CHAPTER III

RESEARCH METHODOLOGY

3.1 Materials and Chemicals

Materials and chemicals used in this study include bagasse, bagasse fly ash, Portland cement, river sand, crushed stone, water, and synthetic wastewater.

3.1.1 Bagasse

Bagasse was collected from a local sugar factory in Saraburi province and was preserved in suitable containers (such as clean, dry, have a lid) to prevent extraneous contamination. As bagasse is a very heterogeneous material containing various fibrous fractions of different properties, a large and uniform sample lot of bagasse was carefully selected and placed in an oven and dried at 110°C. The various samples of bagasse used in this study were drawn from this dried sample for all experiments to maintain the uniformity and homogeneity of the starting material.

The samples of bagasse taken for this study were subjected to treatment under acidic condition to eliminate all soluble sugars within bagasse (Janusa, et al., 2001). Sugars in concentrations as low as 0.03 to 0.15 weight percent in cement will retard the setting time and strength of cement (Janusa, et al., 2001). The bagasse was boiled with 0.1 M HCl for approximately 45 minutes, with the residue washed free of sugars and hydrolysis products. This procedure was repeated 3-4 times until the filtrate was virtually colorless. The residual product was oven dried at 110°C overnight. Ground it to 200 μm fineness, this size was the most available of ground bagasse which shown from pretest. These materials were stored separately in a vacuum desiccator until use. The before and after treated bagasse were shown in Figure 3.1 (a) and (b), respectively.

3.1.2 Bagasse Fly Ash

Bagasse fly ash was collected at same place as bagasse and was preserved in suitable containers to prevent extraneous contamination. It was oven dried at 110°C overnight and sieved to the desired particle size of 150 μm before use, this size was the most available of bagasse fly ash which shown from pretest. The bagasse fly ash (Figure 3.2) was stored in a vacuum desiccator for further use. Gupta and Ali (2000) studied the effect of particle size of bagasse fly ash for adsorb copper and zinc, they reported that particles with smaller size may have higher adsorption capacity than those with bigger size, while it was very difficult to prepare and may be require some special attention and labor during experiment. Therefore, the selected size (150 μm) should have sufficient adsorption capacity, easiness of preparation, does not require any special attention and labor during experiment.

3.1.3 Portland Cement

Ordinary (Type I) Portland cement according to ASTM C150-95, Elephant brand (Figure 3.3) was used throughout the study. This is the most common cement used in general concrete construction when there is no exposure to sulphates in the soil or in groundwater.

3.1.4 River sand and Crushed Stone

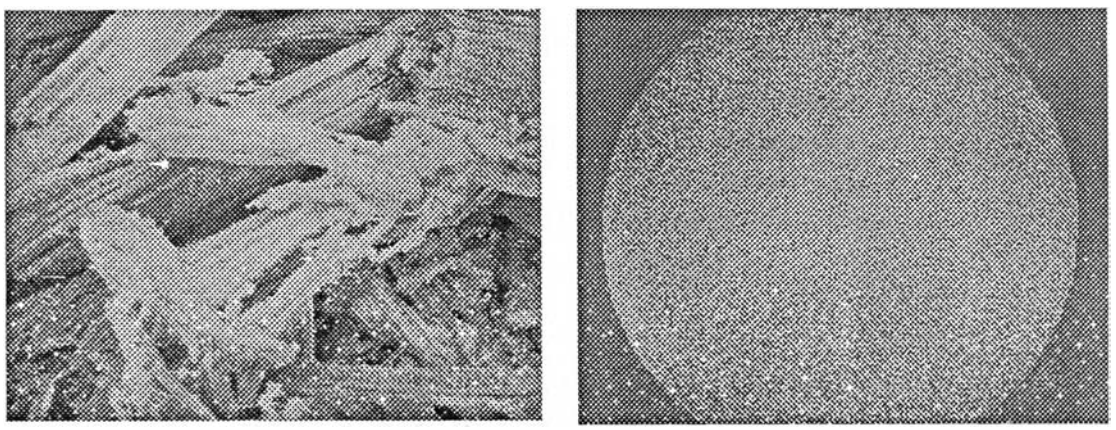
River sand (Figure 3.3) sieved pass through an ASTM standard sieve No.4 (4.75-mm openings) was used as a fine aggregate for all mixes. It was conforms to requirements for graded sand as specified by ASTM C778-92. The crushed stone (Figure 3.3) was used as a coarse aggregate in this study.

3.1.5 Mixing Water

All mixes incorporated tap water which supplied at Hazardous waste laboratory, Chulalongkorn University at normal room temperature.

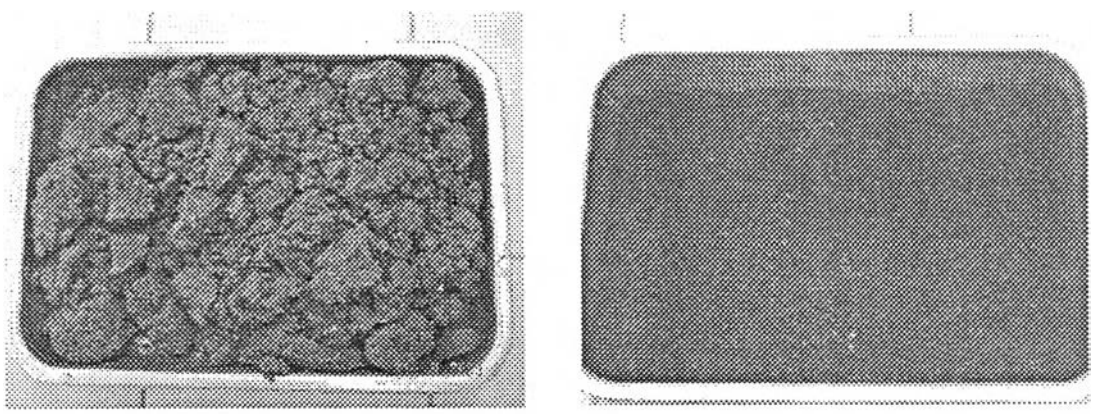
3.1.6 Synthetic Wastewater

Synthetic wastewater samples containing Pb(II) and Cr(VI) were prepared from lead nitrate ($Pb(NO_3)_2$) and potassium dichromate ($K_2Cr_2O_7$), respectively. The synthetic wastewater samples were prepared by dissolving known quantity of analytical-grade chemical in double distilled water and used as a stock solution. Buffer, sodium acetate, was used for contain pH solution on through experiment.



(a) (b)

Figure 3.1 Bagasse (a) Before Acid Treatment and (b) After Acid Treatment.



(a) (b)

Figure 3.2 Bagasse Fly Ash (a) Before Sieving and (b) After Sieving.

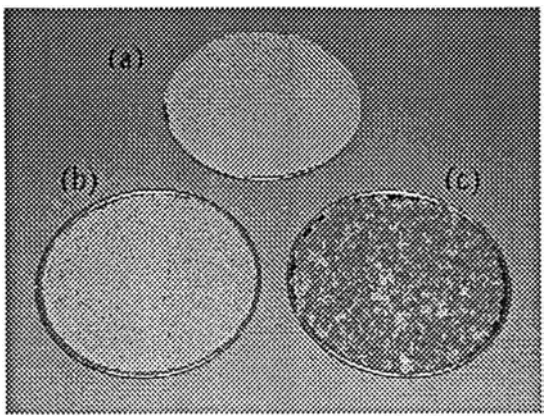


Figure 3.3 (a) Ordinary (Type I) Portland Cement, (b) River Sand and (c) Crushed Stone.

