Chapter III

Experimental Part

Description and Scope

The experimental part of the thesis is devided into two sections. These are the development of a long-range dilatometer and the sintering of glass powders. The shrinkage of samples was detected by the developed dilatometer or calculated by measuring length and diameter of sample before and after firing. Specimens were designed into cylindrical shape about 15 mm of length and 12 mm of diameter. The experiments can be described in 5 steps; preparation of glass powders, specimen preparation, construction of the dilatometer, sintering of specimen, and characterization of fired specimen compared to the specimen before firing, as shown in the following flow chart. Further information to each step is given in figure 3.2.

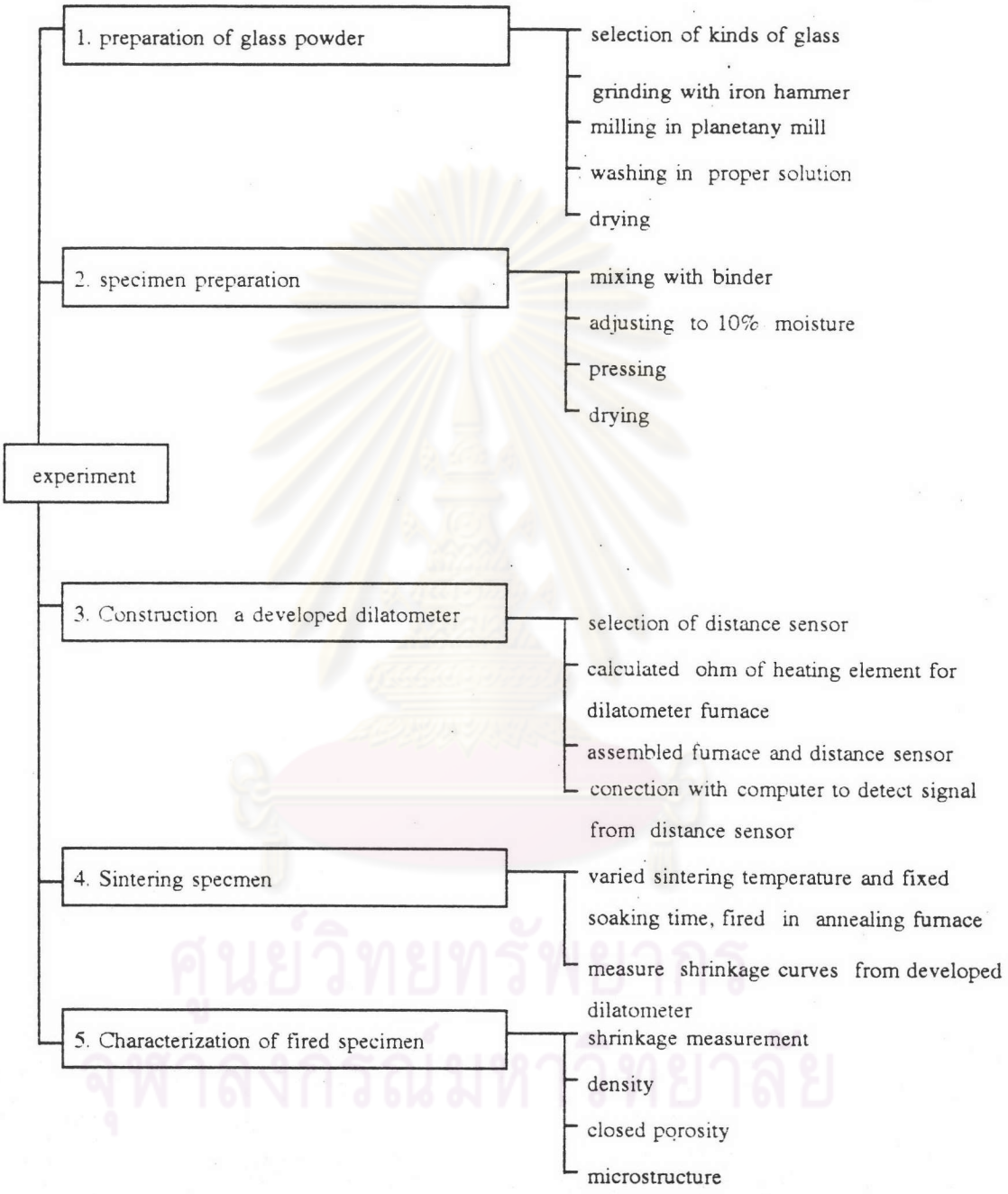

Fig. 3.1 Experiment description flow chart.

