# IMPREGNATION DEPTH OF SILANE PENETRANT SYSTEM AND ITS EFFECT ON ASR EXPANSION

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**Abstract**

In order to investigate the impregnation depth of silanes, a visual method with colored water is applied. This paper deals with the basic investigations of the amount of impregnated silane in addition to the impregnation depth by applying thermo-gravimetry and differential thermal analysis (TG-DTA) of samples taken at different depths in concrete specimens. The amount of impregnated silane is important to the performance of the water-repellent effect. Cement paste powders mixed with silane at different ratios were subjected to differential thermal analysis. A good linear relationship between the exothermic peak area of the heat flow curve and the content of silane was obtained. The results of the length change of the concrete specimens incorporating reactive aggregate and stored under outdoor exposure and the results of differential thermal analysis of powder samples obtained from the surface of the specimens were considered. Methods to estimate the total amount of impregnated silane and the amount needed to control ASR expansion are discussed.

**Keywords**: differential thermal analysis, silane, impregnation, alkali aggregate reaction, ASR

## 1       INTRODUCTION

Silanes are known to control the ASR expansion of concrete because the water content of concrete is kept at low level as a result of its water-repellent effect and vapor permeability. These effects are affected by the impregnated amount and the impregnation depth. The impregnation depth and impregnated amount are thought to be affected by the mix proportions and the surface moisture of concrete. In order to obtain good results as a repair method, quantitative estimation of the impregnated amount and impregnation depth is recommended.

In this paper, the differential thermal analysis of samples obtained from concrete specimens was used to measure the impregnation depth of silanes. The analysis focuses on the peak area of the heat flow curve and the peak temperature. Differential thermal analysis was also applied to mixtures of cement paste powder and silane, and the quantity of impregnated silane required to control the ASR expansion and the estimation method of impregnated silane are discussed.

## 2       EXPERIMENTAL METHODS
### 2.1     Differential thermal analysis of exposed concrete specimens (Experiment 1)

This experiment was carried out in order to determine the relationships between the impregnated depth, the amount of silane, and the effect on expansion. The impregnated depth and the amount of silane were estimated by the peak area of the heat flow curve and the peak temperature in differential thermal analysis. Figure 1 shows the flow of the experiment. The samples for differential thermal analysis were taken at different depths in cores drilled from exposed concrete specimen (100×100×400 mm). Three concrete specimens were made with reactive aggregate and treated with layers of alkyl alkoxy silane together with polymer cement (PCM) and acrylic resin. After five years of outdoor exposure, the PCM and acrylic resin layers of one specimen in three were removed, and the specimen was exposed outdoor for approximately nine years. In such conditions, the silane impregnated specimen without the PCM and acrylic resin layers showed no expansion [1][2].

Table 1 shows the mix proportions of the concrete and the applied coating system is listed in Table 2. The sampling depths of mortar in cores for differential thermal analysis (9th step in Figure 1) are shown in Table 3.

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Grinding of the core surface was performed by 1-mm steps on both ends down to a certain depth with a cylinder grinding machine, and the depth was measured as a feed distance of the machine by displacement gauge graduated in 0.01mm. And samples for analysis were obtained from both ends at each grinding steps. In addition, samples (mainly paste) were taken at each surface scratching with a pick hammer, and were grinded finer with a mortar. And other samples obtained from the hole of exposed specimen (100×100×400mm) at certain depths with a pick hammer and were grinded. The differential thermal analysis was performed at a rate of temperature increase of 10ºC/min, and the weight of the sample was approximately 30 mg.

Figure 2 shows the result of a differential thermal analysis as a control test, and the exothermic peak area of the heat flow curve is indicated by the hatched area. In the figure, the DTA curve shows the differential temperature between the sample and the standard material (aluminum oxide), and the TG curve shows the weight change of the sample.

As a control test, sampling and differential thermal analysis were carried out for a concrete specimen without silane impregnation. The result is shown in Figure 3. There are clear differences between Figure 2 and Figure 3. The heat flow curve has an exothermic peak at around 350ºC in Figure 2, which does not appear in Figure 3. Based on these results, it is assumed that the exothermic peak around 350ºC in the heat flow curve is due to silane.

In the outdoor exposure test (10th step in Figure 1), in order to estimate the silane effect, the side surface of the core specimen was sealed with resin to prevent water exposure. The length change was measured with a contact gauge span of 50 mm at the center, as shown in Figure 4, and with a height gauge for the entire length, as shown in Figure 5. The length was measured every week for up to 13 weeks, and once every four weeks thereafter.

## 2.2 Differential thermal analysis (DTA) of mixture of cement paste powder and silane (Experiment 2)

The purpose of this experiment is to estimate the quantity of silane in concrete. As shown in Figure 6, cement paste was molded and cured for 28 days and then cut into discs of approximately 2 cm in thickness, which were then crushed into powder with a hammer and a mortar. Cement paste powders were mixed with silane at different ratios and then dried in a room at 20ºC and 60% RH. The powders with mixing ratios of 1:0.2 and 1:0.5 were in a dry state, but those of 1:1 and 1:2 were not dry. So they were stored in a drying chamber at 60ºC. Each mixed sample was grinded finer with a mortar and was used for differential thermal analysis.

