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# EFFECTS OF CHLORIDE CONTENT ON THERMAL PROPERTIES OF CONCRETE

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**ABSTRACT:** The thermal properties of cement-based materials have gained more attention not only for the thermal analysis but also for the application of Non-Destructive Tests for building, bridge and other structures. Presence of chloride ions in pore structure was also found to affect thermal properties of concrete. This paper aims to study effects of chloride content on thermal properties of concrete. Specimens were submerged in sodium chloride solution for different period of time. Then, they were subjected to the heating test. It was found out that temperature of specimens with presence of chloride ions in pore solution increased faster compared to specimens without chloride contaminations. As the amount of chloride content in pore structure increased, concrete temperature also rose faster. The results obtained from this study can be used to accurately estimate thermal properties of concrete so that thermal analysis and application of Non-Destructive Tests such as Infrared Thermography can be effectively implemented.

*Keywords: Chloride, Thermal properties, Specific heat, Temperature*

## 1. INTRODUCTION

The thermal behavior of cement-based materials, whether they are mass concrete, conventional concrete or lightweight concrete, has gained more attention not only for the thermal analysis but also for the application of Non-Destructive Tests for building, bridge and other structures. Particularly, in attempt to know the ability of generating, retaining and conducting the heat inside concrete, the thermal properties are required. Since concrete is a compound of many materials, thus, its thermal properties is computed based on the volumetric fraction and the thermal properties of those compound materials respectively [1]. Table 1 shows the thermal properties of materials [2-6]. According to Neville [7], the specific heat of concrete has little effect by the mineralogical character of aggregate, but mainly depend on the amount of moisture content. Schutter and Taerwe [8] showed that the specific heat of harden cement paste made with blast furnace and slag cement decreases linearly with the degree of hydration. Xu and Chung [9] found out that with silica fume, the specific heat of cement paste increases about 7% while sand addition decreases it by approximately 13%. The fact is that sand particle is relatively larger and its specific heat is lower than silica fume. Another recent study investigated the thermal properties of fly ash concrete [1]. The results showed that fly ash replacement results in high specific heat at young age but decreases in later age due to pozzolanic reaction. Choktaweekarn [1] also proposed that the concrete with different mix proportion will result in different thermal properties.

In term of Non-Destructive Tests, Infrared Thermography was developed to detect defects beneath concrete which is mainly based on the different thermal properties of concrete and investigated defects during the process of heating and cooling. To effectively study this application, the thermal properties of concrete, such as specific heat and thermal conductivity, will be highly taken into consideration.

Obviously, all cement-based material is subjected to deterioration and also lead to the change of it properties. These deterioration are results of many mechanisms. A present literature review also showed that in term of chemical phenomenon, chlorides ions can be transported into concrete by the force of diffusion, capillary, ion adsorption and hydraulic pressure. Plus, the movement of chloride in concrete is very vital since it can interact and change the integrity of concrete structure [10]. In marine zone, reinforced concrete structure will have high risk suffering to chloride attack. The presence of chloride ions in pore structure and its effect to the thermal behavior of concrete still have not been studied. Thus, in actual structure, chloride content in concrete have to be highly considered for the long term thermal analysis. Checking the effect of chloride content on the thermal behavior of reinforced concrete must be carried out. This paper aims to study effects of chloride content on thermal properties of concrete.

Table 1 The thermal properties of different materials

| Materials | Thermal Conductivity (w/m.°C) | Specific Heat (J/kg. °C) | Ref. |
|---|---|---|---|
| Quartz Sand | 3.49 | 0.19 | [3] |
| Lime stone | 2.56 | 0.2 | [4] |
| Water | 0.593 | 1 | [3] |
| Sea water | 0.596 | 0.956 | [4]-[5] |
| Cement | 1.55 | 0.18 | [6] |

## 2. METHODOLOGY

### 2.1 Specimens

This study was interested on Ordinary Portland Cement concrete with different mix proportions. The water to binder ratio was fixed to 0.4 and 0.6. Rectangular reinforced concrete specimen of dimension 100mm×100mm×400mm were prepared with deformed steel bar of diameter 16mm, as shown in Fig.1.

