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THESIS

PARTIAL REPLACEMENT OF CLINKER BY AGRICULTURAL WASTE, BAGASSE ASH, FOR TYPE I PORTLAND CEMENT PRODUCTION

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A Thesis Submitted in Partial Fulfillment of
the Requirements for the Degree of
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There are various kinds of agricultural waste ashes throughout the industrial processes in Thailand such as bagasse ash (BA), rice husk ash, oil palm ash etc. They are currently exploited as pozzolanic materials and supplements to improve the compressive strength in terms of chemical composition of cement by partly replacement of clinker for cement production with them. One of their advantages is to decrease CO_2 gas emission from decreasing consumption of clinker to produce cement. Either mortar or concrete production needs cement as main material. Appropriate ratio of clinker replacement by fine (<45 micron) BA and w/c ratio as well as effects of BA on properties of cement were investigated in this research. Initially, BA was designed to replace clinker with the weight percentage of 0, 10, 20, 30 and 40, respectively, whereas gypsum was constantly added. Specimens were casted as cement mortars and pastes and, finally, analyzed for particle size, fineness, compressive strength, normal consistency, setting time, flowability, chemical composition and microstructure according to curing ages of 3, 7, 28, 56 and 90 days. Their properties were carried out and compared with the results of commercial type I Portland cement. The increasing amount of BA affects the increase of w/c ratio and setting time of resultant cement. Furthermore, clinker replacement with BA is a process for reduction of cost of cement raw materials. The experimental results indicated that clinker replacement with 20 wt% BA was appropriate for production in laboratory scale and it would be benefit for scale expanding as production scale in the near future.

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Student’s signature Thesis Advisor’s signature

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Piyanut Muangtong
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LIST OF ABBREVIATIONS

PC = Portland cement

SCBA = Sugar cane bagasse ash

Al = Aluminium

Al_2O_3 = Alumina, aluminium oxide

C = Carbon

Ca = Calcium

$CaSO_4$ = Gypsum, calcium sulfate

$Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$ = Ettringite, calcium aluminum sulfate hydroxide hydrate

Ca_2SiO_4 = Dicalcium silicate

Ca_3SiO_5 = Tricalcium silicate

$CaCO_3$ = Calcite, calcium carbonate

CFCs = Chlorofluorocarbons

CH, $Ca(OH)_2$ = Calcium hydroxide

CH_4 = Methane

C-S-H, $Ca_{1.5}SiO_{3.5}.xH_2O$ = Calcium silicate hydrate

CO_2 = Carbon dioxide

FeO = Iron (II) oxide

Fe_2O_3 = Iron (III) oxide

HFCs = Hydrofluorocarbons

H_2O = Water

K_2O = Potassium oxide

MgO = Magnesium oxide

Na_2O = Sodium oxide

N_2O = Nitrous oxide

O = Oxygen

O_3 = Ozone

PFCs = Perfluorocarbons

P_2O_5 = Phosphorus pentoxide

LIST OF ABBREVIATIONS (Continued)

Si = Silicon

SiO_2 = Quartz, silicon oxide

SO_3 = Sulfur trioxide

TiO_2 = Titanium dioxide, titanium (IV) oxide

EDS = Electron dispersive spectroscopy

SEM = Scanning electron microscope

TGA = Thermogravimetric analysis

SiO_2 = Quartz, silicon oxide

UTM = Universal testing machine

XRD = X-ray diffractometer

XRF = X-ray fluorescence

ASTM = American society for testing and materials

LOI = Loss on ignition

max. = maximum

N = Newton

N/cm^2 = Newton per square centimeter

MPa = Mega Pascal

cm^2 = Square centimeter

cm^3 = Cubic centimeter

mm = Millimeter

mm^2 = Square millimeter

µm = Micron

kg/m^3 = Kilogram per cubic meter

wt% = Weight percentage

°C = Degree of Celsius

PARTIAL REPLACEMENT OF CLINKER BY AGRICULTURAL WASTE, BAGASSE ASH, FOR TYPE I PORTLAND CEMENT PRODUCTION

INTRODUCTION

The cement industry is the second largest CO_2 emitting industry behind the power generation (Worrell *et al.*, 2001). It is found that each ton of cement production produces approximately one ton of CO_2 emission (Ogbeide, 2010), which is one of the important greenhouse gases as the global warming reason (Fairbairn *et al.*, 2010). The partial replacement of clinker for ordinary Portland cement by agricultural waste or agro-waste is an alternative solution for the decreasing of CO_2 emission due to less clinker consumption in cement processing for construction industry. The areas for agriculture are approximately 41% of total areas in Thailand (Ministry of Agriculture and Cooperatives, 2010). Agricultural products are mostly processed annually in the industrial plants such as sugar cane, rice, palm, and etc., therefore, the agricultural wastes has turned up enormously. Fortunately, agricultural wastes are exploited as energy sources in industrial processes to become ash. Though, bagasse ash (BA) is a valueless agricultural wastes of sugar industry (Cordeiro *et al.*, 2008), it is a pozzolan material used to replace part of cement because its chemical composition consisted of high SiO_2 which is the main phase of pozzolanic reaction in cement. It is a reaction between calcium hydroxide ($Ca(OH)_2$, CH), from hydration reaction of cement and water, and SiO_2, a pozzolan from BA, to originate phase of calcium silicate hydrate ($Ca_{1.5}SiO_{3.5}.xH_2O$, C-S-H). The C-S-H from pozzolanic reaction is a supplementary cementing phase to increase the compressive strength of cement (Nontananandh *et al.*, 2011).

The aim of the experiment is to investigate the appropriate ratio of clinker replacing by BA to produce the cement, effects of BA preparation and comparison of properties of resultant cement and type I Portland cement which is a commercial cement. These results are focused to find out the possibility for cement production in laboratory scale and soon for industrial scale production.

OBJECTIVES

1. To increase value of BA as raw material in type I Portland cement production instead of disposing into the environment.

2. To investigate the appropriate ratio of clinker replacement by fine BA to produce as the cement with the best mechanical property.

3. To research the mechanical, physical and chemical properties as well as cost of production of resultant cements and compare with a commercial cement.

LITERATURE REVIEW

Now, the global warming is the most important pollution in the world. Effect of this is the rise in the average temperature of the Earth's atmosphere and oceans since the late 19th century and its projected continuation. Since the early 20th century, Earth's mean surface temperature has increased by about 0.8 °C, with about two-thirds of the increase occurring since 1980. Warming of the climate system is unequivocal, and scientists more than 90% are certain that it is primarily caused by increasing concentrations of greenhouse gases produced by human activities such as CO_2, CFCs, HFCs, PFCs and SF_6 especially, concentrations of CO_2 has increased by 36% since 1750. It occurred from the burning of fossil fuels during industry processing, deforestation and energy using etc. Other causes from nature activities such as H_2O, O_3, CO_2, CH_4 and N_2O were produced from cycles of nature and a variety of natural phenomena (Kiehl and Trenberth, 1997).

The cement industry is one of the most CO_2 emitting industries due in large part to the thermal energy required to produce clinker. The world produced 3 billion tons of cement which calculated as the emitting more than 2.4 gigatons (Gt) of CO_2 into the atmosphere. The industry predicts global cement production is projected to grow to 5.9 billion tons by 2020 amounting to annual CO_2 emissions from the production of cement to more than 4.8 Gt. China alone is expected to produce an extra 4 billion tons of cement annually by 2020.

The current situation of cement industry is more growing to obey the economic growth. The CO_2 emission is high intensity according to high volumes of cement production and it is difficult to reduce capacity of cement production for control amount of CO_2 emission produced from industry. Robert McCaffrey (McCaffrey, 2002) proposed solution for decreasing of CO_2 emission by method of replacing amount of cement with pozzolan materials such as agricultural ash and industrial wastes. It is one of choices to be interesting and suitable solution for Thailand where there are full of agricultural wastes.

Thailand is an agricultural country. It has a total 210,560 million square meters of agricultural areas which by 5% of area for sugar cane growing. Here, it was able to produce approximately 70.89 million tons of sugar cane in 2010 (Ministry of Agriculture and Cooperatives, 2010). Almost all sugar canes are sent to the sugar factory and finally products as sugar are produced. Bagasse ash (BA) is a by-product after sugar cane is used as fuel for boilers to generate steam during production of sugar and it is an agricultural waste to be removed from the factory. In general, BA is used for the treatment of acidic soils and disposed of in landfill that is now becoming an ecowaste to decrease environmental problems. Many inert waste materials consist of high silica and alumina contents, e.g., fly ash, silica fume and agricultural wastes such as BA, rice husk ash and oil palm ash. BA is an outstanding waste consisting of very high silica content approximately 60%. It is claimed as a pozzolanic material reacting with calcium hydroxide (CH), a by-product of the hydration of cement, to form additional calcium silicate hydrate (C-S-H) as new products from the pozzolanic reaction. C-S-H phases increase a supplementary cementing material to enhance the higher compressive strength of cement.

1. CO_2 emission produced from cement industry

The global cement industry contributes around 20% of all man-made CO_2 emissions and is consequently responsible for around 10% of man-made global warming. The energy consumption by the cement industry is estimated at about 2% of the global primary energy consumption, or almost 5% of the total global industrial energy consumption. Cement production increases at about 3% per year at the moment. This rate is set to increase as developing nations rapidly become richer, and spends proportionately more on cement-intensive infrastructure.

There are two sources of CO_2 emissions from the cement plant which are by virtue of the energy it uses and the evolution of CO_2 as a by-product in the calcination process. The cement plant releases one ton of CO_2 for every ton of cement produced, half of it from the fuel it uses and the other half from calcinations process.

1.1 Process of cement production related to CO_2 emission

The basic process of cement production as shown in Fig. 1 consists of -1) acquisition of raw materials, 2) preparation of the raw materials for pyroprocessing, 3) pyroprocessing of the raw materials to form Portland cement clinker and 4) grinding the clinker to Portland cement.

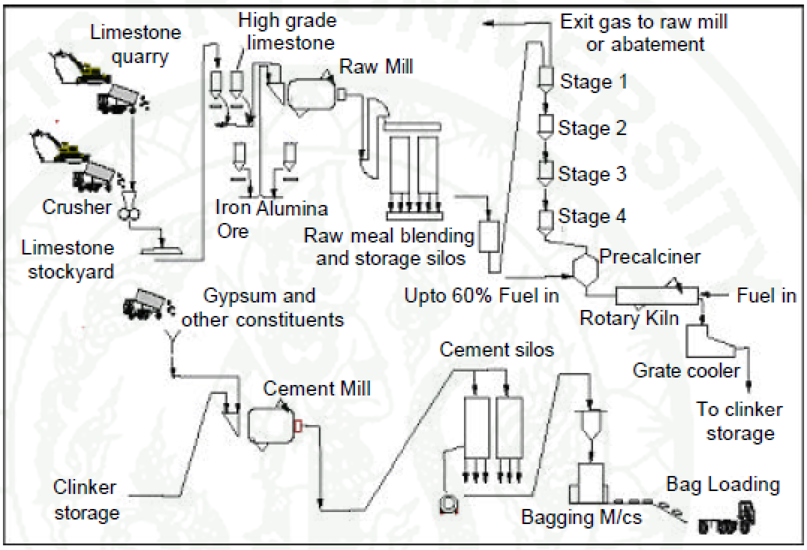


Figure 1 Process of cement production

1.1.1 Mining

Limestone, the main raw material is mined in the quarries with compressed air drilling and subsequently blasting with explosives. The mined limestone is transported through dumpers or ropeways to the plant.

1.1.2 Crushing

The limestone as mined is fed to a primary and secondary crusher where the size is reduced to 25 mm. A late even a tertiary crusher is used to further reduce the inlet size to the mill. The crushed limestone is stored in the stockpile through stacker conveyors. The crushed limestone, bauxite and ferrite are stored in feed hoppers from where they are fed to the raw mill via a weighing feeders in the required proportion

1.1.3 Raw materials preparation

Roller mills for grinding raw materials and separators or classifiers for separating ground particles are the two key energy consuming pieces of equipment at this process stage. For dry-process cement making, the raw materials need to be ground into a flowable powder before entering the kiln. Generally ball mills and vertical roller mills are used.

1.1.4 Coal milling

In plants using coal, coal mills are part of the system to provide dried pulverized coal to kiln and precalciner. The raw coal from stock yard is crushed in a hammer crusher and fed to the coal mill. The coal mill can be an air swept ball mill or vertical roller mill where the coal particles are collected in the bag filter through a grit separator. The required size is 80 % on 90 µm and less than 2% on 212 µm. Hot air generated in a coal fired furnace or hot air from clinker cooler/preheater exhaust is used in the drying of coal in the mill.

1.1.5 Pyro processing

The function of the kiln in the cement industry is to first convert $CaCO_3$ into CaO and then react Silica, Aluminum Oxide, Ferric Oxide, and Calcium Oxide with the free lime to form clinker compounds: C_3S, C_2S, C_3A, and C_4AF. The raw material mix enters the kiln at the elevated end, and the combustion fuels generally are introduced into the lower end of the kiln in a countercurrent manner. The materials are continuously and slowly moved to the lower end by rotation of the kiln. Pulverized coal, gas, pet coke or oil are the fuels generally used. This system transforms the raw mix into clinkers, which are gray, glass-hard, spherically shaped nodules that range from 0.32 to 5.1 cm in diameter. The chemical reactions and physical processes that constitute the transformation are quite complex.

1.1.6 Pre heater and pre calciner

Preheaters are cyclones are arranged vertically, in series, and are supported by a structure known as the preheater tower. Hot exhaust gases from the rotary kiln pass counter currently through the downward-moving raw materials in the preheater vessels. Compared with the simple rotary kiln, the heat transfer rate is significantly increased, the degree of heat utilization is more complete, and the process time is markedly reduced owing to the intimate contact of the solid particles with the hot gases. The improved heat transfer allows the length of the rotary kiln to be reduced and increases the production.

Additional thermal efficiencies and productivity gains have been achieved by diverting some fuel to a calciner vessel at the base of the preheater tower. This system is called the preheater/precalciner process. While a substantial amount of fuel is used in the precalciner, at least 40 percent of the thermal energy is required in the rotary kiln. Up to 95 % of the raw meal gets calcined before entering the kiln. Calciner systems sometimes use lower-quality fuels as a means of improving process economics.

From pre-heater and pre-calciner, 60% of flue gases travel towards raw mill and 40% to conditioning tower where water injection is used to condition the gases. These gases are ultimately passed through electrostatic precipitator (ESP) for the maximum removal of particulate matters.

1.1.7 Clinker cooler

The hot clinker is cooled from 1100 °C to 90 °C in the grate cooler with a series of fans. The cooler has two tasks: to recover as much heat (up to 30% of kiln system heat) as possible from hot (1450 °C) clinker so as to return it to the process; and to reduce the clinker temperature to a level suitable for the equipment downstream. The hot air from recuperation zone is used for main burning air (secondary air) and precalciner fuel (tertiary air). The remaining air is sent to the stack through multiclones or ESP. Once clinker leaves the kiln it must be cooled rapidly to ensure the maximum yield for the compound that contributes to the hardening properties of cement. The main cooling technologies are the reciprocating grate cooler and the tube or planetary cooler.

1.1.8 Finish milling

In this final process step, the cooled clinker is mixed with additives to make cement and ground using the mill technologies described above. These materials are then sent through mills which perform the remaining grinding. The grinding process occurs in a closed system with an air separator that divides the cement particles according to size. Material that has not been completely ground is sent through the system again. Finish milling is the grinding of clinker to produce a fine grey powder. Gypsum ($CaSO_4$) is blended with the ground clinker, along with other materials, to produce finished cement. Gypsum controls the rate of hydration of the cement in the cement-setting process. The cement thus produced is collected in the bagfilter and taken to cement silos through a vertical pneumatic pump. The energy used for cement grinding depends on the type of materials added to the clinker and on the desired fineness of the final product. Cement fineness is generally measured in a unit called Blaine, which has the dimensions of cm^2/g and gives the total surface area of material per gram of cement. Higher Blaine indicates more finely ground cement, which requires more energy to produce. Portland cement commonly has a Blaine of 3000-3500 cm^2/g.

1.2 Greenhouse gas (GHG) linkages

In the cement production process, carbon dioxide emissions can be grouped as “energy related”, referring to emissions that result from the combustion of fossil fuel, and “process related”, referring to the emissions from the decomposition of calcium carbonate. Studies have shown that one ton of carbon dioxide gas is released into the atmosphere for every ton of Portland cement which is made anywhere in the world. The only exceptions are so-called 'blended cements', using such ingredients as coal fly ash, where the CO_2 emissions are slightly suppressed, by a maximum of 10%-15%. Cement, (Portland cement), results from the calcination of limestone (calcium carbonate) at very high temperatures of approximately 1450-1500 °C, and silico-aluminous material according to the reaction of Eq.1.

$$5CaCO_3 + 2SiO_2 \longrightarrow (3CaO.SiO_2) + (2CaO.SiO_2) + 5CO_2 \qquad (1)$$

This means that the manufacture of 1 ton of cement generates 1 ton of CO_2 greenhouse gas.

2. Pozzolan materials

Pozzolan materials are used as a mineral admixture in concrete which consist of high silica and alumina. They demonstrated the pozzolanic property when is very small particle size (normally use particle size less than 45 µm). Their reaction is occurred between calcium hydroxide (CH), from hydration reaction of cement and water as Eq. 2, SiO_2 or Al_2O_3, a pozzolan material reacts with CH, to generate phase of calcium silicate hydrate (C-S-H) or aluminum silicate hydrate (A-S-H) following the pozzolanic reaction in Eq. 3. Both C-S-H and A-S-H from pozzolanic reaction is a supplementary cementing phase inside the microstructure of cement according to ASTM 168 (Glasser, 1996; ASTM C 168, 2001).

