CHAPTER 6

EXPERIMENTAL INVESTIGATION

Select some raw materials, proportion them, grind, heat, cool
and grind again. Reduced to its simplest terms, this is the process for
manufacturing Portland cement.

6.1 Raw materials

The raw materials used for the experiment were limestone, spent
shale and clay. They were in lump form. To crush them into small
pieces, each of the raw materials was put separately into a jaw crusher
(Fig. 6.2) for primary crushing. The output was less than four inches.
They were furthur ground by secondary crushing in a roll crusher (Fig.
6.3). The particles smaller than 0.4 inches were selected out and then
crushed by pulverizer (Fig. 6.4). The ground products were passed
through sieves (Fig. 6.5) no. 20 (850 µm), no. 35 (500 µm), no. 60 (250
µm), no. 100 (150 µm), no. 140 (106 µm), and no. 200 (75 µm). The
collected materials, which passed through sieve no. 200, were kept in
containers. Each raw material in its separate container was analysed
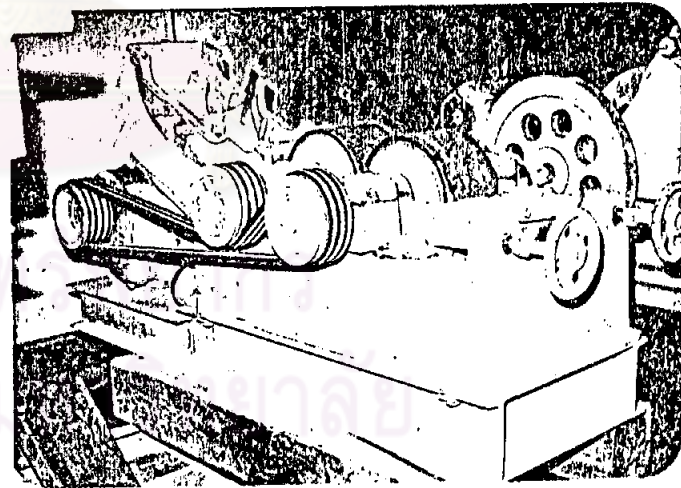for chemical composition by the method described in appendix A.
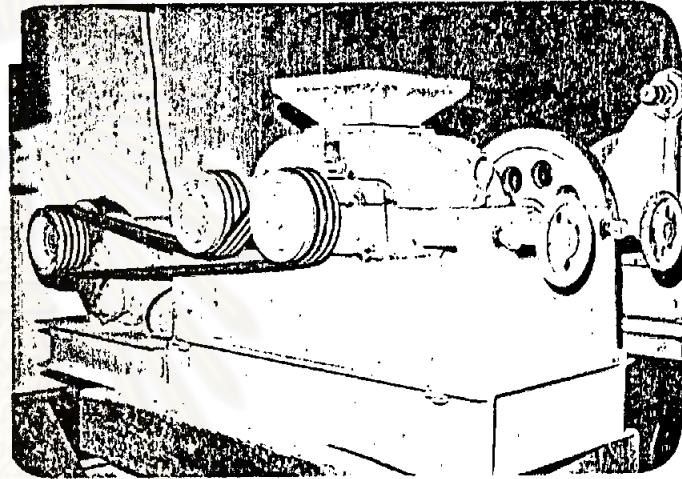
FIGURE 6.2 Jaw Crusher
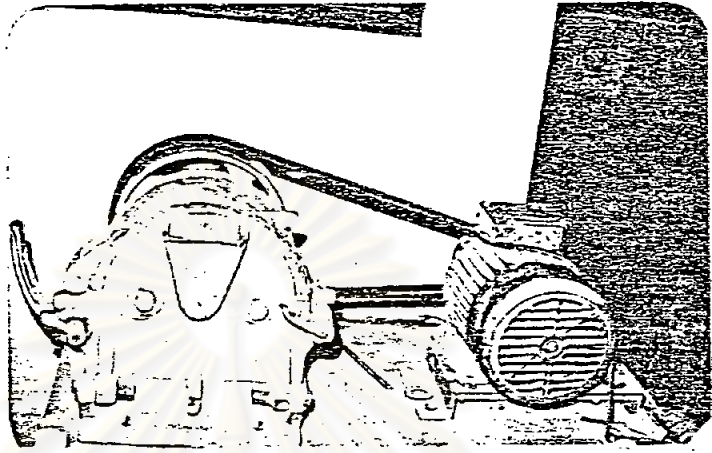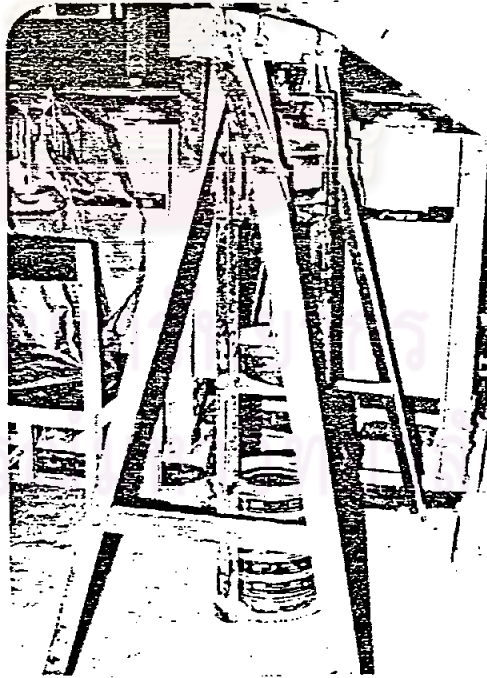

