TriDurLE

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Durability of Transverse Sawcut Joints in Mid-Western Jointed Concrete Pavements

Final Report

by
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Executive Summary

This research aims to investigate Calcium Oxychloride (CAOXY) formation in concrete pavement joints due to the interaction between Calcium Hydroxide ($Ca(OH)_2$) and chloride ions (Cl^-) from deicing salts, notably Calcium Chloride ($CaCl_2$). Common in the US Midwest, CAOXY induces joint deterioration in heavily deiced concrete pavements. Unlike previous studies, our focus is on understanding the combined effects of key parameters, including water-to-cementitious ratio (W/CM), salt solution concentration, age, and temperature, on CAOXY formation. The primary goal is to develop an energy-based model, emphasizing temperature and salt concentration. Visual observation, analysis, and Thermogravimetric Analysis (TGA) reveal temperature, along with salt concentration, as critical factors causing harmful CAOXY formation and joint deterioration in concrete pavement. The findings of this study are expected to be useful for developing strategies to reduce the CAOXY formation and prevent the deterioration of concrete pavement joints, especially in regions where deicers are frequently used.

Chapter 1. Introduction[*]

1.1 Problem Statement

Jointed concrete pavements are constructed with transverse joints, achieved by saw cutting notches into the pavement surface. This technique primarily serves to manage the impact of concrete shrinkage due to drying, thus regulating the formation and positioning of transverse cracks. Subsequently, these notches are expanded to accommodate joint sealant materials, crucial for bonding to the joint sidewalls and preventing infiltration. The absence of a secure bond poses the risk of infiltration and potential saturation of surrounding concrete, particularly problematic for pavements in freeze-thaw environments. Our research endeavors are concentrated on addressing the vulnerability of such pavements to deicing chemicals.

In cold regions of North America, the presence of ice on pavement surfaces necessitates the application of deicing salts, including sodium chloride (NaCl), calcium chloride ($CaCl_2$), magnesium chloride ($MgCl_2$), potassium acetate, sodium acetate, and potassium formate [1]. Furthermore, the durability of concrete pavements is significantly compromised by damage from freezing and thawing, especially in areas with high fluid saturation [2]. This damage is deteriorated by a chemical reaction between chloride-based deicers and calcium hydroxide (CH) in concrete, resulting in the formation of calcium oxychloride (CAOXY), a common problem in concrete pavements located in midwestern parts of the US [3].

1.2 Objectives

Investigate CAOXY formation under different conditions: Utilizing TGA tests, the effects of different parameters including Temperature, aging, W/C ration, as well as the salt solution concentration on CAOXY formation leading to detrimental effects on the concrete pavements can be investigated.

Determine of expansion in cement pastes: To investigate the effects of the aforementioned parameters on the expansion of cement paste samples, strain gauges can be used over a period of time of exposing the samples to deicing salt solutions.

Visual observation: To verify the data from the aforementioned tests and see how severe the effects of deicing salt solution under different conditions are, visual observation can be used.

Analyze TGA test, and strain gauge results: By analyzing the obtained data, the importance of each parameter on CAOXY formation and deterioration in concrete pavements can be derived which may lead to find a way to mitigate the CAOXY formation, and having long lasting pavements with better performances.

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[*] Babavalian, A. et al., Investigation of Deicing Salt Solution in Process of Calcium Oxychloride Formation in Cement Paste, International Conference on Transportation and Development 2024. https://doi.org/10.1061/9780784485538.033

1.3 Report Overview

This research aims to investigate Calcium Oxychloride (CAOXY) formation in concrete pavement joints due to the interaction between Calcium Hydroxide ($Ca(OH)_2$) and chloride ions (Cl^-) from deicing salts, notably Calcium Chloride ($CaCl_2$). Common in the US Midwest, CAOXY induces joint deterioration in heavily deiced concrete pavements. Unlike previous studies, our focus is on understanding the combined effects of key parameters, including water-to-cementitious ratio (W/CM), salt solution concentration, age, and temperature, on CAOXY formation. The primary goal is to develop an energy-based model, emphasizing temperature and salt concentration. Visual observation, analysis, and Thermogravimetric Analysis (TGA) reveal temperature, along with salt concentration, as critical factors causing harmful CAOXY formation and joint deterioration in concrete pavement. The findings of this study are expected to be useful for developing strategies to reduce the CAOXY formation and prevent the deterioration of concrete pavement joints, especially in regions where deicers are frequently used.

Chapter 2. Literature Review[†]

This literature review mainly summarizes the previous studies conducted on CAOXY formation as a result of application of deicing materials on concrete, their effects, and the applicable tests for investigation, as well as different deicing salts.

Deicing Salts

The traditional method for winter road maintenance, especially on unpaved roads or areas where deicers are impractical, involves the direct application of sand onto pavement surfaces [4, 5]. Nonetheless, the utilization of sand as a traction control agent has diminished in many states due to its rapid dispersion by vehicles and issues associated with drain obstruction [6]. Presently, the predominant deicing agents in use encompass sodium chloride (NaCl), calcium chloride ($CaCl_2$), and magnesium chloride ($MgCl_2$). While calcium chloride and magnesium chloride are comparatively more expensive, they exhibit effectiveness at significantly lower temperatures [4-6].

Among these three different kinds of deicing salts, sodium chloride (NaCl), calcium chloride ($CaCl_2$), and magnesium chloride ($MgCl_2$), the most commonly used one is $CaCl_2$. Moreover, the AASHTO T365-20 recommends the use of regent grade $CaCl_2$ to prepare a salt solution for laboratory experiments [7]. According to the report, it has been noted that sodium chloride may not affect CAOXY formation significantly [8]. Therefore, calcium chloride can be selected as a preferred deicing salt for experimental studies.

Effects of Deicing Salts on Concrete's Durability

Concrete pavement undergoes repeated F/T cycles in regions requiring snow removal, leading to two primary types of deterioration including physical deterioration, such as concrete cracking due to expansion, and the second type results from CAOXY formation as a product of the chemical reactions between chloride ions found in anti-icing solutions and components of hardened concrete [9]. Commonly accepted is the role of higher permeability and porosity levels in concrete in contributing to chemical deterioration, often caused by the dissolution of calcium hydroxide from the concrete matrix. Although substantial progress has been made in comprehending the freezing behavior of porous materials exposed to deicing/anti-icing chemicals, certain aspects of the process remain unclear, necessitating further investigation to clarify the detrimental effects of such chemicals [10]. It is generally agreed that deterioration caused by deicing materials is primarily physical [11, 12]; but the significance of chemical mechanisms cannot be ignored. The combination of freezing/dissolving phenomena and deicing material application can lead to more severe deterioration compared to physical one. Furthermore, the concentration of deicers in the concrete plays a significant role in the pressures development generated during F/T cycles [6, 9, 10].

[†] Babavalian, A. et al., Investigation of Deicing Salt Solution in Process of Calcium Oxychloride Formation in Cement Paste, International Conference on Transportation and Development 2024. https://doi.org/10.1061/9780784485538.033

The findings of a study on the effects of concentrated brines, including magnesium chloride, calcium chloride, sodium chloride, and calcium magnesium acetate, on Portland cement concrete, showed significant evidence of chemical interactions between magnesium chloride and calcium chloride with hardened Portland cement paste, resulting in expansive cracking, increased permeability, and reducing compressive strength significantly [13]

seven sites were assessed in a field investigation conducted by the Wisconsin Department of Transportation, to determine the impact of deicing/anti-icing materials on concrete durability. Notably, these sites were at the county borders using different types of deicing/anti-icing materials with 8 different application rates. Comparing the sections, having same pavement structures, traffic level, construction histories, and climate conditions showed that counties using higher quantities of NaCl, $CaCl_2$, and $MgCl_2$ experienced faster concrete deterioration rates, and the deterioration type started as joint spalling leading to fully or partially replacing the slab [14].

Calcium Oxychloride Formation in Concrete Pavements

Calcium Oxychloride (CAOXY) formation leading to damages in pavements is typically observed in the joints and areas where the sealant failed and trapped water in the joint saturating the concrete with high amount of deicing salt concentrations. This damage can be seen as extensive concrete flaking, leading to the filling the concrete joints with flake [15]. It is premature and observed in numerous concrete pavements, frequently within the initial pavement service years; this damage is costly to repair.

Suraneni's research in 2017 was conducted on the relationship between CAOXY formation and deicing solution concentration and proportion. It was found that the reaction leading to CAOXY formation is controlled by Calcium Hydroxide at higher proportions of $CaCl_2$ solution (exceeding 20% in salt blends). Depending on the amount of CH in the paste, this switch can occur on different concentrations. Increasement in the $CaCl_2$ proportions leads to increasing the CAOXY formation as the Calcium Hydroxide content increases in the paste. Using the deicing salt blends with lower proportions of $CaCL_2$ can lead to less CAOXY formation, but the potential reduction in deicing performance at lower temperature, and public safety should be considered [16].

In the constructed pavements in Midwest which are commonly treated with deicing salts, frequent observations show deteriorated and spalled sections in and around around sawcut joints. Spalling damages exhibit the characteristics such as: regardless of the water source, longer period of concrete saturation leads to increasement of distress risk significantly; many distressed pavements show marginal air void systems; on these surfaces, a variety of potentially aggressive deicing salts may have been applied; and damage progresses rapidly once it. Initial signs of deterioration typically are observed as darkening or shadowing near the joints, likely because of the development of micro-cracks perpendicular to the joint. These cracks lead to water penetration, and therefore substantial material loss, as severe joint damage was revealed by coring the concrete pavement. However, it is probable that water which previously infiltrated and trapped within the joint is the water source leading to concrete saturation [17]. Exposure of concrete to water for a long time, if capillary pores become filled with water, may lead to saturated concrete. While water in capillary pores can be evaporated into the environment, freezing, particularly from previously infiltrated water which was trapped in the joint, for an extended time, prevents evaporation. Such saturation is more prevalent near joints, especially if in the case of the lack of sufficient bonding of joint sealants [18]. In the case of debonded joint sealants, water can directly infiltrate the joint. Particularly if the base layer is not design for water drainage, infiltrated moisture can remain trapped leading to remaining the joints full and exposed to water for a long period of time, maybe for months. This is likely a major factor contributing to reduce F/T durability of joints in concrete pavements which are exposed to freezing temperatures [17].

Common Experiments to Investigate Cementitious Materials Exposed to Deicing Salt

Different tests are commonly used to study the behavior of cementitious materials when exposed to deicing chemicals, including LT-DSC (Low-Temperature Differential Scanning Calorimetry), TGA (thermogravimetric analysis), and LGCC (Longitudinal Guarded Comparative Calorimetry). Each test yields different data; for instance, LT-DSC provides information on CAOXY formation levels, while TGA is useful to determine calcium hydroxide content, helping in estimation of potential amount of CAOXY which can be formed. Additionally, LGCC test is effective to determine the damage because of CAOXY formation. In research by Xiao et al. an investigation on the effects of different deicing salts (NaCl, $CaCl_2$, and $MgCl_2$) on concrete durability was conducted. It was found that higher concentration of deicing salts led to accelerated deterioration; also, early-stage joint spalling resulted in partial or full slab replacement. The use of calcium chloride, and magnesium chloride resulted in increasement of extensive cracking, penetrability, and reduced compressive strength. In the samples saturated in the solutions with more than 15% concentration at room temperature, cracking occurred, although this damage was not due to the freeze-thaw effects [19].

Qiao et al. investigated cement paste specimens containing fly ash exposed to $CaCl_2$ solution at temperatures of 5°C and 23°C. The salt solution was made using calcium chloride dihydrate dissolved in deionized water. In order to measure the mass loss of the cement paste after 7-day exposure to the solution, TGA tests were conducted. The temperature cycle mentioned in AASHTO T 365-20 was used to measure the heat flow by LT-DSC tests. CAOXY formation was not observed in samples containing 40and 60 percent fly ash. However, samples exposed to $CaCl_2$ solution exhibited significant amount of temperature-dependent chloride binding by C-S-H (for example, 19.8-70.8% of total binding); using fly ash led to changes chloride binding by C-S-H. A linear increasement in chloride binding by C-S-H was observed by reduction in the pH amount of the solution [20].

Farnam et al. studied on the freeze-thaw behavior of cementitious materials exposed to NaCl solutions with various concentrations including zero, 5, 15, and 23.3 percent. Conducted LT-DSC tests observed an unexpected phase change at zero to 8°C in the specimens which were made using hydrated cement powder, and exposed to high-concentration NaCl solution [21].

Jones et al. studied on the deterioration in concrete materials due to the CAOXY formation as a result of exposure to 30% calcium chloride solution over 202 days at temperature of 5 degrees Celcius. Changes in flexural and compressive, length, mass, as well as chloride penetration were assessed in this investigation. It was found that using fly ash and entrained air can help to compensate the negative effects on strength; in other words, the deterioration due to CAOXY formation in the specimens can be mitigated when entrained air and fly ash are present in them. To mitigate the deterioration in the compressive and flexural strength of the samples exposed to 30% $CaCl_2$ concentration, 30 and 15 percent of fly ash respectively, as well as 5% entrained air should be used. Notably, in order to the mitigation of deterioration in the strengths of non-air entrained (NAE) samples, 45% and 15% fly ash were required for compressive, and flexural strength respectively which means regardless of the no-n-air or air entrained sample, the deterioration in flexural strength of them can be mitigated with the presence of the same fly ash content [22].

Chapter 3. Methodology[‡]

In this chapter, the materials which were used to prepare the samples, the sample preparation process, as well as designing and executing the test programs are explained.

Materials

Ordinary Portland cement type I/II, and distilled water, were used in this study in order to prepare cement paste samples. In addition, reagent-grade Calcium Chloride dihydrate with a molecular weight of 147.01 g/mol was used as a deicing salt. The relevant chemical and physical properties of this deicing salt obtained from the SDS are shown in Table 1.

Table 1 Chemical and physical properties of Calcium Chloride dehydrate

	Form	Color	PH	Density	Melting Point
Calcium chloride dihydrate	Solid	White	4.5 - 9.2 at 50 g/l at 20 °C (68 °F)	1.85 g/cm3 at 20 °C (68 °F)	176 °C (349 °F)

Sample Preparation

To address the objective of finding the relationship between the amount of calcium hydroxide and the formation of CAOXY, the paste specimens with three different water-to-cement ratios (W/CM), including 0.38, 0.43, and 0.48, were prepared. Using a cooking mixer, the required amount of cement and distilled water were mixed and cast into plastic cubic molds with dimensions of 51 x 51 x 51 mm (2 x 2 x 2 in.) (Figure 1). In addition, 8 more cement paste samples with dimensions of 51 x 51 x 254 mm (2 x 2 x 10 in.), and W/CM ration of 0.38, and 0.43 were casted through the same process. It should be mentioned that strain gauges were fixed on top of the samples using anchor studs while casting (Figure 2). After casting, the molds were covered by plastic covers to prevent water evaporation and kept in a room with 23.0 ± 2.0°C [73.5 ± 3.5°F] and 99.9% relative humidity. The samples were demolded after 24 ± 8 hours and returned to the room for another 27 days to complete 28 days of curing procedure and obtain a high degree of hydration [23, 24].

A B

Figure 1 51 x 51 x 51 mm mold (A) and specimens (B).

[‡] Babavalian, A. et al., Investigation of Deicing Salt Solution in Process of Calcium Oxychloride Formation in Cement Paste, International Conference on Transportation and Development 2024. https://doi.org/10.1061/9780784485538.033

A B

Figure 2 51 x 51 x 254 mm mold (A) and specimens with strain gauges (B).

Table 2 shows the factors and levels for the design of experiments using paste specimens. Three different salt solutions with 10%, 20%, and 30% concentrations were studied to find out the effect of chlorine on this chemical reaction.

In order to see the effect of temperature in the formation of CAOXY, the cubic samples with and without exposure to salt solutions were kept for 7 and 28 days in rooms with temperatures of 4°C, 20°C, and 40°C. The whole amount of the generated powder materials was sieved through the No. 200 sieve to make the sample ready for the TGA test (Figure 3). The minus No. 200 sieve material was kept in tubes and sealed to prevent carbonation.

Figure 3 Ground specimen passed No. 200 sieve.

Table 2 Factors and Levels in the Design of Experiments

Low/Mid/High	W/CM	$CaCl_2$ Solution Concentration (%)	Temperature (°C)
Low	0.38	without exposure to solution (0)	4
Mid	0.43	10	20
		20	
High	0.48	30	40

In accordance with the Table 2, the required number of paste specimens at three selected W/CM were prepared. Three paste specimens at each W/CM were immersed in salt solution with a particular concentration in 3 different containers. Each container was then kept under three selected temperatures. Therefore, a total of 27 paste specimens covering 3 solution concentrations and 3 temperatures, in addition to 9 samples not exposed to salt solution in 3 different temperatures, with 3 different water-to-cement ratios were used.

The specimen nomenclature that was followed is as follows:

W/CXClYTZ where X represents the selected level for W/CM, Y represents the level for Cl (solution concentration), and Z represents the level for T (temperature). For example, the specimen with W/C38Cl10T20 identification indicates, 0.38 as W/CM, 10% as solution concentration, and 20°C as the temperature.

Methods

Three different test programs were used to investigate the CAOXY formation in cement paste specimens as a result of exposure to calcium chloride. One of which consisted of conducting a TGA test on 28-day specimens after seven days of exposure to the salt solution to determine the amount of calcium hydroxide ($Ca(OH)_2$). The other one is strain readings on the 28-day specimens after different periods of time of exposure to deicing salt solutions to record the expansion values. The last one involved visual observation, which were done on prepared 28-day specimens after 28 days, 6 months, and 15 months of exposure to a salt solution.

TGA test

According to ASTM C1872 – 18 and a thesis by Traore, the range of temperature for determination of calcium hydroxide in hydraulic cement is from 380 to 500/600 °C [25, 26]. This procedure is carried outs at a heating rate of 10 °C/min after drying the samples before carrying out the test. Kim and Olek noted the specimens need to be dry before TGA is carried out [27]. Although the decomposition of $Ca(OH)_2$ occurs approximately between 350°C and 550°C, they heated their specimens to 1000°C as part of a modification to the ASTM method. In the modified method, the effect of carbonation is included in the determination of $Ca(OH)_2$; the mass loss due to the decomposition of $CaCO_3$ occurs in temperature between 600 and 700 °C. Thus, in this method, platinum or alumina pans should be used since they can operate up to 1500°C, that alumina 6.5mm sample pans were used in this study (figure 4).