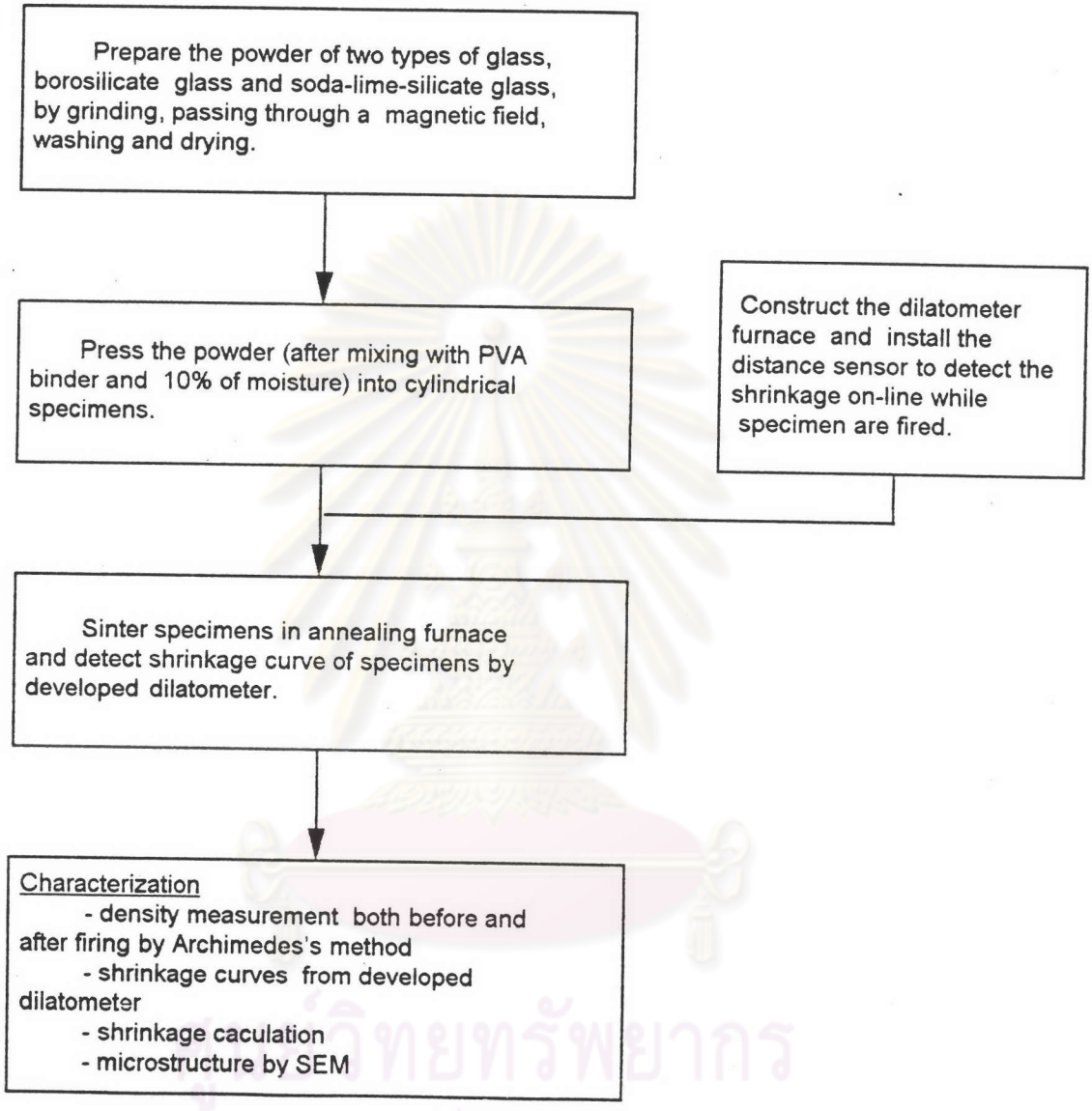

Fig. 3.2 Information in each step of experiment

Experimental Procedure and Equipment

3.1 Apparatus and Instruments

The apparatus and instruments used in the thesis are listed below

1. test tube
2. beaker
3. stirring rod
4. spatula
5. wash bottle
6. volumetric flask
7. thermocouple type K
8. hot plate
9. oven
10. agate mortar
11. planetary mill
12. iron hammer
13. sieve
14. annealing furnace
15. self-constructed furnace
16. distance sensor
17. scanning electron microscope (SEM)

