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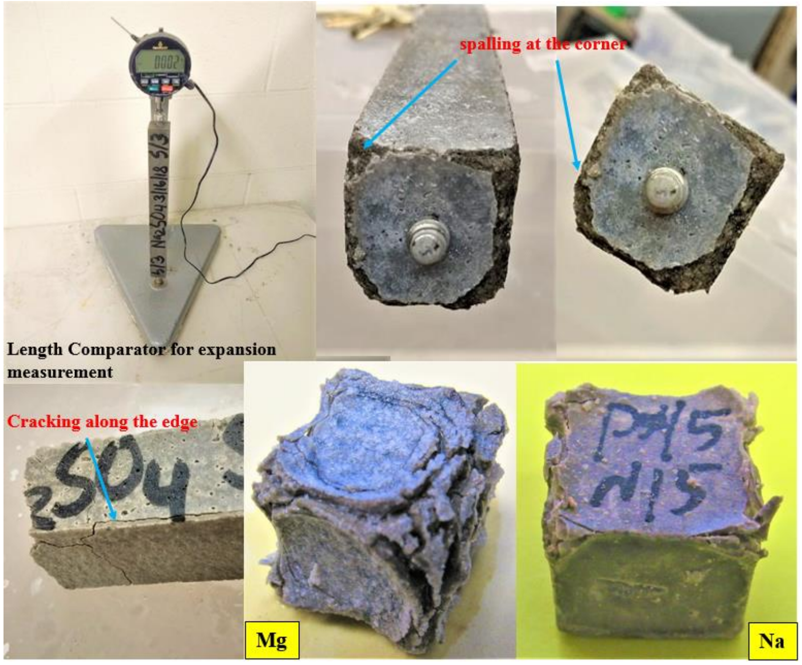

Development of Specifications for Portland-Limestone Cement

Study SD2016-04
Final Report

Prepared by
South Dakota School of Mines and Technology

Rapid City, SD 57701 **January 2019**

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16. Abstract

Sulfate attack can occur in concrete due to external sulfate ions reacting with hydrated cement paste. The sulfate attack resistance of portland-limestone cements (PLCs) has been questioned due to their high limestone content, which has the potential to initiate a rare type of sulfate attack that forms thaumasite. This research evaluates the performance of portland-limestone cements in sulfate prone environments by investigating changes in the physical, chemical, and mechanical properties of specimens. Mortar and paste specimens prepared by replacing Type I/II and Type V cement with 4.4, 10, 14.6 and 20 percent of calcitic and dolomitic limestone powders and fly ash are examined for their sulfate resistance. An accelerated cube test for measuring strength loss due to sulfate attack was developed using 33,800 ppm sodium and magnesium sulfate solutions at 5°C and 23°C. Results from this testing are compared to ASTM C1012 expansion measurements. The physical and chemical transformation in paste specimens are analyzed using visual observation, mass loss measurements, and X-ray diffraction.

Results revealed higher expansion of Type I/II cement with increased calcitic limestone contents, especially in sodium sulfate solution. Type V cement showed greater sulfate resistance in both expansion and strength measurements compared to Type I/II, and the addition of calcitic limestone to Type V cement decreased its expansion. Increased calcitic limestone contents did not significantly impact strength loss for either cement. The addition of a small dosage (4.1% by mass) of dolomitic limestone improved sulfate resistance by exhibiting lower loss of strength in magnesium sulfate and lower expansion in both solutions in part due to ettringite stabilization. The incorporation of Class F fly ash with 14.6% PLCs showed higher sulfate resistance than other mixtures. Higher expansion (up to 80%) at 180 days and greater loss of strength (up to 62%) at 120 days was observed in sodium sulfate compared to magnesium sulfate. Greater loss of strength (up to 62%) was observed at 5°C compared to 23°C for most mixes in both solutions, especially for magnesium sulfate exposure. More surface deterioration, including extensive cracking at the corners and along the edges, bulging on the surfaces, and spalling was found in the paste samples at 5°C. Samples with higher limestone contents, in general, showed greater deterioration. At 5°C, thaumasite was detected in all samples in addition to gypsum and ettringite.

Although many PLCs tested here were not sulfate-resistant, one PLC exhibited excellent sulfate attack resistance. This, in combination with an extensive literature review, indicated that PLCs can be used in sulfate-prone applications if they have the proper composition. It is recommended to SDDOT that PLCs with up to 15% limestone by mass be accepted for use in sulfate environments given they meet sulfate expansion limits specified in ASTM C595 as measured by ASTM C1012.

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AASHTO	American Association of State Highway and Transportation Officials
ACI	American Concrete Institute
AFm	Monosulfoaluminates
Aft, E	Ettringite
ASTM	ASTM International, formerly American Society for Testing and Materials
B	Brucite
C	Calcitic Limestone
CH	Calcium Hydroxide
Cr	Concrete
CSA	Canadian Standard Association
CSH	Calcium Silicate Hydrate
D	Dolomitic Limestone
DOT	Department of Transportation
EN	European Standard
FAA	Federal Aviation Administration
G	Gypsum
GGBFS	Ground Granular Blast Furnace Slag
GU	General Use
HEL	High Early Strength
LF	Limestone Filler
LHL	Low Heat of Hydration
M	Mortar
MHL	Moderate Heat of Hydration
NRCS	National Resources Conservation Service
Pa	Paste
PC	Portland Cement
PI	Principal Investigator
PLC	Portland Limestone Cement
SCM	Supplementary Cementitious Materials
SDDOT	South Dakota Department of Transportation
SRPC	Sulfate-resistant Portland Cement
T	Thaumasite
TEG	Thaumasite Expert Group
TF	Thaumasite Formation
TSA	Thaumasite Sulfate Attack
USDA	United States Department of Agriculture
VR	Visual Rating
w/c	Water/Cement Ratio
XRD	X-Ray Diffraction

1 EXECUTIVE SUMMARY

1.1 Problem Description

One concern with the use of portland limestone cements (PLCs) is the potential development of a unique form of sulfate attack called thaumasite due to the presence of the limestone. This research seeks to determine if SDDOT can use PLCs, with 5-15% by mass replacement by limestone, for sulfate attack-prone projects in South Dakota. Further, this research clarifies whether PLCs with one additional pozzolan should be classified as a binary or ternary cement based on existing and future specifications. A pozzolan is defined as an alumino-siliceous powder that will react with water in the presence of calcium hydroxide to form cementitious compounds.

1.2 Literature Review

Different forms of classical sulfate attack have been identified in laboratory and field experiments in many parts of the world. Among them, the thaumasite form of sulfate attack is highly deleterious for mortar and concrete because it disintegrates the binding capacity of cementitious materials and turns them into a mushy mass. Some influential factors that are required for the formation of thaumasite are the availability of sulfate, carbonates (potentially from limestone powder), moisture, and low temperatures (0°C - 15°C). Moreover, the pH of the exposure and alumina content in cement (C_3A > 8% can accelerate sulfate damage) are also controlling factors. The addition of limestone filler into cements at <15% by mass will likely not result in thaumasite sulfate attack at low temperatures if combined with low C_3A cements (max 5%), low w/c ratios (<0.5), and used in concretes that comply with ACI 201 for sulfate environments. Although several investigations on PLCs have reported an increase in the susceptibility of concrete to thaumasite sulfate attack (TSA) produced with PLCs with limestone contents <15% (and more often at higher dosages >15%) if the concrete is not properly designed to resist sulfate attack. Still local cementitious materials must be tested prior to their use in sulfate-prone environments.

Studies have indicated that the thaumasite type of sulfate damage can be mitigated if the conventional sulfate attack (gypsum and ettringite formation) is properly controlled. This is likely because thaumasite sulfate attack requires prior formation of ettringite. Further, reducing the cracks formed from conventional sulfate attack will significantly limit the ingress of sulfate ions and moisture necessary for thaumasite formation. To date, although a fail-proof mitigation procedure for TSA in cement-based materials has not been found, the sulfate resistance of most concrete materials with PLCs can be achieved by using low w/c (0.50 or preferably lower), minimum cement contents (<650 lb/yd^3), sulfate-resistant cements, and proper placement, consolidation, and curing practices. The addition of appropriate dosages of supplementary cementitious materials (SCMs) is also almost certainly required to achieve sulfate resistance with PLCs. CSA A3004-C8 recommends specific dosages of SCMs for moderate and high sulfate resistance PLC blended cement. For binary blends, use of 25% Class F fly ash (lower CaO contents perform better), 40% slag, and 15% metakaolin are recommended. For ternary blends, it prescribes the use of >5% silica fume plus 25% slag or >5% silica fume plus 20% Class F fly ash.

In practice, many state DOTs currently allow the use of PLCs, but its use in the field has been limited due to low availability. Therefore, most state DOTs do not have much experience with its performance to date. South Dakota has very severe sulfate conditions compared to many other states in addition to cold temperatures, so extra precautions to prevent sulfate attack (particularly with PLCs) are warranted. The severe sulfate conditions were illustrated by the NRCS study on sulfate, magnesium, and sodium content in South Dakota soil, which indicated that sulfate contents can be very concentrated (sometimes near the concentrations of the accelerated test methods). Further, the sulfates in South Dakota can be associated with both sodium and magnesium, which is not necessarily captured in the ASTM C1012 test. Overall, TSA could potentially be a concern when using PLCs due to the introduction of additional carbonates. To prevent sulfate attack associated with PLCs, mixture design standards using local materials will need to be developed.

1.3 Materials and Test Methods

Mixture designs were developed to assess the influence on sulfate attack of varying limestone percentages (0-20%), limestone type (dolomitic vs. calcitic), cement type (Type I/II vs. Type V), and the addition of Class F fly ash. PLCs produced at two separate cement plants with 10.8% and 14.6% limestone were tested in addition to lab-manufactured cements using ground limestone filler. The 14.6% PLC was confirmed to be undersulfated and additional gypsum was added to achieve optimal sulfate levels. Dolomitic limestone powders ($CaMg(CO_3)_2$) were included in the study because little research has been performed on these materials and their influence on thaumasite-related sulfate degradation.

Specimens were tested in both sodium sulfate and magnesium sulfate solutions at 5°C and 23°C. Test methods on the specimens included ASTM C1012, an accelerated strength testing regime, mass loss measurements, visual ratings, and X-ray diffraction analysis. ASTM C1012 is a sulfate attack test method that primarily measures ettringite expansion, which does not include the sulfate attack damage associated with gypsum and thaumasite formation. Gypsum formation is related with loss of adhesion and strength whereas thaumasite can destroy the C-S-H gel and make the concrete non-cohesive. Still, the state-of-the-art in research indicates that using the standard ASTM C1012 test at room temperature can be used to measure the resistance of PLCs to sulfate attack and is used in this study. The reasoning being that if ettringite expansion is controlled the subsequent thaumasite can also be controlled because ettringite works as a precursor for thaumasite formation. Nevertheless, it is more accurate to use test methods that can capture the failure mechanisms of gypsum and thaumasite formation. Specifically, an accelerated test method was performed to investigate the strength loss, mass loss, and visual appearance change over time. Specimens were tested in both sodium sulfate (traditional) and magnesium sulfate (less traditional) solutions, since magnesium sulfate can have a more deleterious impact on concrete especially related to strength loss. Strength tests were also tested at two temperatures, 5°C and 23°C, since formation of thaumasite is more favorable at low temperatures.

1.4 Results and Discussion

1.4.1 Expansion of mortar bars

The expansion of Type I/II replaced PLCs increased with higher dosages of calcitic limestone in both sulfate solutions. However, the addition of calcitic limestone reduces the expansion of Type V replaced PLCs especially when placed in magnesium sulfate exposure. Type V modified cements performed better than Type I/II modified-cements, in general. The combination of dolomitic and calcitic limestone reduces sulfate expansion significantly compared to calcitic limestone alone. This can be attributed to the ettringite stabilization due to the carbonates released from the dolomite. The addition of fly ash with limestone improved the sulfate resistance of PLCs by reducing expansion, especially in sodium sulfate exposure. Overall, higher expansion was observed in mortar bars placed in sodium sulfate compared to magnesium sulfate.

The two interground PLCs (10.8% and 14.6% limestone replacement) had starkly different sulfate attack resistance performances. The 14.6% PLC performed poorly and exceeded sulfate expansion limits provided in ASTM C595 even with the addition of fly ash. These limits were also exceeded after sulfate optimization was performed on this cement although expansion was reduced. The 10.8% PLC performed well and met ASTM C595 sulfate expansion limits at 6-months.

1.4.2 Compressive strength testing

Greater loss of strength was observed for the paste specimens placed at a low temperature (5°C) and in magnesium sulfate. Type V cement showed comparatively lower loss of strength even at 5°C in both solutions. Strength loss was not directly related to the percentage of limestone added to the control Type I/II and Type V cements, which is different from expansion results. The strength gain and loss over time observed is due to the changes in hydration and differences in the deposition of hydration products over the entire exposure period. The compressive strength results in this study showed a dependency on the solution cation type, temperature, and cement properties. The influence of limestone addition on strength loss is less clear compared to expansion testing.

1.4.3 Visual rating and mass loss

Greater surface deterioration was observed with increased limestone addition especially in sodium sulfate. More cracking, bulging, and spalling on pastes was observed when placed at 5°C compared to 23°C. The mass of each of the mixtures did not change significantly over time for the paste samples placed at 23°C in both solutions. However, a considerable mass decrease was observed when samples were stored at 5°C, especially in magnesium sulfate solution. Mass loss was higher for higher limestone contents in both solutions.

1.4.4 Mineralogical results measured by X-ray diffraction (XRD)

The sulfate attack in sodium sulfate was dominated by ettringite and thaumasite whereas gypsum and thaumasite were the main phases that triggered magnesium sulfate attack as shown in the XRD analysis. The addition of dolomitic limestone resulted in the formation of fewer sulfate attack products. Fewer sulfate attack products were also detected in Type V cements compared to Type I/II cements, and when fly ash was added. Sulfate attack products were not correlated to limestone addition rates.

1.4.5 Complementary concrete testing

The interground 14.6% PLC had higher early strength (7-day) and similar 28-day strength to the Type I/II cement. The PLC also had higher cumulative heat than the Type I/II cement after 24 hours, which correlates with the observed strength trends. The addition of fly ash for all mixes reduced early-age strength, slightly extended setting time, and lowered cumulative heat release. 28-day strength of fly ash mixes was on par with complementary plain mixes.

1.5 Recommendations

1.5.1 Use of Type IL and IT cements

SDDOT should allow the use of Type IL and IT cements as specified in ASTM C595 and AASHTO M240 with up to 15% limestone by mass. These cements must meet limits specified in ASTM C595 and AASHTO M240 for moderate sulfate (MS) or high sulfate (HS) resistance if used in sulfate environments.

This recommendation is based on the extensive literature review and experimental testing conducted in this report. Although it was shown that PLCs can exhibit poor sulfate attack performance, it was also shown that PLCs can have high sulfate attack resistance depending on the cement properties. In this study, Type I/II and Type V cements also exhibited poor sulfate attack performance and were used as the base cements for the PLC blends. Using a more sulfate-resistant base cement prior to the addition of limestone would likely have improved their performance.

In the SDDOT Standard Specifications for Roads and Bridges, the following sections could be modified to include Type IL and IT cements instead of Type I, II, or V cement:

- "380.2 MATERIALS, Part A. Cement: Type II cement shall be used for all concrete pavement."
- "460.2. Section 750. Type II cement shall be used, unless otherwise specified."
- "462.2. Section 750. Type II cement shall be used, unless otherwise specified."
- "550.2 A Cement: Section 750, Type I cement"
- "560.2 6. Cement: Section 750, Type II cement shall be used, unless otherwise specified. For pretension prestressed concrete beams, Type I, II, or III cement may be used."
- Section 750.

Two examples of state DOT specifications including PLCs are included in Appendix C and D.

1.5.2 Cement testing

Sulfate attack testing on Type IL and IT cements using ASTM C1012 should occur yearly at a minimum.

It is recommended that any Type IL or IT cement must be tested using ASTM C1012 prior to their use in aggressive sulfate environments and meet specified limits. SDDOT must ensure that the cements are sulfate-resistant on a yearly basis. Current PLCs produced locally do not meet these specifications as evidenced in this research.

1.5.3 Fly ash content

For cements used in applications with sulfate exposure, the use of 20-25% Class F fly ash is recommended.

The use of Class F fly ash can be an effective strategy to reduce sulfate attack. However, in this study the addition of fly ash did not significantly improve the sulfate attack performance for certain PLCs. This is potentially due to its moderately high calcium content.

1.5.4 Pozzolan blend testing

The use of fly ash alone may not reduce sulfate attack expansion of certain cements to below specified limits, which warrants the testing of blends using fly ash and an additional pozzolan for sulfate resistance.

It is recommended that SDDOT research the allowance of fly ash to be used in combination with an additional pozzolan such as silica fume or microsilex to improve performance. For example, CSA A3004-C8 recommends the use of >5% silica fume plus 20% Class F fly ash. Testing by ASTM C1012 can be used to evaluate the effectiveness of the sulfate resistance of pozzolan blends.

1.5.5 Blend classification

For cements with less than 5% limestone classified by ASTM C150 or AASHTO M85, the addition of one pozzolan should be classified as a binary blend and the addition of two pozzolans should be classified as a ternary blend. For cements with 5-15% limestone classified by ASTM C595 or AASHTO M240, the addition of one pozzolan should be classified as a ternary blend in accordance with the standard's nomenclature.

Type I-V cements are classified using the traditional nomenclature when adding pozzolans since the limestone in these cements is considered to be part of the cement. For PLCs with greater than 5% limestone, the limestone is classified as an additional filler material separate from the cement. Therefore, the addition of one pozzolan to a PLC is classified as a ternary blend.

1.5.6 Sulfate-resistant mixes

Specific guidance should be provided for developing sulfate-resistant concrete mixture designs in the SDDOT Standard Specifications for Roads and Bridges as recommended by ACI 201.2R. Concrete should be classified by severity of potential sulfate exposure and designed to protect against this exposure.

It is well known that the concrete mixture design and its method of placement and curing has a significant influence on its sulfate performance beyond the selection of an adequate cement type. The water-soluble sulfate content in soils should be tested for each project to measure the severity of sulfate exposure potential as defined by ACI 201.2R. Once the site is classified, the proper w/c, strength, and cement type can be selected for sulfate attack resistance. Additional mixture design requirements and measures for placement and curing should be specified based on guidance from this report.

2 PROBLEM DESCRIPTION

Due to economic and environmental factors, the cement industry is transitioning to the use of portland-limestone cements (PLCs) instead of cements with low or negligible limestone contents. In PLCs, limestone can replace between 5-15% of the cement, and they are specified as either Type IL and IT blended cements in ASTM C595 [1]. The SDDOT needs to determine the appropriateness of including PLCs in their Standard Specification for Roads and Bridges. Also, the SDDOT needs clarification on whether PLCs with one additional pozzolan should be classified as a binary or ternary cement based on existing and future specifications.

ASTM C595 also classifies a PLC with one additional pozzolan as a "ternary blend". However, this does not agree with some current DOT specifications which consider this to be a "binary blend". Research is needed to clarify this issue before PLC cements can be specified for SDDOT projects.

Over the past few decades, there has been a fair amount of research conducted on the effect of PLCs on concrete properties. A major portion of this project will involve an extensive literature review and discussions with other state DOTs, federal agencies, and cement manufacturers to document their current PLC specifications and to assess the potential limitations of the use of PLCs. This will inform the experimental portion of the project, which will test important concrete properties using local materials (i.e., aggregates, cements, and SCMs such as fly ash). Binary and ternary blends will be tested and compared to control mixtures. PLCs will be gathered from multiple local manufacturers. Additionally, PLCs with higher limestone contents than those currently produced in this region could be manufactured by either intergrinding or blending limestone with cement.

One concern with the use of PLCs is the potential development of sulfate attack due to the presence of the limestone. This research will determine the potential for the three forms of sulfate attack with PLCs using local materials including: (1) ettringite formation (expansion) with ASTM C1012, (2) gypsum formation (loss of strength), and (3) thaumasite formation (binder deterioration). PLCs are most at risk for thaumasite sulfate attack so testing for this reaction will be highlighted. Standardized tests do not exist for gypsum and thaumasite formation so proven test methods from literature will be used instead or new tests will be developed.

In addition to sulfate attack testing, this research will assess the impact of PLCs on both fresh and hardened properties of concrete using a suite of standard analytical testing. This research is important as the supply of standard portland cement (<5% limestone) becomes more limited for use in the U.S. Upon completion of the project, all findings will be communicated to the SDDOT. Recommendations for specifications will address the appropriate use of PLCS and binary/ternary blends. All research will be conducted by principal investigator (PI) Shearer and one graduate MS student at SD Mines.

3 RESEARCH OBJECTIVES

For Project SD2016-04, SDDOT outlined three objectives for this project in the Request for Proposals (RFP) as follows:

1) Investigate other state DOT's specifications and experience using portland-limestone cements and perform a comprehensive review of publications and work done by others.
2) Verify that the properties of concrete made with portland-limestone cements and materials available in South Dakota are comparable to those of standard portland cement concrete.
3) Develop recommendations for changes to the SDDOT's Standard Specifications for Roads and Bridges.

We opted to not add additional research objectives to the three given by SDDOT in the RFP. We felt that the three outlined objectives were adequate for meeting the need SDDOT stated in the RFP. All three of the objectives required a comprehensive paper study of the literature. They also required interviews and communication with practitioners, DOT personnel, and contractors. Additionally, an experimental testing program sought to determine the impact of PLCs on sulfate attack and other important concrete properties.

3.1 Investigated Cement Specifications and Use

Investigated other state DOT's specifications and experience using portland-limestone cements and performed a comprehensive review of publications and work done by others

Objective 1 was accomplished by a review of published and unpublished data from a variety of sources including state DOTs, federal agencies, and potentially international sources (namely regions where higher limestone contents are used including Canada, South America, and Europe). This resulted in a better understanding about their current PLC specifications and potential limitations of the use of PLCs as well as their use of binary/ternary blends. A discussion with cement manufacturers (local and national) and the concrete industry provided further insight on the use of PLCs and binary/ternary blend classifications. Also, an extensive literature review on the topic of PLC concrete, especially related to sulfate attack, was performed. Ultimately, this work helped with writing the new specification for SDDOT and determined the necessary additional experimental research to be performed to accomplish Objective 2.

3.2 Verified Concrete Properties

Verified that the properties of concrete made with portland-limestone cements and materials available in South Dakota are comparable to those of standard portland cement concrete.

Sulfate attack testing using an accelerated and standard method was the primary focus of the experimental research. In addition to sulfate attack testing, this research assessed the impact of PLCs on set time, workability, and mechanical properties. Additionally, isothermal calorimetry was used to determine if any material incompatibilities existed for PLCs (e.g., with admixtures, aggregates, or SCM's). Other durability testing including alkali-silica reactivity testing was not requested by the technical panel. This testing on local materials indicated whether the performance (including sulfate resistance) of local concrete mixtures would be satisfactory given the physical and chemical characteristics of the materials including limestone, and if additional specifications needed to be drafted.

3.3 Developed Recommendations

Developed recommendations for changes to the SDDOT's Standard Specifications for Roads and Bridges

Objective 3 was accomplished by reviewing and analyzing all collected data from Objectives 1 and 2. During the research process, the most important criteria regarding concrete performance with the use of PLCs was selected and evaluated for approval and used to determine if the specifications need to be adjusted given the results. For example, limits for the sulfate resistance of PLC mortars were sought to be established for SDDOT. The specifications could have included limestone quantity limits for particular applications, limestone material property specifications, and appropriate mixture design specifications using PLCs. Lastly, this research addressed the binary vs. ternary discrepancy in the standard specification regarding PLC Type IT cement.

4 TASK DESCRIPTIONS

4.1 Met with Technical Panel

Met with the project's technical panel to review project scope and work plan.

Prior to beginning work on the project we met with the technical panel in person to discuss project scope, schedule, budget, and goals within the first month after the contract is signed. The meeting included a review of the RFP and the proposal. This meeting clarified contractual obligations of SDDOT and SDSM&T for the project.

4.2 Conducted Literature Search

Conducted a thorough literature search and reviewed other state DOTs' specifications regarding the use of portland-limestone cement.

The graduate student performed a three-month search of the cement and concrete literature for pertinent experience and data related to the use of PLC concrete. This literature review focused on the impact of PLCs on sulfate attack and other important concrete properties. The PLC specifications of other state DOTs and federal agencies were also examined including their treatment and differentiation between binary and ternary blends. This involved interviews and a survey with personnel from these agencies. Industry contacts were also interviewed (primarily cement manufacturers and ready-mix concrete producers) regarding their opinions about changes in specifications regarding PLCs.

4.3 Met with Technical Panel

Met with the project technical panel to present findings from Task 2 and to review the proposed testing plan for Task 4.

At the conclusion of Task 2, the PI and the graduate student presented the findings in person from Task 2 with the project technical panel. Following this presentation, there was a discussion about finalizing the proposed testing plan for Task 4. This discussion resulted in the amendment of the proposed research currently presented in Task 4. Some experimental testing (particularly some of the sulfate testing) had to be conducted concurrently with Task 2, given the duration of those tests (12 months or greater).

4.4 Tested Concrete Mixes

Tested mixes made with portland-limestone cements available in South Dakota, one coarse aggregate source with and without fly ash and compared results to mixes made with standard portland cement for sulfate resistance, set time, compressive and flexural strength, workability and durability.

The detailed mix designs and testing procedures are included under Section 5.0 Findings and Conclusions.

4.5 Recommended Specifications

Developed recommendations for specifications for portland-limestone cements based on the literature search and the test results.

Using the results from Tasks 2 and 4, specifications for the appropriate use of PLCs for SDDOT projects and the required test methods for their use were drafted. As stated in Objective 3, these specifications could have potentially included recommendations on limestone types and quantities, appropriate mixture design specifications for PLCs, and any other concrete performance issues regarding the use of PLCs including sulfate resistance. The difference between binary and ternary blends in SDDOT specifications in relation to ASTM specifications was also addressed.

4.6 Met with Technical Panel

Met with the project technical panel to review findings from Tasks 4 and 5.

We met with the technical panel to discuss the results and recommendations developed from Tasks 4 and 5.

4.7 Prepared Final Report

In conformance with Guidelines for Performing Research for the South Dakota Department of Transportation, a final report was prepared summarizing the research methodology, findings, conclusions, and recommendations.

The PI supervised the preparation and submittal of the final report (mainly written by the graduate student but edited and revised by the PI) once SDDOT and the technical panel for the project reviewed the recommendations for specifications and other deliverables. All previous Tasks are summarized, and all recommendations are included.

4.8 Executive Presentation

An executive presentation was given to the South Dakota Department of Transportation Research Review Board at the conclusion of the project.

As part of submittal of the final report, an executive presentation was delivered to SDDOT to summarize the project findings and present the recommended policies, procedures, and/or specifications. This presentation was made by the PI.

5 FINDINGS AND CONCLUSIONS

5.1 Literature Review

5.1.1 Advantages of using portland-limestone cements

Portland cement clinker is manufactured through an energy intensive process. Additionally, it produces a considerable amount of greenhouse gases during cement production, particularly CO_2 that annually contributes to more than 5% of global anthropogenic CO_2 discharge [2]. CO_2 release is primarily a result of decalcination of the limestone during clinkering in addition to the fuel consumption needed to generate the high temperatures necessary to form clinker. It is predicted that the reduction of portland cement clinker will substantially cut back the environmental impacts associated with concrete by reducing carbon emissions. To reduce the environmental impact of cement, most plants have produced blended cements, containing SCMs like slag, silica fume, and fly ash. Currently in the US, a small percentage of limestone powder is used to replace cement as a filler material to produce portland-limestone cement (PLC). PLCs require comparatively less clinker to produce an equivalent amount of cement, and therefore less energy is consumed and CO_2 emissions and other greenhouse gases are reduced.

5.1.2 Overview on limestone cement usage

During the last few decades, PLCs have been widely used in the cement industry to reduce the use of raw materials (e.g., calcium carbonate, silica, alumina, and iron ore), save fuel energy, and curtail CO_2 emissions. PLCs have been formally adopted by many specifications around the world. The majority of the portland cement specifications permit adding up to 5% limestone by mass in portland cement mixtures. Above this allowable limit, PLCs are classified depending on the proportion of limestone added to the parent cement. The European Standard (EN 197-1-2011) has designated 5% limestone as a minor additional component. It also identifies four types of PLCs containing 6-20% limestone (types II/A-L and II/A-LL) and 21-35% limestone (types II/B-L and II/B-LL), respectively [3].

Canadian Standards Association (CSA) A 3001 has allowed the inclusion of 5% limestone since 1983. As of 2008, CSA responded to increasing pressure to reduce the use of clinker content in cement by revising A 3001 to allow PLCs at higher percentages. CSA 3001–13 set the limit to allow PLCs containing up to 15% limestone. Based on the application, the revised standard classified PLCs into four categories including: (1) general use (GU), (2) moderate heat of hydration (MHL), (3) high early strength (HEL), and (4) low heat of hydration (LHL). China and Russia both have permitted up to 10% limestone. Mexico NMX C–414 has defined cement Type CPC as blended portland cement which may contain 6–35% limestone.

In the U.S., the ASTM C150M-17 [4] standard currently permits up to 5% limestone content as a filler material. To meet this standard, the amount of calcium carbonate ($CaCO_3$) calculated from the limestone should be a minimum of 70% by mass. On the other hand, ASTM C595M - 17 [1] (hydraulic cement) classifies cement based on its performance requirement which allows up to 15% limestone replacement.

In the U.S., almost half of the state Departments of Transportation (DOTs) have accepted the use of blended PLCs and others are still considering (Figure 1). Please refer to map in Appendix A for the version of the map developed by the SDDOT survey.

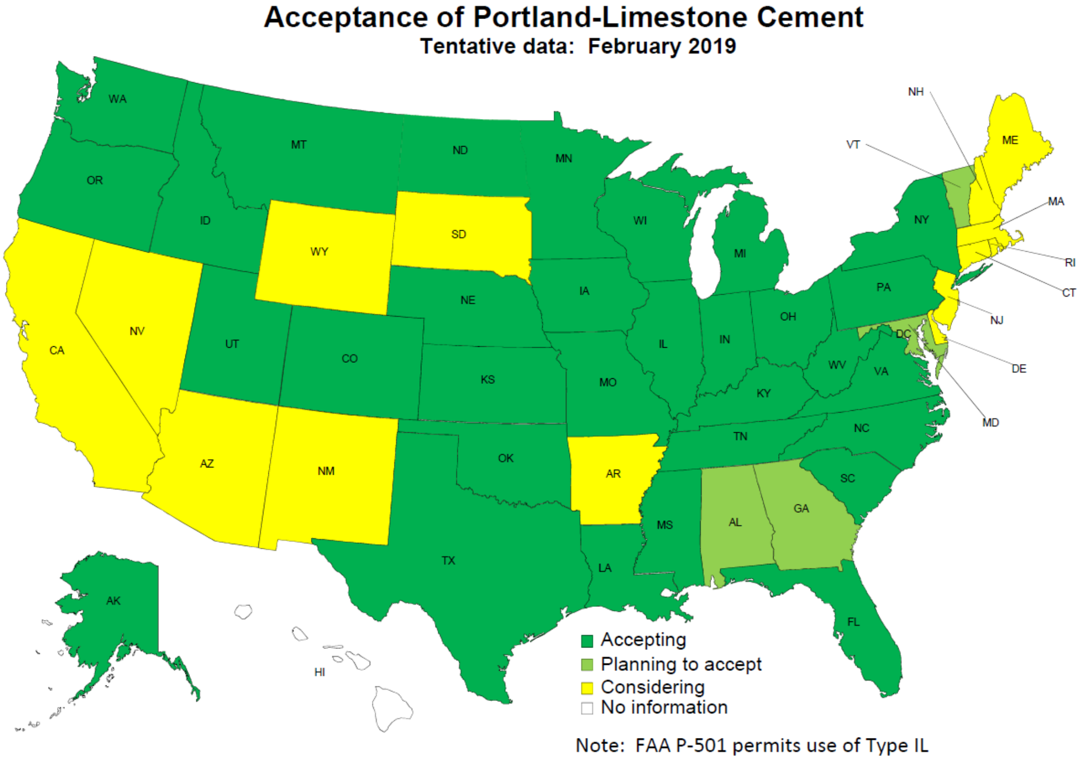

Figure 1: Acceptance of blended PLC cements by state DOTs (data courtesy Steve Wilcox, Argos USA). Reference map in Appendix A for complementary results.

5.1.3 Summary of SDDOT PLC survey

A nation-wide survey was sent to all 50 state DOTs regarding their use of PLC. The survey questionnaire was comprised of 11 questions (see Appendix A for full survey results). Thirty-two state DOTs responded to the survey thus far. The earliest adoption of PLCs was in 2006, however, the majority of the states have adopted the use of PLCs after 2012. The majority of the DOTs allow use of PLCs for both structural and nonstructural applications without restriction. However, there are some exceptions. One state indicated that its use must be approved by an engineer. Another indicated that they use it primarily on “low risk” items.

The survey indicated that the only problem encountered thus far by DOTs with the use of PLCs is the lack of a reliable supply. The availability of PLC was seen as an issue because concrete producers have limited silo capacity and it’s not being used as a mainstream product yet. Further, one DOT noted that it is important for the cement producers to identify a margin of target limestone content (within a 1% range) to keep the material properties consistent. The survey results indicated that with regard to other potential problems with PLC use (e.g., workability, strength, durability, etc.) more than half of the DOTs did not know if there were issues likely due to lack of experience using the material. The remainder of the DOTs indicated that they did not observe any problems with the use of PLCs, however, one DOT noted that it was too early to tell if there were any durability concerns. Fourteen DOTs categorize PLCs as Type IL or IT cements as defined in ASTM C595. The remainder primarily used AASHTO M240 (Type IL) for classification. One state further limits their maximum limestone content to 10% instead of 15%.

The further comments revealed some additional information. Virginia DOT reported no problem using PLCs based on the preliminary laboratory testing, however, the only concern that has arisen is the potential for increased creep, which could be an issue for prestressed concrete. One DOT indicated that the industry is moving quickly towards more use of PLCs. Another indicated that, higher strength and consistency can be achieved using PLCs compared to Type I/II cements if it is blended with Class F fly ash. Overall, it appears that although many state DOTs currently allow the use of PLCs, it has not been used very frequently yet due to limited availability.

5.1.4 ASTM blended hydraulic cement classification

In ASTM C595M-17, the binary and ternary classification consider limestone content as a separate material from cement. According to ASTM C595, the nomenclature of blended cements has been categorized as four types stated below in Table 1.

Table 1: ASTM C595M-17 Blended Hydraulic Cements Classification

Cement Type	Notation
Portland-Limestone Cement	Type IL
Portland Blast-Furnace Slag Cement	Type IS
Portland-Pozzolan Cement	Type IP
Ternary Blended Cement	Type IT

5.1.5 Binary blended cement

Based on the above classification, Type IL (Portland-Limestone Cement) is considered a binary blended cement which is a blend of ordinary portland cement and limestone filler (5 - 15% by mass). Similar to limestone powder, if slag or another pozzolan is added to the ordinary portland cement then it is also classified as a binary blended cement. Some blended cements have special performance requirements in different exposure conditions. To examine their performance, these cements require additional testing to verify certain properties. These special properties are designated by specific letters in the parenthesis followed by the cement type. Some other types of blended hydraulic cements based on the special properties are given below in Table 2.