Figure 4 Alumina 6.5mm Sample pan.

In the work done by Suraneni et al., the same approach of heating up to 500°C with the heating rate of 10°C/min under a nitrogen atmosphere was used [16]. Similar to what others had done, the mass loss during decomposition between 380 and 460°C was used to estimate of the amount of $Ca(OH)_2$.

In this effort, the objective is the determination of the effects of different parameters including W/CM, temperature, and salt concentration on the formation of CAOXY and to enhance the understanding of the relationship between these parameters on the formation of CAOXY. In this regard, it was ascertained that the simple method would be good enough to analyze the data obtained from TGA testing. To analyze the data obtained from TGA test, the decomposition of $Ca(OH)_2$ temperature range was achieved to find the mass loss for different specimens. The results were used to find the relationship between the parameters listed above based on the amount of calcium hydroxide, as well CAOXY. The following is the chemical reaction leading to CAOXY formation [8]:

$$xCa(OH)_2 + yCaCl_2 + zH_2O \rightarrow xCa(OH)_2 \bullet yCaCl_2 \bullet zH_2O$$

Higher mass loss due to the decomposition of calcium hydroxide means that a lesser amount of $Ca(OH)_2$ has participated in the chemical reaction of CAOXY formation. Thus, considering the theoretical chemical reaction, it can be inferred that a lesser amount of CAOXY ($CaOCl_2$) has been formed in the test specimen. To summarize, the greater the mass loss means a greater amount of $Ca(OH)_2$ and a lesser amount of CAOXY, and vice versa.

For example, Figure 5 shows the data obtained from TGA testing for a specimen with a W/CM = 0.38 exposed to a 30% CaCl2 solution kept at the temperature of 20°C. As can be seen, at a temperature of approximately 400°C, a noticeable mass loss has occurred due to the decomposition of $Ca(OH)_2$.

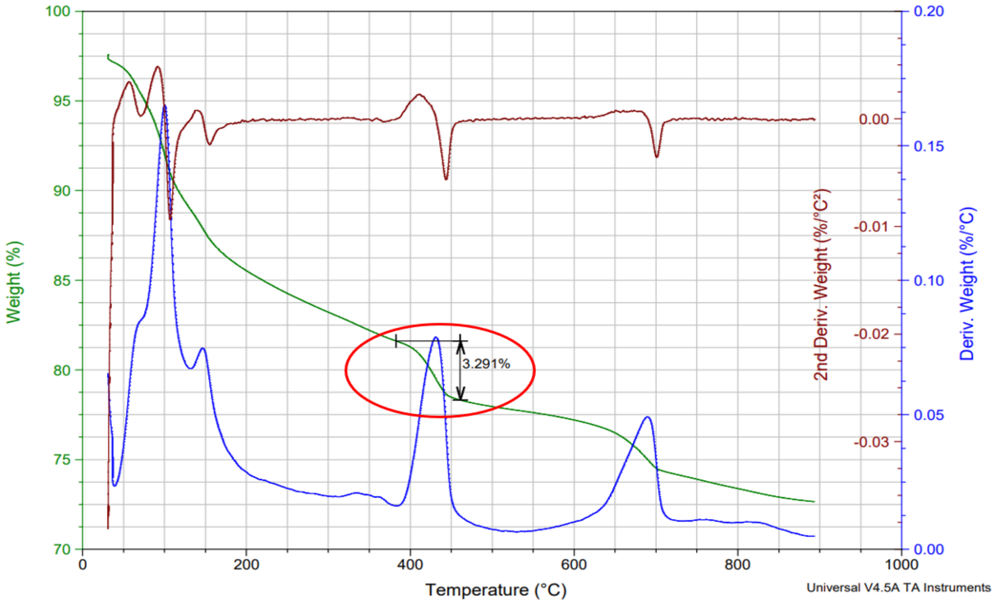


Figure 5 Mass Loss due to the decomposition of $Ca(OH)_2$ using data obtained from TGA test on the W/C38Cl20T20 specimen.

Strain readings

In order to determine the expansion in the cement paste specimens as a result of exposure to deicing salt solutions during the time, strain gauges were used. Table 3 demonstrates the technical specifications of a standard strain gauge.

Table 3 Technical specifications of GEOKON strain gauge-Model 4000

Standard Range	Resolution	Accuracy	Nonlinearity	Temperature Range	Active Gauge Length
3000 με	1.0 με	±0.5% F.S.	<0.5% F.S.	-20 °C to +80 °C	150 mm (5.875 in.)

Figure 6 shows two of the specimens exposed to deicing salt solutions, and the strain gauge reader which is connected to the strain gauges on the sample using a red PVC cable.

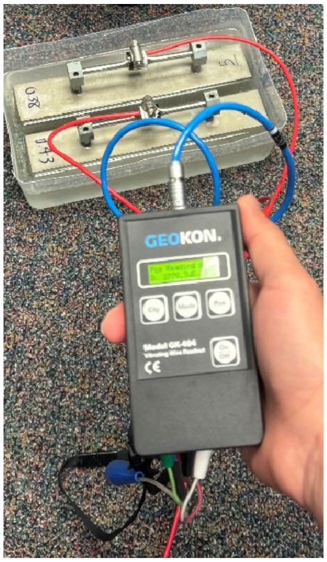


Figure 6 Attached strain gauges to cement paste specimens exposed to deicing salt solution, and strain gauge reader.

In this test program, the specimens with two different W/CM of 0.38 and 0.43 were exposed to two salt concentrations of 10 and 20 percent. In order to see the effects of temperature on expansion, 4 out 0f 8 specimens were kept in room temperature (around 23 °C), and 4 other were kept in refrigerator, in which the temperature depending on the location of the sample was in the range of -4°C to +4°C approximately

Chapter 4. Results and Discussion[§]

In this chapter, the result of all 3 test programs, including TGA tests, visual observation, and strain readings are presented and analyzed.

Based on the method previously described, the data obtained from the TGA testing along with the mass loss due to the decomposition of $Ca(OH)_2$ is shown in Table 4. All the graphs showing results and calculations of the conducted TGA tests are provided in appendix A.

Table 4 Mass loss due to the decomposition of $Ca(OH)_2$

Name	Mass loss due to the decomposition of $Ca(OH)_2$ (%)	Name	Mass loss due to the decomposition of $Ca(OH)_2$ (%)
W/C38Cl0T4	3.376	**W/C43Cl10T4**	3.508
W/C38Cl0T20	3.445	**W/C43Cl10T20**	3.284
W/C38Cl0T40	3.650	**W/C43Cl20T4**	3.307
W/C38Cl10T4	3.264	**W/C43Cl20T20**	3.367
W/C38Cl10T20	3.306	**W/C43Cl30T4**	3.320
W/C38Cl10T40	3.378	**W/C43Cl30T20**	3.428
W/C38Cl20T4	3.288	**W/C48Cl0T4**	3.610
W/C38Cl20T20	3.291	**W/C48Cl0T20**	3.778
W/C38Cl20T40	3.448	**W/C48Cl10T4**	3.600
W/C38Cl30T4	3.175	**W/C48Cl10T20**	3.480
W/C38Cl30T20	3.372	**W/C48Cl20T4**	3.536
W/C38Cl30T40	3.590	**W/C48Cl20T20**	3.496
W/C43Cl0T4	3.442	**W/C48Cl30T4**	3.327
W/C43Cl0T20	3.590	**W/C48Cl30T20**	3.700

Figure 7 indicates that by increasing the W/CM, the mass loss increases indicating a greater amount of calcium hydroxide exists in the specimens. The rate of this increment in mass loss is greater for higher W/CM, which infers a greater susceptibility to CAOXY formation. However, the other parameters such as the temperature of the reaction and solution concentration may also affect CAOXY formation.

[§] Babavalian, A. et al., Investigation of Deicing Salt Solution in Process of Calcium Oxychloride Formation in Cement Paste, International Conference on Transportation and Development 2024. https://doi.org/10.1061/9780784485538.033

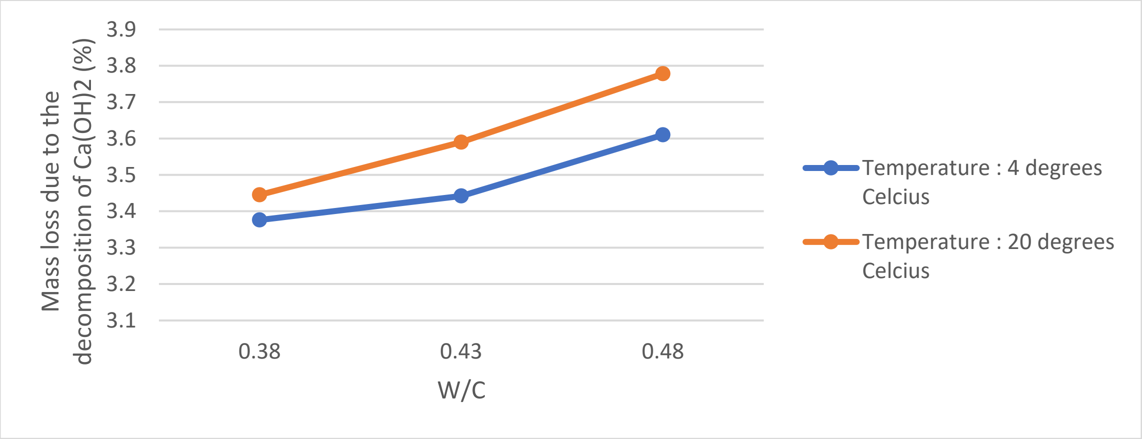


Figure 7 Mass loss values of the specimens without exposure to $CaCL_2$ solution obtained from conducted TGA tests.

Figure 8 indicates that a greater amount of mass loss shows that a greater amount of $Ca(OH)_2$ existed in the sample. On the other hand, there is a reverse relation between the presence of $Ca(OH)_2$ and CAOXY. Again, this means that the amount of CAOXY formed in the specimens is higher in the samples manifesting a lower mass loss and decomposition of $Ca(OH)_2$, and vice versa . By increasing the temperature of the reaction, the mass loss increases, so the amount of calcium hydroxide increases, or in other words, the amount of CAOXY decreases. The amount of CAOXY is changed by increasing the W/CM and/or the salt concentration. A W/CM of 0.43 at higher temperatures leads to more CAOXY formation. Also, the same results for a W/CM of 0.48 or for increasing the salt solution concentration to 20%. As shown in Figure 2, the highest amount of salt solution concentration, 30%, the formation of CAOXY was less affected by increasing the W/CM; and the same trend of decrease in CAOXY formation has been found in all specimens with different water to cement ratios by increasing the reaction temperature. Figure 9 shows the formed CAOXY crystals on the test specimens after 28 days of exposure to salt $CaCl_2$ salt solution validating the results obtained from TGA testing.

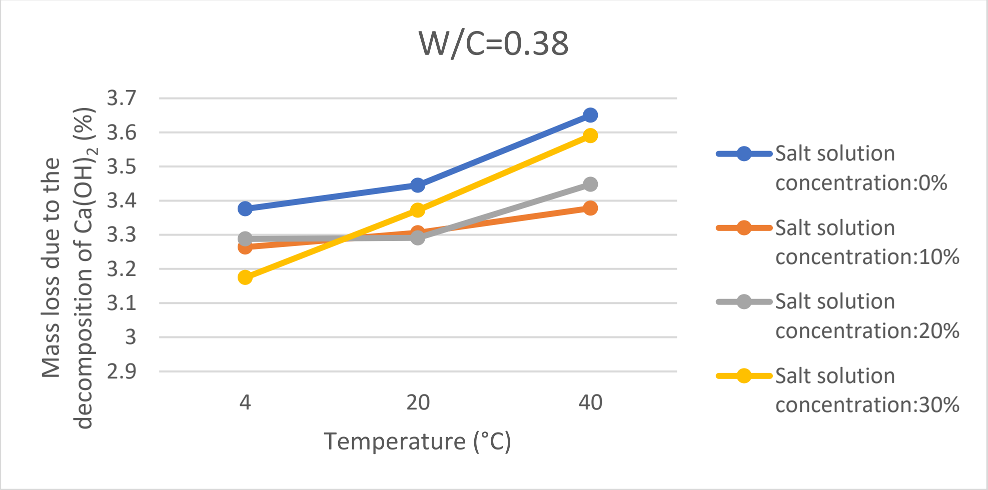
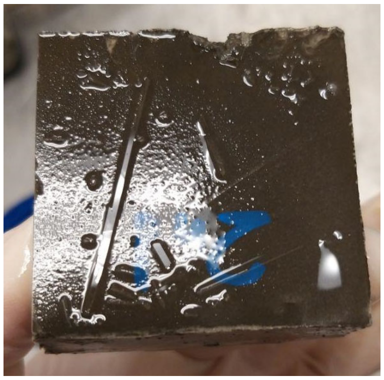


Figure 8 Mass loss values of the specimens obtained from conducted TGA tests.

Figure 9 shows that fewer crystals were formed in the specimen exposed to 30% salt concentration, while for both other samples exposed to 20 and 10 %, respectively, a greater amount of CAOXY crystals formed on the specimens and the amount of CAOXY between the two concentrations were approximately the same, but for the 20% concentration, it appears to be a bit more, which can be verified from the TGA test results shown in Figure 8.

W/C38Cl10T20 **W/C38Cl20T20**



W/C38Cl30T20

Figure 9 CAOXY crystals formed on the specimens after 28 days of exposure solution.

For the temperature of 4 °C, exposure to greater amounts of salt concentration led to a greater amount of CAOXY formation as seen in Figure 10. However, this trend is reversed by changing the temperature from 20 to 40 °C. As the salt concentration increases, the amount of CAOXY formation decreases especially for salt solution concentrations, greater than 20%.

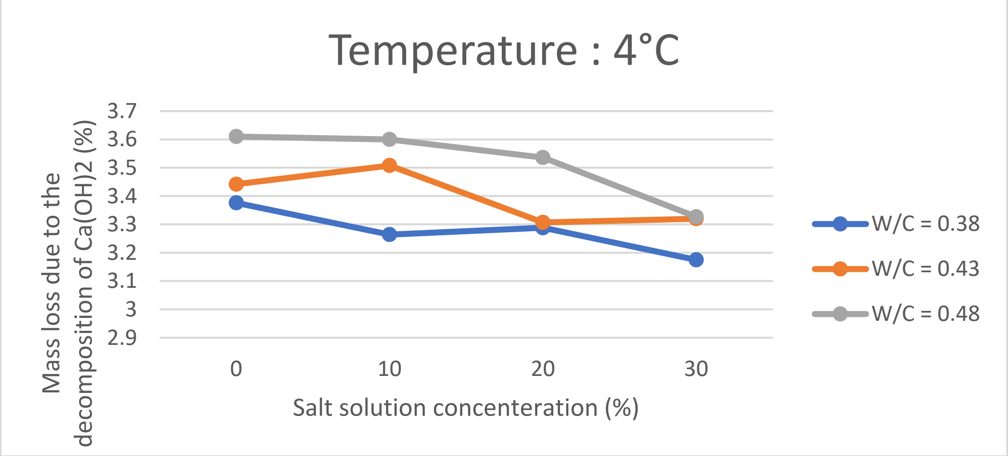


Figure 10 Mass loss values of the specimens obtained from conducted TGA tests.

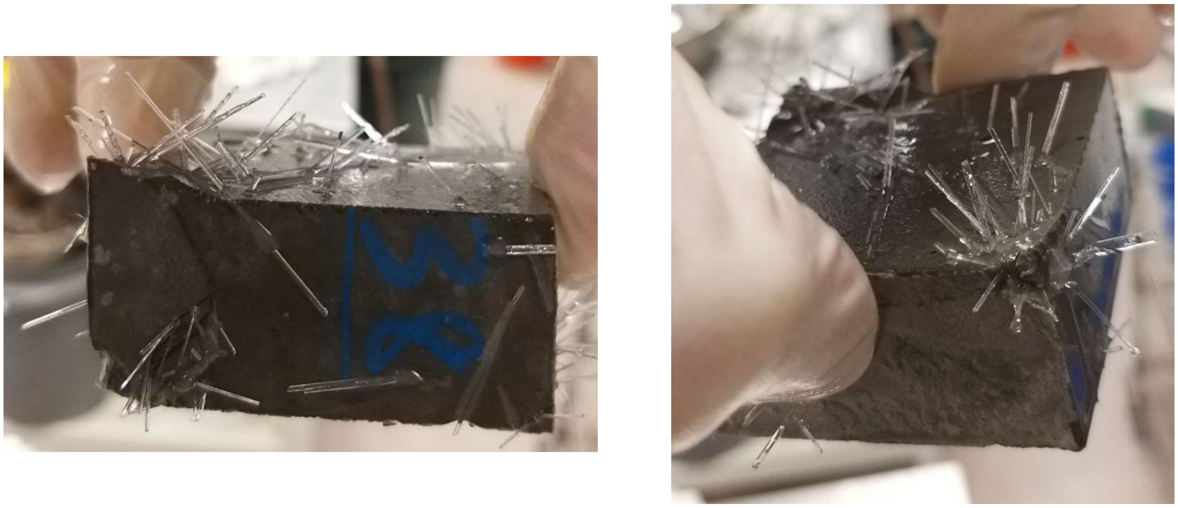


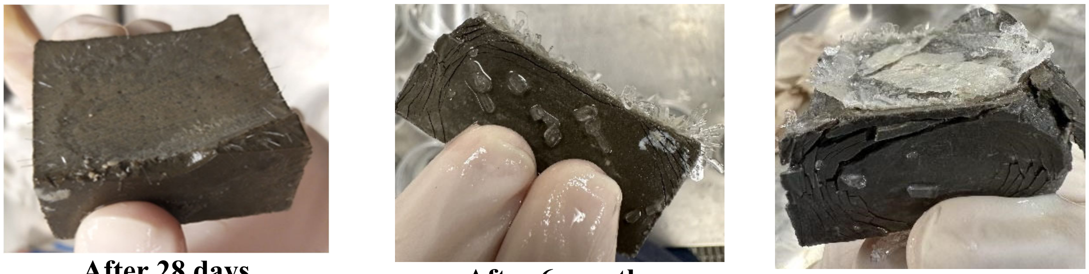
Figure 11 Areas with more concentration of presence of CAOXY crystals.