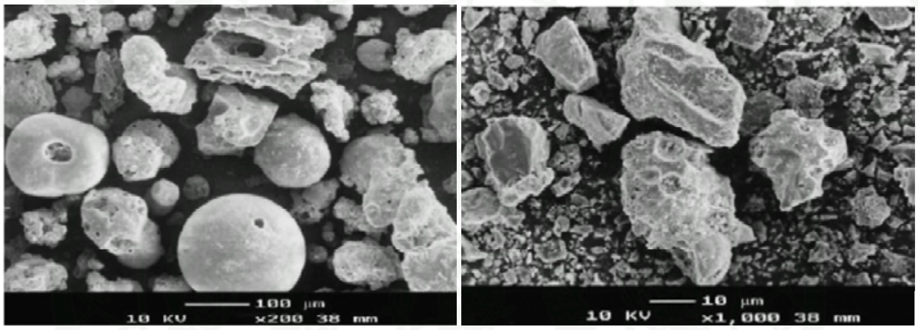
$$\text{Cement} + H_2O \longrightarrow \text{C-S-H} + Ca(OH)_2 + \text{Heat} \qquad (2)$$

$$Ca(OH)_2 + SiO_2\ (\text{Pozzolan}) + H_2O \longrightarrow \text{C-S-H} \qquad (3)$$

Thailand is rich of agricultural wastes which is by-product from the agricultural industry such as bagasse ash (BA) is produced from sugar refinery, rice husk ash (RHA) is produced from rice mill and oil palm ash (OPA) is produced from biodiesel factory etc. Three kinds of ashes were found that the most quantity in the country which are classified as one of pozzolan materials.

2.1 Oil palm ash

OPA is a by-product from oil palm industry which is high capacity according to increasing of population. It contains high SiO_2 approximately 60% up, therefore, it can use as pozzolan material to form C-S-H phase. Moreover, morphology is characterized by a spongy and porous structure in nature, of which its main components are in the angular and irregular form. Meanwhile, raw palm ash before grinding was a rather spherical particles following Fig. 2. Its advantage is chlorine ion protection from normal atmosphere and decreased expansion rate.

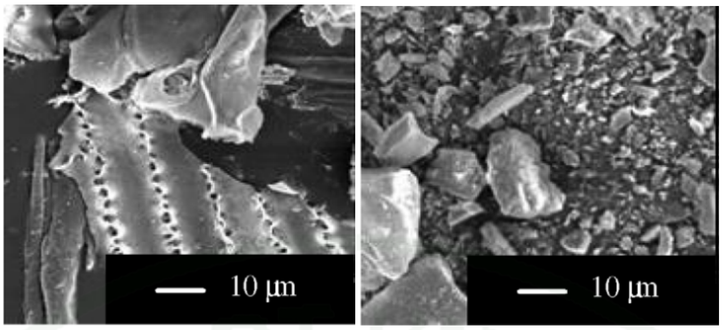


(a) Raw oil palm ash (b) After grinding

Figure 2 Morphology of oil palm ash

2.2 Rice husk ash

RHA is produced from rice mill. It is rich amount of SiO2 approximately more than 90% to affect on much more generation of C-S-H. Morphology is full the spongy structure and irregular shape according to Fig. 3. It reduced the rapid chloride penetrability of concrete from a moderate to a low, and increasing of compressive strength on late time



(a) Unground RHA (b) Ground RHA

Figure 3 Morphology of rice husk ash

2.3 Bagasse ash

BA is by-product of sugar refinery in the sugar industry. It consisted of high SiO_2 approximately 60%. Morphology is rich the porous and irregular shape, it is cause of water requirement to more during mixing of cement and BA. C-S-H phases from pozzolanic reaction between SiO_2 and CH, by-product of hydration reaction, increased compressive strength at late time. Moreover, BA reduced heat of hydration to affect as decreasing of cracking of mortar or concrete.

MATERIALS AND METHODS

Materials

1. Type I Portland cement (PC) has the commercial name as INSEE PETCH, Siam City Cement Public Co., Ltd., in Saraburi Province

2. Clinker, Siam City Cement Public Co., Ltd., in Saraburi Province

3. Gypsum, Siam City Cement Public Co., Ltd., in Saraburi Province

4. Bagasse ash, Kaset Thai Co., Ltd., in Nakhon Sawan Province

5. River sand

6. Deionized water

7. Towel

8. Tamper

9. Vernier caliper

10. Cube steel mold (5×5×5 cm^3)

11. Rectangular plastic mold (4×4×2 cm^3)

12. Sieve 20 Mesh (850 Micron), 30 Mesh (600 Micron), 100 Mesh (150 Micron) and 325 Mesh (45 Micron), Endecotts Ltd., England

13. Analytical balance (2 digits), Ohaus, Adventurer Pro, U.S.A.

14. Oven, Espec, PH-101, U.S.A.

15. Centrifugal ball mill, Retsch, S2, Germany

16. Carbon steel ball mill

17. Sieve shaker

18. Mortar mixer, Eastman Way, Herts HPZ ZHB, England

19. Smarter particle sizing, Malvern Instruments, Mastersizer 3000, England

20. Flow table and flow brass mold

21. Blaine air permeability apparatus

22. Vicat needle apparatus

23. Helium pycnometer, Micromeritics, Accupyc 1330, U.S.A.

24. X-ray fluorescence (XRF), Bruker, S8 Tiger, Germany

25. X-ray diffractometer (XRD), Philips, X'pert, The Netherlands

26. Scanning electron microscope (SEM), Philips, XL-30, The Netherlands

27. Universal testing machine (UTM), Versa-Tester (Evanston), CT-746, U.S.A.

Methods

Procedure of this research is described in Fig. 4.

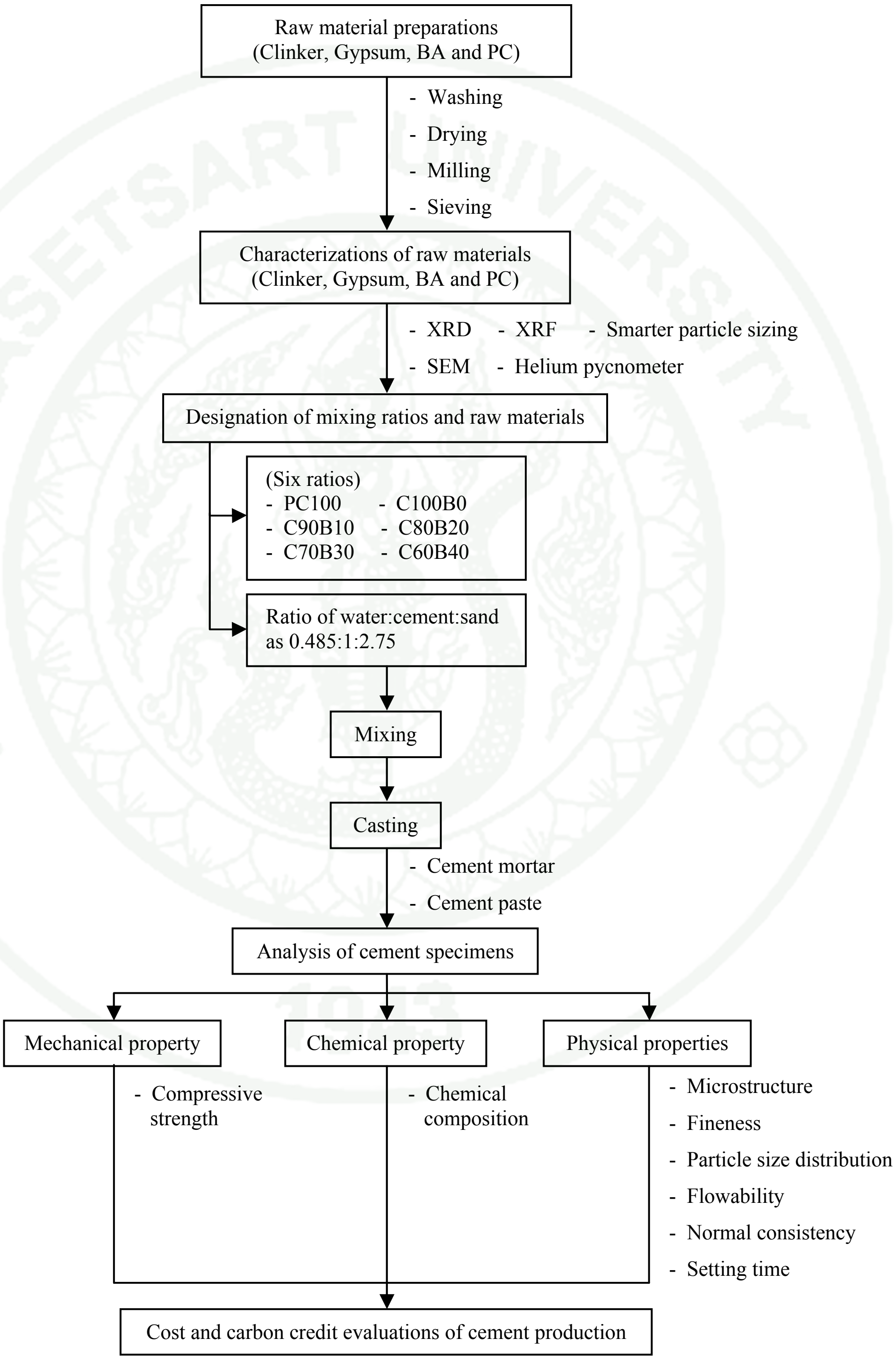


Figure 4 The experimental diagram

1. Raw material preparations and characterizations of material

Type I Portland cement, clinker, gypsum, river sand and as-received BA were chosen as local raw materials for laboratory experiments. Type I Portland cement (INSEE PETCH type) of Siam City Cement Public Company Limited was the commercial cement used to compare with the resultant cement from laboratory. Clinker and gypsum were received from the same company. They were dried in an oven at 100 °C for 24 hr and ground by a ball milling machine made of carbon steel for 30 hr. Then, they were sieved through mesh finer than 149 µm.

For as-received BA, it was obtained from Kaset Thai factory, Nakhonsawan Province and burnt as a heat fuel on production of sugar at approximately 700 °C in boilers. It was prepared by washing with deionized water to ensure impurities removing and drying at 100 °C (Cordeiro *et al.*, 2009a). As other raw materials, it was ground in high speed ball mill (S2, Retsch) for 60 min and sieved through finer than 45 µm (Cordeiro *et al.*, 2008; Cordeiro *et al.*, 2009b).

The chemical composition of BA was carried out by X-ray diffraction between 10^{o}-65^{o} 2θ is shown in Fig. 5, which consists of quartz (SiO_2; JCPDS 85-1054), calcite ($CaCO_3$; JCPDS 83-1762), iron oxide (FeO; JCPDS 01-1223) and carbon (C; JCPDS 26-1077), respectively. The microstructure of BA is shown in Fig. 6 which revealed particles of angular and irregular shape. Surface of particles were rough and plenty of pores. Table 1 presented the mineral admixture class of pozzolanic material according to ASTM C 168 (ASTM C 168, 2001) which the chemical and physical properties of BA correspond to pozzolanic material class N.

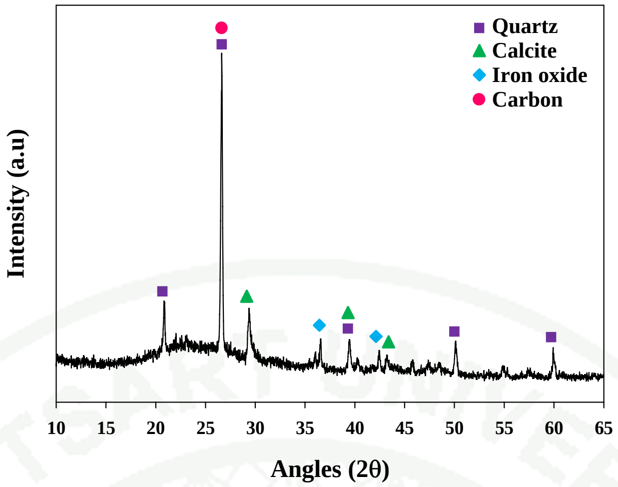
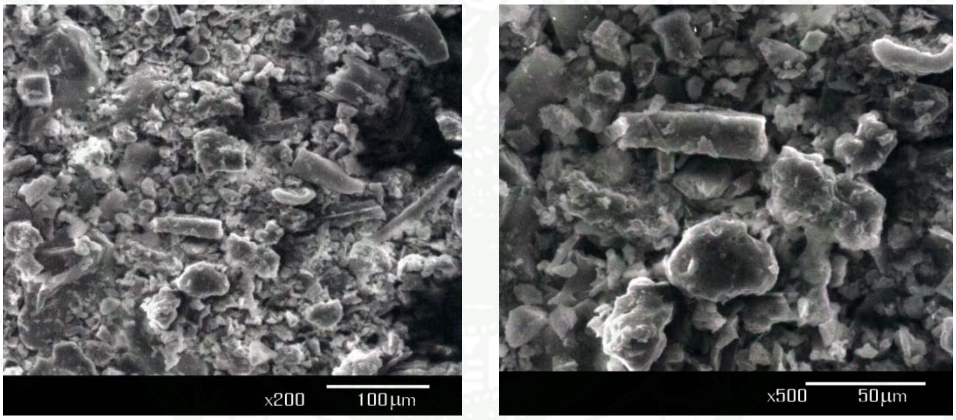


Figure 5 XRD pattern of BA burnt approximately 700 °C



(a) BA, 200X (b) BA, 500X

Figure 6 SEM images of BA after grinding at a magnification of 200X and 500X

Table 1 Properties of BA compared with ASTM C 168

Chemical requirements	**Mineral admixture class**			**BA**
	N	**F**	**C**	
$SiO_2+Al_2O_3+Fe_2O_3$, min. %	70.0	70.0	50.0	72.15
SO_3, max. %	4.0	5.0	5.0	0.41
Loss on ignition (L.O.I), max. %	10.0	6.0	6.0	15.09
Na_2O, max. %	1.5	1.5	1.5	0.32
Physical requirements				
Strength activity index Portland cement				
7-day, min. % of control	75	75	75	103.24
28-day, min. % of control	75	75	75	111.83
Water requirement, max. % of control	115	105	105	115.75

Note Mineral admixture class of pozzolanic material is consist of N, F and C classes according to ASTM C 168

Properties of raw materials analyzed by X-ray fluorescence (XRF, Bruker, S8 Tiger, Germany) for chemical compositions, helium pycnometer (Micromeritics, Accupyc 1330, U.S.A.) for density and smarter particle sizing distribution (Malvern Instruments, Mastersizer 3000, England) for particle size are shown in Table 2 according to ASTM C150 (ASTM C150, 2002). The result of weight loss during calcinations via technique of loss on ignition, LOI, was paid attention rather than that via Thermal gravimetric analysis (TGA) because the raw materials used in the research were prepared for resultant cement merely at room temperature. In process of mortar preparation, particle size of river sand was selected between 600 and 850 μm which prepared by drying first with natural air and sieved through mesh No. 20 and No. 30.

Table 2 Properties of raw materials

Composition	**Portland cement (wt%)**	**Clinker (wt%)**	**Gypsum (wt%)**	**BA (wt%)**
SiO_2	17.84	19.09	2.12	64.11
CaO	66.83	68.14	42.48	5.75
Al_2O_3	3.88	4.02	0.87	5.26
Fe_2O_3	3.71	4.22	0.46	2.78
K_2O	0.67	0.78	0.02	2.59
Na_2O	0.17	0.19	-	0.32
MgO	1.40	1.49	0.13	1.28
TiO_2	0.26	0.26	0.06	0.38
P_2O_5	0.07	0.06	-	1.37
SO_3	4.10	1.11	50.28	0.41
Loss on ignition, L.O.I	0.90	0.48	3.48	15.09
Density (kg/m^3)	3214.60	3215.30	2392.00	2330.40
Particle size at D_v 50 (µm)	18.80	244.00	220.00	18.60

2. Designation of mixing ratios and raw materials

The cement replacement by bagasse ash was designed as shown in Table 3 for sample preparations (cement mortar and paste). The clinker/BA samples were adjusted by replacing clinker with amount of BA as:-1) 0% (C100B0 as control cement) 2) 10% (C90B10) 3) 20% (C80B20) 4) 30% (C70B30) and 5) 40% (C60B40) and all samples were added fine gypsum for 3.5 wt%. Commercial type I Portland cement (PC100) was used for comparing with the resultant cements. The ratio of water:cement:sand was used as 0.485:1:2.75 for experiments according to ASTM C305 (ASTM C305, 2002).

Table 3 Sample preparation

Samples	Portland cement (wt%)	Clinker (wt%)	BA (wt%)	Gypsum (wt%)
C100B0	-	96.5	-	3.5
C90B10	-	86.85	9.65	3.5
C80B20	-	77.2	19.3	3.5
C70B30	-	67.55	28.95	3.5
C60B40	-	57.9	38.6	3.5
PC100	100	-	-	-

3. Casting of samples

Both resultant cement and commercial cement were mixed and prepared for mortar and paste samples. For cement mortars, they were mixed with sand, cement and water. They were cast into molds for compressive strength and flowability of cement mortar testing. Cement pastes were prepared from cement and water only. They were mixed and cast into molds for normal consistency, setting time, chemical composition and microstructure characterizations.