FIGURE 6.3 Roll Crusher

FIGURE 6.4 Pulverizer

FIGURE 6.5 Rotap-shaker
[sieving test]

6.2 Preliminary study of the range of ordinary portland cement

In deciding on the proportion of raw materials, the chemical composition of the raw mix should be within the allowable range. For Portland cement type I, the range limit[26] is shown in Table 6.1.

Table 6.1 The chemical composition of Portland cement Type I by percentage.

%	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Alkali Oxides	SO_3
Minimum	18.58	3.86	1.53	61.17	0.60	0.66	0.82
Maximum	23.26	7.44	6.18	66.92	5.24	2.90	2.26
Average	21.08	5.79	2.86	63.85	2.47	1.40	1.73

The exact amount of each compound in the clinkers depends on the degree to which equilibrium conditions are attained during burning. Table 6.2 gives an analysis of the average composition[26] of Portland cement in terms of compounds.

Table 6.2 Percentage composition of Portland cement Type I in terms of compounds.

%	C_3S	C_2S	C_3A	C_4AF	MgO
Minimum	35.30	0.00	0.00	4.70	0.60
Maximum	70.60	33.20	15.50	18.40	5.24
Average	51.70	21.40	10.50	8.70	2.47

6.3 Proportioning

The proportions of raw materials were calculated by Graphical-determination[21] (Grün and Kunze). Then their moduli values were calculated from their chemical compositions. The details are discussed in section 6.8.

There are many possible proportions which can be divided into 2 types, i.e., two component and three component mixtures (Table 7.2 and 7.3). For this study, a three component mixture was chosen because the raw mix must be made into nodule forms of about 1 cm.[29] It was possible to make smoother and more homogeneous nodules from a three component mixture than from a two component mixture because the third component, clay, has plasticity while limestone and spent shale have none. The nodules tend to segregate and deform unless clay is used.

