

TEST METHODS TO SCREEN CONCRETE MIXTURES FOR CALCIUM OXYCHLORIDE DAMAGE RESISTANCE

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1. Background

1.1. Deicing and Anti-icing Salts

In cold regions of the United States, deicing and anti-icing salts are commonly used to enhance driver safety by removing or preventing freezing conditions on pavement surfaces. Due to availability and cost reasons, the most commonly used deicing and anti-icing salts are chloride-based, including sodium chloride (NaCl), calcium chloride (CaCl₂), magnesium chloride (MgCl₂), and their blends (Suraneni et al. 2017).

1.2. Concrete Pavement Joint Damage

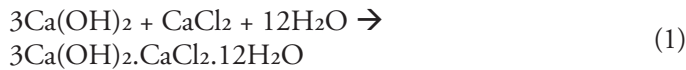
In cold conditions, freeze-thaw damage in concrete pavements with high degrees of saturation can occur as a result of internal stresses caused by the freezing and expansion of water. Chloride ions from the deicers affect freeze-thaw damage in several complex ways, and they can also interact with concrete in nonfreezing conditions.

Three deterioration mechanisms—freeze-thaw, reinforcement corrosion, and salt scaling—are well understood as causes of deterioration of concrete pavements in cold regions. However, there is another deterioration mechanism due to the formation of calcium oxychloride that is less known but possibly as damaging as freeze-thaw deterioration. Calcium oxychloride is a salt that is formed from the reaction of calcium hydroxide (Ca(OH)₂) in the concrete matrix with CaCl₂ or MgCl₂ deicing salts in the presence of moisture (Jones et al. 2020).

1.3. Calcium Oxychloride

Severe damage to cement-based materials exposed to high concentrations of CaCl₂ has been known since the 1960s and 1970s (Lawrence and Vivian 1960, Chatterji et al. 1978). Pioneering studies at this time showed that, typically, this damage was observed with CaCl₂ and MgCl₂ but not NaCl (Smolczyk 1968). Since then, numerous premature failures of concrete pavements in cold regions have been attributed to this mechanism (Jones et al. 2020). Damage manifests as significant spalling and scaling concentrated near joints. A Federal Highway Administration (FHWA) tech brief and American Concrete Institute (ACI) report provide details regarding calcium oxychloride formation, joint damage, and mitigation (Van Dam 2018, ACI Committee 201 2019). A detailed state of the art of calcium oxychloride formation, damage, testing, and mitigation is provided in Jones et al. (2020).

Most research agrees that the dominant cause of damage is due to the formation of oxychloride phases, as shown in equation (1) (Galan et al. 2015). However, exposure to CaCl₂ and MgCl₂ can also lead to the formation of aluminate-based Friedel's salt (Qiao et al. 2018, Qiao et al. 2019) and possibly Kuzel's salt (Balonis et al. 2010). Under such conditions, calcium hydroxide is also leached from the pavement (Jones et al. 2020). In MgCl₂ systems, brucite (Mg(OH)₂) can be formed (Qiao et al. 2018).



The stoichiometry described in equation (1) is the most commonly reported (Galan et al. 2015, Jones et al. 2020), but other forms have been reported, such as $3\text{Ca}(\text{OH})_2 \cdot \text{CaCl}_2 \cdot 11\text{H}_2\text{O}$ and $\text{Ca}(\text{OH})_2 \cdot \text{CaCl}_2 \cdot \text{H}_2\text{O}$. Oxychloride phases are not particularly stable and can be decomposed by changes in temperature and relative humidity, making it hard to observe them in the laboratory, let alone in the field (Shi 2001, Julio-Betancourt 2009).

Exactly why calcium oxychloride damages concrete is still debated. Some researchers have described volume changes of up to 303% (Jones et al. 2020), while others have claimed that crystallization pressure (Chatterji 1978) or “pore wall pressures” due to local supersaturations (Scherer 2004) are the cause of damage.