3.2 Preparation of Glass Powders

Two types of glasses were studied in this thesis. The composition of these glasses is shown in table 3.1

Table 3.1 Chemical composition of borosilicate glass and soda-lime-silicate glass (by weight)

Compound	% in borosilicate glass	% in soda-lime-silicate glass
SiO_2	63.40	72.42
Al_2O_3	5.10	1.62
Fe_2O_3	0.04	0.024
B_2O_3	4.80	-
MgO	3.10	3.90
CaO	6.20	7.31
Na_2O	15.60	14.02
SO_3	1.00	0.21
K_2O	0.20	-

The two glasses, borosilicate glass and soda-lime-silicate glass, were crushed with an iron hammer, then ground with a planetary mill to get a fine powders. The powders were separated into 6 ranges of size; 1000 -500 μm, 500 - 250 μm, 250 - 180 μm, 180 - 125 μm, 125 - 63 μm, and smaller than 63 μm, respectively, and the sizes studied were 180 - 125 μm and 125 - 63 μm. After sieving, the powders were passed through a magnetic field to separate iron impurities from the powders. Then the powders were washed in tap water, diluted hydrochloric acid, and distilled water, and dried in an oven at 120 °C. The powders were kept in a plastic box. The preparation route can be seen in figure 3.3.

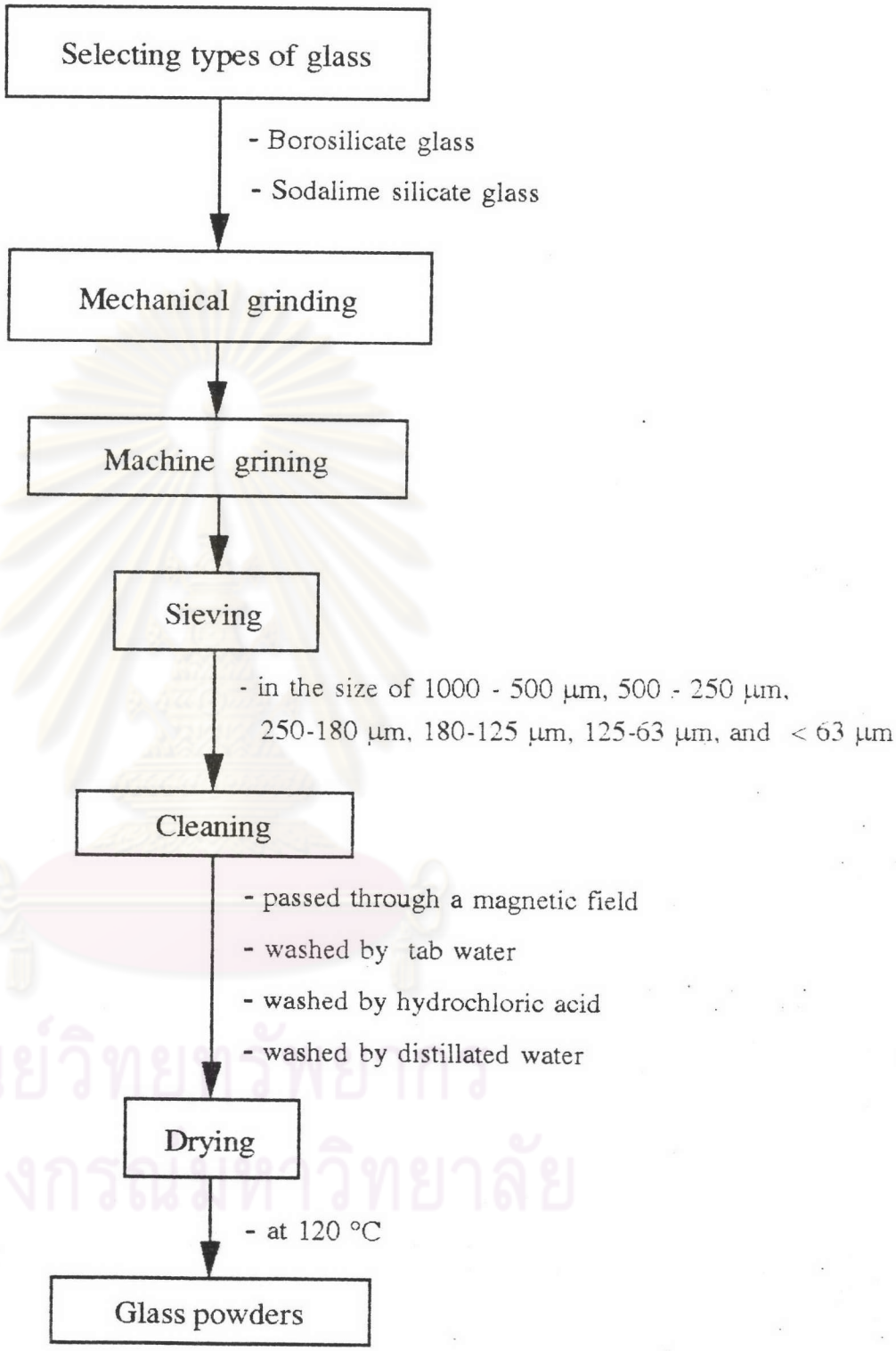

Fig. 3.3 Preparation route of glass powder.

3.3 Specimen Preparation

After the glass powder preparation was finished, specimens were prepared. The glass powders were wet-mixed with 1 % PVA (polyvinyl alcohol) by weight of the powders and dried at 80 °C for 24 hours, then ground in an agate mortar. Next, the mixed powders were weighed and remixed with 10 % water (by weight). The weight of glass powders is calculated close to 60 - 70 % of the standard density which is the density of a well - annealed monolithic pore - free glass at room temperature. The powders and water were blended and granulated in a plastic bag. After that, the powders were pressed from a pellet press to get specimen in a cylindrical shape of about 12 - 13 mm in diameter and about 15 - 16 mm in height, These specimens were dried in the oven at 120 °C. for 24 hours. The route of specimen preparation is shown in figure 3.4.

When the specimens were finished, they were characterized by volume measurement and density measurement before firing.