3.2 Experimental Process Diagram

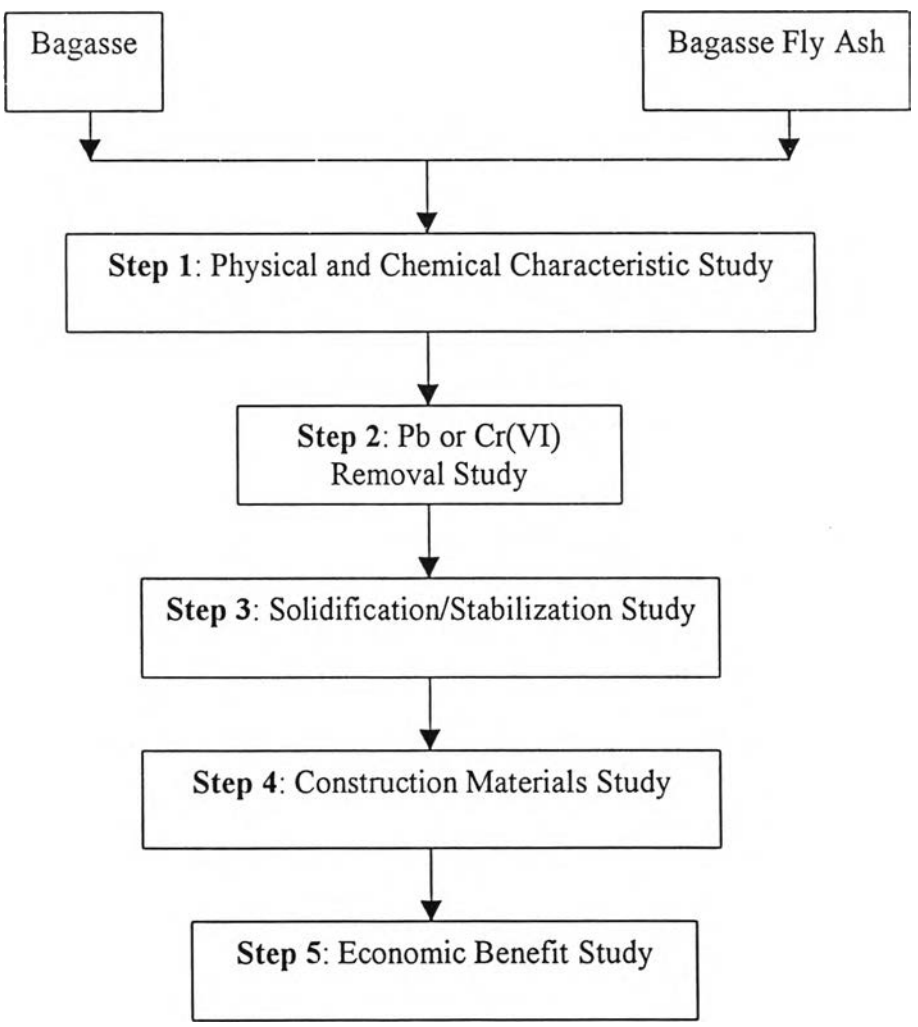


Figure 3.4 Schematic Diagram of the Research

3.2.1 Step 1: Physical and Chemical Characteristic Study

Table 3.1 Physical Characterization of Bagasse and Bagasse Fly Ash

Physical characteristics	Analytical method
1. Bulk specific gravity	ASTM C 128-93
2. Porosity / Pore volume / Pore size	Brunauer Emmet and Taylor analyzer
3. Particle size	Particle size analysis
4. Specific surface area	Brunauer Emmet and Taylor analyzer
5. Morphology	Scanning Electron Microscopy

Table 3.2 Chemical Characterization of Bagasse and Bagasse Fly Ash

Chemical characteristics	Analytical method
1. Bulk chemical composition	X-ray fluorescence spectroscopy (XRF)
2. Mineralogy composition	X-ray diffractometry (XRD)
3. Loss on ignition	ASTM C311-02
4. pH	U.S. EPA SW-846 Method 9045C
5. Absorption capacity	Oven-dried
6. Functional group	Fourier Transformation-Infar Red Spectrometry