1.4. Damage Prevention

While the cause of damage is not totally understood, it is known how to prevent damage. Given that the damage arises because of a reaction between $\text{Ca}(\text{OH})_2$ and $\text{CaCl}_2/\text{MgCl}_2$ in the presence of moisture, it can be prevented by eliminating or reducing either of the reactants. Eliminating CaCl_2 or MgCl_2 is impractical because they are often selected to maintain adequate levels of service in specific weather conditions (Claros et al. 2021). On the other hand, reducing $\text{Ca}(\text{OH})_2$ in concrete is straightforward and can be achieved through the use of supplementary cementitious materials (SCMs) (Monical et al. 2016, Suraneni et al. 2018). All SCMs at a sufficient dosage reduce calcium oxychloride damage.

SCMs reduce $\text{Ca}(\text{OH})_2$ due to pozzolanic reactions (Monical et al. 2016) and refine the pore structure of the concrete to limit the ingress of chlorides (Hosseinzadeh et

al. 2021, Hosseinzadeh et al. 2022). Damage is reduced as SCM replacement increases and as the pozzolanic reactivity of the SCM increases.

The use of inert fillers such as limestone (as in Type II cements) and an increase in the water-to-cementitious materials (w/cm) ratio could theoretically reduce damage by diluting the amount of $\text{Ca}(\text{OH})_2$ in the system. However, these methods have not been found to have a major impact on calcium oxychloride content or on damage (Monical et al. 2016, Monical et al. 2016b, Jones et al. 2020); furthermore, increasing the w/cm ratio has negative impacts on strength and durability.

Entrained air cannot prevent calcium oxychloride formation, but it reduces the degree of saturation of the concrete and provides space for growth of the expansive calcium oxychloride phases (Hosseinzadeh et al. 2021, Hosseinzadeh et al. 2022, Ghantous et al. 2022).

Sealers provide a moisture barrier between the concrete and the salt solution and may be effective at preventing calcium oxychloride formation (Monical et al. 2016, Wang et al. 2019, He et al. 2022). However, they may have to be reapplied periodically. Work is also needed to determine key characteristics that determine sealer effectiveness.

Exposing concrete to carbon dioxide (CO_2) reduces the amount of calcium hydroxide and has been shown to eliminate calcium oxychloride formation. Interestingly, calcium oxychloride is not formed even when there is some residual $\text{Ca}(\text{OH})_2$ in the system, likely because the calcium carbonate (CaCO_3) that forms provides a barrier layer on the $\text{Ca}(\text{OH})_2$ (Ghantous et al. 2016).

Table 1 provides a summary of the various methods used to reduce calcium oxychloride damage.

Table 1. Summary of the various methods used to mitigate calcium oxychloride damage

Method	Mechanism(s)	Advantages	Disadvantages
Avoidance of CaCl_2 and MgCl_2	<ul style="list-style-type: none"> Other deicing salts do not show calcium oxychloride damage. 	<ul style="list-style-type: none"> No calcium oxychloride damage. 	<ul style="list-style-type: none"> Issues with maintaining needed levels of service and operability. Other deicing salts can also cause damage.
Increased usage of SCMs	<ul style="list-style-type: none"> Consumes calcium hydroxide. Dilution reduces calcium hydroxide amounts. Reduces chloride ingress due to reduced permeability. 	<ul style="list-style-type: none"> Practical. Damage reduced with SCM replacement. Improved concrete CO_2 footprint. Other durability benefits. 	<ul style="list-style-type: none"> Early-age strength reductions and property development. In some regions, SCM availability limited.
Air entrainment	<ul style="list-style-type: none"> Reduces concrete degree of saturation. Provides space for the growth of calcium oxychloride. 	<ul style="list-style-type: none"> Practical. Air entrainment needed for freeze-thaw and salt scaling. 	<ul style="list-style-type: none"> Strength reductions. Can be hard to get consistent and accurate air entrainment, especially with some SCMs.
Use of sealers	<ul style="list-style-type: none"> Provides moisture barrier between concrete and salt solution. 	<ul style="list-style-type: none"> Novel method and could have other durability benefits. 	<ul style="list-style-type: none"> Might have to be reapplied. Limited studies and lack of understanding.
Preferential carbonation	<ul style="list-style-type: none"> Consumes calcium hydroxide. Formed calcium carbonate provides a barrier on the CaCl_2. 	<ul style="list-style-type: none"> Novel method. CO_2 sequestration. 	<ul style="list-style-type: none"> May not be practical. Limited studies and lack of understanding, especially in how this could scale.

