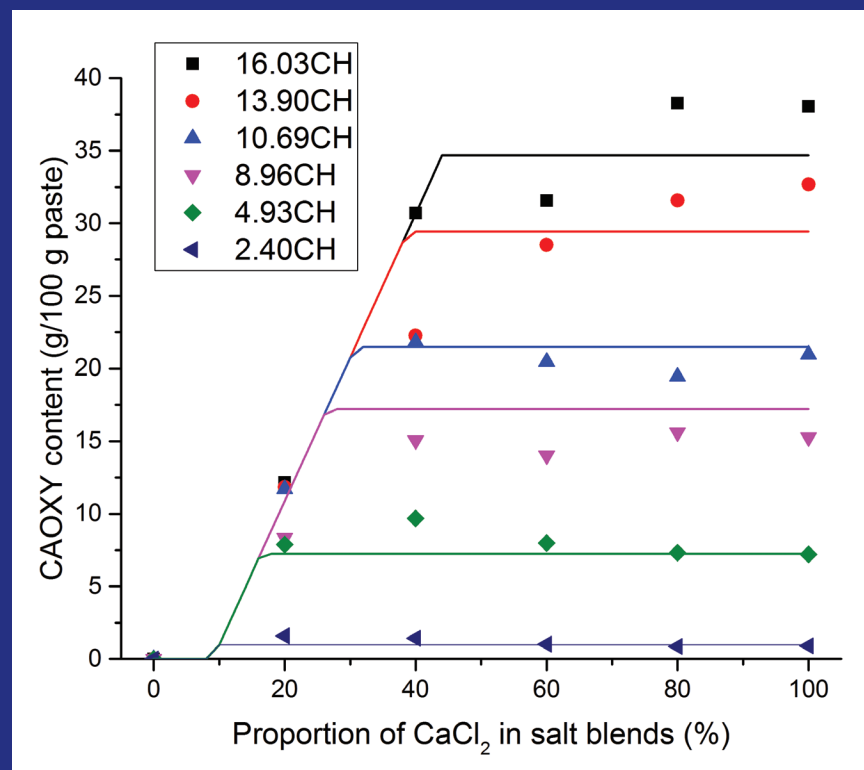


JOINT TRANSPORTATION RESEARCH PROGRAM

INDIANA DEPARTMENT OF TRANSPORTATION
AND PURDUE UNIVERSITY



Performance of Concrete Pavement in the Presence of Deicing Salts and Deicing Salt Cocktails



Prannoy Suraneni, Jonathan Monical, Erol Unal, Yaghoob Farnam,
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JOINT TRANSPORTATION RESEARCH PROGRAM

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16. Abstract <p>Deicing salts are widely used for anti-icing and de-icing operations in pavements. While historically sodium chloride may have been the deicer most commonly used, a wide range of deicing salts have begun to be used to operate at lower temperatures, to “stick to the road better” and to improve other aspects of performance such as environmental impact or corrosion resistance. It has been observed that some chloride based deicing salts can react with the calcium hydroxide in the mixture resulting in the formation of calcium oxychloride an expansive phase that can damage concrete pavements, especially at the joints. This report describes the two main objectives of this work. First, the report documents the development a standardized approach to use low temperature differential scanning calorimetry (LT-DSC) to assess the influence of cementitious binder composition on the potential for calcium oxychloride formation. Second, this work will assess the influence of blended salt cocktails on the formation of calcium oxychloride.</p>			
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EXECUTIVE SUMMARY

PERFORMANCE OF CONCRETE PAVEMENT IN THE PRESENCE OF DEICING SALTS AND DEICING SALT COCKTAILS

Introduction

This report is a summary of work performed to assess the performance of concrete paving materials in the presence of deicing salts and deicing salt cocktails as a part of the Joint Transportation Research Program (JTRP) through SPR-3864. This report describes the two main outcomes of this work. First, the report documents the development a standardized approach to use low temperature differential scanning calorimetry (LTDSC) to assess the influence of cementitious binder composition on the potential for calcium oxychloride formation. Second, this work will assess the influence of blended salt cocktails on the formation of calcium oxychloride.

Findings

- Some concrete pavements have shown premature deterioration at the joints. It has been proposed that this can be attributed to two primary factors: increased fluid saturation and a chemical reaction that occurs between deicing salts and the cement matrix.
- A test method was developed/formalized that uses a low temperature differential scanning calorimeter (LTDSC) test method to quantify the chemical reaction that occurs between the cementitious matrix and the deicing salt to form calcium oxychloride.

- It is proposed that the LTDSC test be used to qualify the potential for calcium oxychloride formation in a cementitious matrix. Currently two primary approaches appear poised to have the potential to mitigate calcium oxychloride formation. These include the replacement of a portion of cement with supplementary cementitious materials and the use of concrete sealers such as soy methyl ester polystyrene blends.
- This report has shown that as the calcium hydroxide (CH) content in the paste increases, so does the potential for calcium oxychloride (CAOXY) formation. CAOXY contents increase with the proportion of CaCl_2 solution in the blends. A simple model has been developed to estimate the amount of calcium oxychloride formed in the pastes, depending on the calcium chloride and calcium hydroxide contents.

Implementation

This report describes the development of a standardized approach to use low temperature differential scanning calorimetry (LTDSC) to assess the influence of cementitious binder composition on the potential for calcium oxychloride formation. This procedure is well founded and is written in ITM format and can be considered for acceptance by INDOT as a test method and forwarded to AASHTO for national consideration as well. The work is documented, accurate and peer reviewed. Second, this work assessed the influence of blended salt cocktails on the formation of calcium oxychloride in various cementitious systems. The work indicates that calcium oxychloride formation can be reduced with the use of supplementary materials, the use of topical treatments, and judicious selection of blend formulations.

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1. OVERVIEW OF RESEARCH

Deicing salts are widely used for anti-icing and deicing operations. While historically sodium chloride may have been the deicer of choice, a wide range of deicing materials have begun to be used to operate at lower temperatures, to adhere to the road better, and to improve other aspects of performance such as environmental impact or corrosion resistance. It has recently been observed that intermediate phases can form when the deicing salt reacts with the matrix of the concrete resulting in a reduction in the durability of concrete pavements. Blended deicing materials can result in changes in melting capacity of ice and intermediate phase compositions forming with the paving materials. This project examined the potential reaction that can occur with different binders and different salt cocktails. Further this project developed the use of a new test method based on low temperature differential scanning calorimetry (LTDC) to assess the freezing point for liquid deicers and their potential to form deleterious reactions that impact the durability from a fundamental scientific perspective. This can guide INDOT operations providing information on the potential interaction between the salt and the pavement composition. This may enable pavement binders to be selected that are least resistant to salt damage since they will be more compatible with deicing salts.