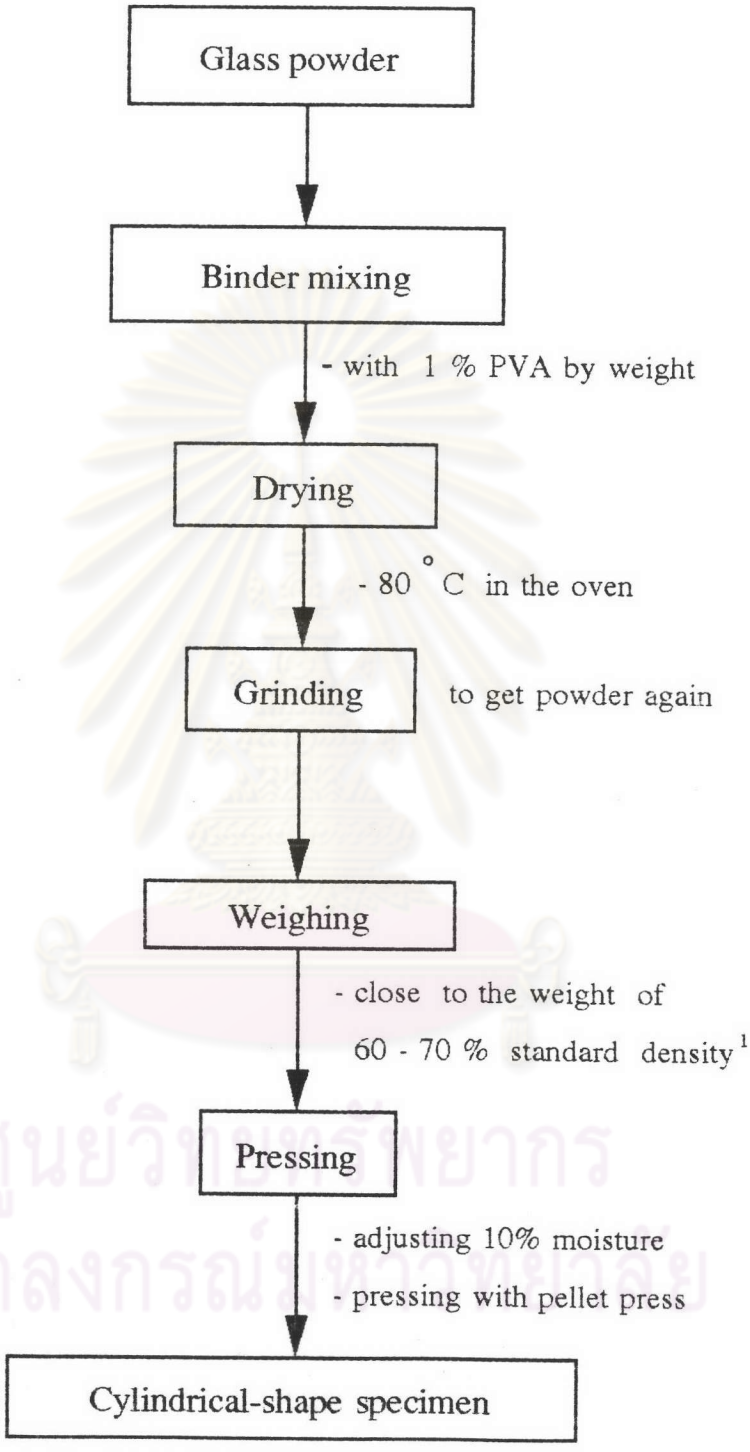

Fig. 3.4 Preparation route of specimen.

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[1] The standard density is the density of a well - annealed, monolithic, pore - free glass at room temperature.

3.4 Construction a Long - Range Dilatometer

First, a small vertical furnace was built. The heater part was sillimanite tube (26 cm long, inner diameter 42 mm). The tube carried the heating element which was nikel-chromium (NrCr) wire, and was covered with refractor wool and refractory brick. The heating element had 11 Ω resistance at room temperature. When operated with 100 V, this provided a power of 1000 W, sufficient to reach a temperature of 900 °C. After that a distance sensor was assembled above the furnace on top of a tripod which could be moved up and down. The voltage supply for the sensor was an automobile battery. The signal output from the sensor was detected by a computer (analogue to digital card) in a units of volt (V). By a controller unit, temperature - time programs, such as constant heating rate, soaking time, etc. could be set. The whole composed instrument is shown in figure 3.5.