Table 2: ASTM C595M-17 Blended Hydraulic Cements with Special Properties

Suffix	Property
A	Air entraining
MS	Moderate sulfate resistance
HS	High sulfate resistance
MH	Moderate heat of hydration
LH	Low heat of hydration

Using this nomenclature, a portland-limestone cement with low heat of hydration properties would be designated as Type IL(LH). As another example, Type IS-A(MS) is an air-entraining portland-blast furnace slag cement with moderate sulfate resistance. During this research project, ASTM C595 changed their previous language that did not permit Type IL and IT cements with greater than 5% limestone to be classified as moderate sulfate resistance cements (MS) or high sulfate resistance cements (HS). Therefore, Type IL and IT cements containing limestone contents >5% can now be classified as MS and HS under ASTM C595.

The percentage of partial replacement of ordinary portland cement either by limestone, slag, or pozzolan is noted by adding a suffix (X) followed by the cement type, where (X) is the selected proportion of limestone, slag, or pozzolan. For instance, binary blended cement with 90% portland cement and 10% limestone is labeled as IL(10) and binary blended cement with 85% portland cement and 15% pozzolan is labeled as IP(15). If air entrainment is included, the letter 'A' is added, thus Type IL(15)A would be an air-entraining cement with 85% portland cement and 15% limestone.

5.1.6 Ternary blended cement

Ternary blended cements are blended hydraulic cements consisting of portland cement with either a combination of: (1) two pozzolans, (2) slag and pozzolan, (3) pozzolan and limestone, or (4) slag and limestone. Ternary blends are generally classified by two suffixes following the cement type. Additionally, the mass percentage of the two respective added materials are shown. Some examples of ternary blended cements are shown in *Table 3* below.

Table 3: ASTM C595M-17 Ternary Blended Hydraulic Cement Classification

Cement Type	Description
IT(L10)(P10)	Ternary blended cement with 80% portland cement, 10% limestone, and 10% pozzolan.
IT(L15)(S10)	Ternary blended cement with 75% portalnd cement, 15% limestone, and 10% slag.
IT(S20)(P10)	Ternary blended cement with 70% portland cement, 20% slag, and 10% pozzolan.
IT(P25)(P10)	Ternary blended cement with 65% portland cement, 25% of one pozzolan, and 10% of another pozzolan.

If it is requested to categorize cement based on performance, such as with air entrainment (A), then the notations are also added. For example, Type IT(S25)(L15)(A) indicates an air-entraining cement containing 60% portland cement, 25% slag, and 15% limestone.

5.1.7 Sulfate attack in concrete

One important concern with the use of PLCs is the potential development of a special type of sulfate attack called thaumasite formation due to the presence of limestone. Research has shown that the amount of limestone in PLCs can have an impact on the sulfate attack of cementitious materials, but also that it can be mitigated through proper mix design and placement techniques.

Sulfate attack in concrete and mortar is a chemical reaction that can either be caused by internal or external sulfate sources. Internal sulfate attack occurs when the source is from either sulfate-rich aggregates, higher amounts of gypsum in the cement, or another source may result in such an attack. One common internal sulfate attack issue is delayed ettringite formation (DEF). External sulfate attack is caused when sulfates ingress into concrete from a sulfate-rich environment like soil, seawater, decaying organic matter, or industrial effluent [5]. These external sulfate ions react with the components of cement paste resulting in concrete deterioration over time where significant microstructural changes weaken the cement paste binder. Sulfate attack in concrete can manifest in the form of expansion and cracking, which increases the permeability of concrete and thus accelerates the aggressive penetration of deleterious ions into the concrete. Sulfate attack can also cause the concrete to become mushy and lose its strength.

As opposed to the chemical forms of sulfate attack, physical sulfate attack (PSA) on concrete is related to surface scaling and flaking of concrete due to the crystallization of salt in pores near the drying surface [6]. The damage process involves capillary rise and evaporation of groundwater especially when the rate of evaporation of salt solution from the exposed surface is higher than the rate of solution uptake [7]. There are several factors that may affect the salt crystallization damage including salt type and concentration, evaporation rate, surface tension, vapor pressure, and properties of the pore structures [8]. This type of attack usually occurs at the interface of concrete structures partially submerged in soils and water. It many times causes more damage than chemical sulfate attack.

5.1.7.1 Ettringite formation

Ettringite is the mineral name of calcium sulfoaluminate ($3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 32H_2O$), which is a hydration product of portland cement. It has a needle-like morphology and contributes to stiffening of the mixture at early ages. If it is formed at later ages in the system, it can lead to significant damage to the concrete.

Alumina phases tricalcium aluminate (C_3A) and tetra calcium aluminoferrite (C_4AF)) in portland cement clinker are susceptible to this form of sulfate attack.[1] In the presence of calcium hydroxide (CH) and water (H_2O), monosulfate hydrate ($C_3A \cdot C\bar{S} \cdot H_{18}$) and calcium aluminate hydrate ($C_3A \cdot CH \cdot H_{18}$) react with sulfate ($\bar{S}$) to produce ettringite in the following reactions [9]:

$$C_3A \cdot CH \cdot H_{18} + 2CH + 3C\bar{S} + 11H \rightarrow C_3A \cdot 3C\bar{S} \cdot H_{32}$$
$$C_3A \cdot C\bar{S} \cdot H_{18} + 2CH + 2C\bar{S} + 12H \rightarrow C_3A \cdot 3C\bar{S} \cdot H_{32}$$

The formation of a limited amount of ettringite may be acceptable; however, excessive amounts of this mineral may cause expansion and cracking of the hardened cement paste. Even though the expansion mechanism due to ettringite formation is still not fully known, two particular mechanisms have been widely published: (1) the topochemical reaction mechanism and (2) the swelling mechanism [10]. In the topochemical reaction mechanism, the reaction between C_3A and the sulfate and calcium ions in the concrete pore fluid is topochemical (i.e., in solid state) [11]. According to swelling theory, adsorption of water into poorly crystalline ettringite can lead to expansion [12].

5.1.7.2 Gypsum formation

The formation of gypsum takes place when the hydration product calcium hydroxide (CH) reacts with sulfates of sodium (Na^+), magnesium (Mg^{2+}), or potassium (K^+) in the presence of water. The migration process of sulfates into concrete depends on the transport properties (e.g., permeability of concrete). Gypsum formation occurs due to cation exchange reaction between sulfates and CH. Depending on the cation types, both CH and calcium silicate hydrate (C-S-H) are prone to conversion into gypsum by external sulfate attack in addition to the formation of brucite. These reactions are as described as follows [9]:

$$Na_2SO_4 + CH + 2H_2O \rightarrow CaSO_4 . 2H_2O \text{ (Gypsum)} + 2NaOH$$
$$MgSO_4 + CH + 2H_2O \rightarrow CaSO_4 . 2H_2O \text{ (Gypsum)} + 2Mg(OH)_2 \text{ (Brucite)}$$
$$3MgSO_4 + 3C\text{-}S\text{-}H + 8H2O \rightarrow 3(CaSO_4 . 2H_2O) + 3Mg(OH)_2 + 2SiO_2 . H_2O$$

In the gypsum formation process, the pH of the system is initially reduced and there is a signifcant loss in stiffness and strength in concrete. As the damage from the strength and loss of adhesion progresses, the concrete is eventually transformed into a non-cohesive mass. The exact process and nature of disintergration caused by gypsum is not completely understood. In concrete that is detoriorated by sulfate attack, gypsum is primarily observed close to the surface, especially in cracks and voids [13, 14].

The formation of gypsum does not likely lead to significant expansion of the samples [11, 15, 16] although some research has shown that with the right conditions gypsum formation can lead to some expansion and

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[1] Cement chemistry notation is often used to describe reactions: C=CaO, S=SiO_2, H=H_2O, A=Al_2O_3, F=Fe_2O_3, $\bar{S}$=SO_3, $\bar{C}$=$CaCO_3$, CH=$Ca(OH)_2$, C-S-H=$C_xS_2H_y$ where x and y vary

cracking [17]. The precise measurement of mechanical damage due to gypsum formation is difficult because it sometimes is masked by the formation of ettringite during sulfate attack [18]. The ASTM C1012 test does not really capture the damage from gypsum, because it only measures expansion. Therefore, compressive strength testing is a better tool to assess this form of sulfate attack.

5.1.7.3 Thaumasite formation

Thaumasite ($C_3S\overline{S}\overline{C}H_{15}$) is a type of mineral that has a complex hexagonal crystal structure of sulfate salt and is usually found in metamorphic rocks and limestone [19]. During thaumasite sulfate attack in concrete, calcium-silicate-sulfate-carbonate hydrates ($CaSiO_3 \cdot CaCO_3 \cdot CaSO_4 \cdot 15H_2O$) forms in the cement paste by reaction of calcium-silicate-hydrates (C-S-H) with sulfates in the presence of carbonate ions and water (all must be available for reaction to occur). As a result, carbonate ions from limestone in PLCs could potentially lead to greater thaumasite formation. The formation of thaumasite usually takes place in very wet environments and its rate of formation is higher at low temperatures. The type and concentration of sulfates, water-cement ratio, cement type, and type and dosage of limestone additive in cement, carbonate sources, curing methods, relative humidity, the proportion of SCMs are important controlling factors for thaumasite formation [20].

Thaumasite sulfate attack (TSA) was first recognized in portland cement concrete sewer pipes, cement grout, and in the base of pavements by Erlin and Stark in 1965 [21]. Thaumasite again attracted noticeable consideration in 1998 when it was discovered in some motorway bridge foundations in the United Kingdom (UK) [22]. The transformation of C-S-H into thaumasite transforms concrete into a non-cohesive mass and can completely damage its binding and load bearing capacities over time.

The formation of thaumasite is not always catastrophic. A recent report from the Thaumasite Expert Group (TEG) distinguishes two mechanisms in which thaumasite can precipitate as a reaction product within cementitious materials**.** These are (1) thaumasite formation (TF), and (2) thaumasite form of sulfate attack (TSA). TF refers to scenarios where thaumasite can be found in preexisting voids and cracks without necessarily affecting the integrity of the host concrete or mortar. On the other hand, TSA can lead to the complete disintegration of a concrete or mortar due to the transformation of calcium silicate hydrates (C-S-H) in the hydrated portland cement paste to thaumasite. During TSA, the damaged cement paste loosely holds aggregates due to its loss of binding capacity. Visible cracks fill with thaumasite and white haloes around the aggregates are formed [23]. In buried concrete structures, TSA starts attacking at the surface and progresses inwards, which causes gradual disintegration of the C-S-H matrix.

5.1.7.4 Mechanisms of thaumasite formation

Generally, TSA favorably occurs at temperatures $\leq 15^{\circ}$ C in the presence of calcium silicate, sulfate, and carbonate ions [22]. However, TSA has also been reported in cement-based materials at higher temperatures [24, 25]. There are two possible routes for thaumasite formation: (1) the direct route and (2) the indirect route. The schematic diagram (Figure 2) shows the mechanisms of the two possible routes. In the direct route, thaumasite is formed through the reaction of C-S-H with carbonate ions (potentially from limestone) in the presence of moisture and sulfate ions, according to following equation [26].

$$3Ca^{2+} + SiO_3^{2-} + CO_3^{2-} + SO_4^{2-} + 15H_2O \rightarrow CaSiO_3 \cdot CaCO_3 \cdot CaSO_4 \cdot 15H_2O$$

According to this hypothesis, initially hydration products including ettringite, C-S-H gel, and CH are formed. Once a significant amount of C_3A is reacted, the external sulfate ions react with Ca^{2+}ions and additional CH decomposed into the pore solution, and gypsum crystallization starts. As more gypsum is produced due to the continuous removal of CH, hydroxyl (OH^-) ions in the system will eventually be depleted and as a result instability and decalcification of C-S-H will occur. In sodium sulfate (Na_2SO_4) solution, the disintegration of C-S-H is attributed to be the source of silica available in the pore solution that reacts with the carbonate and sulfate ions to form thaumasite. However, when magnesium ions are present ($MgSO_4$), the reaction mechanism is different. In this case, the overall reaction to form thaumasite has been outlined as follows [27]:

$$C_3S_2H_3 + 3CH + 2CC + 4MS + 32H \rightarrow C_3SCSH_{15} + 2CSH_2 + 4MH$$

In the indirect route, ettringite acts as a predecessor for thaumasite formation [28]. Ettringite formation takes place in the presence of moisture carrying sulfate ions, where ettringite reacts with C-S-H and carbonates and thus transforms into thaumasite according to the following equation:

$$C_3S_2H_3 + C_6A\bar{S}_3H_{32} + 2C\bar{C} + 4H \rightarrow 2C_3S.\bar{C}\bar{S}H_{15} + C\bar{S}H_2 + AH_3 + 4CH$$

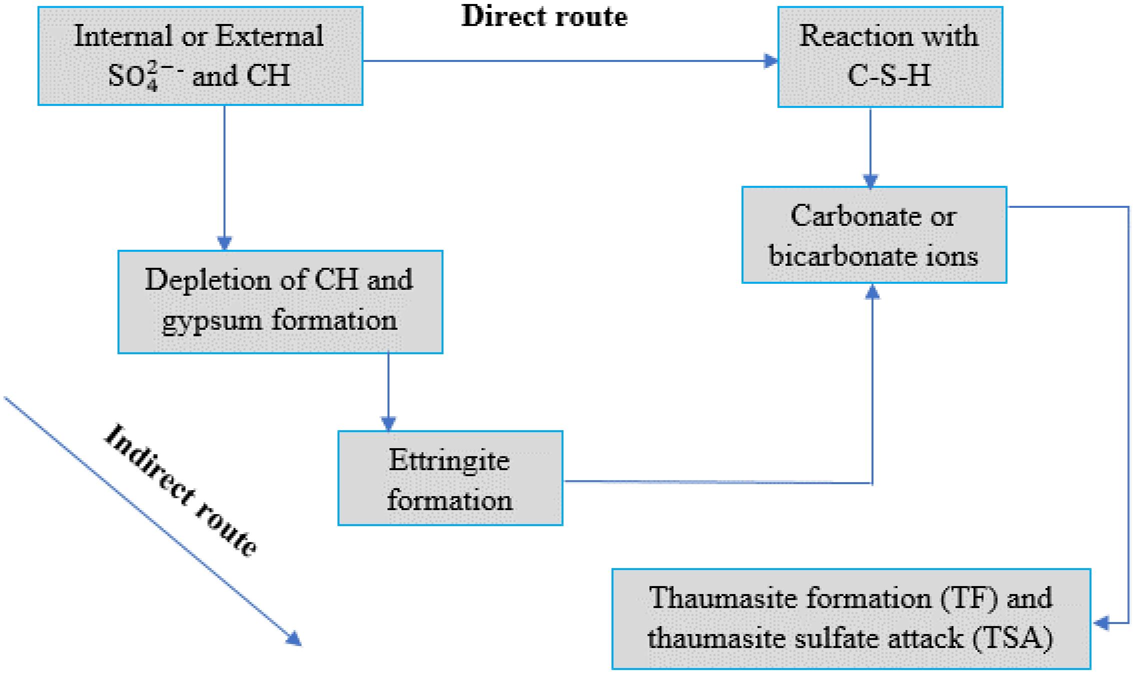


Figure 2 : Simplified schematic for the direct and indirect routes of TSA.

Studies show that the formation of thaumasite is inversely proportional to ettringite [29]. It is assumed that TSA occurs after the accumulation of aluminum at a molar ratio of SO_3/Al_2O_3 goes above 3, leading to ettringite formation [30]. Moreover, some other phases like gypsum, tri-calcium aluminate (C_3A), and calcium aluminoferrite (C_4AF) affect TSA [31]. Several case studies related to TSA reveal that there is usually a coexistence between ettringite and thaumasite in the microstructure of concrete [32].

5.1.7.5 Features of TSA

The primary characteristics of TSA on concrete is rapid loss of its binding ability and strength. An acute TSA can transform hardened concrete from artificial rock to slurry. Some have reported up to a 30% reduction in flexural and compressive strength due to TSA [33]. The bonding between the concrete and reinforcement steel can also be significantly reduced [34].

If TSA takes place in concrete or mortar, its cement paste matrix can be transformed into a white pulpy mass composed of thaumasite, which loosely holds the surrounding aggregates together. The typical visual features of concrete which is damaged by TSA shown in **Figure 4**. It shows a soft mass with loose aggregates.

According to Crammond [35], concrete subjected to TSA can have four zones shown in Figure 3:

Zone 1:	No visual evidence of attack; occasional voids are lined with ettringite or thaumasite
Zone 2:	Thin cracks lined with thaumasite appear running sub-parallel to the concrete surface. Little portlandite is observed in the paste and calcium carbonate sometimes lines cracks.
Zone 3:	Sub-parallel, thaumasite-filled cracks become wider and the amount of non-attacked cement paste is greatly reduced. Haloes of pure white thaumasite are observed around the aggregate pieces. Little portlandite is observed in the paste and calcium carbonate sometimes lines cracks.
Zone 4:	Transformation of cement paste to thaumasite is complete, all that remains is aggregates particles embedded in extremely soft white mush. Localized anaerobic corrosion occurred in isolated chloride-rich areas, where the depth of attack had penetrated through the concrete cover to the steel.

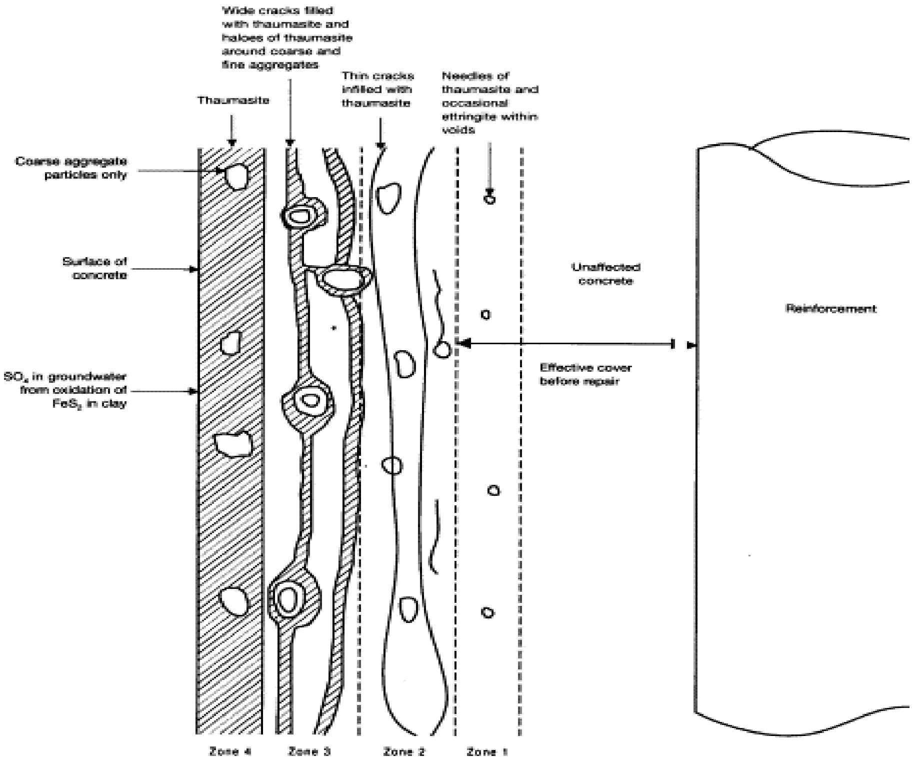


Figure 3: Sketch of idealized form of TSA degradation in high quality structural concrete (from [35])

Figure 4: Visual appearance of specimens disintegrated by TSA (**from** [32])

5.1.7.6 Field and laboratory case studies of TSA

TSA has been found in many countries around the world including the UK, Germany, Norway, China, and South Korea [36-42]. The majority of the TSA resulted in softening and cracking of the concrete. For most cases, the limestone aggregate was the primary source of carbonates needed for the TSA formation. However, in Germany, PLCs may have contributed to the formation of TSA**.** In one case study [38], Freyburg found wet mush and scaling on a train tunnel surface in Germany potentially due to the use of a PLCs in the presence of magnesium in the groundwater. In North America, TSA has also been identified in structural and non-structural concrete primarily in Canada also due to carbonated aggregates [43, 44].

5.1.7.7 Influence of portland limestone cement on sulfate attack

A selection laboratory studies which measured the effect of PLCs on both the classical and thaumasite type of sulfate attack are presented in

Table 4. It can be seen that a wide variety of experimental set-ups have been used as there is no standard for thaumasite sulfate attack measurements. Results of these studies have shown that the addition of limestone filler into cements will likely not show early damage at low temperatures if combined with low C_3A cements (max 5%), low w/c ratios (<0.5), and used in concretes that comply with ACI 201 for sulfate environments [45].

Hooton et al. [46] conducted research on sulfate resistance testing on mortars (laboratory) and concrete (both laboratory and under simulated field condition) for a period of 5 years. Different types of cement-based materials including portland cement (PC) with and without SCMs, portland limestone cement (PLC) having 5 to 15% limestone content with SMCs (e.g., fly ash, slag, metakaolin, and silica fume), and Type II and Type V were used to investigate the performance in sulfate exposures. Concrete made with ASTM C595 Type IL and IT cements incorporating an appropriate dosage of SCMs performed better than ASTM Type V cements in very severe sulfate exposure (Class S3) for up to 5 years. This indicates that PLCs can perform as well if not better compared to sulfate-resistant cements, but appropriate mix designs must be used.

Others have found that PLCs with greater than 15% limestone can increase sulfate vulnerability. Further, even some PLCs with lower than 15% limestone can reduce the sulfate resistance of cement paste. This may be in part due to the "equivalent performance" requirement of PLCs for use in concrete with regard to strength and durability. If PLCs do not, for example, produce concrete with similar strength results to OPC concretes there is less likelihood they will perform as well with regard to sulfate attack. One important strategy to reach "equivalent performance" is to achieve higher Blaine fineness values in PLCs compared to OPC. The fineness values of interground limestone may be significantly higher (upwards of 1000 m^2/kg) than the cement (closer to 400-500 m^2/kg) making the PLC more reactive. This phenomenon will be important to consider when mixing ground limestone with OPC during the experimental phase.

5.1.7.8 External sulfate sources

There are a wide variety of sulfate sources available in the environment. Most soils contain a considerable amount of sulfate. Higher concentrations of sulfate in groundwater is found due to the presence of magnesium, sodium, and potassium sulfates. Similarly, ammonium sulfate is prevalent in agricultural water and soil when effluents from furnaces and chemical industries, and organic matter decompose (especially in lakes, sewer pipes, and mining pits) produce sulfuric acid. Even water used in concrete mixtures and for curing may contain a certain concentrations of sulfate ions [9]. Some important factors that influence the potential of sulfate attack are the amount and nature of sulfates, seasonal variation of groundwater level, soil porosity and groundwater flow, and most importantly the overall quality of concrete.

5.1.7.9 Sulfate ion concentrations in South Dakota soils

Roughly 1,300 sulfate concentrations in South Dakota soils were studied to determine appropriate solution compositions for experimental sulfate attack testing. The ionic concentrations of saturated pastes were provided by measurements conducted by the Natural Resources Conservation Service (NRCS) under the United States Department of Agriculture (USDA). The saturated paste extraction was performed on water extracted from the soil at saturation and on soils with an electrical conductivity of greater than 0.25 dS/m. In addition to measuring sulfate concentrations, the sodium and magnesium concentrations associated with sulfate ions were measured for all test samples. Soil samples were extracted from a certain depth range in each county called horizons. Horizons are the naturally occurring layers formed by the interaction of soil forming factors (i.e., climate, organisms, relief, and parent material) over time. Note that the soil samples analyzed in the study are not completely representative for South Dakota due to limited sampling. There can also be substantial variability in soil properties within short lateral and vertical distances within a soil profile at a single point.

Table 4: Results of most important experimental research on PLCs and sulfate attack

Specimen size (mm)	Material	Time (month)	% LF	% C_3A	SO_4^{2-} (mg/L)	Mg^{2+} (mg/L)	Water /binder	Temp. °C	Curing (day)	Compound D	Compound T	Compound G	Compound B	Compound P	Main Conclusion
$25 \times 25 \times 159$	M	11	0 10 20 30	11	33800	-	0.70 0.78 0.88 1.00	20	28						LF improves sulfate resistance of mortars to a limited time. But it did not produce a sulfate resisting mortar [47].
$25 \times 25 \times 294$	M	12	5 5 3	10.4 9.0 8.0	33800	-	0.51 0.51 0.50	23	2- 3						LF has no influence on sulfate resistance, except when diluting the C_3A content [48].
$25 \times 25 \times 294$	M	12	0 10 20 0 10 20	0.0 1.0	33800	-	0.49 0.54 0.61 0.49 0.54 0.61	20	3-7	E E		G G G G G G		P P P P P P	Penetration of attack, CH depletion and gypsum are deeper when LF content increases [49].
$25 \times 25 \times 294$	M	36	0 12 18	2.0	33800	-	0.49 0.55 0.59	20	28	 E E		G G G			For 0 and 12% LF, expansion was lower than failure criteria. For 18% LF, it failed after 6 months
$40 \times 40 \times 160$	M	36	0 15 12	12	1500	-	0.60 0.71 0.68	8	14	E E	T T T			P P P	Thaumasite formation can be avoided with appropriate pozzolan (Bellmann, 2007).
$100 \times 100 \times 100$	Cr	24	0 5 25 0 5 25	13.1 8.5	18000	-	0.60 0.63 0.80 0.60 0.63 0.80	20	28	No component reported	No component reported	No component reported	No component reported	No component reported	Sulfate performance of concrete was dependent on C_3A content of the cement. Addition of 5% and 25% LF produced no consistent effect; it sometimes improved, but for others it worsened.
$20 \times 20 \times 15$	M	24	20 20 20 25 35	13 10 9 5 0	4200	1100	0.75 0.75 0.75 0.80 0.92	5	21	E E E E	 T T T T	G G G			Faster rate of deterioration with increased C_3A content. For the same C_3A content the attack depended on LF [50].
$30 \times 40 \times 50$	Pa	12	0 15 30	6.7	14400	3600	0.40 0.47 0.57	5	28		T	G	B		Metakaolin (10%) or low Al_2O_3 blast furnace slag (50%) improves the sulfate resistance of PLC with 15% LF [51].
$40 \times 40 \times 160$	M	12 60	10 10 10 10	8.1 0.0 8.1 0.0	3000	800	0.44 0.44 0.44 0.44	5	28	 E E	 T T				Damage was mitigated using a sulfate-resistant portland cement (SRPC) and completely eliminated when this cement was blended with fly ash [52].
$40 \times 40 \times 160$	Pa	7	0 15 30	12.4	67600		0.40 0.47 0.57	5	7	E E E	 T	G		P P P	No significant difference on sulfate resistance performance of PC and PLC exposed to wet-dry cycles [53].
$40 \times 40 \times 160$	M	12	0 0	12.0 4.0	16000	4000	0.6	5	28	E E	T T	G			Cement and SPRC mortars showed signs of deterioration after 4 and 6 months, respectively. Resistance to TSA was improved by addition of silica fume (8%) or GGBFS (60%) [33].

Key: Cr=Concrete, M=Mortar, Pa=Paste, LF=Limestone Filler, E=Ettringite, T=Thaumasite; G=Gypsum, B=Brucite; P=Portlandite

Sodium, magnesium, and sulfate concentration ranges for selected SD counties are shown in Figure 5, Figure 6, and Figure 7. (note: 1mg/L = 1ppm). The average of the county from available NRCS data is shown in addition to the minimum and maximum readings. Clay, Davison, Hyde, and Todd are some of the counties with readings exceeding very severe sulfate exposure class as per ACI 201 (S3 where sulfate concentration is > 20,000 mg/L) (ACI Guide to Durable Concrete) (Figure 7 and Table 5). Although the average sulfate concentrations are much lower for these counties. More than 50% of the counties shown have an average sulfate concentration between 2,000 mg/L to 20,000 mg/L which indicates the severe exposure class (S2). Some counties have higher sodium concentration whereas others have higher magnesium concentrations. It appears that sodium sulfate is more of a concern for most counties. Regardless many of the counties have both magnesium and sodium cations associated with sulfates. Because magnesium sulfate attack is more severe, it is important also to test these materials for magnesium sulfate exposure.

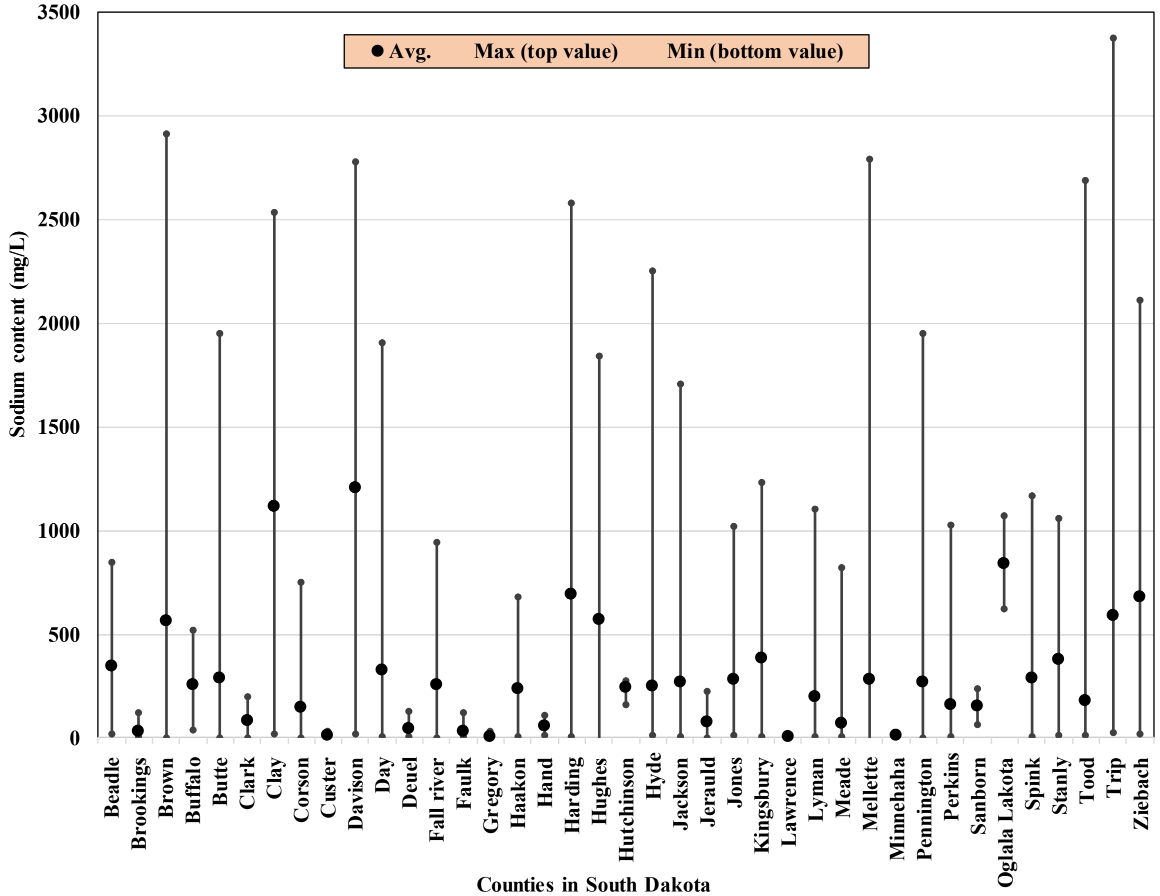


Figure 5: County–wide average Na^+ ion concentration and variation in South Dakota soil (Raw data source: NRCS)

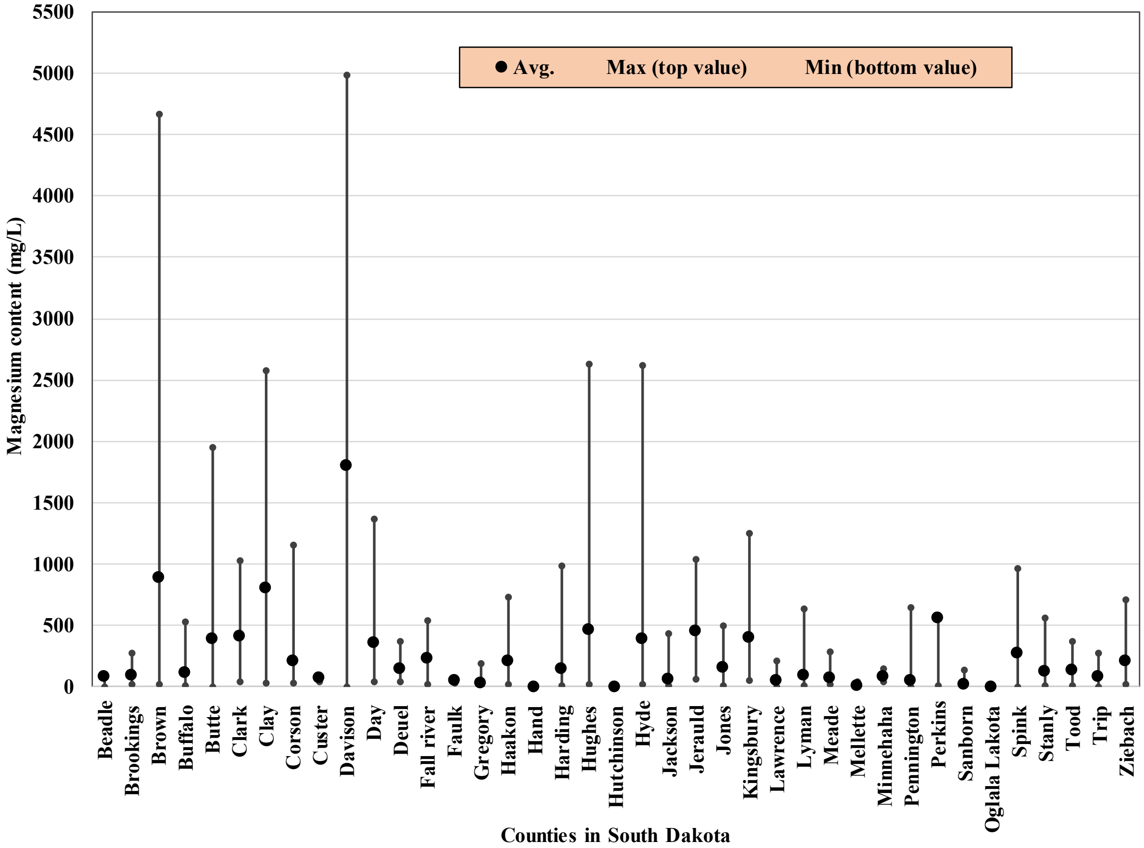


Figure 6: County-wide average Mg^{2+} ion concentration and variation in South Dakota soil (Raw data source: NRCS)

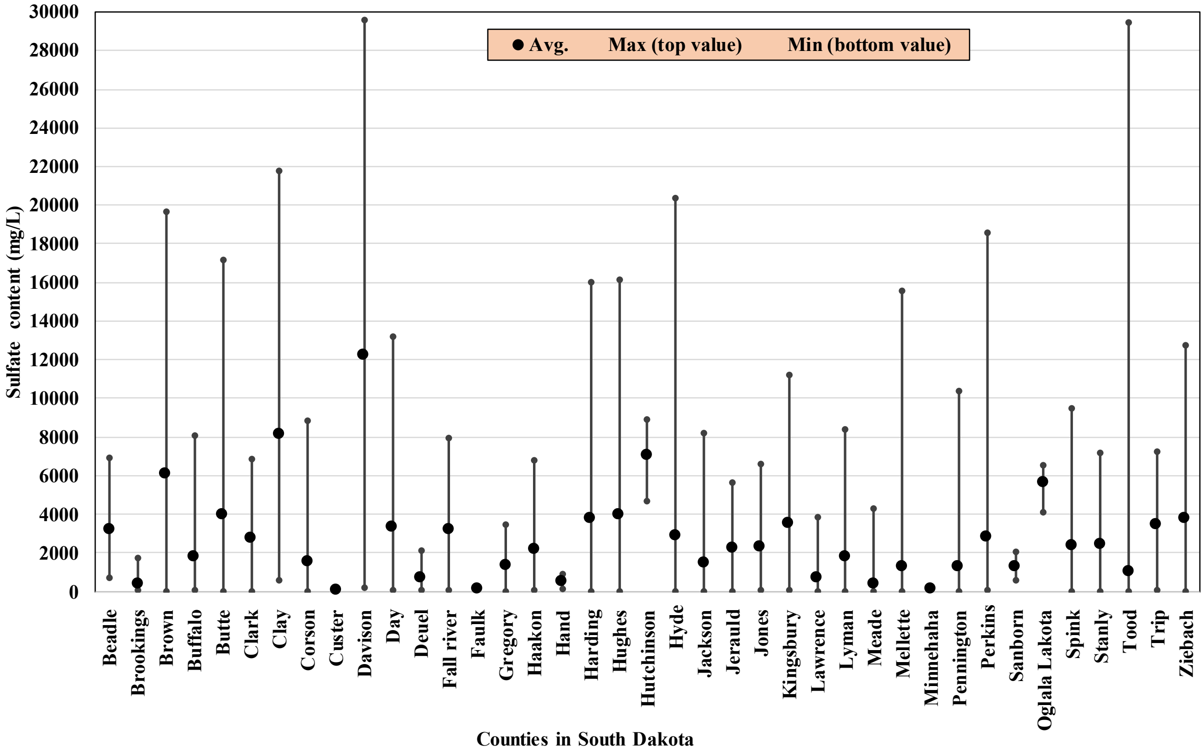


Figure 7: County-wide average SO_4^{2-} ion concentration and variation in South Dakota soil (Raw data source: NRCS). The S3 sulfate limit is 20,000 mg/L.