## 3 RESULTS
### 3.1 Relationship between sampling depth and peak area of heat flow curve (Experiment 1)

Figure 7 shows the relationship between sampling depth and peak area of the heat flow curve. The deeper the sampling depth, the smaller the peak area, that is, a smaller amount of silane is impregnated at a point deeper from surface. At a depth of 5 mm, the existence of a small amount of silane is certified. The dotted line in Figure 7 expresses samples taken at the hole of exposed specimen (100×100×400mm) shown in 8th step in Figure 1.

The results measured for the core specimens by the contact gauge method and by the height gauge method are shown in Figures 8 and 9, respectively. In the case of core No. 2, the results obtained by the contact gauge method show no expansion, whereas the results of the height gauge show some expansion. From these results, it may be inferred that expansion of the core was developed at both ends with water penetration, but that penetration of water was controlled by silane and water did not reach the center of the core. According to the data of the contact gauge method, cores No. 1, 3, and 4, expanded with time. The data obtained by the height gauge method also show expansion, however with a much higher variability. This may confer that on sunny days, the water near the surface of the cores evaporated, and the cores shrunk to a certain degree.

As described above, the length change data show that the cores ground down to depths larger than 3 mm expand significantly, whereas the core ground down to a depth of 2 mm did not. Based on these results, a certain amount of silane exists down to a depth of 2 mm, and this amount is sufficient to control the expansion of concrete under outdoor exposure. From the results of the length change of the cores and differential thermal analysis, the expansion of the cores was controlled by the existence of silane with a peak area of 300 µV·s/mg at a depth of 2 mm but was not controlled with a peak area of 160 µV·s/mg or less at the same depth, though cores contained as much as 9 kg/m³ $Na_2O_{eq}$.

## 3.2    Relationship between the amount of silane and the peak area of the heat flow curve (Experiment 2)

Mixed samples are shown in Figure 10. The sample with a mixing ratio of cement paste powder and silane of 1:2 did not dry completely. Therefore, this sample was not used for differential thermal analysis. A sample with a mixing ratio of 1:0.1 was also made and tested.

The results of differential thermal analysis are shown in Figures 11-14. For the samples with mixing ratios of 1:0.1 and 1:0.2, a peak in the heat flow cure is observed at approximately 330ºC. By contrast, for the samples with mixing ratios of 1:0.5 and 1:1, two peaks in the heat flow curve occur at approximately 250ºC and 320ºC to 370ºC. The existence of two peaks is thought to be a result of the silane rich mix reacting with the cement paste. In addition, it is assumed that the peak at 320ºC to 370ºC corresponds to silane reacting with cement paste and that the peak at approximately 250ºC corresponds to non-reacted silane. And it is assumed that the endothermic peak around 460 ºC shown in Figures 11 ~ 14 is due to the reaction: $Ca(OH)_2 \rightarrow CaO + H_2O$.

Differential thermal analysis of silane was then carried out. An amount of original liquid weighing 9.5 g and containing silane was dried in an oven until reaching a weight of 3.8 g. The results of analysis of the enriched liquid are shown in Figure 15, and a small peak at 240ºC is observed in the heat flow curve. A rapid weight loss occurs before the peak appears due to the white smoke emanating from the cell observed during the experiment. The temperature of 240ºC corresponds to the temperature observed in Figures 13 and 14. The temperature of the exothermic peak of silane reacted with cement paste is higher than that of silane itself because decomposition of reacted silane requires a higher temperature.

The exothermic peak area obtained from heat flow curves are shown in Table 4. In addition, the relationships between the content of silane and the exothermic peak area are shown in Figures 16 and 17.

## 4    DISCUSSION

Figures 8 and 9 show that the expansion of core No. 2 occurred near both ends, but not in the center. This phenomenon suggests that the impregnated silane limits water penetration due to its water-repellent effect, such that water did not reach the center of the specimens.

In the case of cores No. 1, No. 3, and No. 4, which were ground down to depths of 3 mm or more, according to the expansion data measured by the contact gauge, expansion occurred continuously even in the center of the cores which did not dry on sunny days. The data measured by the height gauge also indicate expansion, but with high variability likely due to drying shrinkage near the surface when dry weather.

Thus, the tested concrete specimens contained sufficient impregnated silane to control ASR expansion at a depth of 2 mm. According to the results shown in Figure 8, when the exothermic peak area of the heat flow curve was larger than 300 µV·s/mg at 2 mm, expansion was controlled, and when the area was smaller than 160 µV·s/mg at 2 mm, expansion progressed.

Figures 13 and 14 show two exothermic peaks, from which it may be inferred that some silane did not react with the cement paste powder. Therefore, peaks of reacted silane (320 ~ 370ºC) and non-reacted silane (250ºC) appeared. However, for the lower mixing ratios of 1:0.1 and 1:0.2, silane appears to have completely reacted (Figures 11 and 12).

From Figure 16, the higher the content of silane, the higher the exothermic peak area, and the relationship is approximately proportional. Indeed, a good linear relationship exists between the exothermic peak area (x) and the content of silane (y), which corresponds to the following regression equation:

$$y = 8,660 \ x \qquad\qquad\qquad \text{Eq. (1)}$$

where:
y = exothermic peak area (µV·s/mg),  and
x = silane content (silane / cement paste powder + silane, by weight)

In experiment No. 1, the amount of silane needed to control the expansion of the cores and corresponding to a peak area of 300 µV·s/mg at a depth of 2 mm is equal to 0.0346(silan content), based on above relationship, and the one corresponding to a peak area of 160 µV·s/mg at a depth of 2 mm is equal to 0.0185.