1.1 Organization of This Report

This report is presented as a short summary of three journal papers that were written as a part of this project. This report presents only the most salient points of the three papers, full details may be found in the papers themselves, which are provided in the Appendices. Additionally, the Appendices also contains a developed Indiana Test Method for the low temperature differential scanning calorimetry approach developed here.

The three papers are listed below, and a summary is provided in the following sections:

- **Paper #1:** Monical, J., Villani, C., Farnam, Y., Unal, E., & Weiss, W. J. (2016), "Quantifying Calcium Oxychloride Formation for Different Cementitious Materials in the Presence of CaCl_2 Using Low Temperature Differential Scanning Calorimetry." Paper #1 has been accepted for publication in *Advances in Civil Engineering Materials*.
- **Paper #2:** Monical, J., Unal, E., Barrett, T., Farnam, Y., & Weiss, W. J. (2016), "Reducing Joint Damage in Concrete Pavements: Quantifying Calcium Oxychloride Formation." Paper #2 has been published in *Transportation Research Record: Journal of the Transportation Research Board*.
- **Paper #3:** Suraneni, P., Monical, J., Unal, E., Farnam, Y., & Weiss, W. J. (2016), "Calcium Oxychloride Formation Potential in Cementitious Pastes Exposed to Blends of Deicing Salt." Paper #3 has been submitted for publication to *ACI Materials Journal*.

2. DEVELOPMENT OF THE LTDC TEST METHOD (PAPER #1)

Paper #1 works to quantify the calcium oxychloride that forms when a calcium chloride solution is placed in contact with a ground cement paste using a low temperature differential scanning calorimeter. The paper describes a test method that can be used to quantify the amount of calcium oxychloride that forms from the reaction between a cementitious paste (more specifically the CH in the paste) and calcium chloride (CaCl_2) from the solution. The testing protocol consists of three phases: (1) preparing a powder sample obtained by grinding hydrated cement paste, (2) mixing the hydrated cement paste powder with 20% CaCl_2 salt-water solution (by mass), and (3) exposing the paste-salt water solution mixture to a temperature cycle (-90°C to 50°C , by heating at a rate of $0.25^\circ\text{C}/\text{min}$). Using a low temperature differential scanning calorimeter (LTDC) the heat release signature during heating (between approximately 35°C and 45°C for this concentration of CaCl_2) can be measured and then used to quantify the energy associated with calcium oxychloride phase transition. This protocol was developed after a series of tests performed in the laboratory where several parameters were varied. Details on how the test procedure was developed and the reason of specific choices were made in terms of rates, temperatures and analysis procedures are described in the following sections. Experiments performed using a wide range of mixtures indicate that the use of supplementary cementitious materials (SCM) can reduce the volume of calcium oxychloride produced. As such, mixtures containing SCM would be less likely to demonstrate joint damage. Further, it would be expected that this test can be used to determine the level of SCM that is needed to reduce the calcium oxychloride formation to an acceptable level.

3. QUANTIFYING CALCIUM OXYCHLORIDE FORMATION FOR CONCRETE MADE USING PORTLAND CEMENT, PORTLAND LIMESTONE CEMENT, SUPPLEMENTARY CEMENTITIOUS MATERIALS, AND SEALERS (PAPER #2)

Paper #2 focuses on examining the role of mixture composition on the formation of calcium oxychloride.

Twenty-five cementitious pastes were tested in this study. Plain pastes were made with several type I portland cements and portland limestone cements. Blended cement pastes were made using the plain cements and supplementary cementitious materials (SCMs) including fly ash, slag and silica fume, portland limestone cements, and limestone powder fillers. Fly ash and slag dosages of 20, 40, and 60% were used and silica fume dosages of 1, 2, 3, 6, and 9% were used. Paste samples were mixed with a water-to-cementitious material ratio (w/cm) of 0.36 and 0.42 by mass following ASTM C305-14.

Once mixed, paste samples were cast, cured, and ground using a milling machine to produce a powder passing through a 75- μm sieve. After the powder was ground, it was stored in a sealed container to minimize the potential for carbonation. The calcium chloride solution (20% CaCl_2 by mass) was prepared by mixing granular reagent grade calcium chloride dihydrate and deionized water. The samples were then immediately placed in the LTDC to minimize potential additional hydration reactions and the procedure developed in Paper #1 was used.

As the sample is heated, the formed calcium oxychloride (CAOXY) melts, and the amount of CAOXY that is formed can be determined by normalizing the heat release during the phase change with that of pure CAOXY (186 J/g).

Figure 3.1 shows the amount of CAOXY that is formed in different cement pastes exposed to the 20% CaCl_2 solution with and without SCMs. It is evident that the tested plain cement pastes all show similar amounts of CAOXY. Samples with fly ash or slag show significantly lower amounts of CAOXY.

The benefits of SCM can be seen in Figure 3.2, which shows the amount of CAOXY that is formed in cement pastes with increasing amounts of fly ash, slag, or silica fume. CAOXY amounts are significantly reduced as the fly ash or slag replacement increases. At a replacement level of 40%, CAOXY values reduce by about 60%, and at a replacement level of 60%, CAOXY values are almost zero.

In addition to examining the role of binder composition, six different topical treatments were tested to