Figure 11 shows that the amount of CAOXY crystals along the edge of the samples was greater than in other areas having flatter surfaces. This may be due to a greater amount of exposed surface area to the salt solution in these areas. It can be concluded from this observation that areas of the pavement which are cracked are more susceptible to CAOXY formation; thus, more deterioration can occur in these areas. Table 5 summarizes the outcomes regarding the effects of temperature of reaction, salt concentration, and W/CM coming from analyses of both visual observations and data obtained from TGA test.

Table 5 Effects of W/CM, salt concentration and temperature of reaction on CAOXY formation.

W/CM	Salt concentration		
	10%	20%	30%
	Increasing temperature of reaction from 4 to 40 degrees Celsius		
0.38	↓	↓ (After 20°C)	↓
0.43	↑	↓	↓
0.48	↑	↑	↓

Figure 12 illustrates a direct correlation between the exposure of cement paste specimens to salt solution and the formation of salt and CAOXY crystals. This phenomenon results in a more pronounced deterioration of the specimens.



After 28 days **After 6 months** **After 16 months**

Figure 12 Salt and CAOXY crystals formed on the same specimen after 7 days, 6 and 16 months of exposure to salt solution.

Figure 13 demonstrates the expansion and flaking of cement paste specimens after being exposed to deicing salt solution for several months. The formation of visible cracks is evident.

W/C38Cl30T4 **W/C43Cl30T4** **W/C48Cl30T4**

A

W/C38Cl30T4 W/C43Cl30T4 W/C48Cl30T4

B

Figure 13 CAOXY crystals leading to deterioration of the specimens after couple of months of exposure to salt solution; A: 6 months, and B:15 months.

The following table (Table 6) shows the strain readings obtained from 8 different cement paste specimens exposed to deicing salt solution at different temperatures. The name of each sample tells the W/CM ratio, salt solution concentration, and the temperature where the samples were kept during the time of exposure. As mentioned before, these values have been obtained in order to determine the expansion of the cement paste specimens due to the exposure to deicing salt solution. In this table, the phrase “no data” means that the change in strain readings exceeded the range of strain gauge.

Table 6 Strain readings of the specimens exposed to deicing salt solution.

	Strain (με)							
Time of exposure (days)	**W/C43Cl10T4**	**W/C38Cl10T4**	**W/C43Cl20T-4**	**W/C38Cl20T-4**	**W/C43Cl10T22**	**W/C38Cl10T22**	**W/C43Cl20T22**	**W/C38Cl20T22**
0	0	0	0	0	0	0	0	0
6	335.2	346.8	600.7	598.3	271.6	261	287.2	350.1
13	398.5	443.3	1207.6	1314.5	292.3	301.2	317.2	408
20	469.2	605.8	2156.1	2607.9	305.2	330	331.3	439.9
27	483.9	710.4	2562.7	3214.2	317.3	346.8	337.7	466.3
34	476.7	787.1	2558.7	3309.7	320.7	362.5	335.2	480.9
41	516.7	1000.1	2602.1	3404.4	327	381.3	333.3	496.4
48	326.4	1077.6	2714.8	3422.8	327	391.7	315.1	496.8
55	146.8	1136.1	2834.4	No data	326.1	400.3	297	496
69	288.5	1358.6	No data	No data	325.2	422.2	248.2	482.5
76	421.4	1735.2	No data	No data	329.6	433.5	219.6	469.8
83	520.5	1898.3	No data	No data	328.2	444	184.6	451.6
90	596.7	No data	No data	No data	325.4	452.2	132.8	422.9
104	No data	No data	No data	No data	321	468.1	-14.6	346.2

Figure 14, and 15 show strain readings of the specimens as a result of exposure to different deicing salt solution concentrations of 10 and 20 percents at lower and room temperatures respectively.

It can be seen in Figure 14 that at lower temperatures, there is am increasing trend in strain readings and the rate of this increasement is much higher at the lowest temperature which means that the lower the temperature, the higher the strain readings and its growing rate. On the other hand, both figures show that the lower the W/CM, the higher the strain readings.

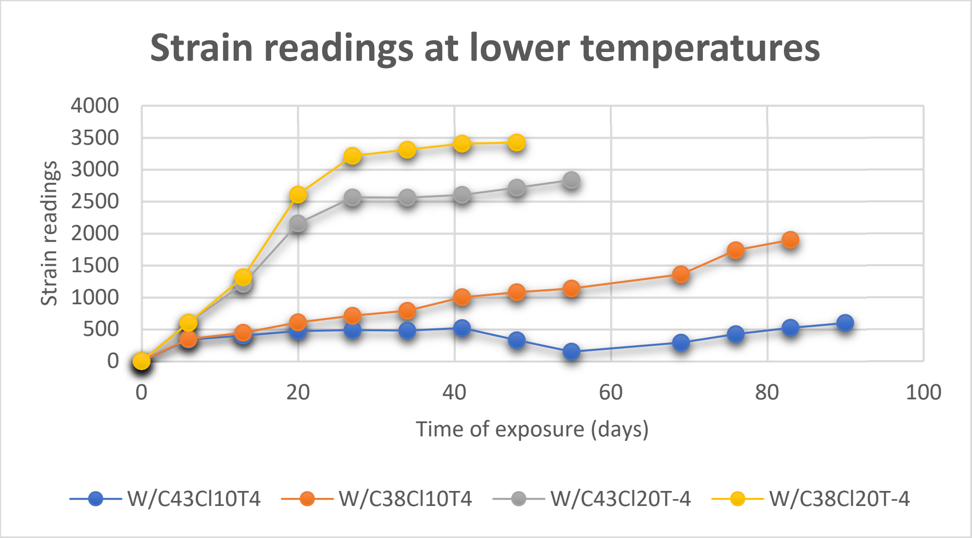


Figure 14 Strain readings on specimens with 0.38, and 0.43 water to cement ratio, and exposed to 10 and 20 percent deicing salt solutions at lower temperatures of 4 °C and -4 °C.

From Figure 15 it can be obtained that as we expected, by increasing the salt solution concentration from 10% to 20%, the strain readings have a more growth rate, but it is surprising that this trend was changed in day of 83 and 69 for the specimens with W/CM 0.38 and 0.43 respectively.

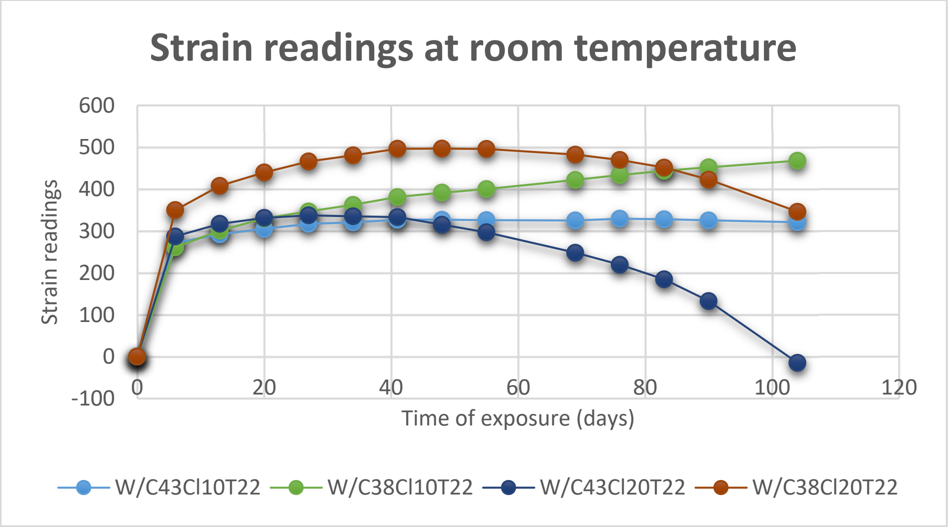


Figure 15 Strain readings on specimens with 0.38, and 0.43 water to cement ratio, and exposed to 10 and 20 percent deicing salt solutions at room temperatures (22 °C).

Strain readings of the specimens as a result of exposure to deicing salt solution concentration of 10 and 20 percent are shown in figures 16, and 17 respectively. These graphs show an increasing trend in the strain readings by decreasing the temperature. For the specimens exposed to salt solution with 10% concentration and W/CM of 0.38, this increasement is major specially after about 3 weeks. Also, the growth in the strain readings for the specimens exposed to salt solution concentration of 20% at the temperature of -4 °C, is outstanding for both W/CM of 0.38 and 0.43, but is slightly more for the specimens with 0.38 water to cement ratio. These graphs obviously show that environment temperature has a direct effect on strain readings which means that by decreasing the temperature, the expansion in the specimens increases which may be as a result of more CAOXY formation in these specimens. The reason of having more CAOXY in lower temperature is that chemical reactions happen more numerously in lower temperatures meaning that a lot of small CAOXY crystals are formed leading to lots of small cracks in the specimens. These cracks will be expanded after the first days of formation more and more until reaching to some points that more expansion is not a lot possible.

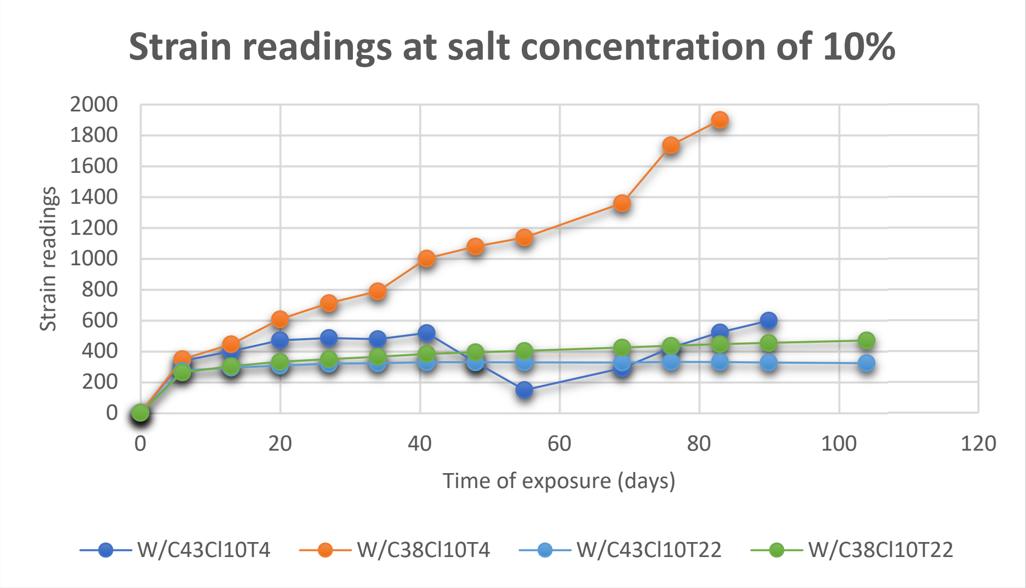


Figure 16 Strain readings on specimens with 0.38, and 0.43 water to cement ratio, and exposed to 10 percent deicing salt solutions at different temperatures.

Figure 17 shows a light decrease in strain readings after around 69 days of exposure to deicing salt solution with the concentration of 20% at room temperature which means some expansions formed in these specimens have been recovered.

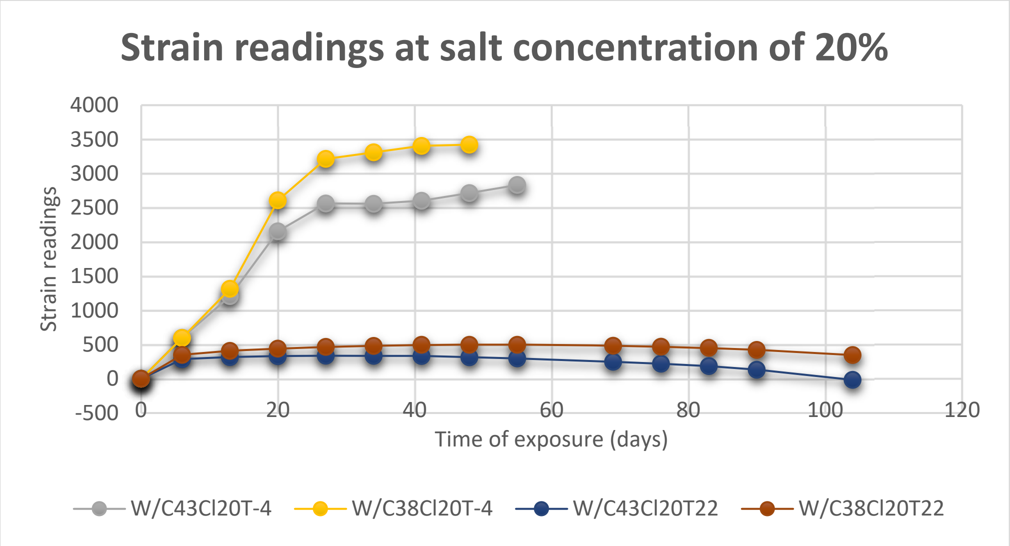


Figure 17 Strain readings on specimens with 0.38, and 0.43 water to cement ratio, and exposed to 20 percent deicing salt solutions at different temperatures.

In order to comparing the strain readings on the specimens with same W/CM at different temperatures and exposed to different salt solution concentrations, following graphs have been developed (Figures 18, and 19). These graphs illustrates that by exposing specimens with same W/CM, although the concentration of deicing salt solution has an effect on expansion of the specimens, the temperature has significant effect on the expansion which can be obviously seen in both specimen with W/CM of 0.38 and 0.43 kept in -4 °C and 20% salt solution concentration in Figures 18, and 19 respectively. This major expansion can be easily observed when you look at the images of these specimens after couple of days of exposure to deicing salt solutions (Figure 20). Also, except these two specimens which have the severe conditions, in all the other specimens we can see that the highest increasement in expansion during 7 days, or the highest rate of increment in strain readings s, occurred in the first 7 days of exposure to deicing salt solutions.

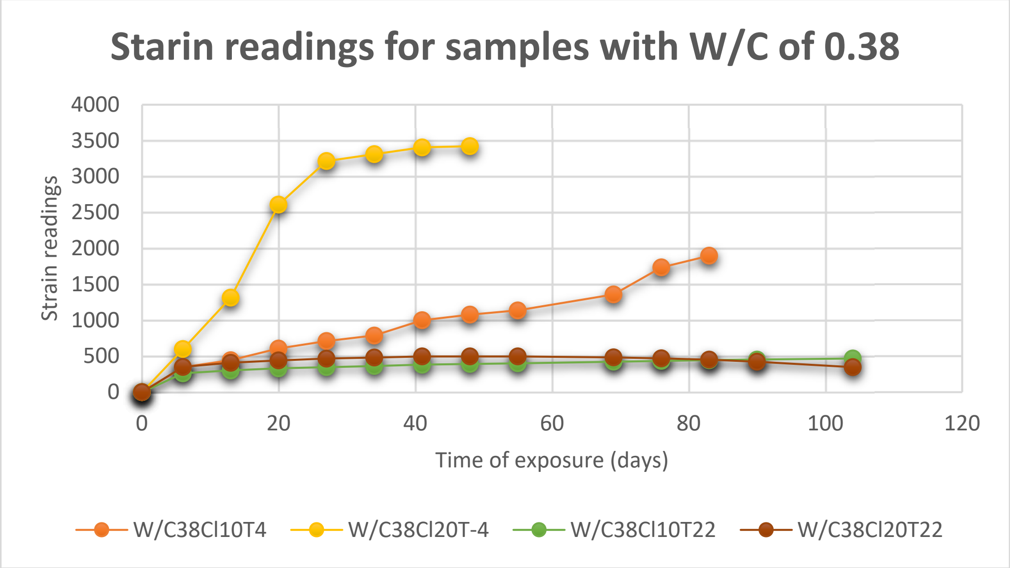


Figure 18 Strain readings on specimens with 0.38 water to cement ratio and exposed to different deicing salt solutions concentration and temperatures.

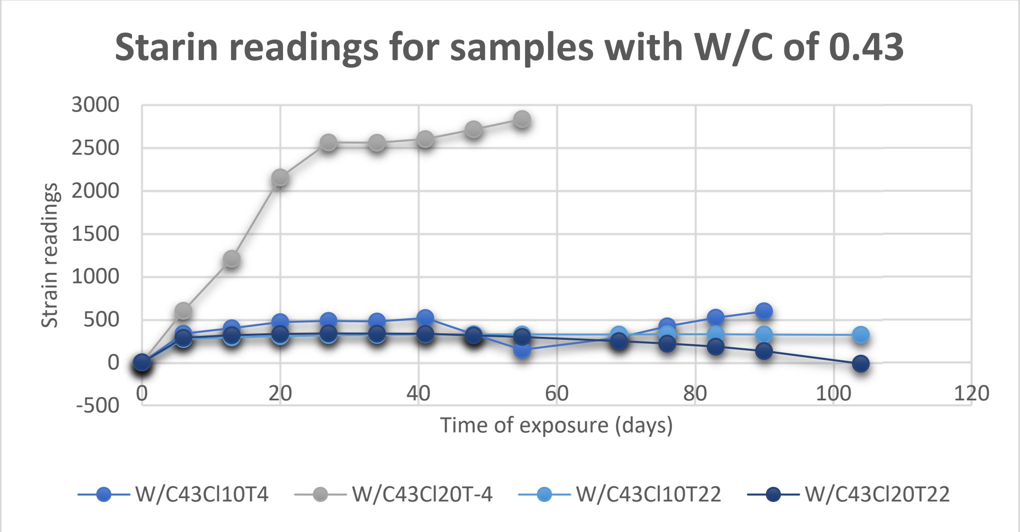
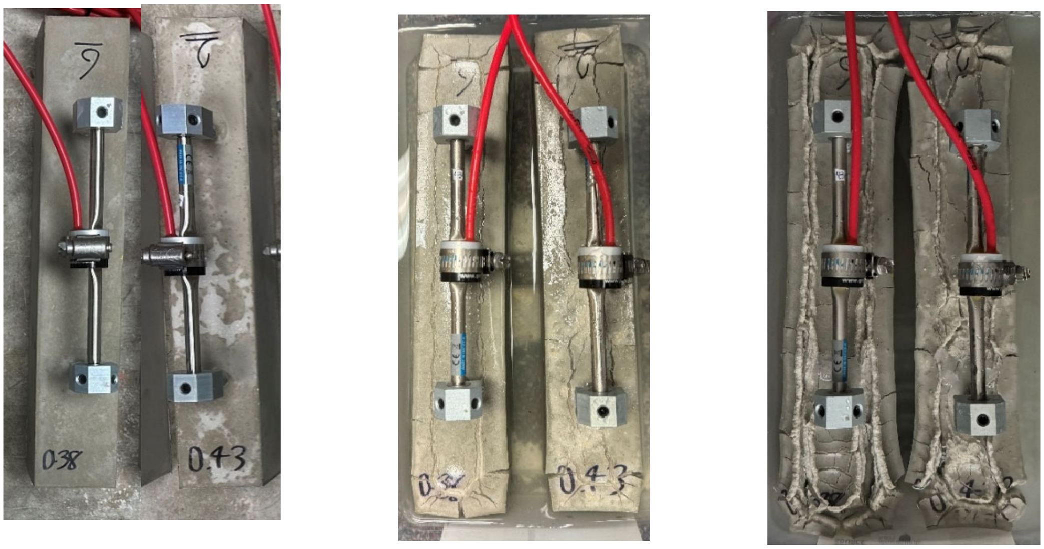


Figure 19 Strain readings on specimens with 0.43 water to cement ratio and exposed to different deicing salt solutions concentration and temperatures.