6.4 Raw mix preparation and firing

From the three component mixtures (Table 7.3), Sample No. 35 was chosen. This proportion was 72.15% limestone; 25% spent shale and 2.85% clay. To prepare a 5 kg raw mix batch, 3607.5 gm of limestone, 1250 gm of spent shale and 142.5 gm of clay were used. Under dry conditions, the components were blended in a ball mill (Fig. 6.6) for two hours without grinding media or balls. The raw components which had passed through sieve no. 200 were fine enough. The purpose in blending was to get homogeneous raw mixes. There, the raw mixes, with the addition of a considerable amount of water, were made into nodules of about 1 cm in diameter.[29] The nodules were air-dried and placed on a high-alumina refractory in the electrical muffle kiln (Fig. 6.7). The time of passage
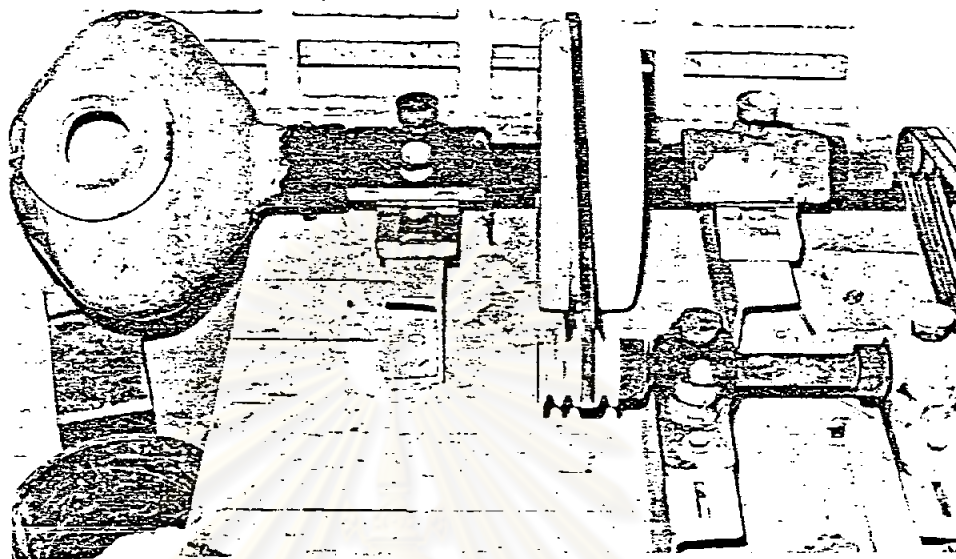
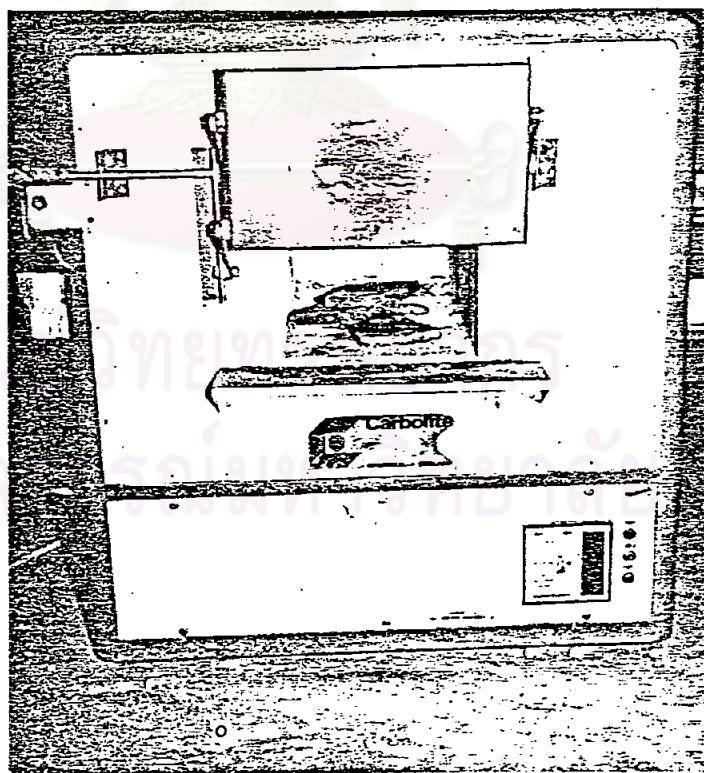FIGURE 6.6   Ball   Mill

FIGURE 6.7   Electrical   Muffle   Kiln

of a cement raw mix through a rotary kiln 200 feet long is about 2.5

hours and it takes about 6 hours for a 450 feet kiln.[16] But for the

burning time in the electrical muffle kiln, these was no data to show

how long it should take. So, a preliminary investigation was necessary.