Using the results described above, the amount of impregnated silane can be calculated. The following assumptions are made:

(1)     A sample obtained from the core surface down to 5 mm contains no coarse aggregate but just mortar, which is composed of water, cement, and fine aggregate in relative proportions of 169 kg/m³, 338 kg/m³, and 823 kg/m³, respectively, based on Table 1.

(2)     In these samples, the fine aggregate does not affect the differential thermal analysis data. (As shown in Figure 3, there is no exothermic peak.)

(3)     The impregnated total depth of silane is assumed to be 5 mm, as shown in Figure 7, and the average exothermic peak area is assumed to be 248 µV·s/mg within the 5 mm surface layer of concrete.

When the average exothermic peak area of 248 µV·s/mg is the value for mortar, the value for cement paste becomes 651 µV·s/mg (=248×[169+338+823]/[169+338]), and the calculated silane content is 0.0752.

On the other hand, the weight of cement paste in the surface layer of concrete down to a depth of 5 mm is calculated as it follows:

$$(169+338) \text{ kg/m}^3 \times 0.005 \text{ m} = 2.54 \text{ kg/m}^2 \text{ of exposed concrete surface.}$$

Assuming the impregnated silane as s, the following relation holds:

$$0.0752 = s / (2.54 + s),$$

and we obtain

$$s = 0.\,206 \text{ kg/ m}^2 \text{ of exposed concrete surface.}$$

As shown in Table 2, the standard weight of applied silane in experiment 1 is:
$$0.12 \text{ kg/m}^2 \times 2 \text{ layers} = 0.24 \text{ kg/m}^2,$$

The measured value thus corresponds to 86% of the design value. The calculated values of the impregnated silane are based on assumptions, which appear to be valid. By additional experimentation and investigation, it seems possible to improve the precision of the estimation of impregnated silane in concrete by differential thermal analysis.

In the future, it will be necessary to confirm the validity of the method of estimating the depth and amount of silane by differential thermal analysis, by applying the method to concrete specimens impregnated with a certain amount of silane. In addition, the reacted compound formed by reaction between cement paste and silane has to be identified.

## 5     CONCLUSIONS

The following results were obtained in the present study:

(1)     It is possible to estimate the impregnation depth of silane by differential thermal analysis (TG-DTA) of powder samples taken at different depths in concrete, based on the presence of a characteristic exothermic peak at 320 ~ 370ºC.

(2)     According to the results obtained, the exothermic peak area of the heat flow curve corresponding to the required amount of impregnated silane to control the expansion of concrete ranged from  160 ~ 300 µV·s/mg at a depth of 2 mm.

(3)     A good linear relationship was confirmed between the exothermic peak area and the content of silane within a practical range. Thus, calculation of the amount of impregnated silane by comparing the differential thermal analysis data of test specimens with data of control specimens containing a known amount of silane appears to be possible.

## 6     REFERENCES

[1]     Matsumoto, S, Sasaki, K, Kanjyo, N, Okuo, M, and Goto, T (2006): Impregnation depth of silane penetration system and its effect on ASR expansion. Upgrade Symposium of Repair and Strengthening of Concrete Structure (6): 139-146.

[2]     Matsumoto, S, Yamaguchi, Y, and Nakaue, A (2002): Results of long term measurement of surface treatment system for controlling ASR. Upgrade Symposium of Repair and Strengthening of Concrete Structure (2): 29-34.

TABLE 1: Mix proportion of concrete used

| Max.size of aggregates (mm) | Slump (mm) | W/C (%) | Air Content (%) | Sand ratio (%) | Unit weight (kg/m³) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Water | Cement | Sand | Gravel | Admixture |
| 20 | 80 | 50 | 3 | 46 | 169 | 338 | 823 | 949 | 845ml |
| Reactive aggregate : Bronzite Andesite, NaCl was added as total alkali equal to 9 kg/m³ of Na2Oe | | | | | | | | | |

TABLE 2: Applied surface treatment system

| Coat | Material | Quantity (kg/m²) |
|---|---|---|
| Bottom coat | reactive silane | 0.12 |
| Bottom coat | (alkyl alkoxy silane : 40%, isopropyl alcohol+ethanol : 60%) | 0.12 |
| Middle coat | | 0.70 |
| Middle coat | polymer cement-based, flexible coating material for acrylic resin-based emulsions | 0.70 |
| Middle coat | | 0.70 |
| Top coat | top-coating material for acrylic resin-based emulsions | 0.10 |
| Top coat | | 0.10 |

TABLE 3: Samples for differential thermal analysis

| Core No. | Sampling depth (mm) | | | | Total depth (mm) | Number of samples |
|---|---|---|---|---|---|---|
| | 2.0 | 3.0 | 4.0 | 5.0 | | |
| 1 | ○ | ○ | ○ | | 4.0 | 6 |
| 2 | ○ | | | | 2.0 | 2 |
| 3 | ○ | ○ | | | 3.0 | 4 |
| 4 | ○ | ○ | ○ | ○ | 5.0 | 8 |