4. Analysis of samples

4.1 Particle size distribution

The raw materials of cement process composed of clinker, BA and gypsum were mixed as cement powders by dry mixing technique. Each cement ratio was measured the particle size distribution by a smarter particle sizing (Mastersizer 3000, Malvern Instruments, England) used the laser diffraction technique. The dry dispersion and pressure of 1 bar were setting as the special condition for testing according to the characteristic of cement powder. The particle size distributions were characterized using D_v 10, D_v 50 and D_v 90, which was the 10, 50 and 90% passing size in the cumulative distribution of cement powder.

Figure 7 Particles size distribution of cement powders analyzed by a smarter particle sizing

4.2 Fineness

Sample powders were prepared as same as the experiment of particles size distribution and analyzed the fineness of cement by using the Blaine air permeability apparatus following ASTM C 204 (ASTM C 204, 2001). Samples were put into the permeability cell and attached cell to the manometer tube. The manometer was slowly evacuated the air from one arm of the machine until the liquid in its tube reached the top mark, and then tightened the valve perfectly. The timer was started when valve was opening, until liquid reached the third mark then timer was stopped. The fineness of cement was calculated and reported as the specific surface area by using data of time as s, second, collected from the experiment, according to Eq. 4.

$$S = \frac{S_s\sqrt{T}}{\sqrt{T_s}} \tag{4}$$

Where

S is specific surface area of the test sample in m^2/kg,

S_s is specific surface area of the standard sample used in calibration of the apparatus in m^2/kg,

T is measured time interval of manometer drop for test sample in s and

T_s is measured time interval of manometer drop for standard sample used in calibration of the apparatus in s

Figure 8 Fineness of cement powders analyzed by a Blaine air permeability apparatus

4.3 Compressive strength

The cement mortars were prepared from water:cement:sand ratio of 0.485:1:2.75, which was fixed to determine for effect of BA on compressive strength of mortars. Samples were mixed in a mechanical mixer. They cast and compacted by tamping for two layers in cube molds (5x5x5 cm^3). Mortar cubes were demolded after casting at room temperature for 24 hr. Consequently, they, 4 cubes of mortar samples for each ratio, were cured in zip plastic bags with saturation of sprayed water until ages of 3, 7, 28, 56 and 90 days for compressive strength testing according to ASTM C 109 (ASTM C 109, 2002) by a universal testing machine (UTM, CT-746, Versa-Tester (Evanston), U.S.A.). The compressive strength was calculated using Eq. 5.

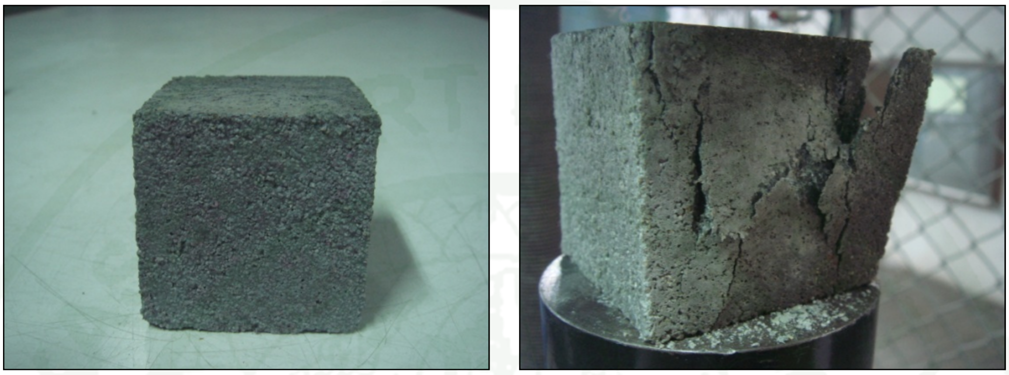
$$f_m = \frac{P}{A} \tag{5}$$

Where

f_m is compressive strength in psi or MPa,

P is total maximum load in lbf or N and

A is area of loaded surface in in^2 or mm^2



(a) Mortar sample before testing (b) Mortar sample after testing

Figure 9 Compressive strength testing by UTM

4.4 To investigate effect of washing and not-washing preparation on compressive strength

The cement mortars were prepared from water:cement:sand ratio of 0.485:1:2.75 and consisted of cement mixed BA which is washed by the deionized water, and cement mixed BA without washing preparation. Mortars of two conditions were mixed and cast in cube molds. They were cured in zip plastic bags with saturation of sprayed water until ages of 3, 7, 28, 56 and 90 days for compressive strength testing by UTM.

4.5 Chemical composition

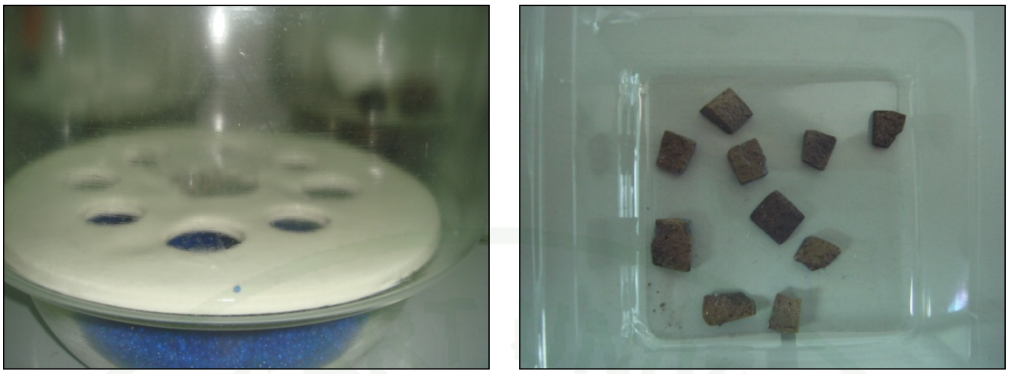
Cement pastes were cast into square plastic molds (4x4x2 cm^3). Paste samples were demolded after 24 hr curing and prolonged curing process as same as mortars. They were prepared as powder by grinding and investigated at ages of 3, 28, 56 and 90 days for chemical composition by an X-ray diffractometer (XRD, X’pert, Philips, the Netherlands) from 10^o - 65^o 2θ and setting the XRD parameters as following in Table 4.

Table 4 XRD parameters for cement sample testing

Parameter	**Value**
Scan mode	continuous
Step size	0.02
Step size	0.02
Time per step (sec)	0.5
Scan speed	0.04
Total time (h:m:s)	0 : 29 : 10

4.6 Microstructure

Paste samples for microstructure analysis by SEM were prepared as same as samples analyzed by XRD technique. Samples were demolded after 24 hr curing and prolonged curing process as same as mortars. Fracture surface of samples was prepared and other sides of cement pastes were ground flat to shape them nearly small cubes (0.5x0.5x0.5 cm^3) as shown in Fig. 10. Samples were dried and removed water from samples immediately to stop any further reactions with a desiccator. Samples were gold sputtered before analysis by SEM technique. Their microstructures were observed at age of 3, 28 and 90 days by a scanning electron microscope (SEM, XL-30, Philips, the Netherlands).



(a) Samples were dried in a desiccator (b) Sample preparation for SEM

Figure 10 Microstructure analysis by SEM

4.7 Flowability

Paste samples were mixed as cement mortar and evaluated the flowability by flow table and flow mold following ASTM C 230 and 1437 respectively (ASTM C 230, 2002; ASTM 1437, 2002). Water/cement ratio was adjusted from standard ratio (0.485:1) by increasing water ratio gradually 0.05 until the value of flowability reached 110 ± 5% with requirement of the standard. Mortar samples were measured the mortar flow value by a vernier caliper and calculated the appropriate of w/c ratio for cement mortars as Eq. 6. The experiment was repeated three times each sample for the appropriate of w/c ratio.

$$M_f = \frac{(D_1-D_0)}{D_0} * 100 \qquad (6)$$

Where

M_f is the percentage of the mortar flow,

D_0 is the diameter of the bottom opening cell of mold should be 100 mm and

D_1 is the diameter of the mortar after it has been spread by operation of the table in mm

Figure 11 Flowability testing by flow table and flow mold

4.8 Normal consistency

Samples were mixed as cement paste and analyzed the normal consistency of hydraulic cement by a Vicat needle (diameter of 1 cm) apparatus following ASTM C 187 (ASTM C 187, 2001). Samples were cast into mold and vibrated for smoother surface. Their surfaces were penetrated by needle of Vicat apparatus within 30 s and measured a range of penetration. Moisture, which is water content used to cement mixing was adjusted from percentage of initial content (25%) by increasing percentage of the moisture content gradually 1% until the penetration reached 10 mm with requirement of the standard. The experiment was repeated three times for each sample the appropriate moisture content and calculated percentage of the moisture content with the interpolation method in Eq. 7.

$$Y_2 = \frac{(X_2-X_1)(Y_3-Y_1)}{(X_3-X_1)} + Y_1 \qquad (7)$$

Where

Y_2 is the percentage of the normal consistency at penetration range of 10 mm,

Y_1 is the percentage of the moisture content before penetration reached 10 mm in %,

Y_3 is the percentage of the moisture content after penetration reached 10 mm in %,

X_1 is the range of penetration used the percentage of the moisture content as Y_1 in mm,

X_2 is the penetration range of 10 mm and

X_3 is the range of penetration used the percentage of the moisture content as Y_3 in mm,

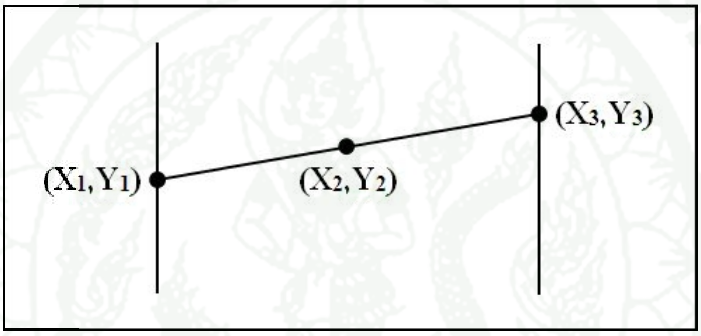


Figure 12 Interpolate model for the normal consistency calculation

Figure 13 Normal consistency of cement testing by a Vicat needle apparatus

4.9 Setting time

Paste samples were prepared as same as the experiment of normal consistency and mixed by using the appropriate moisture content which obtained from the normal consistency testing for each cement ratio. Samples were analyzed by a Vicat needle (diameter of 1 mm) apparatus following ASTM C 191 (ASTM C 191, 2001). Samples were penetrated at the initial time and every 15 min thereafter until a penetration of 25 mm as the initial setting time (Time from moment water is added until the paste ceases to be fluid and plastic). Then samples were penetrated until the needle did not sink visibly into the paste as the final setting time (Time from moment water is added for the paste to acquire a certain degree of hardness) by all the ranges of penetration were measured within 30 s.

Figure 14 Setting time of cement testing by a Vicat needle apparatus

4.10 Cost and carbon credit evaluations of cement production

Cost and carbon credit analysis of raw materials for cement production were calculated as production per 1 ton and compared between selected resultant cement produced from clinker replacing by BA and control cement in order to evaluate the cost and carbon credit for future trend of production in the cement industry.

RESULTS AND DISSCUSSION

1. Particle size distribution

The particle size distributions of the commercial and resultant cement are shown in Fig. 15. The graph of resultant cements replaced with 10%, 20%, 30% and 40% BA (C90B10, C80B20, C70B30 and C60B40) and without BA (C100B0) were observed that they presented similar particle size distributions but little different from graph of the commercial cement. It was found that the commercial cement possessed the smaller particle size than resultant cement because the industrial process could control particle size of cement as expected better than the laboratory process with the efficiency of equipment.

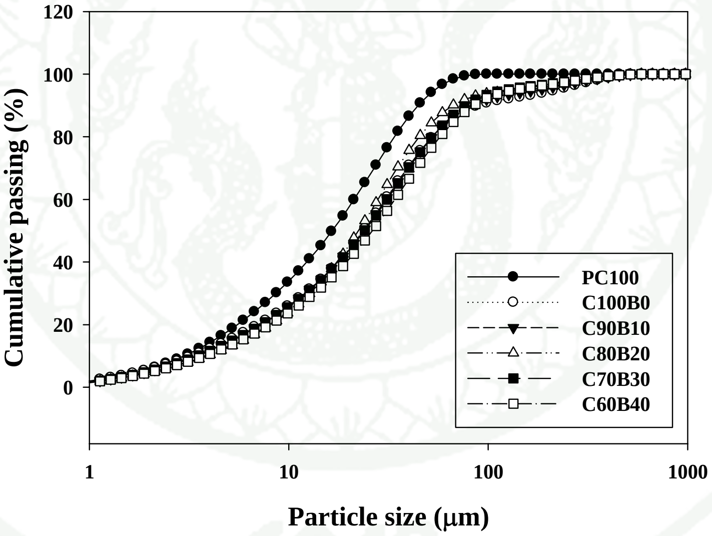


Figure 15 Particle size distribution of cement samples

Results of the average particle size collected at 50% cumulative passing (D_v 50) were reported as 18.8 (PC100), 26.9 (C100B0), 27.0 (C90B10), 25.4 (C80B20), 27.3 (C70B30) and 29.9 μm (C60B40) as shown in Fig. 16. Particle size distribution of resultant cements presented in similar results whereas that of the commercial cement was obviously smeller.

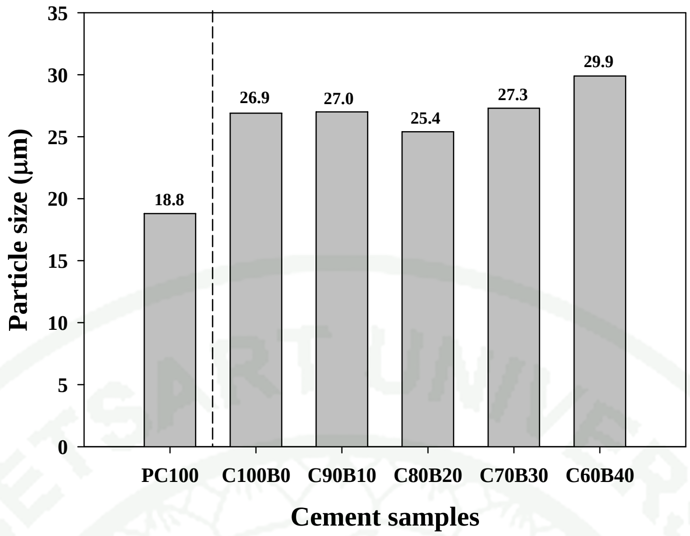


Figure 16 Particle size distribution of cement samples at D_v 50

2. Fineness

Fineness is related to the specific surface area which was analyzed by Blaine air permeability apparatus. In Fig. 17, the specific surface area results were analyzed as 3,546.53 (PC100), 2,688.20 (C100B0), 2,872.86 (C90B10), 3,012.76 (C80B20), 3,129.98 (C70B30) and 3,367.58 cm^2/g (C60B40), respectively. It was observed that the amount of BA influenced the fineness of cement powders, the more BA added, the more specific surface area, i.e., fineness of the resultant cements. Because particle size of BA was than 45 μm which was smaller than particle size of clinker and gypsum (not above 149 μm).

In addition, fineness of commercial cement is more than that of control cement due to the better efficiency of equipment in the industry.

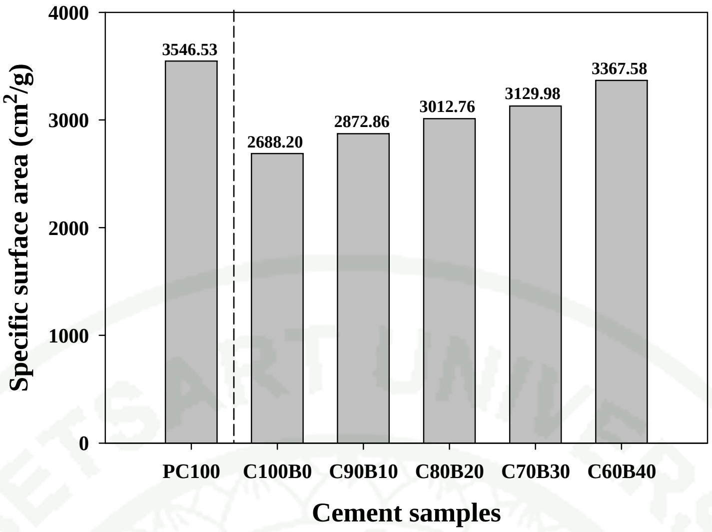


Figure 17 Specific surface area of cement samples

3. Compressive strength

The compressive strength is the first parameter to evaluate the feasibility of the experimental ratio of clinker replacement by BA as resultant cements as shown in Fig. 18. It was considered that the amount of BA influenced the compressive strength of cement mortars and the most effective ratio to the compressive strength was C80B20 which was the replacing clinker with 20% BA cement. Because it presents the best compressive strength (43.57 MPa) comparing among others, 0 10 20 30 and 40% BA, and close to that of commercial cement (44.34 MPa) at 90 days age.