Comparing Figures 20 and 21 can illustrate obviously the negative effects of lower temperature and higher deicing salt concentration on the expansion of cement paste specimens due to the formation of CAXOY crystals.



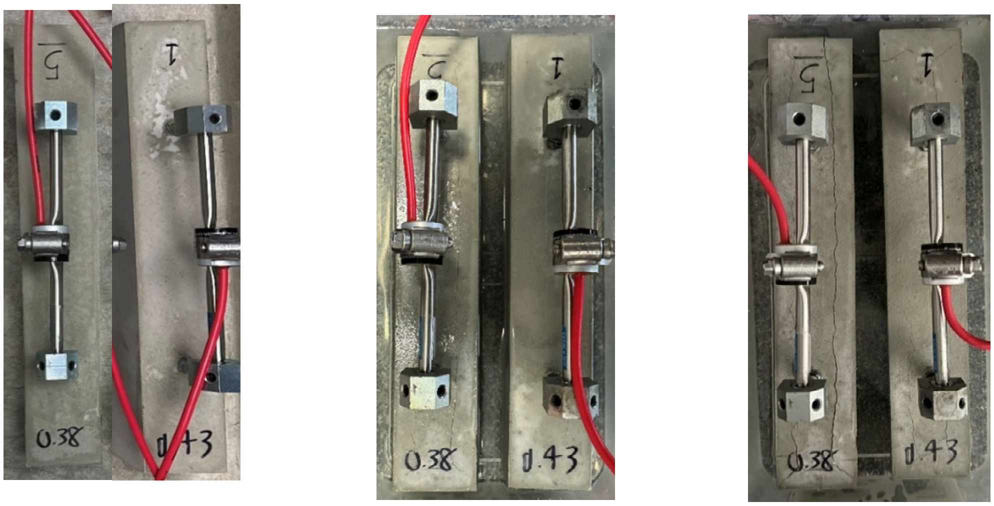
Before exposure to deicing salt solution

After 41 days

After 55 days

Figure 20 W/C38Cl20T-4 and W/C43Cl20T-4 specimens after different time periods of exposure to deicing salt solution.

It can be derived from Figure 21 that the negative effect of deicing salts on the specimen with lower W/CM (0.38) is higher; this effect is more obvious when the crack width and numbers are compared on the specimens with 0.38 and 0.43 water to cement ratio after 55 days of exposure to deicing salt.



Before exposure to deicing salt solution

After 41 days

After 55 days

Figure 21 W/C38Cl10T4 and W/C43Cl10T4 specimens after different time periods of exposure to deicing salt solution.

Finally, considering strain gauge values and visual observations, the worst condition happened for the specimen with W/C of 0.38 kept in -4 °C and exposed to 20% of deicing salt solution with an increasement from 1981.9 to 5404.7 με which is about 172.7% increasement in strain readings in 48 days. On the other hand, the best condition leading to least amount of changing the stain value was observed in the specimen with 0.43 of W/C exposed to deicing salt solution with 10% concentration and kept in the room temperature of 22 °C; in this specimen, the strain readings increased from 1997.8 to 2312.9 με in 48 days showing 15.8 % increasement (Figure22).

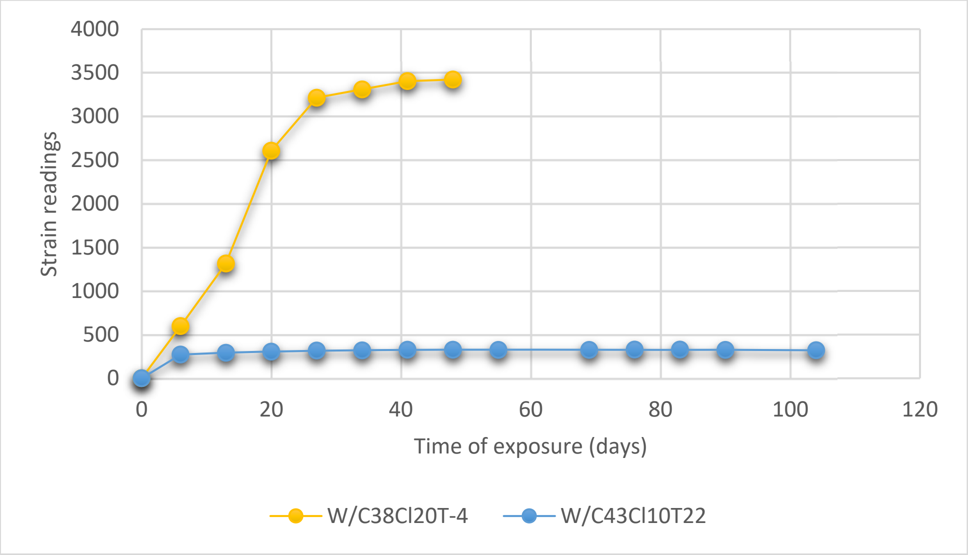


Figure 22 Specimens with highest and lowest changes in strain readings.

Activation Energy:

To calculate the activation energy (E_a) using the strain readings and Arrhenius equation. At the first step, we need to calculate the extent of the reaction (α) using the following formula:

$$\alpha = \frac{Strain\ reading\ (t)}{Strain\ reading\ (end)}$$

Considering the rate law, by relating the reaction rate to the extent of the reaction and as the slope of the strain readings-time curve shows the reaction rate, we have [23]:

$$r = slope\ of\ the\ curve = k\ (1-\alpha)^n$$

In which, k is the rate constant, and n can show that how the non-reacted part of the reaction can affect the reaction rate. Thus, by calculating r,slope at each point of the strain-time graph, and using the solver in excel, we can calculate k for each temperature that samples were exposed.

As each sample with same W/CM and salt solution concentration, exposed to 2 different temperatures, we have two k values for each that can be used in the next steps in calculation of activation energy.

Using the Arrhenius equation, the activation energy can be determined [23]:

$$k = Ae^{-\frac{E_a}{RT}}$$

In this equation, T is temperature in Kelvin, A is pre-exponential factor, and R is gas constant equals to 8.314 J/mol.K. If we take the natural logarithm, we have:

$$\ln(k) = \ln(A) - \frac{E_a}{R}\frac{1}{T}$$

Thus, by plotting $\ln(k)$ versus $\frac{1}{T}$, the slope of the plot gives the $-\frac{E_a}{R}$, so by multiplying the slope by $-R$, the activation energy (E_a) is achieved.

The following table shows an example of calculated k for the sample with 0.43 water to cement ration and exposed to 10% deicing salt solution.

Table 7. Temperature and Rate Constant for W/C43Cl10.

Temperature (°C)	Temperature (K)	Rate Constant (k)	$\ln(k)$	$\frac{1}{T}$ (K^{-1})
4	277.15	55.86814198	4.022994307	0.003608154
22	295.15	46.320363	3.83558167	0.003388108

The following figure is the plotted graph for the mentioned sample.

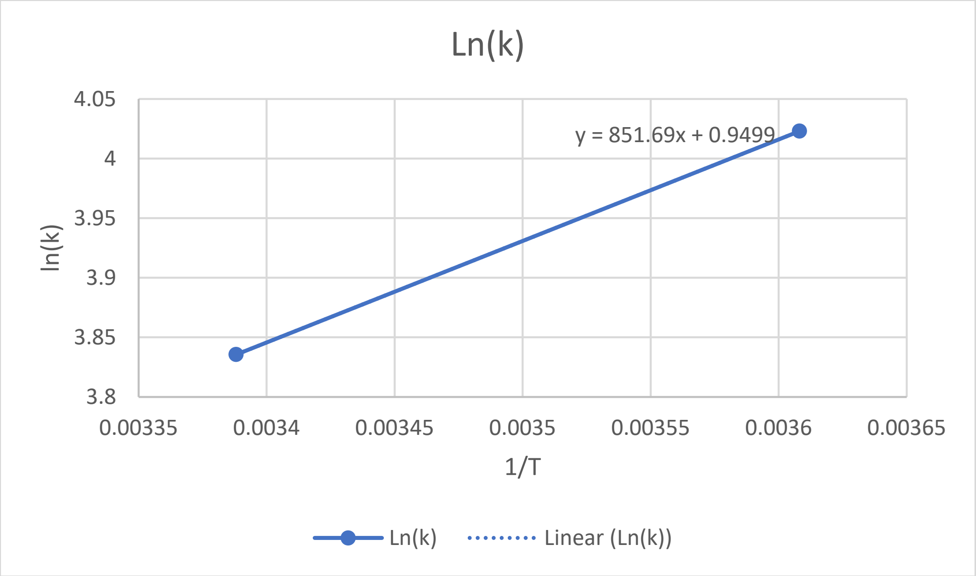


Figure 23. $\ln(k)$ vs. $\frac{1}{T}$ graph for W/C43Cl10 sample.

The slope of this graph is 851.69, so the activation energy can be calculated as follows:

$$E_a = Slope * (-R) = 851.69 \times (-8.314) = -7080.95066\, J$$

Using the equation of the trendline we can calculate pre-exponential factor (A) as follows:

$$\ln(A) = 0.9499$$

$$\mathrm{A} = 2.585451101$$

As we have 4 different samples with 2 different W/CM and exposed to 2 different salt solution concentration, we will have 4 calculated activation energy as can be seen in the next table.

Table 8. Activation energy and Pre-exponential factor for 4 different samples.

Sample	Activation energy (E_a) ($\frac{J}{mol}$)	Pre-exponential factor (A)
W/C38Cl10	21133	245487.179
W/C38Cl20	-19278	0.023
W/C43Cl10	-7081	2.585
W/C43Cl20	-21853	0.007

Comparing the results from the table, it can be seen that at high level of salt solution concentration, changing in W/CM doesn't have significant effect on the activation energy; also, it is shown that by doubling the salt solution concentration from 10 to 20 percent, for the samples with 0.43 W/CM, the activation energy increased to about 3 times which means that increasing

the salt solution concentration affects the activation energy significantly.
In order to relating these calculated activation energies and see the effects of two different parameters including W/CM and salt solution concentration, the overall rate K will be calculated as follows:

$$K = w_1 k_1 + w_2 k_2 + w_3 k_3 + w_4 k_4$$

In which, w_i, and k_i are the weight reflecting the influence of each combination of parameters, and rate constant for that condition respectively.

As we have:

$$k_i = \ A_i e^{-\frac{E_{a_i}}{RT}}$$

We can expand the overall rate K as follows:

$$K = w_1 A_1 e^{-\frac{E_{a_1}}{RT}} + w_2 A_2 e^{-\frac{E_{a_2}}{RT}} + w_3 A_3 e^{-\frac{E_{a_3}}{RT}} + w_4 A_4 e^{-\frac{E_{a_4}}{RT}}$$

The numbers 1, 2, 3, and 4 are referring to the 4 different conditions with 2 different W/CM and 2 salt solution concentration. Using table 2, we have:

$$K = w_1 245487.179 e^{-\frac{21133}{RT}} + w_2 0.023 e^{\frac{19278}{RT}} + w_3 2.585 e^{\frac{7081}{RT}} + w_4 0.007 e^{\frac{21853}{RT}}$$

or

$$K = w_1 245487.179 e^{-\frac{2541.9}{T}} + w_2 0.023 e^{\frac{2318.7}{T}} + w_3 2.585 e^{\frac{851.7}{T}} + w_4 0.007 e^{\frac{2628.5}{T}}$$

Comparing the rate values for the samples exposed to temperature of 22 °C and the mentioned equation, weights can be determined to get the closest and most accurate results as follows:

$$K = 0.27 \times 245487.179 e^{-\frac{2541.9}{T}} + 0.1 \times 0.023 e^{\frac{2318.7}{T}} + 0.1 \times 2.585 e^{\frac{851.7}{T}} + 0.53 \times 0.007 e^{\frac{2628.5}{T}}$$

Comparing the weights, it can be seen that the part of equation related to the sample with highest salt solution concentration and W/CM has the significant effect on the overall rate meaning that higher salt solution concentration leads to more expansion as a result of the chemical reaction occurred when concrete pavement is exposed to deicing salt solutions.

Chapter 5. Summary and Conclusions[**]

The equation that represents the reaction between calcium hydroxide and chlorine demonstrates that larger amounts of $Ca(OH)_2$ and Cl_2 can produce a greater amount of CAOXY. When exposing identical samples, which contain the same quantity of $Ca(OH)_2$, to varying salt solutions and conditions, some of the $Ca(OH)_2$ is consumed by the chemical reaction, leaving behind a portion that has participated in the reaction and contributed to CAOXY formation. A smaller amount of remaining calcium hydroxide indicates that a greater amount of it has been consumed, leading to a higher quantity of CAOXY being produced. This theory supports the conclusions obtained from the TGA test results. Therefore, by exposing specimens to the salt solution and analyzing the amount of remaining $Ca(OH)_2$ using TGA test results, the formation of CAOXY can be determined. For example, a greater amount of mass loss due to the decomposition of $Ca(OH)_2$ indicates that a larger amount of $Ca(OH)_2$ has remained in the samples, which has not participated in the chemical reaction, leading to a lower amount of CAOXY being produced. Additionally, visual observations of the samples after exposure to the salt solution have been conducted to validate the conclusions derived from this theory. The conclusions drawn from TGA testing on different cement paste samples with varying parameters including:

- W/CM of 0.38, 0.43, and 0.48,
- Exposure to $CaCl_2$ salt concentration of 10, 20, and 30%,
- Room temperature of 4, 20, and 40 °C, and
- 7 and 28 days of exposure after 28 days of curing

are as follows:

- A higher W/CM ratio leads to the formation of more $Ca(OH)_2$, indicating a greater potential for CAOXY formation. However, other factors such as temperature and solution concentration can also affect CAOXY formation, which means that an increase in W/CM may not necessarily lead to an increase in CAOXY formation.
- The effect of temperature on the formation of CAOXY is influenced by the W/CM ratio. When the W/CM ratio is low, increasing the temperature leads to a decrease in CAOXY formation. Conversely, for higher W/CM ratios, an increase in temperature leads to an

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[**] Babavalian, A. et al., Investigation of Deicing Salt Solution in Process of Calcium Oxychloride Formation in Cement Paste, International Conference on Transportation and Development 2024. https://doi.org/10.1061/9780784485538.033

increase in CAOXY formation, especially for the samples exposed to lower salt concentrations. In other words, increasing the salt concentration counteracts the effect of reducing the W/CM ratio, resulting in a lower rate of concrete deterioration.

- Visual observations indicate that areas where cracks have formed in the samples show an increased amount of CAOXY crystal formation. Therefore, minimizing cracking may help limit CAOXY formation in concrete.
- Exposing cement paste specimens to deicing salt solution for an extended period, a direct relationship was observed between the period of exposure and the formation of CAOXY crystals leading to the deterioration of the specimens. This deterioration includes visible cracks, expansion, and flaking, which ultimately decreases the performance of concrete pavements.

Using strain gauges to determine the expansion in the specimens with different parameters including:

- W/CM of 0.38, and 0.43,
- Exposure to $CaCl_2$ salt concentration of 10, and 20%.
- Room temperature of 22 °C and refrigerator temperature of 4 to -4 °C, and
- Around 104 days of exposure after 28 days of curing

Led to the following conclusions:

- Although in theory by increasing the W/CM, $Ca(OH)_2$ increases leading to an increase in CAOXY formation because of being one of the main components of the chemical reaction of CAOXY formation, it is not the only parameters having effect on the formation of Calcium Oxychloride, so the other parameters like temperature and salt solution concentration can change this expected trend that it can be seen specimens with

0.38 W/CM has higher expansion comparing to the ones with 0.43; this changes were seen in TGA test as well.

- Strain readings obtained for the specimens exposed to deicing salt solution, show that by increasing the temperature, less expansion will occur in the specimens which can be interpreted as less CAOXY crystal formation; this conclusion can be verified by both visual observations on these samples, as well as the outcomes of TGA tests. This trend can obviously be seen on the specimens with same conditions but more temperature range, from -4 to 22 °C, even for the specimen with W/CM of 0.38 and exposed to 10% deicing salt solution specifically after 27 days, but it is slightly less severe for the specimen with 0.43 W/CM and exposed to 10% deicing salt solution; although in this case we can still see the same trend specially after more period of exposure (around 76 days) that after this longer period of time, the growth rate of expansion I higher than the first couple of days for lower temperature. It can be concluded that the lower the temperature the less time is needed to have more sever conditions.
- These results show that specially in longer period of time of exposure to deicing salt solution, the more W/CM can help specimens to resist more and having less deterioration.
- It is also surprising that at room temperature, the effects of higher concentration of deicing salt solution is slightly more significant at the beginning, but by passing the days, although the strain readings of specimens exposed to lower solution concentration, have increased slowly or were constant in some parts, the strain readings of the specimens exposed to higher concentration were beginning to slightly recover after 69, and 83 days of exposure for the samples with 0.43, and 0.38 water to cement ratio respectively.