TABLE 4: Result of DTA (Exothermic peak area of heat flow curve)

| Mixing rate silane/cement | Content silane/ (silane+ cement) | Exothermic peek area (μV·s/mg) | | | | | | | | Total |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Peak at around 250°C | | | | Peak at around 330°C | | | | |
| | | (1) | (2) | (3) | Ave. | (1) | (2) | (3) | Ave. | |
| 1:0.1 (0.1) | 0.09 | — | — | — | — | 676 | 690 | 740 | 702 | 702 |
| 1:0.2 (0.2) | 0.17 | — | — | — | — | 1,180 | 1,629 | 1,662 | 1,490 | 1,490 |
| 1:0.5 (0.5) | 0.33 | 247 | 229 | 224 | 233 | 2,619 | 2,453 | 2,509 | 2,527 | 2,760 |
| 1:1 (1.0) | 0.50 | 106 | 111 | 98 | 105 | 3,725 | 3,725 | 3,749 | 3,733 | 3,838 |

1. Casting specimen with reactive aggregate ( 100 × 100 × 400 mm )

2. Accelerated curing ( 28 days, 40°C, R.H.100% )

3. Treatment of surface

4. Curing in room ( one week )

5. Outdoor exposure ( five years )

6. Removing of surface layers ( PCM and acrylic resin)

7. Outdoor exposure ( 9 years )

8. Drilling of cores

Specimen without surface layer ( 100 × 100 × 400 mm )

Drilled cores (68 × 100 mm)

No.1　No.2　No.3　No.4

9. Grinding surface, sampling and differential thermal analysis of the samples

Grinding surface ( 1-mm step )

Differential thermal analysis

No.1 4.0 mm Grinding depth　No.2 2.0 mm Grinding depth　No.3 3.0 mm Grinding depth　No.4 5.0 mm Grinding depth

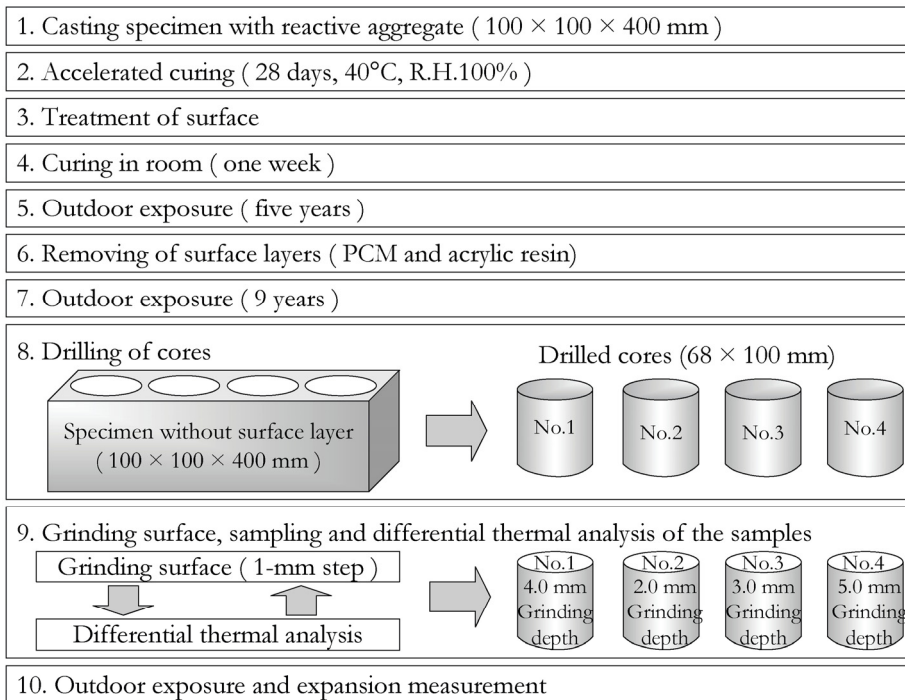10. Outdoor exposure and expansion measurement
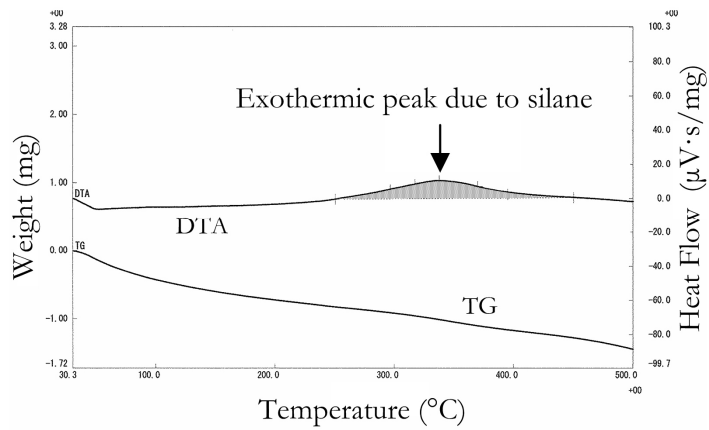
Figure 1: Flow chart of experiment 1