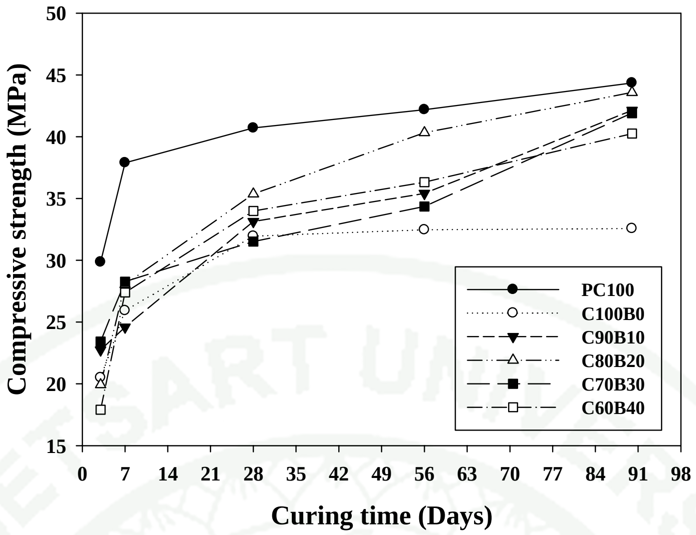


Figure 18 Compressive strength of cement mortars

The compressive strength of resultant cements developed with the curing time elucidated by the rate of development of compressive strength which was presented by the slope of graph between 7 and 56 days. The slopes were analyzed as 0.09 (PC100), 0.13 (C100B0), 0.22 (C90B10), 0.25 (C80B20), 0.12 (C70B30) and 0.18 (C60B40), respectively. It was found that the most developed slope of compressive strength between two age (7 and 56 days) was C80B20. It was implied that C80B20 possessed the possibility of more development of compressive strength than other ratios in longer curing time. The reason of increasing compressive strength is, probably, from the proper proportion of SiO_2 (from BA) and $Ca(OH)_2$ (the by-product of hydration reaction) to become C-S-H from the pozzolanic reaction and to cause the higher compressive strength of samples.

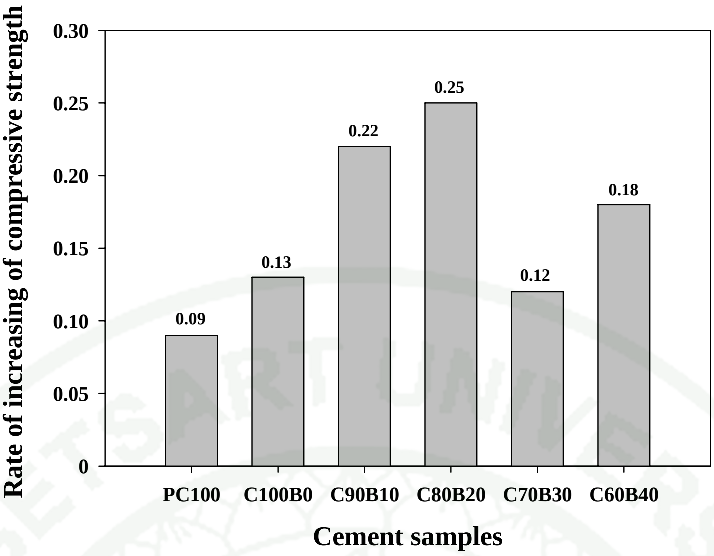


Figure 19 Development of compressive strength of cement mortars in term of slope of 7 and 56 days

4. Effect of pozzolan on compressive strength in term of washing and not-washing preparation

Furthermore, the relation of compressive strength and method of BA preparation is shown in Fig. 20. The values of compressive strength from two methods as:-1) Adding BA (C90B10, C80B20, C70B30 and C60B40) and 2) Not adding BA (C90B10N, C80B20N, C70B30N and C60B40N) are compared. Comparison result indicates that the washing method for BA preparation does not affect on the compressive strength of cement mortar which replacing by BA, due to the values of compressive strength from two methods are not much difference and some values are close to each other.

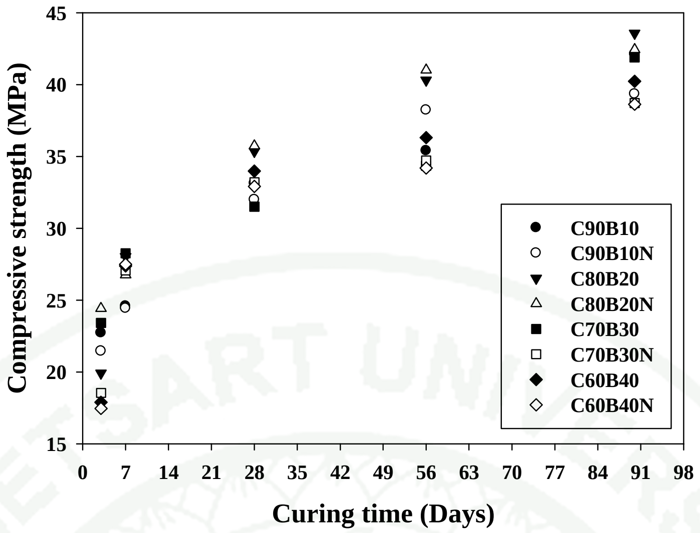


Figure 20 Comparison of washing and not-washing methods for BA preparation on compressive strength

5. Chemical composition

The chemical composition of resultant cements is an aim to search for supplementary cementing phase, C-S-H, which influences to increase the compressive strength (Cordeiro *et al.*, 2008; Cordeiro *et al.*, 2009b). XRD patterns are detected as tricalcium silicate (Ca_3SiO_5, C_3S; JCPDS 49-0442), dicalcium silicate (Ca_2SiO_4, C_2S; JCPDS 29-0369), calcium silicate hydrate ($Ca_{1.5}SiO_{3.5}.xH_2O$, C-S-H; JCPDS 33-0306), calcium hydroxide ($Ca(OH)_2$, CH; JCPDS 44-1481), quartz (SiO_2; JCPDS 85-1054), and ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$; JCPDS 41-1451), respectively. At initial ages, the result of curing time at 3 and 28 days indicates that the intensity of CH phase is increasing both the cement replaced with BA and without BA which as a result of the hydration reaction between cement and water to become the CH phase and other products from reaction. After that at older ages, the result is observed that the intensity of CH phase decreases whereas that of C-S-H phase increases in the cement replaced with BA comparing to without BA. It is indicated that CH phase reacts with SiO_2 phase to transform into C-S-H phase in the pozzolanic reaction as shown in Fig. 21-23 of commercial and resultant cement at 3, 28 and 90 days.

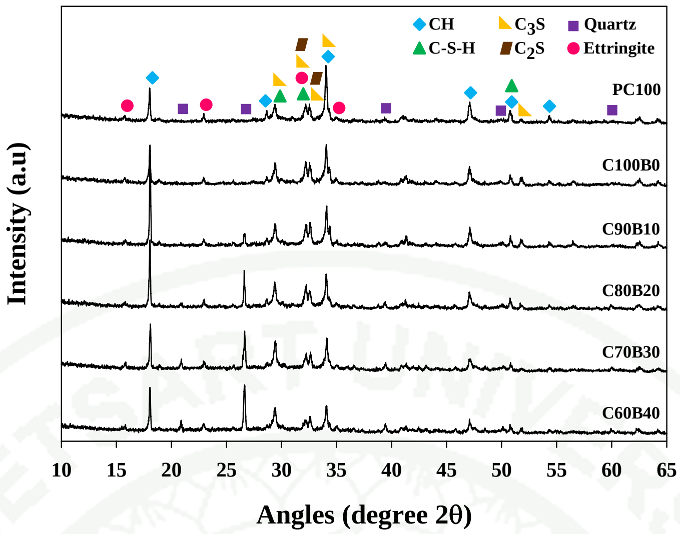


Figure 21 XRD patterns of commercial and resultant cement at 3 days

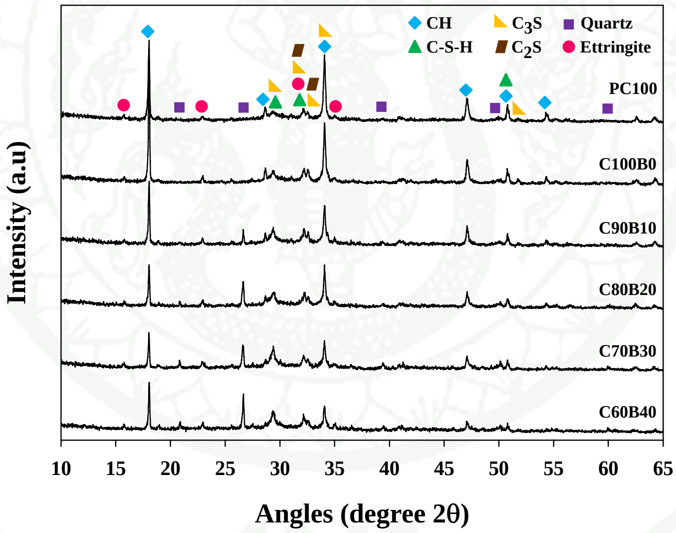


Figure 22 XRD patterns of commercial and resultant cement at 28 days

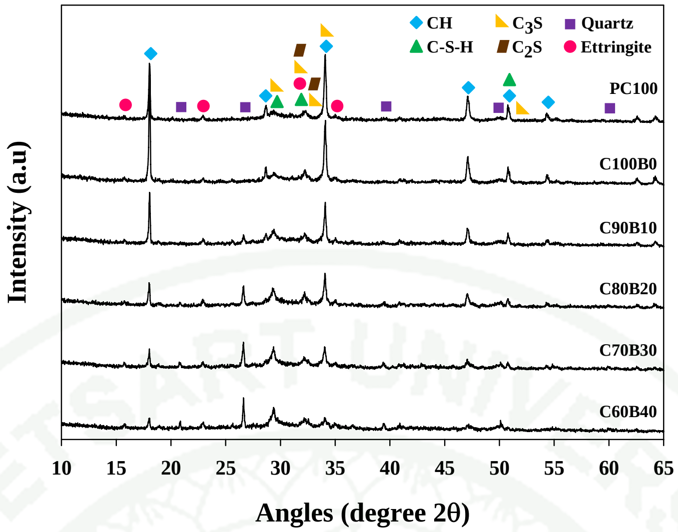


Figure 23 XRD patterns of commercial and resultant cement at 90 days

6. Microstructure

In Fig. 24, the microstructure of cement pastes of the clinker replacing with 20% BA (C80B20) supports the result of compressive strength and chemical composition mentioned above that the cement structure is developed with higher packing density according to the curing time. SEM image of 3 days, in Fig. 24 (a) reveals plenty of pores and needlelike ettringite structures which is similar to SEM image of 28 days, Fig. 24 (b). But it shows smaller and less pores than structure at curing age of 3 days. At the late age of 90 days, Fig. 24 (c) shows more dense structure of resultant cement due to the supplementary cementing phase of C-S-H. C-S-H gel of the pozzolanic reaction is a principal coordination phase to increase compressive strength of resultant cement (Cordeiro *et al.*, 2008; Cordeiro *et al.*, 2009b).

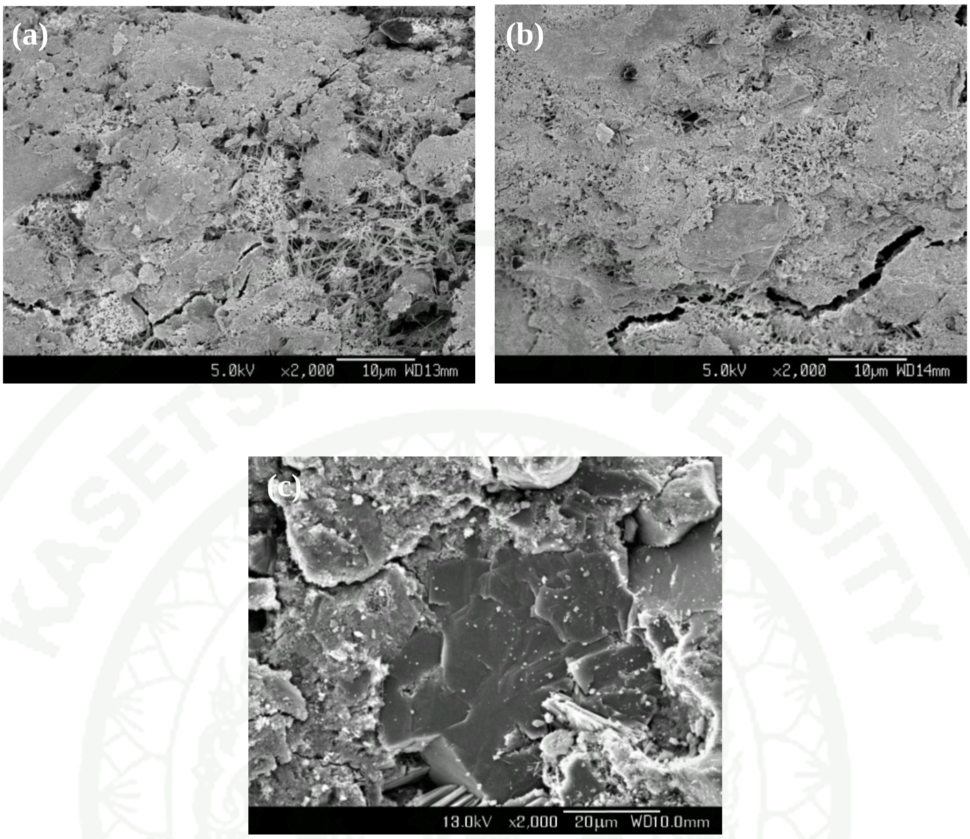
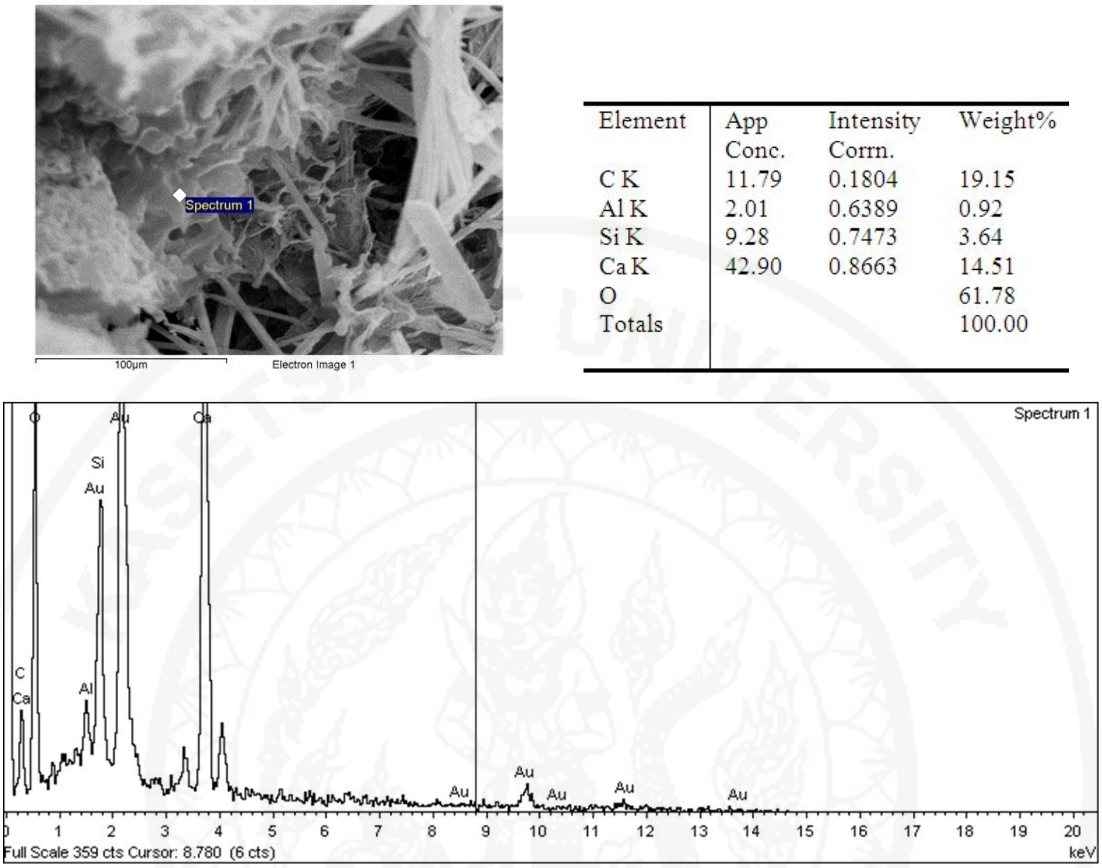


Figure 24 SEM image of C80B20 at curing times (a) 3 days, (b) 28 days and (c) 90 days at a magnification of 2000X

In Fig. 25, the EDS result indicates the chemical composition of the clinker replacing with 20% BA (C80B20) in the late age of 90 days which consists of carbon, aluminium, silicon, calcium and oxygen. These elements are main composition in C-S-H phase according to chemical formula as $Ca_{1.5}SiO_{3.5}.xH_2O$, which support reason of the increasing of compressive strength and the C-S-H phase is found by the XRD technique as shown in Fig. 21-23.



Element	App Conc.	Intensity Corrn.	Weight%
C K	11.79	0.1804	19.15
Al K	2.01	0.6389	0.92
Si K	9.28	0.7473	3.64
Ca K	42.90	0.8663	14.51
O			61.78
Totals			100.00

Figure 25 EDS analysis of C80B20 at curing times 90 days

7. Flowability

The w/c ratio indicates flow behavior, for example, flowability of resultant cement influencing on workability of the cement. From Fig. 18, w/c ratio of 0.485 for all cement ratios was first fixed for compressive strength testing to find out the best cement which was C80B20. Not only w/c ratio of 0.485 was used but also that of 0.735. It was found that mortar flow of all cement at 0.485 w/c ratio was lower than that of standard (110±5%). Then the w/c ratio of 0.735 for all cement ratios was selected to present the effect of BA on percentage of mortar flow as shown in Fig. 26, the more replacing amount of BA, the lower percentage of mortar flow (shown by dotted lines).