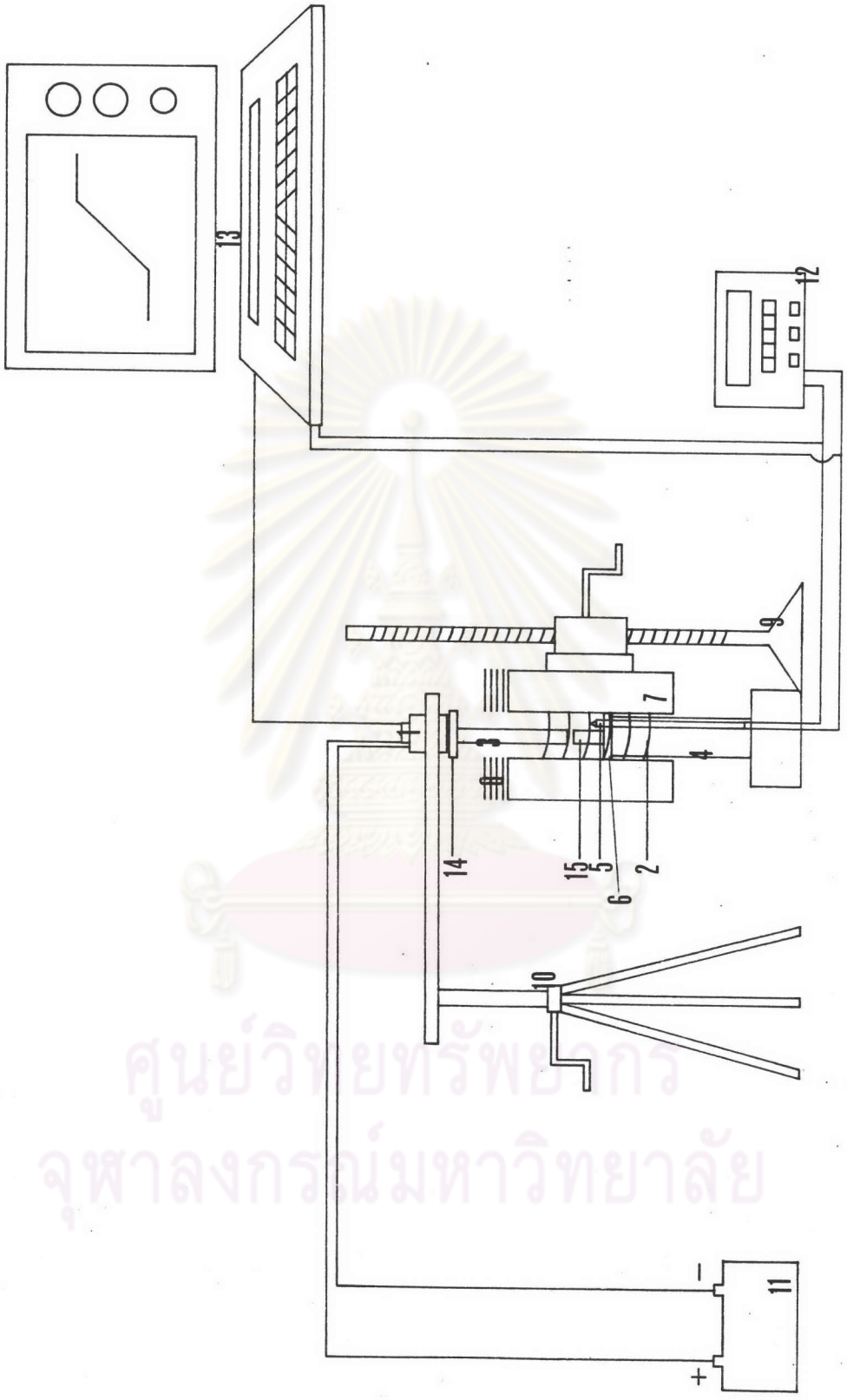

Fig. 3.5 Schematic of an assembled long-range dilatometer system.

The lables of the figure 3.5 have the following meaning:

1. distance sensor
2. heating element
3. silica rod
4. silica tube
5. thermocouple
6. platinum plate
7. furnace
8. heat shield plates
9. furnace stand
10. tripod stand for sensor
11. voltage supply
12. controller
13. computer
14. iron plate
15. sample

3.4.1 Distance Sensor

The types of the distance sensor are Bi20 - G47 - Y1 (type A) and Bi15 - CP40 - LIU (type B). These sensors react to the approach of ferromagnetic substances and are able to translate the distance into a voltage signal. Two sensors were tested: Type A was a proportional on/off output sensor, while type B was a long - range proportional analog output sensor. The sensor type A needs 12 V supply, while the sensor type B needs 24 V. An iron plate was used as approaching ferromagnetic object. This plate was 56.70 mm in diameter and 0.76 mm thick. To set up a calibration curve, a micrometer scew was used. Only sensor type B has a proportional distance wide enough. It detects distances over a range of 12 mm. This range is wide enough to record even large shrinkage of specimen during firing. The sensor type A cannot detect the distance as effectively. Its range was shorter than 5 mm. Besides this, problem occured with the on/off characteristics of the sensor. So in this experiment, the sensor type B was used. The calibration curve from sensor type B is shown in figure 3.6.

The circuit of connecting sensors type A and B is shown in figure 3.7. For the sensor type B, the output signal can be measured in both voltage and current by switching the connecting joint. In the experiments, the voltage option was applied.