6.5 Preliminary Investigation

The air dried nodules were fired at $1300^{\circ}C$, $1350^{\circ}C$ and $1400^{\circ}C$

for 45 minutes, 1 hour and 2 hours. They were fired according to the

following procedure:

1. Set the temperature of the electrical muffle kiln at $500^{\circ}C$

and maintain it for 30 minutes. The water is evolved from the clay at

this temperature.[16]

2. Set the temperature to $900^{\circ}C$ for 30 minutes. CO_2 from $CaCO_3$

is evolved and amorphous dehydration products of clay crystallise.[16]

3. Set the temperature to the desired one i.e., $1300^{\circ}C/1350^{\circ}C/$

$1400^{\circ}C$ and maintain it for 45 minutes/1 hour/2 hours.

The temperature of the electrical muffle kiln rises rapidly.

Hence, the temperature should be carefully controlled at $500^{\circ}C$ and $900^{\circ}C$

for 30 minutes each to prevent the nodules from cracking. An analysis

of the free lime in the clinkers gave the following results:

Table 6.3 The percentage of free lime in three-component mixture

clinkers at various temperatures and times.

Temp. °C \ Time	45 min.	1 hr	2 hr
1300	26.95	16.14	2.30
1350	9.72	5.20	0.22
1400	0.25	0.17	n.d.

The lower the amount of free lime, the more complete the reaction.[16] The amount of free lime must be as low as possible. An excess of free lime can become combined with the acidic oxides of the cement mix and give rise to unsoundness. As seen in table 6.3, the lowest amount of free lime was 0.17 and it was obtained by firing the mixture to 1400°C for 1 hour.

6.6 Products

The results of the preliminary investigation were used as a guide-line for burning sample no 35. This, the sample no. 35 nodules were fired at 1400°C for one hour in the electrical muffle kiln and the firing procedure was the same as the preliminary investigation.

The colour of the clinkers produced changed from brownish to greyish green and were harder than before firing. They were ground to a fineness of which only 30 percent were retained on 75 μm (sieve no. 200). The test sieves were as follow; no. 60 (250 μm), no. 80 (180 μm), no. 100 (150 μm), no. 140 (106 μm) and no. 200 (75 μm) respectively. 5% gypsum was added to this mixture. The resulting cement powder was stored in a plastic container for the following test.

6.7 X-Ray Diffraction Analysis

The cement powder was subjected to x-ray diffractometric studies for both the identification of crystalline phases and their roughly quantitative estimation. A mixture and the component to be identified should be presented in sufficient quantities to yield a good diffraction pattern. The cement powder was packed in a sample holder and placed parallel to the x-ray beam (Fig. 6.8, 6.9). According to the x-ray diffracted peak (Fig. 7.1), Bragg angle could be determined as follows:

For CuKα radiation,

$$2\theta = 29.30 \text{ degree}$$
$$= 32.10 \text{ degree}$$
$$= 32.40 \text{ degree}$$
$$= 34.30 \text{ degree}$$

The spacing d of the reflecting lattice planes which produced the line can be calculated. All the peaks of the x-ray diffraction patterns could be broadly assigned to C_3S, C_2S, C-S-H (Appendix D.3).