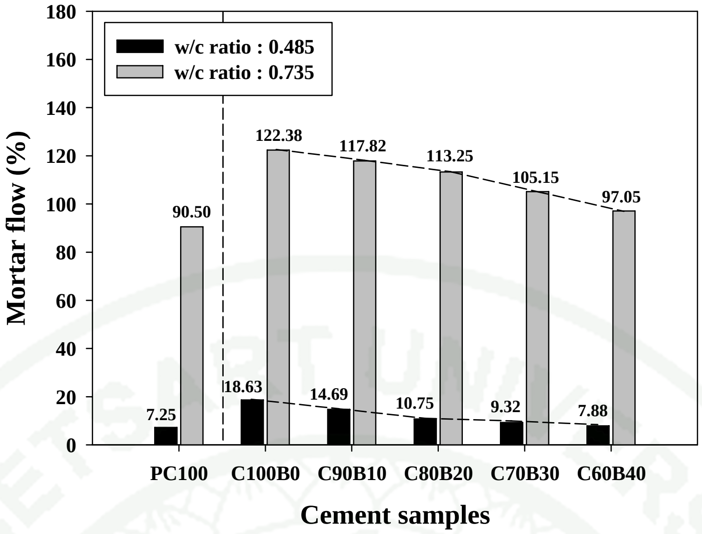


Figure 26 Flowability of cement mortars

Therefore, all cement ratios were repeated to clarify the appropriate of w/c ratio for cement mortars preparation as shown in Fig. 27. The w/c ratios of the cement replaced with 0% BA (control cement or C100B0), 10% BA (C90B10), 20% BA (C80B20), 30% BA (C70B30), and 40% BA (C60B40) and the commercial cement (PC100) were 0.635, 0.685, 0.735, 0.765, 0.785 and 0.785, respectively. This result of behavior describes that the increasing amount of BA also affects the increase of w/c ratio. Due to BA is a hydrophilic material, therefore, water attends with BA before it attends with cement (Ali *et al.*, 2009) and its structure as an irregular shape with porous surfaces results in lot of water to confine inside the structure (Chusilp *et al.*, 2009).

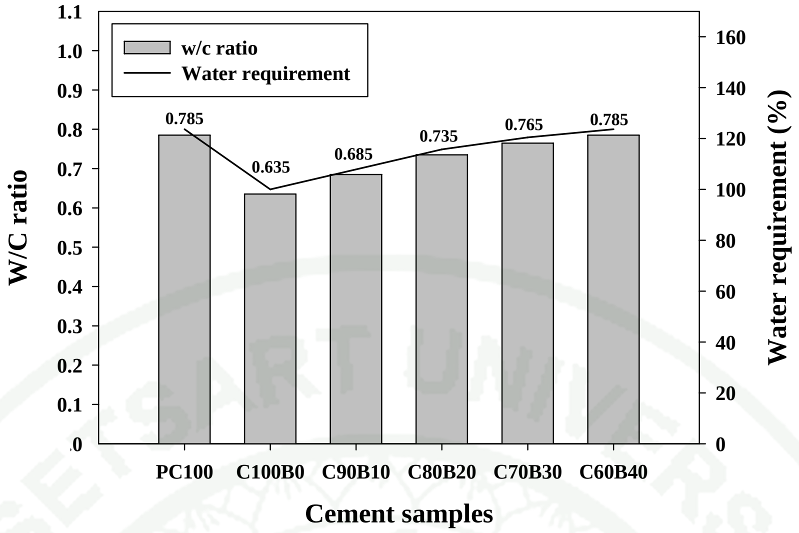


Figure 27 Appropriate w/c ratio for cement mortars preparation

8. Normal consistency

The normal consistency of cement pastes were analyzed in order to search the suitable w/c ratio for using to the examination of setting time of cement pastes. In Fig. 28, the normal consistency of the cement replaced with 0% BA (control cement or C100B0), 10% BA (C90B10), 20% BA (C80B20), 30% BA (C70B30), and 40% BA (C60B40) and the commercial cement (PC100) were analyzed as 22.44, 28.67, 34.71, 39.83, 50.55 and 26.31, respectively. The result presents the effect of BA on the normal consistency that the increasing amount of BA also affects the increase of normal consistency. Due to BA is a hydrophilic material (Ali *et al.*, 2009) and its structure as an irregular shape with porous surfaces (Chusilp *et al.*, 2009) results in lot of water attend with BA and cement to react as the hydration and pozzolanic reactions. It is the same reason as the flowability of cement mortars.

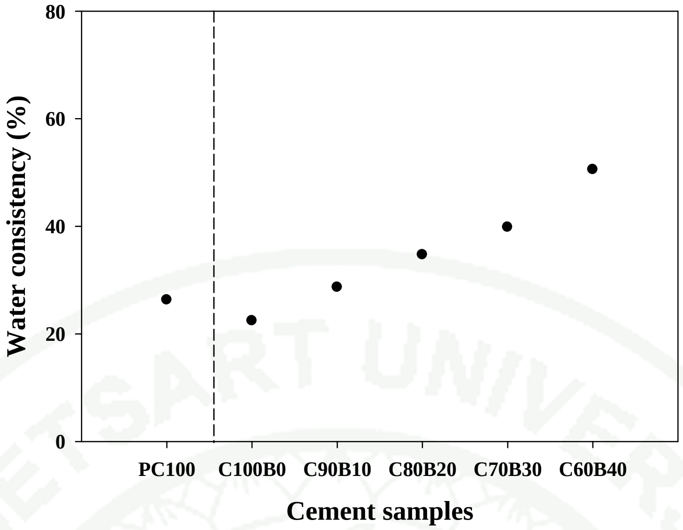


Figure 28 Normal consistency of cement pastes

9. Setting time

The setting time is a method to analyze the determination of the time of setting of cement paste which relates amount of water to fill in the mixing process of cement paste. the result was observed that the effect of BA on setting time as the initial time and final time of resultant cements which replacing by BA (10-40 %BA) had the time increased when increasing the amount of BA as shown in Fig. 29. Because it fluctuated according to the amount of water which obtained from the evaluation of normal consistency experiment, therefore, if amount of BA increase, the value of normal consistency and the time of setting time will increase accordingly.

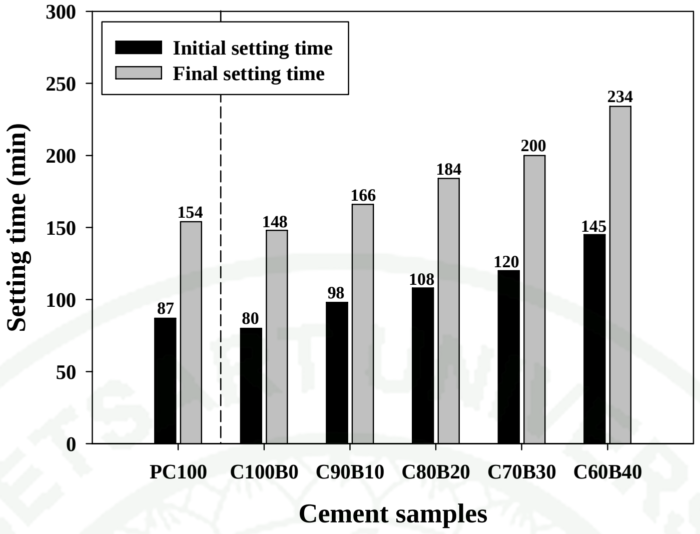


Figure 29 Setting time of cement pastes

In Fig. 30, the setting results of commercial (PC100) and control cement (C100B0) were evaluated as 78 and 80 for initial setting time, and final setting time as 138 and 148. Results were indicated that the effect of fineness and particle size of cement on setting time which the control cement was larger particle size and less fineness than the commercial cement. Therefore, cement of laboratory production was longer setting time than Portland cement from industry, due to much fineness and small particle size increased the react area of cement and water to occur the hydration reaction rapidly, therefore, Portland cement would be used less time for setting than control cement.

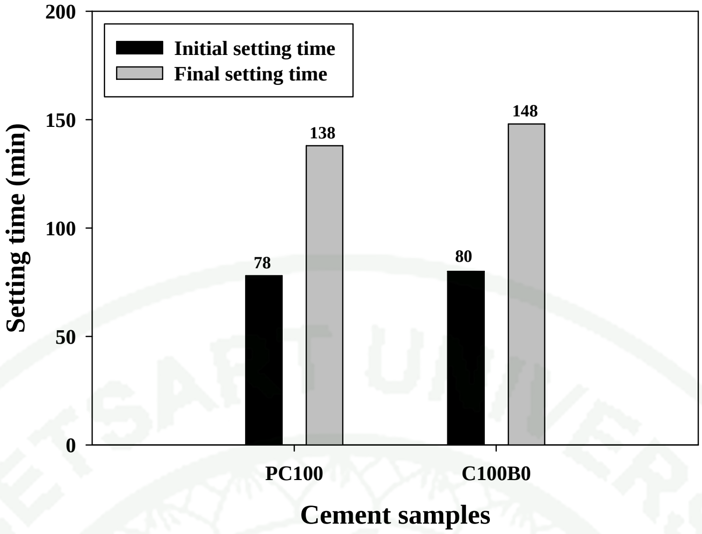


Figure 30 Setting time of PC100 and C100B0 at water consistency of 22.44%

10. Cost and carbon credit analysis of cement production

Table 5 presents the cost analysis used for cement production for 1 ton between control cement (C100B0) and the best ratio of resultant cement which replacing with 20% BA (C80B20). The comparison result is observed that cost of control cement as 885.83 Thai Baht and cost of resultant cement as 712.13 Thai Baht which it can reduce the raw material cost of 19.61%. Due to BA which replacing clinker is valueless material and free of cost. Reduction cost of BA is one of choices to saving of raw material cost in the industrial production.

Table 5 Comparison of the cost analysis used to cement production for 1 ton

Material	**Unit cost (THB/kg)**	**Control cement (C100B0)**		**Resultant cement (C80B20)**	
		Quantity (kg)	**Price (THB)**	**Quantity (kg)**	**Price (THB)**
Clinker	0.9	965	868.50	772	694.80
Gypsum	0.495	35	17.33	35	17.33
BA	**Free of cost**	-	-	193	-
Total	-	1000	**885.83**	1000	**712.13**
			Reduction cost (%)		**19.61**

Table 6 shows the carbon credit analysis used to cement production for 1 ton between control cement (C100B0) and resultant cement which replacing with 20% BA (C80B20). The comparison result is observed that carbon emission of control cement as 100% and carbon emission of resultant cement as 80.7% which it can reduce the carbon emission of 19.3%. Because BA which replacing clinker is directly used and decrease the carbon emissions according to ratio of BA is using to replace amount of clinker.

Table 6 Comparison of the carbon credit used to cement production for 1 ton

Material	**Control cement (C100B0)**		**Resultant cement (C80B20)**	
	Quantity (kg)	**CO_2 emission (%)**	**Quantity (kg)**	**CO_2 emission (%)**
Clinker	965	96.5	772	77.2
Gypsum	35	3.5	35	3.5
BA	-	-	193	-
Total	1000	**100**	1000	**80.7**
		Reduction carbon credit (%)		**19.3**

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

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

1. The compressive strength of cement mortar which replacing by BA does not depend on the washing method for BA preparation.

2. The appropriate proportion of clinker replaced by fine bagasse ash is 20% BA, and for future trend in industrial scale production.

3. The specific surface affects on water requirement and setting time and indicates reaction ability and time of reaction of cement.

4. The increased amount of BA influences the increasing of water requirement or w/c ratio both cement mortar and paste and range of setting time both initial and final setting time.

5. The BA can reduce the raw material cost 19.61% and carbon credit 19.3% which is one of choices to decrease raw material cost of the cement industry, moreover, CO_2 emission is also less.

Recommendations

1. The grinding process for raw material preparation should improve to higher efficiency than old process. The properties of new samples will be better than old samples.

2. BA preparation by washing did not affect on properties of resultant cement, therefore, BA preparation process will change water type as water supply which replacing deionized water for removing some impurities from ash.

3. Compressive strength testing should be examined as longer time than curing time of 90 days, may be 180, 360 or 720 days, to observe the increasing of compressive strength in the long time.

4. The best ratio of resultant cement should be tested in the actual usage such as masonry and wall plaster.

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APPENDICES

Appendix A

Particle size distribution results

Appendix Table A1 The particle size distribution of raw materials

Sample	D_v 10 (μm)	D_v 50 (μm)	D_v 90 (μm)
PC	3.38	18.8	50.6
Clinker	12.9	244	930
Gypsum	12.3	220	641
BA	2.68	18.6	76

Appendix Table A2 The particle size distribution of commercial and resultant cements

Ratio	D_v 10 (μm)	D_v 50 (μm)	D_v 90 (μm)
PC100	3.38	18.8	50.6
C100B0	3.70	26.9	101
C90B10	3.91	27.0	93.7
C80B20	4.40	25.4	75.3
C70B30	3.95	27.3	87.7
C60B40	4.29	29.9	96.0

Note D_v 10 is 10% below this size for a volume distribution in μm,

D_v 50 is the median for a volume distribution in μm and

D_v 90 is 90% below this size for a volume distribution in μm

Appendix B

Fineness results

Appendix Table B1 The fineness of PC100

No.	**S_s (cm^2/g)**	**T (s)**	**$\sqrt{T}$ (s)**	**T_s (s)**	**$\sqrt{T_s}$ (s)**	**S (cm^2/g)**
1	3380	120.30	10.9681	111	10.5356	3518.75
2	3380	123.73	11.1234	111	10.5356	3568.58
3	3380	122.60	11.0725	111	10.5356	3552.25
					Avg.	3546.53

Appendix Table B2 The fineness of C100B0

No.	**S_s (cm^2/g)**	**T (s)**	**$\sqrt{T}$ (s)**	**T_s (s)**	**$\sqrt{T_s}$ (s)**	**S (cm^2/g)**
1	3380	69.23	8.3205	111	10.5356	2669.36
2	3380	69.05	8.3096	111	10.5356	2665.86
3	3380	72.38	8.5076	111	10.5356	2729.38
					Avg.	2688.20

Appendix Table B3 The fineness of C90B10

No.	**S_s (cm^2/g)**	**T (s)**	**$\sqrt{T}$ (s)**	**T_s (s)**	**$\sqrt{T_s}$ (s)**	**S (cm^2/g)**
1	3380	80.42	8.9677	111	10.5356	2876.99
2	3380	79.35	8.9079	111	10.5356	2857.81
3	3380	80.80	8.9889	111	10.5356	2883.79
					Avg.	2872.86

Appendix Table B4 The fineness of C80B20

No.	**S_s (cm^2/g)**	**T (s)**	**$\sqrt{T}$ (s)**	**T_s (s)**	**$\sqrt{T_s}$ (s)**	**S (cm^2/g)**
1	3380	88.42	9.4032	111	10.5356	3016.71
2	3380	87.35	9.3461	111	10.5356	2998.39
3	3380	88.80	9.4234	111	10.5356	3023.19
					Avg.	3012.76

Appendix Table B5 The fineness of C70B30

No.	S_s (cm^2/g)	T (s)	$\sqrt{T}$ (s)	T_s (s)	$\sqrt{T_s}$ (s)	S (cm^2/g)
1	3380	95.28	9.7611	111	10.5356	3131.53
2	3380	94.17	9.7041	111	10.5356	3113.24
3	3380	96.11	9.8036	111	10.5356	3145.16
					Avg.	3129.98

Appendix Table B6 The fineness of C60B40

No.	S_s (cm^2/g)	T (s)	$\sqrt{T}$ (s)	T_s (s)	$\sqrt{T_s}$ (s)	S (cm^2/g)
1	3380	110.28	10.5014	111	10.5356	3369.03
2	3380	109.17	10.4484	111	10.5356	3352.02
3	3380	111.11	10.5409	111	10.5356	3381.70
					Avg.	3367.58

Appendix Table B7 The average fineness of commercial and resultant cements

Ratio	S (cm^2/g)
PC100	3546.53
C100B0	2688.20
C90B10	2872.86
C80B20	3012.76
C70B30	3129.98
C60B40	3367.58

Note S is specific surface area of the test sample in cm^2/g,

S_s is specific surface area of the standard sample used in calibration of the apparatus in cm^2/g,

T is measured time interval of manometer drop for test sample in s and

T_s is measured time interval of manometer drop for standard sample used in calibration of the apparatus in s

Appendix C

Compressive strength results

Appendix Table C1 The compressive strength of PC100

No.	Compressive strength (MPa)				
	Curing time (Days)				
	3	7	28	56	90
1	29.46	37.16	44.03	42.54	44.49
2	29.68	37.53	38.66	42.58	45.66
3	30.41	38.96	39.42	41.42	42.88
Avg.	29.85	37.88	40.70	42.18	44.34

Appendix Table C2 The compressive strength of C100B0

No.	Compressive strength (MPa)				
	Curing time (Days)				
	3	7	28	56	90
1	19.78	26.46	31.75	31.39	33.57
2	20.06	26.73	32.36	32.95	31.63
3	21.66	24.56	31.75	33.03	32.49
Avg.	20.50	25.92	31.95	32.46	32.56

Appendix Table C3 The compressive strength of C90B10

No.	Compressive strength (MPa)				
	Curing time (Days)				
	3	7	28	56	90
1	23.74	25.62	33.22	38.00	42.03
2	23.55	24.35	32.81	34.15	43.33
3	20.91	23.79	33.36	34.06	40.99
Avg.	22.73	24.59	33.13	35.40	42.12

Appendix Table C4 The compressive strength of C80B20

No.	Compressive strength (MPa)				
	Curing time (Days)				
	3	7	28	56	90
1	21.06	27.90	33.91	41.65	43.21
2	18.58	28.36	35.82	38.13	44.58
3	20.13	27.83	36.31	41.16	42.91
Avg.	19.92	28.03	35.35	40.31	43.57

Appendix Table C5 The compressive strength of C70B30

No.	Compressive strength (MPa)				
	Curing time (Days)				
	3	7	28	56	90
1	22.82	29.12	31.30	36.82	41.45
2	24.43	27.85	32.46	33.22	42.49
3	23.01	27.8	30.77	33.02	41.76
Avg.	23.42	28.26	31.51	34.35	41.90

