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HYDROCHLORIC ACID HEAT REACTION METHOD TO MEASURE CEMENT CONTENTS IN CEMENT MIXED SOILS

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ABSTRACT: The mixing cement with soft soil to increase their strength has been used in many construction sites and it is important that soil and cement are well mixed. In order to evaluate the mixing accuracy during construction, it may be required to measure the cement content by sampling the cement mixed soil. While there are several methods for measuring cement content, the hydrochloric acid heat reaction (HAHR) method is easiest and quickest and is relatively high in precision to measure the cement content in fresh concrete. However, to apply HAHR to the fresh soil cement, there were many questions about a test condition. This study investigated conditions to apply the HAHR method to cement mixed soil. At first, cement are mixed to the local soil samples in the ratio of 0 to 10g/100g. Initial temperatures (T_0) of the mixed soil and hydrochloric acid are measured. 100 g of mixed soil is put in an insulated container. 100mL of hydrochloric acid is added, and reaction temperature (T_1) is measured. Relationship of temperature rise (T_1-T_0) and cement content is a calibration graph. The relation is proportional. And, the temperature rises are measured about 100g of cement mixed soil of the site. Its cement content is obtained using the calibration curve. It is optimal to use 6M hydrochloric acid for this method. It is necessary to examine it with local soil and local cement to prepare a calibration curve. When the water content ratio of the soil greatly changes, it is necessary for the calibration curve to be updated. HAHR tests are done in 10 to 60 minutes after having mixed soil and cement in the case of samples containing a little water. But, in the case of containing much water, the tests are done under the specified elapsed time. As an example of the result, the cement content of soil can be determined from the rising temperature of the sample soil.

Keywords: Cement content, Hydrochloric acid, Soil, Temperature, Dissolution heat

1. INTRODUCTION

A method of improving the engineering properties of soil by mixing cement powder or cement milk with soil is often adopted in construction works**.** Prior to a construction work, the amount of cement to be added is designed so that target strength can be obtained based on the result of laboratory test using the local soil. The construction method includes a method in which cement is added to the soil in situ and a method in which cement is mixed by transferring the soil to a mixing-plant. The field to laboratory strength ratio in deep mixing column method was investigated [1]. It is known that the strength of soil cement is affected by mixing accuracy from experience. It is important to determine the mixing time depending on the local soil properties so that the mixing is well-done.

One method to investigate the mixing accuracy of soil and cement collects many samples of cement mixed soil, and measures each cement content. The cement content can be measured by analyzing calcium hydroxide and calcium carbonate in the samples of cement hydrate by a chemical analysis and a thermal analysis [2] [3]. Further, the cement content can be measured by analyzing calcium in the samples using a fluorescence X-ray (XRF) apparatus [4] [5]. However, it is necessary for the method to analyze soil because a mineral including calcium such as calcium carbonate may be included in the soil. The results of cement content must be corrected by the chemical component of the soil in chemical, thermal and X-ray methods. In addition, these methods need many expensive analytical instruments and an expert technique. It is desirable for the on-site test method to be simple and quick. On the other hand, the hydrochloric acid heat reaction (HAHR) method was developed for the management of cement content in the fresh concrete [6]. HAHR was applied to the cement mixed soil [7]. Because HAHR was simple and quick, the authors thought that it adapted to an on-site test. However, to apply HAHR to the soil cement, there were many questions about a test condition.

This study focused on measuring cement content of fresh cement mixed soils considering many factors affected temperature rise in HAHR such as hydrochloric acid concentration, cement type, the water content of the soil, and time after mixing of soil cement. Furthermore, this report describes the result that applied the HAHR method to construction.

2. METHODOLOGY

2.1 Materials

The soil used is of two types, sandy soil, and clay. The clay is mainly composed of kaolin minerals produced in Gifu Prefecture in Japan. The sand was produced in Chiba Prefecture in Japan. Table 1 shows the physical properties of each soil. The particle size distribution curves for the clay and the sand are shown in Fig. 1.

X-ray diffraction analysis showed that these soils did not include portlandite $Ca(OH)_2$ and calcite $CaCO_3$ which had exothermic reactions with hydrochloric acid. And, these soil showed pH 6-6.5.

The cement mainly used is blast furnace cement (slag content: 40 to 60 %). For comparison, ordinary Portland cement, special cement for ground improvement, quicklime and hydrated lime were also used.