5.1.7.10 Testing and measurement of conventional sulfate attack

In the US, the resistance of cement-based materials associated with sulfate attack is generally evaluated by ASTM C1012 [54] (expansion of mortar prism). In ASTM C1012, mortar specimens ($25 \times 25 \times 285$ mm) are immersed into 5% (50g/L) sodium sulfate solution at a temperature of $23 \pm 2\,°\mathrm{C}$ without controlling the pH. This test is performed for 12-18 months and expansion is measured at certain intervals (1, 2, 3, 4, 8, 13 weeks and 4, 6, 9, 12, 15, and 18 months) time. This test method has been recommended for blended cements and cement-based materials incorporating SCMs. For concrete in field exposure, the ACI 201.2R has categorized different classes (Table 5 and

Table 6) of sulfate exposure based on the concentration of the external sulfate ($\mathrm{SO_4}$) sources. According to this guide, for any type of portland blended cements, the limit for expansion is set up at 0.10% after 18 months of exposure Class S3 (more than 10,000 ppm) following the procedure ASTM C1012. For reinforced concrete exposed to different sulfate environments (Class S0, S1, S2, and S3), the required maximum w/c ratio for the mixture and minimum compressive strength of concrete materials are also specified by ACI 318 (Table 5 and Table 6).).

Table 5: Requirement to protect against damage to concrete by external sulfate attack

Severity of potential exposure	Water-soluble sulfate (SO_4^{2-}) in soil, % by mass	Water- soluble sulfate (SO_4^{2-}) in soil, ppm	Sulfates (SO_4^{2-}) in water, ppm	w/c by mass, max	Minimum comp. strength, psi
Class S0	$SO_4^{2-} < 0.10$	1000	$SO_4^{2-} < 150$	N/A	2500
Class S1	$0.10 \leq SO_4^{2-} < 0.20$	$1000 \leq SO_4^{2-} < 2{,}000$	$150 \leq SO_4^{2-} < 1{,}500$	0.50	4000
Class S2	$0.20 \leq SO_4^{2-} \leq 2.0$	$2000 \leq SO_4^{2-} \leq 20{,}000$	$1500 \leq SO_4^{2-} \leq 10{,}000$	0.45	4500
Class S3	$SO_4^{2-} > 2.0$	$SO_4^{2-} > 20{,}000$	$SO_4^{2-} > 10{,}000$	0.45	4500

Table 6: Requirement to protect against damage to concrete by external sulfate attack

	Cementitious material	Cementitious material	Cementitious material
Severity of potential exposure	**ASTM C 150**	**ASTM C595**	**ASTMC1157**
Class S0	No type restriction	No type restriction	No type restriction
Class S1	II	Type IP, IS, or IT with (MS) designation	MS
Class S2	V	Type IP, IS, or IT with (HS) designation	HS
Class S3	V plus pozzolan or slag cement	Type IP, IS, or IT with (HS) designation plus pozzolan or slag cement	HS plus pozzolan or slag cement

The current ASTM test method for evaluating the sulfate resistance of cement-based materials has been criticized because it neglects important factors including temperature, humidity, pH level, and the type of sulfate solutions which usually control the field performance of concrete structures [55]. Therefore, modified versions of the sulfate attack test have been reported in the literature for the effect of temperature and humidity variations [56], pH level [57], type of cation and solution concentrations [58]. The US Bureau of Reclamation conducted a long term (20 years) experimental program to investigate the length change of concrete cylinders exposed to 2.1 % sodium sulfate solution [59]. In that study, the cylinder specimens were also placed in a cyclic wetting/drying (accelerated) exposure**.** The test results indicated that one year in the wetting/drying exposure caused similar damaging effects on concrete specimens to eight years in the continuous immersion exposure. This study was later verified by Stark [60] who conducted long-term (16 years) field and laboratory studies, which reported that a wetting/drying exposure is more deleterious to concrete than a regular immersion exposure.

The ASTM C1012 mortar bar test and the proposed accelerated cube testing use a concentration of 33,800 ppm of sulfate for testing. Although this concentration is higher than any seen in the field, it is appropriate due to accelerated nature of the test and the high sulfate concentrations observed in some of the South Dakota counties.

5.1.7.11 Testing and measurement of thaumasite sulfate attack

As discussed earlier, TSA has been reported to occur preferentially at low temperatures (0°C-15°C). Standard methods for the measurement of deterioration due to TSA have not been established. Therefore, to study the resistance of cementitious materials to TSA, studies [27, 61] have adopted a modified version of ASTM C1012 in which temperature was kept constant at 5°C. Canadian Standards Association (CSA) A3000 introduced a standard test method for TSA (CSA A3004 – 08, procedure B) in its 2010 amendment, which is identical to ASTM C1012 (CSA A3004 – 08, procedure A) except that the temperature was changed to 5°C**.** In procedure A, the expansion of mortar bars was limited to 0.1% and 0.05% for moderate and high sulfate-resistant cement, respectively, after a period of 6 months. However, in CSA A3004 – 08 (procedure B), the expansion limit (0.1%) was set at 18 months instead of 6 months and the standard recommended to run the test up to 24 months.

However, a recent study conducted by the Portland Cement Association (PCA) has revealed that the modification of ASTM C1012 to CSA A3004 – 08 (procedure B at 5°C) is not a representative test method for measuring damage due to TSA (Hooton, 2016). This research showed that the low temperature mortar bar test does not reliably predict the performance of concrete made with PC–SCM or PLC–SCM blends. This is likely due to the fact that the pastes are not mature enough when testing begins, which results in excessive damages unrelated to the sulfate attack due to the very cold temperatures. By mitigating conventional sulfate attack using materials fulfilling the traditional expansion limits as specified in ASTM C1012, TSA can be mitigated.

This new study recommends that the standard ASTM C1012 test method be used to test for TSA, not modified to be conducted at 5°C. The modified version (at 5°C) of ASTM C1012 test results indicated that non-sulfate-resistant mixtures are always initially affected by ettringite-based sulfate attack and then thaumasite is only observed after significant damage occurs from conventional sulfate attack. Therefore, measuring conventional sulfate attack should be a strong indicator of the formation of thauamasite sulfate attack, because it is theorized that it will not occur unless ettringite is first formed. The study also recommends that it be used for determining the sulfate resistance of ASTM C595 Type IL and IT cements. ASTM C1012 should also be used to evaluate the sulfate resistance of cement based-materials with SCMs [46].

However, thaumasite does not cause expansion, which is the only form of attack measured by ASTM C1012, so additional testing is also warranted. Most investigations have included a description of visual appearance of specimens. Several techniques including visual rating, photographical records, and proportion of surface or edge of specimens damaged are generally considered for this purpose. At the initial stage of attack, sulfate attack products accumulate in the concrete pores and does not manifest any visible deterioration. The damage starts from the corners and is followed by extensive cracking along the edges and leads to spalling and disintegration on the surface of the specimens. Irassar [45] has shown in Table 7 the visual rating used in research on PLCs.

Table 7: Visual rating used to classify surface deterioration

Rating	Description
0	No visible detorioration
1	Detorioration at corners and edges
2	Cracking along the edges
3	Extensive cracking and expansion
4	Spalling and disintegration of surface

This researcher also developed a graph based on many research studies conducted previously on the cementitious materials with limestone filler exposed to sodium and magnesium sulfate solutions. Some of the important factors such as w/c ratio, percentage of limestone content, and the amount of tricalcium aluminate (C_3A) were considered (Figure 8).

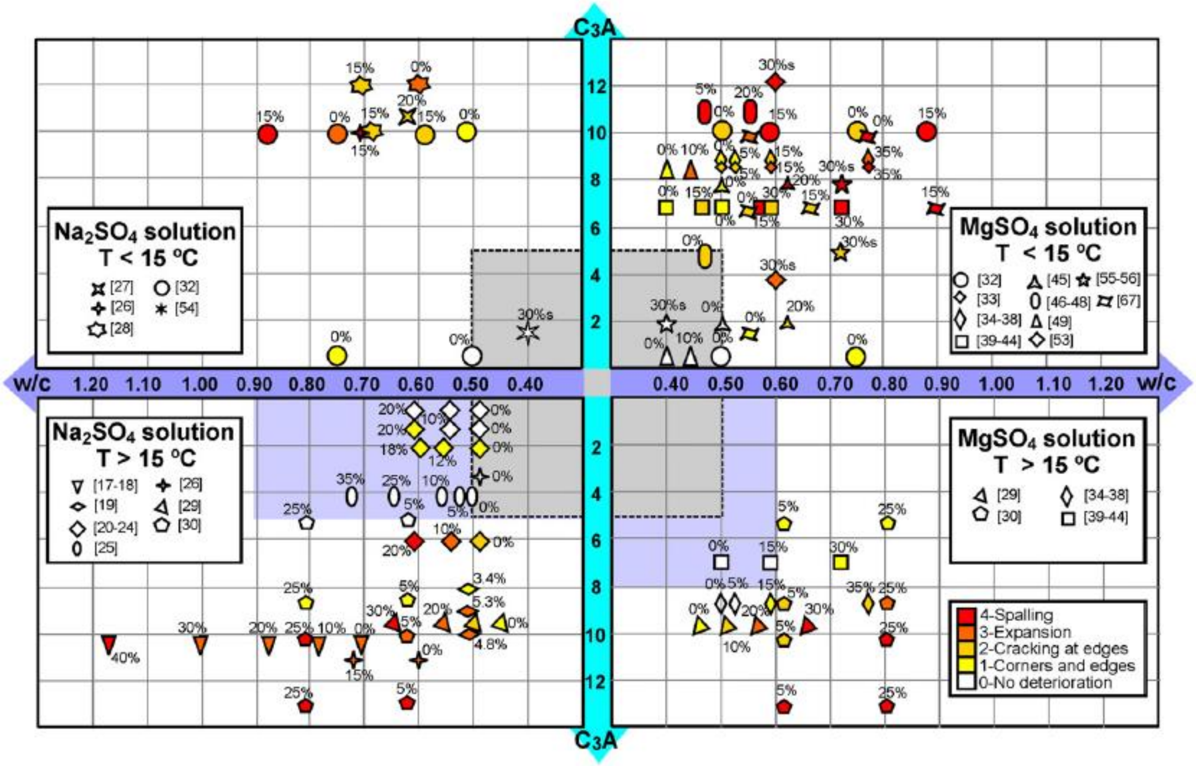


Figure 8: Conceptual plot showing different visual ratings of surface deterioration due to sulfate attack based on the w/c ratio and C3A content. Limestone filler content is shown as % value [45].

Figure 8 shows that surface deterioration is worse for specimens exposed to $MgSO_4$. For testing using $MgSO_4$ solutions at temperatures less than 15 °C, compared to those at temperatures above 15 °C, the specimens made with w/c $<$ 0.50 and moderate sulfate-resistant cement (C_3A <6%) [58, 62-64] showed no deterioration in this environment (see light grey zone in Figure 8). In the case of Na_2SO_4 solution, at temperature $>$15 °C no significant surface deterioration was observed with low C_3A cement even with high limestone filler (LF) contents. The deterioration depended on pH of the environment and C_3S/C_2S ratio which promotes gypsum formation and the decomposition of C-S-H.

TSA investigations also usually include the measurement of sulfate attack crystalline products (e.g., ettringite, gypsum, thaumasite) using X-ray diffraction techniques to determine deterioration. Figure 9 shows the formation of thaumasite at the surface layer as measured by XRD from many studies. A combination of thaumasite, gypsum, ettringite, CH, and brucite have been detected on the surface layer (paste, mortar, and concrete) after external sulfate attack occurred.

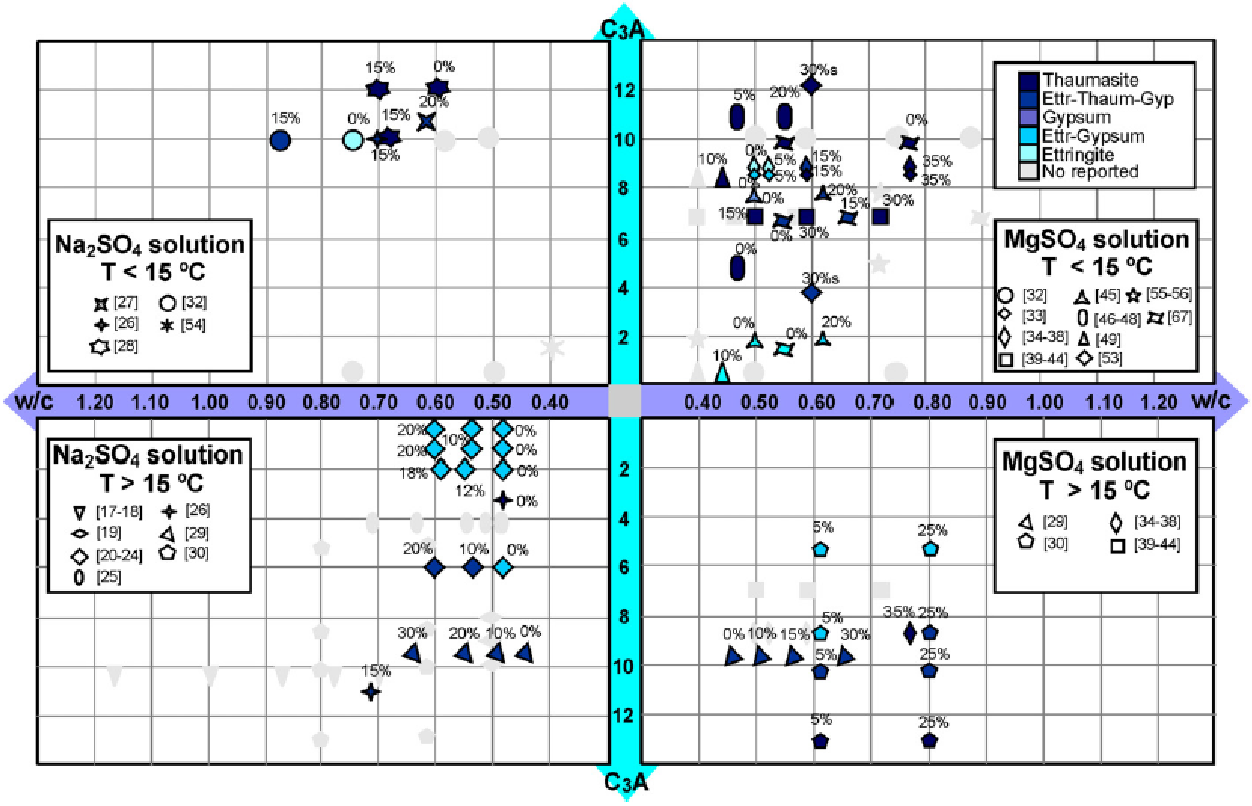


Figure 9: Conceptual plot showing the mineralogical composition of damaged specimens based on w/c ratio and C3A content. Limestone filler content is shown as % value [45].

Thaumasite formation has been observed for all types of specimens with different dimensions exposed to both Na_2SO_4 and $MgSO_4$ solutions [45]. A large amount of thaumasite accompanied by gypsum or/and ettringite is observed when the C_3A content is higher than 6% with a w/c >0.50 at temperautres below 15 °C in $MgSO_4$ exposures. The formation of thaumasite was less likely when the exposures (especially in Na_2SO_4) temperature is > 15 °C (Figure 9).

Finally, the change in compressive strength of specimens is also measured as a complement to the ASTM C1012 test when assessing TSA formation. Kurtis et al. (2001) developed an accelerated test for sulfate resistance of portland cements by assessing compressive strength. In this test method, paste (0.5 × 0.5 × 0.5 inch) cubes are immersed in 4% Na_2SO_4 solution and controlled pH is controlled at 7.2 to better simulate field conditions (whereas the CH leaching in the ASTM C1012 test tends to increase pH in the solution). A modified version of this test set at a temperature of 5°C will be used for this research.

5.1.7.12 Factors affecting TSA

Thaumasite only forms in portland cement concrete if certain conditions are satisfied. The formation of TSA mainly depends on factors including the presence of sulfate, the presence of carbonate, the amount of tricalcium aluminate in the cement, moisture content, temperature, and the pH of the sulfate exposure conditions. These factors are described in more detail as follows:

Source of SO_4^{2-} ions

Sulfate ions either provided inside the concrete or ingressed from the exterior must be present for thaumasite formation to occur. The internal sources are mainly from sulfates provided by the cement and aggregates. Additionally, there is a possibility of sulfate generation from the sulfide oxidation of aggregates (i.e., iron sulfide – pyrite – which can be oxidized to form a sulfate pore solution in the presence of oxygen and moisture) [26]. Most common sulfates in the field that may result in TSA are associated with sodium, magnesium, potassium, and calcium in soils or groundwater. Among them, magnesium sulfate has shown to produce the most damaging effects on the hardened cement paste made with PLCs especially compared to sodium sulfate [28]. In magnesium sulfate solutions, thaumasite, gypsum, and brucite are formed according to the following equation:

$$C_3S_2H_3 + 3CH + 2C\overline{C} + 4M\overline{S} + 32H \rightarrow 2C_3S\overline{S}\overline{C}H_{15} + 2C\overline{S}H_2 + 4MH$$

Thaumasite and brucite (MH) are often removed in the mush spalling away from the surface of cementitious materials leaving behind gypsum and ettringite in the sound parts of cement-based materials [65].

Source of carbonates

Availability of carbonate ions is an integral part of TSA [30]. If carbonates are available in the cementitious matrix with sufficient moisture and a prevailing low temperature, thaumasite can easily form and further lead to TSA. Several studies on TSA reveal that cement, aggregates, groundwater, atmospheric CO_2, and admixtures are the primary sources of carbonate ions. In a case study, mortar specimens were made with cement containing either 20% limestone or 20% quartz as filler material and investigated in the same experimental exposure. The test results revealed a large amount of thaumasite in limestone cement and only a negligible amount of ettringite in quartz cement [66]. The test results hinted limestone as a probable source of carbonate ions which were deemed to be responsible for TSA. Carbonate aggregates have been found to cause TSA compared to siliceous aggregate, which performed satisfactorily [67]. De-dolomitization (a partial/complete transformation of dolomite to calcite on the scale of individual crystals) of dolomitic aggregate may also contain carbonates [68]. Some external sources that generally accelerate TSA could be CO_2 in the air and CO_3^{2-} in groundwater, surface water, or seawater. The atmospheric CO_2 may supply necessary carbonates through the formation of bicarbonate ions, and thus TSA can take place in the system without the addition of limestone filler or aggregate [69].

Alumina content in cement

The sulfate resistance of cement–based materials usually decreases as the C_3A content is increased. This compound can react with external SO_4^{2-} to form ettringite (AF$_t$ phase). Furthermore, monosulfoaluminates (AF$_m$ phases) in hardened cement paste formed from C_3A can also react with sulfates to result in sulfate attack. Similarly, AF$_t$ and AF$_m$ phases may also result due to the hydration of the C_4AF compound, where aluminum is exchanged for iron [70]. C_4AF reacts more slowly in sulfate exposures, however, the mechanism for sulfate attack is anticipated to be the same as for the C_3A phase [71]. According to Hobbs [22] , TSA requires advance formation of classical sulfate attack products (ettringite, gypsum, and depletion of CH) along with the availability of calcium carbonate to occur. When limestone is present in binder materials, hydrated compounds of alumina are affected in two ways: (1) the dilution effect that controls the C_3A content in PLC; and (2) the effect between $CaCO_3$ and C_3A phases due to chemical interplay.

Depending on the SO_3/C_3A and $CaCO_3/C_3A$ ratios, carbonate ions originating from limestone filler can adjust C_3A hydration products. The monocarboaluminate are thermodynamically more stable than monosulfoaluminates and thus the conversion of monosulfoaluminates to monocarboaluminate can take place at an early age [72].

Matthews [58] reported that the sulfate resistance of PLCs (5 and 25% LF) presents a clear dependency on C_3A content. Nobst and Stark [74] reported that the rate of thaumasite formation is proportional to their C_3A and Al_2O_3 contents. Even small Al_2O_3 contents can increase the probability of thaumasite formation, such as in SRPC (sulfate-resistant portland cement). Some researchers observed thaumasite in mortar specimens at low temperature (5 ° C) made with cement without C_3A [75] whereas no thaumasite was detected in the same experiment at 20 ° C [76]. This indicates that the effect of C_3A on TF depends on temperature. However, no obvious relationship was observed between TF and the C_3A content with a C_3A content ranging from 1-8 % [77]. A recent study by Felekeglu revealed that the susceptibility of cement–based materials made by PLCs to TSA depends on C_3A content of the cement [78]. In this study, PLC mortar specimens with different limestone content (5, 10; 20; and 40%) and C_3A (4.59% and 11.25%) content exposed to sodium and magnesium sulfate solution were studied at two different temperatures (20 ° C and 5 ° C). Higher C_3A content accelerates the deterioration rate of mortar specimens exposed to both sodium and magnesium sulfate solutions. Even at low temperature (5 °C), the PLC with lower (4.29%) C_3A and limestone content (less than 20%) performed significantly better than other blends, which was also confirmed by the microstructural investigations. The effect of different dosages of C_3A (8-9% as moderate and 11-12% as high) content on the severity of sulfate attack in PC and PLCs with SCMs was investigated by other researchers [79], where the test results reported much better sulfate resistance of the specimens made by moderate C_3A (8-9 % C_3A*)* containing PLC.

Temperature

The favorable temperature for thaumasite formation ranges from 5-15 ° C. The rate of thaumasite formation is governed by the exposure temperature and usually increases with decreased temperature. This is due to insolubility of thaumasite, the stability of $Si(OH)_6$ groups, solubility of CO_2, and extent of portlandite solubility at these temperatures [23]. However, thaumasite can also form at higher temperatures because it can be stable at 20-25 °C. Thaumasite collected at low temperature from a historic structure found to be stable when stored at 40 °C and started to disintegrate at a low relative humidity (around 35%) and higher temperatures 60 ° C [80]. Thaumasite was also found in some historic buildings at a higher temperature (>20 ° C) in South Italy [25]. Additionally, in laboratory experiments, TSA was identified under cyclic temperatures (20 °C and 40 °C) with a range of relative humidity (35-100%) [24]. Diamond [81] examined TF in a field study (Orange County, Southern California) with a mean exposure temperature around 20 ° C for a decade which concluded that thaumasite can form outside of the optimal formation temperatures and stable at higher temperatures, but the relative humidity also impacts its stability.

Moisture

W/c ratio is one of the fundamental mixture design parameters of cement–based materials which controls its resistance (characteristic of pore structure) to the ingression of moisture and aggressive sulfate ions. All components (sulfate and carbonate ions, calcium silicate or calcium silicate hydrate) that are necessary to form thaumasite require that water is present at the reaction site or they are transported by water. Water transport in cement-based materials relies upon capillary porosity and its connectivity. These components are closely related to w/c and the development of cement hydration. To improve the resistance of cementitious materials against any type of sulfate attack (including TSA), low w/c (typically less than 0.45) is recommended to lower the ingress and movements of attacking ions and moisture, which ultimately accelerates chemical reactions with the hardened cement paste [26]. Low w/c helps to produce concrete with less porosity, and a finer and disconnected pore structure which reduces its susceptibility to TSA.

pH value

The effect of pH has a significant impact in the aggressiveness of the sulfate attack [64]. Classical sulfate attack is more aggressive at low pH because it can decalcify the concrete (and the C-S-H) which is very deleterious. Zhou et al. [40] studied the role of pH regarding TSA in OPC, PLC, and SRPC both in acidic and alkaline media which reported that the acidic media does not promote thaumasite formation. Additionally, it revealed that the combination of higher sulfate concentration and alkalinity can escalate the kinetics of TSA on cement–based materials. Based on laboratory and field experiments some other researchers concluded that thaumasite does not from in cementitious materials at pH levels below 10.5 [29] and can be disintegrated and transformed into popcorn calcite if the pH level falls below 10.5 [36]. The reactivity of some ions (phosphate, carbonate, and bicarbonate) during thaumasite formation decreased with increased pH levels [82]. Results from these studies indicate that the process of thaumasite formation and subsequent TSA might not be favorable in acidic sulfate exposure (lower pH level < 7.0), where the deterioration process in such environment is more likely to be gypsum formation.

5.1.7.13 Prevention of sulfate attack

Although there is no fail-proof guideline that can help to mitigate the sulfate deterioration of cement-based materials, there are some good rules of thumb which can be followed to prevent classical and thaumasite sulfate attack. It is difficult to prevent, in part due to the potential wide variations in material properties and exposure conditions (sulfate concentration, temperature, and humidity). For concrete in aggressive environments some key factors including type of cement, w/c, and SCMs control the resistance of cement-based materials to chemical sulfate attack (including TSA). Using low cement contents with low alumina contents, SCMs, low w/c, and dense (well-compacted) concrete in addition to proper curing will all help prevent the formation of sulfate attack (BRE, 2005).

Water content

The w/c ratio is the leading parameter in concrete mixture design which controls the penetration of moisture and deleterious ions into the concrete matrix. To improve the durability of concrete against sulfate attack, a low w/c ratio is recommended in ACI 201.2R. A lower w/c minimizes the internal transport of ions including Ca^{2+}, CO_3^{2-}, SO_4^{2-}, and water [83]. It has been shown that low w/c produces concrete with less porosity, which reduces sulfate deposition and consequently reduces the susceptibility of the concrete to TSA. Bruckner et al. [84] investigated concrete with two different types of cement having variable w/c, and reported a higher rate of thaumasite deterioration (mm/year) with increased w/c.

Cement and aggregate content

To mitigate sulfate detorioration, the European Standard (EN 206 -1) imposes limitations on maximum cement content (300-360 kg/m^3). The maximum cement content is prescribed to enhance the physical resistance (lower permeability) of concrete susceptible to sulfate attack and reduce the volume of paste available for conversion to sulfate attack products. Carbonated aggregate should also be avoided if possible to prevent thaumasite formation.

C_3A content

It is generally believed that there is a correlation between alumina content and sulfate attack. The reduction of aluminate content in cement-based materials might be an effective way to mitigate ettringite formation and eventually TSA. To improve the sulfate resistance lower C_3A cement is available in the market. ASTM C 150 Type II cement (moderate sulfate resistance) with less than 8%C_3A, and Type V cement (high sulfate resistance) having C_3A below 5% are typically recommended for sulfate ions bearing exposures. However, in some cases, it has been reported that the use of sulfate-resistant cement (Type V) having less than 5% C_3A may not control damage due to sulfate attack likely because it does not prevent the formation of gypsum.

Use of SCMs

The use of SCMs including ground granular blast furnace slag (GGBS), fly ash, and silica fume has been proven to mitigate TSA in concrete [85]. The amount of SCMs required to control the expansion due to external sulfate attack depends on the composition of the both the portland cement and SCMs, as well as the exposure conditions [45].

Higgins [86] reported that 70% replacement of cement with GGBS showed no evidence of TSA in any solution including magnesium sulfate solutions (1.8%, 0.42%, and 0.14% as SO_4) and sodium sulfate solutions (1.8 % as SO_4). Another study on OPCs and PLCs using different dosages of slags (15; 30; 50, and 70%) as a filler at normal and low temperatures reported that the OPCs and PLCs with 30% or 50% slag was effective in making the mixes highly sulfate resistance at both 5 °C and 23 °C [87]. Yet, only 50% slag was found to be highly sulfate-resistant at 5 °C. This result led to the revision of the slag content to be 40% in the CSA A3001 standard where TSA is a concern. Terneray blends of slag and silica fume have shown to provide better resistance to external sulfate attack in PLCs mortars compared to slag alone [79].

The pozzolanic activity of fly ash binds calcium hydroxide released in the hydration process of portland cement, thus it reduces the availability of calcium hydroxide which can react with external sulfate compounds. The use fly ash also helps to reduce the amount of tricalcium aluminate. Mulenga (2003) examined TF in concrete and mortar prepared with a combination of PLC and a fly ash (4.0% of CaO) where 40% fly ash replacement has reported moderate sulfate resistance and no thaumasite was observed at a fly ash replacement level of 50%. Another study conducted by the United States Bureau of Reclamation (USBR) showed that properly proportioned concrete using up to 35% of class F fly ash will resist sulfate deterioration far better than conventional portland cement [88]. The test results indicated a descending order of sulfate resistance: (a) Type V plus fly ash – most resistant to sulfate attack; (b) Type II plus fly ash; (c) Type V; (d) Type II; (e) Type I plus fly ash; and (f) Type I – least resistant.

The effect of fly ash on sulfate damage depends on the class (Class C and Class F), amounts, and the individual physical and chemical characteristics of fly ash and cement. A recent study on sulfate resistance of PC and PLC with different SCMs (class F fly ash, slag, silica fume, and metakaolin) showed that PLC (22% limestone filler) with 20% class F fly ash (CaO < 8%) and 5% silica fume outperformed the other mixes [79] however, excessive levels of fly ash is not beneficial to the prevention of TSA [33]. For binary blended PLC, CSA A3000 specified the use of 25% Class F fly ash by mass of the binder. Generally, ASTM C 618-15 fly ash with CaO less than 15% is believed to improve the sulfate resistance of cement-based materials.

The utility of silica fume to improve the resistance of cementitious materials in severe sulfate environments has been investigated for many years. The replacement of cement with silica fume reduces the amount of lime (CaO) and C_3A which eventually can minimize the amount of ettringite and gypsum formed in the hardened concrete. Moreover, the higher level of C-S-H formed and the fine particle size of silica fume decrease the permeability of the concrete and thus the sulfate diffusion into the cement paste is reduced. The effect of varying sodium sulfate concentration (2700 mg/L, 18000 mg/L, and 72000 mg/L) on the sulfate resistance of portland cement mortars with and without silica fume (10% replacement of cement by mass) has been examined by some researchers [89]. This study revealed a significant sulfate resistance even at a high solution concentration (72000 mg/L) when blended with 10% silica fume. Lee (2005) [90] studied the sulfate attack and strength loss of portland cement mortars exposed to 5% sodium and magnesium sulfate solutions with different levels of silica fume replacement and found 5-10 % addition of silica fume replacement worked best. Others investigated the effect of silica fume (2-15% by mass) replaced portland cement mortars exposed to magnesium sulfate solution and reported better sulfate resistance at a level of 8% replacement.

5.2 Experimental program

5.2.1 Materials

In this study, the sulfate resistance of portland limestone cements (PLCs) in pastes and mortars placed in sodium sulfate and magnesium sulfate solutions were used for expansion testing and pastes were used for strength, visual rating, and mass loss. The results of PLCs mortar and pastes were compared to the performance of Type I/II and Type V cement [91]. The Type I/II portland cement contains 4.4% calcitic limestone (by mass) interground with the clinker during the manufacturing process while the Type V cement does not contain any added limestone. PLCs were lab-produced by adding powdered limestone rock to these cements. Both calcitic limestone (the same rock used in Type I/II cement) and dolomitic limestone rock were used. Class F fly ash was also added as an SCM in this research. In this study, standard graded sand [92] was used making mortar specimens for all mixes. The chemical composition and physical characteristics of cement and filler materials are presented in Table 8.