Appendix Table C6 The compressive strength of C60B40

No.	Compressive strength (MPa)				
	Curing time (Days)				
	3	7	28	56	90
1	16.63	28.99	32.23	35.97	41.95
2	20.44	26.87	33.72	34.96	36.72
3	16.63	26.28	35.98	38.00	42.06
Avg.	17.90	27.38	33.98	36.31	40.24

Appendix Table C7 The compressive strength of C90B10N

No.	**Compressive strength (MPa)**				
	Curing time (Days)				
	3	**7**	**28**	**56**	**90**
1	21.85	24.32	28.28	36.42	38.94
2	21.96	24.71	34.10	38.08	39.19
3	20.57	24.30	33.58	40.18	39.91
Avg.	21.46	24.44	31.99	38.23	39.35

Appendix Table C8 The compressive strength of C80B20N

No.	**Compressive strength (MPa)**				
	Curing time (Days)				
	3	**7**	**28**	**56**	**90**
1	24.62	24.99	34.76	41.09	42.18
2	23.00	27.71	34.88	40.91	41.97
3	25.65	27.57	37.55	41.05	43.18
Avg.	24.42	26.76	35.73	41.02	42.44

Appendix Table C9 The compressive strength of C70B30N

No.	**Compressive strength (MPa)**				
	Curing time (Days)				
	3	**7**	**28**	**56**	**90**
1	18.37	23.51	32.48	35.93	38.19
2	18.51	28.51	31.41	34.35	38.49
3	18.74	29.17	35.70	33.88	39.45
Avg.	18.54	27.06	33.20	34.72	38.71

Appendix Table C10 The compressive strength of C60B40N

No.	Compressive strength (MPa)				
	Curing time (Days)				
	3	**7**	**28**	**56**	**90**
1	19.12	26.90	31.42	33.64	38.13
2	16.25	27.79	34.03	34.05	39.43
3	17.02	27.79	33.27	34.87	38.32
Avg.	17.46	27.49	32.91	34.19	38.63

Appendix Table C11 The average compressive strength of commercial and resultant cements

Ratio	Compressive strength (MPa)				
	Curing time (Days)				
	3	**7**	**28**	**56**	**90**
PC100	29.85	37.88	40.70	42.18	44.34
C100B0	20.50	25.92	31.95	32.46	32.56
C90B10	22.73	24.59	33.13	35.40	42.12
C80B20	19.92	28.03	35.35	40.31	43.57
C70B30	23.42	28.26	31.51	34.35	41.90
C60B40	17.90	27.38	33.98	36.31	40.24
C90B10N	21.46	24.44	31.99	38.23	39.35
C80B20N	24.42	26.76	35.73	41.02	42.44
C70B30N	18.54	27.06	33.20	34.72	38.71
C60B40N	17.46	27.49	32.91	34.19	38.63

Note C90B10, C80B20, C70B30 and C60B40 are the group of BA was cleaned by the deionized water and

C90B10N, C80B20N, C70B30N and C60B40N are the group of BA wasn’t cleaned by the deionized water

Appendix D

Flowability results

Appendix Table D1 The mortar flow of PC100

No.	W/C ratio	D_0 (mm)	D_{1x} (mm)	D_{1y} (mm)	D1 (mm)	Mortar flow (%)
1	0.785	100	210	211	214.88	**114.88**
			220	218		
			219	219		
			210	212		
		Avg.	214.75	215		
2	0.785	100	203	211	212.63	**112.63**
			209	205		
			210	222		
			219	222		
		Avg.	210.25	215		
3	0.785	100	210	213	212.25	**112.25**
			212	208		
			215	213		
			215	212		
		Avg.	213	211.50		

Appendix Table D2 The mortar flow of C100B0

No.	**W/C ratio**	**D_0 (mm)**	**D_{1x} (mm)**	**D_{1y} (mm)**	**D1 (mm)**	**Mortar flow (%)**
1	0.635	100	208	211	208	**108.00**
			209	202		
			210	213		
			208	203		
		Avg.	208.75	207.25		
2	0.635	100	216	217	213.88	**113.88**
			215	212		
			211	212		
			210	218		
		Avg.	213	214.75		
3	0.635	100	204	202	205.13	**105.13**
			200	204		
			209	207		
			209	206		
		Avg.	205.50	204.75		

Appendix Table D3 The mortar flow of C90B10

No.	W/C ratio	D_0 (mm)	D_{1x} (mm)	D_{1y} (mm)	D1 (mm)	Mortar flow (%)
1	0.685	100	210	222	211.63	**111.63**
			209	209		
			208	207		
			209	219		
		Avg.	209	214.25		
2	0.685	100	205	201	205.75	**105.75**
			202	208		
			209	206		
			210	205		
		Avg.	206.50	205		
3	0.685	100	211	207	209.75	**109.75**
			202	214		
			212	207		
			209	216		
		Avg.	208.50	211		

Appendix Table D4 The mortar flow of C80B20

No.	**W/C ratio**	**D_0 (mm)**	**D_{1x} (mm)**	**D_{1y} (mm)**	**D1 (mm)**	**Mortar flow (%)**
1	0.735	100	219	213	214.25	**114.25**
			215	212		
			211	218		
			212	214		
		Avg.	214.25	214.25		
2	0.735	100	215	206	213.25	**113.25**
			209	210		
			218	218		
			214	216		
		Avg.	214	212.50		
3	0.735	100	215	213	213.50	**113.50**
			217	214		
			213	212		
			210	214		
		Avg.	213.75	213.25		

Appendix Table D5 The mortar flow of C70B30

No.	W/C ratio	D_0 (mm)	D_{1x} (mm)	D_{1y} (mm)	D1 (mm)	Mortar flow (%)
1	0.765	100	201	216	207.75	**107.75**
			218	217		
			195	203		
			204	208		
		Avg.	204.50	211		
2	0.765	100	202	215	206.63	**106.63**
			210	202		
			201	216		
			203	204		
		Avg.	204	209.25		
3	0.765	100	210	217	208.88	**108.88**
			215	218		
			204	201		
			203	203		
		Avg.	208	209.75		

Appendix Table D6 The mortar flow of C60B40

No.	W/C ratio	D_0 (mm)	D_{1x} (mm)	D_{1y} (mm)	D1 (mm)	Mortar flow (%)
1	0.785	100	211	209	213.50	**113.50**
			214	218		
			216	212		
			215	213		
		Avg.	214	213		
2	0.785	100	215	214	212.88	**112.88**
			213	211		
			212	214		
			211	213		
		Avg.	212.75	213		
3	0.785	100	210	207	214.88	**114.88**
			207	210		
			220	223		
			222	220		
		Avg.	214.75	215		

Note D_0 is the diameter of the bottom opening shall of mold be 100 mm and D_1 is the diameter of the mortar after it has been spread by operation of the table in mm and it was calculated from the average of D_{1x} and D_{1y}

Appendix Table D7 The appropriate w/c ratio and water requirement of commercial and resultant cements for cement mortars preparation

Ratio	W/C ratio	Water requirement (%)
PC100	0.785	123.62
C100B0	0.635	100.00
C90B10	0.685	107.87
C80B20	0.735	115.75
C70B30	0.765	120.47
C60B40	0.785	123.62

Appendix E

Normal consistency results

Appendix Table E1 The normal consistency of PC100

No.	Before the penetration reached 10 mm			After the penetration reached 10 mm			Normal consistency (%)
	Moisture content		Penetration in 30 s (mm)	Moisture content		Penetration in 30 s (mm)	
	%	cc		%	cc		
1	26	130	8.5	27	135	15.0	26.23
2	26	130	8.0	27	135	13.5	26.36
3	26	130	8.0	27	135	14.0	26.33
						Avg.	**26.31**

Appendix Table E2 The normal consistency of C100B0

No.	Before the penetration reached 10 mm			After the penetration reached 10 mm			Normal consistency (%)
	Moisture content		Penetration in 30 s (mm)	Moisture content		Penetration in 30 s (mm)	
	%	cc		%	cc		
1	22	110	10.0	23	115	11.5	22.00
2	22	110	8.0	23	115	10.0	23.00
3	22	110	9.5	23	115	11.0	22.33
						Avg.	**22.44**

Appendix Table E3 The normal consistency of C90B10

No.	Before the penetration reached 10 mm			After the penetration reached 10 mm			Normal consistency (%)
	Moisture content		Penetration in 30 s (mm)	Moisture content		Penetration in 30 s (mm)	
	%	cc		%	cc		
1	28	140	7.5	29	145	10.5	28.83
2	28	140	8.0	29	145	11.0	28.67
3	28	140	9.0	29	145	11.0	28.50
						Avg.	**28.67**

Appendix Table E4 The normal consistency of C80B20

No.	Before the penetration reached 10 mm			After the penetration reached 10 mm			Normal consistency (%)
	Moisture content		Penetration in 30 s (mm)	Moisture content		Penetration in 30 s (mm)	
	%	cc		%	cc		
1	34	170	8.0	35	175	11.5	34.57
2	34	170	7.0	35	175	10.5	34.86
3	34	170	7.5	35	175	11.0	34.71
						Avg.	**34.71**

Appendix Table E5 The normal consistency of C70B30

No.	Before the penetration reached 10 mm			After the penetration reached 10 mm			Normal consistency (%)
	Moisture content		Penetration in 30 s (mm)	Moisture content		Penetration in 30 s (mm)	
	%	cc		%	cc		
1	39	195	7.5	40	200	10.5	39.83
2	39	195	7.0	40	200	10.0	40.00
3	39	195	8.0	40	200	11.0	39.67
						Avg.	**39.83**

Appendix Table E6 The normal consistency of C60B40

No.	Before the penetration reached 10 mm			After the penetration reached 10 mm			Normal consistency (%)
	Moisture content		Penetration in 30 s (mm)	Moisture content		Penetration in 30 s (mm)	
	%	cc		%	cc		
1	50	250	7.5	51	255	11.0	50.71
2	50	250	8.0	51	255	12.5	50.44
3	50	250	8.5	51	255	11.5	50.50
						Avg.	**50.55**

Appendix Table E7 The normal consistency of commercial and resultant cements

Ratio	Normal consistency (%)
PC100	26.31
C100B0	22.44
C90B10	28.67
C80B20	34.71
C70B30	39.83
C60B40	50.55

Appendix F

Setting time results

Appendix Table F1 The setting time of PC100 at the normal consistency as 26.31%

Time (min)	**Penetration (mm)**		
	1	**2**	**3**
30	40	40	40
45	38	38	39
60	30	37	38
75	27	28	30
90	12	11	13
105	5	4	5
120	2	2	1.5
135	1	1	1
150	0.5	0.5	0.5
165	0	0	0
180			
195			
210			
225			
240			
255			
270			
Initial setting time (min)	85	87	88
		Avg.	**87**
Final setting time (min)	154	152	156
		Avg.	**154**

Appendix Table F2 The setting time of C100B0 at the normal consistency as 22.44%

Time (min)	**Penetration (mm)**		
	1	**2**	**3**
30	40	40	40
45	40	40	40
60	38	37	36
75	36	34	30
90	20	20	19
105	8	10	10
120	4.5	6	6
135	1	2	3
150	0	0	0
165			
180			
195			
210			
225			
240			
255			
270			
Initial setting time (min)	82	81	78
		Avg.	**80**
Final setting time (min)	149	145	150
		Avg.	**148**

Appendix Table F3 The setting time of C90B10 at the normal consistency as 28.67%

Time (min)	**Penetration (mm)**		
	1	**2**	**3**
30	40	40	40
45	40	40	40
60	40	40	40
75	40	37	38
90	30	29	28
105	24	20	20
120	17	16	14
135	7	10	10
150	2	5	5
165	0	0	2
180			0
195			
210			
225			
240			
255			
270			
Initial setting time (min)	100	98	95
		Avg.	**98**
Final setting time (min)	165	162	170
		Avg.	**166**

Appendix Table F4 The setting time of C80B20 at the normal consistency as 34.71%

Time (min)	**Penetration (mm)**		
	1	**2**	**3**
30	40	40	40
45	40	40	40
60	40	40	40
75	40	40	40
90	38	39	38
105	26	27	26
120	15	19	14
135	9.5	11.5	8
150	4	6	3.5
165	2	3	2
180	0.5	1	0.5
195	0	0	0
210			
225			
240			
255			
270			
Initial setting time (min)	108	110	107
		Avg.	**108**
Final setting time (min)	184	187	182
		Avg.	**184**

Appendix Table F5 The setting time of C70B30 at the normal consistency as 39.83%

Time (min)	**Penetration (mm)**		
	1	**2**	**3**
30	40	40	40
45	40	40	40
60	40	40	40
75	40	40	40
90	40	39	38
105	36	32	30
120	26	23	25
135	20	17	19
150	14	12	12
165	10	5	7
180	6	3	4
195	2	1	1
210	0	0	0
225			
240			
255			
270			
Initial setting time (min)	122	119	120
		Avg.	**120**
Final setting time (min)	202	197	200
		Avg.	**200**

Appendix Table F6 The setting time of C60B40 at the normal consistency as 50.55%

Time (min)	**Penetration (mm)**		
	1	**2**	**3**
30	40	40	40
45	40	40	40
60	40	40	40
75	40	40	40
90	40	40	40
105	39	38	39
120	34	32	37
135	26	27	30
150	20	18	21
165	18	14	17
180	10	9	14
195	6	5	8.5
210	3	2	4
225	1	1	2
240	0	0	0
255			
270			
Initial setting time (min)	147	143	145
		Avg.	**145**
Final setting time (min)	236	232	233
		Avg.	**234**

Appendix Table F7 The setting time of PC100 and C100B0 at the normal consistency as 22.44%

Time (min)	Penetration (mm)					
	PC100			C100B0		
	1	2	3	1	2	3
30	40	40	40	40	40	40
45	40	40	40	40	40	40
60	39	38	38	38	37	36
75	34	33	32	36	34	30
90	17	15	15	20	20	19
105	5	4.5	4	8	10	10
120	2	1.5	1	4.5	6	6
135	1	0.5	0.5	1	2	3
150	0	0	0	0	0	0
165						
180						
195						
210						
225						
240						
255						
270						
Initial setting time (min)	80	78	77	82	81	78
Avg.		**78**			**80**	
Final setting time (min)	140	138	137	149	145	150
Avg.		**138**			**148**	

Appendix Table F8 The setting time of commercial and resultant cements

Ratio	Initial setting time (min)	Final setting time (min)
PC100	87	154
C100B0	80	148
C90B10	98	166
C80B20	108	184
C70B30	120	200
C60B40	145	234

Appendix G

Tables

Appendix Table G1 Databases of JCPDS for analysis the XRD pattern in this thesis

Reference code	Mineral name	Chemical formula
00-001-1223	Iron Oxide	FeO
00-026-1077	Carbon	C
00-029-0369	Calcium Silicate	Ca_2SiO_4
00-033-0306	Calcium Silicate Hydrate	$Ca_{1.5}SiO_{3.5}.xH_2O$
00-041-1451	Ettringite, Calcium Aluminum Sulfate Hydroxide Hydrate	$Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$
00-044-1481	Portlandite, Calcium Hydroxide	$Ca(OH)_2$
00-049-0442	Calcium Silicate	Ca_3SiO_5
01-083-1762	Calcite	$Ca(CO_3)$
01-085-1054	Quartz, Silicon Oxide	α-SiO_2

Appendix Table G2 Rate of increasing of compressive strength between 7 and 56 days

Ratio	Rate of increasing of compressive strength
PC100	0.09
C100B0	0.13
C90B10	0.22
C80B20	0.25
C70B30	0.12
C60B40	0.18

Appendix Table G3 The cost analysis of BA preparation for 1 ton

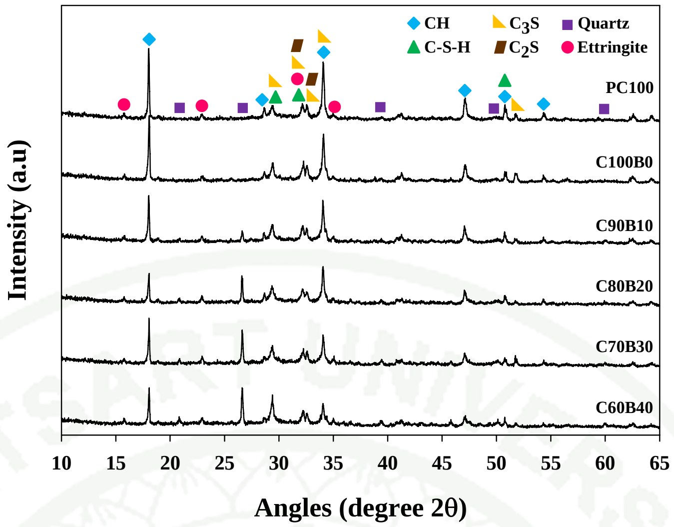
List of BA preparation cost	Price (THB/ton)	
	Deionized water	Water supply
Shipping cost	999.57	999.57
Washing cost	416.68	50.00
Electricity cost	330.40	330.40
Total	**1746.65**	**1379.97**