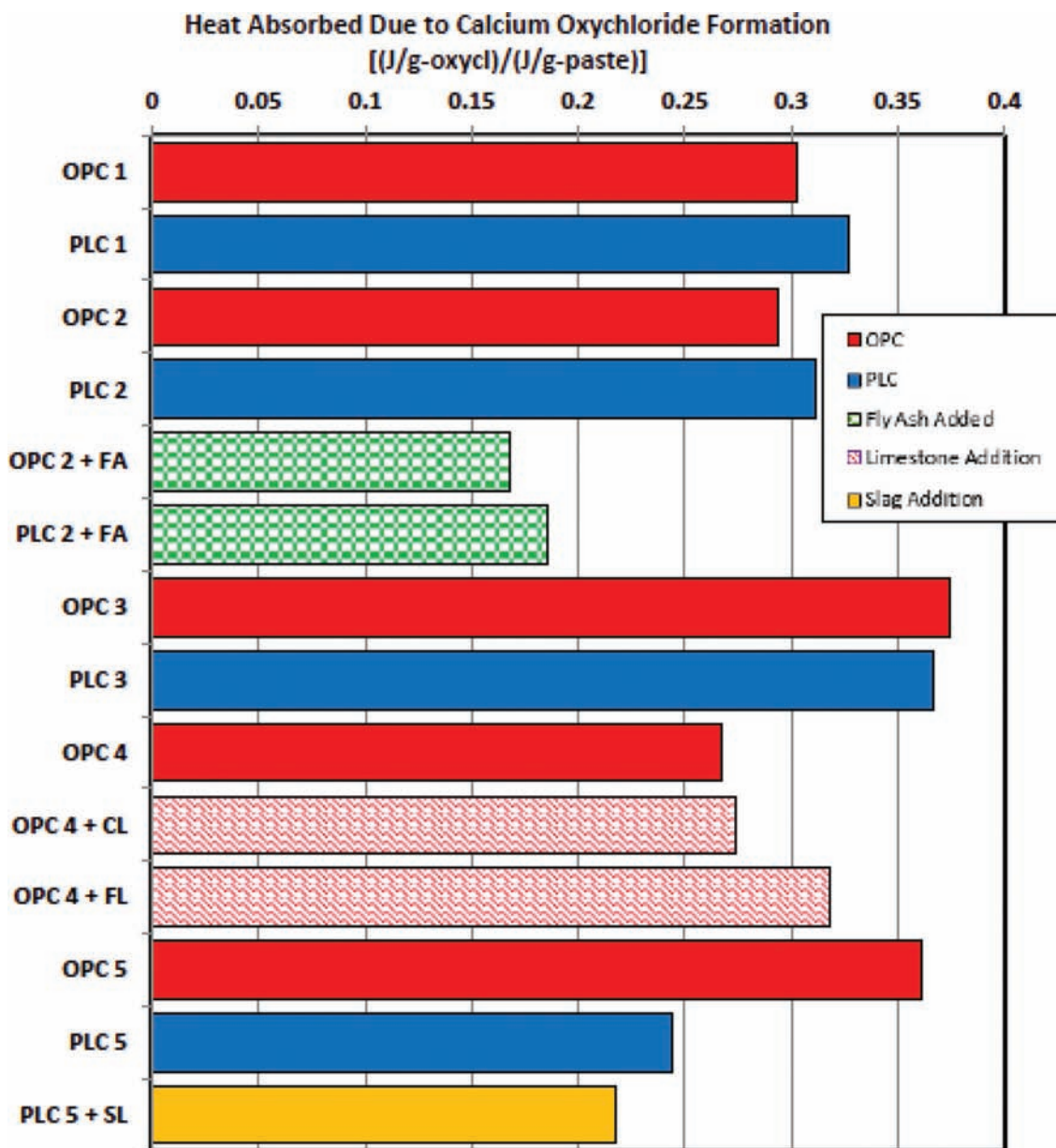


Figure 3.1 CAOXY amounts formed in cement pastes exposed to 20% CaCl_2 solution.

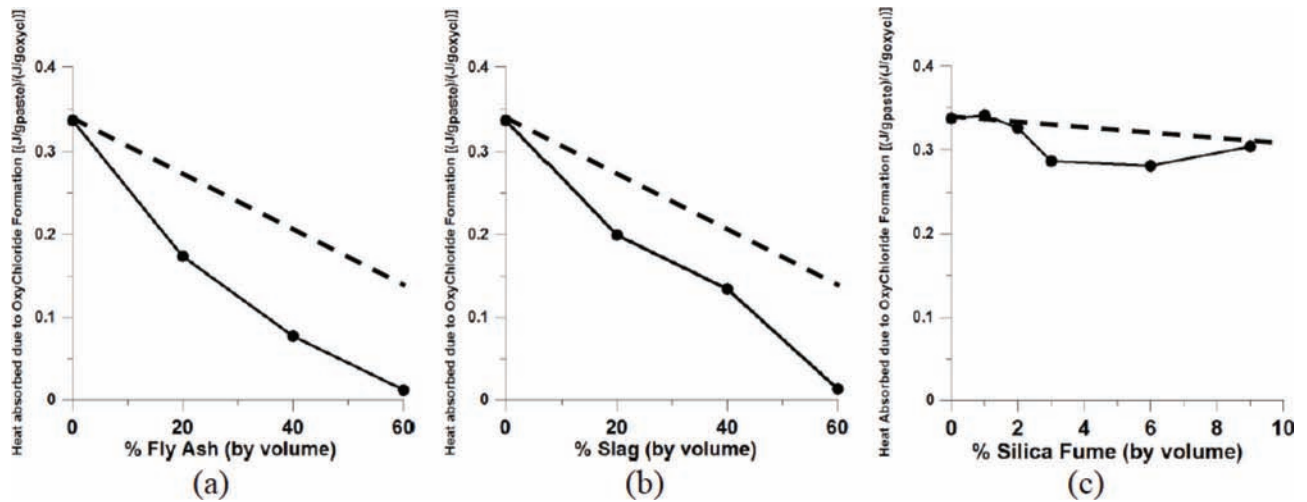


Figure 3.2 Amount of CAOXY formed with various amounts of different SCMs. The dashed lines in the figure indicate the expected reduction in CAOXY due to dilution of the cement by the SCMs.