For quantitative estimation, the relation between diffracted intensity and concentration was based on the exact expression for the intensity diffracted by a single-phase powder specimen.[7]

$$I = \left(\frac{I_o e^4}{m^2 c^4}\right)\left(\frac{\lambda^3 A}{32 \pi r}\right)\left(\frac{1}{v^2}\right)\left[|F|^2 P \left(\frac{1+\cos^2 2\theta}{\sin^2\theta \cos\theta}\right)\right]\left(\frac{e^{-2M}}{2\mu}\right) \quad \ldots\ldots\ldots\ldots 6.1$$

where

I = integrated intensity per unit length of diffraction line
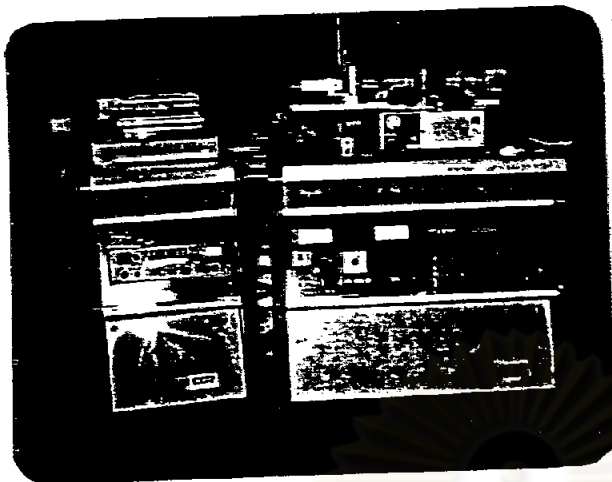
Io = intensity of incident beam

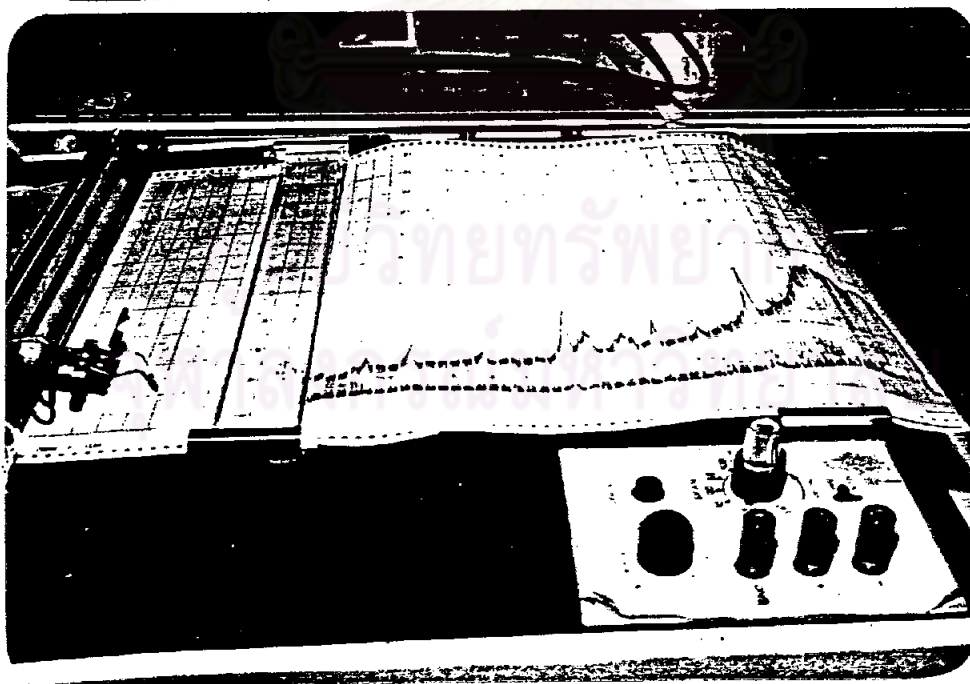FIGURE 6.8 X—Ray Diffractometer

FIGURE 6.9 Sample Holder

FIGURE 6.10   Diffraction Recorder

e,m = charge and mass of the electron

c = velocity of light

λ = wavelength of incident radiation

r = radius of diffractometer circle

Ac = cross-sectional area of incident beam

v = volume of unit cell

$|F|$ = structure factor

P = multiplicity

Θ = Bragg angle

e^{-2M} = temperature factor (a function of Θ)

μ = linear absorption coefficient

Simplify equation 6.1, hence became[7]

$$\frac{I\alpha}{I\alpha\rho} = W\alpha \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad 6.2$$

where $I\alpha$ = the intensity of the selected line of the α phase, subscript ρ denotes diffraction from the pure phase

$W\alpha$ = weight fraction

Equation 6.2 was used in roughly quantitative estimate. Under the same conditions, Elephant brand cement was subjected to x-ray dif-fractometric studies too, to compare the cement from spent shale and the Elephant brand cement.