Appendix Table G4 The cost of commercial and resultant cements for 1 ton

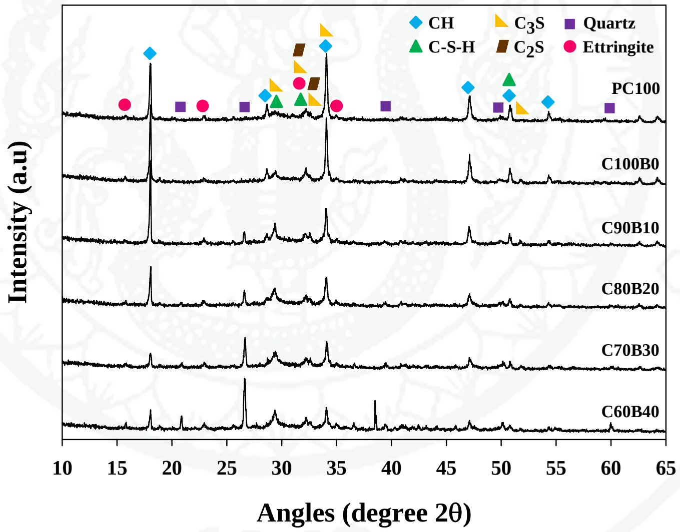
Ratio	Price (THB)				Total (THB)
	Clinker	BA		Gypsum	
		Deionized water	Water supply		
PC100	-	-	-	-	**2694.00**
C100B0	868.50	-	-	17.33	**885.83**
C80B20	694.80	337.10	-	17.33	**1049.23**
C80B20	694.80	-	266.33	17.33	**978.46**

Appendix H

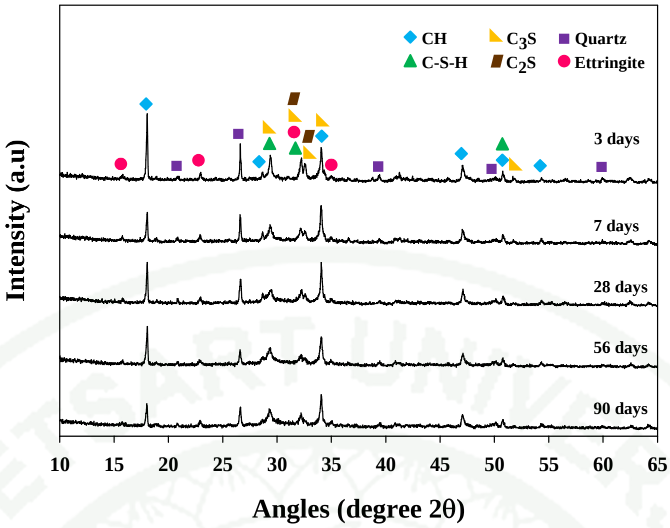
Figures



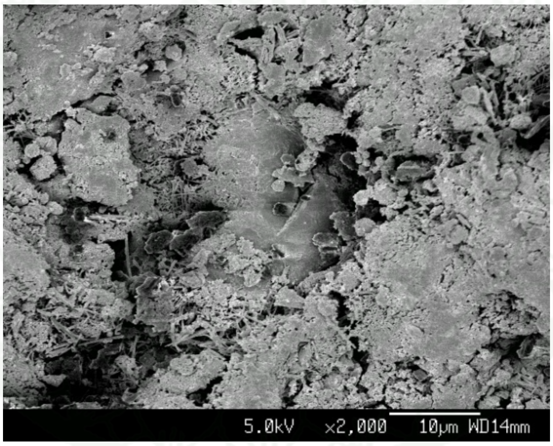
Appendix Figure H1 XRD patterns of commercial and resultant cement at 7 days



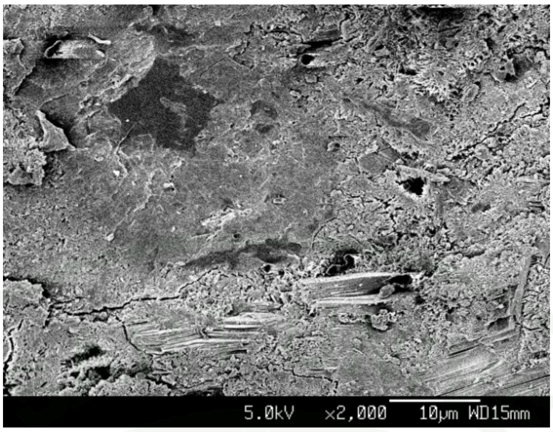
Appendix Figure H2 XRD patterns of commercial and resultant cement at 56 days



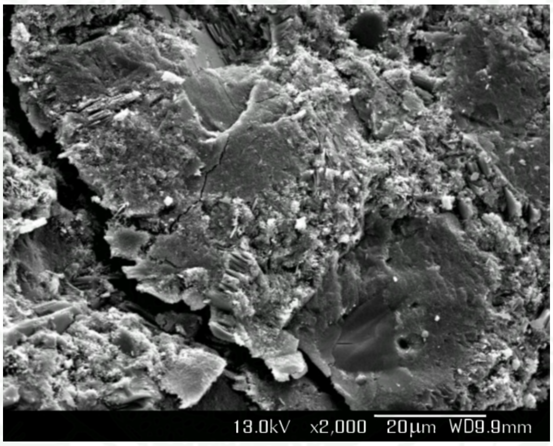
Appendix Figure H3 XRD patterns of C80B20 at 3, 7, 28, 56 and 90 days



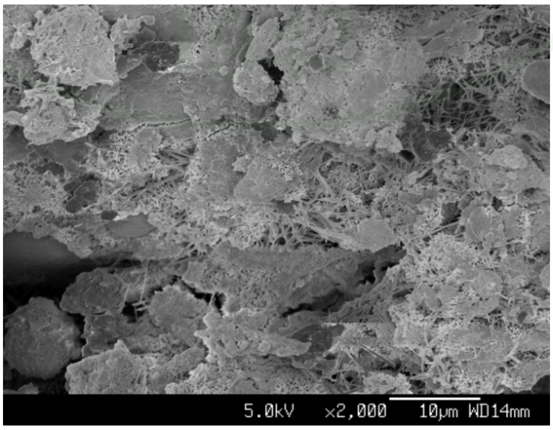
Appendix Figure H4 SEM image of PC100 at curing times 3 days at x2,000



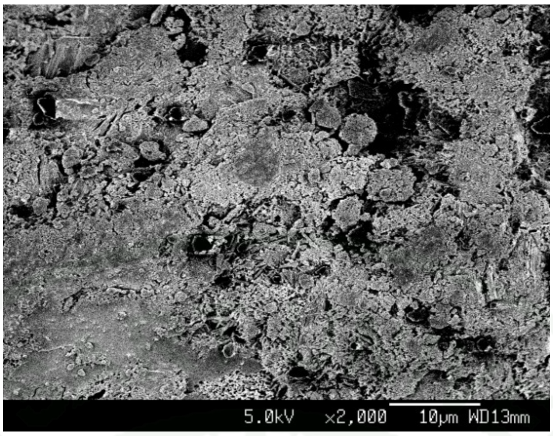
Appendix Figure H5 SEM image of PC100 at curing times 28 days at x2,000



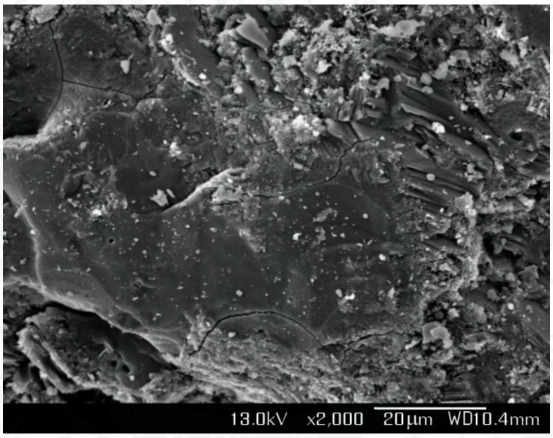
Appendix Figure H6 SEM image of PC100 at curing times 90 days at x2,000



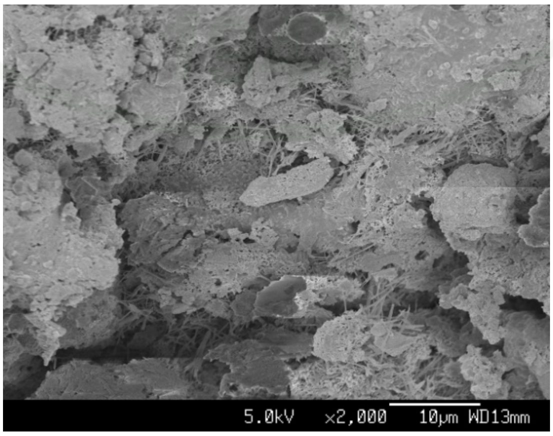
Appendix Figure H7 SEM image of C100B0 at curing times 3 days at x2,000



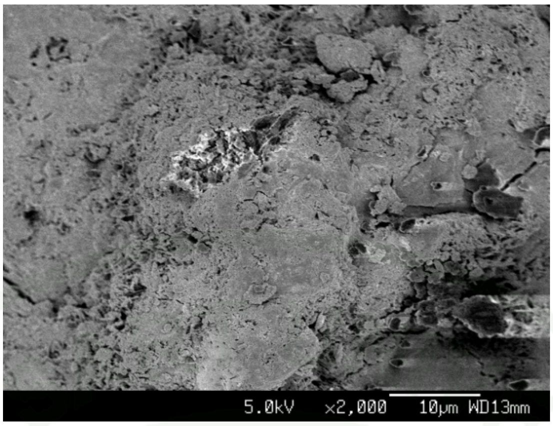
Appendix Figure H8 SEM image of C100B0 at curing times 28 days at x2,000



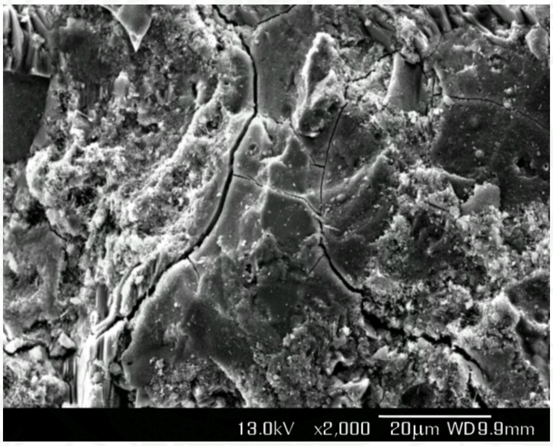
Appendix Figure H9 SEM image of C100B0 at curing times 90 days at x2,000



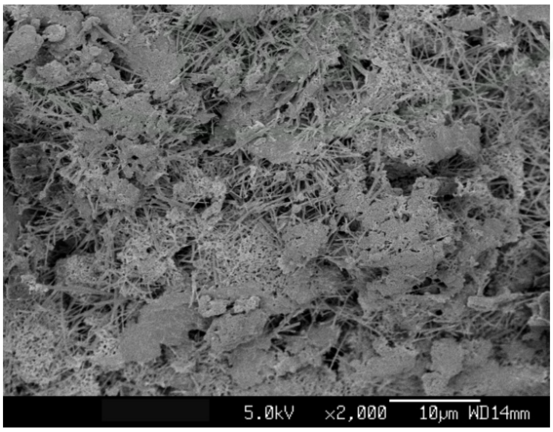
Appendix Figure H10 SEM image of C90B10 at curing times 3 days at x2,000



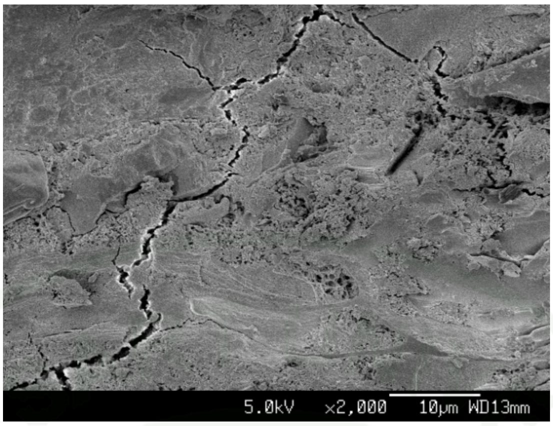
Appendix Figure H11 SEM image of C90B10 at curing times 28 days at x2,000



Appendix Figure H12 SEM image of C90B10 at curing times 90 days at x2,000

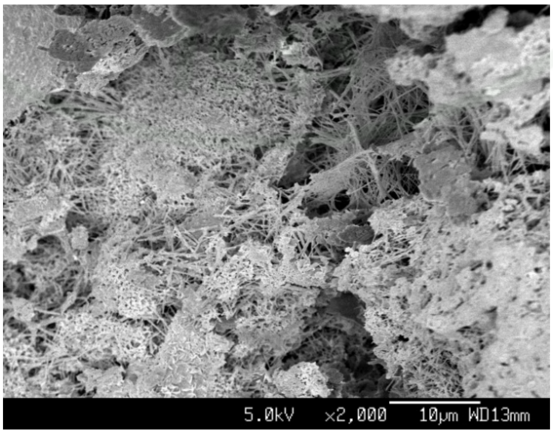


Appendix Figure H13 SEM image of C70B30 at curing times 3 days at x2,000

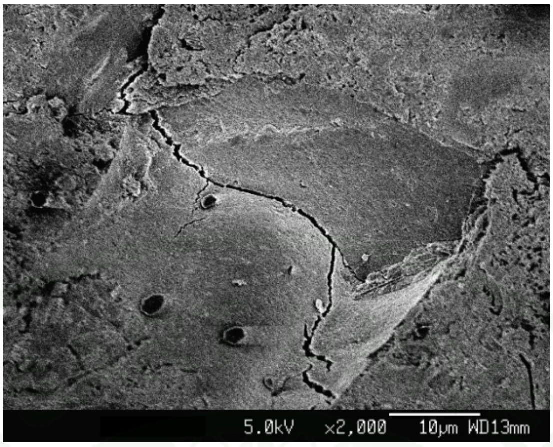


Appendix Figure H14 SEM image of C70B30 at curing times 28 days at x2,000

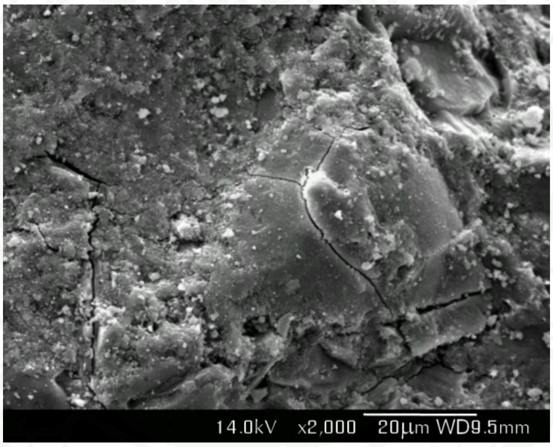
Appendix Figure H15 SEM image of C70B30 at curing times 90 days at x2,000



Appendix Figure H16 SEM image of C60B40 at curing times 3 days at x2,000



Appendix Figure H17 SEM image of C60B40 at curing times 28 days at x2,000



Appendix Figure H18 SEM image of C60B40 at curing times 90 days at x2,000

Appendix I

Research paper

Chiang Mai Journal of Science
Journal of the Science Faculty of Chiang Mai University

Chiang Mai Journal of Science
Published by Faculty of Science
Chiang Mai University
Chiang Mai 50200, Thailand

July 2, 2012

Dear Duangrudee Chaysuwan,

I am pleased to inform you that, following the satisfactory completion of your revisions in response to the comments of the referees, your paper **“Effects of Fine Bagasse Ash on the Workability and Compressive Strength of Mortars”** has now been accepted for publication as a Research Paper. The article will be published in the next available issue. You will also receive a complimentary free copy of that issue. Reprints of your paper will be available for download free of charge from our journal website http://it.science.cmu.ac.th/ejournal/.

On behalf of our Editorial Board, may I thank you very much indeed for publishing your work in our **Chiang Mai Journal of Science** and I sincerely hope that you will consider submitting further articles in the future.

Yours sincerely,

Wasu Pathom-aree

(Dr. Wasu Pathom-aree)
Editor-in-Chief

Chiang Mai J. Sci. 2012; 39(X) : 1-9
http://it.science.cmu.ac.th/ejournal/
Contributed Paper

Effects of Fine Bagasse Ash on the Workability and Compressive Strength of Mortars

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ABSTRACT

There are various kinds of agricultural waste ashes throughout the industrial processes in Thailand such as sugar cane bagasse ash (SCBA), rice husk ash, oil palm ash etc. They are currently exploited as pozzolanic materials and supplements to improve the compressive strength in terms of microstructures of cement by partly replacement of cement with them. One of their advantages is to decrease CO_2 gas emission from decreasing consumption of cement in either mortar or concrete production. Appropriate ratio of replacing clinker by fine (<45 micron) SCBA and w/c ratio as well as effects of SCBA on properties of cement are being studied in this research. Initially, clinker and SCBA proportion were designed by replacing clinker with the amount of SCBA at 0, 20 and 40%, respectively, whereas gypsum was constant added. Specimens were casted as cement mortars and pastes and, finally, analyzed for compressive strength, flow ability, chemical composition and microstructure according to curing ages of 3, 7 and 28 days. Their properties were carried out and compared with the results of commercial type I Portland cement. These test results indicated that replacing clinker with 20% SCBA was appropriate for production in laboratory scale and w/c ratio of 0.735 is suitable on workability of the resultant cement.

Keywords: agricultural waste, clinker, fine bagasse ash, w/c ratio, workability.

1. INTRODUCTION

The cement industry is the second largest CO_2 emitting industry behind the power generation [1]. It is found that each tonne of cement production produces approximately one tonne of CO_2 emission [2], which is one of the important greenhouse gases as the global warming reason [3]. The partial replacement of ordinary Portland cement by agricultural waste or agro-waste is an alternative solution for the decreasing of CO_2 emission due to less cement consumption for construction industry. The areas for agriculture are approximately 41% of total areas in Thailand [4]. Agricultural products are mostly processed annually in the industrial plants such as sugar cane, rice, palm, and etc., therefore, the agricultural wastes has turned up enormously. Fortunately, agricultural wastes are exploited as energy sources in industrial processes to become sugar cane bagasse ash (SCBA), rice husk ash, and oil palm ash. Though, SCBA is a valueless agricultural wastes of sugar industry [5-10], it is a pozzolan or pozzolanic material used to replace part of cement because its chemical composition consisted of high SiO_2 is the main phase of pozzolanic reaction in cement.