3.2.2 Step 2: Pb(II) and Cr(VI) Removal Study

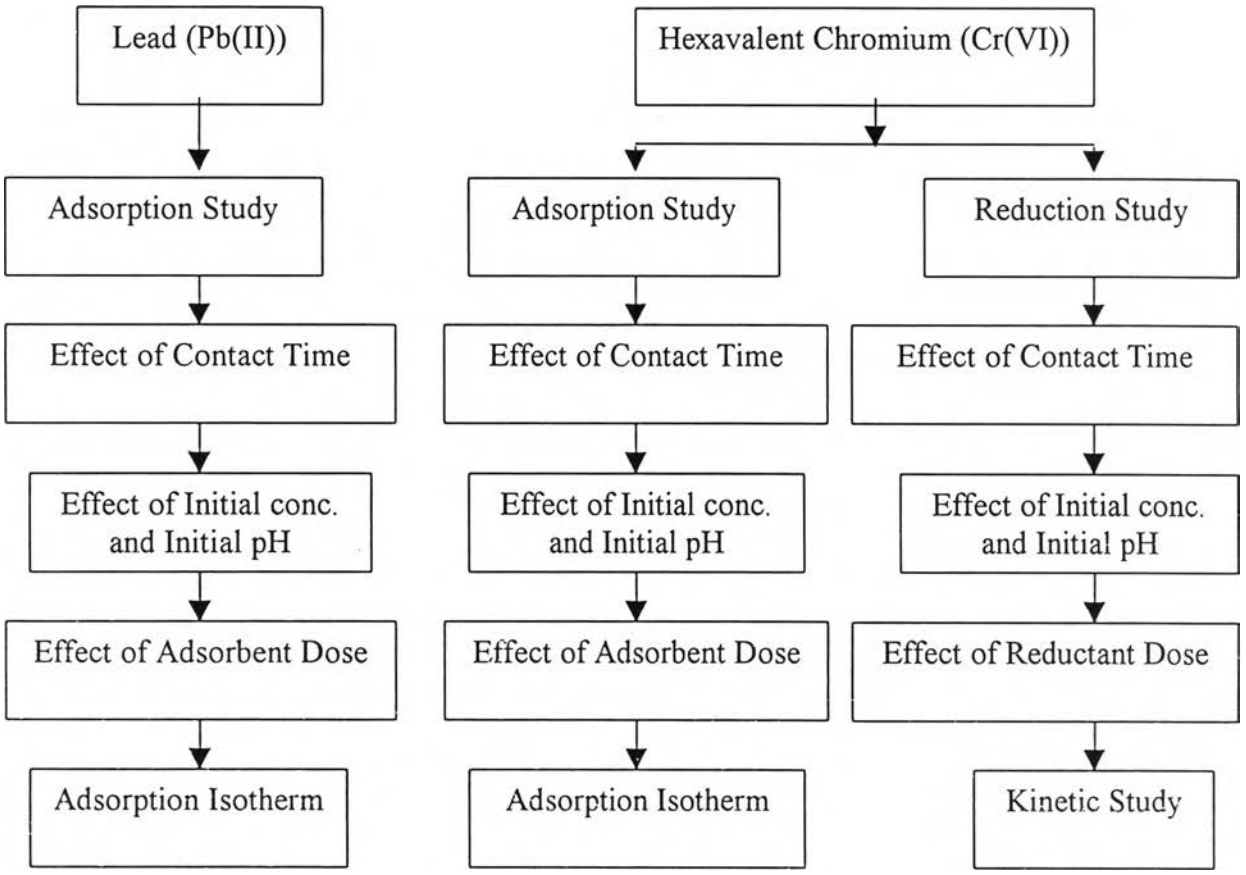


Figure 3.5 Schematic Diagram of Step 2: Pb(II) and Cr(VI) Removal Study

Table 3.3 Removal Experiments

Factor	Independent variable	Controlled variable	
		Pb(II)	Cr(VI)
Contact time	3, 6, 9, 12, 15, 30, 45, 60, 90, 120, 150, 180, 240, 300 and 360 min	- Conc. =10 mg/L - pH = 4 - Dose = 10 g/L	- Conc. =10 mg/L - pH = 2 - Dose = 20 g/L
Initial Conc. and pH	5, 10, 20, 30, 40 and 80 mg/L pH 1, 2, 3, 4, 5 and 6	- Time = **optimum** - Dose = 10 g/L	- Time = **optimum** - Dose = 20 g/L
Dosage	0.5, 1, 5, 15,and 20 g/L	- Time = **optimum** - Conc. = **optimum** - pH = **optimum**	- Time = **optimum** - Conc. = **optimum** - pH = **optimum**

3.2.3 Step 3: Solidification/Stabilization Study

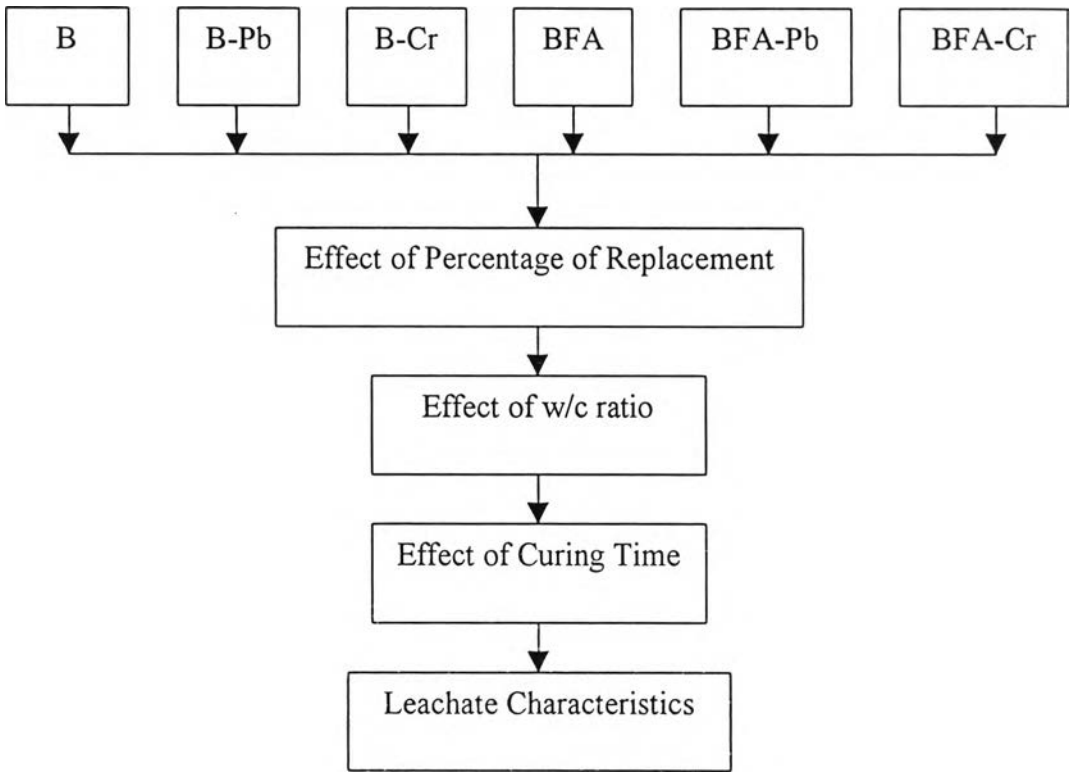


Figure 3.6 Schematic Diagram of Step 3: Solidification/Stabilization Study

Table 3.4 Solidification/Stabilization Experiments

Study	Independent variable		Controlled variable
	Bagasse	Bagasse Fly Ash	
Percentage of replacement	0, 5, 10, and 15 %	0, 10, 20, and 30%	curing time = 7 d
w/c ratio	0.40, 0.50, 0.60,and 0.70		curing time = 7 d
Curing time	3, 7, 14, and 28 d	3,7,14,28,and 60 d	w/c ratio = **optimum** **% R = optimum**