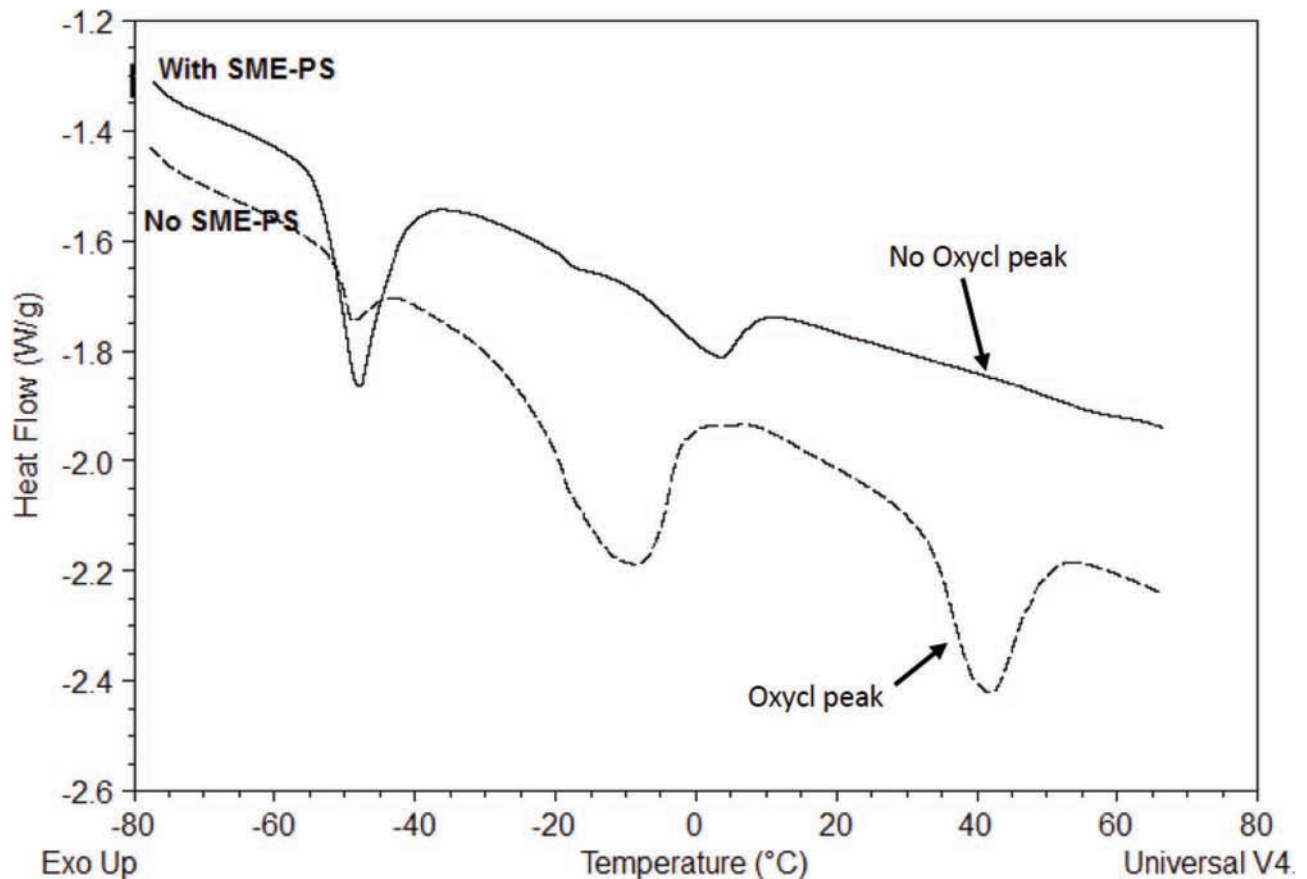


Figure 3.3 CAOXY amounts with and without topical treatment.

understand whether they can reduce CAOXY formation. The topical treatments showed little benefit when testing ground powders as grinding the sample exposes the calcium hydroxide that would have been protected by the physical barrier of the topical treatment to the salt. Therefore, to overcome this limitation, topical treatment using a topical soy methyl ester polystyrene

blend was applied to small cement paste cores (cylinders 5 ± 1 mm in diameter and 2.5 ± 0.5 mm in height). Results are shown in Figure 3.3, and they indicate a substantial reduction in CAOXY amount. It has been shown elsewhere that sealers soy methyl ester polystyrene blends, alkylalkoxysilane sealer and a water-based alkylalkoxysilane penetrating sealer (WBS) can prevent

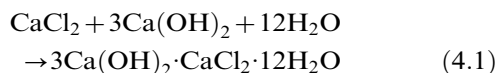
the ingress of salts solutions into concrete and therefore can be effective at reducing oxychloride formation and damage. Further studies on the action of topical treatments are needed to confirm these preliminary findings.

4. PERFORMANCE OF SALT COCKTAILS (PAPER #3)

Chloride-based deicing salt solutions can react chemically with the calcium hydroxide in the cementitious matrix, leading to the formation of an expansive salt known as calcium oxychloride. This study examined the formation of calcium oxychloride in the presence of blends of different chloride-based deicing salts (sodium chloride and calcium chloride).

In this study twenty-eight cement pastes with w/cm 0.36 were tested using cements, fly ashes, slag, one silica fume that are typical of use in INDOT projects. Fly ash and slag were used at 20% replacement, whereas silica fume was used at 3 and 6% replacement. Pastes were mixed as earlier, and cured 4 months at a temperature of 23 °C. Two solutions were prepared consisting of only one salt with 20% CaCl₂ and 20% NaCl by mass, respectively. Using the two pure solutions several salt blends were prepared. TGA and LTDS were used to determine CH and CAOXY contents, in a manner similar to the other papers.

Figure 4.1 shows the relationship between CAOXY and CH contents for different salt blends tested. There are two clusters of CH values, one around 10 g/100 g paste and the other from around 15 g/100 g paste; the first cluster corresponds to pastes with fly ash or slag; the second cluster corresponds to plain pastes or pastes with silica fume. The reaction to form CAOXY is the given in Eq. 4.1:



If all the CH reacts as in Eq. 4.1, then 549.44 grams of CAOXY are formed for 222.28 grams of CH reacting, this is shown as a bold line in Figure 4.1. The theoretical value from chemistry provides an upper bound of the amount of CAOXY that can form. For a given mixture, the CAOXY values are similar for the salt blends containing larger proportions of CaCl₂. In these cases, CAOXY values are well-correlated with CH values and approach the theoretical limit based on chemistry. The addition of SCMs such as fly ash and slag therefore reduces the CAOXY values due to a reduction in CH values. It should be noted that the CH – CAOXY best-fit lines do not pass through zero, but intersect the X-Axis at 3 (g CH/100 g paste), indicating that some amount of CH is not reacting to form CAOXY. For blends with lower proportions of CaCl₂, there is poor correlation between CAOXY and CH contents, and less CAOXY forms. Very little CAOXY is measured with pure NaCl salt solutions.

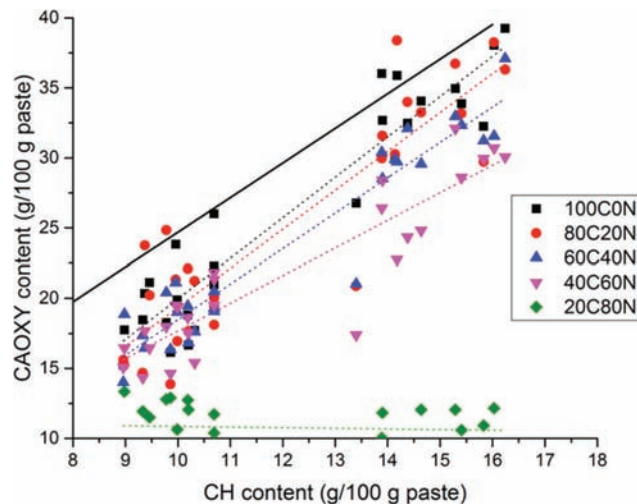


Figure 4.1 Relation between CAOXY and CH contents for several salt blends (where aCbN denotes a salt blend having proportions a % CaCl₂ and b % NaCl).