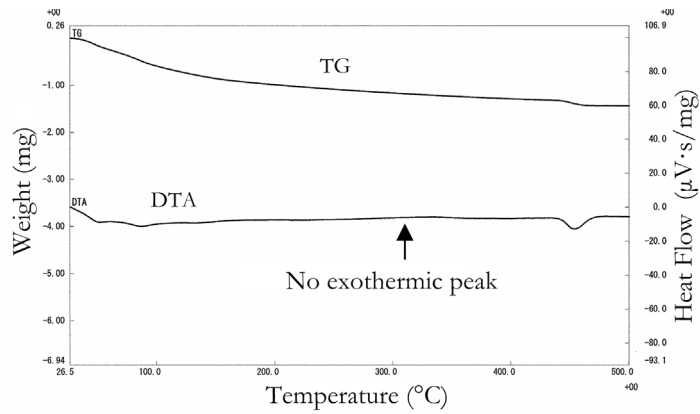Figure 2: Result of TG-DTA of a concrete sample containing silane

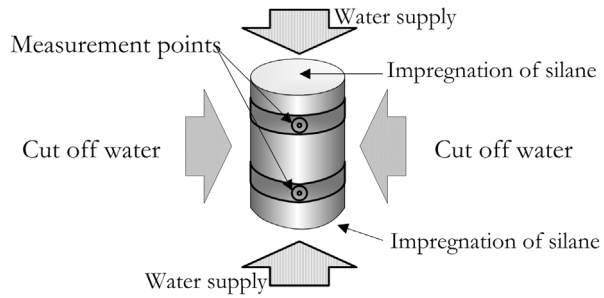Figure 3: Result of TG-DTA of a concrete sample containing no silane

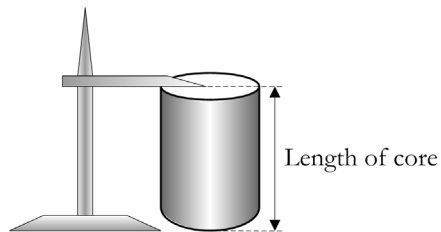Figure 4: Core specimen and measurement with a contact gauge

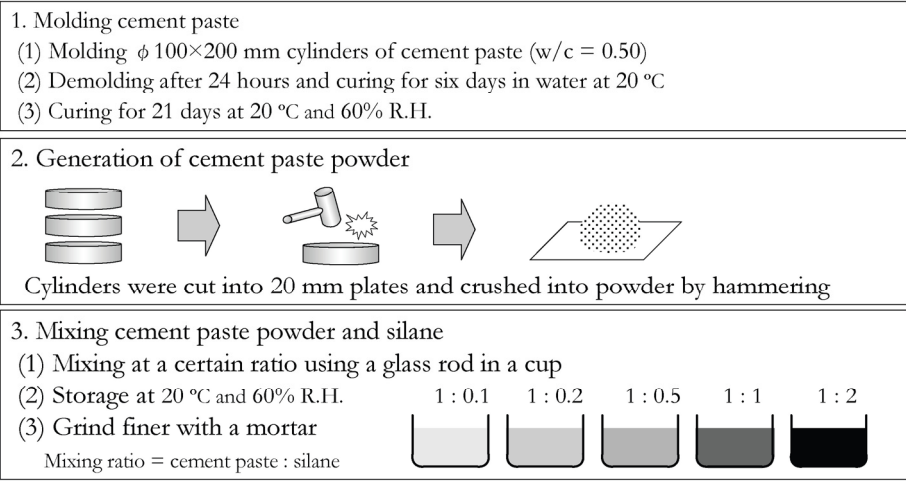Figure 5: Length measurement of cores with a height gauge

1. Molding cement paste
 (1) Molding φ100×200 mm cylinders of cement paste (w/c = 0.50)
 (2) Demolding after 24 hours and curing for six days in water at 20 ℃
 (3) Curing for 21 days at 20 ℃ and 60% R.H.

2. Generation of cement paste powder

Cylinders were cut into 20 mm plates and crushed into powder by hammering

3. Mixing cement paste powder and silane
 (1) Mixing at a certain ratio using a glass rod in a cup
 (2) Storage at 20 ℃ and 60% R.H.       1 : 0.1    1 : 0.2    1 : 0.5    1 : 1    1 : 2
 (3) Grind finer with a mortar
    Mixing ratio = cement paste : silane

Figure 6: Preparation of cement paste/silane mix (experiment 2)
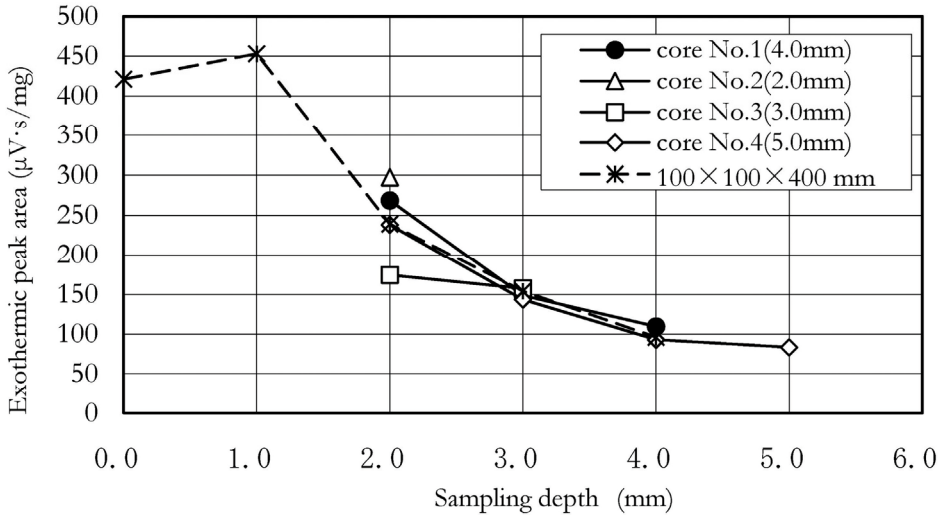