- The visual observations of these samples, in addition to verification of the effect of lower temperature on concrete deterioration, can indirectly verify that these expansions are not because of ice crystals since there we no ice in the solution even in -4 °C; so, it can be derived that these deteriorations are as a result of CAOXY crystals.
- The first major effect leading to expansion happens in the first week of exposure to salt solution. Also, the rate of deterioration is increasing specially for the specimens kept in lower temperature specifically -4 °C which can be as a result of having more cracks leading to exposing more surfaces and areas to deicing salt solutions and finally resulting in wider cracks and more sever conditions which leads to expanding the cement paste sample, or in the other word exploding it which is unrecoverable deterioration. Thus, by continuous exposure to harsh weather and deicing salt solution, the cement paste specimens will almost be changed to powder and lose their performance.

All the test programs including TGA tests, strain readings, and visual observations clearly show that from among all different parameters including W/CM, temperature, and salt solution concentration, temperature has the most significant effect on CAOXY formation leading to concrete deterioration; decreasing the temperature negatively affects the performance of the concrete specially at low range of temperatures (4 to -4 °C) as a result of deterioration occurring due to exposure to deicing salt solution; it was also found that at lower temperature, in addition to high amount of deterioration, the rate of deterioration is significantly higher than higher temperatures which means that same specimens may experience same deterioration at different low temperatures like 4 and -4 °C, but the speed of getting worst condition for the specimens kept in lower temperature (-4 °C) is much higher and this deterioration will occur in shorter period of time. Needless to say, same as what has been seen in previous studies mentioned in the literature review, another parameter, salt solution concentration, has negative effects leading to increase the rate of deterioration; this negative effect on deterioration can also be seen with changes in W/CM ratio parameter. Thus, it is important to consider all these parameters at the time of designing both concrete pavements and deicing salt solution concentration, and remember that based on the weather condition, the design may need to be changed to minimize the negative effects of these parameters on concrete pavement performance in order to have the least deterioration while the best performance is being achieved over the concrete pavement's design life.

Chapter 6. Recommendations to Minimize CAOXY Formation

As the tensile strain capacity of cement paste is around 150-250 με, by exposure the sample to salt solution, when the strain meets this number, it leads to failure of the concrete and affects its performance. It can be seen in table 6 that even after 6 days of exposure to deicing salts solution, all the samples showed strain higher that tensile strain capacity of concrete; this can be seen even in lower salt solution concentration of 10% which is usually the concentration that is used when applying deicing salts to concrete pavements. This shows the significant effect of deicing salts on concrete pavements deterioration since the expansion of cement paste occurs even at lower deicing salt solution concentration and only after couple of days. It means that regardless of the environment temperature, W/CM, and salt solution concentration, cement paste will face deterioration when it is exposed to the deicing salt solution even for few days. Thus, in order to not having the joint deterioration problem in concrete pavements, we need to prevent the joint from exposure to deicing salt solution for couple of days which happens when the salt water is trapped in the joints. Two main conditions that can lead two CAOXY being a problem is failed joint sealant and inactivated joints. It is obvious that when the joint sealant is failed, it leads to deicing salt solution penetration to joints, and if the joints are inactivated, the salt water will be trapped leading to deterioration since when the joints are activated, the salt solution will pass through the crack from the bottom of the joint to the bottom of the pavement. Thus, resealing and maintaining the functionality of the sealant system are preventive measures that should be considered to tackle this problem; it is important prior to resealing, to wash out the joint and removing surface salt, short of a full depth repair, before installation of the new sealant. However, if full depth repair was needed that would certainly establish a working joint rather than a non-working joint. These measures can prevent concrete pavement joint deterioration leading to enhancement the life span of pavements.

References

[1] Shi, X., et al., Evaluation of alternative anti-icing and deicing compounds using sodium chloride and magnesium chloride as baseline deicers–Phase I. 2009, Colorado. Dept. of Transportation. Applied Research and Innovation Branch.
[2] Li, W., et al., Water absorption and critical degree of saturation relating to freeze-thaw damage in concrete pavement joints. Journal of Materials in Civil Engineering, 2012. 24(3): p. 299-307.
[3] Suraneni, P., et al., Deicing salts and durability of concrete pavements and joints. Concr. Int, 2016. 38(4): p. 48-54.
[4] Blackburn, R.R., Snow and ice control: Guidelines for materials and methods. Vol. 526. 2004: Transportation Research Board.
[5] Walker, D., The truth about sand and salt for winter maintenance. Crossroads. Fall, 2005.
[4] Ghafoori, N. and R.P. Mathis, Scaling resistance of concrete paving block surfaces exposed to deicing chemicals. Materials Journal, 1997. 94(1): p. 32-38.
[5] O'Keefe, K. and X. Shi. Anti-icing and pre-wetting: improved methods for winter highway maintenance in North America. in Proceedings of the Transportation Research Board Annual Meeting. 2006. Citeseer.
[6] Wang, K., D.E. Nelsen, and W.A. Nixon, Damaging effects of deicing chemicals on concrete materials. Cement and concrete composites, 2006. 28(2): p. 173-188.
[7] AASHTO (American Association of Highway and Transportation Officials). 2020. Standard Method of Test for Quantifying Calcium Oxychloride Formation Potential of Cementitious Pastes Exposed to Deicing Salts. AASHTO T 365-20.
[8] Jones, C. et al., Calcium oxychloride: A critical review of the literature surrounding the formation, deterioration, testing procedures, and recommended mitigation techniques. Cem. Concr. Compos., 2020. 113: 103663.
[9] Sutter, L., et al., Long-term effects of magnesium chloride and other concentrated salt solutions on pavement and structural Portland cement concrete. Transportation research record, 2006. 1979(1): p. 60-68.
[10] Olek, J., et al., Investigation of anti-icing chemicals and their interactions with pavement concretes. 2013.
[11] McDonald, D. and W. Perenchio, Effects of salt type on concrete scaling. Concrete international, 1997. 19(7): p. 23-26.
[12] Collepardi, M., L. Coppola, and C. Pistolesi, Durability of concrete structures exposed to CaCl 2 based deicing salts. Special Publication, 1994. 145: p. 107-120.
[13] Sutter, L., et al., The deleterious chemical effects of concentrated deicing solutions on Portland cement concrete. 2008, South Dakota Department of Transportation, Office of Research.
[14] Xiao, D.X., S. Owusu-Ababio, and R. Schmitt, Evaluation of the Effects of Deicers on Concrete Durability. 2018.
[15] Jones, W., et al., An overview of joint deterioration in concrete pavement: Mechanisms, solution properties, and sealers. 2013.
[16] Suraneni, P. et al. 2017. "Calcium oxychloride formation potential in cementitious pastes exposed to blends of deicing salt." ACI Mater. J., 114 (4), 631-641.
[17] Weiss, J., et al., Guide to the Prevention and Restoration of Early Joint Deterioration in Concrete Pavements. 2016.
[18] Taylor, P., R. O. Rasmussen, H. Torres, G. Fick, D. Harrington, and T. Cackler., Interim guide for optimum joint performance of concrete pavements. 2012, National Concrete Pavement Technology Center: Ames, IA 50011.
[19] Xiao, D. et al., Evaluation of the Effects of Deicers on Concrete Durability. WisDOT., 2018. WHRP 0092-17-03.
[20] Qiaoa, C. et al., Chloride binding of cement pastes with fly ash exposed to $CaCl_2$ solutions at 5 and 23 °C. Cem. Concr. Compos., 2019. 97, 43-53.
[21] Farnam, Y. et al., Acoustic Emission and Low Temperature Calorimetry Study of Freeze and Thaw Behavior in Cementitious Materials Exposed to NaCl Salt. Transp. Res. Rec., 2014. 2441 (1), 81-90.

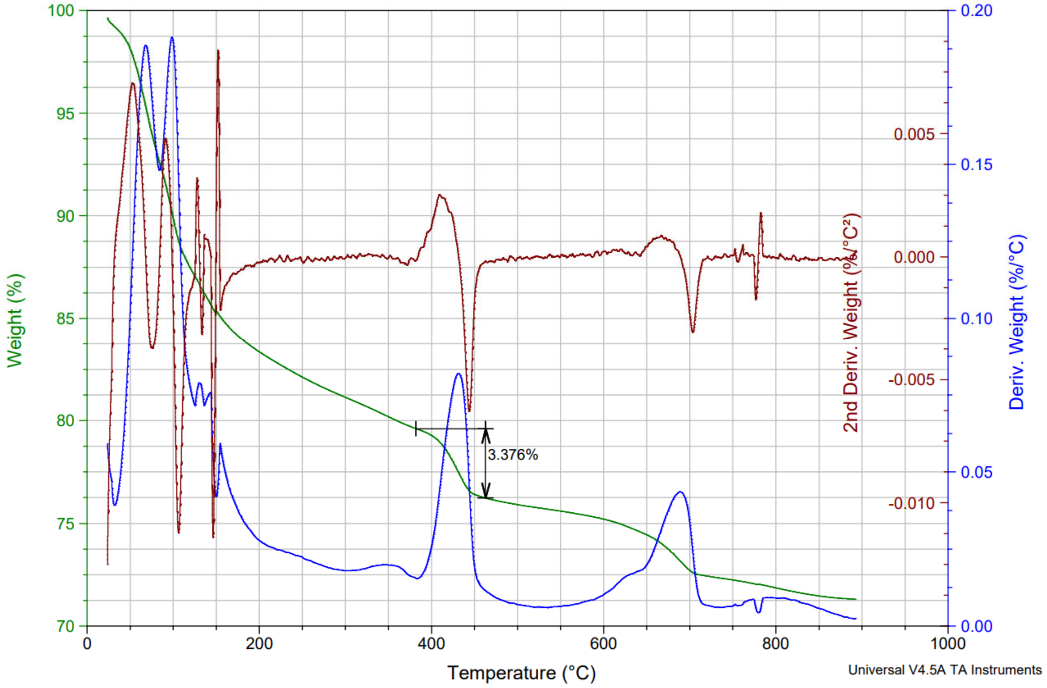
[22] Jones, C. et al., Investigating concrete deterioration due to calcium oxychloride formation. Constr. Build. Mater., 2022. 320: 125600.
[23] Callister, Jr. William D. and Rethwisch, David G., Fundamentals of Materials Science and Engineering. 4th edition, John Wiley & Sons, Inc.

APPENDIX A

TGA TEST RESULTS

The following graphs show the results of the conducted TGA tests on different specimens and the calculation of the percentage of mass loss due to the decomposition of Calcium Hydroxide as a result of heating up the specimens during the TGA tests.

Specimen W/C38Cl0T4:



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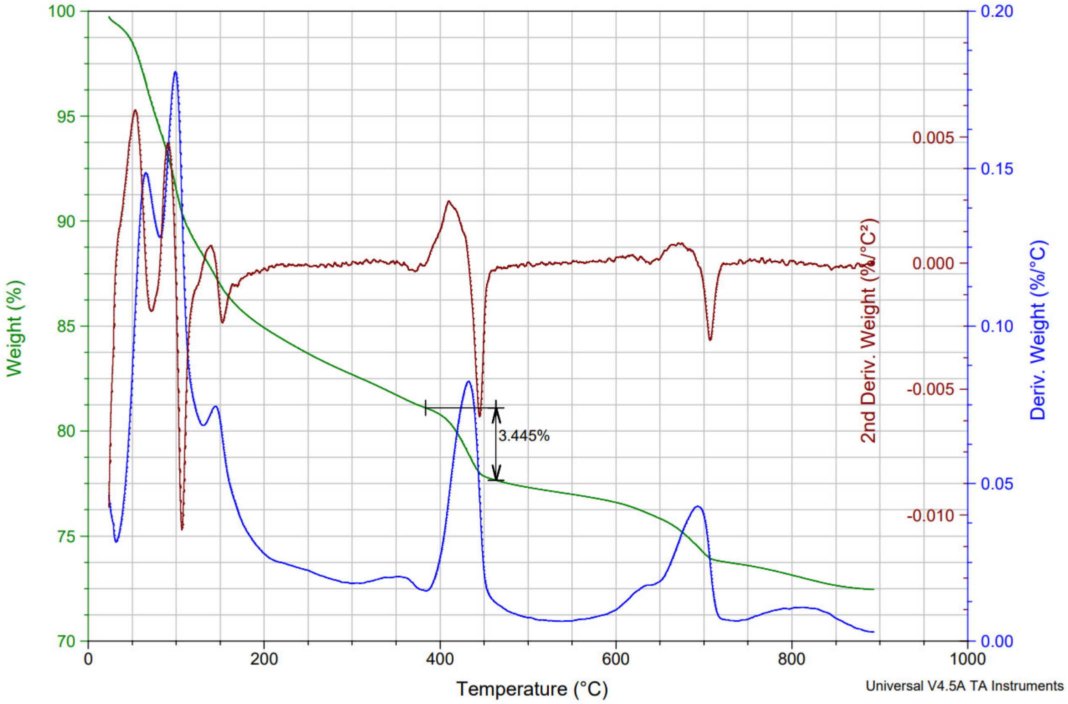

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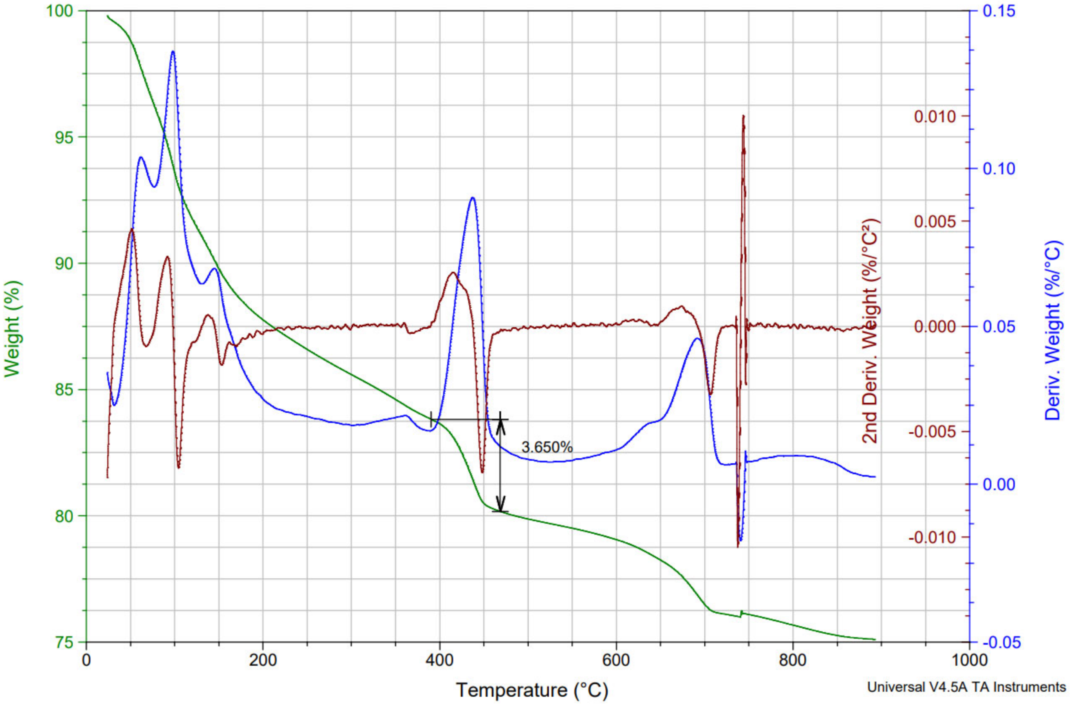