3.2.4 Step 4: Construction Materials Study

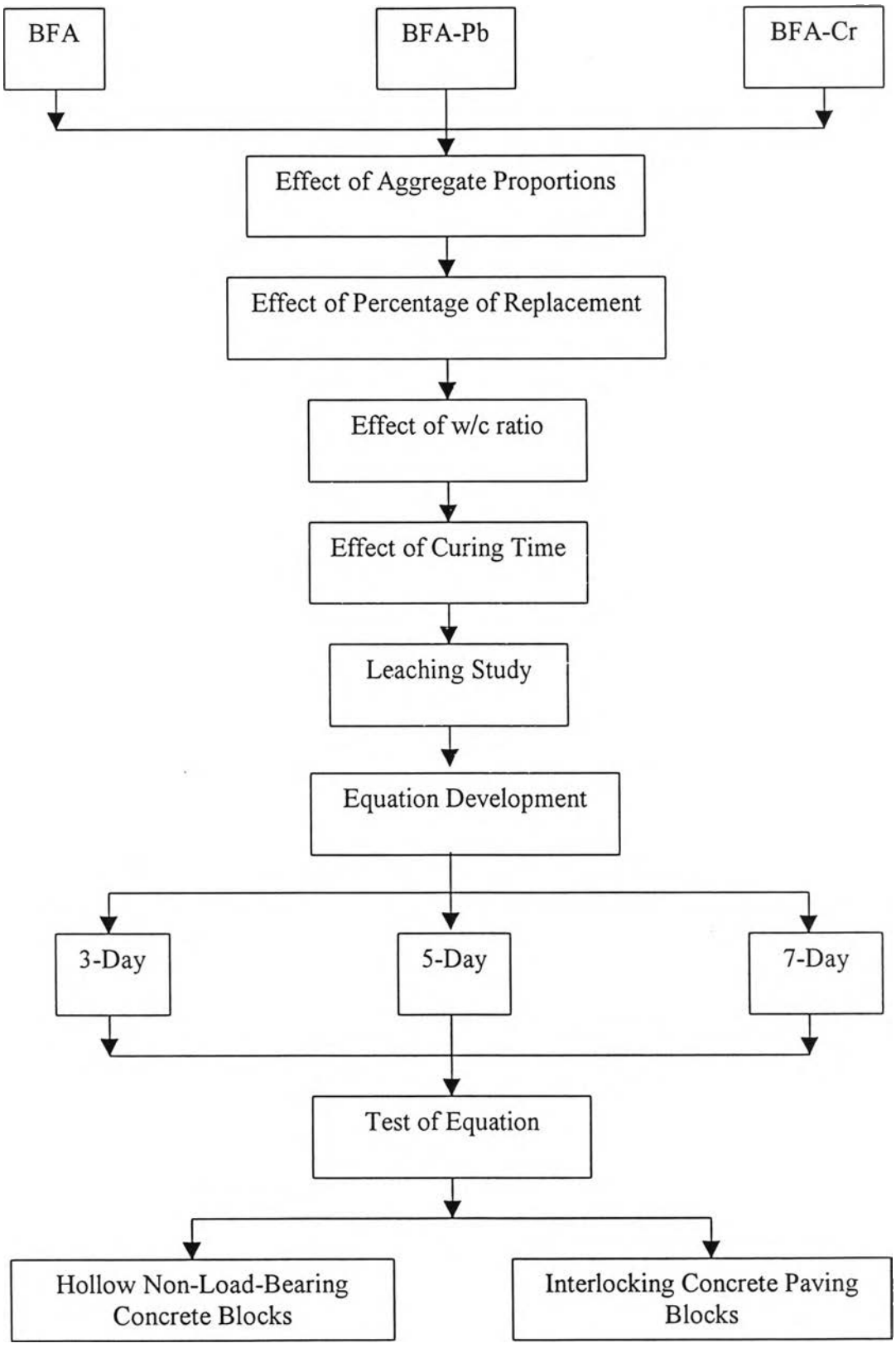


Figure 3.7 Schematic Diagram of Step 4: Construction Materials Study

Table 3.5 Construction Materials Experiments

Factor	Independent variable	Controlled variable
Aggregate proportions	cement : sand : crushed stone = 1:1:2, 1:1.1:1.9, 1:1.5:2.5, 1:2:3, and 1:3:5	curing time = 7 d w/c ratio = 0.5
Percentage of replacement and w/c ratio	0, 10, 20, and 30% 0.40, 0.50, 0.60, and 0.70	curing time = 7 d Aggregate = **optimum**
Curing time	3, 5, 7, 14, 28, and 60 d	w/c ratio = **optimum** Aggregate = **optimum**

3.3 Experimental Programs

3.3.1 Physical Characteristic Study

3.2.1.1 Particle Size Analysis

All bagasse and bagasse fly ash samples were subject to particle size analysis by Malvern Particle Size Analyzer model Mastersizer 2000 equipped with the Scirocco 2000 that measures particle sizes ranging from 0.02-2000 microns.

Particle size of cement and binder has a significant effect on the hydration reaction rate. Finer particles cause reduction in the setting time and increase the compressive strength development due to it has more specific surface area to react with water than coarser particles.

The size distribution of particles in the waste often indicated the potential for water movement trough the material and the compressibility. Also, very fine-grained materials have been shown to produce poorly stabilized material. Presence of large particles may require the use of size reduction equipment. The best material for forming a strong interlocking matrix is well graded, with few particles in extreme sizes.

3.3.1.2 Bulk Specific Gravity

Bulk specific gravity depends on its physical properties and chemical compositions. It is defined as the ratio of weight of a given volume of a sample to the weight of an equal volume of water. It is used to design the mixture proportion of concrete. Unit weight of concrete product is also dependent on the specific gravity of its mixture. Specific gravity provides an indication of the material, voids in the particles and existence of non-combusted materials. Specific gravity of bagasse and bagasse fly ash was measured according to the standard method described in ASTM C188-95.

3.3.1.3 Specific Surface Area

Specific surface area is used to represent the fineness of the sample and relate to the rater of interaction with the surrounding. There are several methods to determine it such as air permeametry or gas adsorption. This study measured surface area of bagasse and bagasse fly ash by Surface Area Analyzer, Thermo Finnigan, Sorptomatic 1990.

3.3.1.4 Porosity / Pore Volume / Pore Size

Porosity is the ratio of the volume of pores to the total volume of sample. There are several indications that the compressive strength does not depend solely on porosity. The relation between strength and porosity is markedly dependent on the broad characteristics of the microstructure such as volume and specific binding capacities of hydration products. At high porosities, the better bonding properties of ill-crystallized material augmented the strength, but at low porosities, the greater intrinsic strength of the dense, crystalline particles was more important. The strength increased with the proportion of fine pores. A volume of hydration products contributed more to the strength than the same volume of unreacted cement, but this effect was distinctly less than that of porosity. This study measured pore specific

volume, pore size and porosity of bagasse and bagasse fly ash by Surface Area Analyzer, Thermo Finnigan, Sorptomatic 1990.

3.3.1.5 Morphology

Scanning Electron Microscopy (SEM) is a technique for examining the surfaces of solid materials. The bagasse and bagasse fly ash features were investigated by a JEOL JSM-6400 scanning electron microscope (SEM), as shown in Figure 3.8. SEMs can be used to understand the particle shape, surface texture, or morphology of the sample. Magnification of an SEM can be varied form 5x to 1,000,000x, almost 300 times higher than optical instruments, yielding the resolutions of approximately 5 nm. The samples were initially glued on an aluminum stub and coated with foal-palladium alloy so that it was not electrically conductive.

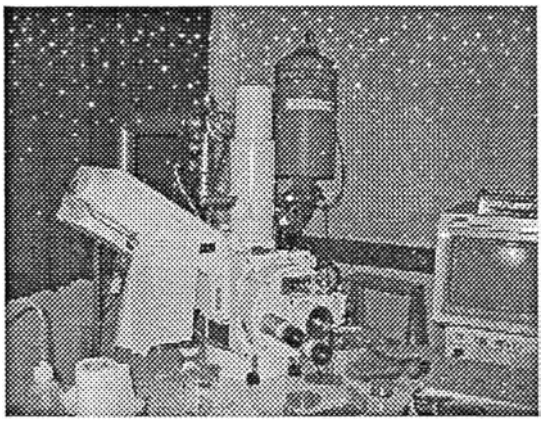


Figure 3.8 Scanning Electron Microscope JEOL JSM-6400

3.3.2 Chemical Characteristic Study

3.3.2.1 Bulk Chemical Composition Analysis by XRF

ASTM C618 lists the required chemical compositions for coal fly ash used in concrete. These limitations are based on oxides of silica, aluminum, iron, calcium, and sulfur. Silica and alumino silicate are the major composition in the pozzolanic reaction, while sulfer and alkali content have the adverse effect on the durability of concrete. X-ray Fluorescence Spectrometer Philips PW 2400 was used to determine the elemental composition of the bagasse and bagasse fly ash in this study, it is shown it Figure 3.9 (a).It was wavelength dispersive type (WDS) with Rh target X-ray tube excited source, maximum 3 kW power and detectable elements form B to U.

To obtain a good representative, firstly, a sample was ground in a ceramic mortar to homogeneously fine powder (size was below 45 microns) because the X-ray only penetrates up to a few millimeters form surface of a sample. After that, 1.5 grams of H_3BO_3 (2.5% by weight) binder, was added to approximate 4.5 grams of ground sample. Then, mix of sample and binder was pressed into a pellet for convenient handling and measurement. The pilled sample was put in a sample cup as shown in Figure 3.9 (b), before running, and loaded on a feeder tray of the XRF instrument. Each sample would take 30 minutes for the instrument to detect characteristic X-rays of elements emitted from the sample in helium environment.