Table 8: Chemical composition and physical data for the cements and fly ash

	Type I/II	Type V	Class F fly ash
Chemical composition (wt. %)			
SiO_2, %	19.8	21.8	52.2
Al_2O_3, %	4.7	4.4	15.9
Fe_2O_3, %	3.1	3.9	5.7
CaO, %	64.8	64.7	13.0
MgO, %	1.1	1.2	4.4
SO_3, %	3.1	2.2	0.6
Na_2O, %	0.12	0.13	2.5
K_2O, %	0.64	0.67	2.4
CO_2, %	1.8	1.3	-
LOI, %	2.7	1.2	0.1
Mineralogical compound (wt. %)			
C_3S, %	64.2	59.5	-
C_2S, %	10.9	20	-
C_3A, %	4.3	4.0	-
C_4AF, %	12.1	13.3	-
Equivalent alkalis, %	0.54	0.57	1.5
Physical characteristics			
Blaine fineness (m^2/kg)	429	408	-
Residue 45 µm sieve (%)	3.9	4.7	21.0
Specific gravity	3.13	3.15	2.53

5.2.2 *Preparation of limestone powder*

To manufacture the limestone powder, calcitic and dolomitic limestone rocks were kept in water for 24 hours and then washed to remove any residue. The rocks were then dried in an oven at 23°C for 24 hours to remove the moisture. A Denver 2HP in laboratory scale Jaw Crusher and pulverizer were used to break the limestone rock into small pieces. The pulverized limestone was then placed into a ball mill system. Using a wet grinding process, 300 g of pulverized limestone and 1 liter of water was used with a complete set of steel balls (approximately 8 kg) and ground for 20 minutes with a speed of 100 rpm. This wet mixture was then oven dried at 35°C for 8 hours. In a dry grinding process, 100 g of limestone was ground using the same equipment for 15 minutes at 150 rpm. Afterward, the limestone powder was sieved using a #325 sieve (45 µm) and analyzed by Sympatec Mytos system with dry-dispersion and laser diffraction measurement. The particle size distributions of the limestone powders are shown in Figure 10. The mineralogical composition of the limestone powders as measured by QXRD is presented in Table 9.

Table 9: Mineralogical composition of limestone powder

Limestone type	Weight %							
	Quartz (%)	Pyrite (%)	Illite (%)	Kaolinite (%)	Albite (%)	Dolomite (%)	Calcite (%)	Fineness (m^2/kg)
Calcitic	1.7	0.01	0.3	1.2	0.0	0.4	96.4	778
Dolomitic	8.0	0.26	0.6	0.4	0.7	81.0	9.0	657

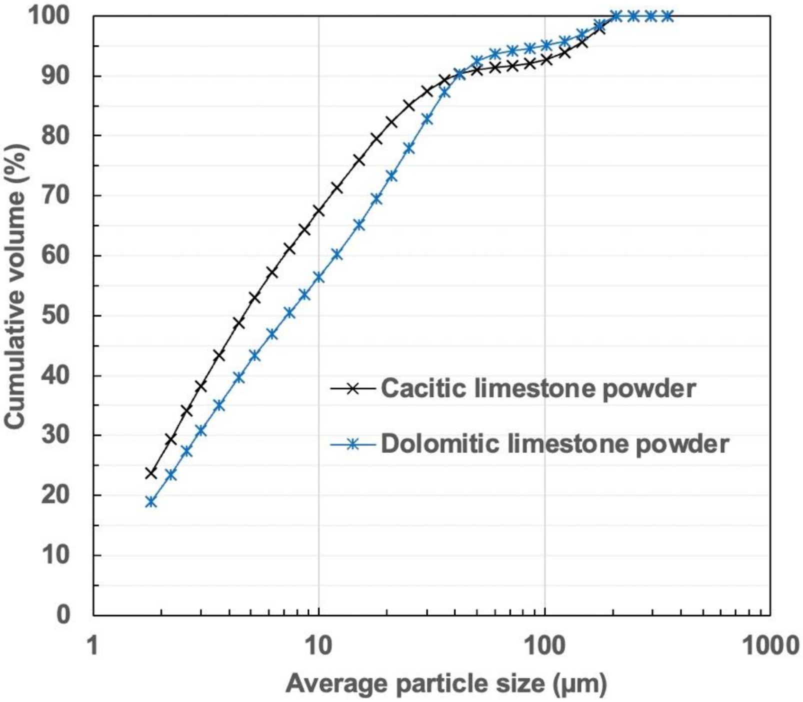


Figure 10 : Particle size distribution of limestone powder

5.2.3 Mixture designs

The details of the mixture design for the PLC mortars and pastes is shown in Table 10 and Table 11, respectively. The Type I/II cement itself contains 4.4% calcitic limestone powder. The cement was replaced by 5.6%; 10.2%; and 15.6% calcitic limestone powder to make 10%, 14.6%, and 20% PLCs, respectively. There is some level of potential error with the exact quantity of limestone in each mixture due to the manufacturing method. To evaluate the effect of adding fly ash, 20% (by mass) Class F fly ash was used to replace the 14.6% PLCs. Similarly, high sulfate-resistant Type V cement was replaced by 14.6% limestone powder (combinations of calcite and dolomite) and 20% (by mass) Class F fly ash.

Based on QXRD test results, the percentage of $CaCO_3$ in Type I/II cement, calcitic limestone powder, and dolomitic limestone powder was found to be 91%, 96.4%, and 9.0%, respectively. According to the standard specification for blended hydraulic cements, the limestone used to manufacture PLCs shall have a $CaCO_3$ content of at least 70% by mass [93]. To meet this requirement in some blended mixes the percentage of calcitic and dolomitic powder have been adjusted when added to the Type I/II and Type V cements. The percentage of dolomitic limestone powder to reach at least 70% of $CaCO_3$ content was calculated for the mixtures M-I-10.5C-4.1D and M-V-10.5C-4.1D (refer to Table 10 and Table 11). A sample calculation can be found in Appendix B.

The mixture designs are denoted using the generic placeholders "X-Y-##Z-F", where the designator "X" represents mortar (M) or paste (P), "Y" designates the base cement type (Type I/II or Type V), "XX" represents the percentage of limestone in the cement, "Z" indicates the type of limestone (i.e., calcitic, C, or dolomitic, D), and F indicates the use of 20% fly ash. Additionally, Na and Mg represent submersion of the specimens in either sodium or magnesium sulfate solutions.

Table 10: Mix design for mortar bars expansion test exposed to sulfate solution at 23°C

Designation	Mixture proportion by mass	Mixture proportion by mass	Mixture proportion by mass	Mixture proportion by mass	Mixture proportion by mass	Sulfate solution types
	% control cement	% calcitic powder	% dolomitic Powder	% fly ash	w/c	
M-I-4.4C	95.6	4.4	-	-	0.485	Na, Mg
M-I-10C	90	10	-	-	0.485	Na, Mg
M-I-14.6C	85.4	14.6	-	-	0.485	Na, Mg
M-I-10.5C-4.1D	85.4	10.5	4.1	-	0.485	Na, Mg
M-I-20C	80	20	-	-	0.485	Na, Mg
M-I-14.6C-20	65.4	14.6	-	20	0.485	Na, Mg
M-I-10.5C-4.1D-20	65.4	10.5	4.1	20	0.485	Na
M-V-0C	100	-	-	-	0.485	Na, Mg
M-V-14.6C	85.4	14.6	-	-	0.485	Na, Mg
M-V-10.5C-4.1D	85.4	10.5	4.1	-	0.485	Na
M-V-14.6D	85.4	-	14.6	-	0.485	Na
M-V-14.6C-20	65.4	14.6	-	20	0.485	Na

The details of mixture designs for the paste specimens is presented in Table 11. The pH of the solution was controlled for some of the mixtures, which is denoted by a “(pH)”: next to Na (refer to Table 11).

Table 11: Mix design for paste cubes exposed to sulfate solution at 23°C and 5°C

Designation	Mixture proportion by mass	Mixture proportion by mass	Mixture proportion by mass	Mixture proportion by mass	Mixture proportion by mass	Sulfate solution types
	% control cement	% calcitic powder	% dolomitic powder	% F Fly ash	w/c	
P-I-4.4C	95.6	4.4	-	-	0.485	Na(pH), Mg
P-I-10C	90	10	-	-	0.485	Na, Mg
P-I-14.6C	85.4	14.6	-	-	0.485	Na(pH), Mg
P-I-10.5C-4.1D	85.4	10.5	4.1	-	0.485	Na(pH), Mg
P-I-20C	80	20	-	-	0.485	Na, Mg
P-I-14.6C-20	65.4	14.6	-	20	0.485	Na(pH), Mg
P-I-10.5C-4.1D-20	65.4	10.5	4.1	20	0.485	Na(pH)
P-V-0C	100	-	-	-	0.485	Na(pH), Mg
P-V-14.6C	85.4	14.6	-	-	0.485	Na(pH), Mg
P-V-10.5C-4.1D	85.4	10.5	4.1	-	0.485	Na
P-V-14.6D	85.4	-	14.6	-	0.485	Na
P-V-14.6C-20	65.4	14.6	-	20	0.485	Na(pH)

5.2.4 Mixture designs for interground PLC cements

14.6% interground PLC was supplied by the GCC cement plant for sulfate attack testing (20% by mass). In addition to this, Type IL (10.78) cement from Holcim was evaluated and compared to the results with the PLC supplied by GCC. Class F fly ash was used to replace these PLCs to evaluate the effect of SCMs on sulfate attack. The chemical composition and physical characteristics of cement and filler materials are presented in Table 12.

Table 12: Chemical composition and physical data for the cements and fly ash

	GCC IL (14.6%)	**Holcim IL (10.78%)**
Chemical composition (wt. %)		
SiO_2, %	17.5	18.9
Al_2O_3, %	4.3	3.4
Fe_2O_3, %	3.0	4.1
CaO, %	63.6	61.6
MgO, %	1.1	4.0
SO_3, %	3.0	2.5
Na_2O, %	0.10	0.49
K_2O, %	0.48	-
CO_2, %	6.1	-
LOI, %	7.5	0.5
Mineralogical compound (wt. %)		
C_3S, %	57	49
C_2S, %	6	17
C_3A, %	6	2
C_4AF, %	9	12
Equivalent alkalis, %	0.42	0.57
Physical characteristics		
Blaine fineness (m^2/kg)	639	494
Residue 45 µm sieve (%)	99.1	99.6
Specific gravity	3.08	3.15

The mixture designs are denoted using the generic placeholders "X-IL-Y-##-F-S-I/C", where the designator "X" represents mortar (M) or paste (P), "Y" designates the brand of Type IL (PLC) cement, G represents cement from GCC and H represents cement from Holcim, "##" represents the percentage of limestone in the cement, "S" represents 1% SO_3, "I" and "C" indicate interground and combined limestone to cement clinker, respectively, and F indicates the use of 20% fly ash. Additionally, Na and Mg represents submersion of the specimens in either sodium or magnesium sulfate solutions.

The mixture design of mortar bar and paste samples are presented in Table 13 and Table 14, respectively.

Table 13: Mix design for mortar bars expansion test exposed to sulfate solution at 23°C

Designation	**% control cement**	**% SO_3**	**% fly ash**	**w/c**	**Sulfate solution types**
M-IL-G-14.6-I	100	-	-	0.485	Na, Mg
M-IL-G-14.6-S-I	99	1	-	0.485	Na, Mg
M-IL-G-14.6-20-I	80	-	20	0.485	Na, Mg
M-IL-G-14.6-20-S-I	79	1	20	0.485	Na, Mg
M-IL-H-10.78-I	100	-	-	0.485	Na, Mg
M-IL-H-10.78-20-I	80	-	20	0.485	Na, Mg

Table 14: Mix design for paste cubes exposed to sulfate solution at 23°C and 5°C

Designation	**% control cement**	**% SO_3**	**% fly ash**	**w/c**	**Sulfate solution types**
P-IL-G-14.6-I	100	-	-	0.485	Na, Mg
P-IL-G-14.6-S-I	99	1	-	0.485	Na, Mg
P-IL-G-14.6-20-I	80	-	20	0.485	Na, Mg
P-IL-G-14.6-20-S-I	79	1	20	0.485	Na, Mg

The mixing, casting, and measurements for mix designs are the same as previously described.

5.2.5 Mixing, casting, and measurement procedures for mortars and pastes

5.2.5.1 Mortar bar expansion measurement

The procedure outlined in ASTM C1012 [54] was followed to investigate the expansion of mortar specimens exposed to external sulfate. Following this standard, each mixture was proportioned as one part cement and 2.75 parts standard graded sand, and a water-to-cementitious materials ratio of 0.485. Before preparing the mortar mixtures, the filler materials and control cements were mixed properly as per the mixture designs presented. The limestone powders, fly ash, and original cement was weighed as per the mixture design and mixed in an ASTM compliant mixer (Hobart H – 3844) for 5 minutes. The mortar mixtures were prepared according to ASTM C305 [94] and ASTM C109 [95]. Each mix consisted of 9 -2 inch × 2 inch × 2 inch mortar cubes and 6 -1 inch × 1 inch × 11.25 inch mortar bars. A thin coat of release agent (form oil) was applied to the interior surfaces of the standard cube and prism molds. Once the mortar was prepared it was cast into the metal cube and prisms molds. Hand tamping of the mortar was performed according to ASTM C109 with a 0.5 inch × 0.8 inch × 6 inch non-absorbent oak wood. Immediately after placement, the molds were covered by a plastic plate and placed over a riser in a closed container filled to 0.5 inches below the bottom of the molds with preheated water (35°C). Afterward, the container was covered by a lid and stored in an oven at 35°C for 24 hours.

After 24 hours of initial curing, all bars and cubes, except two cubes, were demolded and submerged in saturated $Ca(OH)_2$ water at 23°C. The 24-hour compressive strength of the two cubes was tested, and subsequently, the compressive strength measurements were monitored daily until the average strength of mortar cubes reached 2850 psi. Once the mortar cubes in a batch gained the specified strength, the initial length of the mortar bars was measured with a digital length comparator according to ASTM C490 [96]. Next, 6 mortars bars were submerged in sodium or magnesium sulfate solution with a SO_4^{2-} concentration of 33800 mg/L and stored at 23°C. 50 g and 43.36 g of anhydrous sodium and magnesium sulfate respectively were diluted in deionized water to prepare the sulfate solutions. See Appendix B for sulfate concentration calculations.

750 ml of sulfate solution for each mortar bar was used and the initial pH of the sulfate solution fell in a range of 6.0 to 8.0 as specified in the standard. Afterward, the length of the mortar bars was measured at 1, 2, 3, 4, 8, 13, and 15 weeks after immersion in the sulfate solution. The length of mortar bars was measured every month after 15 weeks. The sulfate solution was refreshed after 4, 8, and 13 weeks, and then 6 and 9 months. No attempt was taken to alter the pH of the sulfate solutions during the experiment.

5.2.5.2 Strength measurement, mass loss, and visual rating of pastes

Although the ASTM C1012 standard measures the expansion of mortar samples related to the ettringite form of sulfate attack, there is no standard procedure to measure the gypsum (or thaumasite) formation ($CaSO_4 \cdot 2H_2O$) during sulfate attack. Gypsum formation can take place due to the reaction between calcium hydroxide and external sulfate ions. The accelerated test methods adopted by some researchers use the loss in strength as an indication of sulfate resistance [12, 98].

In this study, a modification of the accelerated test method developed by Kurtis et al. has been followed to evaluate sulfate deterioration which measures the compressive strength reduction of paste specimens [98]. In this experiment, the compressive strength change over time of 0.5 inch × 0.5 inch × 0.5 inch paste specimens were tested. Steel molds were fabricated to cast the specimens. A standard mixing procedure (ASTM C305) for paste was followed for making the paste samples using a w/c = 0.485 (same as for ASTM C1012) for all mixtures referred to Table 11. After molding, the specimens were covered to avoid shrinkage and kept at 23°C for 24 hours. After demolding, the paste cubes were submerged in water and kept in an oven at 50°C for 6 more days to accelerate their maturity. For each mixture, 100 cubes were made (specimens with imperfections were rejected).

Once the initial curing was finished, dimensions of the cubes were measured using a slide caliper. The size of the cubes generally varied from 0.50 inch to 0.52 inch. Afterward, the 7-day compressive strength of 12 cubes for each mixture was determined. This strength is referred to the initial strength of the paste specimens. The loading rate for the compressive strength test was 10 lb/sec.

Because of the small sample size, there was a considerable variability in strength results. A statistical approach outlined in ASTM C109 was followed to identify the outliers. In this method, the average strength was calculated from 12 cubes tested at each age and the standard deviation was computed thereafter using the following equation.

$$SD_b = \sqrt{\left(\frac{\sum (X - X_b)^2}{N_b - 1}\right)}$$

Where,

SD_b = standard deviation of a single batch
X_b = average of test values in single batch
N_b = number of cubes per batch

Then, maximum normal deviation (MND) was calculated using the Excel function "=norminv (1-0.25/N_b, 0, SD_b)"

The normal range used to find the outliers was as follows:

Maximum = (X_b + MND)
Minimum = (X_b – MND)
Outlier = any test value falling outside the calculated normal range.

In each testing age, 20 cubes were selected for mass loss measurements and visual appearance ratings, and 12 cubes were selected for strength testing. The mass of paste specimens was measured at every testing period for all mixtures placed in sodium and magnesium sulfate at both temperatures. The initial mass (7 days after elevated curing) was measured after placing the paste cubes into the sulfate solutions for 24 hours. Soft facial tissue paper was used to soak out the water from the surfaces of the cubes before weighing. All specimens were placed in a large bin of sodium and magnesium sulfate solutions placed at 23°C and 5±1°C.

Sulfate attack in select mixtures (refer to the mixtures presented in Table 11) was measured in sulfate solution with a constant pH to better simulate field conditions. For these samples, the pH of the sodium sulfate solution was maintained at 7.2 using a pH meter and a dosing pump (Milwaukee MC720). The dosing pump added aliquots of 0.1N H_2SO_4 from a flask (placed outside of the refrigerator) until the pH of the sulfate solution reached 7.2. The concentration of sodium and magnesium sulfate solution was kept constant at 33800 ppm. The initial mass of the paste cubes was determined after 24 hours of immersion in sulfate solutions. For this test, the excess water on the surface of samples was removed using paper towels and then the samples were weighed. The mass loss, visual inspection, and compressive strength were measured at 14, 28, 56, 91, and 120 days after the immersion of samples in sulfate environments.

5.2.5.3 X-ray diffraction testing on pastes

The paste specimens tested for strength at 28 days and 120 days placed in sodium and magnesium sulfate solutions at 23°C and 5°C were saved to perform a microstructural investigation using X-Ray diffraction (XRD). As sulfate attack is more severe at low temperatures, XRD was performed only on the specimens placed at 5°C. The broken cubes were ground into powder using a mortar and pestle and then sieved through a #200 sieve. The hydration was stopped using isopropanol alcohol and all samples were stored in a sealed bottle until testing to avoid carbonation.

5.2.5.4 Mixture designs and test methods for complementary concrete testing

Additional fresh and hardened concrete properties were measured using selected cement blends with and without fly ash. The mixture designs were provided by SDDOT. Fine and course aggregates from local sources were used. The properties of materials used is shown in Table 15 and the mixture designs of different concrete are presented in Table 16, Table 17, Table 18, and Table 19.

These tests include:

- Setting time (ASTM C191)
- Slump (ASTM C143)
- Compressive strength (ASTM C39, ASTM C109)
- Flexural strength (ASTM C78)
- Isothermal Calorimetry (ASTM C1679) to measure the early age hydration kinetics

Given information by SDDOT:

Table 15: Properties of materials used in concrete testing

Materials	Specific gravity	FM	Absorption (%)
Cement	3.15	-	-
Fly ash	2.5	-	-
Fine aggregate	2.62	2.8	1.1
Coarse aggregate	2.68	-	0.4

Table 16: Mix design for complementary concrete testing

Air content	6.5%
Maxium aggregate size (in)	0.75
Slump (in)	1 to 2
w/c	0.42
Mixing water requirement (lb/yd^3)	280
Weight of cementitous materials (lb/yd^3)	666.67

Table 17: Mix design for compressive strength, slump, electrical resistivity, and flexural strength testing (w/c = 0.42)

Mix Name	Cement (lb/yd$^{3)}$	Fine agg. (lb/yd$^{3)}$	Coarse agg. (lb/yd$^{3)}$	Fly ash (lb/yd$^{3)}$	Water (lb/yd$^{3)}$	Air content (%)
Type I/II (4.4% LF)	667	1720	1160	-	280	6.5
Type I/II (4.4% LF)	534	1720	1160	133	280	6.5
Type IL (14.6% LF)	667	1720	1160	-	280	6.5
Type IL (14.6% LF)	534	1720	1160	133	280	6.5

Table 18: Mix design of paste for setting time (w/c = 0.42)

Mix No	Cement type	Cement (g)	Fly ash (g)	Water (g)
1	4.4 % PLC (Type I/II)	650	-	273
2	4.4 % PLC (Type I/II)	520	130	273
3	14.6 % PLC(interground)	650	-	273
4	14.6 % PLC (interground)	520	130	273

Table 19: Mix design of paste for isothermal calorimetry (w/c = 0.42)

Mix No	Cement type	Cement (g)	Fly ash (g)	Water (g)
1	4.4 % PLC (Type I/II)	100	-	42
2	4.4 % PLC (Type I/II)	80	20	42
3	14.6 % PLC(interground)	100	-	42
4	14.6 % PLC (interground)	80	20	42

5.3 Results and Discussion

5.3.1 Expansion of mortar bars

5.3.1.1 Influence of limestone percentage

The expansion results of the prismatic mortar specimens incorporating an increasing percentage of calcitic limestone (4.4% – 20%) powder submerged in sodium sulfate and magnesium sulfate solutions are presented in Figure 11 and Figure 12, respectively. The interground PLC results are shown in a later section.

All mixtures experienced a similar trend of expansion at early ages in both sulfate solutions. Previous research has shown that mortar bars in this test expand slowly at the beginning and can have significantly increased expansion after 28 days of sulfate exposure [99]. After 91 days in solution, all mortar bars showed a gradual expansion trend. The expansion trend observed in magnesium sulfate up to 91 days of exposure was similar to sodium sulfate for all mixtures although lower in magnitude. Afterward, the mortar samples submersed in sodium sulfate expanded more rapidly than those in magnesium sulfate up to 7 months.

In general, the percent expansion increased with an increasing dosage of limestone filler over the exposure time. In sodium sulfate, the percent expansion of PLCs (using Type I/II cement as a base) was proportional to the ratio of the calcitic limestone replacement up to 4 months of exposure and continued thereafter except for the M-I-20C mixture. This is in agreement with the results conducted on PLCs in other studies [100, 101]. In contrast, the expansion results of Type I/II replaced PLCs in magnesium sulfate were less affected by an increase in limestone content. Similar results on PLC mortars in magnesium sulfate are reported elsewhere [69, 102]. Interestingly, in both sulfate solutions, the M-I-14.6C and M-I-20C mixtures followed a close expansion pattern after 120 days. This might be due to the filler effect of limestone powder which reduces the C_3A content of the cement, and thus any negative affects due to a higher limestone content are negated by the lower C_3A content [103-105]. All mixtures placed in sodium sulfate were completely disintegrated after 210 days except the control cement (M-I-4.4C). On the other hand, none of the PLC mixtures were disintegrated when placed in magnesium sulfate during the same exposure period.

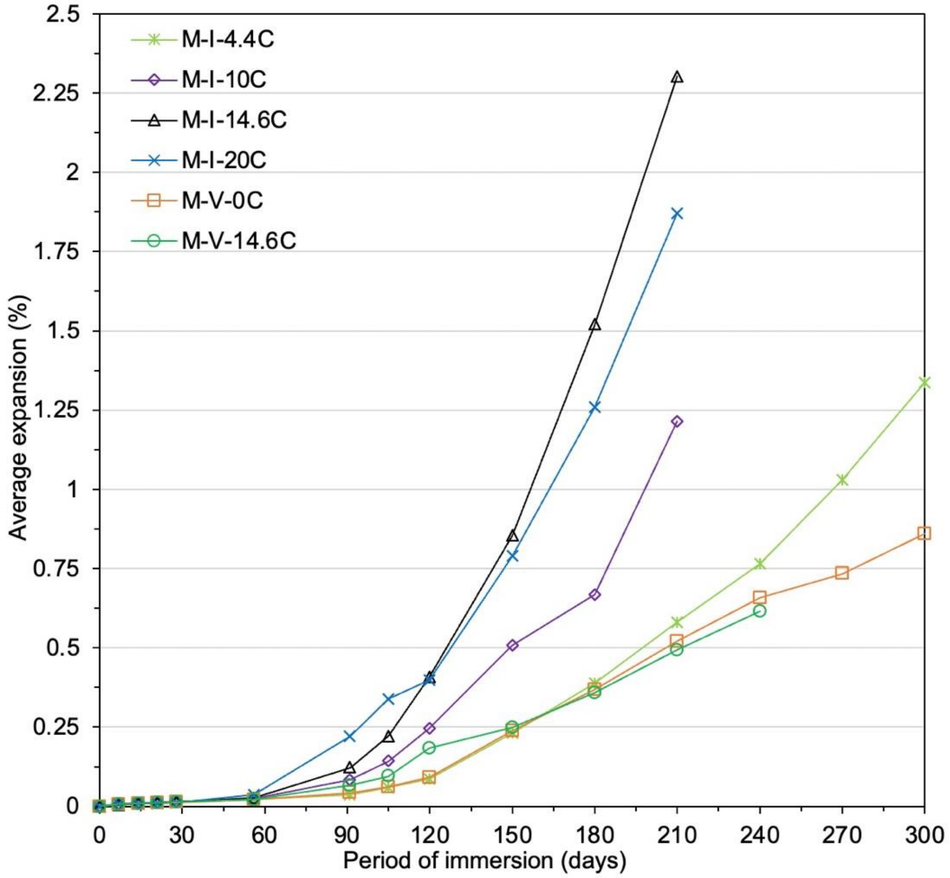


Figure 11: Expansion of different dosages of PLC mortars placed in 5% sodium sulfate solution

In sodium sulfate, the control cement (M-I-4.4C) performed better than other similar blends while in magnesium sulfate the M-I-10C mixture performed best among Type I/II replaced PLCs. Still, the M-I-4.4C mixture in sodium sulfate exceeded the ASTM C595 12-month expansion limit at 120 days (Figure 11) while the M-I-10C mixture in magnesium sulfate exceeded this limit roughly at 170 days (Figure 4) [106]. The other Type I/II replaced PLC mixtures in sodium sulfate exceeded this expansion limit roughly between 65 to 95 days whereas in magnesium sulfate this occurred between 105 to 120 days.

It is evident from Figure 11 and Figure 12 that the percent expansion of M-V-0C mortar samples in both sulfate solutions was approximately the same until 8 months. In magnesium sulfate, the M-V-0C mortar showed a sudden rise in expansion with 0.05% at 28 days of exposure followed by a constant expansion until 3 months. Then, a gradual expansion was noticed until 8 months followed by an accelerated expansion after 9 months of exposure. This can be attributed either to the instability of the brucite layer or due to the expansive forces exerted by the ettringite resulting from the decomposition of the C-S-H matrix.

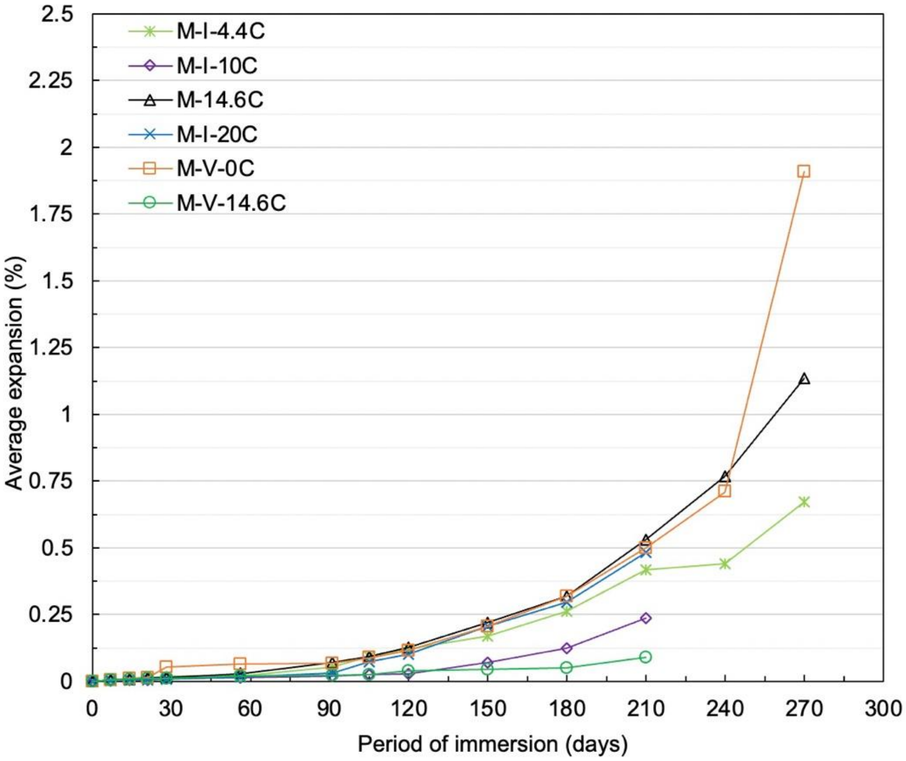


Figure 12: Expansion of different dosages of PLC mortars placed in 4.23% magnesium sulfate solution

The incorporation of 14.6% calcitic limestone to the original Type V cement (M-V-14.6C) substantially improved the expansion over the exposure time. The M-V-14.6C passed the ASTM C595 6-months expansion limit, however, it showed an expansion of 0.09% at 7 months (Figure 4) which is close to exceeding the ASTM C595 12-month expansion limit (0.1%). The expansion of M-V-14.6C was similar to the sample with no limestone at the same immersion time when placed in sodium sulfate solution (Figure 11), which is in contrast with the behavior exhibited when adding limestone to the Type I/II cement. It is well known that the most important factor in the sulfate resistance of portland cement is the C_3A content [26, 107]. ASTM C150 [91] restricts the C_3A percentage to <5% for Type V cement to control the ettringite expansion when used in aggressive sulfate environments. In this study, the lower C_3A (4.0%) and higher fineness (778 m^2/kg) of calcitic limestone powder could have contributed to its lower expansion with the added limestone. However, since both Type I/II and Type V cements have similar C_3A content, there is likely another reason. Perhaps its higher C_2S content or lower SO_3 content also contributed to its lower expansion with added limestone especially in magnesium sulfate solution.

Overall, the Type V cement (M-V-0) showed less expansion in sodium sulfate than Type I/II cement (M-I-4.4) (Figure 11). The M-V-0C performed worst in magnesium sulfate during the entire exposure period (Figure 12), however, the addition of 14.6% calcitic limestone improved the sulfate resistance of this mixture, which outperformed all other mixtures.

5.3.1.2 Influence of limestone type and composition

The mortar bar expansion results of different 14.6% PLCs made with both calcitic and dolomitic limestone placed in sodium sulfate and magnesium sulfate with and without fly ash are shown in Figure 13, Figure 14, and Figure 15. Although the M-I-14.6C mixture showed the maximum expansion in both solutions, the addition of dolomitic limestone improved the sulfate resistance of this mixture both in sodium and magnesium sulfate solutions. The approximate percent expansion of the M-I-10.5C-4.1D mixture was 0.42% at 8 months exposure in both solutions (Figure 5 & 6). The Type V mortar bars (M-V-10.5C-4.1D) expanded even less (Figure 15).

When the dolomitic limestone (4.1% by mass) was incorporated into M-I-14.6C to make M-I-10.5C-4.1D, the expansion at 6 months exposure decreased by 84% and 59% in sodium and magnesium sulfate, respectively (Figure 13 and Figure 14). Similar results on mortar bar expansion with dolomitic limestone have also been reported elsewhere [108]. Further, the expansion of M-V-10.5C-4.1D was 54% lower than M-V-14.6C in sodium sulfate at 180 days (Figure 15). The replacement of Type V cement by 14.6% dolomitic limestone powder improved the sulfate resistance even more by 59% at 180 days in sodium sulfate (refer to Figure 11 and Figure 15).

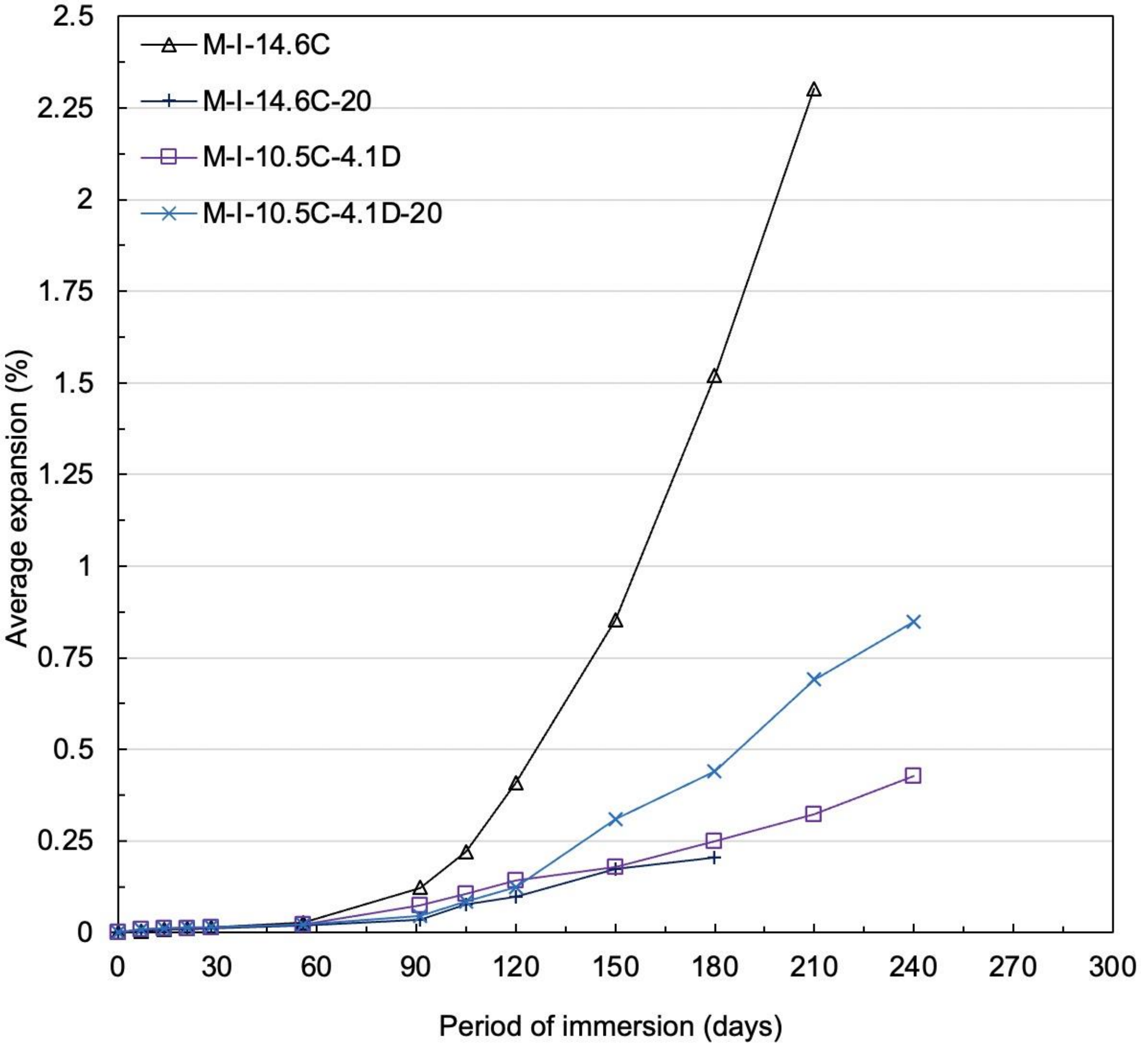


Figure 13: Expansion of different dosages of PLC mortars placed in 5% sodium sulfate solution

Although some consider limestone to be an inert material, investigations have reported reactions between limestone and other components when added as a filler material in portland cement [109, 110]. These reactions are likely influencing the sulfate attack results here. Dolomite contains calcium, magnesium, and two carbonate ions with the formula $CaMg(CO_3)_2$. Compared to calcite ($CaCO_3$), dolomite provides an additional source of magnesium and carbonate. Because of this additional carbonate released from the dolomite, more stable AFm (alumina, ferric oxide, mono-sulfate) phases, like hemicarbonate ($Ca_4Al_2(CO_3)_{0.5}(OH)_{13}\cdot 5.5H_2O$) and monocarbonate ($Ca_4Al_2(CO_3)(OH)_{12}\cdot 5H_2O$) are formed during the reaction between limestone and aluminate in portland cement [72, 111-113]. These AFm phases are more stable than monosulfate ($Ca_4Al_2(SO_4)(OH)_{12}\cdot 6H_2O$) [73]. This phase change does not allow ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$) to transform into monosulfate even when the sulfate sources are consumed (e.g., $CaSO_4 \cdot 2H_2O$).