6.8 Determination of the chemical properties of cement from spent shale

The cement powder was analysed for SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, K_2O, Na_2O, SO_3, Loss on Ignition, free lime, gypsum and insoluble residue

by the methods described in appendix A.

Then C_3S, C_2S, C_3A and C_4AF were calculated from the chemical composition by substitution into the following equation.[2]

$$C_3S = (4.071 \times \%CaO) - (7.600 \times \%SiO_2) - (6.718 \times \%Al_2O_3) -$$
$$(1.430 \times \%Fe_2O_3) - (2.852 \times \%SO_3) \dots\dots\dots 6.3$$

$$C_2S = (2.867 \times \%SiO_2) - (0.7544 \times \%C_3S) \dots\dots\dots 6.4$$

$$C_3A = (2.650 \times \%Al_2O_3) - (1.692 \times \%Fe_2O_3) \dots\dots\dots 6.5$$

$$C_4AF = (3.043 \times \%Fe_2O_3) \dots\dots\dots 6.6$$

Their moduli values were calculated including liquid phase.[14,21]

$$L.S.F. = \frac{CaO - (0.70\ SO_3)}{2.80\ SiO_2 + 1.20\ Al_2O_3 + 0.65\ Fe_2O_3} \dots\dots 6.7$$

$$L.C.F. = \frac{(CaO - Free\ CaO) - 0.70\ SO_3}{2.80\ SiO_2 + 1.20\ Al_2O_3 + 0.65\ Fe_2O_3} \dots\dots 6.8$$

$$H.M. = \frac{CaO}{SiO_2 + Al_2O_3 + Fe_2O_3} \dots\dots\dots 6.9$$

$$S.M. = \frac{SiO_2}{Al_2O_3 + Fe_2O_3} \dots\dots\dots 6.10$$

$$A.M. = \frac{Al_2O_3}{Fe_2O_3} \dots\dots\dots 6.11$$

The liquid Phase is usually calculated by the Lea and Parker formula[16] which is:

$$L.P. = 2.95 \ Al_2O_3 + 2.20 \ Fe_2O_3 + K_2O + Na_2O + MgO$$

If A.M. $\geq$ 1.38 .... 6.12

$$L.P. = 8.50 \ Al_2O_3 - 5.22 \ Fe_2O_3 + K_2O + Na_2O + MgO$$

If A.M. < 1.38 .... 6.13

6.9 Determination of Physical Properties of Cement from Spent Shale

There are many physical requirements for Portland cement type I but the important ones are as follows:

6.9.1 Fineness (specific surface area, cm^2/gm)

There are two alternate methods to test fineness, the turbidimeter test and the Air permeability test. The latter was used for this determination. The fineness of the cement expressed as the total superficial area in cm^2/gm. The apparatus (Figure 6.11) consists of a permeability cell, a manometer, and a flowmeter. The procedure follows ASTM:C 204-55 which is described in appendix B.1.