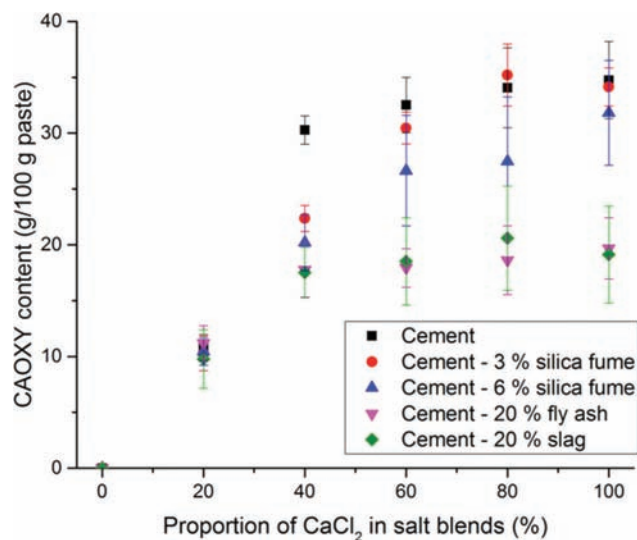


Figure 4.2 Relation between CAOXY and proportion of CaCl₂ in salt blends.

Figure 4.2 shows a plot of the CAOXY formed in the different pastes as a function of the proportion of CaCl₂ solution to NaCl solution in the salt blends. Data points have been grouped into different groups based on their CH contents. CAOXY contents increase with the proportion of CaCl₂ solution in the blends. At lower proportions of CaCl₂ solution in the blends, the reaction is controlled by the amount of CaCl₂. At higher proportions of CaCl₂ solution in the blends, the reaction is controlled by CH. The concentration at which this switch occurs depends on the amount of CH in the paste. Therefore, all mixtures show the same CAOXY contents at low proportions of CaCl₂ in the salt blends, at higher proportions of CaCl₂ in the salt blends, mixtures with higher CH show higher CAOXY contents.

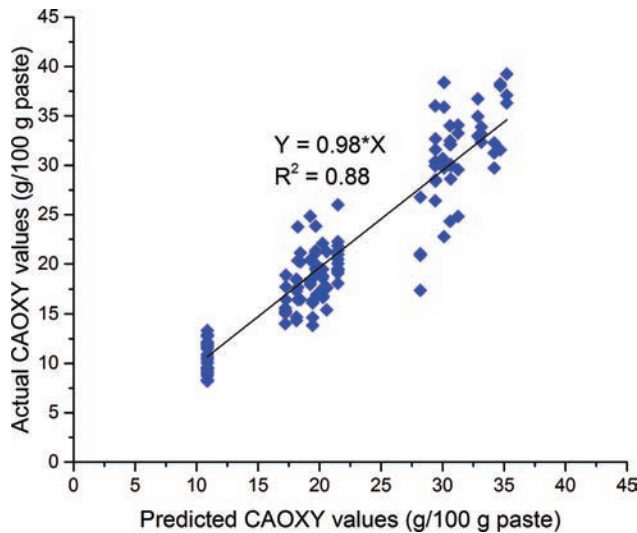


Figure 4.3 Predicted and expected CAOXY values.

A general model to estimate CAOXY contents can be developed. Consider a case where 100 g of ground cement paste is mixed with 100 g of CaCl₂ and NaCl blends (overall strength 20%). Three assumptions are made:

1. NaCl has a negligible contribution to the CAOXY formation.
2. Not all the CH reacts to form CAOXY; 1.8 g/100 g CH is encapsulated.
3. Some of the CaCl₂ is bound by cement hydrates; 2 g/100 g CaCl₂ is bound.

As presented in Eq. 4.1, whenever there is excess CH, the reaction is controlled by CaCl₂, and vice versa. This leads to the following conditions:

$$\text{If } CH < 2 \text{ or } CaCl_2 < 1.8, \text{ then CAOXY} = 0 \quad (4.2)$$

$$\text{If, } 2 \times CaCl_2 - 1.6 < CH, \text{ then} \\ \text{CAOXY} = \frac{549.44}{110.98} \times (CaCl_2 - 1.8) \quad (4.3)$$

$$\text{If, } 2 \times CaCl_2 - 1.6 > CH, \text{ then} \\ \text{CAOXY} = \frac{549.44}{222.28} \times (CH - 2) \quad (4.4)$$

Applying the model to the entire data set results in Figure 4.3; as can be seen from the figure, the agreement between predicted and actual CAOXY values is excellent.

The model can be used to predict CAOXY values for various CH and CaCl₂ values. Results are shown in Figure 4.4, with experimental points being shown as symbols and modeled data being shown as straight lines. At low proportions of CaCl₂, the CAOXY value depends on CaCl₂, and at high proportions of CaCl₂, the CAOXY value depends on CH. In other words, the slope of the initial part (a linear increase) is determined by CaCl₂ and the plateau value is determined by the

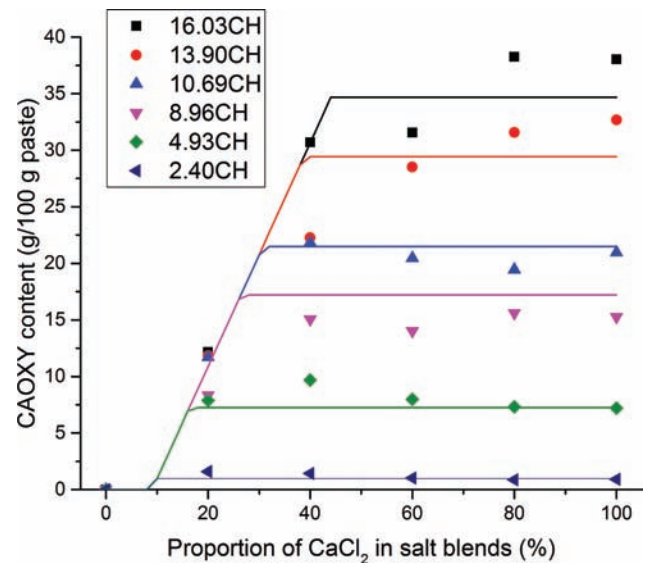


Figure 4.4 Application of the model to estimate CAOXY values for various CH and CaCl₂ values. Experimental data is shown as points and modeled data as straight lines.

CH. The model allows for the development of this entire plot for different CaCl₂ and CH contents, thereby significantly reducing experimental effort.

5. CONCLUSIONS

5.1 Project Overview

The Indiana Department of Transportation commissioned a study to better understand how the composition of different salts can interact with the binder of concrete paving mixtures to form damage. The outcomes of this project were threefold.

- First, the project developed a test procedure that can be used to quantify the potential extent of the calcium oxychloride reaction that can occur. This test procedure (a first of its kind) can be used to quantify the amount of calcium oxychloride that can be formed for a given binder system. It is anticipated that this test can be used to improve concrete mixture design to reduce the potential for joint deterioration.
- Second, research was performed to quantify the calcium oxychloride formation for concrete made using portland cement, portland limestone cement, supplementary cementitious materials, and sealers. The results provide an indication that sealers and supplementary materials can both be used to reduce damage caused by the reaction between the cementitious matrix and the deicing salt.
- Third, a study was conducted which is believed to be the first examination that the authors are aware of to document the impact of salt blends or salt cocktails. The results clearly show that some compositions are more aggressive than other compositions.