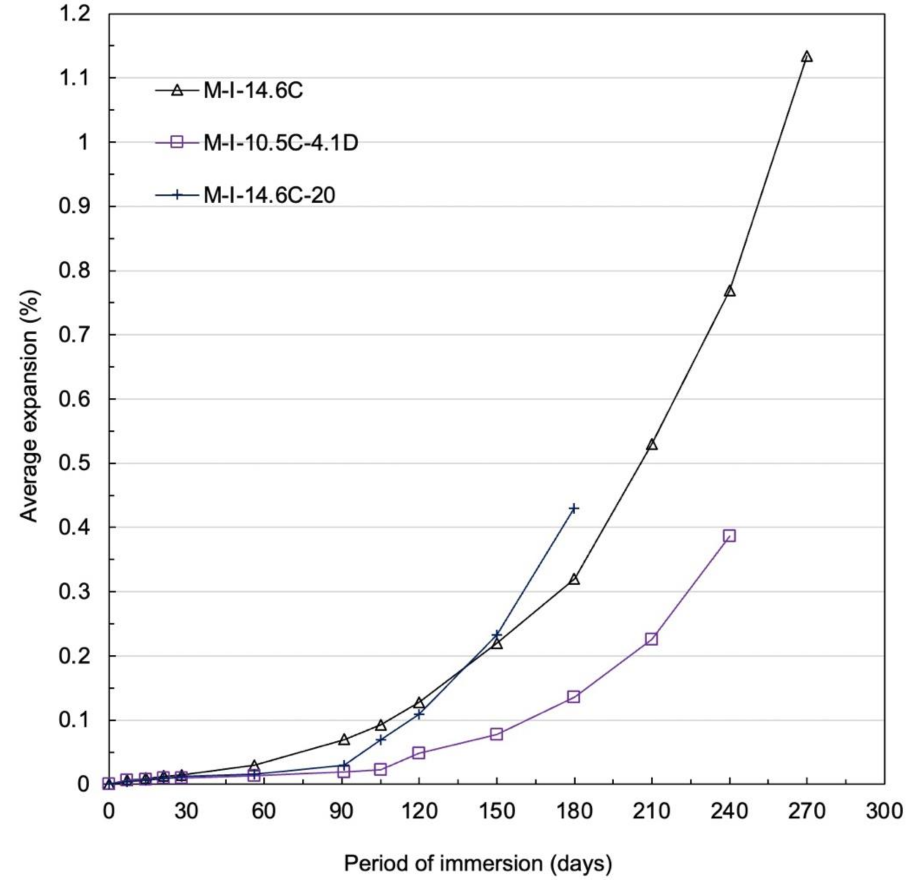


Figure 14: Expansion of different dosages of PLC mortars placed in 4.23% magnesium sulfate solution

This phase alternation phenomenon, called ettringite stabilization, can increase the volume of hydrates and consequently reduce the porosity [109, 110, 114]. This, in addition to less monosulfate available for conversion to ettringite in the matrix, could be a potential reason for the improving sulfate resistance of all mixtures where dolomitic limestone was used to replace calcitic limestone. Another potential reason that could allow dolomitic limestone to improve sulfate resistance could be the chemical interaction that accelerates the hydration of tricalcium silicate when calcium carbonate is added to the cements. This phenomenon was reported in another study [115] but an opposite finding has also been found [116]. It appears the differences in fineness between the two limestones had less effect than the differences in their chemistry. That is because a higher limestone fineness would typically perform better, but the higher calcitic limestone fineness compared to the dolomitic limestone did not result in better sulfate resistance.

Nevertheless, M-V-10.5C-4.1D and M-V-14.6D mixtures still exceeded the ASTM C595 12–month expansion limit between 135 to 145 days in sodium sulfate, but at a later age than the same cement with only calcitic limestone. Similarly, while the M-I-14.6C mixture exceeded this expansion limit roughly at 80 days and 105 days in sodium and magnesium sulfate solution, respectively, the time required for M-I-10.5C-4.1D mixture to cross this limit was 100 days and 165 days for the corresponding sulfate solutions.

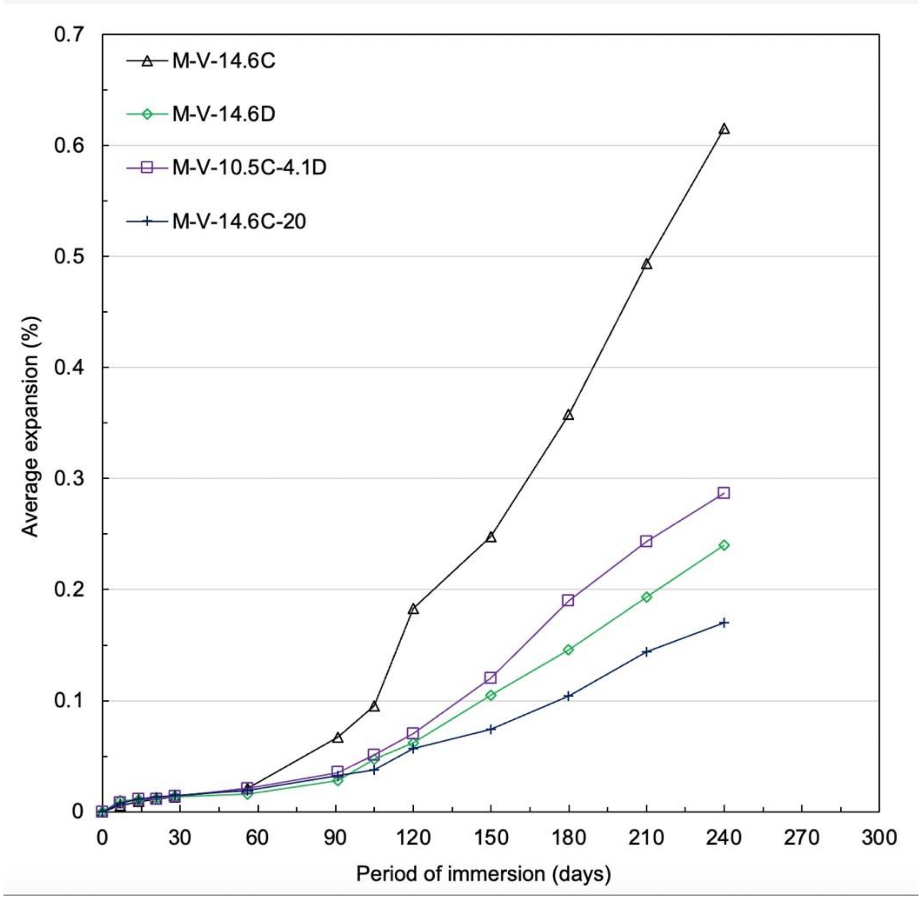


Figure 15: Expansion of different dosages of PLC mortars placed in 5% sodium sulfate solution

5.3.1.3 Influence of fly ash

The effect of fly ash on the sulfate attack expansion of different 14.6% PLCs (calcitic and dolomitic) in both sulfate solutions are presented in Figure 13, Figure 14, and Figure 15. The replacement of M-I-14.6C with 20% fly ash reduced the expansion approximately 645% at 180 days in sodium sulfate (Figure 13). The probable reason for this is the pozzolonic activity of fly ash that reacts with the calcium hydroxide ($Ca(OH)_2$) released in the hydration process of portland cement, thus reducing the availability of $Ca(OH)_2$ which can react with external sulfate compounds. The addition of fly ash also helps to reduce the amount of tricalcium aluminate (C_3A), which mostly influences the expansion of cementitious materials. This effect is similar to other research that has found that adding Class F fly ash (4.0% of CaO) with PLCs results in moderate sulfate resistance with 40% fly ash replacement [74].

Still, both the M-I-14.6C and M-I-14.6C-20 mixtures in sodium sulfate exceeded the ASTM C595 6-months expansion limit roughly at 83 days and 120 days, respectively. Generally, the percentage of CaO is the governing factor for a fly ash's resistance to sulfate attack. PLCs with 20% fly ash (CaO <8%) perform better in sulfate environments compared to fly ashes with higher calcium contents [79] in part due to the higher C_3A contents of high CaO ashes. In this study, the fly ash used contains 13.03% of CaO (which lies closer to the range of Class C fly ash), which could be a potential reason for not vastly improving the sulfate resistance of these PLCs.

Adding dolomite to the mix (M-I-10.5C-4.1D-20) resulted in a better expansion performance up to 90 days with the addition of fly ash, but had higher expansion thereafter, with 76% higher expansion with the fly ash than M-I-10.5C-4.1D at 180 days (Figure 12). The pH of the sodium sulfate solution measured in this study varied in between 12.2-13.5 which is highly alkaline in nature. Studies have shown that dolomite can undergo a dedolomitization reaction in alkaline sulfate environments where dolomite forms brucite and calcite by reacting with portlandite [117-119]. The combined effect of this brucite formation and the high CaO content of the added fly ash may be the reason for the higher expansion of the M-I-10.5C-4.1D-20 mixture.

The fly ash addition increased the expansion of M-I-14.6C mortar specimens when placed in magnesium sulfate (Figure 14). The mortar bars expanded rapidly starting at 90 days and by 6 months had an increased expansion of about 34% compared to the M-I-14.6C mixture at the same exposure time. The expansion of M-I-14.6C-20 at 180 days was even 65% higher than the control cement (M-I-4.4C) in magnesium sulfate (Figure 12 and Figure 14). On the other hand, the expansion of M-I-14.6C-20 reduced expansion by 37% in sodium sulfate at the same immersion time (Figure 11 & Figure 13). To summarize, the addition of calcitic limestone and fly ash increased the expansion of mortar samples in magnesium sulfate and reduced expansion in sodium sulfate for the same mixture (M-I-14.6C-20) at the same exposure time.

For Type V cement, although the percent expansion of M-V-0C and M-V-14.6C was the same (0.36%) at 180 days in sodium sulfate exposure, the addition of fly ash reduced expansion by 71% (Figure 14). Still, both samples exceeded the ASTM C595 12–month expansion limit by 6 months. Moreover, M-V-14.6C-20 showed overall better performance at any given age among all other PLC mortars placed in sodium sulfate exposure. The reason that the M-V-14.6C-20 mixture showed better sulfate resistance could be due to its lower SO_3 (2.2%) content. Similar results were reported on Type V cement replaced by fly ash in other studies [88, 120, 121]. Also, the lower C_3A (4.0%) and higher fineness (778 m^2/kg) of the calcitic limestone powder along with the addition of fly ash could have reduced the expansion of the mortar specimens.

Overall, the addition of fly ash and limestone helped to reduce the expansion of Type V replaced PLCs more than Type I/II replaced PLCs. C_3S releases more $Ca(OH)_2$ than C_2S during the hydration of portland cement. The proportion of C_2S to C_3S in Type V cement is higher than the Type I/II cement which could be a reason for the lower amount of $Ca(OH)_2$ and subsequently reduced expansion of these mortars in sulfate environments.

5.3.2 Mg and Na expansion trend

In this study, the mortar bar expansion results showed a lower expansion trend in magnesium sulfate than in sodium sulfate for the same mixtures at the same exposure period. The calcitic limestone addition helped to reduce the expansion in magnesium sulfate, but it increased the expansion of mortar samples in sodium sulfate at 180 days of the exposure period. Overall, the calcitic limestone replaced PLCs showed reduced expansion in magnesium sulfate compared to sodium sulfate, but the reduction was higher at a higher addition of limestone (see Figure 16).

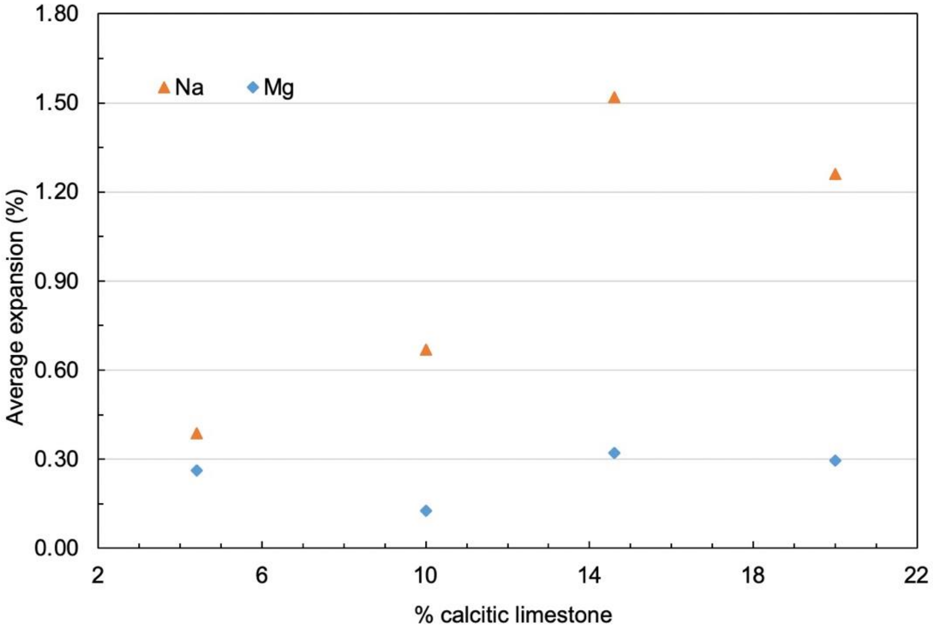


Figure 16: Expansion trend of different PLCs (calcitic limestone) in sulfate solutions at 180 days

Moreover, the overall expansion of all other cements made by replacing M-V-0C and M-I-4.4C cements with calcitic/dolomitic limestone and fly ash was higher in sodium sulfate than magnesium sulfate over the entire study period (refer to Figure 11, Figure 12, Figure 13, Figure 14, and Figure 15). Several studies have revealed the higher expansion of PLC mortars in sodium sulfate compared to magnesium sulfate using the same experimental setup [28, 78, 100, 101].

Another difference observed between Na and Mg expansion data is the rate of expansion over time. The expansion of mortar samples from all of the mixtures placed in sodium sulfate solution occurred in two-stages (Figure 11, Figure 13, and Figure 15). In the initial stage (until 2 months), the expansion was very low but was followed by a sudden increase in expansion due to excessive ettringite and gypsum formation in the final stage and continued in some cases until the mortar bars were completely disintegrated. This two-stage expansion trend for sodium sulfate is also reported in other studies [122-124].

On the other hand, the mortar specimens stored in magnesium sulfate solution followed a steady expansion (Figure 12 and Figure 14). This is due to the formation of a brucite layer at the exposed surface of the specimens. The low solubility of this brucite layer restricts the magnesium ion penetration into the interior matrix of mortar samples. However, the brucite layer consumes a high amount of CH and depletes the pH of the pore solution, which eventually leads to decalcification of C-S-H. In a later stage of sulfate attack, the calcium ion can be completely replaced by magnesium ion, converting the C-S-H to M-S-H, which has been reported to be a non-cohesive phase. This mechanism of sulfate attack in magnesium sulfate solution has also been reported elsewhere [14, 125].

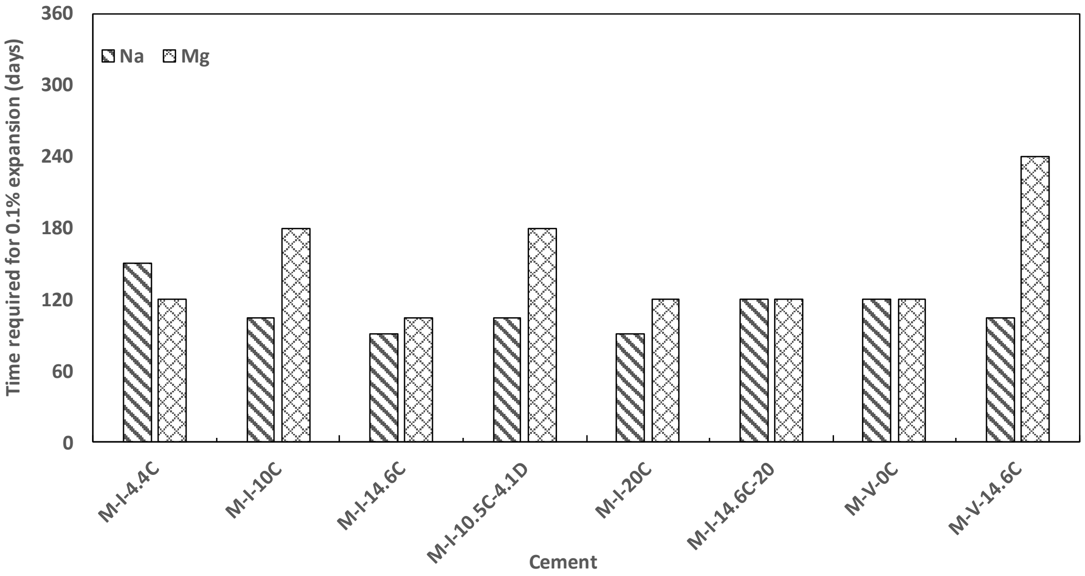
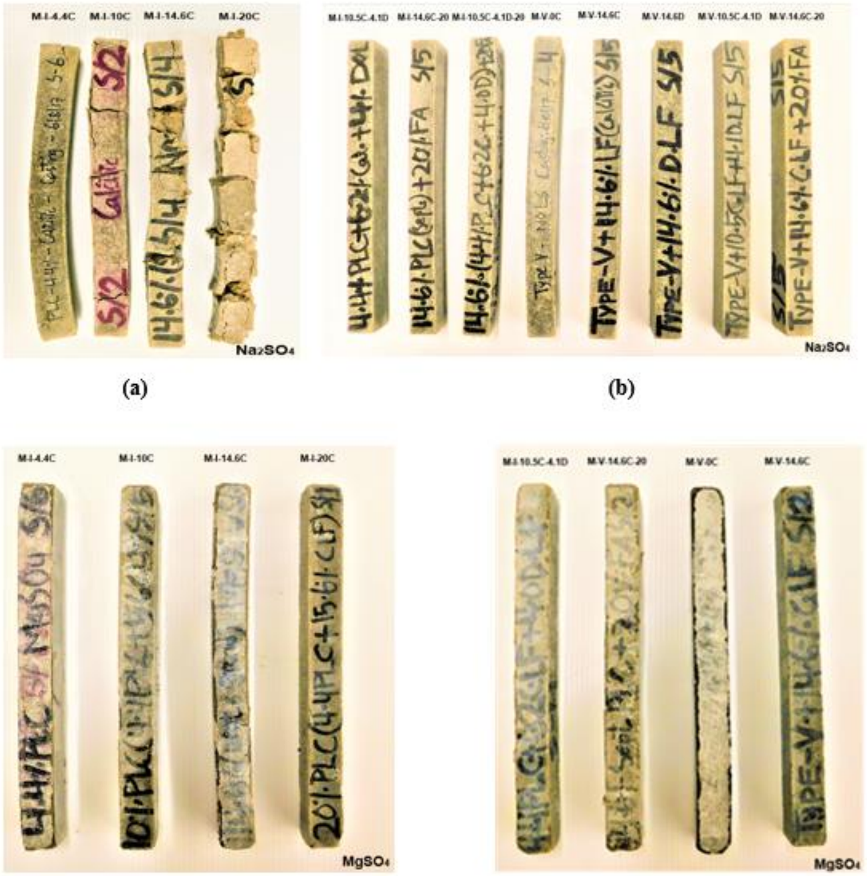


Figure 17: Time required for different PLCs to exceed the average expansion of 0.1% in sulfate solutions

The time required for some of the PLC mixtures (common in both solutions) to exceed the ASTM C595 12-month expansion limit (0.1%) is shown in Figure 17. Eight common mixtures which were tested in both sulfate solutions are presented here. This indicates that all of the mixtures have exceeded the allowable expansion limit well prior to 12 months regardless of the sulfate solution type. The majority of the mixtures exceeded the 12-month expansion limit quicker in sodium sulfate compared to magnesium sulfate.

5.3.3 Visual appearance of mortar specimens

Sulfate ion penetration from external sources can lead to different degrees of deterioration in cement-based materials including changes in porosity, microcracking, expansion, flexural and compressive strength loss, spalling, mass loss and even complete disintegration. It is common for studies to include a description of the visual appearance of specimens to evaluate the sulfate performance of cementitious systems [45, 126]. The photos of mortar specimens (one from each mixture) placed in sodium and magnesium sulfates are shown in Figure 18. At the beginning of observed expansion, the pores are filled with products due to sulfate attack and thus no visible deterioration was detected. Following this, the first sign of attack starts with the deterioration of corners followed by extensive cracking along the edges. Overall, the mortar samples with higher calcitic limestone powder amounts in both solutions showed more damage in both solutions. Mortar bars with 10%; 14.6%, and 20% limestone completely disintegrated after 7 months when placed in sodium sulfate solution (Figure 18-a). The mixtures M-I-10.5C-4.1D, M-I-14.6C-20, and M-I-10.5C-4.1D-20 showed some damage at corners, warping, and cracking along the edges (Figure 18-b). Although M-V-0C mortar bars showed extensive cracking and some spalling at the corners (Figure 18-b), the addition of limestone and fly ash helped to reduce the surface deterioration (Figure 18-b). The mortar bar expansion results of all mixtures placed in sodium sulfate correspond with their surface deterioration (Figure 11, Figure 13, and Figure 15).



(a) (b)

(c) (d)

Figure 18: Images of mortar samples exposed to Na_2SO_4 (a and b) and $MgSO_4$ (c and d) for 7 months

In magnesium sulfate solution, a white powdery coating (probably the brucite layer) was detected, and spalling was observed along the edges in almost all specimens except M-V-14.6C. The calcitic limestone replaced PLCs showed noticeable damage at the corners along with spalling along the edges and some extensive cracking in mortars made from M-I-4.4C and M-I-10C (Figure 18-c). The addition of fly ash increased the surface degradation of M-I-14.C-20 (Figure 10-d) but the addition of dolomitic limestone reduced surface damage (Figure 18-d). However, the addition of fly ash in M-I-14.6C-20 mixture showed less surface damage and expansion in sodium sulfate probably due to the absence of the weak brucite layer. In magnesium sulfate, the worst level of degradation including spalling, cracking, and expansion was observed in M-V-0C mortar whereas M-V-14.6C showed some minor damage at the corners (Figure 18-d). The damaging phases in magnesium sulfate also were correlated with the expansion results.

5.3.4 Change in compressive strength of paste specimens

5.3.4.1 Influence of limestone percentage

The results of the compressive strength testing of paste specimens incorporating different percentages of calcitic limestone powder exposed to sodium and magnesium sulfate solutions at 23°C and 5°C are presented in Figure 19 (a-d). Additionally, the percent reduction at each exposure age in compressive strength of these paste specimens compared to 7-day strength is shown in Figure 20. The compressive strength values at 7 days (before submersion in the sulfate solutions) were slightly higher in general for mixtures placed in sodium sulfate compared to those placed in magnesium sulfate. This can be attributed to the variability of casting conditions, as cubes for sodium and magnesium sulfate were prepared at different times. In this study, trends are analyzed instead of absolute strength values to account for this variability.

Over the 120 day exposure period the samples undergo one of three primary strength change trends: (1) decrease, increase, decrease, (2) increase, decrease, or (3) increase, decrease, increase (less common). These strength increases can be potentially explained by two phenomenon: (1) the continued hydration of unhydrated cement particles (mostly C_3S and C_2S) which produced more hydration products, primarily C-S-H, leading to higher compressive strength and (2) gypsum and ettringite formation due to the reaction between sulfate ions and hydrated cement components [127]. These phenomena may have improved sulfate resistance of these mixtures by making a denser microstructure through filling the void spaces with the hydration products prior to any subsuquent damage.

The reduction of strength is caused by continued sulfate attack, which increases cracking, opening up the microstructure and allowing more sulfate ingress, eventually resulting in greater loss of strength at later ages. These subsequent reactions between sulfate ions and calcium hydroxide lead to higher amounts of ettringite formation, which exerts pressure in capillary pores resulting in significant deterioration and strength loss [128].

It appears that the limestone addition to the cement did not affect strength loss in the same manner it affected expansion for sodium sulfate exposure. That is, higher limestone percentages did not significantly increase strength loss as would have been predicted by their much higher expansion. In 5°C at 120 days, the P-I-10C, P-I-14.6C, and P-I-20 mixtures exhibited a slightly greater loss of strength compared to the 4.4% limestone filler cement, however, the strength loss difference was relatively small.[2] This is in accordance with other studies that have shown higher compressive strength reduction with increased limestone replacement in cold sulfate solutions [100, 129]. This effect is less pronounced in the magnesium solution, where the 20% limestone actually showed less expansion at 120-day exposure time compared to the lower limestone cement.

At 23°C, the higher limestone cements (14.6% and 20% in sodium and 20% in magnesium) had lower loss of strength by 120 days compared to the lower limestone cements. This is an opposite trend to that observed in expansion data in sodium sulfate solution. All PLC mixtures produced from Type I/II cement showed higher loss of strength at later ages at 5°C and 23°C compared to the P-V-0C and P-V-14.6C mixtures, which showed a significant strength increase at 120 days in both sulfate solutions at 23°C (Figure 19-a and c). This can be attributed to the lower C_3S and C_3A contents in the control Type V cement which can improve the sulfate resistance compared to the Type I/II blended PLCs [49, 101, 130, 131]. Although C_3A does not participate in the gypsum formation reaction. This improvement in strength can also be explained as a combined result of better particle packing [132], higher cement hydratiion rate [130] and production of calcium carboaluminate [133]. Type V mixes performed worse at 5°C compared to 23°C in both sulfate solutions throughout the exposure period yet still better than Type I/II mixes.

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[2] The strength values of these samples (and others analyzed in this study) are within one standard deviation of each other at certain ages. This is in part due to the high variability of the compressive strength results observed with the testing of these small samples. Therefore, small differences in strength loss may not be statistically significant with some of these samples.

Figure 19 and Figure 20 clearly reveal that the compressive strength reduction was higher at 5°C than 23°C at later ages in both solutions, but especially in magnesium sulfate. At 5°C, the maximum strength loss in all Type I/II replaced PLCs was recorded at 120 days of magnesium sulfate exposure (Figure 20-d). Generally, the kinetics and solubilities of expansive products formed during sulfate attack depend on temperature. At higher temperatures, the solubility of gypsum [134] and ettringite [135] increase as elevated temperatures make the pore solution supersaturated, which results in more precipitation of these expansive products. However, this study showed opposite results in terms of higher strength reduction at low temperatures. The principal cause of the higher strength reduction at low temperatures is due to the dissolved calcium and carbonate ions [107, 136]. The additional dissolved calcium in the pore solution results in more ettringite and gypsum formation, and the dissolved carbonates are a source for more thaumasite formation [136].

The cation type of sulfate solution affects the compressive strength and expansion results in a different manner. While the increase in the expansion was higher for specimens exposed to sodium sulfate solution, compressive strength decreased more in magnesium sulfate solution exposure. This was supported by another study [137]. Overall, the compressive strength results in this study showed a clear dependency on the solution cation type, temperature, and cement properties.

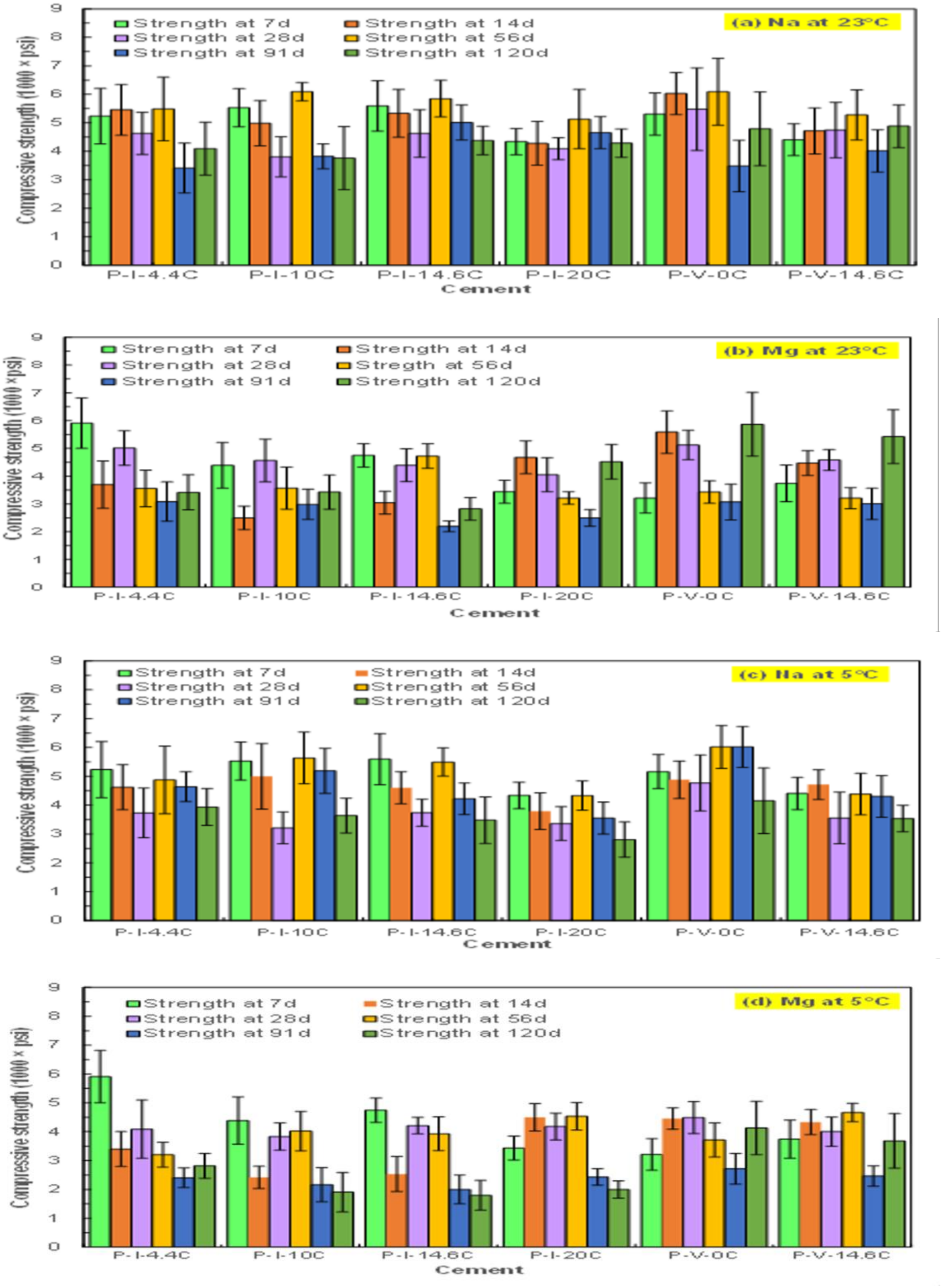

Figure 19: Compressive strength of paste cubes (calcitic limestone only) placed in sulfate solutions (a) Na at 23°C, b) Mg at 23°C, (c) Na at 5°C, and (d) Mg (bars show 1 standard deviation) at 5°C

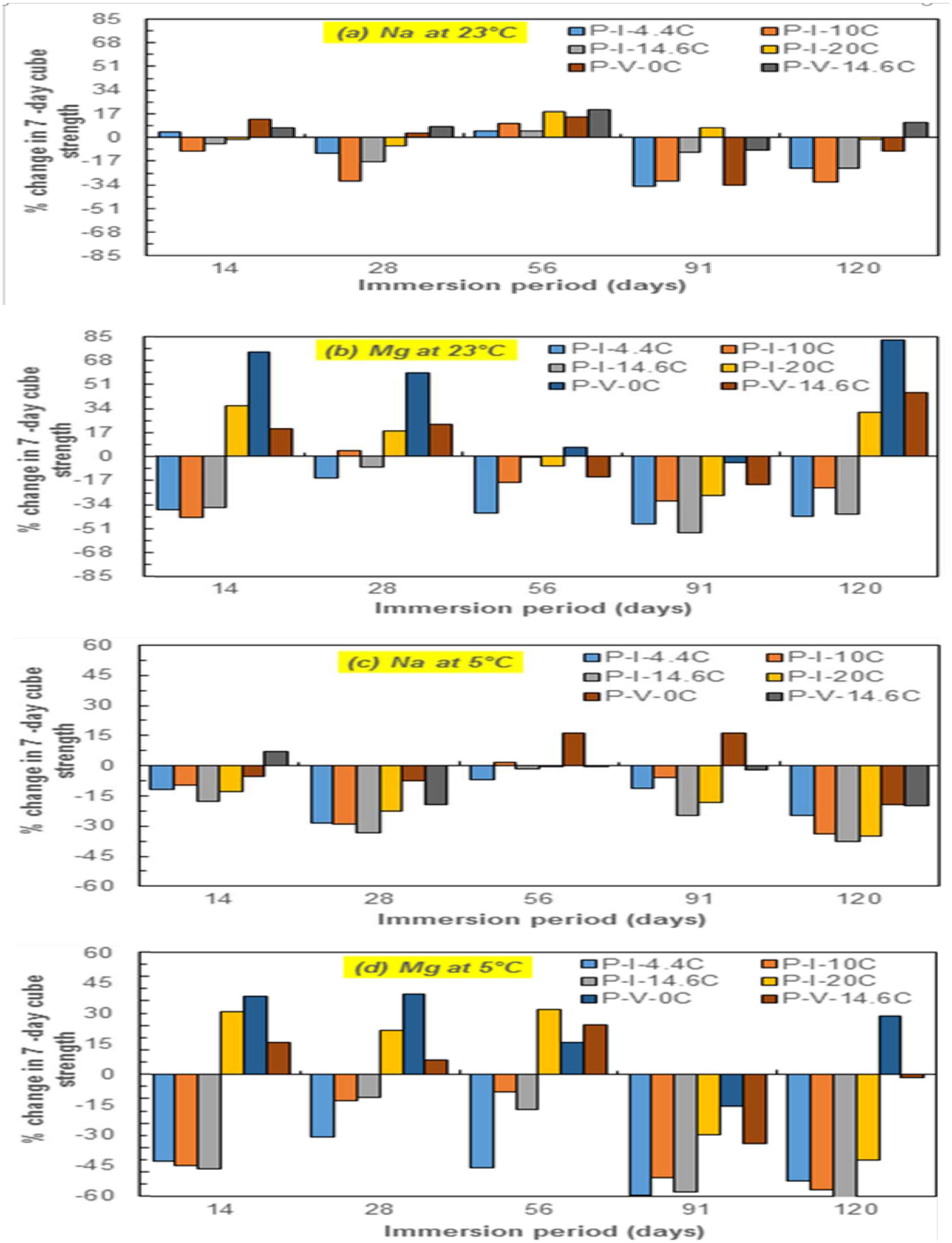

Figure 20: Percent reduction of compressive strength of paste (calcitic limestone only) cubes placed in sulfate solutions

(a) Na at 23°C, (b) Mg at 23°C, (c) Na at 5°C, and (d) Mg at 5°C

5.3.4.2 Influence of limestone type and composition

The compressive strength results of different 14.6% PLCs placed in sulfate environments with and without fly ash are shown in Figure 21, Figure 22, Figure 23, and Figure 24. Similar strength patterns were observed for P-I-14.6C and P-I-10.5C-4.1D mixtures at both temperatures when paste samples were immersed in sodium sulfate solution (Figure 21 -a and c). However, the strength changing pattern was different for these mixtures in magnesium sulfate. The addition of dolomitic limestone led to less strength reduction (and strength increases in some cases) of the P-I-10.5C-4.1D mixture compared to the calcitic-only mixture at both temperatures when placed in magnesium sulfate solution (Figure 22-b & d).