To effectively investigate the mechanism of temperature inside concrete, thermocouples type k were attached at different position and depths from the surface (10mm, 20mm, 45mm & 75mm). After casting the concrete for 24 hours, all specimens were removed from the mold and immersed in curing tank under saturated condition for 28 days before the test. Two types of specimens (A & B) were produced with the same property for the experimental test. Specimen type A was used as a controlled specimen without being submerged in sodium chloride solution while specimen type B was used to induce chloride diffusion at different time of submersion.

Table 2 shows the properties of tested specimens and the different time of chloride submersion.

In this study, the effect of moisture to the chloride diffusion and heat transfer in concrete was taken into consideration. Specimen was kept fully saturated during chloride submersion test and saturated surface dried condition during heating and cooling test.

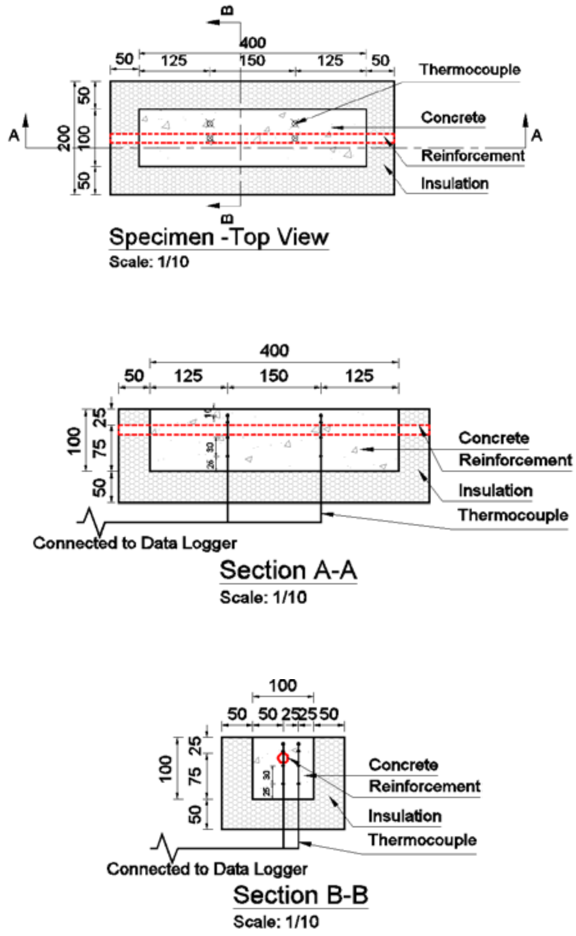


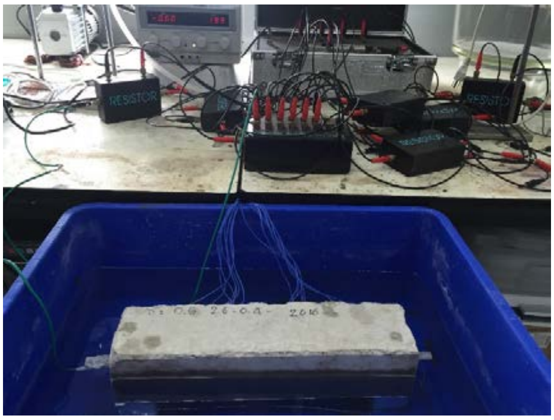

Fig.1 Shape of tested specimen (Unit: mm)