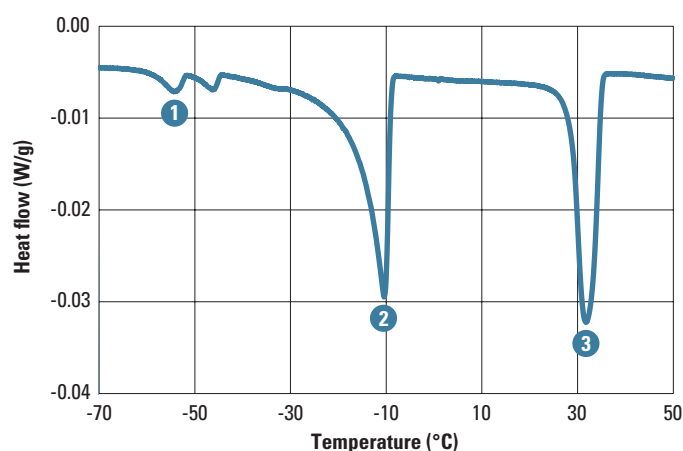
2. Low-Temperature Differential Scanning Calorimetry

2.1. Method Overview

With an understanding of what causes oxychlorides to form and strategies to mitigate or prevent damage, test methods are needed to screen a given mixture for oxychloride formation potential. Low-temperature differential scanning calorimetry (LT-DSC), described in AASHTO T 365, is a standardized method to evaluate the calcium oxychloride resistance of cementitious materials.

In LT-DSC, paste/mortar/concrete specimens are cured to the desired age, ground to a fine powder, and mixed with CaCl₂ solution. In the standard, pastes are used with a 1:1 powder: solution by mass, where the solution is 20% CaCl₂; however, modifications for the purpose of research can be done (Monical et al. 2016b).

Material is mixed in a pan, which is then sealed and inserted into the device. After an isothermal hold for one hour, the temperature is reduced to -90°C at 3°C/minute, ramped from -90°C to -70°C to -90°C, and then heated to 50°C at 0.25°C/minute. During the heating cycle, the heat associated with calcium oxychloride phase transformation—typically between 30°C and 40°C—can be quantified (Monical et al. 2016b, Jones et al. 2020). Based on the known heat absorbed due to the phase transformation of pure calcium oxychloride, the amount of calcium oxychloride in the system can be determined. Figure 1 shows a LT-DSC plot of the heating cycle for a cement paste. The three peaks marked in the figure indicate (1) melting of the eutectic solids, (2) melting of ice, and (3) the calcium oxychloride phase transformation, with the exact locations and intensities of the peaks varying based on mixture composition.



Adapted from Qiao et al. 2017

Figure 1. Heating cycle of a cement paste subject to a standard LT-DSC run, with three peaks showing (1) melting of the eutectic solids, (2) ice melting, and (3) the calcium oxychloride phase transformation

In ordinary portland cement (OPC) pastes without SCMs, the calcium oxychloride content is ~35 g/100 g paste. When 20% fly ash or slag by mass is used to replace the cement, the calcium oxychloride content is ~20 g/100 g paste; this amount decreases to ~10 g/100 g paste at 40% replacement and ~3 g/100 g paste at 60% replacement. In portland limestone cement (PLC) pastes, values tend to be only slightly lower (Monical et al. 2016a).

While this test method provides a direct measurement of oxychloride formation potential, it suffers from a number of disadvantages. The LT-DSC device is a niche piece of equipment that is not generally available in concrete laboratories. The test also takes a rather long time to perform and can be expensive. Interlaboratory reproducibility for the test is not available. The test neglects other important properties, which are part of a concrete mixture and can affect the resistance to calcium oxychloride damage in the field, such as air content and transport properties.