For the magnesium sulfate mixes, the addition of dolomite could have increased the compressive strength through ettringite stabilization [109, 110]. Further, the improved performance of the P-I-10.5C-4.1D mixture at 120 days in magnesium sulfate could be attributed to the formation of hydrotalcite ($Mg_6Al_2(OH)_{18} \cdot 3(H_2O)$) [114]. Hydrotalcite is a magnesium-containing hydrate which forms upon the dissolution of dolomite due to an increased curing temperature (25°C to 60°C) [117-119]. In this study, the elevated curing of paste specimens (50°C) could have increased the compressive strength. Research has shown that hydrotalcite is associated with portlandite consumption, which could have improved its sulfate resistance [138].

In sodium sulfate, the addition of dolomite resulted in greater strength reduction over time (Figure 22-a & c). However, when the samples wereplaced in sodium sulfate, the addition of dolomite resulted in a higher reduction in expansion compared to those placed in magnesium sulfate. There appears to be a negative interaction with regard to strength not observed in magnesium. More research is needed to fully understand this behavior.

The compressive strength results of different 14.6% PLCs (calcitic and dolomitic) replaced by Type V cement placed in sodium sulfate solution with and without fly ash are shown in Figure 23 and Figure 24. The compressive strength of P-V-14.6D and P-V-10.5C-4.1D mixtures followed a similar pattern at 23°C over the entire exposure period (Figure 23–a). The effect of the dolimitic limestone addition on strength is less pronounced for Type V cement compared to Type I/II. At 23°C, the addition of dolomite results in lower loss of strength at later ages echoing the results from mortar bar expansion which were lower for dolomitic mixes. The reason behind this strength improvement is likely the same for those discussed for the observed expansion reduction [108, 114, 139]. For 5°C, differences in trends between strength loss and dolomitic addition are more difficult to identify.

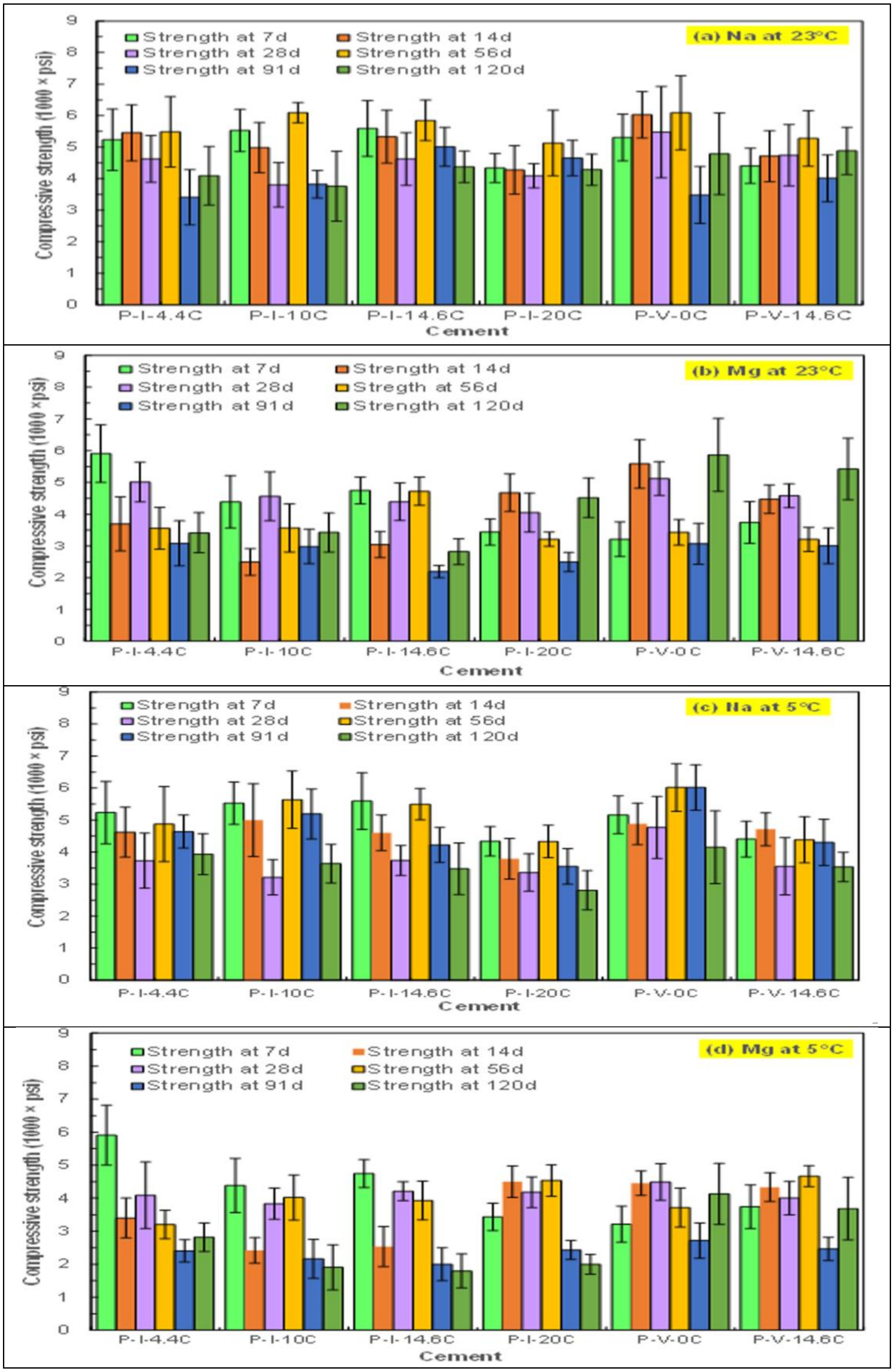

Figure 21: Compressive strength of paste (calcitic and dolomitic limestone) cubes placed in sulfate solutions (a) Na at 23°C, (b) Mg at 23°C, (c) Na at 5°C, and (d) Mg (bars show 1 standard deviation) at 5°C

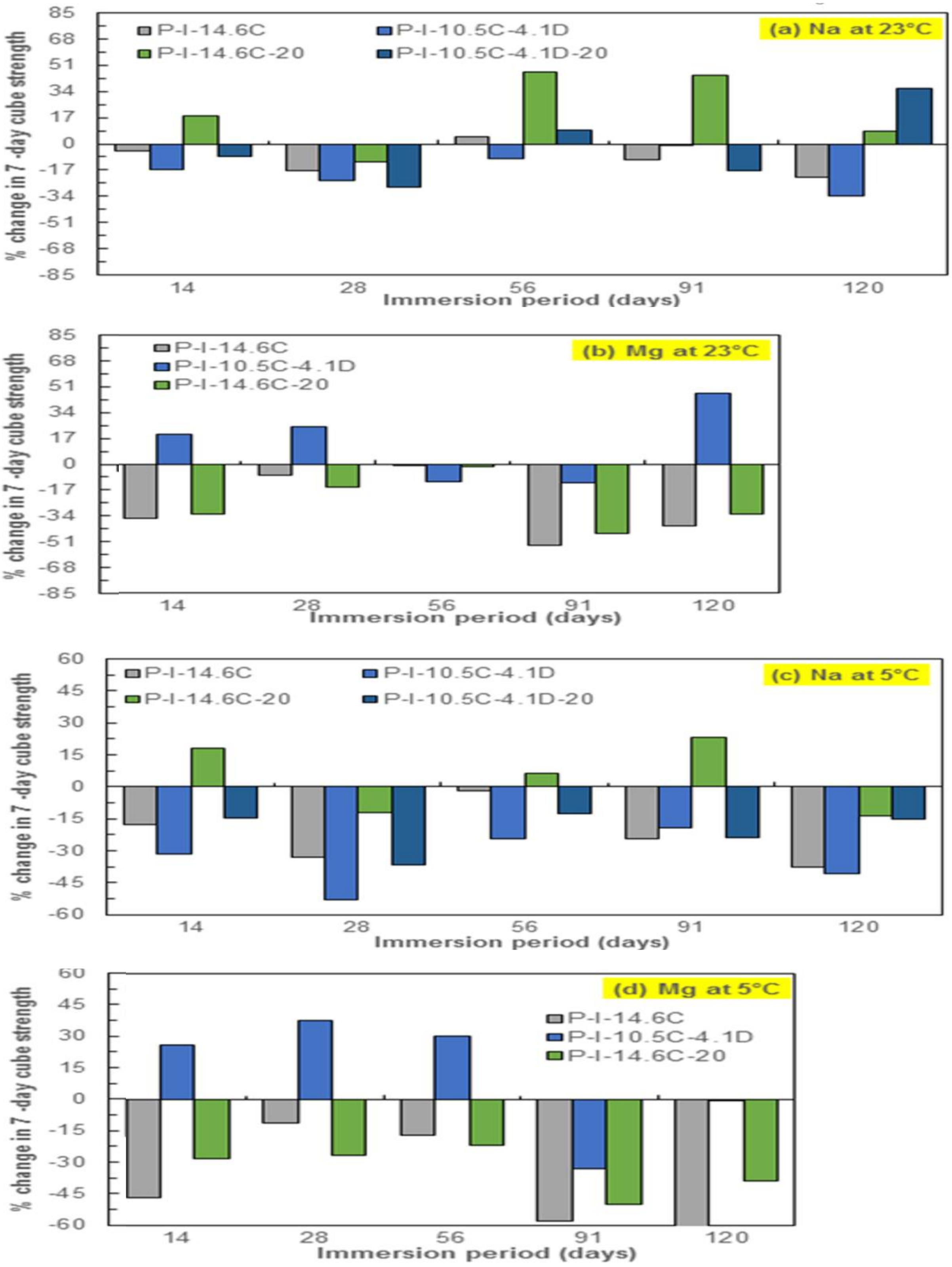

Figure 22: Percent reduction of compressive strength of paste (calcitic limestone only) cubes placed in sulfate solutions

(a) Na at 23°C, (b) Mg at 23°C, (c) Na at 5°C, and d) Mg at 5°C

5.3.4.3 Influence of fly ash

The effect of fly ash addition on the compressive strength of different 14.6% PLCs (calcitic and dolomitic) in both sulfate solutions are presented in Figure 21, Figure 22, Figure 23, and Figure 24. For the Type I/II cement, the addition of the fly ash resulted in lower loss of strength over time at both temperatures and in both solutions. This was true when added to calcitic-only and blended calcitic/dolomitic PLCs. Strength loss for the fly ash mixes was greater in Mg and at 5°C, similar to the mixes without fly ash.

Fly ash is known to have a considerable impact on compressive strength in normal mixtures not undergoing sulfate attack (i.e., reducing it at early ages and increasing it at later ages). Typically, Class F fly ash does not undergo pozzolanic reaction until after 3 months [140]. In this experiment, the elevated curing temperature may have initiated this reaction much earlier, resulting in the enhanced performance of the fly ash mixes seen here. Fly ash and limestone also can have a synergistic effect that results in the formation of calcium carboaluminate hydrate. The lower reactivity of the fly ash mixes in 5°C could be a result of reduced continued hydration of the fly ash often seen at lower temperatures [141, 142].

When comparing these results to the expansion data, fly ash decreased the expansion of the calcitic Type I/II-replaced PLCs, but increased expansion for dolomitic PLCs in sodium sulfate. In magnesium sulfate, expansion was also increased for calcitic PLCs. Perhaps the lower temperature curing of these mortars resulted in less pozzolanic reactivity of the fly ash prior to sulfate attack damage initiation, which could account for the differences between the strength and expansion results.

For the Type V cement, the addition of fly ash resulted in greater loss of strength over time at both temperatures in sodium sulfate. Interestingly, the Type V-replaced PLCs with fly ash had lower expansion (an opposite trend). It's unclear from this data why this phenomenon occurred, but may be related to the differences in maturity between the samples due to the differing curing regimes as well as the impact of the fly ash on sulfate attack with Type V regarding ettringite formation (expansion) vs. gypsum formation (strength loss).

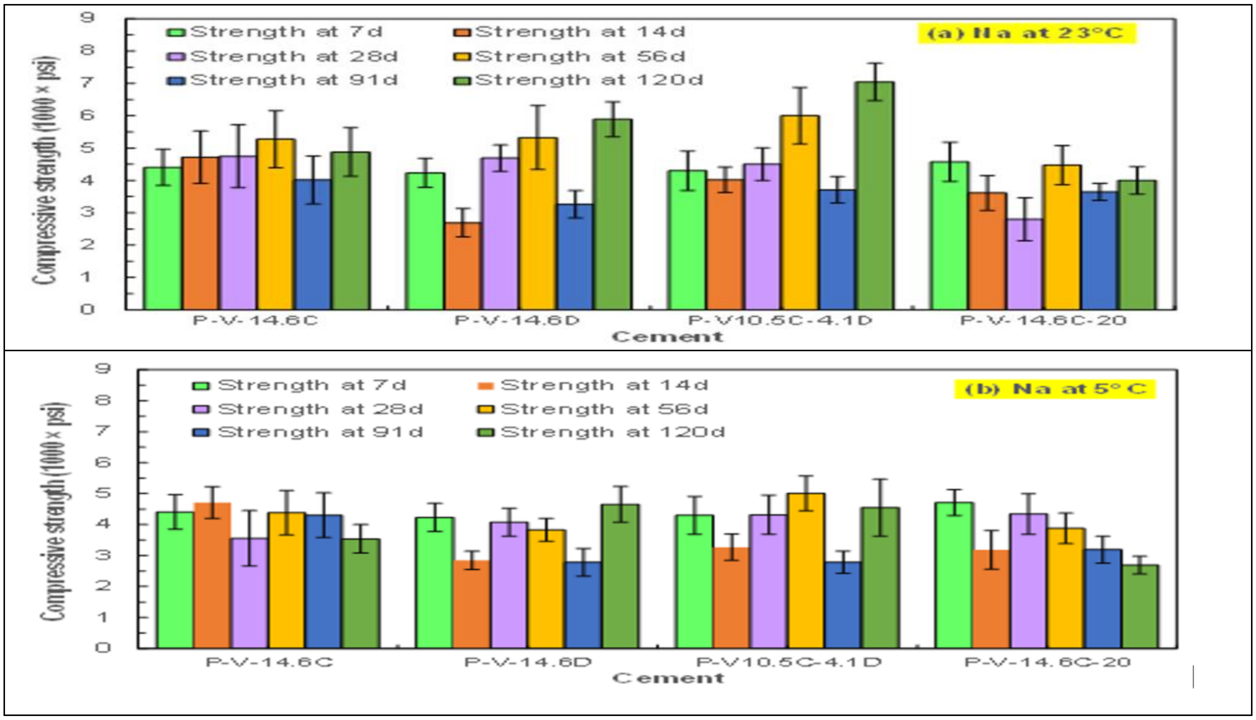

Figure 23: Compressive strength of Type V cement replaced PLC paste cubes placed in sodium sulfate solutions

(a) Na at 23°C and (b) Na at 5°C

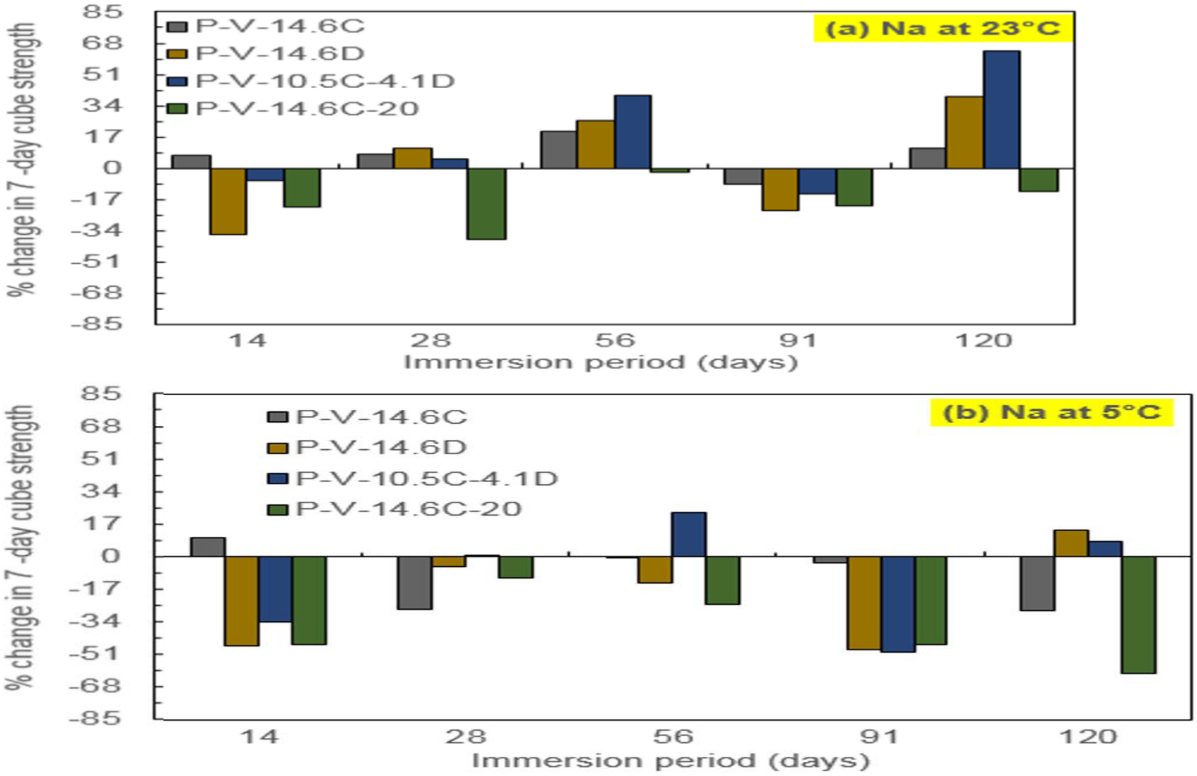

Figure 24: Percent reduction of compressive strength of Type V cement replaced PLC paste cubes placed in sodium sulfate solutions

(a) Na at 23°C and (b) Na at 5°C

5.3.5 Influence of pH

The compressive strength of different PLCs placed in sodium sulfate exposure at 5°C in a controlled pH of 7.2 is presented in Figure 25. The results from this test revealed that most of the mixtures showed greater loss of strength in the controlled pH environment compared to the non-controlled pH sodium sulfate exposure especially at later ages except for the P-I-4.4C, P-V-0C, and P-V-14.6C-20 mixtures. The maximum (79%) and minimum (8%) strength reduction were observed in P-V-14.6C and P-V-0C mixtures, respectively, in pH-controlled sodium sulfate exposure (Figure 25). This indicates that the addition of limestone in Type V cement accelerates the strength reduction under acidic (pH=7.2) sodium sulfate exposure, which was not observed in the alkaline solution.

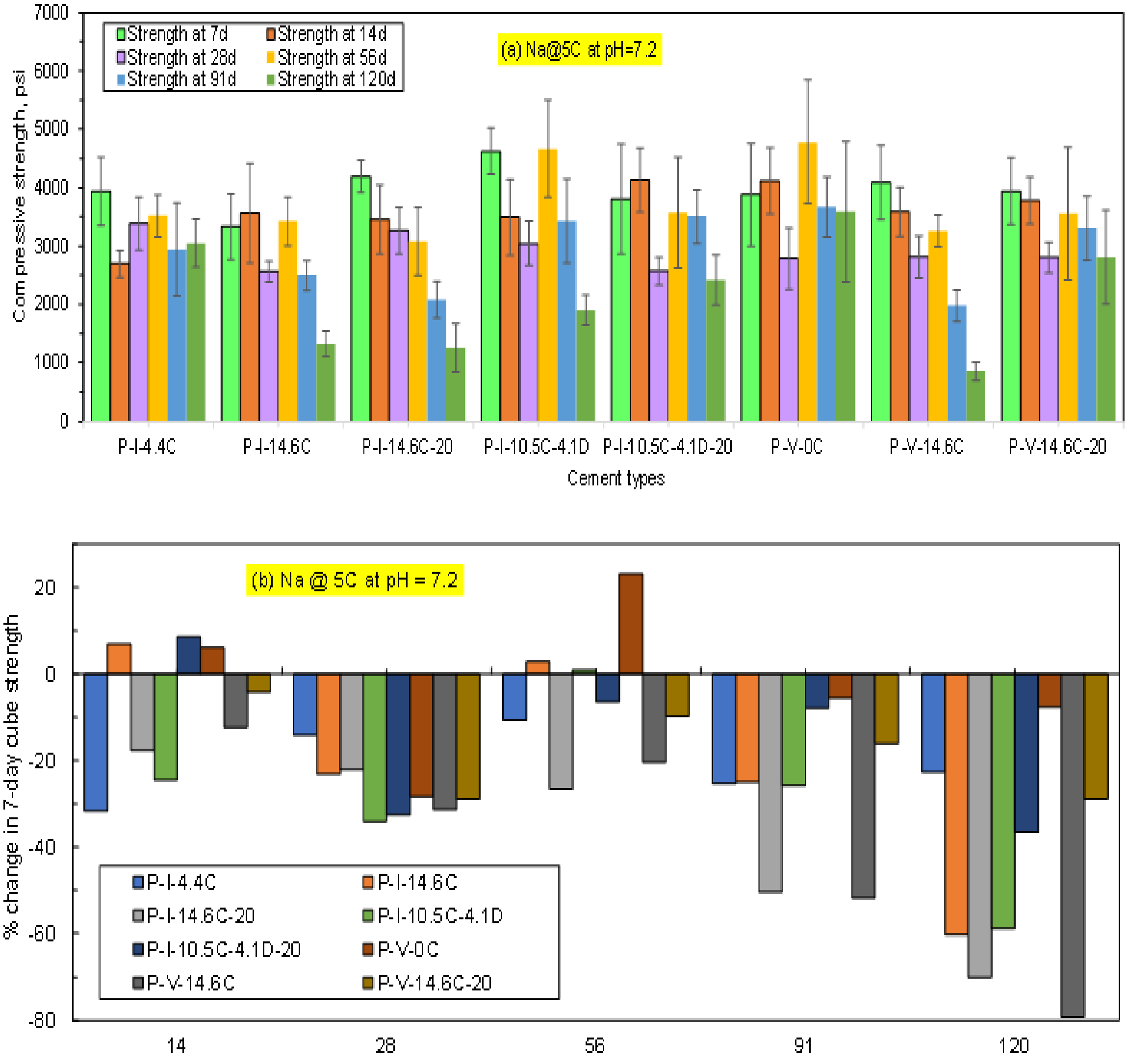

Figure 25: Compressive strength (a) and percent reduction of strength (b) of different PLCs placed in sodium sulfate solution at 5°C at pH= 7.2

There was not any significant change in strength for P-I-4.4C and P-V-0C mixtures in both sulfate environments. However, the solution pH considerably reduced the strength of the P-I-14.6C, P-I-14.6C-20, P-I-10.5C-4.1D, and P-I-10.5C-4.1D-20 mixtures compared to the normal pH condition at 120 days of sodium sulfate exposure. The addition of dolomitic limestone did not show any significant improvement in strength here as it did with the expansion results. Fly ash addition improved Type V PLC strength, but not Type I/II PLC strength at later ages—an opposite trend to the non-pH controlled data. The pH of the concrete and the environment has a significant impact in the aggressiveness of the sulfate attack [64]. Conventional sulfate attack (ettringite and gypsum formation) is more aggressive at a lower pH because it can decalcify the concrete and the C-S-H. However, the lower pH has not been shown to promote thaumasite formation [143].

5.3.6 Visual inspection of paste specimens

Visual inspection of the paste specimens was performed to identify the visible signs of surface damage including cracking, spalling, and softening at 120 days due to sulfate exposure. Photos of specimens immersed in sodium and magnesium sulfate solutions at both temperatures are presented in Figure 26. Between the start of testing until 56 days, some minor corner cracks were observed in all mixtures especially for those placed at 23°C in both sulfate solutions. Generally, the first sign of attack started with the deterioration of corners followed by extensive cracking along the edges and, finally, spalling and disintegration on the specimen surfaces regardless of sulfate solution types. The visual rating system used to classify surface deterioration in this study is shown in Table 20. This visual rating system is widely used to represent the surface deterioration due to sulfate attack. The observations based on this visual rating are presented in Table 21.

Table 20: Visual rating used to classify surface damage

Rating	Description
0	No visible deterioration
1	Deterioration at corners
2	Deterioration at corners and some cracking along the edges
3	Severe cracking along the edges
4	Cracking and expansion
5	Bulge of surfaces
6	Extensive cracking and expansion
7	Extensive spalling
8	Complete disintegration

Table 21: Visual inspection of paste specimens placed in sulfate solutions at 120 days

Specimens designation	at 120 days Na_2SO_4 exposure 23°C	at 120 days Na_2SO_4 exposure 5°C	at 120 days $MgSO_4$ exposure 23°C	at 120 days $MgSO_4$ exposure 5°C
P-I-4.4C	1	5, 6	2	5,6
P-I-10C	2	5,6	1	6
P-I-14.6C	2	7	1	6,7
P-I-20C	3	7	1	4
P-I-10.5C-4.1D	3	5, 6	1	2
P-I-14.6C-20	2	4,5	1	3
P-I-10.5C-4.1D-20	1	4	N/A	N/A
P-V-0C	2	2	1	1
P-V-14.6C	2	2	2	4
P-V-14.6D	2	2	N/A	N/A
P-V-10.5C-4.1D	1	4	N/A	N/A
P-V-10.5C-20	2	3	N/A	N/A

(a) Na @ 23°C

(c) Mg @ 23°C

(b) Na @ 5°C

(d) Mg @ 5°C

Figure 26: Visual appearance of paste specimens after 120 days of sodium and magnesium sulfate exposure at 23°C and 5°C

Overall, the paste samples with a higher percentage of calcitic limestone powder showed more damage in both solutions, especially at 5°C (Figure 26 -b, d). At 5°C, the paste samples from the P-I-14.6C mixture showed extensive cracking and surface spalling. Additionally, a clear bulging on the surfaces was observed at 120 days of exposure. In contrast, the P-V-0C and P-V-14.6C mixtures showed less surface damage at both temperatures in both solutions, which is also supported by the expansion results. At 23°C, none of the paste samples showed significant damage in either solution (ranged from 0 - 3) (Figure 26 -a, c). The addition of fly ash with different PLC mixtures considerably reduced the surface damage at both temperatures in both sulfate solutions. This indicates the surface damage accelerates with higher limestone content and at low temperatures.

5.3.7 Mass loss of paste specimens

The mass of each of the mixture did not change significantly over time for the paste samples placed at 23°C in both solutions. The decrease in mass at this temperature was reported between 0.20 – 1.1% in both solutions. However, a considerable mass decrease was observed when samples were stored at 5°C. Overall, the decrease in mass was more significant for the mixtures immersed in magnesium sulfate solution. The percent change in mass (mass loss) for some calcitic limestone replaced PLCs placed in both solutions at 5°C is shown in Figure 27 and Figure 28. The calcitic limestone replaced PLCs showed a noticeable mass loss compared to all other mixtures. The rate of mass decrease was similar for all samples shown in Na. However, in Mg some of the samples didn’t lose mass at later ages. The increase in mass loss at 120 days was higher for all mixtures placed in magnesium sulfate than in sodium sulfate. In general, the mass change is higher for higher limestone contents in both solutions. Adding limestone to Type V cement has a similar effect to mass loss as it did for Type I/II.

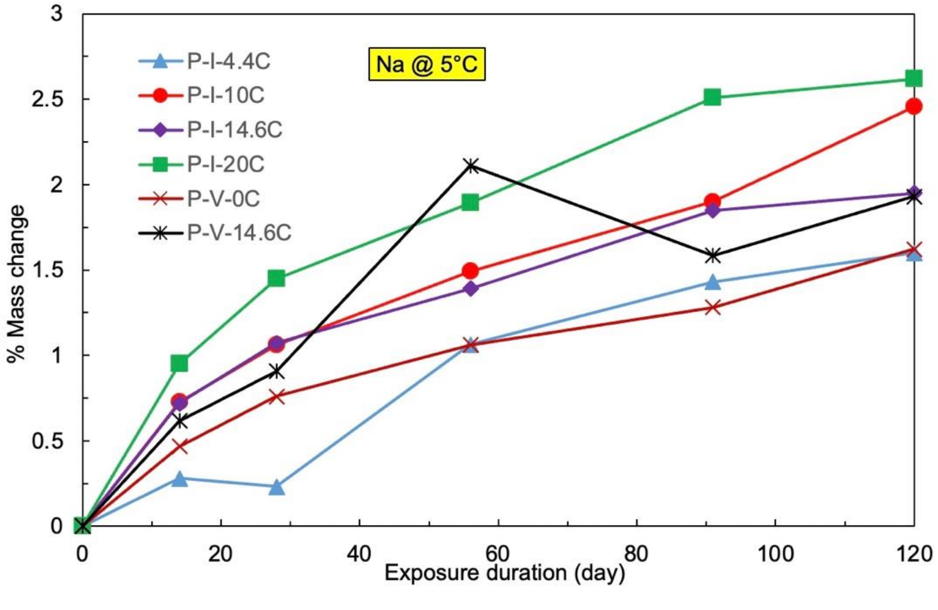

Figure 27: Mass loss of paste specimens placed in sodium sulfate solution at 5°C

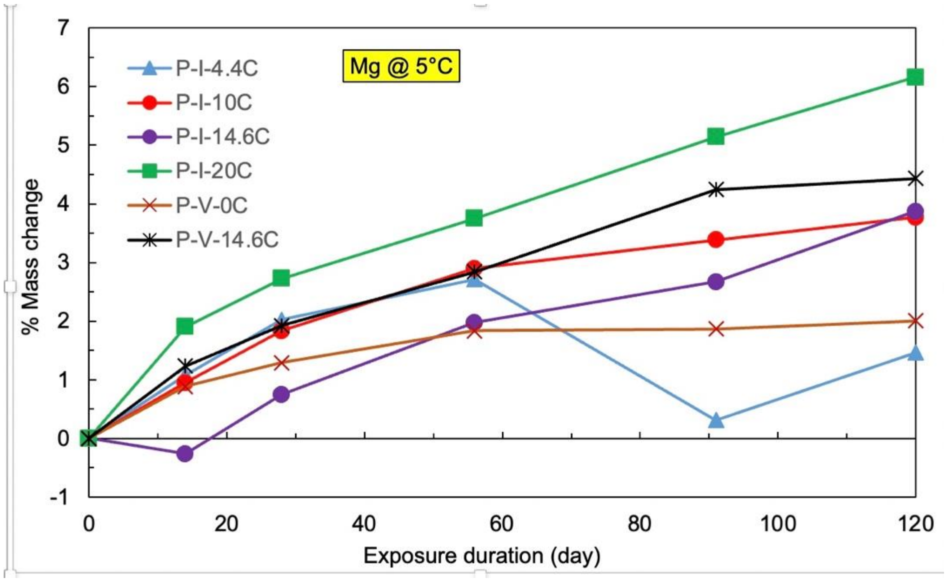

Figure 28: Mass loss of paste specimens placed in magnesium sulfate solution at 5°C

Some paste specimens showed a mass gain over the exposure duration. The mass increase can be attributed to the swelling due to the gypsum or ettringite formation in the damaged paste specimens [144]. Moreover, it could even be due to the filling of pores by expansion reaction products which made the paste denser and thereby increase the weight [145] or the water absorption during the hydration of cement [146]. Therefore, the changes in mass to predict the sulfate resistance of paste specimens is not as accurate as other methods shown in this study.

5.3.8 Mineralogical changes measured by X-ray diffraction

5.3.8.1 X-ray diffraction results in Na_2SO_4 solution

The results of the XRD analysis on paste specimens exposed to sodium sulfate solution at 28 days and 120 days at 5°C are presented in Figure 29, Figure 30, Figure 31, and Figure 32**.** The XRD traces show that the main products associated with sulfate attack are gypsum, ettringite, and thaumasite. Other mineral components detected include calcite, calcium silicate, and portlandite (a hydration product). The peak intensities of gypsum and portlandite observed in all mixtures at both testing ages did not show any correlation to the percentage of to replace the control cements. The main sulfate reaction products found in calcitic limestone replaced PLCs were ettringite and thaumasite at 28 days (Figure 29) and 120 days (Figure 30**)** of sodium sulfate exposure. There was also some gypsum available at both testing ages.