Figure 7: Relationship between sampling depth and exothermic peak area
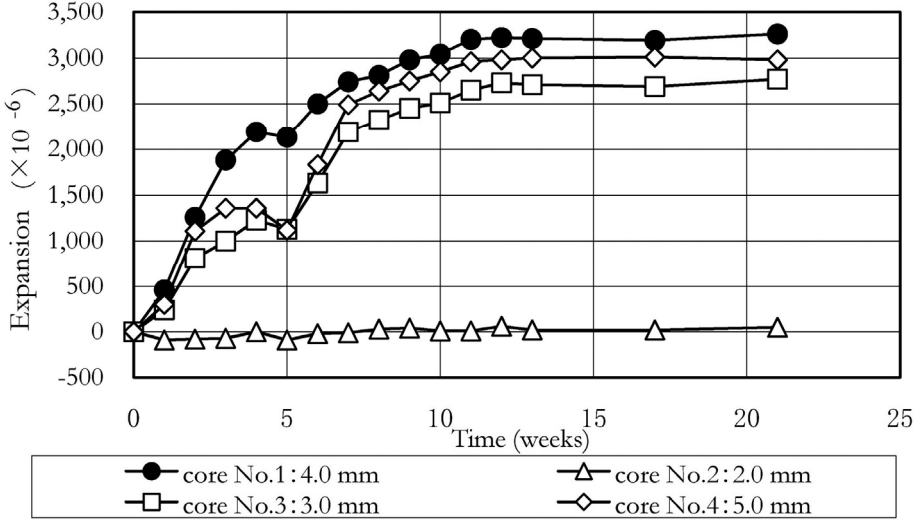


Figure 8: Expansion of cores (contact gauge method)
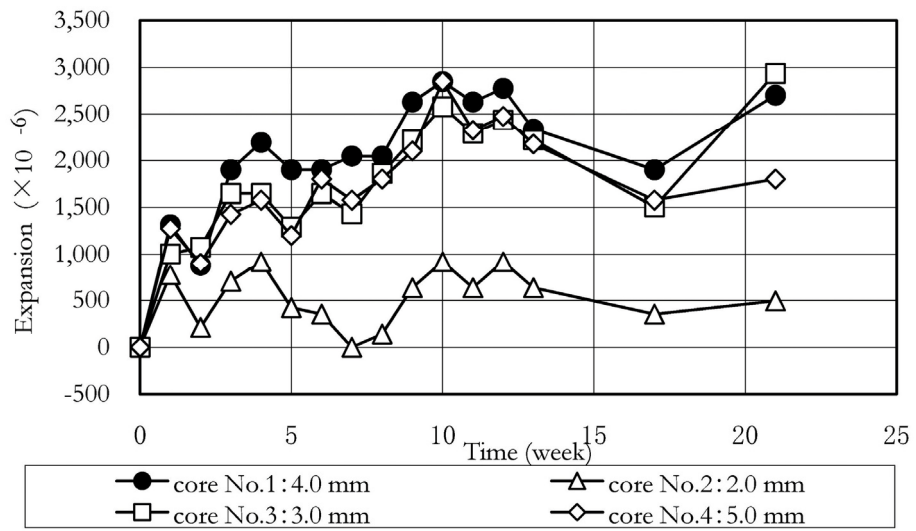
Figure 9: Expansion of cores (height gauge method)