6.9.2 Normal Consistency

This method of determining the quantity of water required to produce a cement paste of standard consistency is commonly employed. The Vicat apparatus (The one on the left in figure 6.12) was used, a plunger 10 mm in diameter being substituted for the needle end. The quantity of water required to produce a paste of standard consistency is the amount required to give a paste which will permit the settlement of the Vicat plunger to a specified point (normally 5 mm to 7 mm) from the bottom of the Vicat mould when the cement paste was tested as described
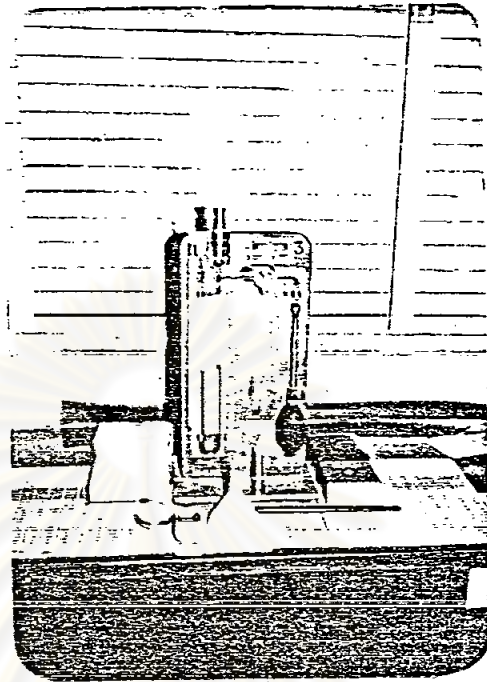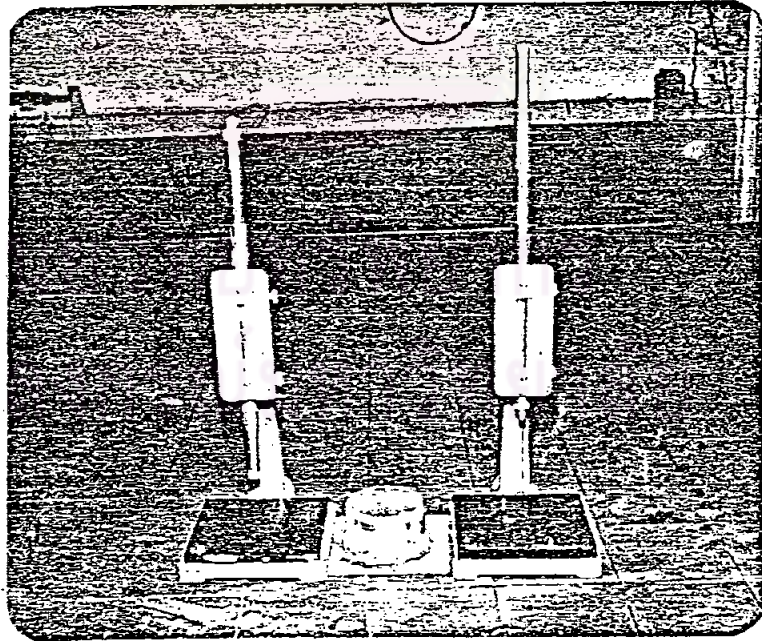
FIGURE 6.11   Air permeability test. Blaine

FIGURE 6.12   Vicat apparatus:- plunger:needles

in appendix B.2. The time of gauging, that is the time elapsing from the moment of adding the water to the dry cement until commencing to fill the mould, should not be less than three minutes nor more than five minutes and the gauging should be completed before any sign of setting occurs.

6.9.3 Time of Setting

Two distinct stages of setting are recorded in the laboratory, namely, the commencement of the setting (called the initial set) and the end or final set. These stages are observed by the use of standard needles. The time elapsing after gauging of the neat cement paste when the needles fail to penetrate to a prescribed depth are recorded as either initial or final set. The results must be interpreted somewhat broadly and are not precise to within a few minutes. Although the method chosen for testing the setting of cement may not give absolutely exact and precise results, it is satisfactory in that the conditions of the test are well defined. The procedure for determining the initial and final setting time of cement following ASTM:C 191-79, is given in appendix B.3.