2.2 Containers and Thermometers

The insulated container and the thermometer used are shown in Fig. 2. The insulated container is glass dewar vessel with a 300 mL. For the temperature sensor, FTNGOPF3 (a resistance bulb thermometer with Pt100 Ω) made by Fuji Electric Co., Ltd. was used. As the digital indicator, SD24 made by Shimaden Co., Ltd. was used.

2.3 Methods and Laboratory Procedures

An insulated container, hydrochloric acid (HCl), soil, cement, and water were used. They were left in the test room for at least one day so as to be at room temperature and equilibrium temperature (T_0 °C.). In the case of tests for only cement, 2 to 10g of cement was put in the insulated container. In the case of tests for cement mixed soil, the cement mixed soil of 100g was put in the container. And, 100 mL of HCl of a given concentration was added and mixed with a stirring rod connected with a thermometer (a thermometer indicating the maximum temperature). The maximum temperature (T_1 °C) was read and obtained the rising temperature (ΔT °C) by Eq. (1).

$$\Delta T = T_1 - T_0 \qquad (1)$$

3. RESULTS AND DISCUSSION

3.1 Influence of Hydrochloric Acid Levels on Temperature Rise

The water content of the sandy soil was adjusted to 10%. 110 g of sandy soil (100 g as dry mass) and 0 to 10 g of blast furnace cement were put and mixed in an insulating container. The reason why blast furnace cement was used is that it is adopted most in ground improvement works in Japan. Then, 100 mL each of HCl having a concentration of 2 to 12 M (mol/L) was added and mixed, and the temperature rise ΔT was measured.

Table 1 Properties of soil samples

	w_n (%)	d_s (g/cm^3)	w_L (%)	w_P (%)	U_c
sand	7	2.71	-	-	2.0
clay	1.3	2.66	41	12	-

Note: w_n;water content, d_s; soil particle density, w_L; liquid limit, w_p; plastic limit, U_c; coefficient of uniformity.

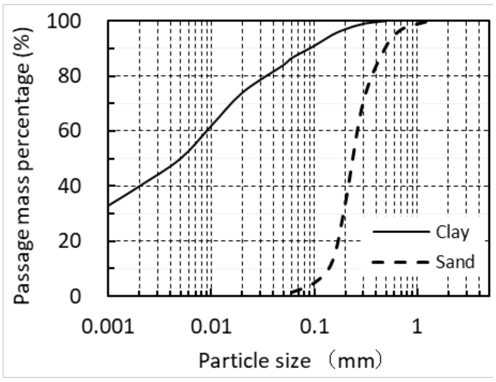

Fig. 1 Particle size distribution of soil samples

Fig. 2 Insulated container and thermometer.

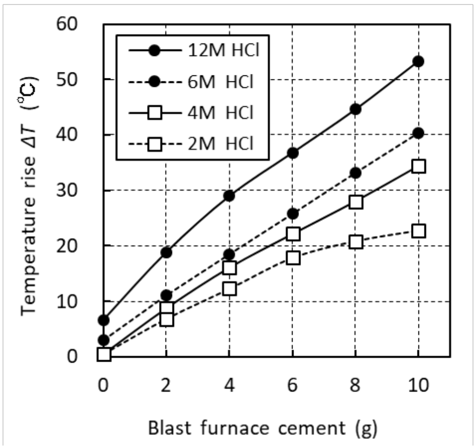

Fig. 3 Relations between cement mass and ΔT as a parameter by HCl concentration. (Sand; 110g, w=10%, HCl; 100mL)

Results are shown in Fig. 3. ΔT increased as the amount of cement increased and as the concentration of HCl increased. 2M-HCl increased the temperature linearly up to 6 g of cement, but the rise slowed at more than 8 g of cement. This may be due to the shortage of HCl in a reaction between cement and HCl. Meanwhile, although 12M-HCl caused the maximum temperature rise, the reaction between cement and HCl was intense, and there was a tendency of slight deviation from a straight line. Moreover, on the handling of 12M-HCl, there are many occurrences of hydrogen chloride gas. The risks of the burn are large when it adheres to the skin, therefor it cannot be said that safety is high. 6M-HCl, and 4M-HCl showed a linear relationship with the amount of cement, the reaction was milder than 12M-HCl, and the risk was greatly reduced. 6M-HCl has an advantage that even when the amount of cement was large, shortage of HCl does not easily occur compared with 4M-HCl. It was concluded that 6M was optimal for the concentration of HCl. Kanda [6] used concentrated hydrochloric acid (about 12M) for measuring cement content in ready-mixed concrete, but 6M-HCl was found to be practical for cement mixed soil. The time before reaching the maximum temperature was less than one minute. It was found that cement content in cement mixed soil can be measured if 6M-HCl was used to prepare a calibration curve as shown in Fig. 3.