Table 2 Tested specimens

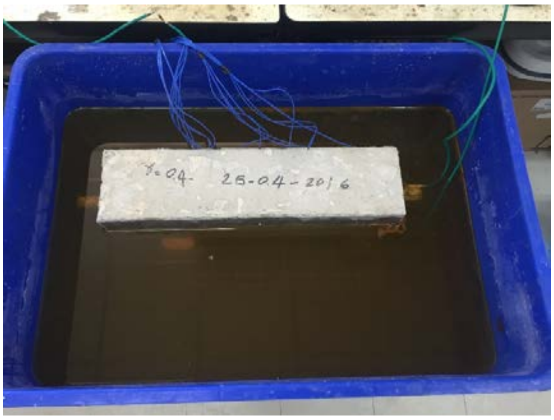
| (w/b) | Specimen type | Geometry (mm) | Cover depth (mm) | Rebar diameter (mm) | Submersion time (hours) |
|---|---|---|---|---|---|
| 0.4 | A | 100×100×400 | 25 | DB16 | 0 (controlled) |
| | B | 100×100×400 | 25 | DB16 | 2.5 |
| | | | | | 5 |
| | | | | | 10 |
| | | | | | 84 |
| 0.6 | A | 100×100×400 | 25 | DB16 | 0 (controlled) |
| | B | 100×100×400 | 25 | DB16 | 2.5 |
| | | | | | 5 |
| | | | | | 10 |
| | | | | | 84 |

### 2.2 Electrochemical Method for Chloride Penetration Acceleration

An electrochemical method for chloride penetration acceleration was adopted to push chloride ions i concrete. This electrochemical method consists of a DC power source, a counter electrode and an electrolyte. During the test, the specimen was partially submerged in a 5% of sodium chloride solution with the applied current intensity of 850 $\mu A/cm^2$. Then a positive electric wire of DC source is connected to the one end of reinforcing steel bar and acted as anode while the negative electric wire is connected to the stainless steel and acted as cathode (see Fig.2).



a)



b)

Fig.2 Electrochemical method for chloride penetration acceleration, a). Specimen before testing, b). Specimen after testing

### 2.3 Infrared Heating Test

To evaluate the different thermal behavior, two specimens (controlled (A) & submerged (B)) with fully saturated condition were subjected to the same heat source and heating time. More importantly, to simulate the real structural condition of one directional heat flow, five boundary surface of tested specimens were controlled by insulators to block the heat flow and only the top surface of specimen exposed to the heat flux as shown in Fig.1.

The testing was carried out in a laboratory room with the controlled ambient temperature at 34℃. The external thermal excitation was operated with a commercial Infrared heater with 1000W of heating power, 17mm of diameter and 300mm of length. The distance from the surface of tested specimens and Infrared heater was fixed to 0.4m. A test was conducted for 8 hours including heating process for 4 hours and cooling process for another 4 hours.

Fig. 3 shows the completed process of the test. Before the heating test, tested specimens were pre-conditioned to maintain the uniform temperature throughout specimen. To start the test, the infrared heater was switched on as to provide the heat radiation to the concrete surface. After finished the heating process, the heater was turned off and moved away to avoid any additional heat radiations during the cooling down period. From the attached thermocouple at different positions and depths, the mechanism of temperature inside concrete specimens were recorded by using data logger every one minute.

### 2.4 Total Chloride Content Measurement

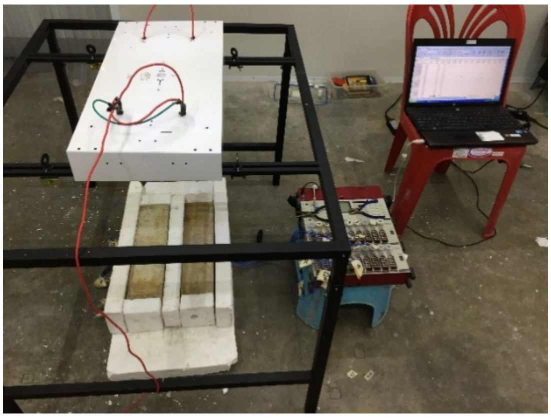
After finished the heating tests, the total chloride content in concrete was conducted by potentiometric titration with silver nitrate ($AgNO_3$), which is based on ASTM C1552 [11]. The samples were extracted from the specimens at every 1cm depth till 5cm depth from surface. The obtained results of total chloride content of specimens after 84 hours submersion for both mix proportion were showed in Table 3. By using Fick's second law and the results of the measurement, the chloride diffusion coefficient, $D_a$ , and chloride surface concentration, $C_s$, can be defined as shown in Eq. (1) .