2.2. Applicability to Concrete

In principle, the LT-DSC test is applicable to paste, mortar, and concrete (Suraneni et al. 2018b). However, the amounts of Ca(OH)₂ in concrete are much lower than in paste due to dilution from the aggregates. As an example, cement pastes without any SCMs are expected to have 20 g Ca(OH)₂/100 g paste forming 40 g calcium oxychloride/100 g paste. In concretes, the paste mass fraction is about 0.25, and thus the Ca(OH)₂ in concrete would be 5 g Ca(OH)₂/100 g concrete, forming 10 g calcium oxychloride/100 g concrete.

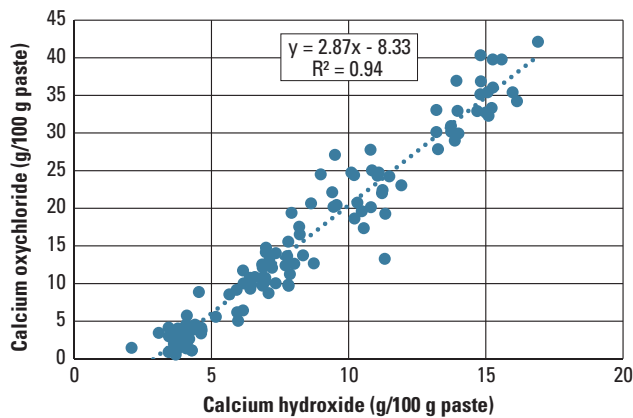
Powdering concrete uniformly is also a major challenge, and the high heterogeneity requires testing of repeat samples to ensure representative results. When testing concrete, studies have suggested using a powder-liquid value of 4 rather than the value of 1 used for pastes and performing three (or more) LT-DSC tests on each sample to obtain representative data for concrete (Suraneni et al. 2018b). Fresh concrete could be sieved to obtain representative mortar samples, as described in AASHTO T 197 (ASTM C403). However, this process is time-consuming and has not been explored for calcium oxychloride studies to the best knowledge of the author.

3. Other Approaches to Predict Calcium Oxychloride Formation/Damage

Given the limitations of the AASHTO T 365 test, and especially the fact that LT-DSC devices are not widely available, alternative test methods are needed for wider-scale implementation of testing for oxychloride damage prediction. Several other test methods that are more familiar to concrete testing laboratories may also be used to screen concrete mixtures for resistance to calcium oxychloride formation.

3.1. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is a well-known technique used to determine the chemical compositions of powders. In TGA, powders are heated and the mass is monitored. $\text{Ca}(\text{OH})_2$ decomposes between 350°C and 500°C, and the mass loss is stoichiometrically linked to the amount of $\text{Ca}(\text{OH})_2$ present. Similar to LT-DSC, paste/mortar/concrete is powdered before testing, but unlike LT-DSC, no solution is needed. Several studies have reported a correlation between $\text{Ca}(\text{OH})_2$ measured from TGA and calcium oxychloride measured from LT-DSC testing (Figure 2) (Suraneni et al. 2016, Suraneni et al. 2018).



Adapted from Suraneni et al. 2016, 2017b, 2018

Figure 2. Strong correlation between paste calcium oxychloride from LT-DSC and paste calcium hydroxide amounts obtained from TGA

Table 2 shows a summary of calcium hydroxide and calcium oxychloride values obtained from TGA and LT-DSC testing of pastes with a w/cm ratio of 0.36 containing various SCMs, including fly ashes, slags, and calcined clays.

One major advantage of TGA is that the equipment is far more common and accessible in many cement and concrete laboratories. In principle, a furnace could also be used as an inexpensive alternative to TGA. One disadvantage is that while there are correlations between $\text{Ca}(\text{OH})_2$ and calcium oxychloride content, there is some data scatter, which has been linked to the lack of availability of the entire $\text{Ca}(\text{OH})_2$ amount to participate in reactions with CaCl_2 to form calcium oxychloride (Suraneni et al. 2016, Suraneni et al. 2018). Given the similarity between TGA and LT-DSC results, TGA can also be considered a challenging method for screening concrete mixtures for LT-DSC, at least in most cases. Performing multiple repeats on specimens, as described in Section 2.2, can make TGA more applicable to concrete.