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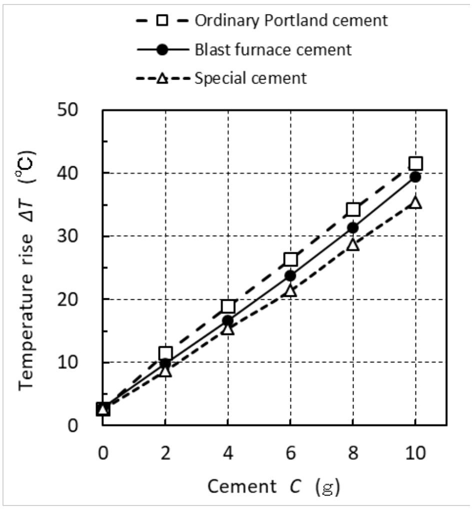

Fig. 4 Relations between three kinds of cements mass and ΔT (Sand; 110g, w=10%, HCl; 6M, 100mL)

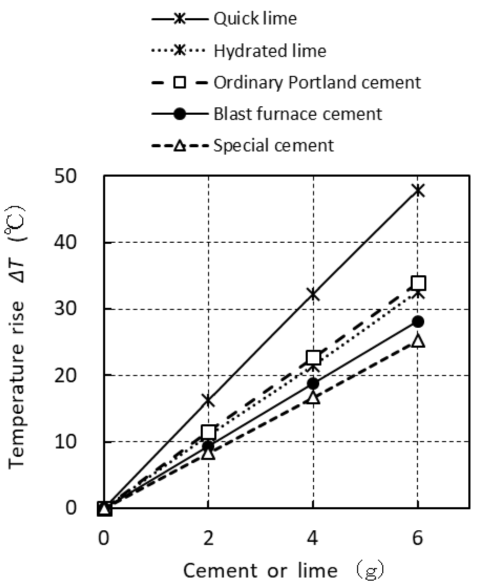

Fig. 5 Relations between cements or limes mass and ΔT (Soil; not included, HCl; 6M, 100mL)

Table 2 CaO content and temperature rise per 1g of limes and cements

	CaO (%)	H (℃/g)
Quick lime	100	8.0
Hydrated lime	76	5.4
Ordinary Portland cement	64	5.7
Blast furnace cement	56	4.7
Special cement	52	4.2

Note: H; inclinations of the straight lines on Fig.5.

3.2 Temperature Rise of Various Cement and Limes

For cement stabilization work, cement other than blast furnace cement may be used. Therefore, ordinary Portland cement and special cement for soil improvement were examined. In the same way, as in the above blast furnace cement, 0 to 10 g of cement was added and mixed with 110 g of sandy soil having 10% of water content, and 100 mL of 6M-HCl was added. The results of temperature rise are shown in Fig. 4.

The slope of the temperature rise line was different for the three types of cement. The magnitude of the inclination was ordinal Portland cement > blast furnace cement > special cement. This cement differs in CaO content and so on. It is considered that the difference in chemical and mineral compositions influenced the magnitude of heat reaction with HCl. It is necessary to prepare a calibration curve for each type of cement to be used.

Furthermore, the examinations to obtain basic data on temperature rise were conducted for limes and cement. Five kinds of quick lime, slaked lime, ordinary Portland cement, blast furnace cement, and special cement for ground improvement were targeted. 100 mL of 6M-HCl was added to 0 to 6 g of limes or cement and mixed to measure ΔT. The examination of this series did not include soil. Results are shown in Fig. 5. The values of the slope of each straight line in Fig. 5, namely H (ΔT °C/g) are shown in Table 2. Table 2 shows CaO content in addition.

H values of the straight line were in the order of quicklime > ordinary Portland cement > hydrated lime > blast furnace cement > special cement. H in Table 2 is not an accurate value in thermochemistry because it is not tested using sufficiently insulated container. However, because it was tested under unified conditions, it is considered that relative evaluation is possible.