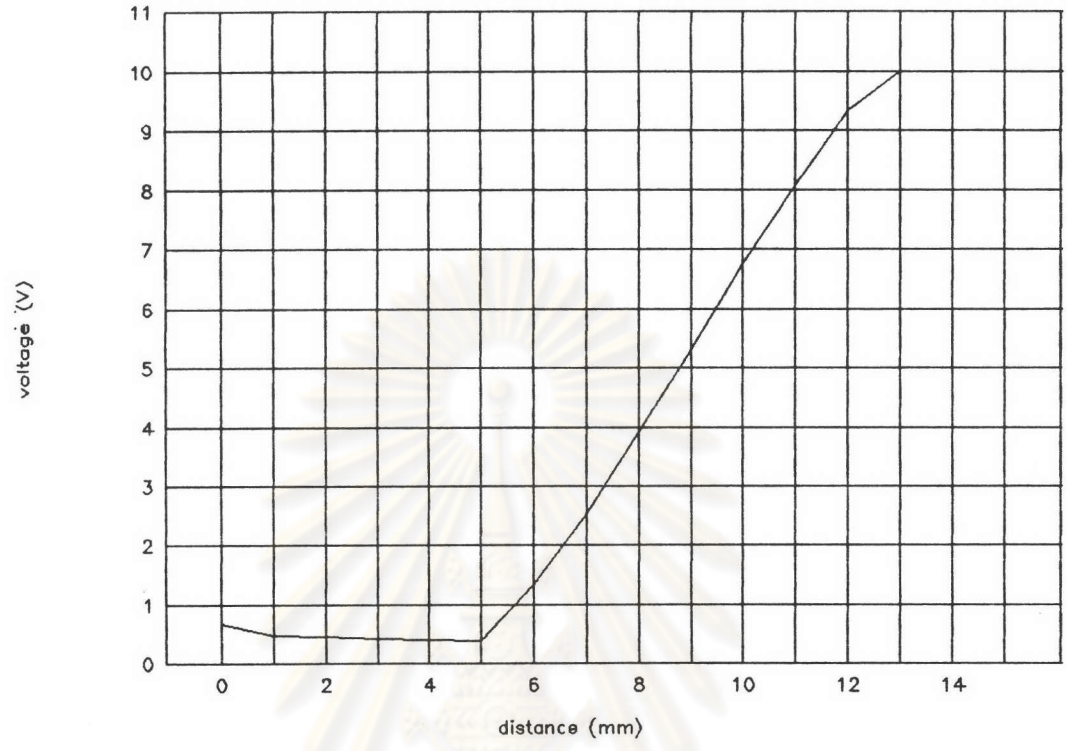

Fig. 3.6 Calibration curve of sensor type B.

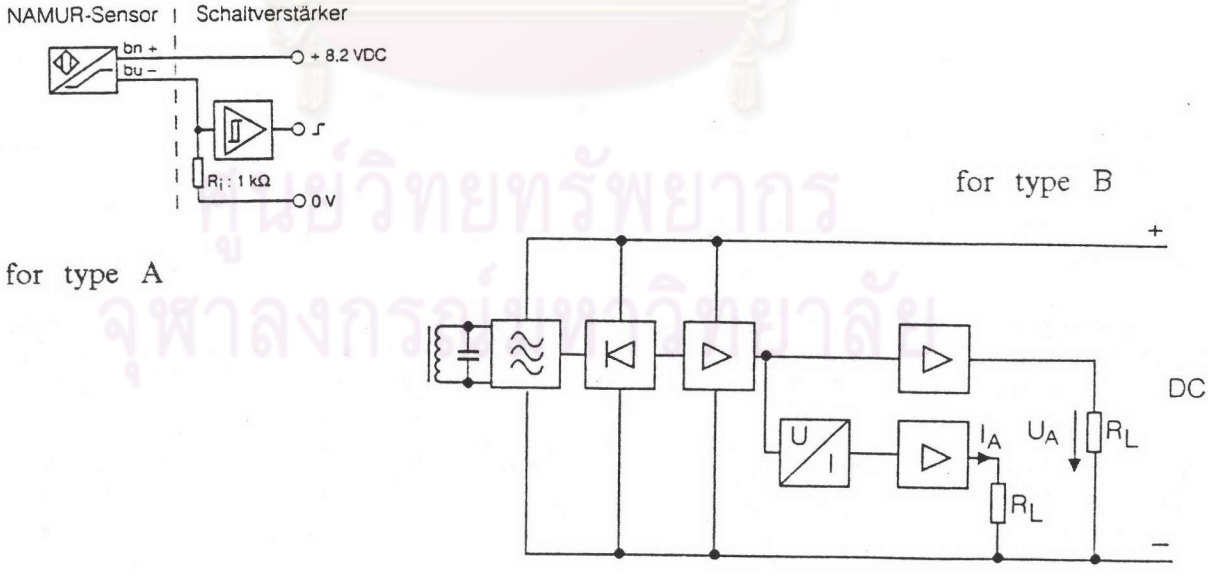

Fig. 3.7 Circiut of connecting sensors

3.4.2 Thermocouple for Detecting Temperature

Thermocouples used in the experiment are type K which is a nickel-chromium - nickel (NiCr-Ni) type. Type K is good for detecting temperatures in the range of room temperature to 1000 °C. Figure 3.7 shows the thermocouple junction.

Fig. 3.8 Single junction for lab purpose of thermocouple.

The signal from this thermocouple is also detected by the analogue to digital card from the computer. The signal is detected in units of mV; convert to °C (see appendix B). The thermocouple wire was kept in a thin alumina tube, the junction at the tip was uncovered.