3.2. Volume Change Measurements

A typical volume change measurement test is performed on a mixture of $\text{Ca}(\text{OH})_2$, CaCl_2 , and water (Qiao et al. 2017, Qiao et al. 2018). Alternatively, $\text{Ca}(\text{OH})_2$ can be replaced with a cement paste that is cured and ground to prepare a sample similar to those used for LT-DSC and TGA testing to infer calcium oxychloride formation potential.

Table 2. Summary of calcium hydroxide and calcium oxychloride values for various SCMs

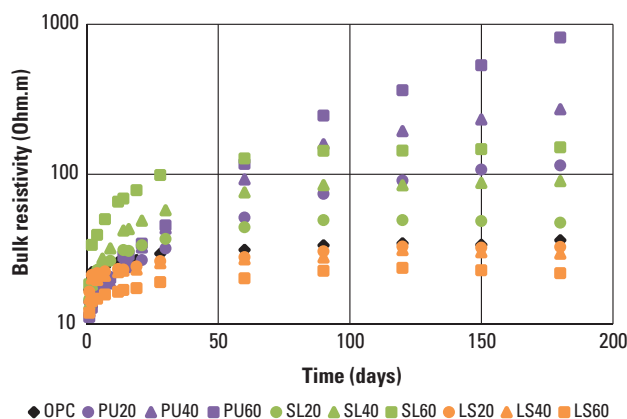
SCM Type	SCM Replacement (mass %)	Calcium Hydroxide (g/100 g paste)	Calcium Oxychloride (g/100 g paste)
None (Control OPC)	0	14.4	33.9
Fly ash	20	10.3	20.4
Fly ash	40	6.9	10.9
Fly ash	60	3.8	2.9
Slag	20	9.8	18.7
Slag	40	7.0	9.9
Slag	60	4.4	3.8
Limestone	20	13.5	32.5
Limestone	40	11.6	25.9
Limestone	60	8.2	17.9
Calcined clay	5	11.3	19.3
Calcined clay	10	9.1	14.0
Calcined clay	15	7.1	6.5
Silica fume	2	11.6	20.6
Silica fume	6	11.9	25.0
Silica fume	10	9.9	21.9

Adapted from Suraneni et al. 2018

The mixture is placed in a glass vial without any air bubbles. A water-insoluble dye is added to the top of the mixture, and then the vial is sealed with a rubber stopper. The temperature is cycled in a water bath from 50°C to 0°C and then back to 50°C, with each step held constant for eight hours for equilibration and a test time of 11 days in total. The volume change, monitored using cameras or visually recorded, is linked to the formation of calcium oxychloride. Phase isopleths and ternary phase diagrams can be developed from this test, which aids in understanding the various phase transitions in the Ca(OH)₂-CaCl₂-H₂O system (Qiao et al. 2017, Qiao et al. 2018). However, this is a laborious and time-consuming test, and the interpretation is complex. The only possible advantage of this test is that the set-up is inexpensive. Limited or no research exists using this test on paste samples. It does not appear that this test could be used to screen concrete mixtures for calcium oxychloride damage resistance.

3.3. Bulk Resistivity

Bulk resistivity (run similarly to AASHTO T 402 or ASTM C1876) has been proposed as a method for screening concrete mixtures for LT-DSC damage resistance. It is well known that as the SCM replacement increases, paste/mortar/concrete bulk resistivity increases (Hosseinzadeh et al. 2021, Chopperla and Ideker 2022, Hosseinzadeh et al. 2022, Wang et al. 2022). As shown in Figure 3, bulk resistivity generally increases with age in mixtures with SCMs; this is shown for pumice (PU) and slag (SL), and the behavior is in stark contrast with that of limestone (LS). Note that the y-axis in the figure is shown on the log scale for better visualization. Bulk resistivity increases with SCM replacement. No significant increase is observed in bulk resistivity in mixtures with inert limestone replacement at any replacement level (Wang et al. 2022).