$$C_{(x,t)} = (C_s - C_i)\left[1 - erf\left(\frac{x}{2\sqrt{D_a \times t}}\right)\right] + C_i \qquad (1)$$

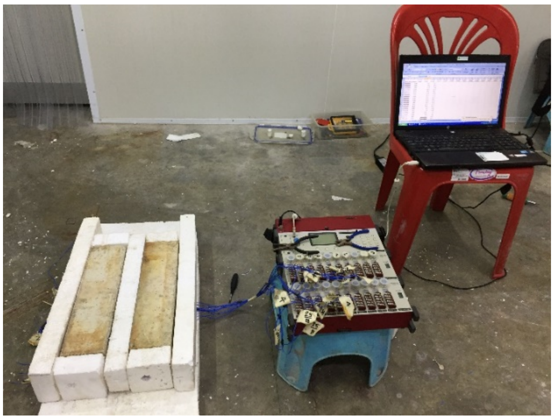
Where $C_{(x,t)}$ is the concentration of chloride at time t and at distance x from the surface [% by weight of concrete]. $C_s$ is the chloride surface concentration and the initial chloride concentration, $C_i$, in this study was assumed to be 0. $D_a$ is chloride diffusion coefficient [$cm^2$/year], x is the distance from concrete surface [cm] and t is exposure time [year].

## 3. RESULTS AND DISCUSSION

Regarding the obtained value of chloride diffusion coefficient, $D_a$, and chloride surface concentration, $C_s$, corresponded to both mix proportions, the percentage of total chloride content at each submersion time were predicted using Fick's second law again as shown in Fig. 4. All results clearly showed that the chloride penetration profile increased as the water to binder ratio increased from 0.40 to 0.60. This is because the higher water to binder ratio generated the greater porosity which leads to greater permeability of chloride ions. Please be noted that at the longest submersion time, 84 hours, chloride ion penetrated to the depth of 25mm and 35mm for concrete with w/b 0.40 and 0.60, respectively.



a)

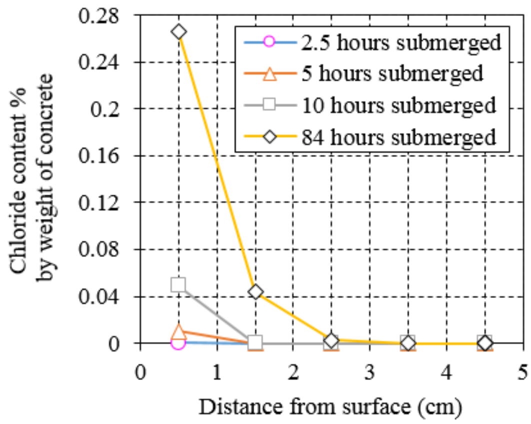


b)

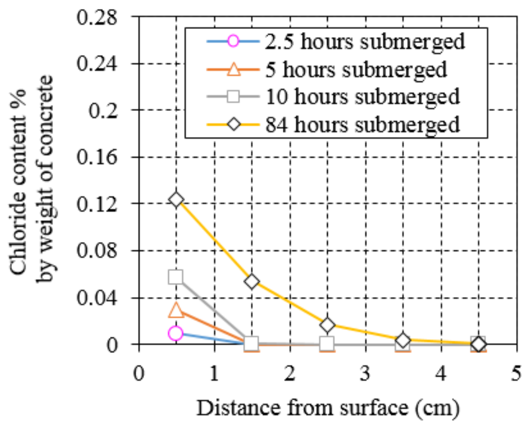
Fig. 3 Tested specimens, a). During heating process, b). During cooling process