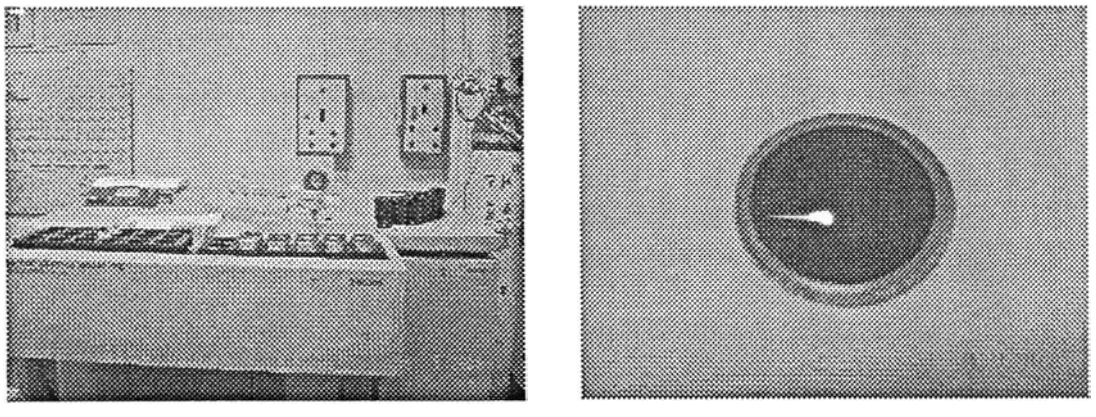
3.3.2.2 Mineralogical Composition Analysis by XRD

X-ray diffraction examines the crystal structure of a material. .X-rays are scattered and diffracted by a lattice structure of crystals, yielding patterns characteristic to various crystals based on the lattice spacing. In this study, the powder X-ray diffraction (XRD) spectrometer, Bruker D8 was used to identify the crystalline phases of the samples, as shown in Figure 3.10 (a). The X-ray diffraction spectrometer with Cu target, graphite monochromator, maximum 3 kW power and

search match program. A graphite monochromator was used to produce diffracted lines according to a single X-ray wavelength with low background. Positions and intensities of the measured peaks are related to crystalline structure, while shapes are related to physical state of the materials.

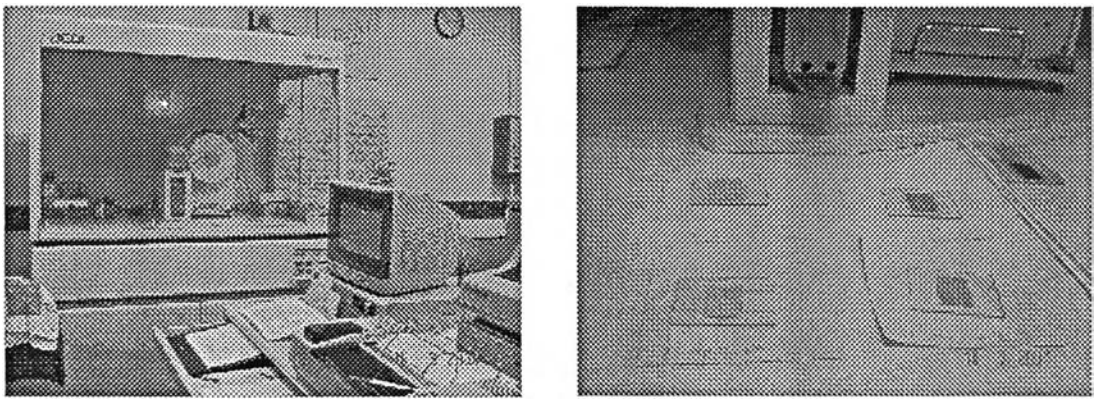
Sample was prepared by oven dried and grinding in a ceramic mortar until homogeneous with particle size of below 45 micron. After that, laid it down on glass plate as shown in Figure 3.10 (b). Instrument, operating conditions, were set at 40 kV accelerating voltage, 40 mA current, and 5° to 70°2θ scanning range.

The crystalline components of a mixture in amounts of 1% or more can be identified individually by characteristic peaks in the X-ray diffraction patterns produced. However, noncrystalline components can not detected; the amorphous phase (Figure 3.11 (a)) is defined as a hump that is the area under the base line of the peaks and above the background curve. Possible phases of the resulting scan were identified using database from International Centre for Diffraction Data (ICDD), a database of more than 60,000 phases. The crystalline phases as shown in Figure 3.11 (b), the software of instrument produced a list of most likely candidate crystalline phases according to well scanned pattern of a given compound matched their reference patterns in the database.



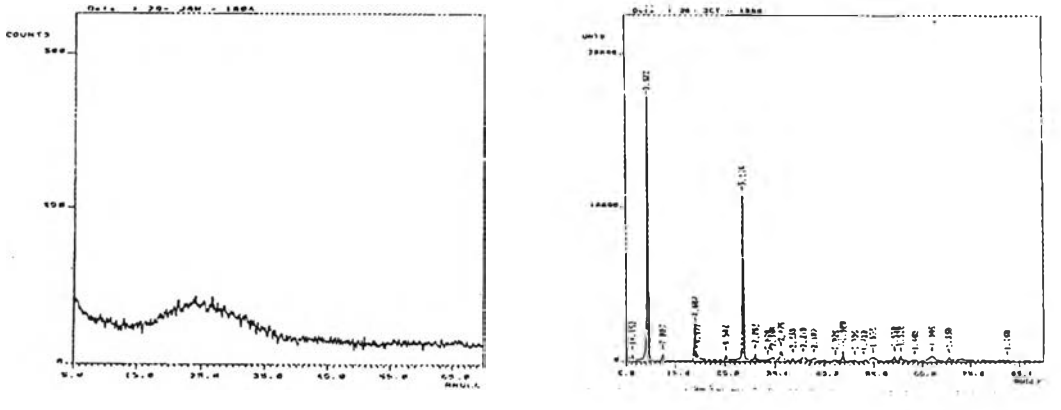
(a) (b)

Figure 3.9 (a) Philips X-ray Fluorescence Spectrometer PW 2400 and (b) Prepared Sample for Analyze



(a) (b)

Figure 3.10 (a) Bruker X-ray Diffraction Spectrometer D 8 and (b) Prepared Sample for Analyze



(a) (b)

Figure 3.11 Example of XRD Spectra (a) Noncrystalline Phase and (b) Crystalline Phases

3.3.2.3 Loss on Ignition (LOI)

Loss on ignition (LOI) is normally used to represent the carbon content in the sample because carbon content will reduce the air entrainment presented in the concrete that effect the workability, strength, and durability of concrete. Then, higher carbon contents can adversely affect the performance of concrete. LOI is defined by ASTM C311 as the weight fraction, expressed as percentage, of material that is lost

by heating the oven-dried sample at 750 ± 50°C. LOI is a measurement of unburned carbon remaining in the ash. It can be used as an important indicator of the degree of burnout in material or combustion efficiency.

3.3.2.4 pH

The pH is a measure of the hydrogen ion activity and indicates the acid-to-base balance of a material. The guidance to determine pH of bagasse and bagasse fly ash is expressed in the U.S. EPA SW-846 Method 9045C. First, prepare aqueous phase sample by adding 100 mL of deionized (DI) water in a 150-mL beaker, and placed approximately 5 g. of sample. The aqueous phase sample was regularly stirred at least 5 minutes and let to gradually stand and settle out for about 15 minutes from the suspension. The digital pH meter Consort model C 830, after complete segregation, were employed to determine the pH of the aqueous phase sample.