Data adapted from Wang et al. 2022

Figure 3. Bulk resistivity of mortar mixtures with SCMs measured on 50 mm mortar cubes after limewater curing, showing resistivity increasing with age and with SCM replacement

Moreover, paste, mortar, and concrete bulk resistivity are correlated (Hosseinzadeh et al. 2021b). Correlations between bulk resistivity in mortar and corresponding calcium hydroxide consumption values in paste are known from literature (Wang et al. 2021, Wang et al. 2022). Finally, bulk and surface resistivity values are known to correlate, and the latter, which is used extensively by agencies for quality assurance/quality control and could also be applied in field structures, could also be used.

Therefore, in principle, bulk resistivity on concrete or even corresponding mortar mixtures could be used to predict mixture calcium oxychloride damage resistance. A major advantage of bulk resistivity is that it is a measure of transport and thus also identifies mixtures that are likely to have reduced chloride ingress, something the other methods described in this document cannot do. However, bulk resistivity is, to a certain extent, independent of air content. Therefore, for damage prediction, an indicator that combines both is likely needed.

It is reported that bulk resistivity may be used to predict concrete mixture resistance for calcium oxychloride and for screening, but it needs to be combined with air content, as highlighted in Table 3. Data are shown for concrete mixtures exposed to 5°C to 20°C cycles for 150 cycles in a 20% CaCl₂ solution. The product of bulk resistivity and air content is generally able to predict the final damage state (from visual observations) and the compressive strength after exposure. However, the predictive ability is improved when using the product of bulk resistivity and the square root of the air content. In laboratory mixtures, both bulk resistivity and air content can be measured/monitored. Bulk resistivity depends on cement and SCM alkali content, curing, and age, among many other factors. If it is to be used to predict concrete calcium oxychloride damage resistance, standardized conditions have to be identified, or the value has to be normalized with some kind of control mixture.

Table 3. Final damage state, products of bulk resistivity (91-day value) and air content, and compressive strength after exposure

Final Damage State	Bulk Resistivity Air Content	Bulk Resistivity Air Content ^{0.5}	Compressive Strength (MPa)
None	2005	742	23.3
Minor	475	288	20.1
Moderate	673	260	9.4
Severe	533	203	4.2
Failure	178	113	0.0

Adapted from Hosseinzadeh 2022

3.4. Other Methods

3.4.1. X-Ray Diffraction

X-ray diffraction (XRD) can be used to identify calcium oxychloride in paste/mortar/concrete and in model systems (Galan et al. 2015). Representative samples of paste/mortar/concrete are powdered below 45 μm and inserted into a holder. XRD is run over a set of angles, typically between 10 and 70 2θ. Peaks are compared to values from known materials to identify the phases present, and quantification can be conducted using internal standards. While sample preparation is complex and the phase is transitory, the peaks of calcium oxychloride are easily identifiable. However, this is likely a test that works only on model systems or pastes. In mortars and concretes, interference/dilution due to aggregates and sampling issues complicates measurements.

3.4.2. Electron Microscopy

In laboratory mortar and concrete exposed to CaCl₂ and MgCl₂, electron and other forms of microscopy have been used to identify calcium oxychloride (Sutter et al. 2006, Peterson et al. 2013). Such testing is useful for identifying reaction processes, damage mechanisms, decomposition pathways, etc. Electron microscopy could be used, as could optical microscopy. Polished specimens or fracture surfaces could be used as could powder specimens. Electron microscopy also needs vacuum conditions. However, testing concrete using electron microscopy is challenging and quantification using electron or optical microscopy even more so.

3.4.3. Mass Change and Visual Observation

In Hosseinzadeh et al. (2021, 2022), mass change and visual observation during the exposure of concrete mixtures to high-concentration CaCl₂ and MgCl₂ solutions were shown to be relatively accurate indicators of damage. The rate of mass change in all cases decreased as the air content and SCM replacement level increased. Increases in air content and SCM replacement level were correlated with reduced damage. Thus, a clear link between mass change and damage was established (Hosseinzadeh et al. 2021, Hosseinzadeh et al. 2022). A visual damage classification scheme was also developed, and visual damage was shown to correlate with compressive strength at the end of the exposure duration. While these two methods are promising, they require exposure of concrete to chloride solutions for up to 600 days and therefore are not practical.