Table 3 The measured total chloride concentration of specimen after 84 hours of submersion

| Measured total chloride concentration, c(x,t) [% by weight of concrete] | | |
|---|---|---|
| Depth [cm] | w/b=0.4 | w/b=0.6 |
| 1 | 0.12236 | 0.08622 |
| 2 | 0.01156 | 0.02720 |
| 3 | 0.00516 | 0.01141 |
| 4 | 0.00407 | 0.00969 |
| 5 | 0.00390 | 0.00784 |




a). w/b=0.4

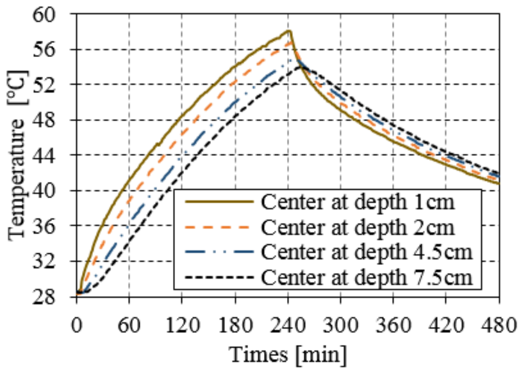



b). w/b=0.6

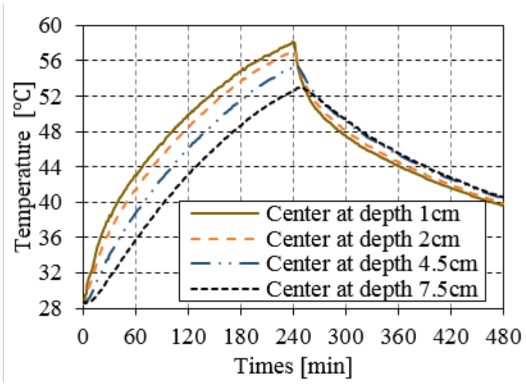
Fig. 4 The prediction of chloride profile of concrete with different submersion time

### 3.1 Effect of Chloride Contamination on Changing of Concrete Temperature

As the results obtained from the heating test, we preliminary observed that the temperature of both specimens started at about 28±0.2℃ (see Fig. 5) which is approximately uniformed since the tested specimens were pre-conditioned as mentioned above. Thus, the temperature profile of both controlled specimens and specimen submerged in sodium chloride solution can be compared properly. Fig. 5 shows absolute temperature of specimen with water to binder ratio 0.4 for two different time of submersion, 0 hour and 84 hours respectively. As observed, the temperature profile at each depth of both specimens tended to have the same tendency.




a). Controlled specimen (No submerged in chloride solution)




b). Specimen submerged in chloride solution for 84 hours

Fig. 5 The absolute temperature of specimen with w/b=0.4 at different time of submersion during the heating and cooling process

However, during the heating process, temperature of specimen submerged in NaCl solution increased faster compared to the controlled specimen as shown in Fig. 6. Since the specimen after 84 hours of submersion had higher amount of chloride content, plus the present of chloride ions in the pore structure in concrete reduce the pH of solution and then accelerate hydration [12]. Thus, its pore structure turned to be more solid and less liquid which is known as a good conductor with low specific heat compared to water.

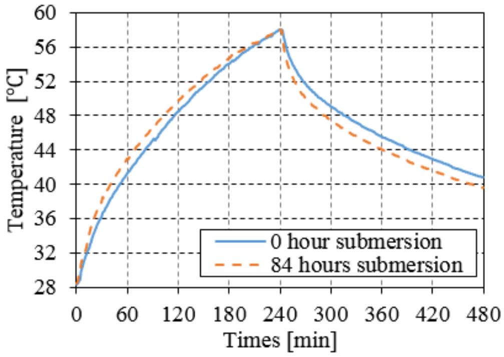
As expected, up to the time of 480 minutes, the temperature generation rise in specimen with the high amount of chloride content is higher than that of the controlled specimen. Fig. 6 compares the temperature profile of both specimens at each depth. Moreover, after 480 minutes, the cooling process stated, and the temperature also dropped. The results obtained, as showed in Fig. 6, the temperature of specimen after 84 hours submersion in NaCl decreased faster compared to the controlled specimen. Due to its low specific heat, it requires to release only a small amount of heat energy to decrease its temperature while the controlled specimen with higher specific heat requires higher heat energy released.