6.9.4 Soundness

The autoclave test (Figure 6.13) is intended to determine the soundness of cement on a 1 inch by 1 inch neat cement specimen. The autoclave expansion test provides an index of potential delayed expansion caused by the hydration of CaO or MgO or both. The procedure for determining the soundness following ASTM:C 151-77, is given in appendix B.4.
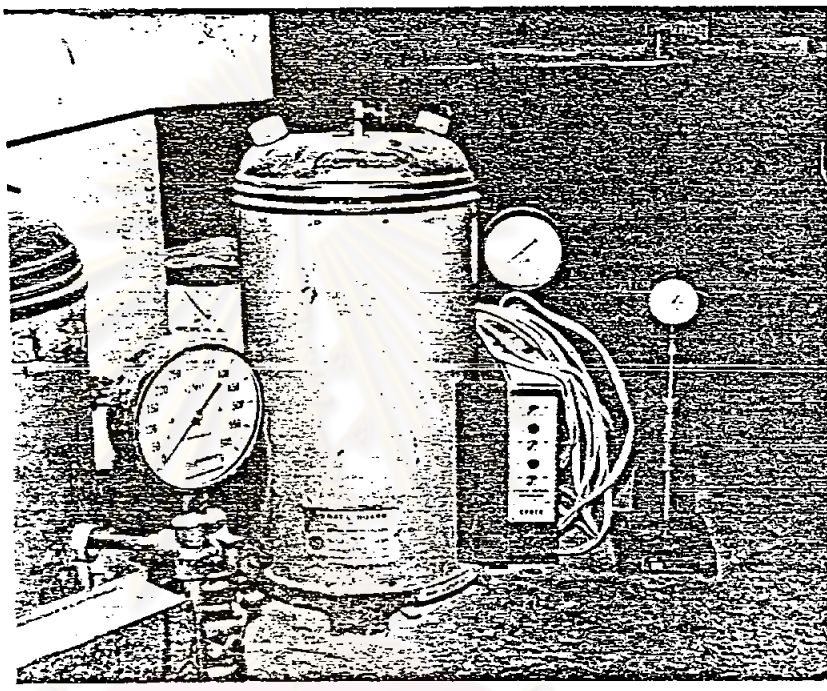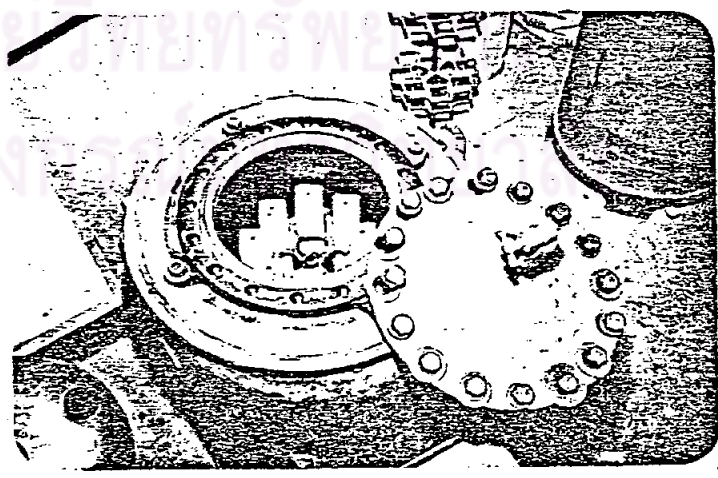
Left: Autoclave

Right: Length comparator

FIGURE 6.13 Autoclave

6.9.5 Air Content of Mortar

The purpose of this method is to determine whether or not the hydraulic cement under test meets the air-entraining or non air-entraining requirements of the applicable hydraulic cement specification. The air content of concrete is influenced by many factors other than the potential of the cement for air-entrainment. The procedure for determining the air content of mortar follows ASTM:C 185-80 as given in appendix B.5.

6.9.6 Compressive Strength

Strength plays a most important part in determining the quality of cement. Compressive strength is a widely used criterion in cement testing and is determined either by crushing mortar cubes or concrete cubes. Mortar cubes of 2 inches or 50 mm were used in this study. The procedure for determining compressive strength follows ASTM:C 109-80 as given in appendix B.6.

The cube specimens were given three different test ages, 3 days, 7 days, and 28 days. After testing them, the broken pieces of each specimen were ground to a fine powder, passed through sieve no. 200 (75 μm) and subjected to x-ray diffraction. Then the results were compared.