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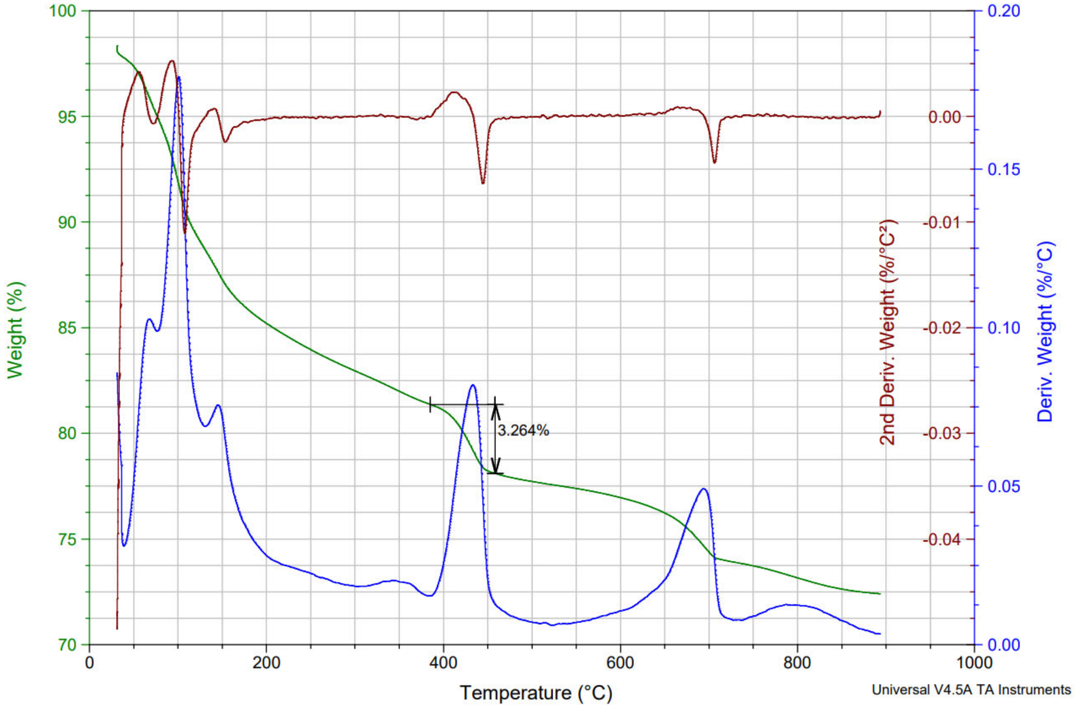
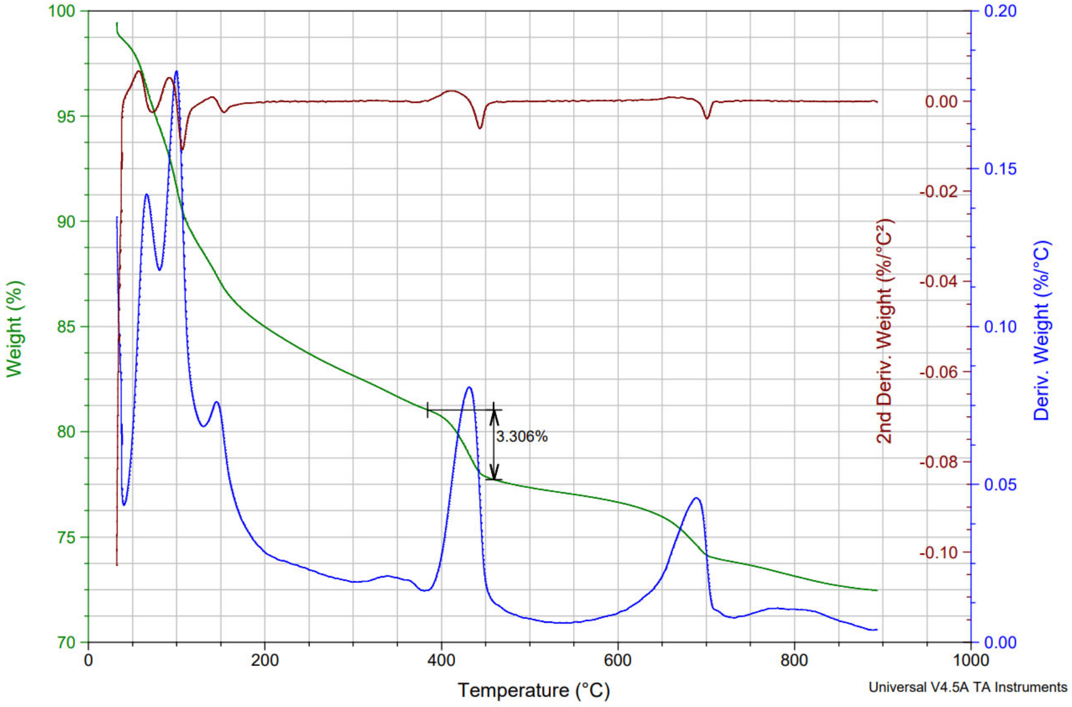
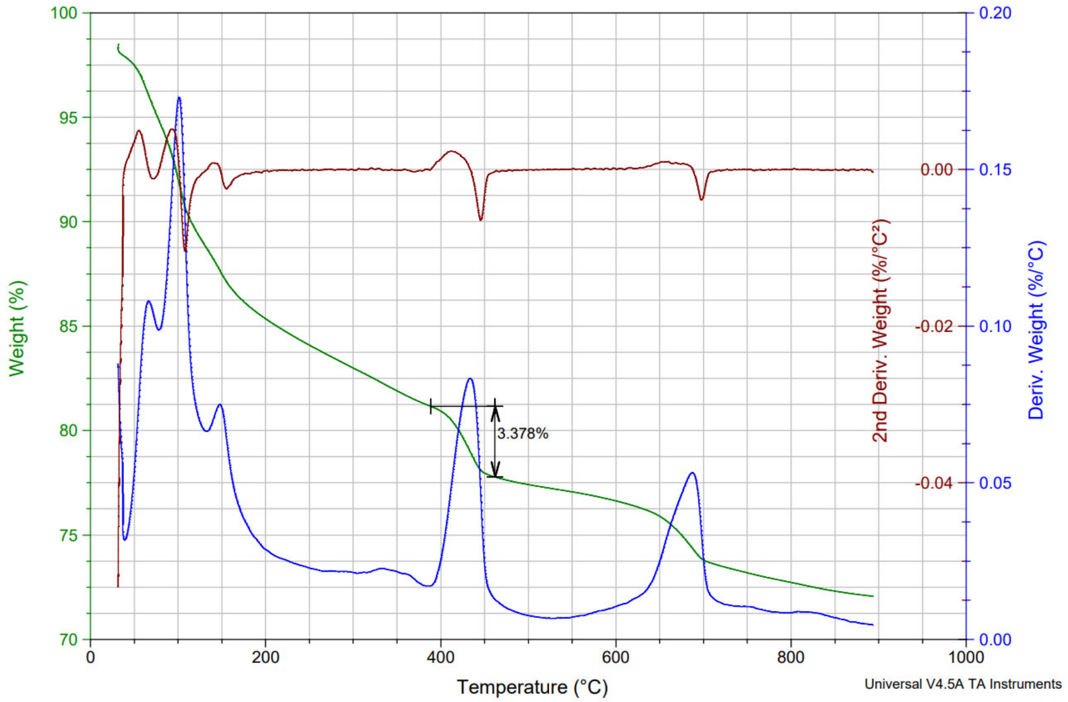


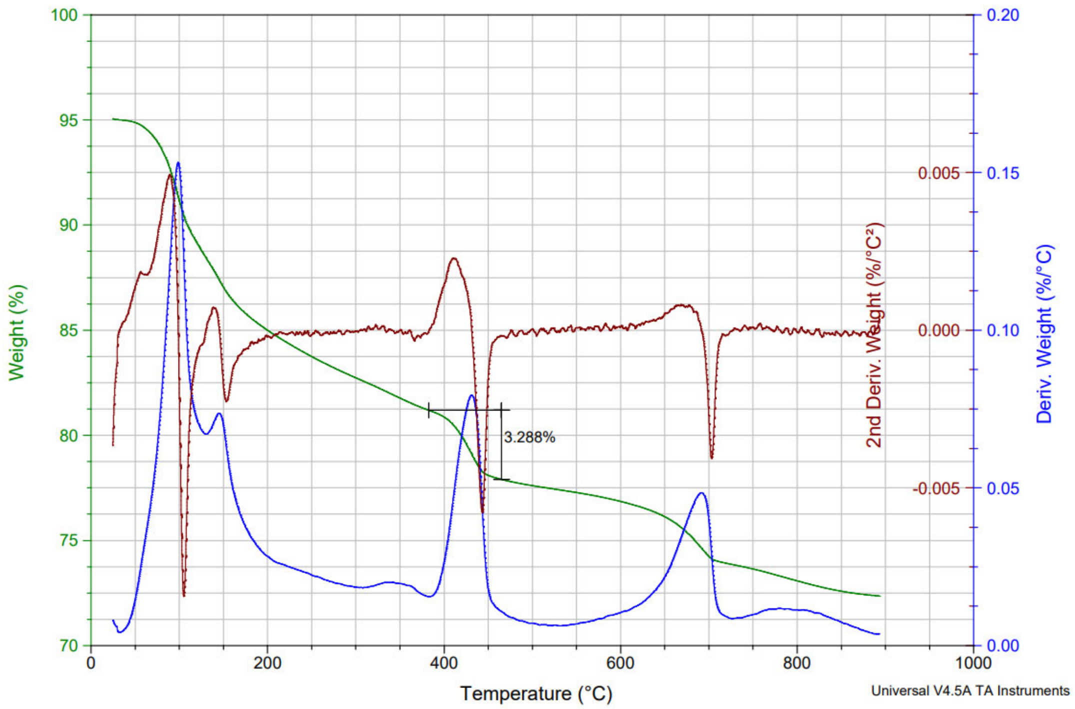
Specimen W/C38Cl10T20:



Specimen W/C38Cl10T40:



Specimen W/C38Cl20T4:



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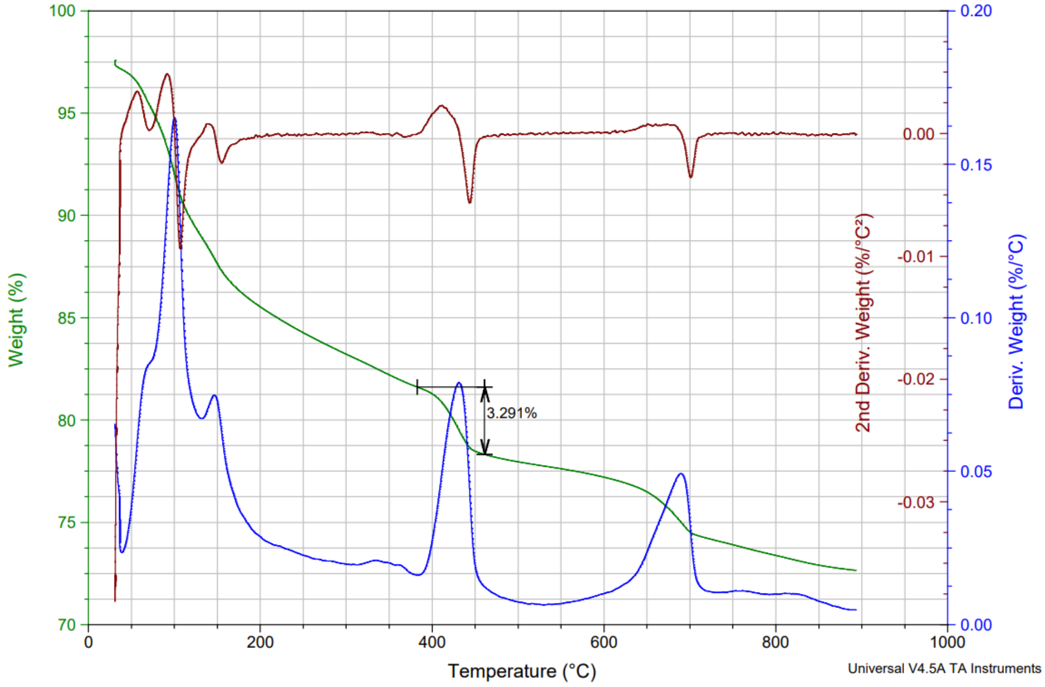

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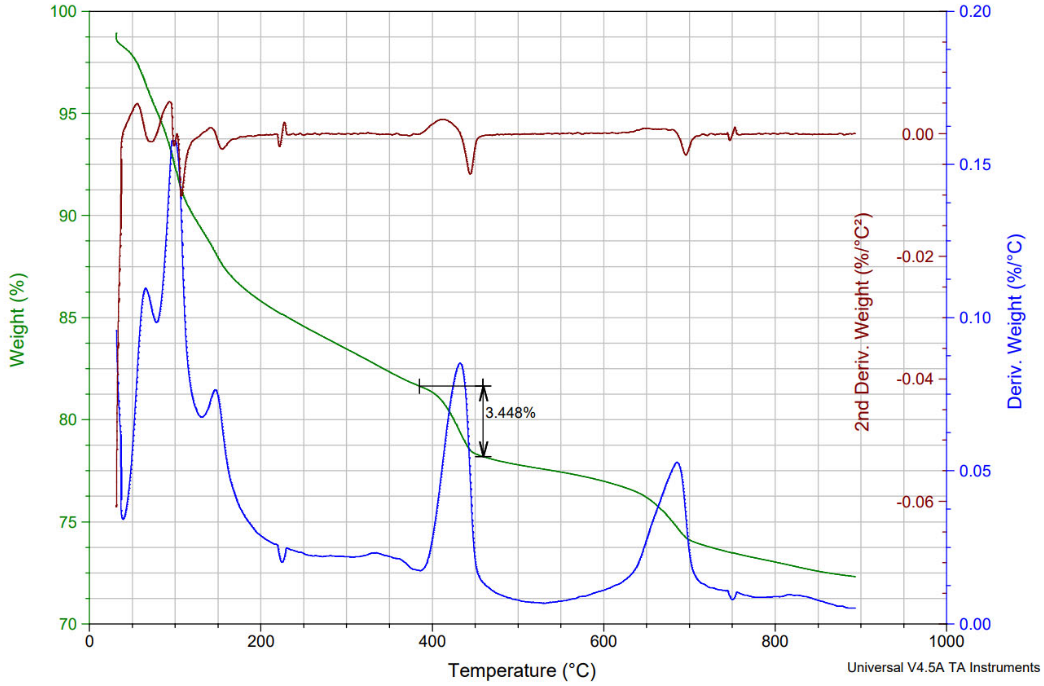

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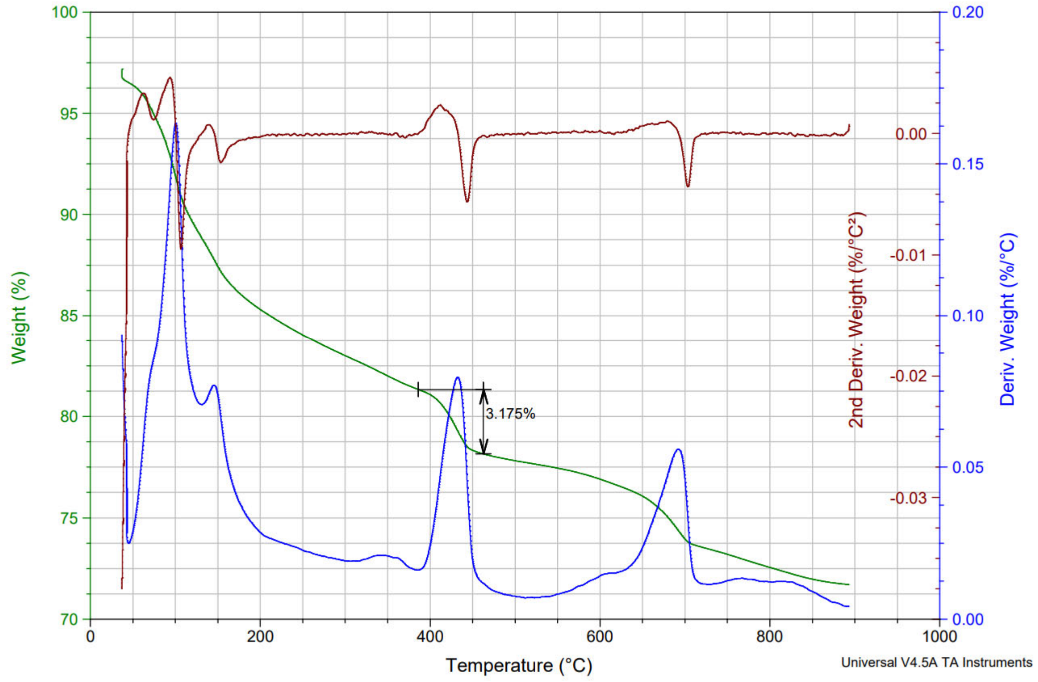

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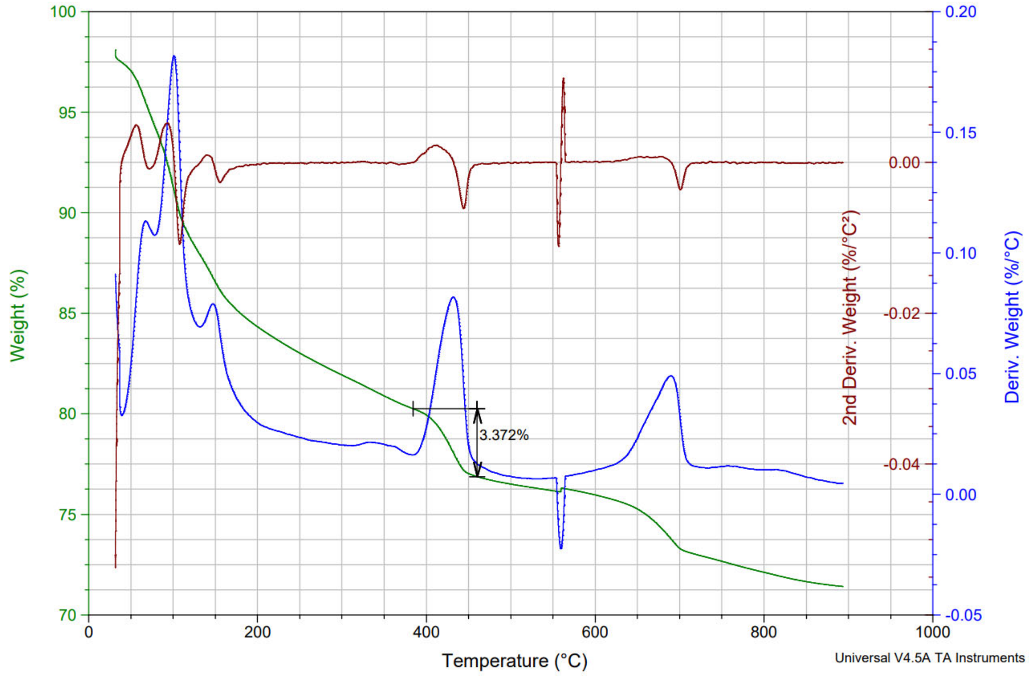

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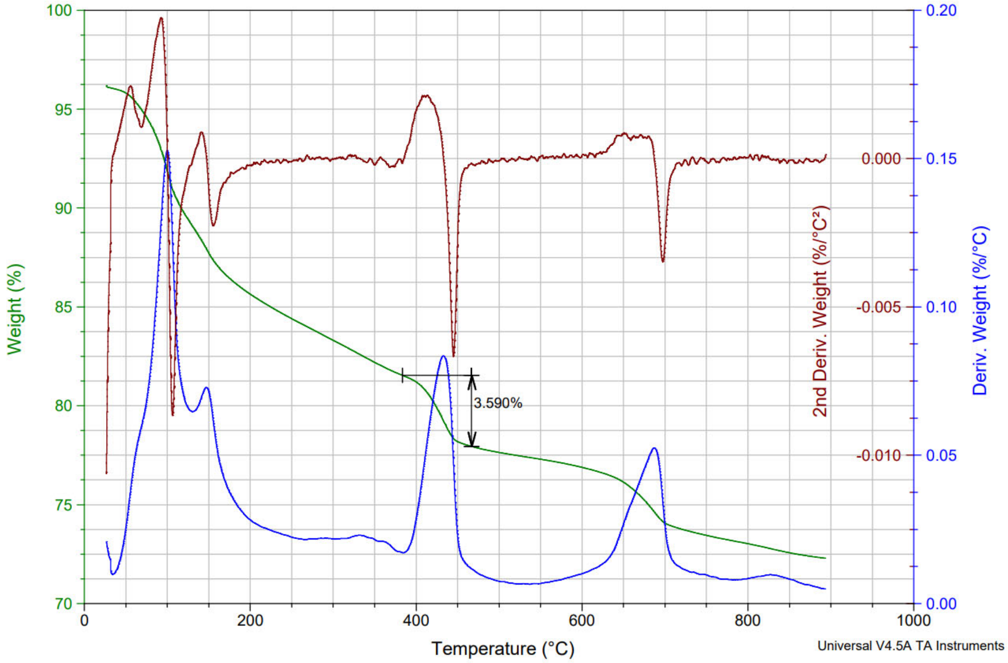