5.2 Summary of the Test Method to Quantify Calcium Oxychloride

- A low temperature differential scanning calorimetry approach was developed to quantify the amount of

calcium oxychloride that forms when cementitious pastes are exposed to calcium chloride and blends of calcium chloride and sodium chloride. This approach consists of placing a ground hydrated cement paste in contact with a salt solution and monitoring heat flow for a sample as the temperature is raised. This test can be extended to mixtures containing a wide variety of deicing materials.

- The testing protocol consists of preparing a cement paste, grinding the paste to obtain a hydrated powder, testing a cement paste–20% CaCl_2 –water mixture in the low temperature differential scanning calorimeter (LTDSC) where the sample is cooled to $-90\text{ }^\circ\text{C}$, then heated at a rate of $0.25\text{ }^\circ\text{C/hr}$ to a temperature of $50\text{ }^\circ\text{C}$. The heat release signature during heating (between approximately $35\text{ }^\circ\text{C}$ and $45\text{ }^\circ\text{C}$) can be used to quantify the heat associated with calcium oxychloride transformation.
- It is recommended that the test method use paste samples that are hydrated to a great extent (to enable both the reaction and pozzolanic reaction to occur. A standard time of at least 91 days of curing at $23\text{ }^\circ\text{C}$ is provided. To help develop a more timely test it is proposed that the test be accelerated to obtain a 91 day equivalent age (on a sealed specimen) as determined using 3 days of curing at $23\text{ }^\circ\text{C}$ followed by 25 days at $50\text{ }^\circ\text{C}$.

5.3 Summary of Mixture Composition Effects

- Some concrete pavements have shown premature deterioration at the joints. This deterioration has been attributed to a variety of factors including a reaction between the deicing salt and the cementitious matrix. The reactions can vary depending on the chemistry of the matrix and the chemistry of the deicing salt. Calcium chloride (CaCl_2) can react with either tricalcium aluminate (C_3A) to form Kuzel's salt or Friedel's salt or calcium hydroxide ($\text{Ca}(\text{OH})_2$) to form calcium oxychloride ($3\text{Ca}(\text{OH})_2 \cdot \text{CaCl}_2 \cdot 12\text{H}_2\text{O}$).
- The straight cement systems (OPC) showed the highest amount of calcium oxychloride formation. The amount of calcium hydroxide can vary slightly depending on the composition of the cement, the authors believe that specifying restrictive limits of C_3S or C_2S in a Type I cement will not resolve this problem.
- The samples made using portland limestone cement (PLC) theoretically show a reduction in calcium hydroxide due to dilution. However many of these mixtures showed an accelerated hydration associated with the finer grind of the PLC resulted in a comparable amount of calcium hydroxide and calcium oxychloride formation to the original OPC.

- Experiments performed using a wide range of mixtures indicate that the use of supplementary cementitious materials (SCM) can substantially reduce the calcium oxychloride that forms. As such, mixtures containing SCM would be less likely to demonstrate joint damage.
- As the calcium hydroxide (CH) content in the paste increases, so does the potential for calcium oxychloride (CAOXY) formation. Fly ash, slag and silica fume have all been shown to reduce the potential for calcium oxychloride formation.
- The use of increased SCM needs to be balanced with concerns over scaling, reduction of the pH buffer leading to increased corrosion potential, and slower early strength development.

5.4 Summary of Salt Blend Performance

- The potential of calcium oxychloride formation was determined for NaCl and CaCl_2 solutions in contact with paste. Calcium chloride solutions result in a greater potential for calcium oxychloride formation.
- CAOXY contents increase with the proportion of CaCl_2 solution in the salt blends. At lower proportions of CaCl_2 solution in the salt blends, the reaction is controlled by the amount of CaCl_2 . At higher proportions of CaCl_2 solution in the salt blends, the reaction is controlled by CH. The concentration at which this switch occurs depends on the amount of CH in the paste.
- A general model to estimate the amount of calcium oxychloride that forms given the salt blend composition and the amount of calcium hydroxide in the cement paste has been developed.

5.5 Summary of Mitigation Strategies

Three mitigation strategies may be used to mitigate calcium oxychloride formation.

- First, the use of supplementary cementitious materials such as fly ash, slag, and silica fume leads to a reduction in calcium oxychloride contents due to a reduction in the calcium hydroxide contents.
- Second, the use of topical sealers, such as those based on topical soy methyl ester polystyrene blend can create a physical barrier between calcium hydroxide and salt solution.
- Finally, the use of salt blends comprising a lower amount of calcium chloride, as sodium chloride does not significantly contribute to calcium oxychloride formation.

APPENDICES

Appendices A, B, and C are available for download at <http://dx.doi.org/10.5703/1288284316350>. Appendix D starts on the following page.

APPENDIX A: PAPER #1

Monical, J., Villani, C., Farnam, Y., Unal, E., & Weiss, W. J. (2016), "Quantifying Calcium Oxychloride Formation for Different Cementitious Materials in the Presence of CaCl₂ Using Low Temperature Differential Scanning Calorimetry."

Paper #1 is the author-accepted manuscript version of an article accepted for publication in *Advances in Civil Engineering Materials*, Copyright © 2016, ASTM International, West Conshohocken, PA.

APPENDIX B: PAPER #2

Monical, J., Unal, E., Barrett, T., Farnam, Y., & Weiss, W. J. (2016). "Reducing Joint Damage in Concrete Pavements: Quantifying Calcium Oxychloride Formation."

Paper #2 has been published in *Transportation Research Record: Journal of the Transportation Research Board*:

From Monical, J., E. Unal, T. Barrett, Y. Farnam, and W. J. Weiss. Reducing Joint Damage in Concrete Pavements: Quantifying Calcium Oxychloride Formation. *Transportation Research Record: Journal of the Transportation Research Board*, No. 2540. Copyright, National Academy of Sciences, Washington, D.C., 2016. Abstract posted with permission of TRB. For complete paper, please link to <http://pubsindex.trb.org/view/2016/C/1393740>.

APPENDIX C: PAPER #3

Suraneni, P., Monical, J., Unal, E., Farnam, Y., & Weiss, W. J. (2016). "Calcium Oxychloride Formation Potential in Cementitious Pastes Exposed to Blends of Deicing Salt."

Paper #3 has been submitted for publication to *ACI Materials Journal*.