To be clear on the effect of chloride content to the temperature generation of concrete, a further investigation on different amount of chloride content by different time of submersion was also analyzed. Since it was expected that the chloride ions in pore structure reduces the specific heat of concrete, thus the higher amount of chloride content in concrete the lower specific heat it will be. The experimental test of specimens with a variation of submersion time in this study was carried out separately. Thus, the starting point of initial temperature of each specimen could be different. To avoid the effect of initial temperature and clearly observes how different amount of chloride content changed the temperature profile, the obtained data were used to analyze and plot the transient temperature rise curve, as shown in Eq. (2).

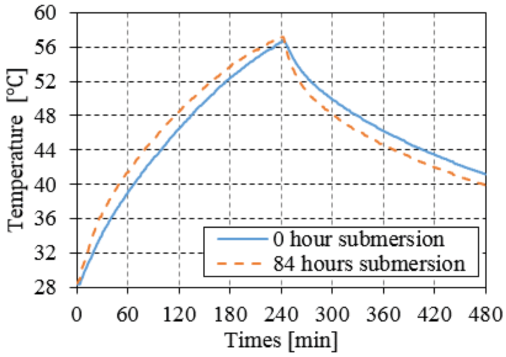
$$\Delta T = T(t) - T(t=0) \tag{2}$$

Where T(t) is the temperature at time t, and T(t=0) is the initial temperature at starting point of test.

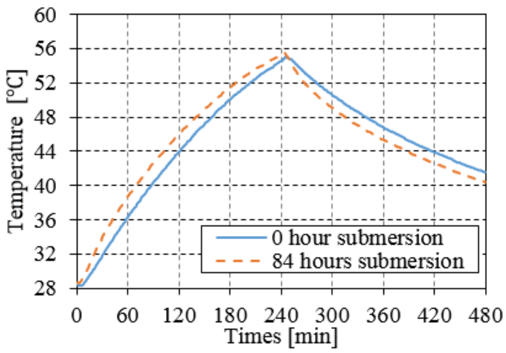
In Fig. 7, the temperature generations at depth 1cm of specimen with the same mixture but different time of submersion were plotted. This graph showed that within the longer time of specimen submerged in NaCl solution, its temperature rise is higher. According to Lizarazo and Claisse [13], it was found out that by using electrochemical methods, the amount of chloride content increases as the applied time gets longer (see in Fig. 4). Millero [14] stated that, at a certain temperature, the specific heat of water solution is lower as the percentage of chlorinity get higher.