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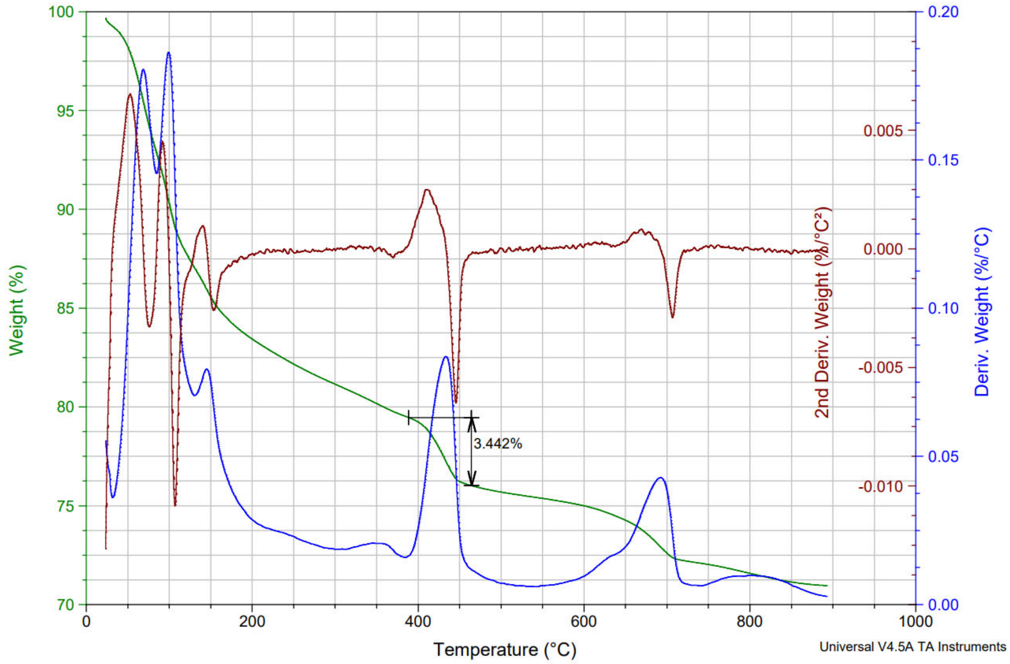

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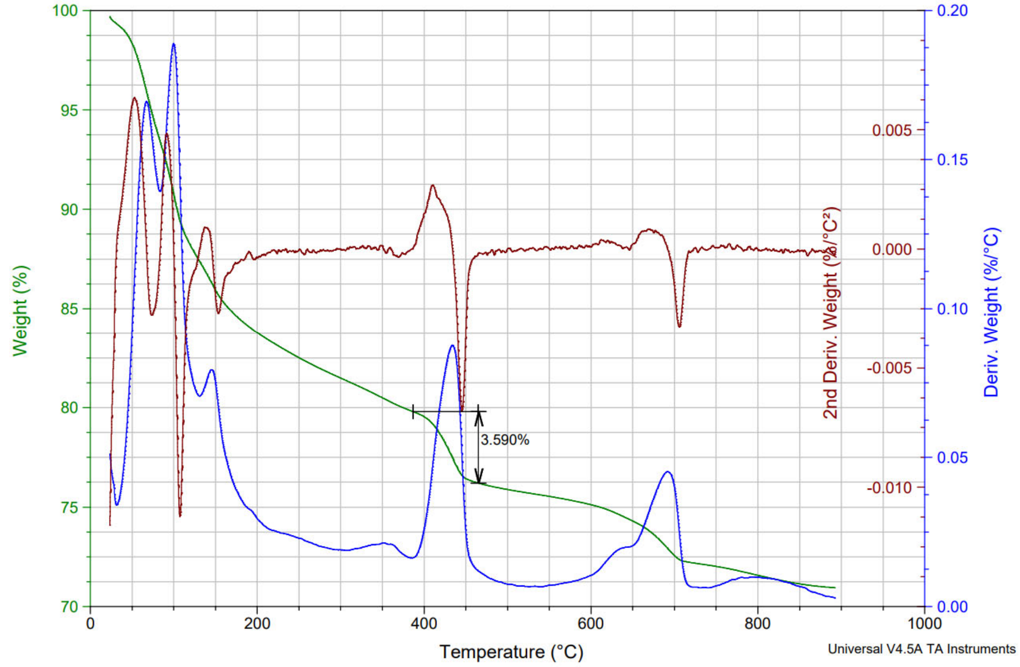

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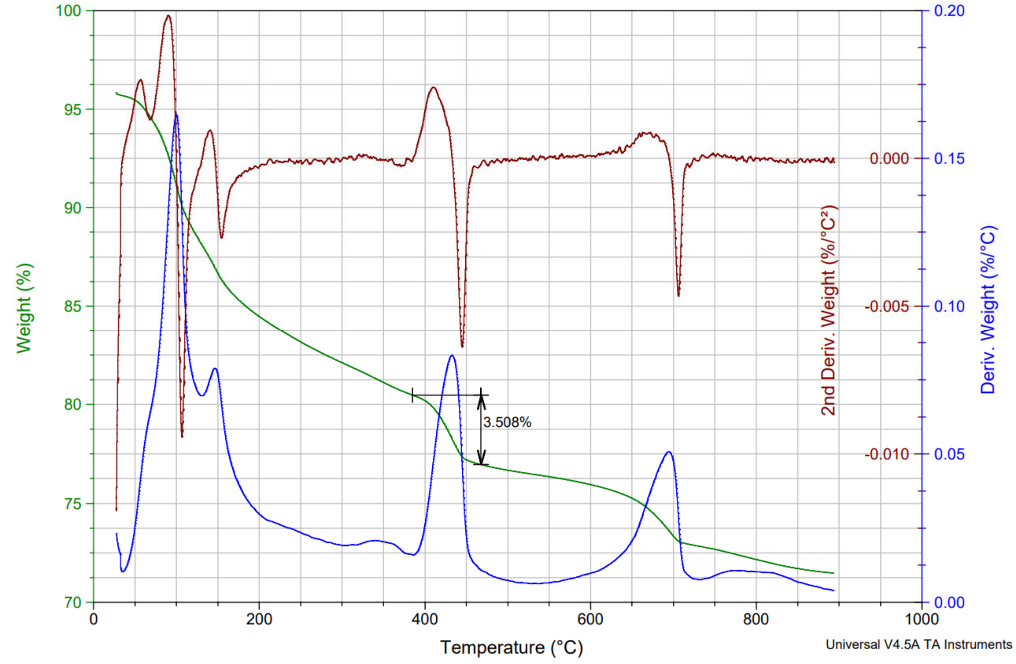

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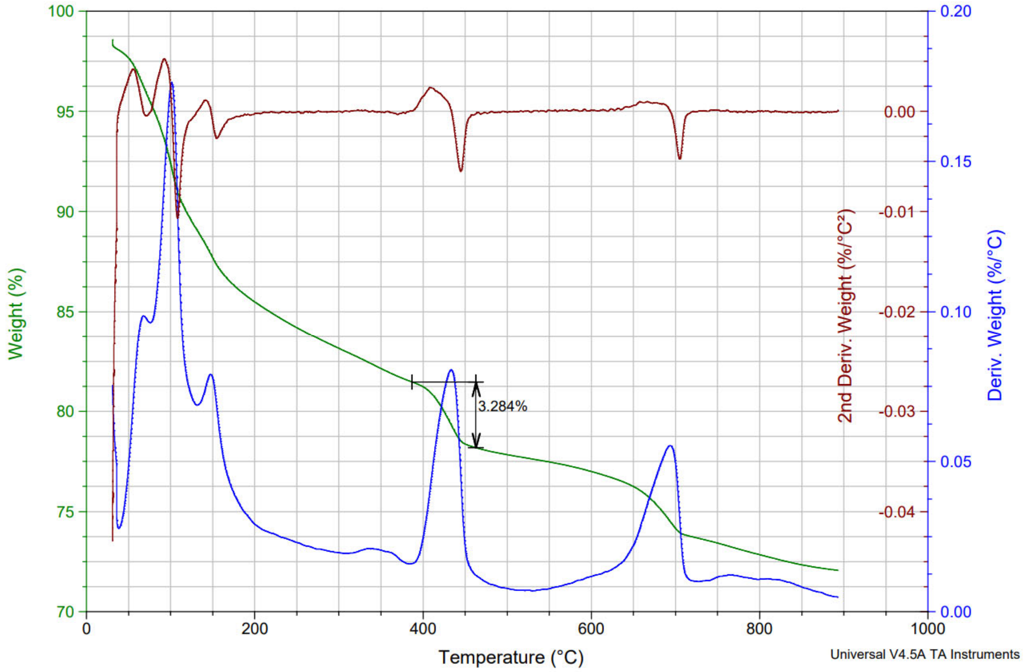

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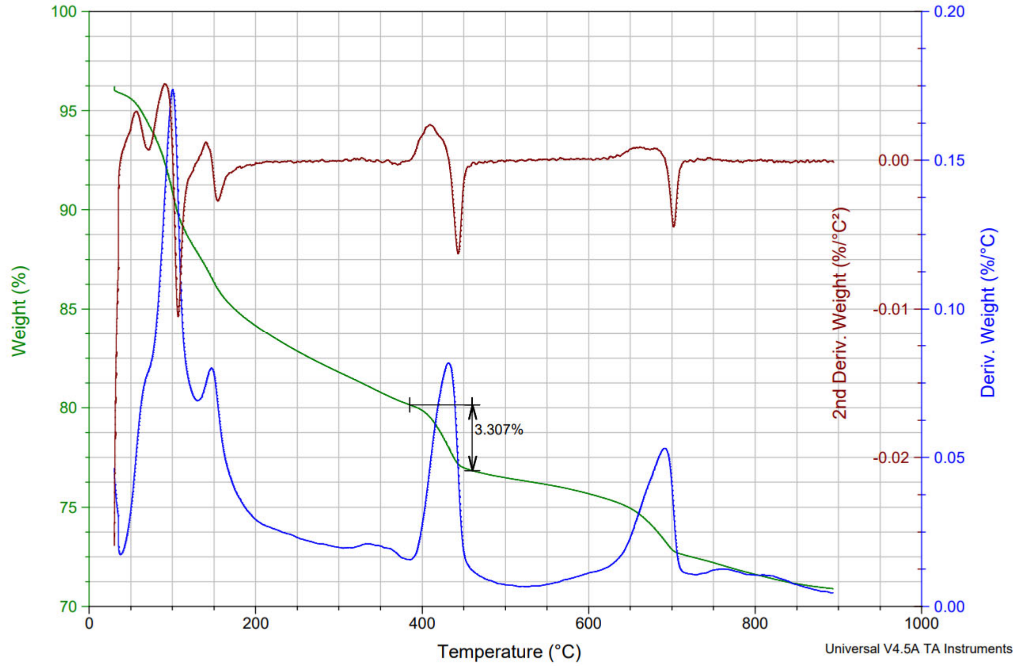
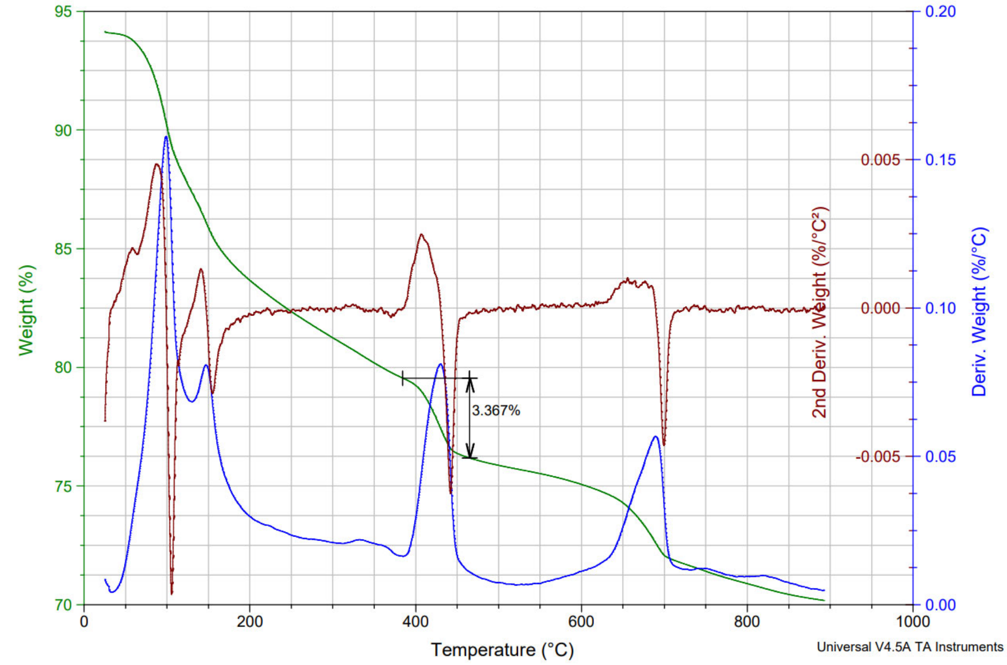


Specimen W/C43Cl20T20:



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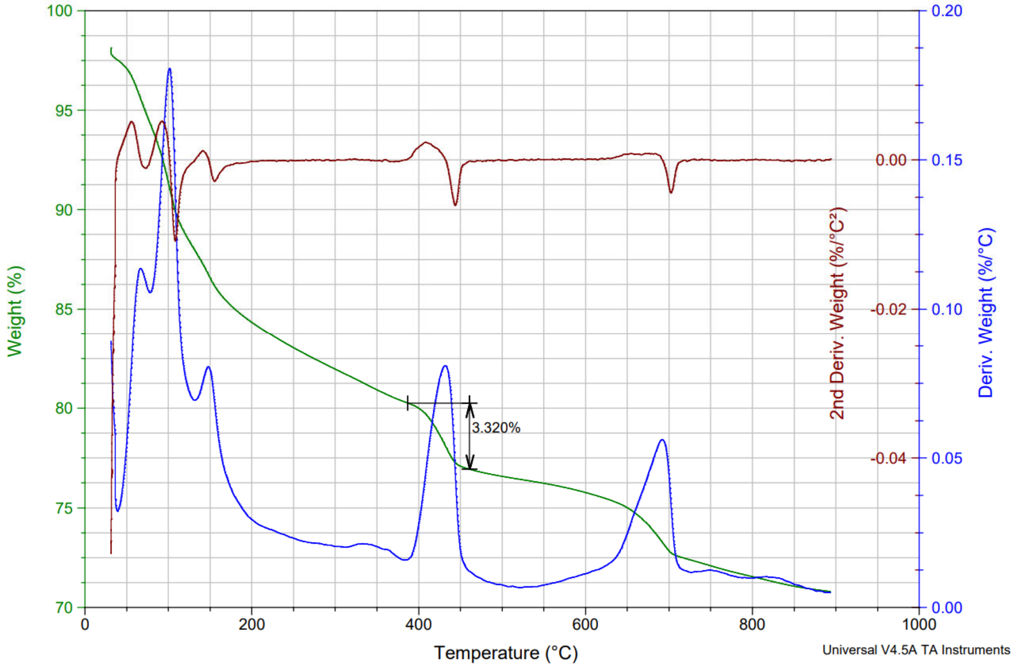

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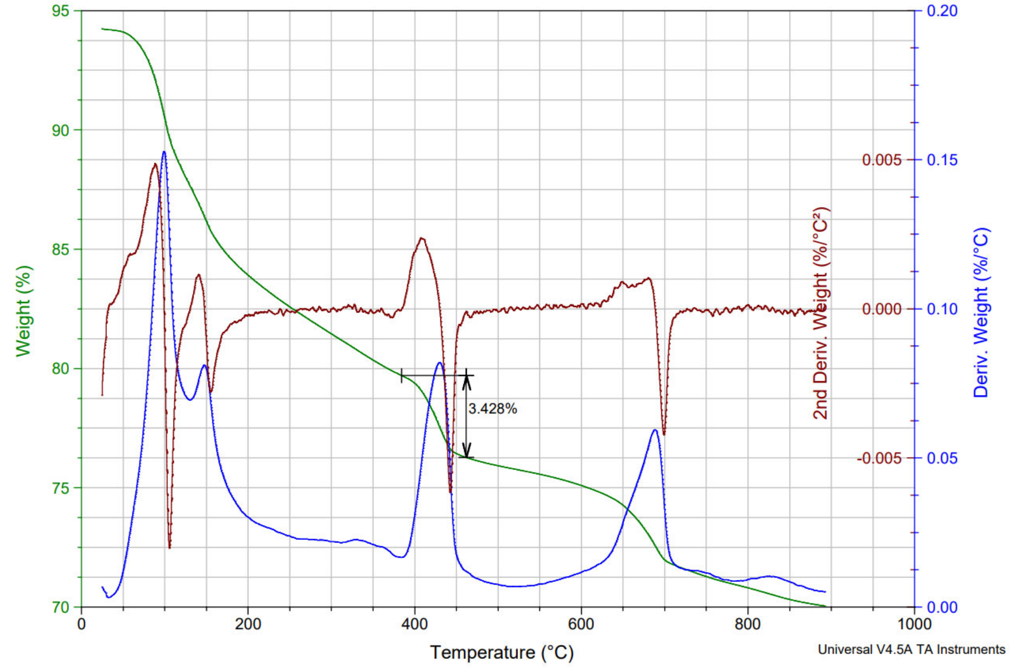