3.3.2.5 Water Absorption Capacity

Water absorption capacity of bagasse and bagasse fly ash samples may be used as an indication of how much the materials would take up water in the mixing with Portland cement. It was reported as a difference in percent of the weight of the moist sample over the dry sample. Oven-dried samples were weighed in ceramic or plastic cups which were then placed in a plastic tray with a cover that let moist air flow through, but not water droplets. The tray was put in the curing room for 24 hours since it is assumed that the surface of the material particles would be saturated with moisture. Then, the cups were weighed and recorded the new weight (Rachakornkij, 2000).

3.3.2.6 Functional Group

The FTIR spectroscopy analytical technique can identify the presence of absence of functional groups within a molecule. The class or type of compound can be deduced, although positive identification of the exact composition of the unknown

is not always possible. The possible functional groups of bagasse and bagasse fly ash were determined by Fourier Transform Infrared Spectrometer (FTIR), Perkin Elmer, 1760-X at the Scientific and Technological Research Equipment Center, Chulalongkorn University.

3.3.3 Removal Study

3.3.3.1 Removal Procedure

Removal studies were conducted by the batch technique to obtain the data. A series of 50-mL plastic conical tubes were used. The tubes were shaken at room temperature (27±2°C) and the shaking speed was 125 rpm. The pH values of solutions were adjusted by addition of HNO_3 and NaOH. The filtrate solution was analyzed the heavy metal concentration by AAS. The removal experiments were carried out as show in Table 3.3.

3.3.3.2 Adsorption Isotherm

Adsorption isotherms for Pb(II) and Cr(VI) onto bagasse and bagasse fly ash: set experiment at the suitable condition found in the previous experiment. This study used Langmuir and Freundlich isotherms to describe the lead and chromium adsorption onto bagasse and bagasse fly ash.

3.3.3.2 Equipment

A Perkin-Elmer model 800 Atomic Absorption Spectrophotometer (AAS), as shown in Figure 3.12, was used for lead and chromium analysis. All of the measurements were made under optimization of wavelength, bandwidth, air/C_2H_2 flame, detection limit 0.05 mg/L. pH meter measurements were obtained using a digital pH meter Consort model C 830 (Figure 3.13). An IKA HS 501 shaker, as shown in Figure 3.14, was used for all adsorption experiments.

3.3.4 Solidification/Stabilization Study

3.3.4.1 Procedure and Equipment

The type I Portland cement was used as the main binder in the experiment and was mixed with water and aggregates by mixer (Hobart) as shown in Figure 3.15. According to ASTM C 192, aggregate and approximately 70% of total mixing water were added to the wetted mixer. Then start the mixer; cement was added simultaneously with bagasse or bagasse fly ash because it was considered as insoluble material admixture that had an amount exceeding 10% by weight of cement. The remaining mixing water was gradually added to ensure the uniform blending. However the total mixing time was dept lower than 10 minutes. After mixing, it was used to consolidate the concrete into the 5x5x5 cm^3 cubic mould (Figure 3.16) and was taken to analyse compressive strength at appropriate time by 30-tons compressive strength test machine (Figure 3.17) according to the ASTM standard. After 24 hours, all of the specimens were demoulded and cured in the moisture room until the time of testing.

3.3.4.2 Compressive Strength Test

Compressive strength is the most important commonly concerned property of hardened concrete, because other properties such as bonding or durability are related to the compressive strength. For S/S product, strength-test values indicated how well a material will hold up under mechanical stresses caused by overburden and earth-moving equipment. Strength-test data also are often used to provide a baseline comparison between unstabilized and stabilized wastes. Unstabilized waste materials generally do no exhibit good shear strength; however, if the waste is stabilized into a concrete-like form, the strength characteristic can be expected to increase significantly. Strength test, unconfined compressive strength, in this study followed ASTM C 109-95.

3.3.4.3 Leaching Test

Leachate extraction procedure described in the Notification of Ministry of Industry No.6, B.E. 2540 (1997) was used to determine toxicity of Leachate. This test does not determine total elemental contents of the specimens, but it indicates the leaching potential of eight elements; namely, Arsenic (As), barium (Ba), Cadmium (Cd), Chromium (Cr), Lead (Pb), Mercury (Hg), Selemium (Se), and Silver (Ag). The maximum permissible concentrations in Leachate from toxic wastes have been set at 100 times the drinking water standard. The Leachate standard for lead and chromium is 5.0 mg/L both (Peralta et al. 1992).

In this test, first, reduce particle size of the waste to smaller than 9.5 mm. The extraction fluid made with 80% of sulfuric acid and 20% of nitric acid in deionized water to a pH of 5.0 which is selected to mimic conditions in a synthetic precipitation. The crushed material is mixed with extraction fluid in a liquid-to-solid weight ratio of 20:1, which based upon the alkalinity of the waste. The extraction vessel is rotated at 30 rpm for 18 hours by agitator as shown in Figure 3.18. The final step is Leachate separation by filtered through a 0.6 to 0.8 μm glass fiber filter, sample preparation, and analysis with AAS.

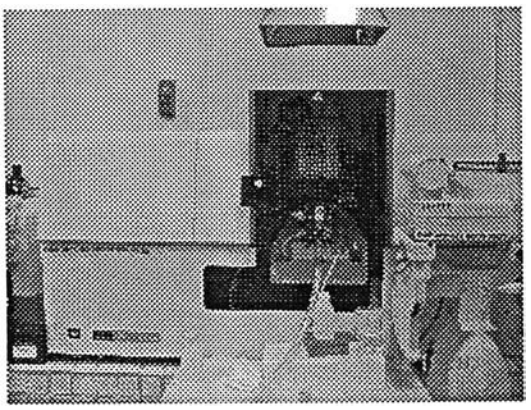


Figure 3.12 Perkin-Elmer model 800 Atomic Absorption Spectrometer

Figure 3.13 pH meter Consort model C 830

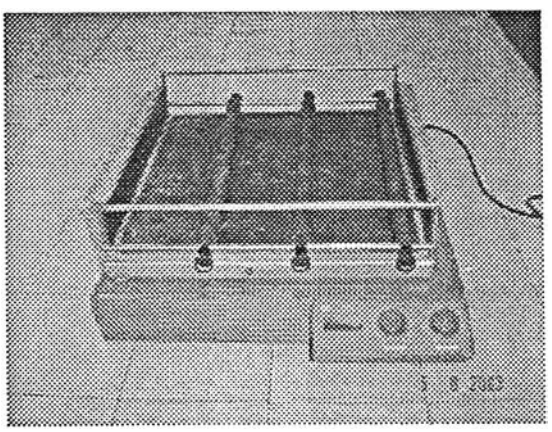


Figure 3.14 IKA HS 501 Shaker.