The heat that causes ΔT is the sum of the heat of dissolution of lime and cement [8], the heat of dissolution of soil, the heat of neutralization, and the heat of dilution of HCl. In Fig. 4, the temperature rise with 0 g of cement is due to the heat of dissolution, neutralization heat, and dilution heat of a part of the soil. The dissolution reactions of quicklime and hydrated lime with hydrochloric acid are represented by Eqs. (2) and (3).

$$\begin{aligned} &CaO(sol.) + 2HCl \\ &\rightarrow CaCl_2(aq.) + H_2O + 194kJ \end{aligned} \tag{2}$$

$$\begin{aligned} &Ca(OH)_2(sol.) + 2HCl \\ &\rightarrow CaCl_2(aq.) + 2H_2O + 129kJ \end{aligned} \tag{3}$$

These are exothermic reactions and have the biggest influence on the temperature rise in Fig. 5. The ratio of H of quick lime to H of slaked lime in Table 2 is 1.12 when H is expressed in temperature rise per one mol. On the other hand, the ratio of the calorific value of Eq. (2) to the calorific value of Eq. (3) is 1.50. This difference is thought to be due to the different rate of exothermic reaction. Cement is a mixture of various minerals and contains many CaO based minerals. Therefore, cement generates ΔT by a dissolution reaction similar to lime.

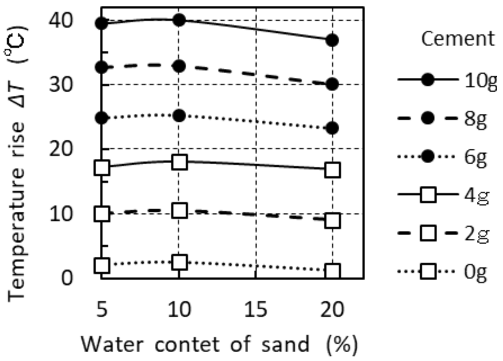

Fig. 6 Relations between water content of sand and ΔT (Sand; 100g as dry mass, HCl; 6M, 100mL)

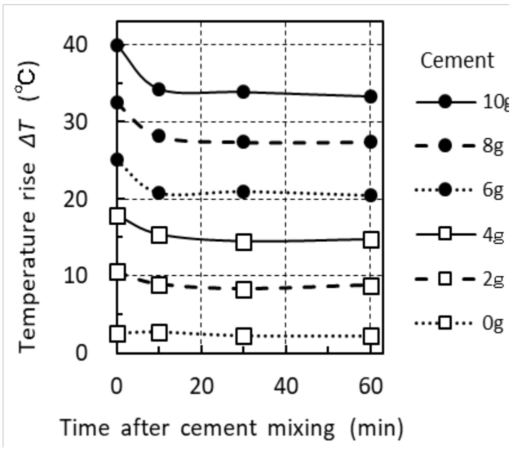

Fig. 7 Relations between time after cement mixing and ΔT (Sand; 100g, w=10%, HCl; 6M, 100mL)

3.3 Influence of Water Content on Temperature Rise

The influence of the water content of sandy soil on temperature rises was tested. Results are shown in Fig. 6.

These were little differences in ΔT with 5% of water content and 10% of water content. Then, when the water content was increased to 20 %, ΔT decreased by 1 to 3 °C. It is considered that the influence of the water content on ΔT basically follows the heat quantity calculation. When the water content of soil falls within ±5 %, it can be used as a common calibration curve.

3.4 Influence of Time after Mixing of Cement and Sand on Temperature Rise

The influence of elapsed time from the mixing of sand and cement on temperature rise was investigated. The elapsed times were up to 60 minutes. The results are shown in Fig. 7.

ΔT showed the maximum when the elapsed time is 0 minute. And, Δ T was almost the same after 10 to 60minutes. The reason why ΔT decreased after 10 minutes is cement hydrations due to moisture in the sandy soil. It is considered that the decrease in ΔT decreased after 10 minutes because the water content was relatively small. Even in the hydrochloric acid heat dissolution test conducted by Kanda [6] on flesh concrete, the decrease in ΔT associated with the elapsed time is greater for the larger amount of water. This suggests that the influence of elapsed time depends on the hydration rate of cement. From Fig. 7, the HAHR method should not be carried out in 0-10 minutes after mixing soil and cement.