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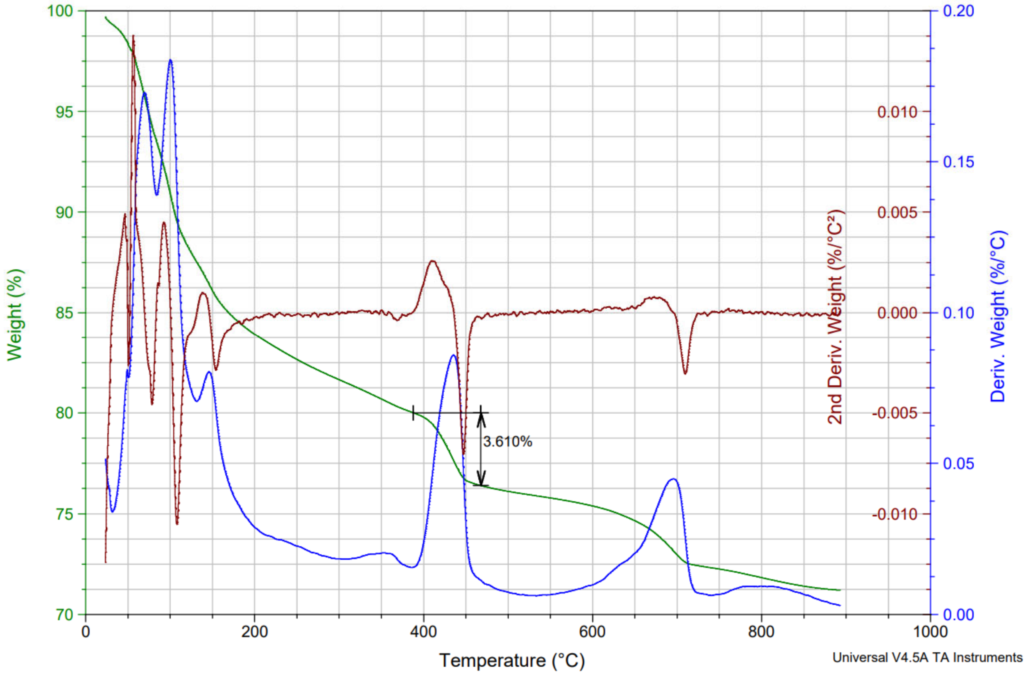
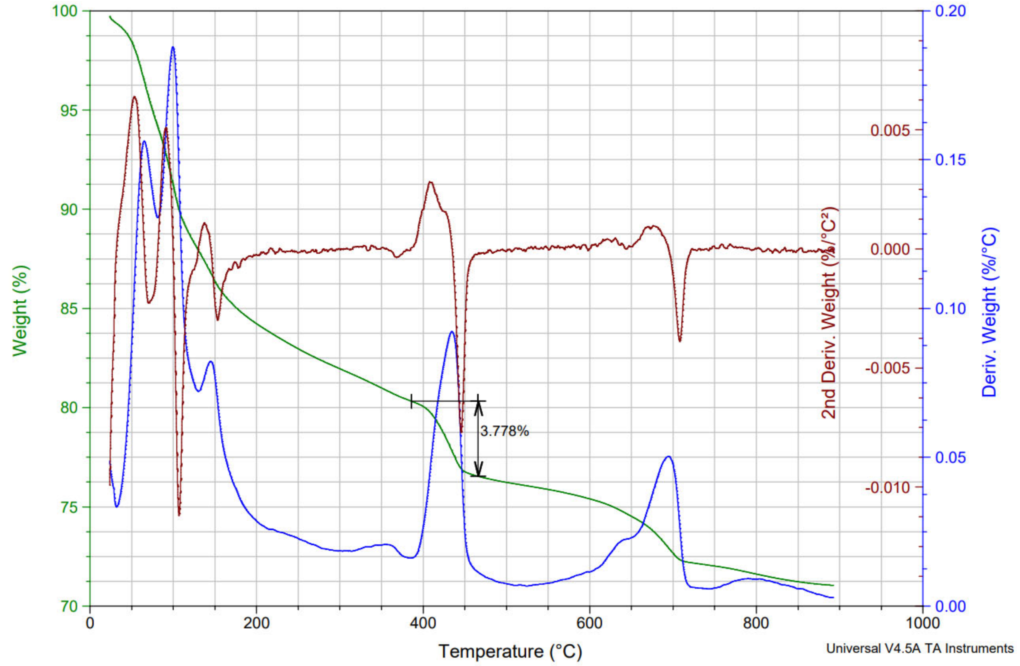


Specimen W/C48Cl0T20:



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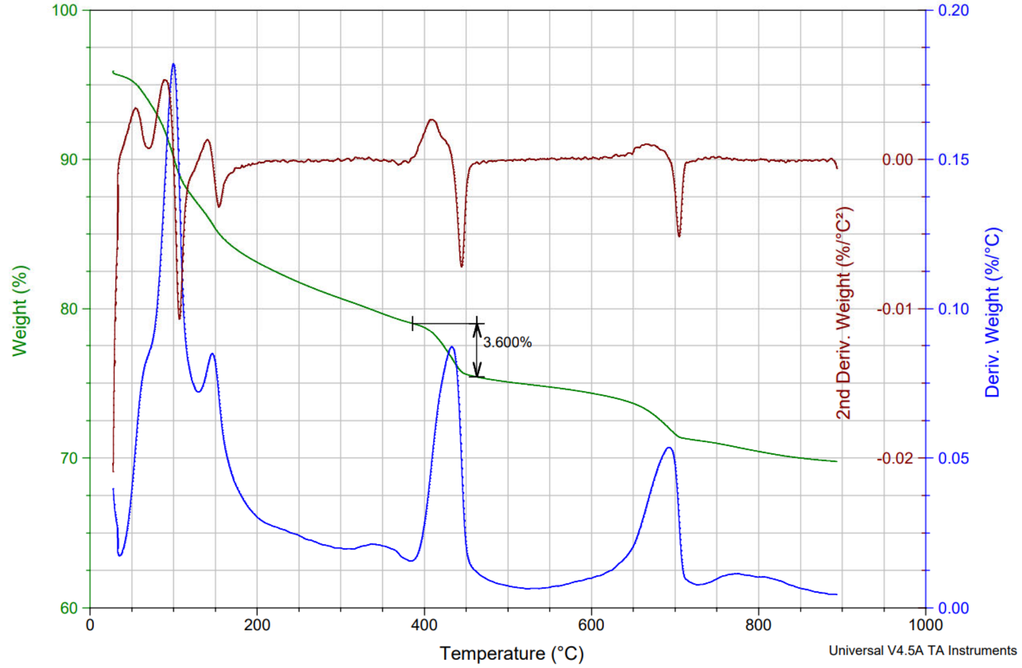
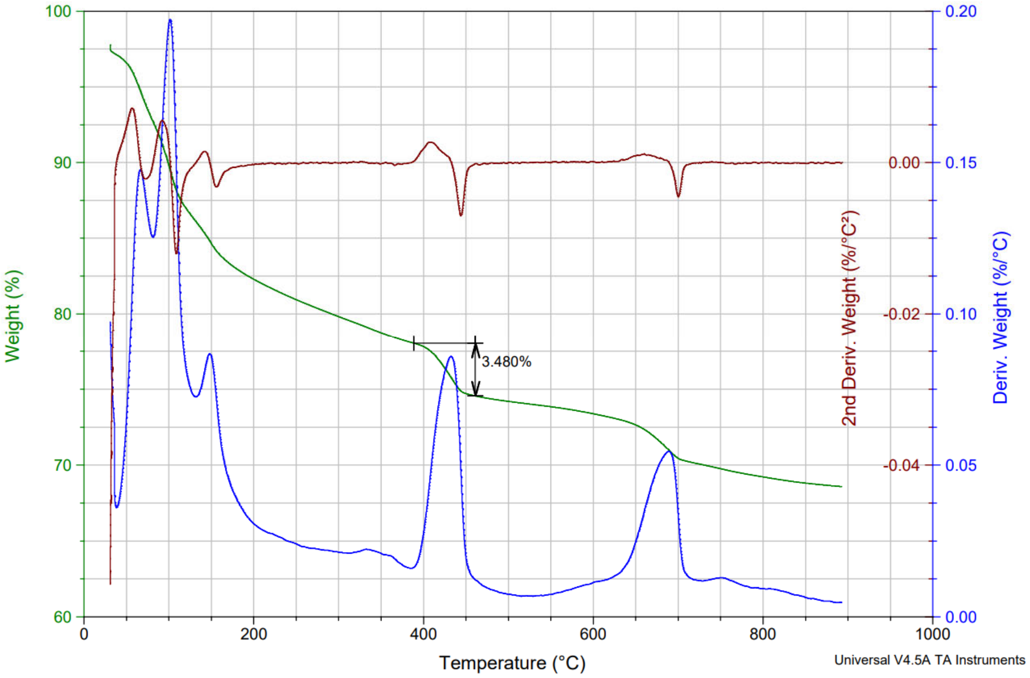
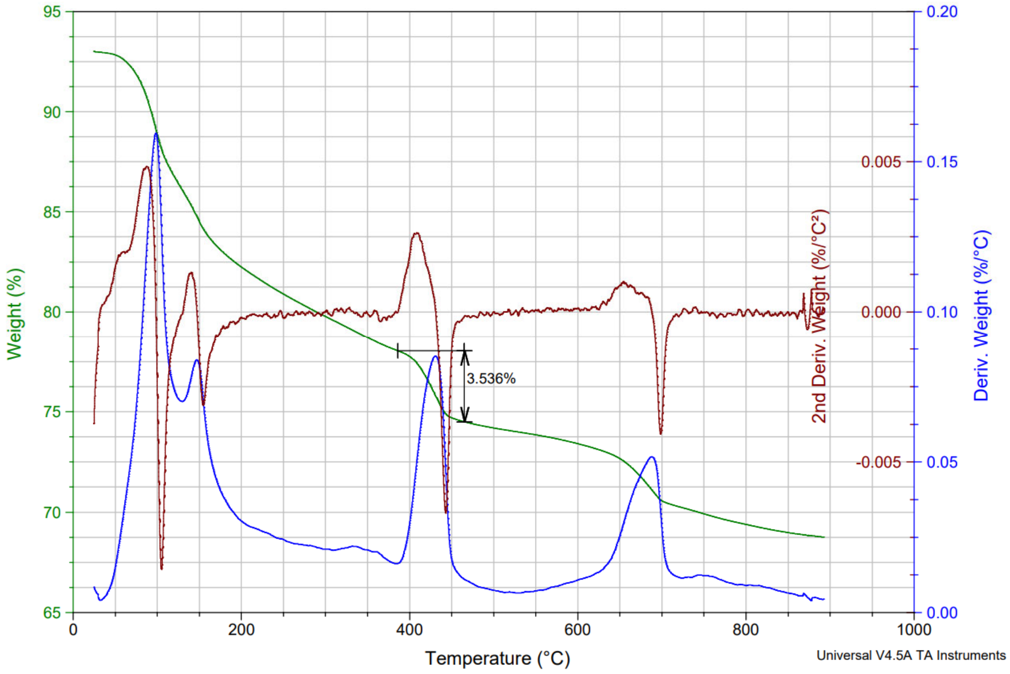


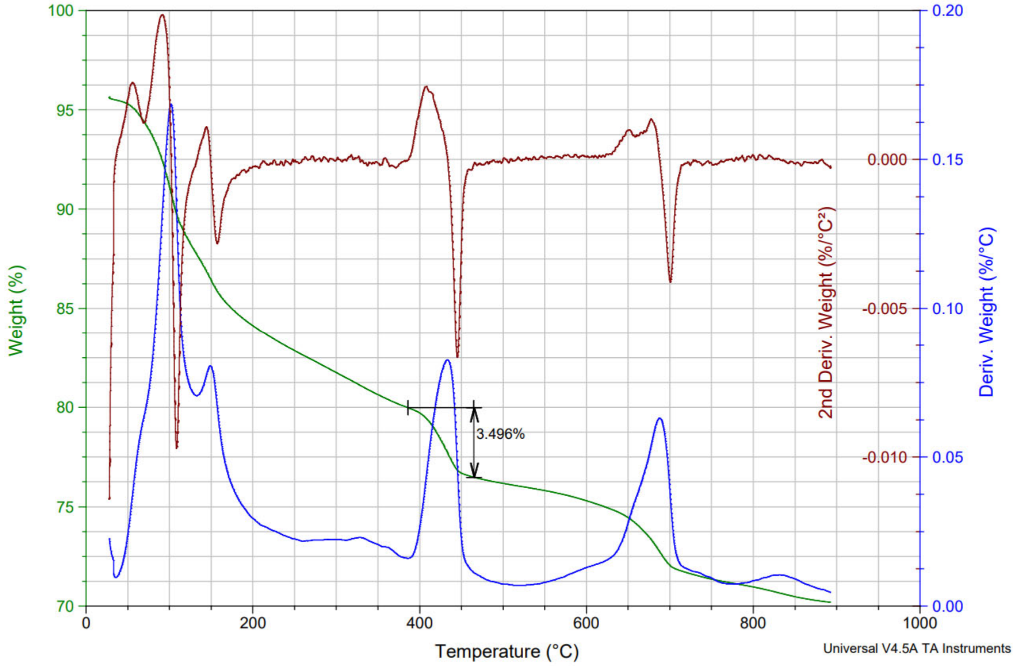
Specimen W/C48Cl0T20:



Specimen W/C48Cl20T4:



Specimen W/C48Cl20T20:



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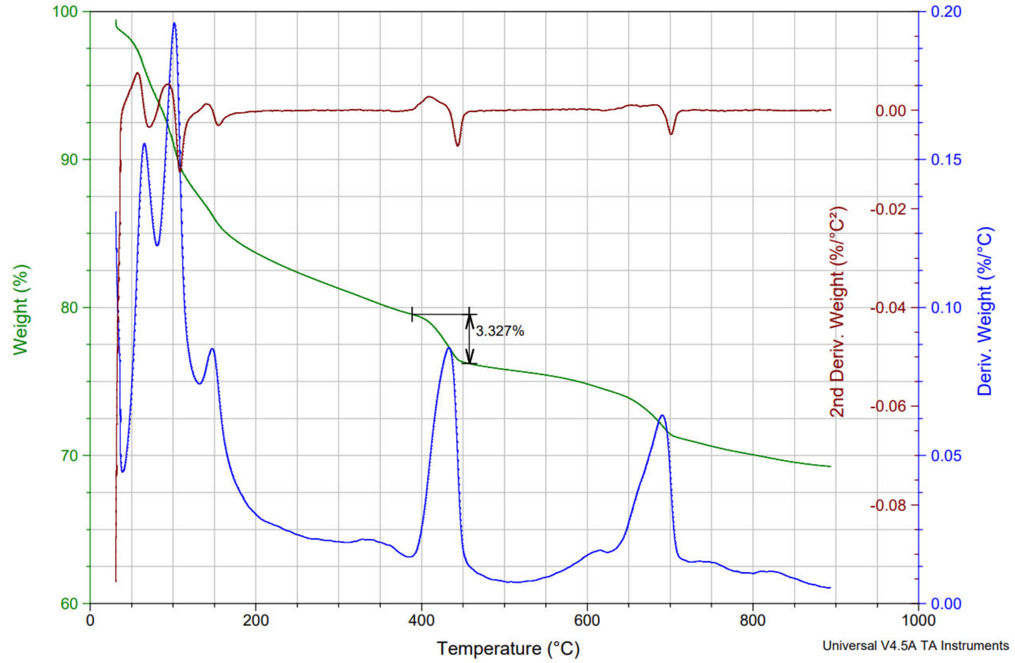

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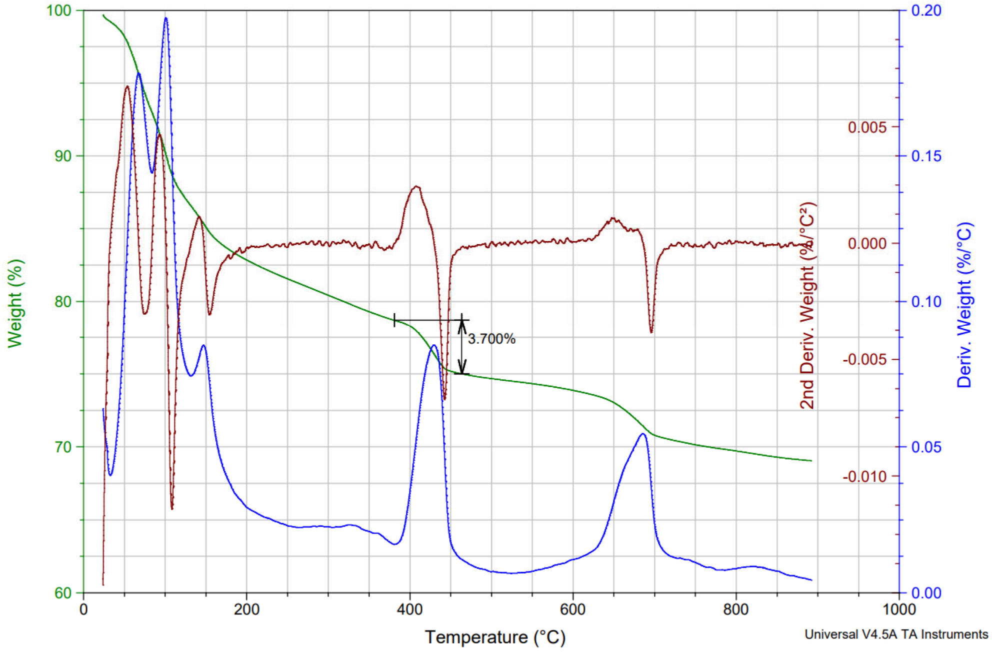

APPENDIX B

A PRACTICAL EXAMPEL FOR EXPANSION MODEL

Using the mentioned model to obtain the overall rates for different temperatures and compare them with the observed k values, it can be seen that this model can predict the rate with an acceptable range of error. The following equation shows the model which was obtained:

$$K = 0.27 \times 245487.179e^{-\frac{2541.9}{T}} + 0.1 \times 0.023e^{\frac{2318.7}{T}} + 0.1 \times 2.585e^{\frac{851.7}{T}} + 0.53 \times 0.007e^{\frac{2628.5}{T}}$$

The following table shows the observed and predicted rate values.

Rate value for different temperatures and samples.

Sample	Temperature (°C)	Temperature (K)	Rate (experimental)	Rate (predicted)
W/C43Cl10T4	4	277.15	56	71
W/C43Cl20T-4	-4	269.15	116	89
W/C38Cl20T-4	-4	269.15	128	89