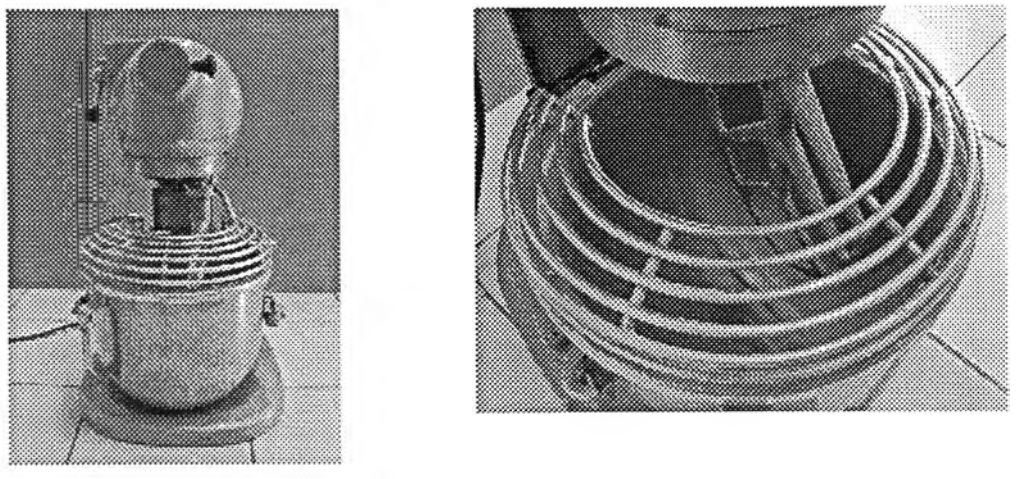


Figure 3.15 Hobart Concrete Mixer

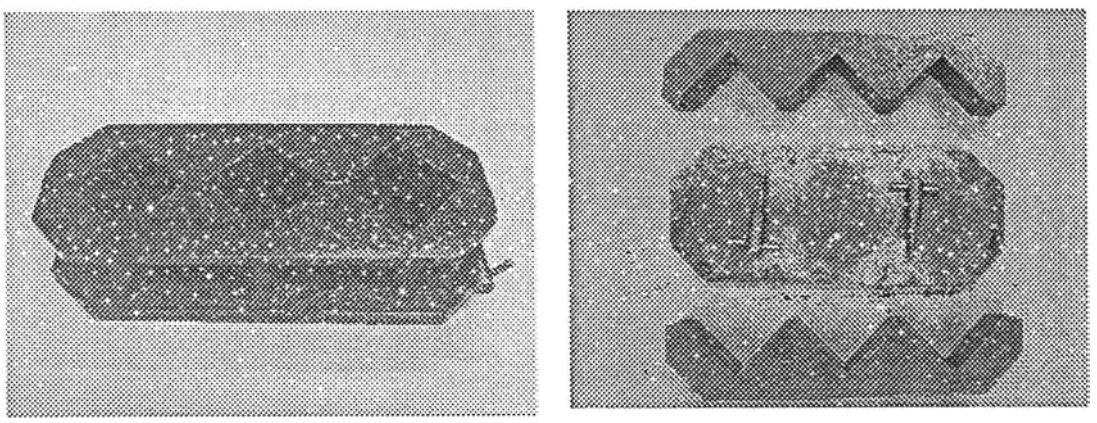


Figure 3.16 Cubic Mould, 5x5x5 cm^3

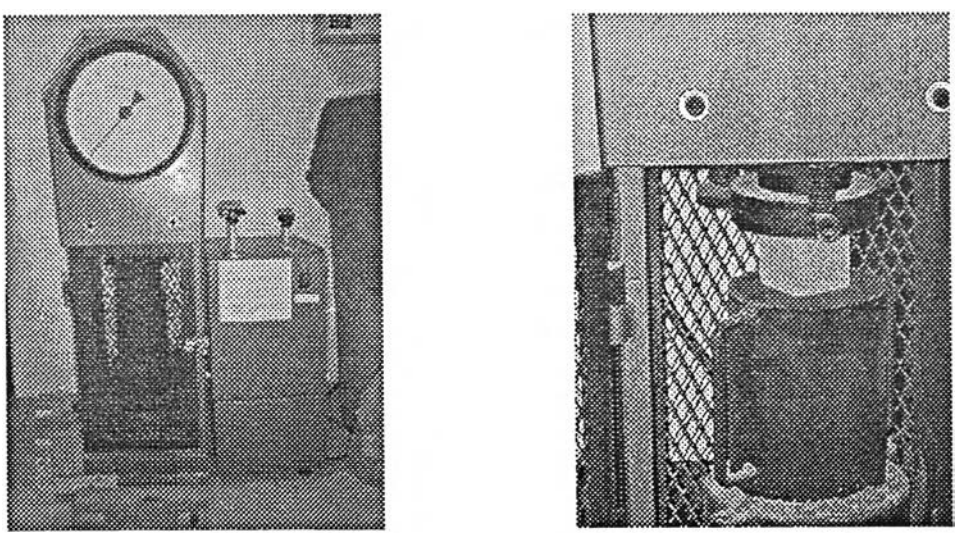


Figure 3.17 30-tons Compressive Strength Test Machine

3.3.5 Construction Material Study

3.3.5.1 Procedure and Equipment

The mixing procedure, curing of specimens and leaching test were same the details in 3.3.4.1 and 3.3.4.3, as mentions above. In part of equation test, the mould was hollow block mould and interlocking paving block mould as shown in Figure 3.19 and Figure 3.20, respectively. In addition, the compressive strength measure by 500-tons compressive strength test machine (Figure 3.21)

3.2.5.2 Development of Equation

The SigmaPlot® 2000 version 6.1, mesh plot graph 3D was used for develop regression equation. Figure 3.22 showed example of type of 3D graphs; plan, gaussian, paraboloid, and lorentzain. Create a 3D mesh graph show as follows:

1. Open the graph wizard by clicking the toolbar Graph Wizard button, by choosing theGraph menu crate graph command. The Graph Wizard appears.
2. Select the type of graph that want to make from the scroll box in the dialog box. Use the scroll bars to view the entire list. Select the desired graph, and then click the Next button.
3. Specify how data is formatted by choosing the appropriate data format from the Data Format list. Select either XYZ triplet data, many Z columns, or single X and Y columns with many Z column, then click Next.
4. Specify which worksheet columns correspond to the data for plot.
5. Click Finish to create the plot and close the Graph Wizard.

3.2.5.3 Test of Equation

The recommended equations were tested for use by build construction materials namely; interlocking concrete paving blocks and hollow non-load-bearing concrete. The equations have three parameter; w/c ratio, percent replacement and compressive strength. Test of equations by set percent replacement and compressive

strength and then find out w/c ratio from equation. After curing time at 3, 5, and 7 days, measuring compressive strength which mean actual strength. Meanwhile compressive strength value which set in first time mean as predicted strength.