| 1 : 0.2 | 1 : 0.5 | 1 : 1 | 1 : 2 |
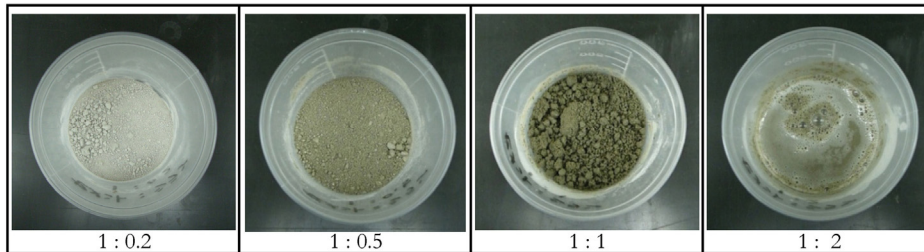
Figure 10: Dry mixtures of cement paste powder and silane
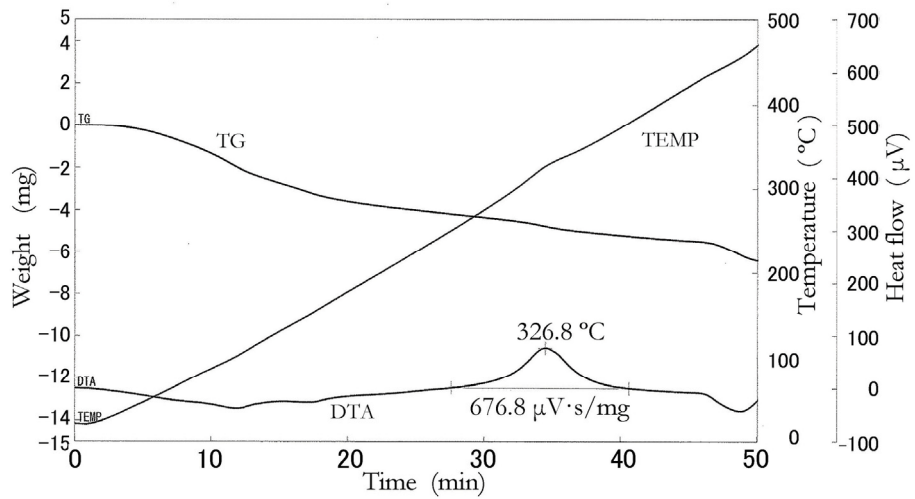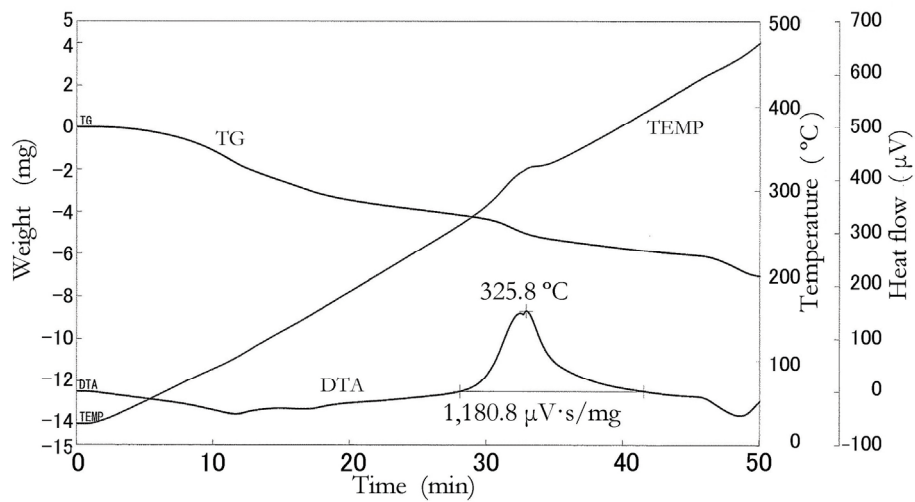


Figure 11: Result of DTA (1:0.1: subsample 1)

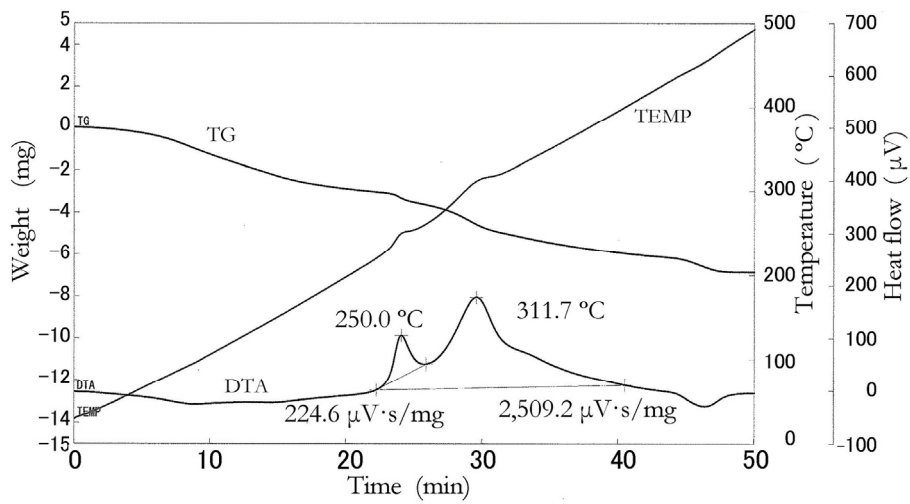Figure 12: Result of DTA (1:0.2: subsample 2)
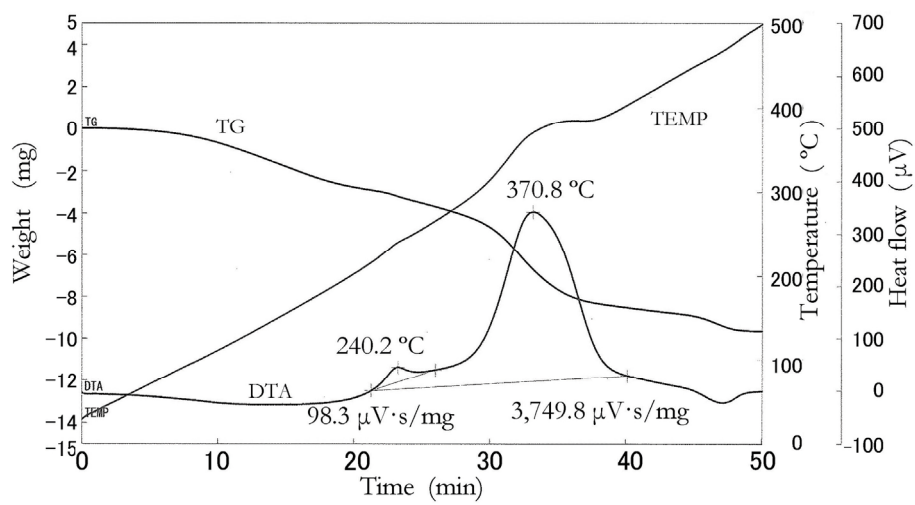
Figure 13: Result of DTA (1:0.5: subsample 3)