Initially, the hydration reaction is the first reaction of cement and water to form calcium hydroxide (CH) and calcium silicate hydrate (C-S-H). Subsequently, the pozzolanic reaction is the second reaction between CH, from hydration reaction, and SiO_2, a pozzolan from SCBA, to originate the second phase of C-S-H. The C-S-H from pozzolanic reaction is a supplementary cementing phase to increase the compressive strength of cement [5,6,9-11]. The cement mortar property as water/cement (w/c) ratio is important to consider in order of real constructions. The w/c ratio directly influences the flowability of cement mortar and also workability of masonry [12,13].

The aim of the experiment is to investigate the appropriate ratio of clinker replacing by SCBA to produce the cement and w/c ratio of the resultant cement. Effects of SCBA on properties of cement such as the flowability, compressive strength, microstructures and chemical compositions are focused to find out the possibility for production of cement in laboratory scale and soon for industrial scale experiments.

2. MATERIALS AND METHODS

2.1 Materials

Type I Portland cement, clinker, gypsum, river sand and as-received SCBA were chosen as local raw materials for laboratory experiments. Type I Portland cement (INSEE PETCH type) of Siam City Cement Public Company Limited was a commercial cement used to compare with the resultant cement from laboratory. Clinker and gypsum were received from the same company. They were dried in an oven at 80°C for 24 hr and ground by a ball milling machine made of carbon steel for 30 hr. Then, they were sieved through mesh finer than 1 mm. For as-received SCBA, it was obtained from bagasse of Kaset Thai factory in Nakhonsawan province and burnt as a heat fuel on production of sugar at approximately 700°C in boilers. It was prepared by washing with deionized water to ensure impurities removing and drying at 100°C [9]. As other raw materials, it was ground in high speed ball mill (S2, Retsch) for 60 min and sieved through finer than 45 μm [5-8]. The chemical composition of SCBA carried out by X-ray diffraction between 10°- 65° 2θ is shown in Figure 1, which consists of quartz (SiO_2; JCPDS 85-1054), calcite ($CaCO_3$; JCPDS 83-1762), iron oxide (FeO; JCPDS 01-1223) and carbon (C; JCPDS 26-1077), respectively.

Properties of raw materials analyzed by X-ray fluorescence (XRF, Bruker, S8 Tiger, Germany) for chemical compositions and helium pycnometer (Micromeritics, Accupyc 1330, U.S.A.) for density are shown in Table 1 according to ASTM C150 [14]. The result of weight loss during calcinations via technique of loss on ignition, LOI, was paid attention rather than that via TGA because the raw materials used in the research were prepared for resultant cement merely at room temperature. In process of mortar preparation, particle size of river sand was selected between 600 and 850 µm which prepared by drying first with natural air and sieved through mesh No. 20 and on No. 30.

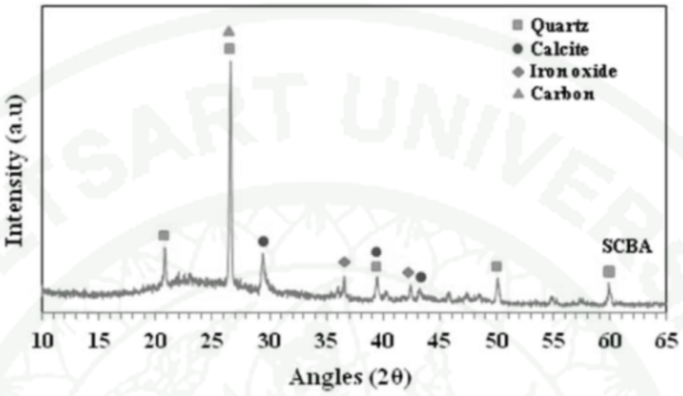

Figure 1. XRD pattern of SCBA burnt approximately 700°C.

Table 1. Properties of raw materials.

Composition	Portland cement (wt%)	Clinker (wt%)	Gypsum (wt%)	SCBA (wt%)
SiO_2	17.84	19.09	2.12	64.11
CaO	66.83	68.14	42.48	5.75
Al_2O_3	3.88	4.02	0.87	5.26
Fe_2O_3	3.71	4.22	0.46	2.78
K_2O	0.67	0.78	0.02	2.59
Na_2O	0.17	0.19	-	0.32
MgO	1.40	1.49	0.13	1.28
TiO_2	0.26	0.26	0.06	0.38
P_2O_5	0.07	0.06	-	1.37
SO_3	4.10	1.11	50.28	0.41
Loss on ignition, L.O.I	0.90	0.48	3.48	15.09
Density (kg/m^3)	3214.6	3215.3	2392.0	2330.4
%Passing 45 µm	48.04	40.52	15.72	52.04

2.2 Designation of mixing ratios and raw materials

The cement replacement by bagasse ash was designed as in Table 2 for sample preparations (cement mortar and paste). The clinker/SCBA samples were adjusted by replacing clinker with amount of SCBA as:-1) 0% (C100B0 as control cement) 2) 20% (C80B20) and 3) 40% (C60B40) and all samples were added fine gypsum for 3.5 wt%. Commercial type I Portland cement (PC100) was used for comparing with the resultant cements. The ratio of water:cement:sand was used as 0.485:1:2.75 for experiments according to ASTM C305 [15].

Table 2. Sample preparation.

Samples	Portland cement (wt%)	Clinker (wt%)	SCBA (wt%)	Gypsum (wt%)
C100B0	-	96.5	-	3.5
C80B20	-	77.2	19.3	3.5
C60B40	-	57.9	38.6	3.5
PC100	100	-	-	-

2.3 Casting of samples

Each resultant cement and commercial cement were mixed and prepared as mortars and pastes. For cement mortars, they were mixed with sand, cement and water. They were cast into cube molds (5×5×5 cm^3) for compressive strength and fluidity of cement mortar testing. Cement pastes were prepared from cement and water only. They were cast into small plastic molds (4×4×2 cm^3) for chemical composition and microstructure characterizations.

2.4 Analysis of samples

2.4.1 Compressive strength

All mortar samples were prepared from w/c ratio of 0.485:1, which was fixed to determine for effect of SCBA on compressive strength of mortars. They were removed from molds after casting at room temperature for 24 hr. Consequently, they, 5 cubes of mortar samples for each ratio, were cured in zip plastic bags with saturation of sprayed water until ages of 3, 7 and 28 days for compressive strength testing according to ASTM C 109 [16] by a universal testing machine (UTM, CT-746, Versa-Tester (Evanston), U.S.A.).

2.4.2 Chemical composition

Cement pastes were removed from molds after 24 hr curing and prolonged curing process as same as mortars. They were investigated at ages of 3, 7 and 28 days for chemical composition by an X-ray diffractometer (XRD, X'pert, Philips, the Netherlands) from 10° - 65° 2θ.

2.4.3 Microstructure

Fracture surface of samples was prepared and other sides of cement pastes were ground to be a small square shape (0.5×0.5×0.5 cm^3). Samples were dried and removed water from samples with a desiccator. Their microstructures were observed at age of 3 and 28 days by a scanning electron microscope (SEM, XL-30, Philips, the Netherlands).

2.4.4 Flowability

Soon after the appropriate ratio of clinker replacing by SCBA was known, samples were cast as cement mortar and evaluated the flowability by flow table and flow mold following ASTM C 230 and 1437 [16-18]. Water/cement ratio was adjusted from standard ratio (0.485:1) by increasing water ratio gradually 0.05 until the value of flowability reached 110 ± 5% with requirement of the standard.

3. RESULTS AND DISCUSSION

3.1 Compressive strength

The compressive strength is the first parameter to evaluate the feasibility of the experimental ratio of resultant cements as shown in Figure 2. It is considered that the amount of SCBA influences the compressive strength of cement mortars by replacing with 20% SCBA as the most appropriate ratio.

Because it presents the best compressive strength (35.35 MPa) comparing among others, 0 and 40% SCBA, and close to that of commercial cement (40.7 MPa) at 28 days age. It is also found that the compressive strength has been developed further at the age of more curing time elucidated with rate of increasing of compressive strength or the slope of graph between 7 and 28 days. The slopes are analyzed as 0.13 (PC100), 0.29 (C100B0), 0.35 (C80B20) and 0.31 (C60B40), respectively. The highest slope in Figure 2 is the clinker replacing with 20% SCBA (C80B20) and it is implied that C80B20 possesses the possibility of more development of compressive strength than other ratios in longer curing time. The reason of increasing compressive strength is, probably, from the proper proportion of SiO_2 (from SCBA) and $Ca(OH)_2$ (the by-product of hydration reaction) to become C-S-H from the pozzolanic reaction and to cause the higher compressive strength of samples.

3.2 Chemical composition

The chemical composition of resultant cements is an aim to search for supplementary cementing phase, C-S-H, which influences to increase the compressive strength [5-10]. XRD patterns are detected as tricalcium silicate (Ca_3SiO_5, C_3S; JCPDS 49-0442), dicalcium silicate (Ca_2SiO_4, C_2S; JCPDS 29-0369), calcium silicate hydrate ($Ca_{1.5}SiO_{3.5}{\cdot}\times H_2O$, C-S-H; JCPDS 33-0306), calcium hydroxide ($Ca(OH)_2$, CH; JCPDS 44-1481), quartz (SiO_2; JCPDS 85-1054), and ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O$; JCPDS 41-1451), respectively. At older ages, the result is observed that the intensity of CH phase decreases whereas that of C-S-H phase increases in the cement replaced with SCBA comparing to without SCBA. It is indicated that CH phase reacts with SiO_2 phase to transform into C-S-H phase in the pozzolanic reaction as shown in Figure 3 of commercial and resultant cement at 3 and 28 days.

3.3 Microstructure of resultant cements

In Figure 4, the microstructure of cement pastes supports the result of compressive strength and chemical composition mentioned above that the cement structure is developed with higher packing density according to the curing time. SEM image of 3 days, in Figure

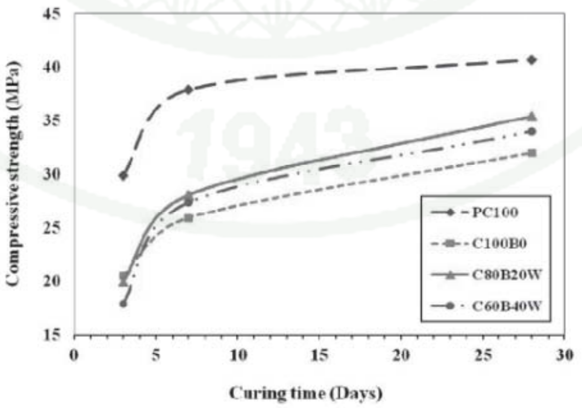

Figure 2. Compressive strength as a function of curing time in commercial and resultant cement

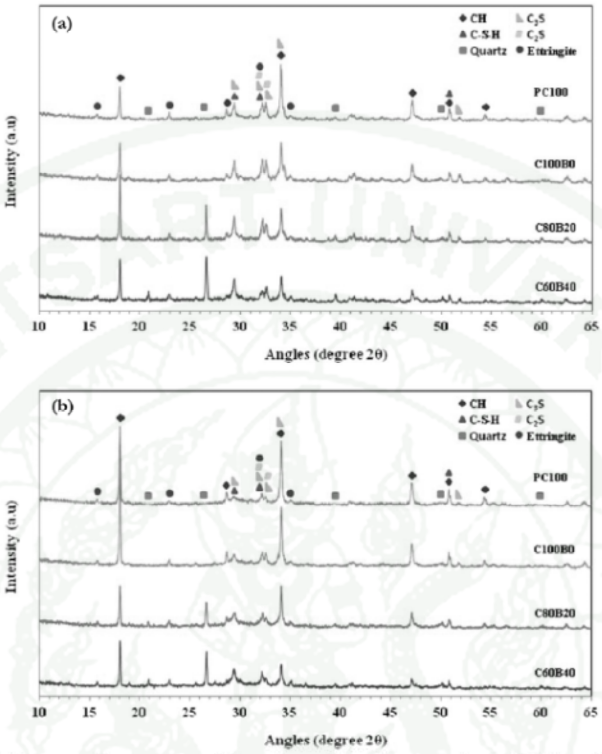

Figure 3. XRD patterns of commercial and resultant cements at (a) 3 and (b) 28 days.

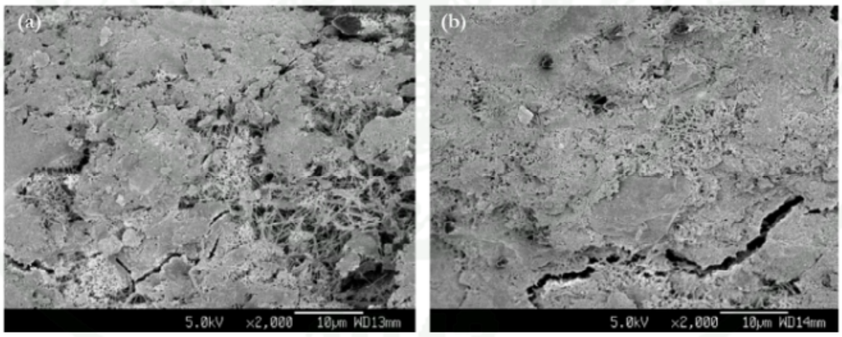

Figure 4. SEM images of C80B20 at curing times (a) 3 days and (b) 28 days at magnification ×2,000.

4(a) reveals plenty of pores and needlelike ettringite structures. At the late age of 28 days, Figure 4(b) shows more dense structure of resultant cement which contains less pores and ettringite needles due to the supplementary cementing phase of C-S-H. C-S-H gel of the pozzolanic reaction is a principal coordination phase to increase compressive strength of resultant cement.

3.4 Flowability of resultant cements

The w/c ratio indicates flow behavior, for example, flowability of resultant cement influencing on workability of the cement. From Figure 2, w/c ratio of 0.485 for all cement ratios was first fixed for compressive strength testing to find out the best cement which was C80B20. Not only w/c ratio of 0.485 was used but also that of 0.735. It was found that mortar flow of all cement at 0.485 w/c ratio was lower than that of standard (110±5%). Then the w/c ratio of 0.735 for all cement ratios was selected to present the effect of SCBA on percentage of mortar flow as in Figure 5, the more replacing amount of SCBA, the lower percentage of mortar flow (shown by dotted lines). Therefore, all cement ratios were repeated to clarify the appropriate of w/c ratio for cement mortars preparation as in Figure 6. The w/c ratios of the cement replaced with 0% (control cement or C100B0), 20% (C80B20), and 40% SCBA (C60B40) and the commercial cement (PC100) were 0.635, 0.735, 0.785 and 0.785, respectively. This result of behavior describes that the increasing amount of SCBA also affects the increase of w/c ratio. Due to SCBA is a hydrophilic material, therefore, water attends with SCBA before it attends with cement [19] and its structure as an irregular shape with porous surfaces results lot of water to confine inside the structure [6,10].

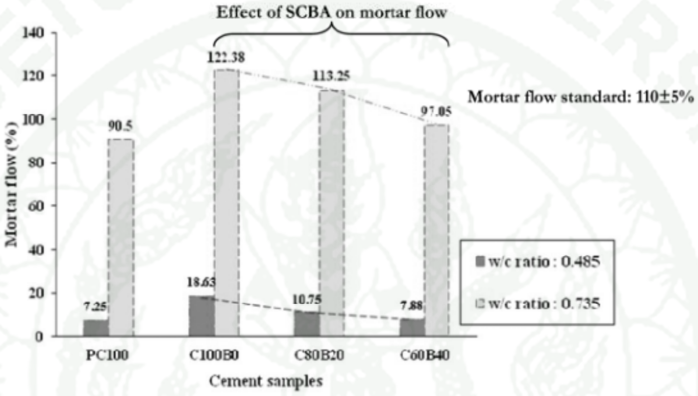

Figure 5. Flowability of cement mortars.

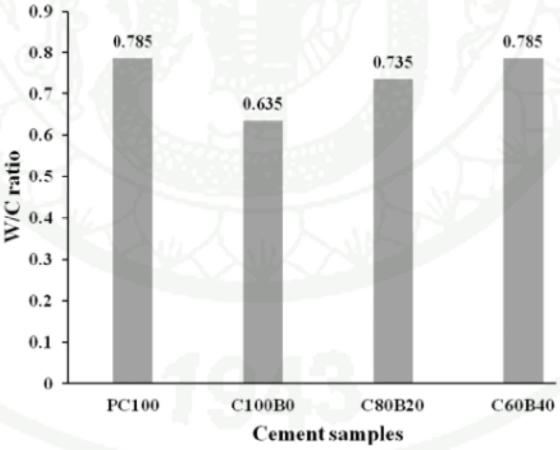

Figure 6. Appropriate w/c ratio for cement mortars preparation.

4. CONCLUSIONS

The results of this research indicated that the appropriate proportion of clinker replaced by fine bagasse ash was 20% SCBA (C80B20). It presented the highest compressive strength comparing to all ratios (0-40% SCBA) of resultant cements and near that of commercial cement. The appropriate w/c ratio of C80B20 was 0.735:1 for good mortar flow (110±5%) and workability of cement mortar. It was ensured that increasing amount of SCBA influenced the increase of w/c ratio. Moreover, this cement procedure was possible for cement preparation in laboratory and would lead to industrial production in the future.

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