3.5 Sintering of Specimen

3.5.1 Density and Shrinkage Measurement Before Firing

The length, upper diameter, and lower diameter of each specimen were measured, the density was calculated by

$$D = m / V \qquad 3.1$$

$$V = \pi r^2 h = \text{volume "before"} \qquad 3.2$$

r is the radius, and h is the height of specimen. After firing, the length, upper diameter, and lower diameter of the specimen was measuerd again, the shrinkage in length and volume shrinkage was calculated following the formula,

$$\% \text{ shrinkage in length , } S_l = \frac{\text{length before - length after}}{\text{length before}} \times 100 \qquad 3.3$$

$$F = \pi/4 \left(r_{up} + r_{low} \right)^2 h = \text{volume "after"} \qquad 3.4$$

$$\% \text{ volume shrinkage , } S_v = \frac{\text{volume before - volume after}}{\text{volume before}} \times 100 \qquad 3.5$$

Because of their shape after firing, the volume calculation had to use the average of the upper radius and lower radius. At higher temperatures, the shape of this specimen was moer and more distructed, and that shape is shown in the figure below.

Fig. 3.9 Specimens after firing at high temperature, 3 hours.

3.5.2 Firing Test (Sintering)

When the specimens were finished , they were tested by firing. The temperatures were selected by viscosity. (The viscosity - temperature relations of the glasses used are shown in table 4.1.)

There were three kinds of specimen studied , borosilicate glass size 125 - 63 μm, borosilicate glass size 180 - 125 μm, and soda-lime-silicate glass size 125 - 63 μm. Borosilicate glass was sintered at T(9.7), T(9.4), T(8.7), T(8.2), and T(7.9), soda-lime-silicate glass was sintered at T(10.1), T(9.9), T (9.3), T(9.0), T(8.8), T(8.6), T(8.1), T(7.7) and T (7.4) in an annealing furnace. The shrinkage of specimens was measured after 3 hours of soaking at each viscosity level. Next, the density of each sample was measured using Archimedes method

3.5.3 Dilatometry Measurement

First, the shrinkage of three specimens, borosilicate glass size 180 - 125 μm borosilicate glass size 125 - 63 μm, and soda-lime-silicate glass size 125 - 63 μm were measured by the new dilatometer, which was set to a heating rate of 5 K/min from room temperature to just above the Littleton temperature. In an alternative test, the specimen were put into the furnace at a pre - selected constant viscosity level for 3 hours. The data were recorded on - line by a computer.

3.6 Characterization of the Specimen.

3.6.1 Density Measurement

After firing, the bulk density of specimens were measured by Archimedes method. Each specimen was weighed at least 5 times. The densities were calculated by using the following equation.

$$S_{glass} = S_{water} / (1 - m_2/m_1) \qquad 3.6$$

for m_1 is weight of glass in air (g)

m_2 is weight of glass in water (g)

S_{water} = density of water in g/cm^3

and S_{glass} = density of glass in g/cm^3

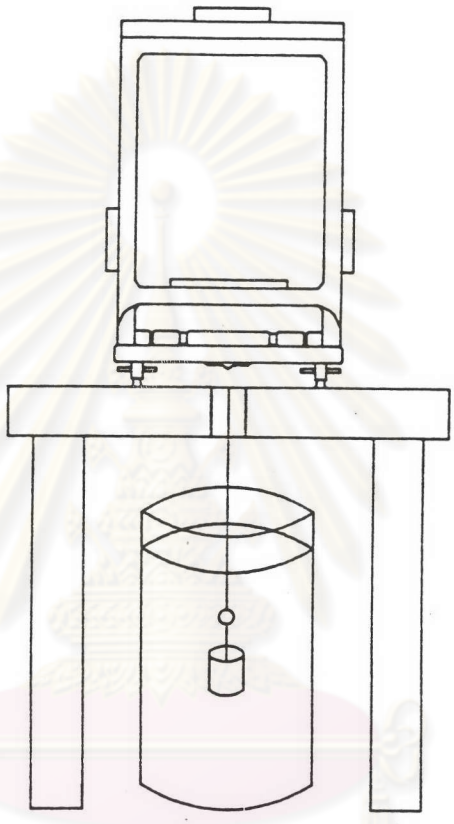

Fig. 3.10 Underhook weighing method.

3.6.2 Microstructure of Specimens

After firing, the specimens were cut by low - speed saw into 2 mm thick slices and polished by sand paper No. 18, cleaned with commercial detergent, water, and dried, Then, they were cleaned with trichloroethylene. After that the specimens' surface were coated with a thin layer of gold and observed by SEM(JEOL - CF35).