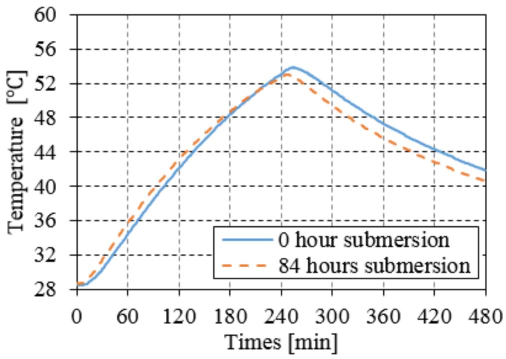

a). Temperature of concrete at depth 1cm




b). Temperature of concrete at depth 2cm



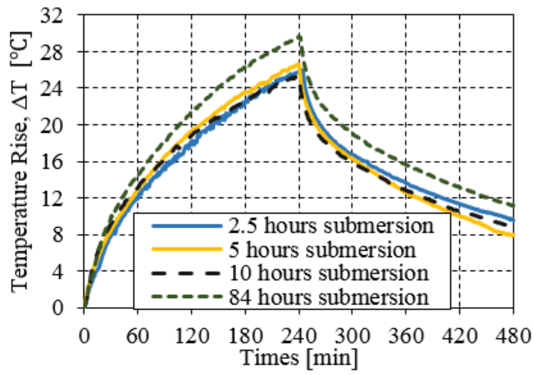

c). Temperature of concrete at depth 4.5cm



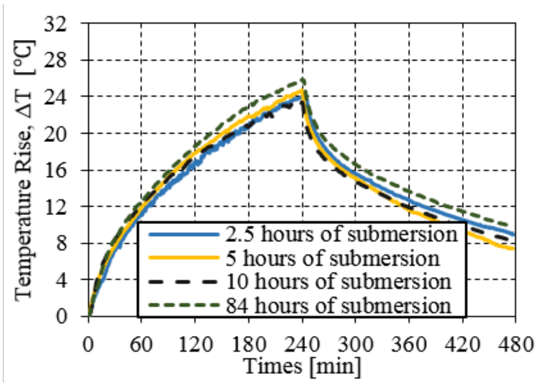

d). Temperature of concrete at depth 7.5cm

Fig. 6 The comparison of temperature of concrete between controlled specimen and specimen submerged in NaCl solution at each depth

When the amount of chloride ions in the pore media in concrete gets higher, it was expected that the specific heat of concrete reduces non proportionally to the amount of chloride concentration. Interestingly, the experimental results as shown in Fig. 7 are confirmed.




a). Temperature rise of specimen with w/b=0.4




b). Temperature rise of specimen with w/b=0.6

Fig. 7 The comparison of temperature rise of specimen with different time of submersion for the completed process of heating and cooling for both mixtures, w/b=0.4 & w/b=0.6

### 3.2 Effect of Water to Binder Ratio on Changing of Concrete Temperature

A proposed model to predicted the specific of concrete by Choktaweekarn [1] clarified that the water to binder ratio significantly affects the specific heat of concrete. Specifically, the predicted model estimates that for concrete with water to binder ratio w/b=0.4, its specific heat is approximately 814.75 $J/kg.$℃ while it is about 933.65 $J/kg$℃ for water to binder ratio w/b=0.6. The results of this study, showed in Fig. 8, verified with result of Choktaweekarn [1]. For the controlled specimens of both mixture, the obtained results clearly showed that due to the low specific heat of water to binder ration w/b=0.4, its temperature increased proportionally higher than that of water to binder ration w/b=0.6. However, the results of total chloride content showed that the percentage of chloride concentration was higher corresponded to the increment of water to binder ratio. Due to the fact that w/b=0.6 produced a greater porosity of cementitious material and leaded to a high risk of chloride migration while w/b=0.4 reduced the pore size and consequently had a low permeability [15]. This behavior indicated that the specimen with higher amount of water to binder ratio should show greater effect of chloride to its specific heat. In contrast, in Fig. 7, the obtained results proved that even though the specimen with water to binder ratio w/b=0.6 had higher percentage of chloride concentration than that of specimen with water to binder ratio w/b=0.4, but temperature rise of specimen with w/b=0.4 still consistently greater than specimen with w/b=0.6. These results showed that high w/b ratio concrete has initially high specific heat. Increasing of chloride content lightly affected to specific heat and temperature rise.

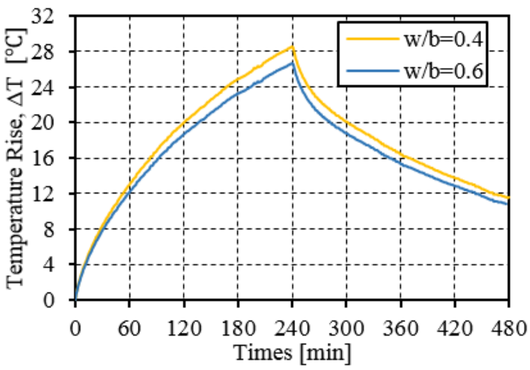



Fig. 8 The comparison of temperature rise of controlled specimen for both water to binder ratio w/=0.4 and w/b=0.6

## 4. CONCLUSIONS

The thermal properties of a long term concrete structure are affected by the amount of chloride content in cementitious materials. It was found out that higher percentage of chloride concentration leaded to the faster temperature rise due to the fact that chloride contamination decreases the specific heat. However, the effects seem to be smaller in case of high water to binder ratio concrete.

## 5. ACKNOWLEDGEMENTS

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