3.5 Temperature Rise of Various Cement Mixed with Clay-Sand Slurry

The clay-sand slurry was prepared using the sand and the clay shown in table 1. 8 g of clay per 100 g of sand as a dry mass was mixed, and 40 mL of water was added and mixed. The amount of slurry was adjusted so that the total amount with cement to this slurry was 100 g. Cement content was 0 to 10 g. HAHR test was carried out for this cement mixed soil. Three kinds of cement were used. The results are shown in Fig. 8.

ΔT increased linearly with any cement. And it showed the same tendency as the result of Fig. 4 which was tested using sand of relatively low water content. And, Fig. 8 shows that the slope of the straight line became smaller than in Fig. 4 because the soil contained much water. ΔT in 10 g of cement decreased by about 10 °C in Fig. 8 compared with Fig. 4. These are due to an increase in the heat capacity accompanying an increase in the amount of water, and it is considered that the estimation of ΔT is possible by calculation of heat quantity.

3.6 Influence of Time after Mixing of Cement and Clay-Sand Slurry on Temperature Rise

The HAHR test was carried out after 10 minutes, 30 minutes, 60 minutes, 1 day, 7 days and 28 days passed after mixing of blast furnace cement and clay-sand slurry. The cement mixed soil samples were covered with a plastic sheet and put at 20 °C until the HAHR test. The results are shown in Fig. 9.

ΔT has begun to decrease from 10 minutes in any case of the cement amount. The decrease in ΔT is more prominent as the cement amount is larger. The decrease in ΔT was caused by the progress of the cement hydration. In these tests, the soil contained a sufficient amount of water for cement hydration. Therefore, it is necessary for HAHR test for the water-rich samples to be done under a specified elapsed time after mixing of soil and cement. On the other hand, ΔT in Fig.7 little decreased in 10 to 60 minutes of elapsed time. In the case of samples with a little quantity of water as Fig.7, the limitation is relaxed.

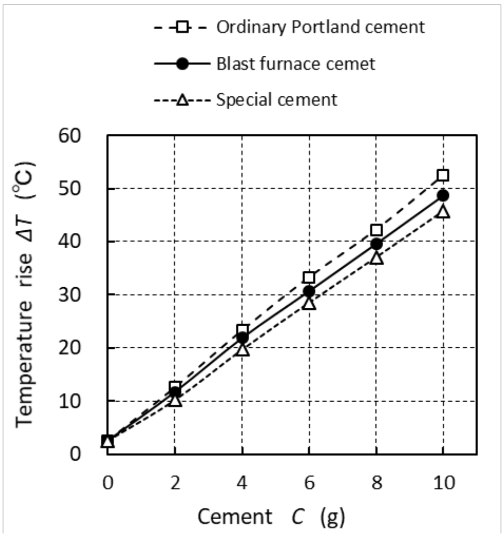

Fig. 8 Relations between cements mass and ΔT (Soils; sand-clay, 100g as dry mass, w=40%, HCl; 6M, 100mL)

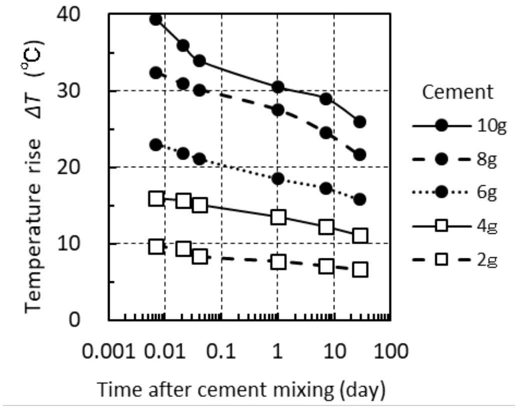

Fig.9 Relations time after cement mixing and ΔT (Soils; clay-sand, 100g as dry mass, w=40%, HCl; 6M, 100mL)

In addition, Δ*T* after 1, 7 and 28 days decreased as compared with Δ*T* after 10 minutes, but a considerable value remained. This suggests that it is possible to measure the cement content for the long-term elapsed samples by devising the method of preparing the calibration curve.