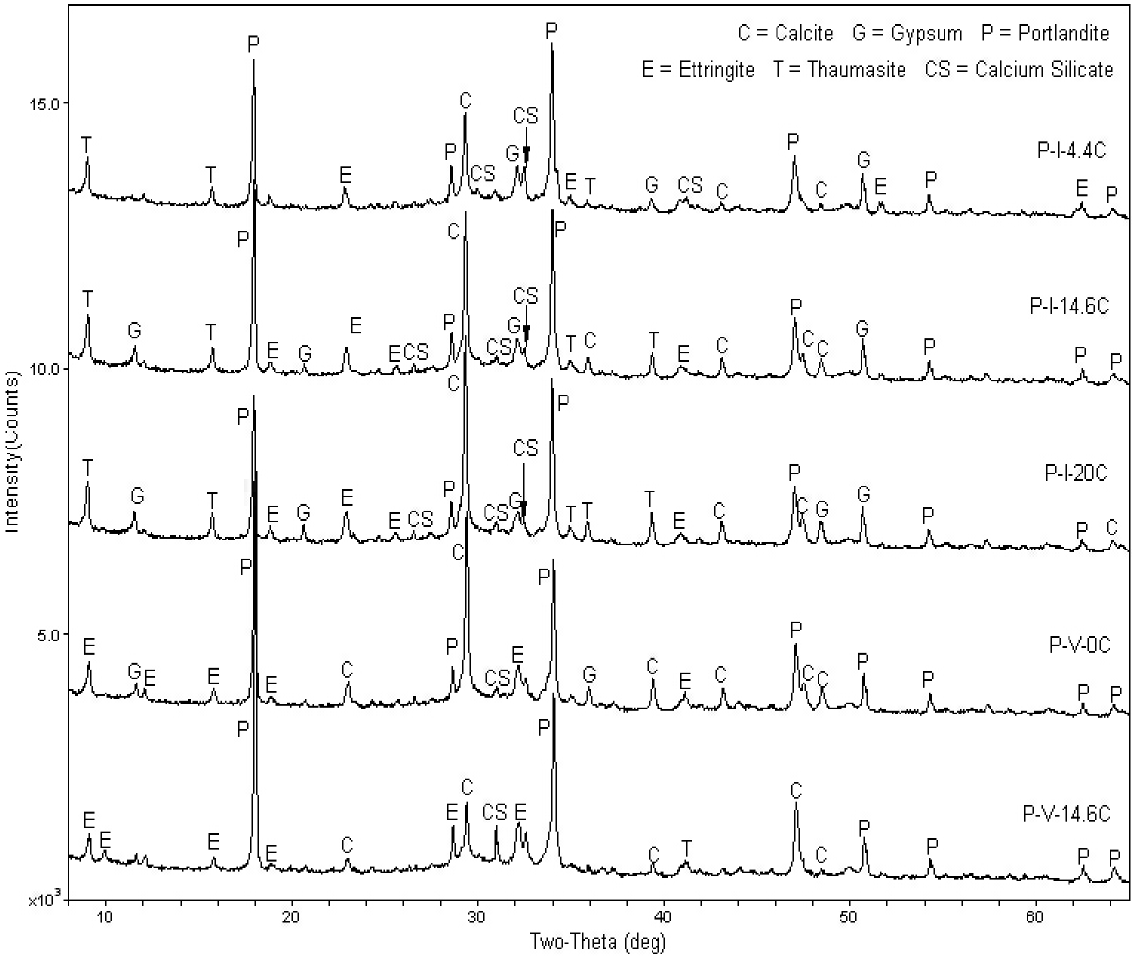

Figure 29: XRD patterns of paste samples exposed to sodium sulfate solution at 5°C for 28 days

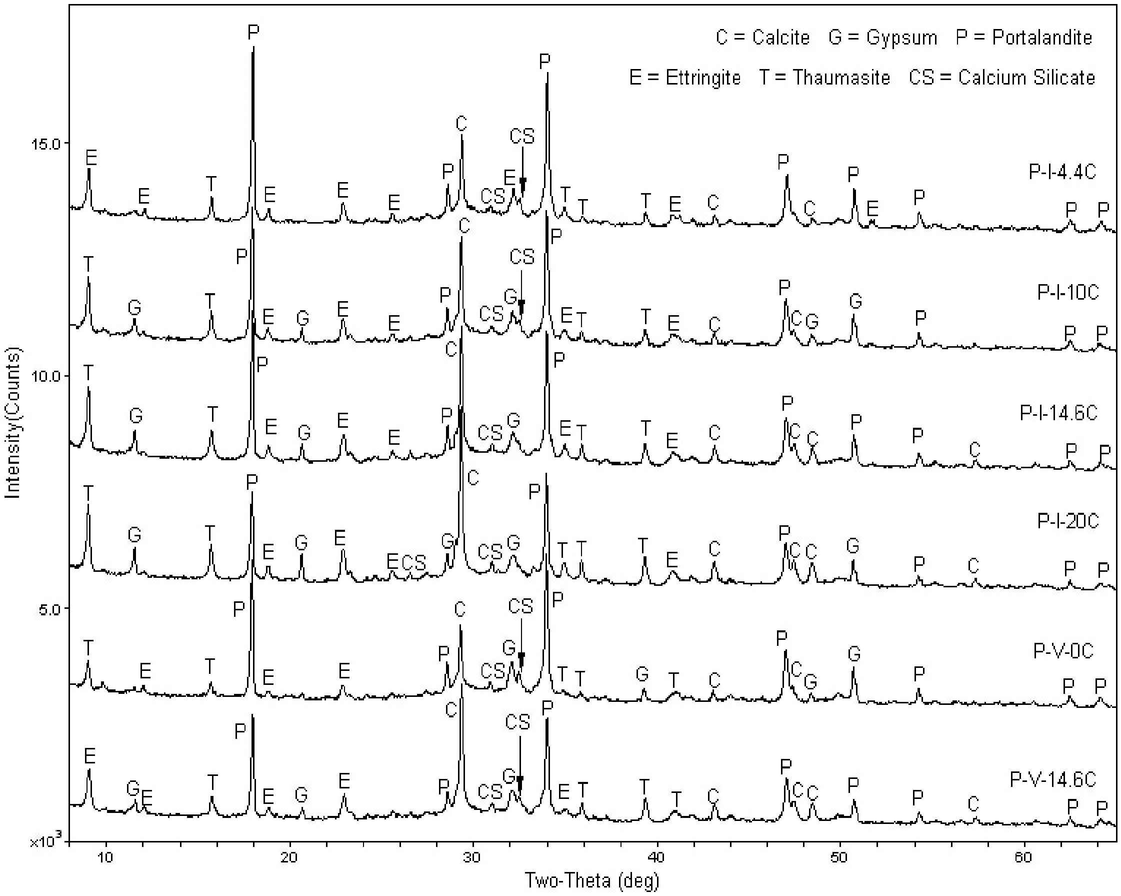

Figure 30: XRD patterns of paste samples exposed to sodium sulfate solution at 5°C for 120 days:

At 28 days, thaumasite was observed in all mixtures except P-V-0C. The intensity of ettringite and thaumasite in all mixtures was higher at 120 days compared to 28 days in addition to more peaks associated with these reaction products (Figure 30). As expected, relatively strong calcite peaks were identified in P-I-4.4C, P-I-10.5C, P-I-14.6C, and P-I-20C paste specimens due to the replacement of the control Type I/II cement by calcitic limestone powder. The increase in calcite peaks with increased limestone (calcitic) content at 28 days and 120 days sodium sulfate exposure was observed at 2θ = 29.4° as shown in Figure 29 and Figure 30, respectively.

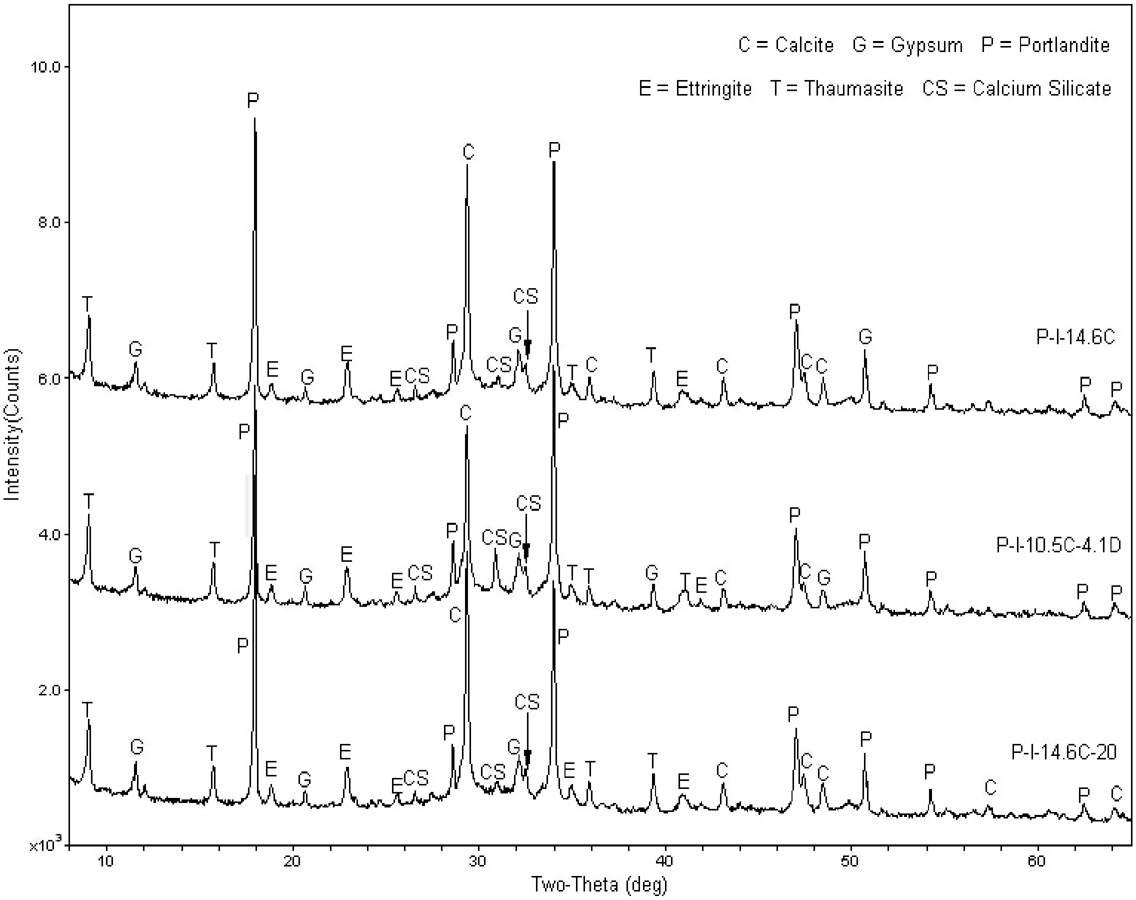

Figure 31: XRD patterns of paste samples exposed to sodium sulfate solution at 5°C for 28 days

At 28 days, P-V-14.6C showed smaller calcite peaks than P-V-0C (Figure 29). The P-V-0C mixture does not contain any added limestone and the presence of calcite could potentially come from the atmospheric CO_2 during sample preparation.

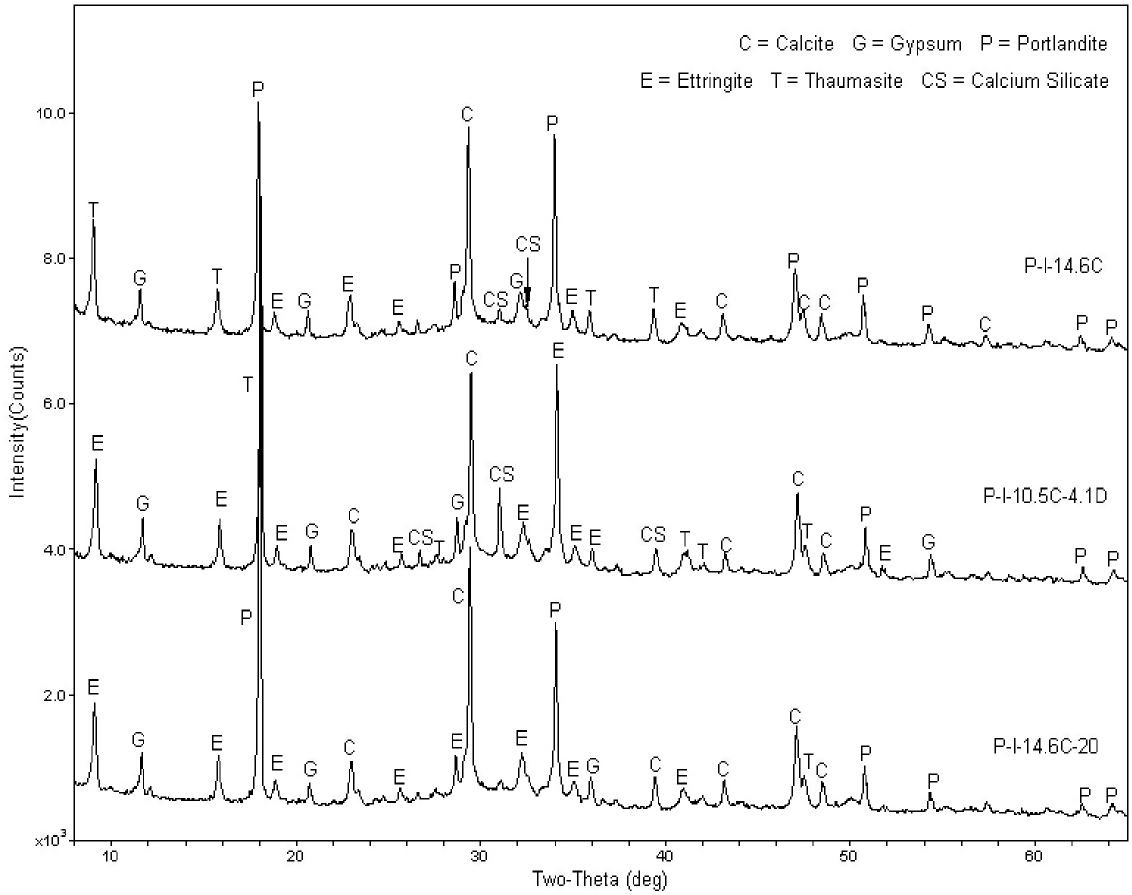

Figure 32: XRD patterns of paste samples exposed to sodium sulfate solution at 5°C for 120 days

The conversion of ettringite to thaumasite was detected at $2\theta = 9.1°$, $2\theta = 15.8°$, and $2\theta = 41.1°$ in P-V-0C sample between 28-120 days (Figure 30). For P-V-14.6C at 120 days, the conversion of other minerals to thaumasite was not observed, but more thaumasite was formed and a reduction in calcite and portlandite peaks was observed compared to 28-day data. To note, there was not any noticeable difference in mortar bar expansion (up to 180 days) and cubes strength (up to 120 days) between P-V-0C and P-V-14.6C mixtures as discussed earlier.

The XRD patterns of P-I-14.6C, P-I-10.5C-4.1D, and P-I-14.C-20 mixtures exposed to sodium sulfate are shown in Figure 31 and Figure 32. There are anomalies between the ettringite and thaumasite products at 28 days and 120 days in P-I-10.5C-4.1D. Specifically, some ettringite was observed at 28 days that converted into thaumasite at 120 days. Literature has revealed that due to structural similarities between ettringite and thaumasite it can be difficult to distinguish between these minerals or it can even be due to the ettringite stabilization [147].

Interestingly, at 120 days, the P-I-10.5C-4.1D mixture showed the highest peak for thaumasite and ettringite at $2\theta = 19.1°$ and $2\theta = 34.2$, respectively, which was converted from portlandite found at 28 days (Figure 31 and Figure 32). Although the P-I-10.5C-4.1D mixture showed higher expansion reduction than P-I-14.6C, greater loss of strength was observed due to the thaumasite formation at later ages.

The P-I-14.6C-20 mixture showed stronger calcite and portlandite peaks at 120 days than P-I-14.6C (Figure 32). At 28 days, the P-I-14.6C-20 mixture showed a combination of thaumasite and ettringite and many of these thaumasite peaks appeared as ettringite at 120 days. There were not any considerable changes in peak intensities at later ages for this mixture. In general, the compressive strength reduction due to sulfate attack is greatest for thaumasite formation. The P-I-14.6C-20 mixture showed less strength reduction than P-I-14.6C at 120 days. The higher strength reduction of P-I-14.6C mixture can be attributed to the progressed thaumasite and ettringite phases at a later age (compared to 28 days) and relatively higher peak intensities at 120 days (Figure 32).

Generally, higher amounts of limestone (a carbonate source) in PLCs and low temperature, which increases the solubility of CO_2 in water, increase the likelihood of thaumasite formation. In this study, the XRD showed that ettringite and thaumasite are responsible for the deterioration of PLC paste specimens at 5°C. Based on the thaumasite formation hypothesis, thaumasite can be formed due to the topochemical conversion of ettringite in the presence of sufficient silicate and carbonate sources [65, 148]. The effect of solution pH is very important. In Na_2SO_4 exposure, another sulfate reaction product, NaOH, is formed which increases the pH (because of higher solubility) of the solution. In our study, the pH of sodium sulfate solution was in the range of 12.2-13.5 over the entire testing period, which may have stabilized the ettringite phases. Thus the conversion of ettringite to thaumasite did not take place. However, it is evident that the sodium sulfate attack is attributed to ettringite and thaumasite formation more so than due to gypsum formation.

5.3.8.2 X-ray diffraction results in $MgSO_4$ solution

The results of XRD analysis of paste specimens exposed to magnesium sulfate solutions at 5°C are presented in Figure 33, Figure 34, Figure 35, and Figure 36**.** The same minerals were observed here as with sodium sulfate in addition to brucite. The dominating sulfate reaction products found in calcitic limestone replaced PLCs were gypsum, ettringite, and thaumasite at 28 days while gypsum and thaumasite were most prevalent at 120 days of magnesium sulfate exposure (Figure 33, Figure 34, Figure 35, and Figure 36).

Figure 25 shows weak peaks of gypsum and strong peaks of portlandite for all calcitic limestone replaced PLCs. At 120 days, the gypsum peaks became much stronger and portlandite peaks became weaker (Figure 34) due to the sulfate attack.

For example, at 2θ = 11.6° and 20.7° at 28 days, there was no considerable change in gypsum peaks with increased limestone content in all mixtures, whereas significantly higher gypsum peaks were identified at this 2θ position at 120 days of magnesium sulfate exposure for cements with higher limestone contents. Interestingly, at 120 days, a strong gypsum peak was found at 2θ = 29.1° between portlandite (2θ = 28.7°) and calcite (2θ = 29.4°) peaks for P-I-10C, P-I-14.6C, P-I-20C, and P-V-14.6C paste mixtures (Figure 34). Similarly, some new gypsum peaks are also observed between 2θ = 30° to 36° at 120 days of sulfate immersion (Figure 34).

On the other hand, a substantial reduction of portlandite peaks was observed at 2θ = 18.1° and 34.1° at 120 days compared to 28 days (Figure 34). For the P-I-14.6C mixture, at 2θ = 34.1°, portlandite was completely consumed and more thaumasite was formed at 120 days. It is clear that the conversion of portlandite to thaumasite is mainly responsible for a significant strength reduction (65% at 120 days) of this mixture (discussed in the compressive strength section). However, there was not any significant change in strength reduction for higher limestone contents in magnesium sulfate exposure (Figure 20).

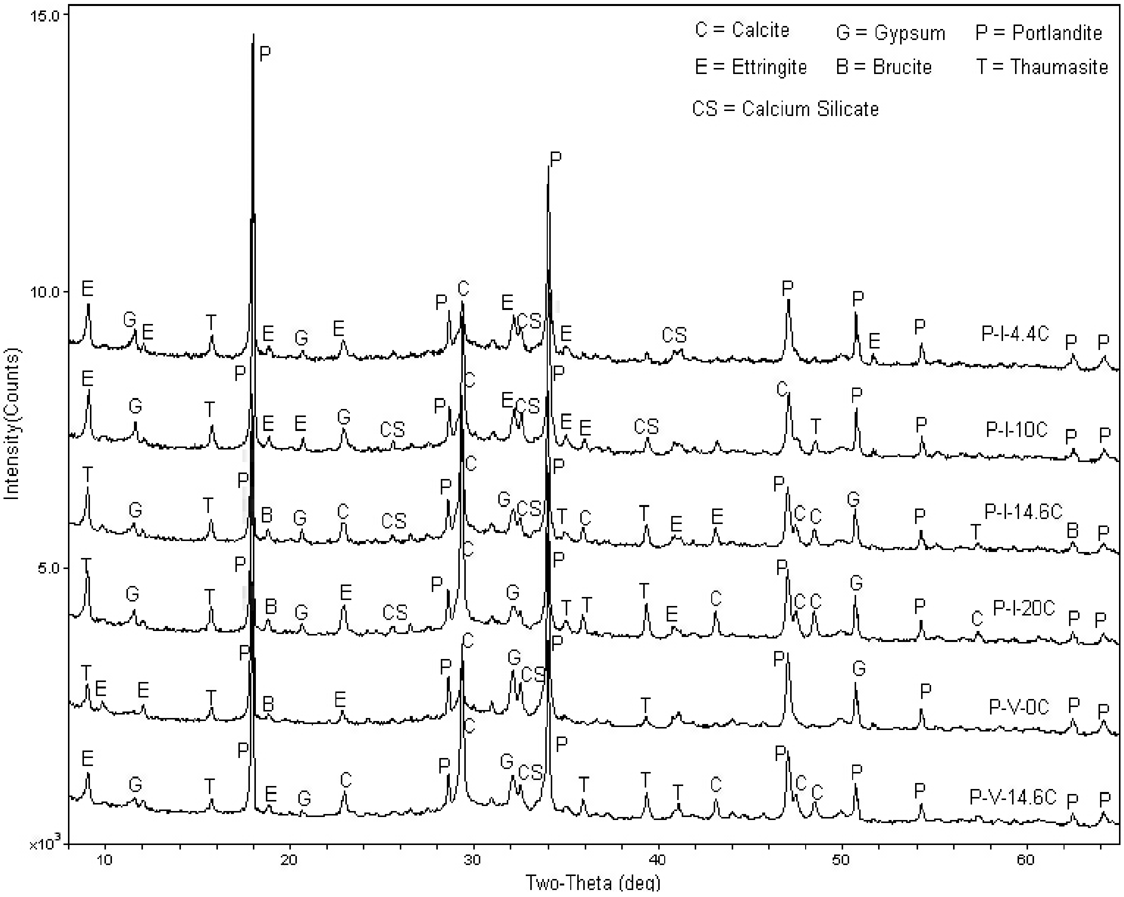

Figure 33: XRD patterns of paste samples exposed to magnesium sulfate solution at 5°C for 28 days

One difference for the samples in magnesium sulfate compared to sodium sulfate is the change of thaumasite to ettringite at later ages. For example, at $2\theta = 9.1°$, P-I-14.6C, P-I-20C, and P-V-0C showed thaumasite at 28 days when it showed stronger ettringite peaks at 120 days. As discussed earlier, this can be the structural similarity or co-existence of these minerals at an early age which is difficult to identify through XRD. The mineralogical phases of P-V-0C and P-V-14.6C mixtures remained unchanged at 120 days. There was not any noticeable strength reduction in these mixtures at 120 days compared to 28 days, which corresponds well to this finding. However, there was 84% expansion reduction in M-V-14.6C compared to M-V-0C at 180 days.

Figure 34: XRD patterns of paste samples exposed to magnesium sulfate solution at 5°C for 120 days

The changes in sulfate attack reaction products at later ages in the P-I-14.6C mixture was quite different than those found in P-I-10.5-4.1D. Fewer gypsum compounds, less thaumasite, and no brucite were found in P-I-10.5C-4.1D sample when compared to P-I-14.6C. The improved performance of P-I-10.5C-4.1D mixture measured by the mortar bar expansion and compressive strength results (discussed earlier) is likely due to these differences.

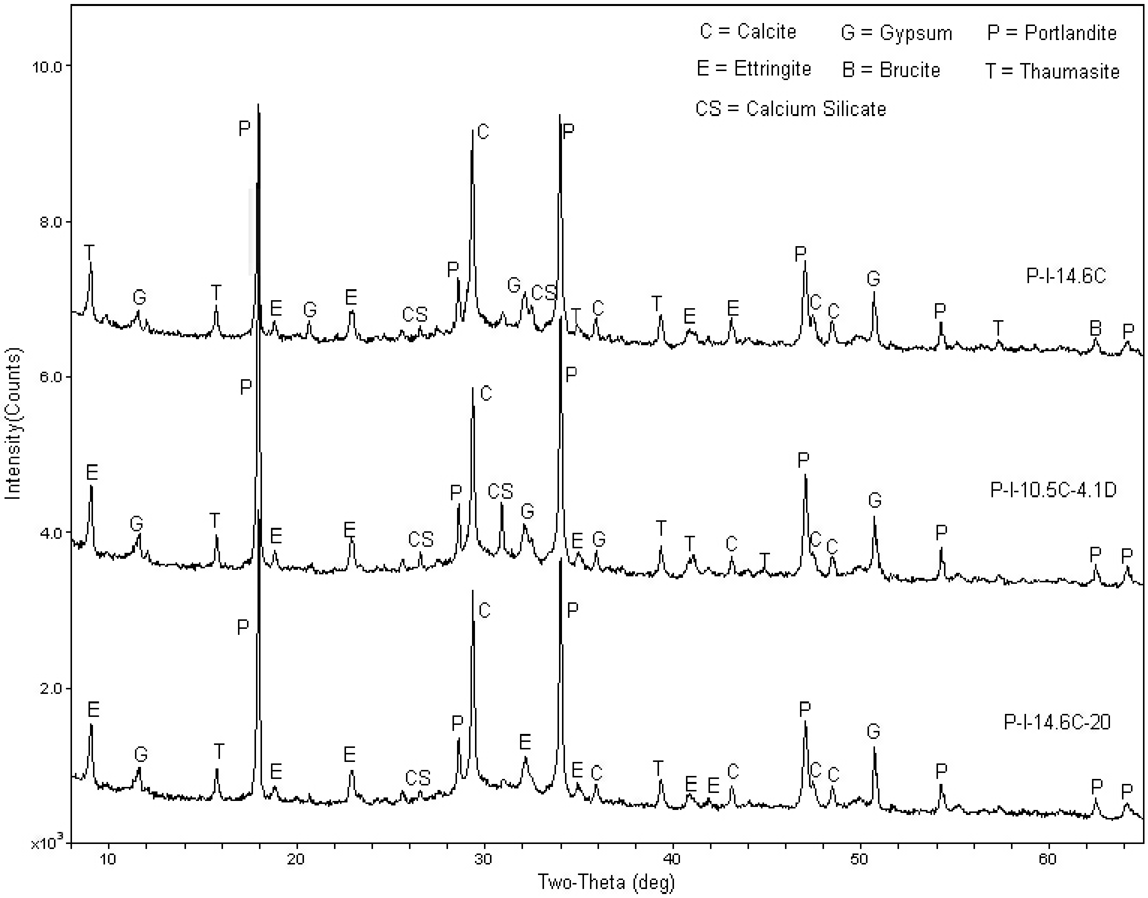

Figure 35: XRD patterns of paste samples exposed to magnesium sulfate solution at 5°C for 28 day

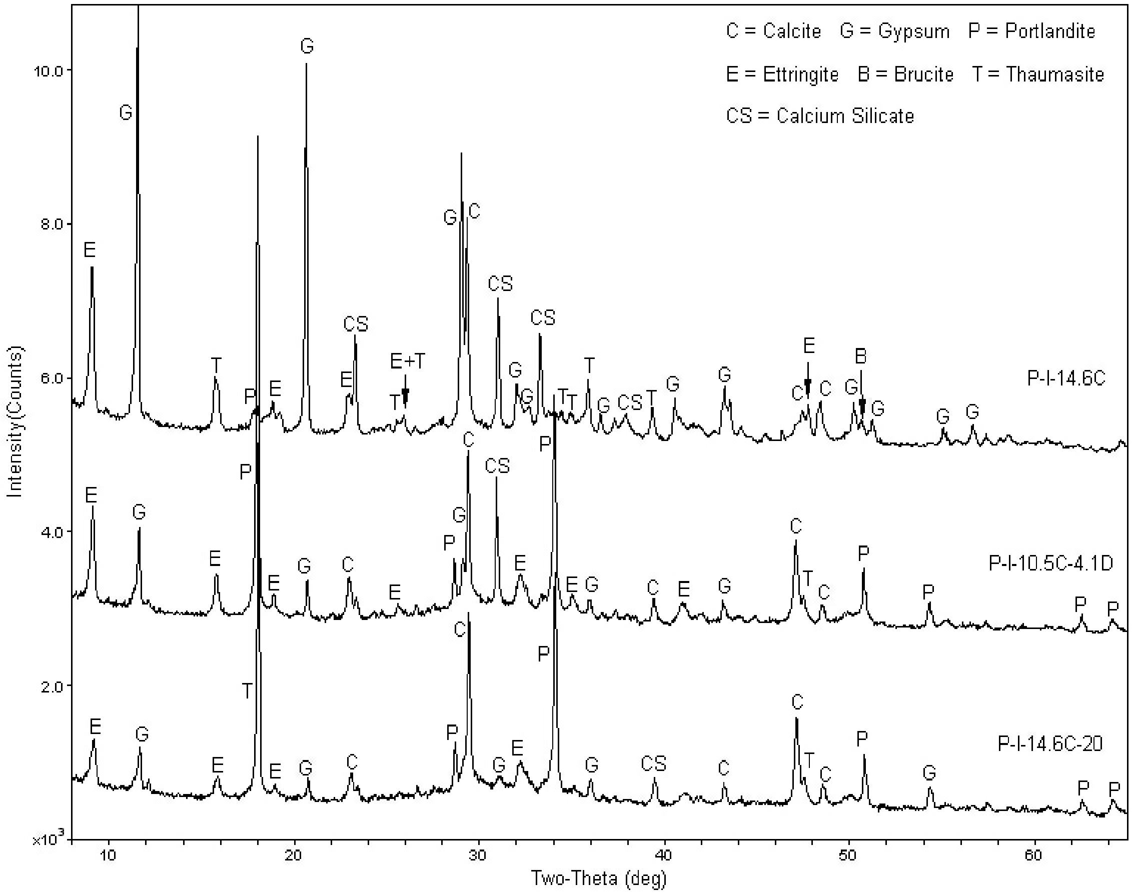

Figure 36: XRD patterns of paste samples exposed to magnesium sulfate solution at 5°C for 120 days

In general, in $MgSO_4$ exposure the pH of the solution does not change significantly due to the limited leaching of $Mg(OH)_2$ formed as a sulfate reaction product. This is because of the low solubility of brucite compared to the portlandite available in the pore solution [101]. In this study, the pH of the magnesium sulfate was in the range of 6.5-10 which indicates that more gypsum was formed over the exposure duration. This can be attributed to C-S-H destabilization due to the lower pH values. Overall, it can be predicted that the damage due to magnesium sulfate attack is primarily from gypsum and thaumasite formation.

5.3.9 Results of interground PLC testing

5.3.9.1 Expansion of mortar bars

The expansion results of the prismatic mortar specimens of different interground and separately made (added finely ground limestone powder to Type I/II cement) PLCs blends submersed in 5% sodium and magnesium sulfate solution are shown in Figure 37 and Figure 38. All mixtures experienced a similar trend of expansion at early ages. Previous research has shown that mortar bars in this test expand slowly at the beginning and can have significantly increased expansion after 28 days of sulfate exposure [99]. The expansion of M-I-4.4C mortar gradually increased after 91 days whereas mortar bars from M-I-14.6C mixture expanded rapidly after 60 days and disintegrated after 7 months. However, the replacement of M-I-14.6C with fly ash showed to reduce 67% expansion at 180 days.

The expansion of mortar specimens of M-I-4.4C, M-I-14.6C, and M-I-14.6C-20 mixtures showed a similar trend where the addition of fly ash did not noticeably reduce the expansion in magnesium sulfate exposure (Figure 38).

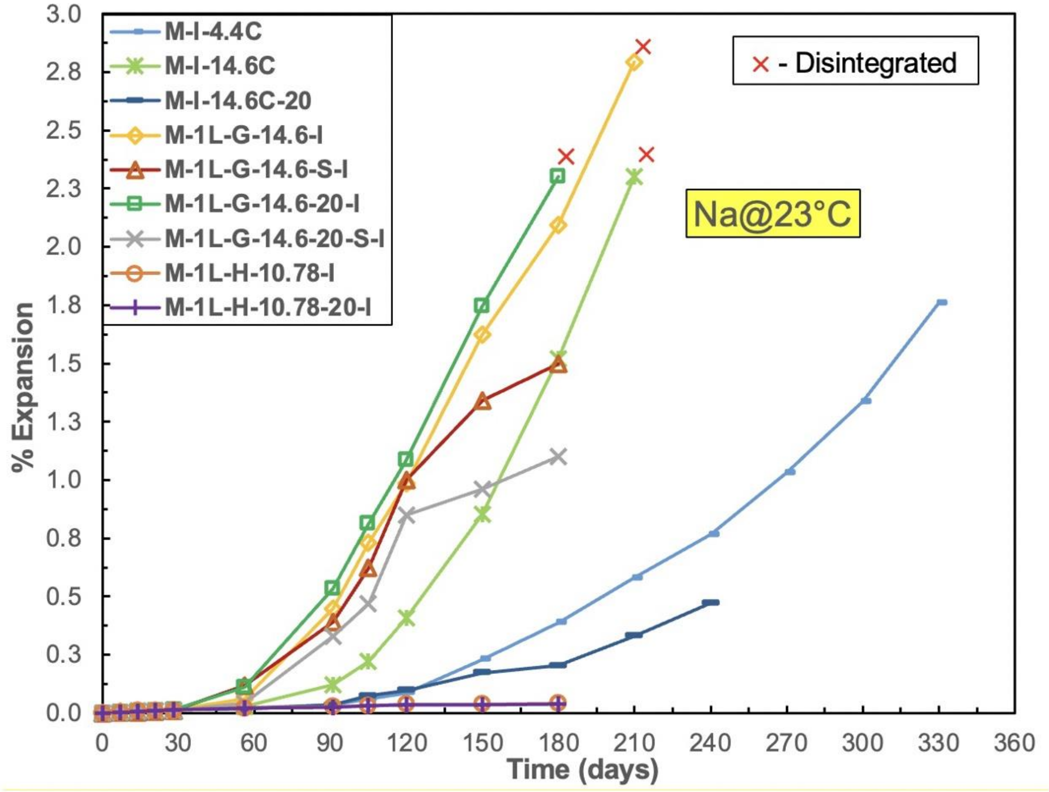

Figure 37: Expansion of different PLC mortars placed in 5% sodium sulfate solution

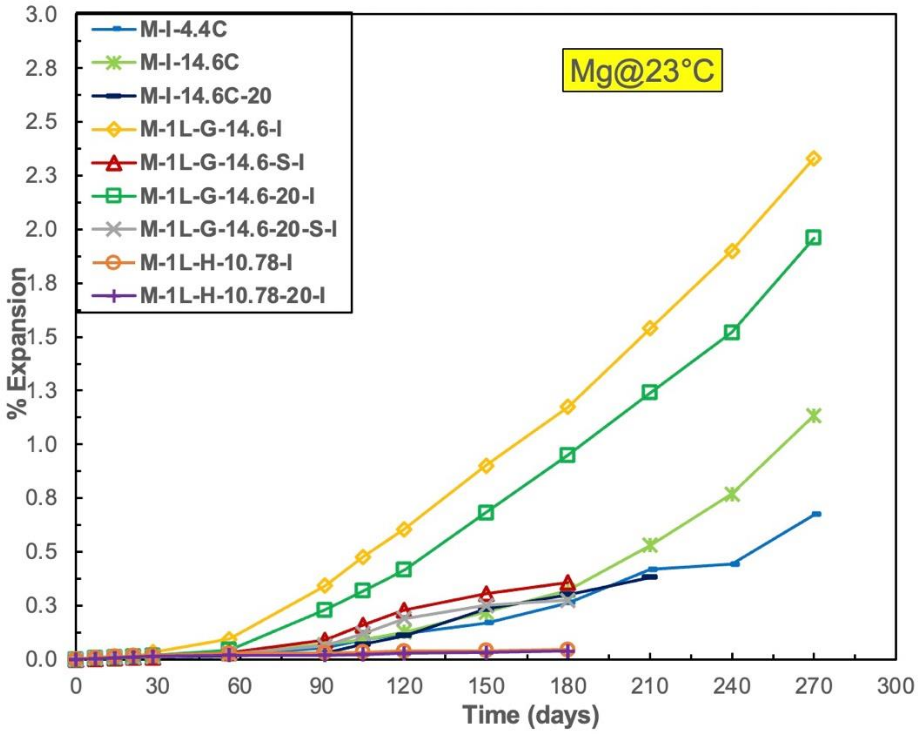

Figure 38: Expansion of different PLC mortars placed in 5% magnesium sulfate solution

The rapid increase in expansion was observed in M-IL-G-14.6-I and M-IL-G-14.6-20-I mixtures just after 60 days in both sulfate solutions. The mortar samples from these two mixtures completely disintegrated after 7 months in sodium sulfate exposure but was not completely damaged until 12 months. The expansion results showed that all mixtures exceeded ASTM C595 12-months expansion limit prior to 4 months exposure in both sulfate exposures. Overall, the mortar bar expansion was relatively higher in all mixtures in sodium sulfate than in magnesium sulfate.