3.4.4. Thermodynamic Modeling

Thermodynamic modeling can be used to predict the amount of calcium hydroxide that will form in paste mixtures, although assumptions about the degree of reaction of SCMs might need to be made (Suraneni et al. 2016). The thermodynamic constants of calcium oxychloride are unknown and are not available in thermodynamic software.

3.5. Overview

Table 4 shows the materials and equipment needed for each of the calcium oxychloride tests.

Table 5 describes the various tests, the specimens required for testing, and the advantages and disadvantages of each test.

Table 4. List of materials and equipment for calcium oxychloride tests

Test	Materials	Major Equipment (Cost)	Other Requirements
LT-DSC	CaCl ₂ , deionized water	LT-DSC device, pans, pipettes, and associated accessories (generally \$50,000)	Mixing equipment, curing chamber, mortar and pestle
TGA	—	TGA device (generally \$50,000)	Mixing equipment, curing chamber, mortar and pestle
Volume change measurements	CaCl ₂ , deionized water, water insoluble dye	Glass vials, stopper, water bath, camera (generally \$10,000)	Mixing equipment, curing chamber, mortar and pestle
Bulk resistivity	—	Bulk resistivity meter and associated accessories (generally \$5,000)	Mixing equipment, curing chamber
XRD	—	XRD device, XRD software, holders, and associated accessories (generally \$120,000 or more)	Mixing equipment, curing chamber, mortar and pestle
Microscopy	Epoxy maybe needed	Scanning electron microscope and associated accessories (generally \$300,000 or more) Optical microscope and associated accessories (generally \$10,000)	Mixing equipment, curing chamber, mortar and pestle Polishing equipment, sputter coater maybe needed
Mass change and visual observations	CaCl ₂	Balance, camera (generally \$5,000)	Mixing equipment, curing chamber, storage chamber
Thermodynamic modeling	—	Thermodynamic modeling software (free versions are available)	—

Table 5. Advantages and disadvantages of various tests for calcium oxychloride

Test and Description	Specimens	Advantages	Disadvantages
LT-DSC run to measure calcium oxychloride amounts in powders	Paste, mortar, concrete (powder)	<ul style="list-style-type: none"> • Test is standardized, relatively rapid. • Data analysis is easy and can be run on concrete. 	<ul style="list-style-type: none"> • Niche, expensive equipment. • Effects of transport and air ignored. • Limited results on concrete. • Aggregate dilution and errors when run on concrete.
TGA run to determine calcium hydroxide amounts in powders	Paste, mortar, concrete (powder)	<ul style="list-style-type: none"> • Test is rapid. • Data analysis is easy. • Equipment is widely available. • Test can be run on concrete 	<ul style="list-style-type: none"> • Niche, expensive equipment. • Effects of transport and air ignored. • Limited results on concrete. • Aggregate dilution and errors when run on concrete. • Relationship between TGA and LT-DSC results shows scatter.
Volume change measurements on powders, including model systems	Paste, mortar, concrete (powder)	<ul style="list-style-type: none"> • Provides information about phases changes. 	<ul style="list-style-type: none"> • Slow test, complex interpretation. • Effects of transport and air ignored. • Limited results on concrete. • Aggregate dilution and errors when run on concrete. • Not a feasible concrete screening test.
Bulk resistivity measured on paste, mortar, or concrete as a proxy for calcium oxychloride resistance	Paste, mortar, concrete	<ul style="list-style-type: none"> • Test is standardized, rapid. • Data analysis is easy and can be run on concrete. • No need for powdering. 	<ul style="list-style-type: none"> • Must be combined with a measure of air content. • Limited studies correlating with calcium oxychloride damage. • Many factors affect bulk resistivity.
XRD run on powdered specimens to measure calcium oxychloride content	Paste, mortar, concrete (powder)	<ul style="list-style-type: none"> • Test is rapid. 	<ul style="list-style-type: none"> • Niche, expensive equipment. • Effects of transport and air ignored. • Limited results on concrete. • Aggregate dilution and errors when run on concrete. • Data analysis is complex. • Not a feasible concrete screening test.
Microscopy, various types run on specimens to study calcium oxychloride and damage	Paste, mortar, concrete	<ul style="list-style-type: none"> • Can provide information about nature of damage. 	<ul style="list-style-type: none"> • Niche, expensive equipment. • Quantification challenging. • Data analysis is complex. • Limited results on concrete. • Not a feasible concrete screening test.
Mass change and visual observations run during exposure of specimens to CaCl₂	Paste, mortar, concrete	<ul style="list-style-type: none"> • Data analysis is easy and can be run on concrete. 	<ul style="list-style-type: none"> • Very slow test. • Not a feasible concrete screening test.
Thermodynamic modeling to quantify calcium hydroxide amounts	Paste	<ul style="list-style-type: none"> • Does not need any equipment. 	<ul style="list-style-type: none"> • Does not provide different information than TGA. • Effects of transport and air ignored. • Limited results on concrete. • Significant challenges when run on concrete. • Not a feasible concrete screening test.