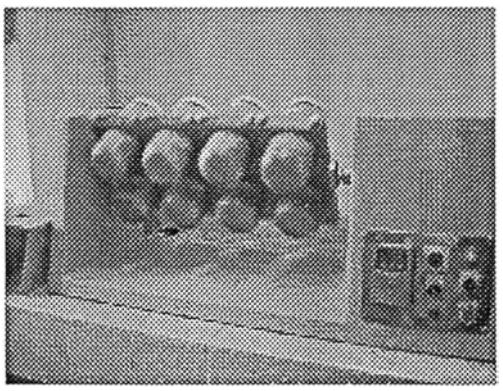


Figure 3.18 Rotary Agitator

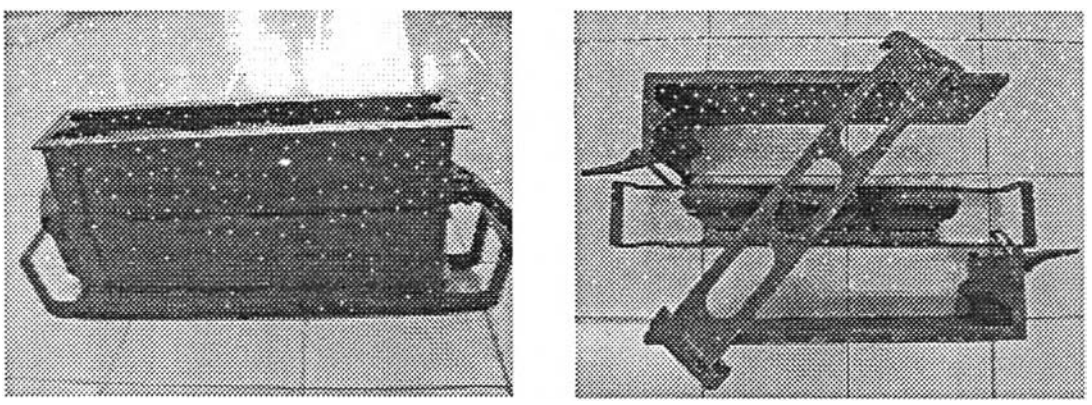


Figure 3.19 Hollow Non-Load-Bearing Concrete Block Mould

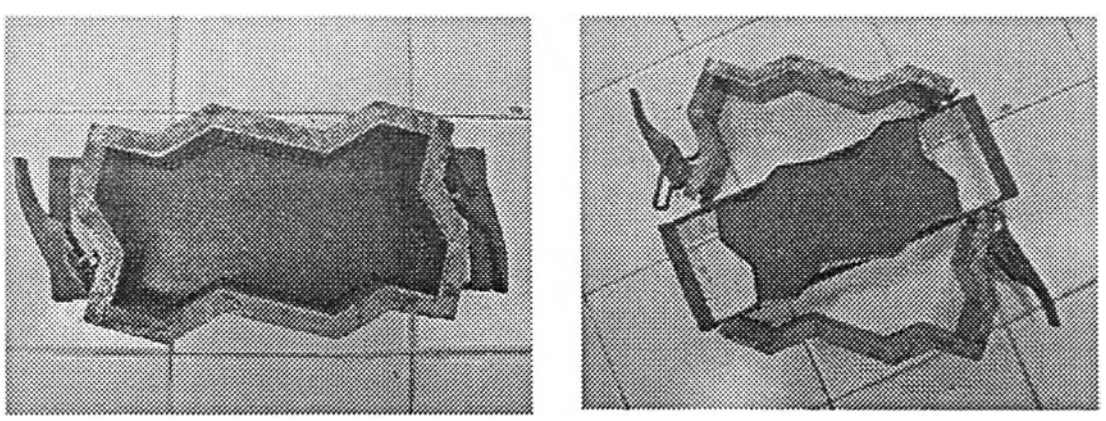


Figure 3.20 Interlocking Concrete Paving Block Mould

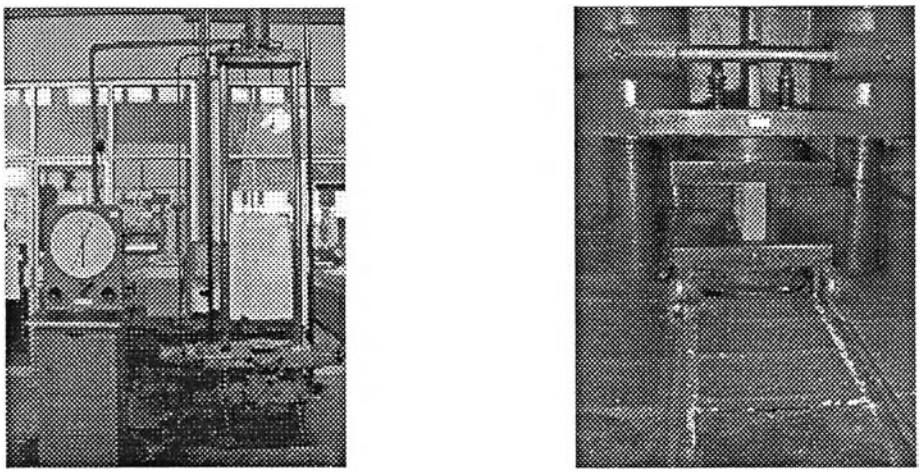


Figure 3.21 500-tons Compressive Strength Test Machine

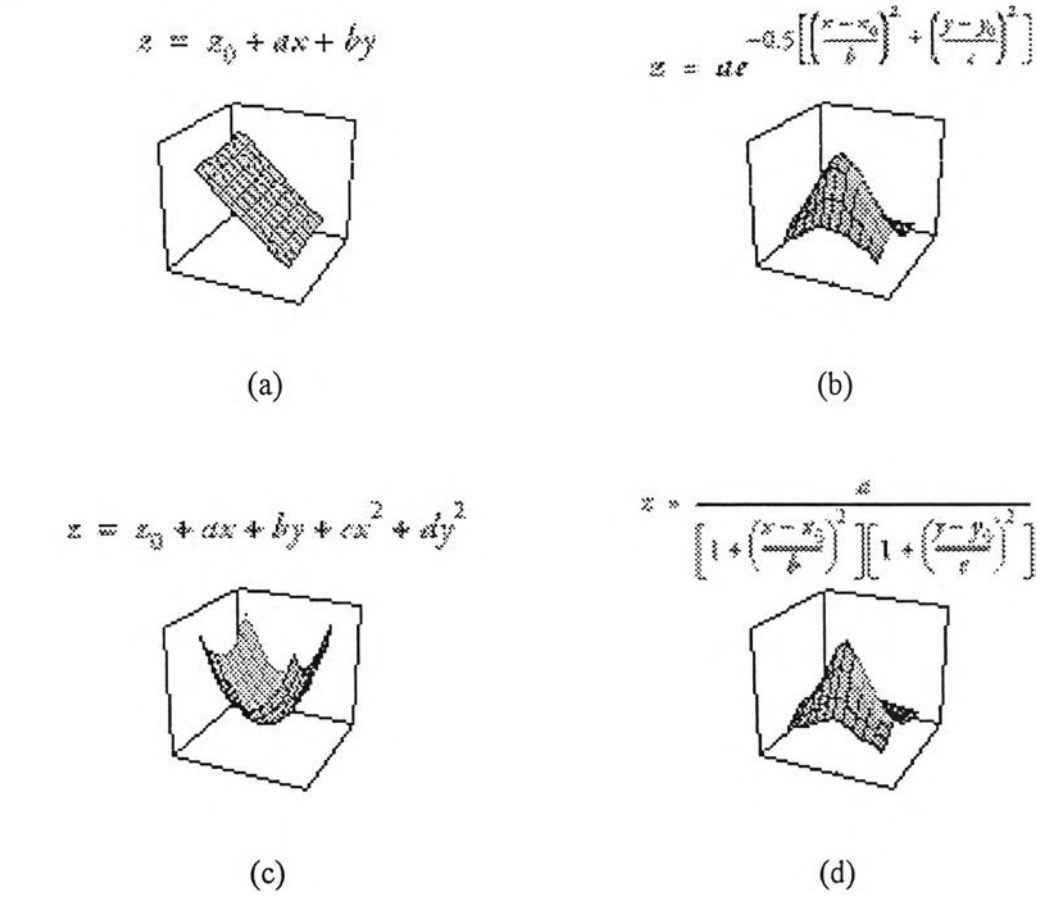


Figure 3.22 Type of 3D Graphs (a) Plan, (b) Gaussian, (c) Paraboloid, and (d) Lorentzain