Figure 14: Result of DTA (1:1: subsample 4)

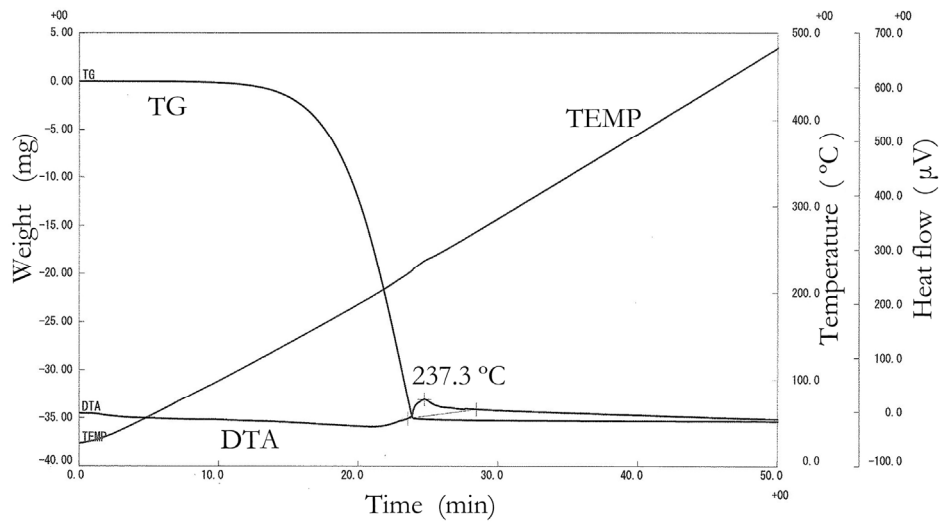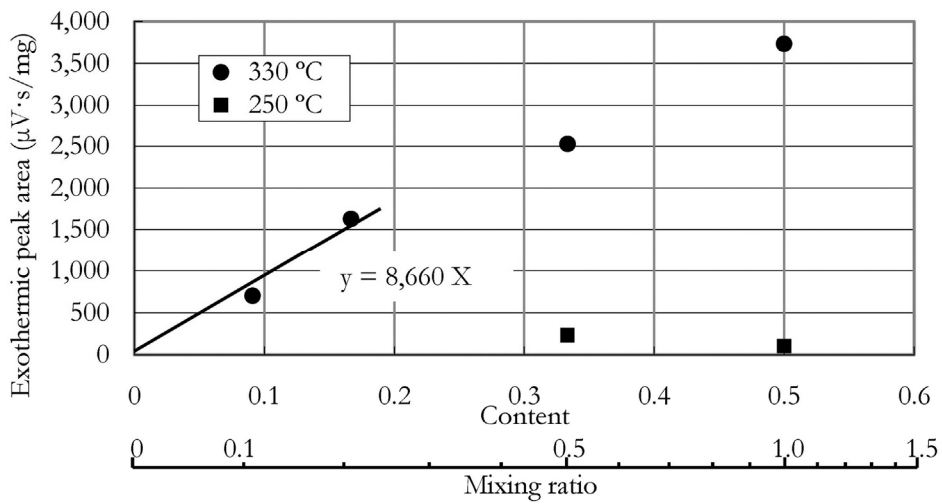Figure 15: Result of DTA (enriched silane)



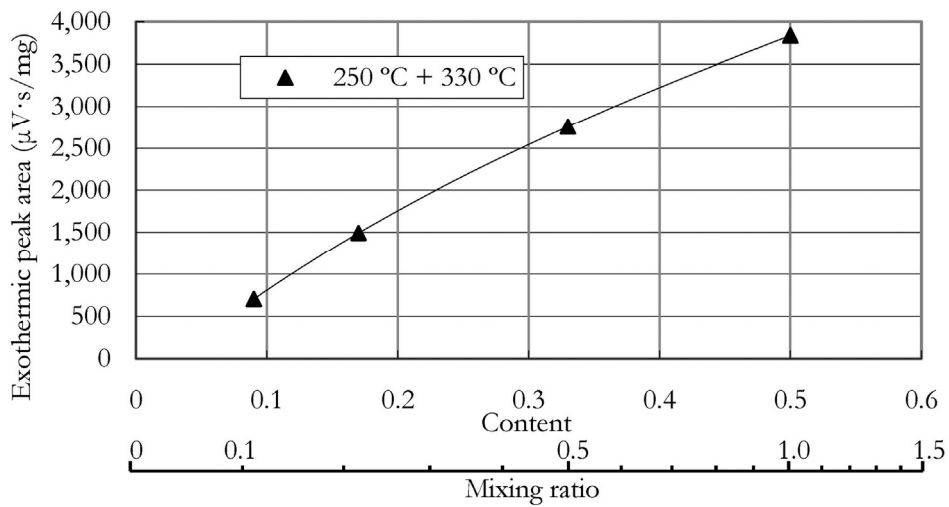Figure 16: Relationship between silane content and exothermic peak area



Figure 17: Relationship between silane content and exothermic peak area