4. Summary and Recommendations

This tech brief summarizes calcium oxychloride formation, damage, and prevention. Test methods that can be used to measure calcium hydroxide and calcium oxychloride are described in some depth. These include LT-DSC, TGA, volume change measurements, bulk resistivity, XRD, scanning electron microscopy, mass change and visual observation, and thermodynamic modeling. Of these, the three methods with the greatest potential to screen concrete mixtures for calcium oxychloride damage are LT-DSC, TGA, and bulk resistivity. All have certain advantages but also suffer from certain disadvantages. Both LT-DSC and TGA work best for paste but have issues with aggregate dilution and representative sampling. These issues can be

overcome by testing repeats and modifying certain test conditions. While LT-DSC is a standard test, it involves a niche piece of equipment. The equipment needed for TGA is more available; however, the correlation between calcium hydroxide and calcium oxychloride content shows scatter. Bulk resistivity is a standardized method that is readily applicable to concrete, especially because paste, mortar, and concrete values correlate. Concrete bulk resistivity, when multiplied by air content or its square root, has been shown to correlate with damage and compressive strength at the end of exposure. However, bulk resistivity is affected by a number of factors, and only limited data comparing bulk resistivity and calcium oxychloride damage are available.

A key concern is the lack of data from various tests. Studies have shown that damage is apparent after 600 days—two years of exposure to high-concentration CaCl_2 solutions and cold temperatures. Therefore, it is suggested to make concrete mixtures with different SCMs, SCM replacements, and air contents and then expose them to these conditions, with visual observations, mass change, and strength at the end of exposure used to track damage. Calcium hydroxide and calcium oxychloride should be measured using TGA, LT-DSC, and bulk resistivity measurements on concrete as well as corresponding paste and mortar samples. Comparison of LT-DSC, TGA, and bulk resistivity results with the damage observed will provide clarity on how well each of these methods can be used to screen concrete for calcium oxychloride damage. Threshold values for measurements will also be an outcome from such a study. Such research, done potentially as a pooled fund study led by state departments of transportation (DOTs) in cold areas, is a critical need and would provide long-term benefits.

Future work should also focus on methods in which aggregate can be rapidly and accurately separated from the paste fraction; the availability of such methods would mean LT-DSC and TGA could be used on concrete to determine the paste calcium oxychloride content. Comparison of LT-DSC, TGA, and bulk resistivity (or surface resistivity) on a number of laboratory and field concretes with known mixture designs would shed further light on the ability of these tests to screen concrete for calcium oxychloride damage.

5. References

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The mission of the National Concrete Pavement Technology Center (CP Tech Center) at Iowa State University is to unite key transportation stakeholders around the central goal of developing and implementing innovative technology and best practices for sustainable concrete pavement construction and maintenance.

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