1.0 SCOPE.

- 1.1 This test method covers the procedures for quantitative determination of the potential for calcium oxychloride formation.
- 1.2 The hydrated cement paste is ground to a fineness sufficient to pass through a No. 200 (75 μm). An example mixture and curing preparation procedure is described in the Appendix. The ground powder is exposed to a 20% CaCl_2 (by mass) salt solution, thoroughly mixed at a mass ratio of 1:1, placed and tested in a Low-Temperature Differential Scanning Calorimetry (DSC) machine. The heat required to change the sample temperature is recorded as a function of temperature throughout the duration of the test.
- 1.3 This ITM may involve hazardous materials, operations, and equipment and this document may not address all of the safety problems associated with the use of the test method. The user of the ITM is responsible for establishing appropriate safety and health practices and determining the applicability of regulatory limitations prior to use.

2.0 REFERENCES.

2.1 AASHTO Standards.

- M 92 Wire-Cloth Sieves for Testing Purposes
- M 231 Weighing Devices Used in the Testing of Materials

2.2 ASTM Standards.

- D 1193 Reagent Water
- E 1269 Determining Specific Heat Capacity by Differential Scanning Calorimetry

3.0 TERMINOLOGY. Definitions for terms and abbreviations will be in accordance with the Department's Standard Specifications, Section 101.

4.0 SIGNIFICANCE AND USE. This ITM is used for the determining the amount of calcium oxychloride formation in a cementitious binder exposed to a deicing salt mixture.

5.0 APPARATUS.

- 5.1 Grinding machine.
- 5.2 Sieve, No. 200, conforming to the requirements of AASHTOM 92.
- 5.3 Mechanical crusher or mortar and pestle.
- 5.4 Analytical balance, Class A, conforming to the requirements of AASHTO M 231.
- 5.5 Micro-pipette.
- 5.6 Encapsulation Device (Tzero Sample Press).
- 5.7 DSC Test Chamber in accordance with ASTM E 1269.

- 5.8 Containers such as high-volume stainless steel pans, and lids which are inert to the sample materials and whose shape and structural integrity can withstand temperatures within the DSC machine.
- 6.0 REAGENTS.**
- 6.1 **Purity of Reagents.** Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society.
- 6.1.1 Calcium chloride (CaCl_2).
- 6.1.2 Sodium chloride (NaCl).
- 6.1.3 Magnesium chloride (MgCl_2).
- 6.2 **Purity of Water.** Unless otherwise indicated, references to water shall be Type II reagent water in accordance with ASTM D 1193.
- 7.0 SAMPLE PREPARATION.**
- 7.1 Crush 100 g of the material (hydrated cement paste) using either a grinding machine or mortar and pestle.
- 7.2 Pass the ground material through a No. 200 sieve.
- 7.3 Crush or grind the portion retained on the sieve, by means that will not contaminate the sample, until substantially all of the material passes the sieve.
- 7.4 Combine all portions of the original 100 g material.
- 7.5 Steps 7.1–7.4 should be done hastily to minimize the effects of carbonation of the cementitious binder to occur.
- 7.6 Combine reagent grade calcium chloride to distilled water to produce a 20% by mass CaCl_2 solution.
- 8.0 PROCEDURE.**
- 8.1 Weigh 10 ± 0.5 mg of ground powder in a DSC high-volume stainless steel pan.
- 8.2 Add 10 ± 0.5 mg of salt solution with micro-pipette to the powder in the pan. It is important to ensure that the liquid and solid masses are exactly the same to ensure a 1: 1 liquid: solid ratio. The total mass of the contents inside the pan should be 20 ± 1 mg.
- 8.3 Mix contents well so that all powder is thoroughly wetted.
- 8.4 Hermetically seal lid containing rubber O-ring to pan using encapsulation device.
- 8.5 Place pan containing ground powder-salt solution mixture in DSC loading cell.
- 8.6 Expose pan to the following temperature cycle:
- 8.6.1 Equilibrate pan at 25 °C for 50–60 minutes.
- 8.6.2 Cool sample to -90 °C at a rate of 3 °C/min.
- 8.6.3 Expose sample to low temperature loop, cycling from -90 °C to -70 °C to -90 °C at a rate of 3 °C/min.
- 8.6.4 Heat sample to 50 °C at a rate of 0.25 °C/min.

9.0 CALCULATIONS. Use TA software to evaluate the heat flow data recorded by the DSC machine. Integrate the heat flow versus time curve associated with the calcium oxychloride melting phase. Calculate the magnitude of the drop in the cumulative heat curve. An example calculation is shown in the Appendix. The gram of calcium oxychloride per gram of cementitious paste is calculated using the following formula:

$$\text{Amount of calcium oxychloride, } M_{\text{oxy}} = \frac{\Delta H}{L_{\text{oxy}}} * 100$$

where:

M_{oxy} = mass in g of calcium oxychloride per 100 g of cementitious paste, g/ 100 g

ΔH = latent heat absorbed during calcium oxychloride phase transformation for cementitious material, J/g

L_{oxy} = specific latent heat associated with calcium oxychloride phase transformation, 186 J/g

10.0 REPORT. The above expression shall be reported to the nearest 0.1 or 0.01.

Appendix

Example Mixing and Curing Preparation Procedure

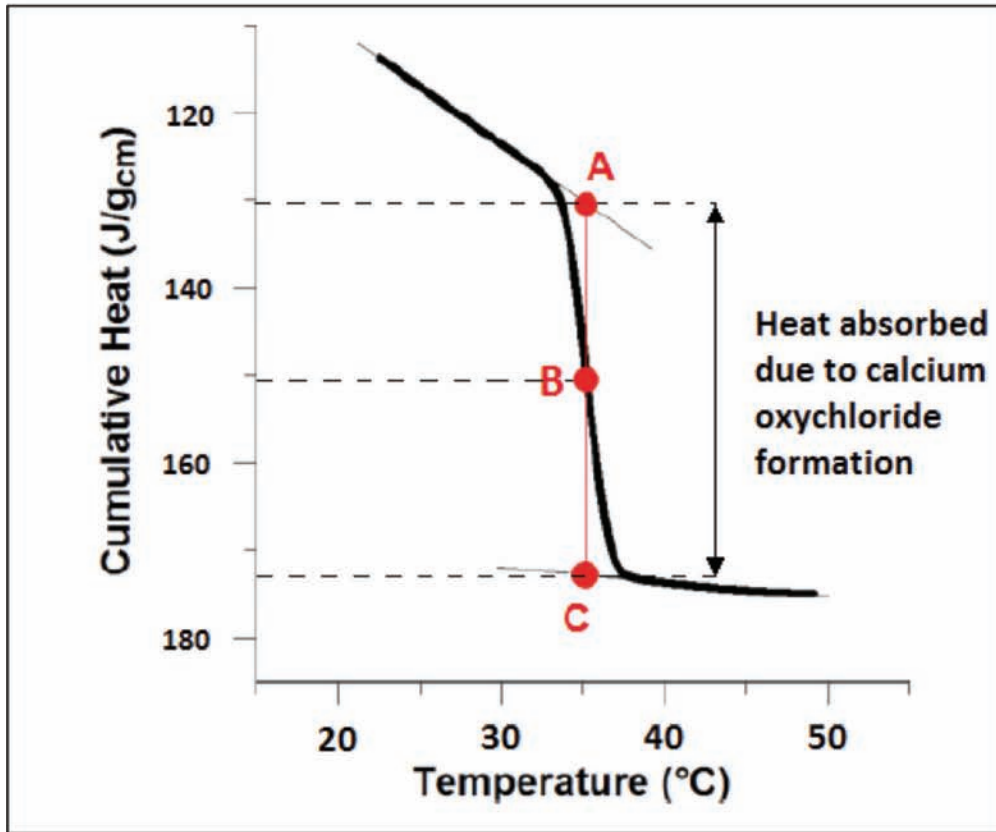
The following is a mixing and curing preparation example procedure for a hydrated cement paste sample:

Prepare a hydrated cement paste sample with a 0.36 water-to-cementitious material ratio conforming to ASTM C305-14. Cast sample in small plastic cylinder with a diameter of 1.5 in. and a height of 2.0 in. Seal containers and cure for 49 days at a temperature of 23 °C.

Mixture Proportions

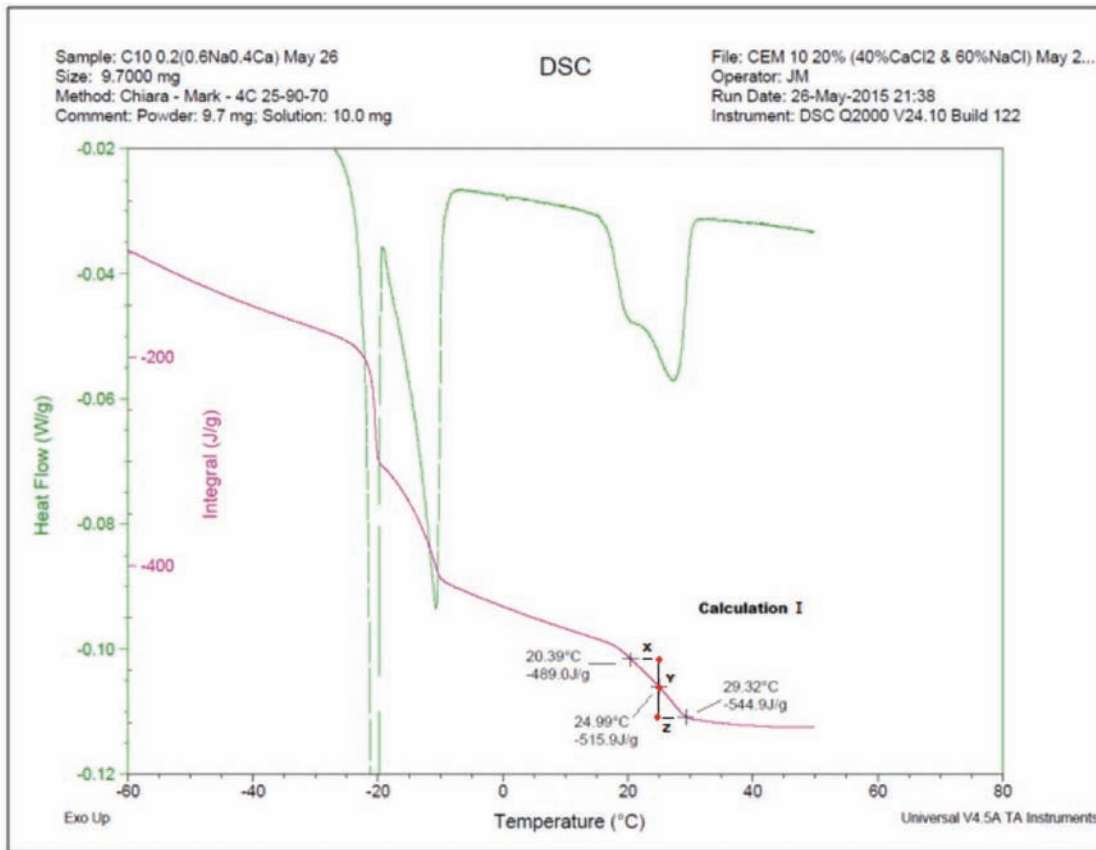
ID	w/c ratio	OPC (g)	Water (g)
Sample A	0.36	658	237

Example Calculation of Latent Heat Absorbed



The heat absorbed due to calcium oxychloride formation is evaluated by integrating the heat flow versus time curve as shown in the figure above. This cumulative heat is estimated by calculating the magnitude of the shift in cumulative heat slopes before and after the phase transformation (between points A and C) with respect to the midpoint of the phase change (point B). Points A, B and C all lie on the same vertical line.

Calculation I in the figure below is performed by choosing a midpoint along the heat accumulation curve (pink line labeled as 'Integral') as described above. This midpoint is an estimation of the temperature which corresponds to a heat accumulation value which should be close to 50% of the total enthalpy value of the phase change. This percentage can be calculated by dividing the drop between points X and Y by the drop between points X and Z (Points X, Y and Z in the figure below correspond to Points A, B and C, respectively, in the figure above).



A temperature of 24.99 °C corresponds to 48.1% completion for this particular heat accumulation curve. The latent heat absorbed during calcium oxychloride phase transformation for cementitious material (ΔH) is 55.9 J/g. Therefore, the mass of calcium oxychloride per 100 g of cementitious paste (M_{oxy}) = 30.05.

About the Joint Transportation Research Program (JTRP)

On March 11, 1937, the Indiana Legislature passed an act which authorized the Indiana State Highway Commission to cooperate with and assist Purdue University in developing the best methods of improving and maintaining the highways of the state and the respective counties thereof. That collaborative effort was called the Joint Highway Research Project (JHRP). In 1997 the collaborative venture was renamed as the Joint Transportation Research Program (JTRP) to reflect the state and national efforts to integrate the management and operation of various transportation modes.

The first studies of JHRP were concerned with Test Road No. 1—evaluation of the weathering characteristics of stabilized materials. After World War II, the JHRP program grew substantially and was regularly producing technical reports. Over 1,500 technical reports are now available, published as part of the JHRP and subsequently JTRP collaborative venture between Purdue University and what is now the Indiana Department of Transportation.

Free online access to all reports is provided through a unique collaboration between JTRP and Purdue Libraries. These are available at: <http://docs.lib.purdue.edu/jtrp>

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