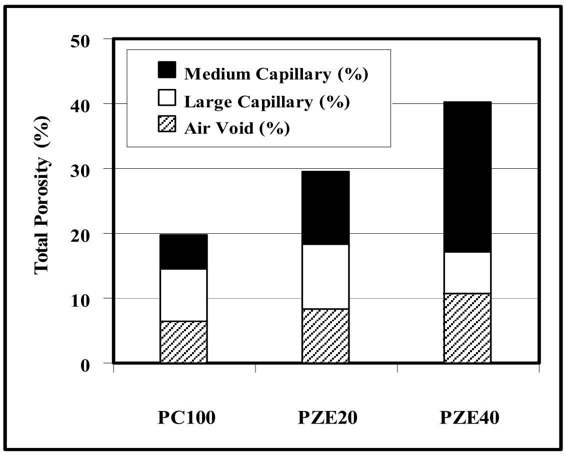


Figure 6. Total porosity of PC100, PZE20 and PZE40 at 28 days

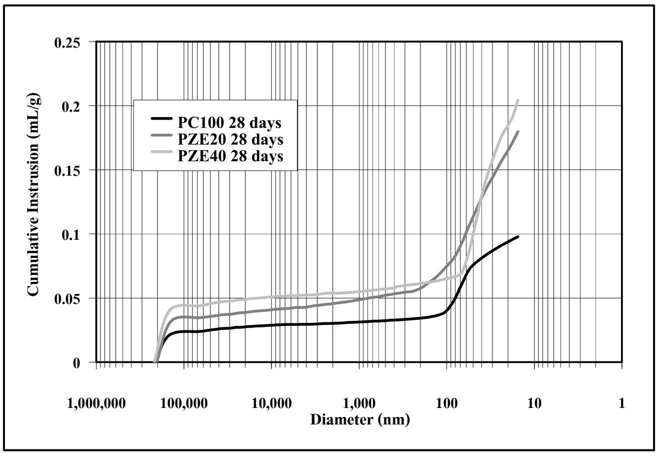


Figure 7. Pore size and accumulation pore volume of PC100, PZE20 and PZE40 paste at 28 days

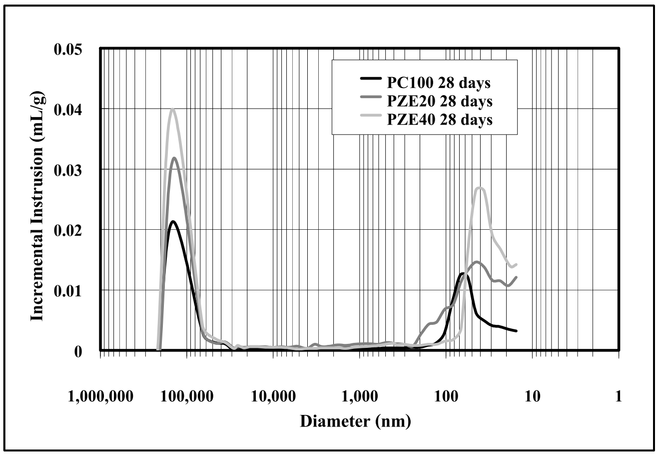
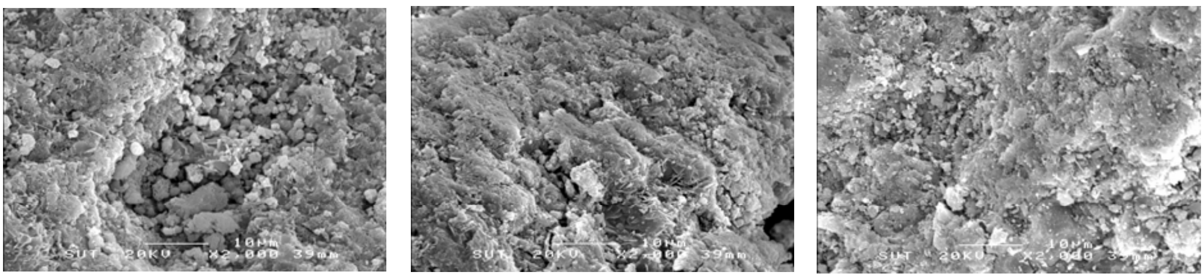


Figure 8. Pore size and incremental pore volume of PC100, PZE20 and PZE40 paste at 28 day

4.2.3 Fracture Surface Analysis by Scanning Electron Microscope (SEM)

The microstructure morphology of fractured surface pastes PC100, PZE20 and PZE40 at 28 and 90 days by SEM are shown in Figs. 9a , b and c respectively. The microstructure of PC100 was porous and had many voids, while PZE20 and PZE40 were formed exhibited a very dense structure. Correspond to 4.2.2 topic, there is The replacement of Portland cement by zeolite decreased the pore size and the structure of paste very dense. It was effect of chemical compound of hydration or either pozzolanic reaction. It was concluded that the replacement of Portland cement by zeolite large amount (PZE40) the structure of paste very dense.



(a) (b) (c)

Figure 9. Fracture Surface (a) PC100, (b) PZE20 and (c) PZE40 paste at 28 days by SEM

5. CONCLUSIONS

Based on the results of this study, the following conclusions can be drawn :

1. the disintegration of $Ca(OH)_2$ decreased with an increase in the zeolite replacement level (PZE20, PZE40) by compare PC100.

2. The replacement of Portland cement by zeolite increased the total porosity but decreased the average pore size of the paste**.**

3. The replacement of Portland cement by zeolite decreased pore size, then the structure of paste was crowded. This effect form hydration reaction and some part of pozzolanic reaction.

6. ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial supports from the School of Civil Engineering, Suranaree University of Technology for providing facilities and equipments.

7. REFERENCES

[1] Feng, N.-Q., Xing, F. and Leng, F.-G. 2000. Zeolite Ceramsite Cellular Concrete. Magazine of Concrete Research. 52 (2): pp. 117-122.

[2] Feng, N.-Q. and Peng, G.-F. 2005. Applications of Natural Zeolite to Construction and Building Materials in China. Construction and Building Matyerials, 19: 579-584.

[3] Quanlin, N. and Naiqian, F. 2005 Effect of Modified Zeolite on Expansion of Alkaline Silica Reaction. Cement and Concrete Research, 35 (9): pp. 1784-1788.

[4] Poon, C.S., Lam, L., Kou, S.C. and Lin, Z. S. 1999. A Study on the Hydration Rate of Natural Zeolite Blended Cement Paste. Construction and Building Materials. 13: pp. 427-432.

[5] Theerawat Sinsiri, "Effect of Zeolite on Properties of Paste and Mortar", Concrete meeting yearly 2, 25-27 October 2006, Udornthanee, page MAT12-MAT17.

[6] El-Jazairi, B. and Illston, J.M. 1977. A Simultaneous Semi-Isothermal Method of Thermo-gravimetry and Derivative Thermogravimetry, and Its Application to Cement Pastes. Cement and Concrete Research, 7: pp. 247-258.

[7] El-Jazairi, B. and Illston, J.M. 1980.The Hydration of Cement Paste using the Semi-Isothermal Method of Derivative Thermogravimetry, Cement and Concrete, 10: pp. 361-366.

[8] Wang, K.S., Lin, K.L., Lee, T.Y. and Tzeng, B.Y. 2004. The Hydration Characteristics when C_2S is Present in MSWI Fly Ash Slag. Cement and Concrete Research, 26: pp. 323-330.