3.7 Practical Application

In March 2017, construction was carried out to supply cement milk to soft ground and stir and mix in the Tohoku region of Japan. The soil is almost homogeneous clay up to a depth of 10 m and has a natural water content of 74.3 %, a wet density of 1.48 g/cm^3, a liquid limit of 77.1 %, a plasticity limit of 44.8 %, a 75 μm to 2 mm content of 12 %, and a <75 μm content of 88 %. The improvement depth of

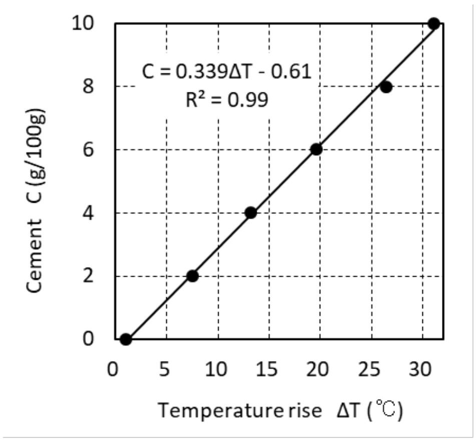

Fig. 10 Example of calibration curve for the site (Soils; 100g as wet mass, w=74%, HCl; 6M, 100mL)

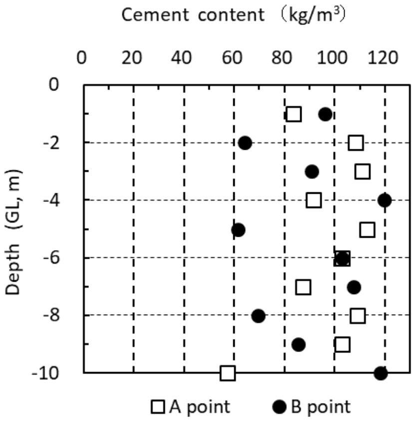

Fig. 11 Example of cement contents for the site

the ground was GL. 0 m to GL -10 m. In order to improve this ground to the target strength, special cement for ground improvement was mixed with designed addition amount of 80 kg/m^3. Cement was supplied in cement milk with a water/cement ratio of 2.28. The stirring and mixing machine is one in which stirring blades are attached to a chain rotating in the vertical direction. Because the adhesiveness of the soil was high so that the mixing with cement was difficult, the water ratio of cement milk was set higher.

In this construction, in order to investigate and control the mixing precision of cement, the authors brought equipment of HAHR method to the site and measured cement content at the site. A sampling tube was inserted at the site where stirring and mixing of the cement was completed at the site, samples were taken for each depth, and the cement content was measured. An example of the calibration curve is shown in Fig. 10.

A calibration curve was prepared each time the local soil quality changed. For the calibration curve, the horizontal axis represents ΔT and the vertical axis represents the cement content C. An example of the results of the HAHR test in the depth direction immediately after cement improvement is shown in Fig. 11.

The points A and B are the points for investigating the construction conditions of horizontal movement (stirring time) of the stirring machine. The mutual distance between the two points is about 3 m. The HAHR method was easily done at the site and the results quickly contributed to the rationalization of construction.

4. CONCLUSIONS

In a cement mixing method to soils, it is important that soil and cement are well mixed. In order to evaluate the mixing accuracy, it may be required to measure the cement content in samples of cement mixed soil. This study investigated the hydrochloric acid heat reaction (HAHR) method to measure the cement content in fresh cement mixed soils. The HAHR methods are established as follows.

At first, step, to prepare a calibration curve indicating temperature rise and cement content is needed. Cement is mixed to the local soil samples in the ratio of 0 to 10g/100g. Initial temperatures (T_0) of the mixed soil and hydrochloric acid are measured. 100 g of mixed soil is put in an insulated container. And, 100mL of hydrochloric acid is added and stirred. Maximum temperature (T_1) by the reaction is measured. Relationship of temperature rise (T_1-T_0) and cement content is a calibration curve which is usually linear.

In this method, it is optimal to use hydrochloric acid of 6mol/L. The quantity of addition of the hydrochloric acid is always 100mL. The quantity of cement mixed soil is usually 100g. But, when the cement content is extremely little or when extremely large, the quantities of samples are changed.

At the second step, the temperature rises of 100 g of the samples whose cement content was unknown were measured in the same way as the method for measurement of the first step. It is desirable that the HAHR tests are done for 10 minutes to 1 hour after mixing soil and cement in the case of the samples containing a little water. But, in the case of water-rich samples, the tests are necessary to be done under the specified elapsed time. And, the cement content (g/100g) were provided by using the calibration curve prepared at first step.

HAHR method is a quick method because a temperature rise is measured within one minute. Because the calibration curves are prepared for each on-site soil, HAHR method can be applied to every soil. HAHR method is applicable without considering chemical composition and mineral composition of the soils. This method is very simple in the calculation of cement content not the only measurement of temperature rise.

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