On the other hand, the interground PLCs from Holcim (M-IL-H-10.78-I and M-IL-H-10.78-20-I) did perform very well. The expansion of M-IL-H-10.78-20-I mixture was relatively lower than M-IL-H-10.78-I in both solutions (Figure 37 and Figure 38). The test results at 6-months sodium sulfate exposure (0.04%) from the experiment at SD School of Mines was a little higher than the test results provided by Holcim (0.03%), however, the samples still met the expansion limit.

5.3.9.2 Sulfate optimization and subsequent expansion of mortar samples

Due to the unusually high expansion observed with the GCC interground cement, it was speculated to be undersulfated, which needed to be verified with experimental work. Different dosages of gypsum (calcium hemihydrate) were added to replace the control cement to determine the optimized sulfate content using isotherm calorimetry. The power and energy plots revealed that this cement was undersulfated (Figure 39 and Figure 40), because the secondary peak associated with sulfate consumption was not observed after the alite peak. The optimized SO_3 content was calculated using the Calmetrix sulfate optimization tool. The isothermal calorimetry results indicate that 1% SO_3 needed to be added to achieve sulfate optimization

(Figure 41). During the hydration phase of C_3A, ettringite is formed through the reaction between aluminate and gypsum. When the amount of gypsum depletes, C_3A itself reacts with the ettringite to form monosulfate. If monosulfate conversion can be reduced, sulfate attack can also theoretically be reduced.

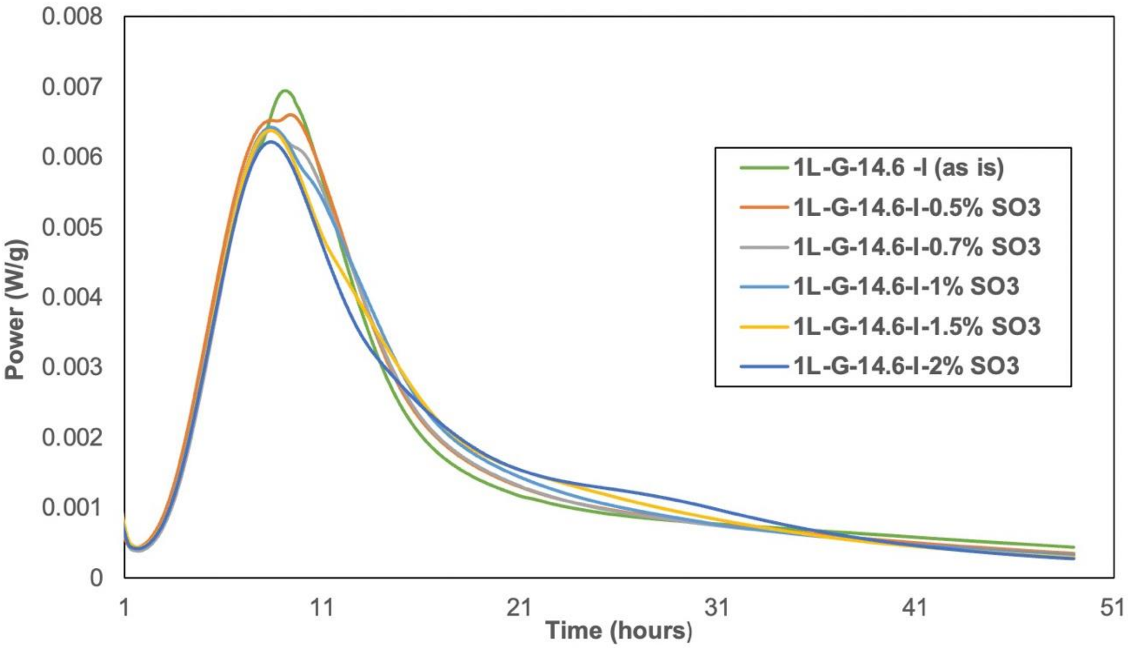

Figure 39: Isothermal calorimetry power graph of M-I-G-14.6 cement with different SO_3 dosages

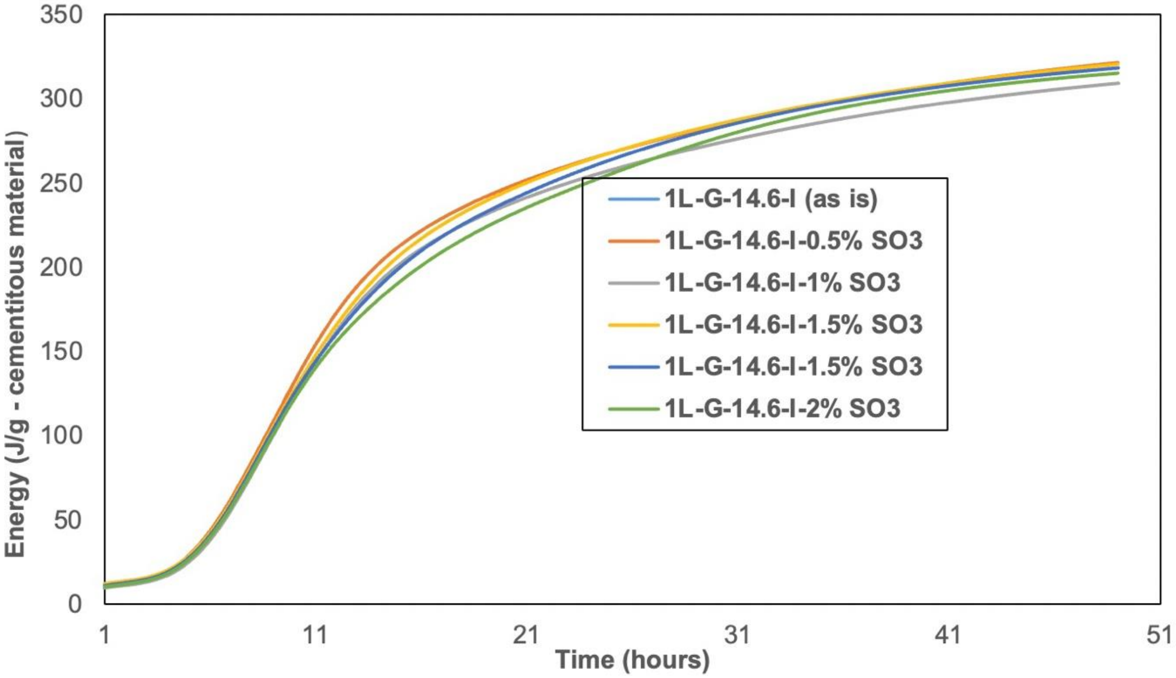

Figure 40: Isothermal calorimetry energy graph of M-I-G-14.6 cement with different SO_3 dosages

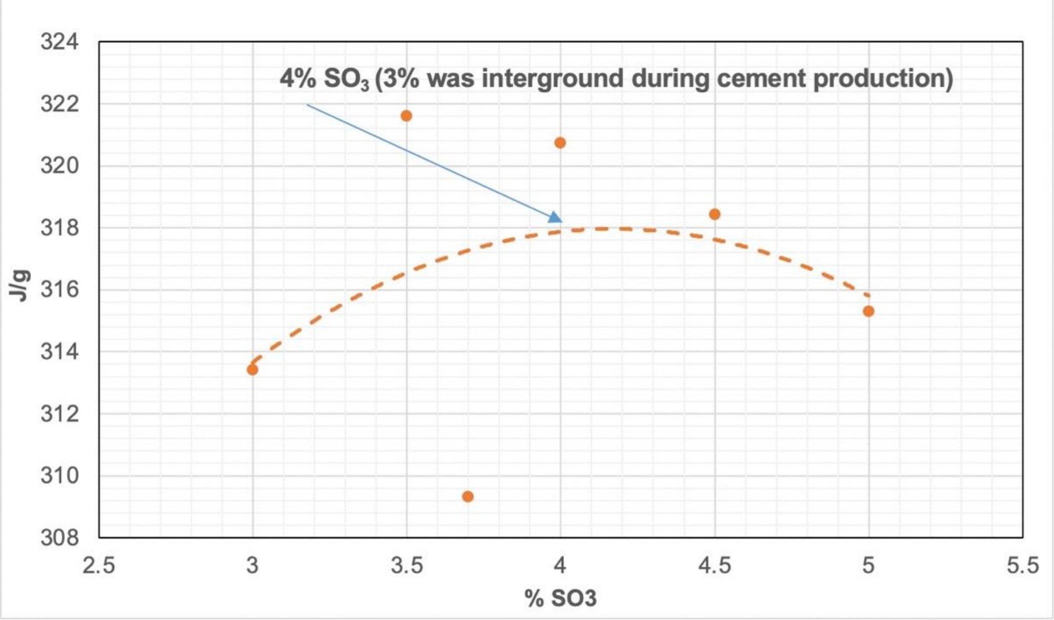

Figure 41: Optimization of SO_3 percentage of M-I-G-14.6 cement

New mortar specimens were cast by adding 1% SO_3 in M-IL-G-14.6-I and M-IL-G-14.6-20-I mixtures and placed in both sulfate environments. This gypsum addition has approximately reduced 28% and 54% expansion in M-IL-G-14.6-S-I and M-IL-G-14.6-20-S-I mixtures, respectively at 180 days in sodium sulfate (Figure 37). In magnesium sulfate, around 69% and 71% expansion reduction was observed at the same exposure period when 1% gypsum was added to the control cements (Figure 38). However, the expansion limits were still exceeded with the sulfate optimized cement.

5.3.9.3 Strength loss of paste cubes

The undersulfated and sulfate-optimized P-IL-G-14.6-I and P-IL-G-14.6-20-I cement mixtures were also evaluated for compressive strength change in a sulfate environment over an exposure period of 180 days. The percent reduction in compressive strength (relative to an initial 7-day strength) at different ages in Na and Mg solution at 5°C is presented in Figure 42 and Figure 43, respectively. Over the 180-day exposure period the samples underwent both strength increases and decreases. The strength increases can be potentially explained by the continued hydration of unhydrated cement particles (mostly C_3S and C_2S) which produced more hydration products, primarily C-S-H, leading to higher compressive. Strength losses are mainly attributed to sulfate attack.

At later ages, strength loss was greater in the Type IL cement compared to the Type I/II cement, which corresponds to expansion data. The addition of fly ash marginally improved strength loss for the undersulfated PLC. Sulfate optimization of the PLC also marginally improved strength loss in both solutions. The sulfate-optimized fly ash blended PLC mix performed best, especially in sodium sulfate. In this experiment, the elevated curing temperature may have accelerated the pozzolanic reaction, resulting in the enhanced performance of the fly ash mix seen here. Fly ash and limestone also can have a synergistic effect that results in the formation of calcium carboaluminate hydrate which stabilizes ettringite and improves mechanical properties. This could have contributed to its improved sulfate attack performance, especially with the sulfate balanced.

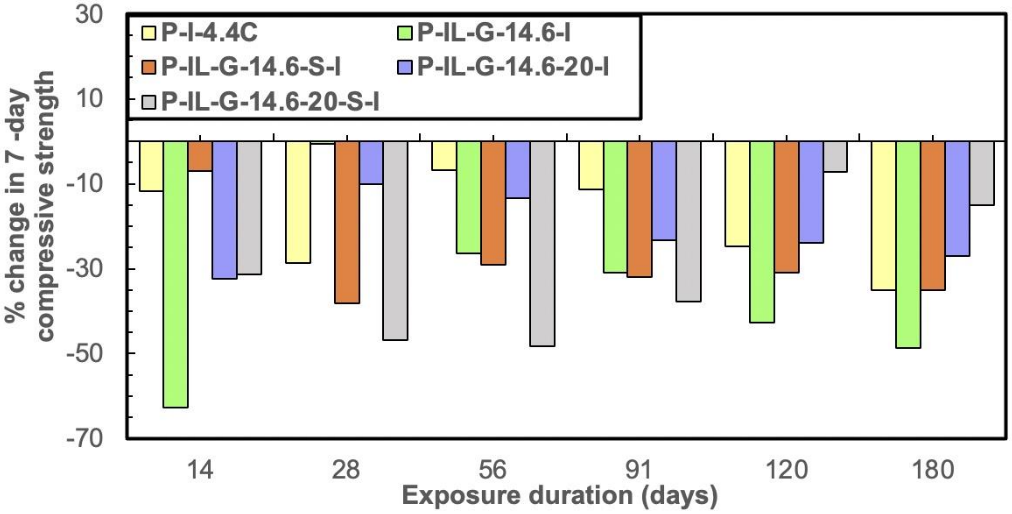

Figure 42: Percent reduction of compressive strength of paste cubes placed in sodium sulfate solution at 5°C

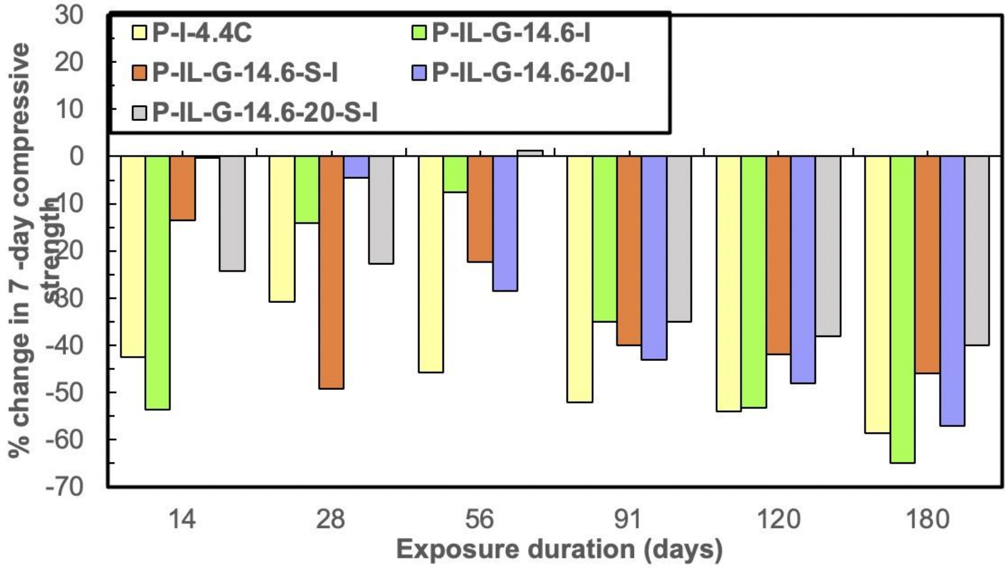

Figure 43: Percent reduction of compressive strength of paste cubes placed in sodium sulfate solution Mg at 5°C

5.3.10 Complementary concrete testing results

The complementary test results for compressive strength, flexural strength, setting time, slump, and density for Type I/II and Type IL(14.6) with and without 20% Class F fly ash are presented in Table 22, Table 23, Table 24, and Table 25 In addition, the heat and energy generated per gram of cementitious materials measured using isothermal calorimetry are presented in Figure 44, Figure 45, Figure 46, and Figure 47. Workability for all mixes was very poor (zero slump), and no admixtures were added to improve workability. However, consolidation of the mixes appeared satisfactory. The interground PLC from GCC had higher early strength (7-day) and similar 28-day strength to the Type I/II cement. The PLC also had higher cumulative heat than the Type I/II cement after 24 hours, which correlates with the observed strength trends. The addition of fly ash for all mixes reduced early-age strength, slightly extended setting time, and lowered cumulative heat release. 28-day strength of fly ash mixes was on par with complementary plain mixes.

Table 22: Test results for Type I/II cement

Test	Testing age					
	3 days	3 days	7 days	7 days	28 days	28 days
	Average	Stdv.	Average	Stdv.	Average	Stdv.
Compressive strength of 2" × 2" mortar cube (psi)	2600	320	2430	210	3140	650
Compressive strength of 4" × 8" cylinder mortar (psi)	4940	220	5640	340	6720	250
Flexural strength of beam (psi)	-	-	-	-	880	30
Initial setting time (min)	270	270	270	270	270	270
Final Setting time (min)	340	340	340	340	340	340
Slump (inch)	0	0	0	0	0	0
Fresh Density (lb/ft^3)	150	150	150	150	150	150

Table 23: Test results for Type I/II cement with fly ash

Test	Testing age					
	3 days	3 days	7 days	7 days	28 days	28 days
	Average	Stdv.	Average	Stdv.	Average	Stdv.
Compressive strength of 2" × 2" mortar cube (psi)	2120	320	2940	710	3830	760
Compressive strength of 4" × 8" cylinder mortar (psi)	4750	180	5830	310	6840	350
Flexural strength of beam (psi)	-	-	-	-	885	50
Initial setting time (min)	280	280	280	280	280	280
Final Setting time (min)	340	340	340	340	340	340
Slump (inch)	0	0	0	0	0	0
Fresh Density (lb/ft^3)	152	152	152	152	152	152

Table 24: Test results for 14.6% PLC cement

Test	Testing age					
	3 days	3 days	7 days	7 days	28 days	28 days
	Average	Stdv.	Average	Stdv.	Average	Stdv.
Compressive strength of 2" × 2" mortar cube (psi)	2530	770	2700	1160	3690	440
Compressive strength of 4" × 8" cylinder mortar (psi)	6380	110	6750	160	6870	300
Flexural strength of beam (psi)	-	-	-	-	815	40
Initial setting time (min)	210	210	210	210	210	210
Final Setting time (min)	275	275	275	275	275	275
Slump (inch)	0	0	0	0	0	0
Fresh Density (lb/ft^3)	140	140	140	140	140	140

Table 25: Test results for 14.6% PLC cement with fly ash

Test			Testing age			
	3 days	3 days	7 days	7 days	28 days	28 days
	Average	Stdv.	Average	Stdv.	Average	Stdv.
Compressive strength of 2" × 2" mortar cube (psi)	1880	330	3070	290	2480	280
Compressive strength of 4" × 8" cylinder mortar (psi)	5620	190	5940	200	6880	640
Flexural strength of beam (psi)	-	-	-	-	825	30
Initial setting time (min)	240	240	240	240	240	240
Final Setting time (min)	285	285	285	285	285	285
Slump (inch)	0	0	0	0	0	0
Fresh Density (lb/ft^3)	149	149	149	149	149	149

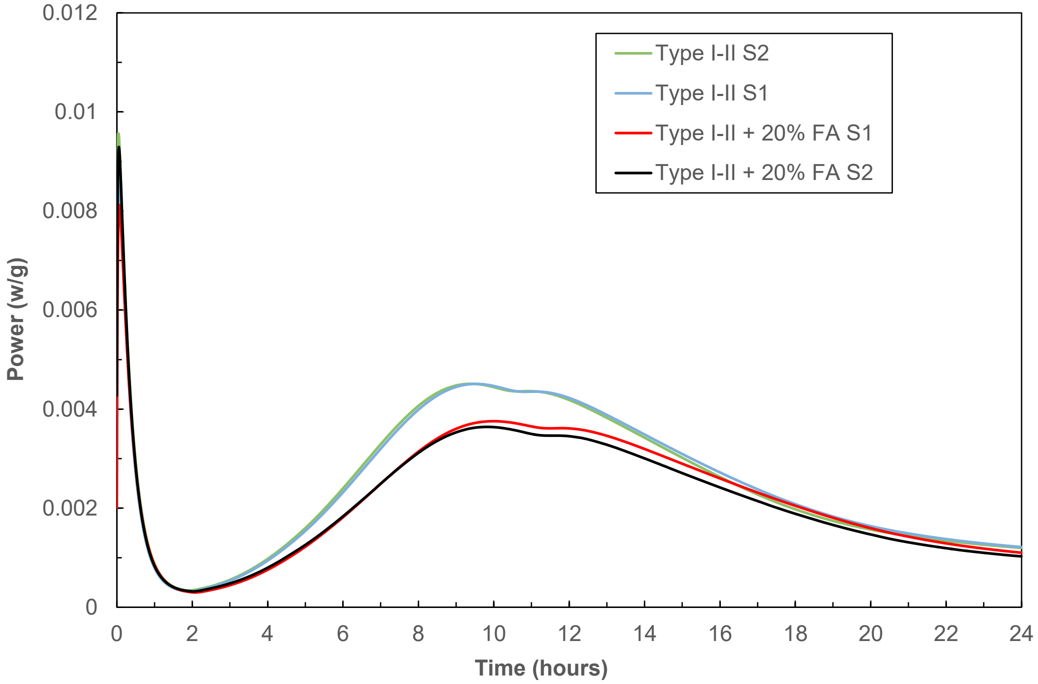

Figure 44: Isothermal calorimetry power graph of Type I/II cement with fly ash

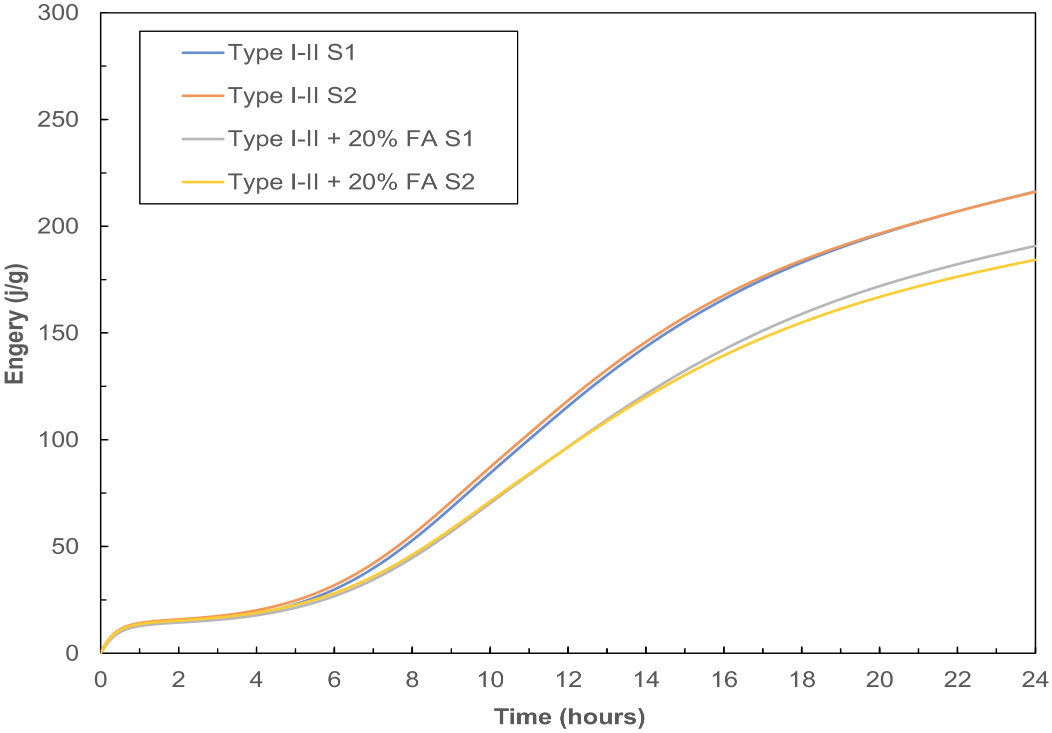

Figure 45: Isothermal calorimetry energy graph of Type I-II cement with fly ash

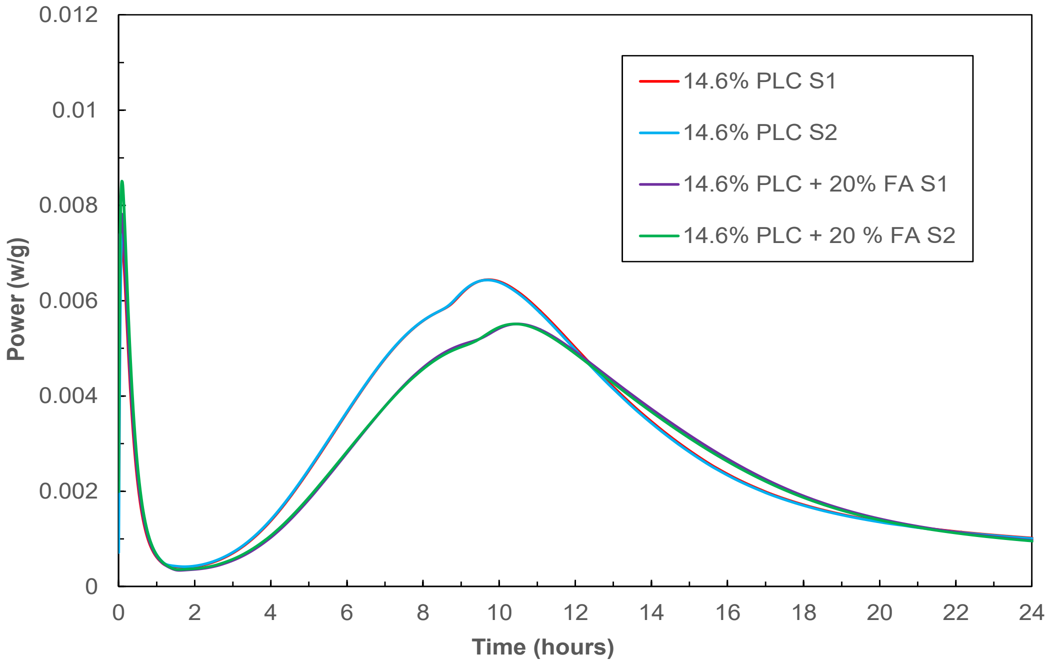

Figure 46: Isothermal calorimetry power graph of 14.6% PLC cement with fly ash

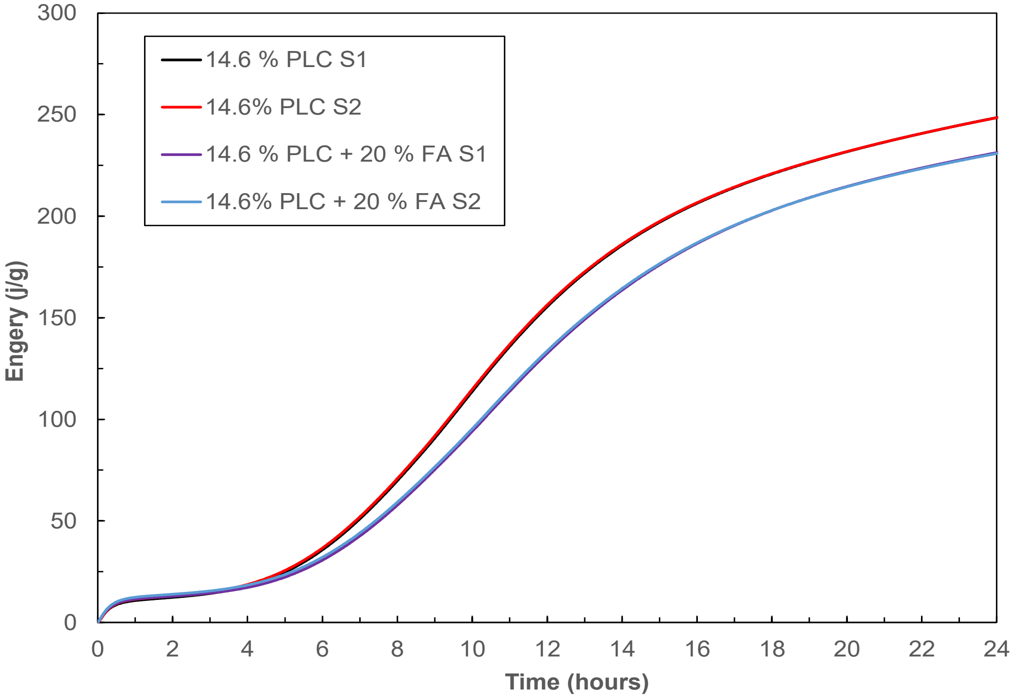

Figure 47: Isothermal calorimetry energy graph of 14.6% PLC cement with fly ash

6 RECOMMENDATIONS

6.1 Recommendations

6.1.1 Use of Type IL and IT cements

SDDOT should allow the use of Type IL and IT cements as specified in ASTM C595 and AASHTO M240 with up to 15% limestone by mass. These cements must meet limits specified in ASTM C595 and AASHTO M240 for moderate sulfate (MS) or high sulfate (HS) resistance if used in sulfate environments.

This recommendation is based on the extensive literature review and experimental testing conducted in this report. Although it was shown that PLCs can exhibit poor sulfate attack performance, it was also shown that PLCs can have high sulfate attack resistance depending on the cement properties. In this study, Type I/II and Type V cements also exhibited poor sulfate attack performance and were used as the base cements for the PLC blends. Using a more sulfate-resistant base cement prior to the addition of limestone would likely have improved their performance.

In the SDDOT Standard Specifications for Roads and Bridges, the following sections could be modified to include Type IL and IT cements instead of Type I, II, or V cement:

- "380.2 MATERIALS, Part A. Cement: Type II cement shall be used for all concrete pavement."
- "460.2. Section 750. Type II cement shall be used, unless otherwise specified."
- "462.2. Section 750. Type II cement shall be used, unless otherwise specified."
- "550.2 A Cement: Section 750, Type I cement"
- "560.2 6. Cement: Section 750, Type II cement shall be used, unless otherwise specified. For pretension prestressed concrete beams, Type I, II, or III cement may be used."
- Section 750.

Two examples of state DOT specifications including PLCs are included in Appendix C and D.

6.1.2 Cement testing

Sulfate attack testing on Type IL and IT cements using ASTM C1012 should occur yearly at a minimum.

It is recommended that any Type IL or IT cement must be tested using ASTM C1012 prior to their use in aggressive sulfate environments and meet specified limits. SDDOT must ensure that the cements are sulfate-resistant on a yearly basis. Current PLCs produced locally do not meet these specifications as evidenced in this research.

6.1.3 Fly ash content

For cements used in applications with sulfate exposure, the use of 20-25% Class F fly ash is recommended.

The use of Class F fly ash can be an effective strategy to reduce sulfate attack. However, in this study the addition of fly ash did not significantly improve the sulfate attack performance for certain PLCs. This is potentially due to its moderately high calcium content.

6.1.4 Pozzolan blend testing

The use of fly ash alone may not reduce sulfate attack expansion of certain cements to below specified limits, which warrants the testing of blends using fly ash and an additional pozzolan for sulfate resistance.

It is recommended that SDDOT research the allowance of fly ash to be used in combination with an additional pozzolan such as silica fume or microsilex to improve performance. For example, CSA A3004-C8 recommends the use of >5% silica fume plus 20% Class F fly ash. Testing by ASTM C1012 can be used to evaluate the effectiveness of the sulfate resistance of pozzolan blends.

6.1.5 Blend classification

For cements with less than 5% limestone classified by ASTM C150 or AASHTO M85, the addition of one pozzolan should be classified as a binary blend and the addition of two pozzolans should be classified as a ternary blend. For cements with 5-15% limestone classified by ASTM C595 or AASHTO M240, the addition of one pozzolan should be classified as a ternary blend in accordance with the standard's nomenclature.

Type I-V cements are classified using the traditional nomenclature when adding pozzolans since the limestone in these cements is considered to be part of the cement. For PLCs with greater than 5% limestone, the limestone is classified as an additional filler material separate from the cement. Therefore, the addition of one pozzolan to a PLC is classified as a ternary blend.

6.1.6 Sulfate-resistant mixes

Specific guidance should be provided for developing sulfate-resistant concrete mixture designs in the SDDOT Standard Specifications for Roads and Bridges as recommended by ACI 201.2R. Concrete should be classified by severity of potential sulfate exposure and designed to protect against this exposure.

It is well known that the concrete mixture design and its method of placement and curing has a significant influence on its sulfate performance beyond the selection of an adequate cement type. The water-soluble sulfate content in soils should be tested for each project to measure the severity of sulfate exposure potential as defined by ACI 201.2R. Once the site is classified, the proper w/c, strength, and cement type can be selected for sulfate attack resistance. Additional mixture design requirements and measures for placement and curing should be specified based on guidance from this report.

7 RESEARCH BENEFITS

This research has provided a set of recommendations and guidelines for SDDOT that specify appropriate limits for limestone contents in PLCs for use in sulfate environments. Additionally, these guidelines have addressed the proper definitions of binary and ternary blends including limestone for use by SDDOT. This project has supported student research and increased the research capacity at SD Mines. Another benefit will be more sustainable infrastructure by improving concrete durability through these specification changes, which will lower the cost of maintenance and future infrastructure investments while also helping the environment. This will be particurlary true when SDDOT places concrete in sulfate attack-prone areas. This benefit could be defined as the increase in the longevity of a structure or road due to proper specification as compared to a structure or road that was designed without the specification changes (athough PLC concrete would likely not be poured in SD without the change in specifications). Ultimately, this research will increase the service life of transportation assets.

The sustainability of the SD infrastructure will also be increased by the use of PLCs, because part of the CO_2 and energy-intestive clinker phase is removed in the cement by the limestone. This could be defined and estimated by a life-cycle anlaysis (LCA), which was out of the scope of this research. The savings in CO_2 emissions could then be tracked for all PLC concrete poured in SD. As local cement manufacturers begin to only produce PLCs, SDDOT could also have a cost savings from this research by not having to ship ordinary cement from distant locations for their projects if PLCs are not yet allowed. This cost savings could be quantified by the difference in cost for freight shipping of cement from various locations compared to using local cement sources.

This research was warranted, because it will enable SDDOT to adapt to modern cement-making practices. There is a strong potential that PLCs may be the only available cements in the U.S. in the future. This research enables SDDOT to be prepared for this significant change.

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Appendix A: STATE DOT SURVEY ON PORTLAND-LIMESTONE CEMENT

Appendix B: Limestone Dosage and Magnesium Sulfate Concentration Calculation

B.1 Limestone dosage calculation

Based on the QXRD test results, the percent the amount of $CaCO_3$ in control Type I/II cement, calcitic limestone, and dolomitic limestone were 91, 95, and 9, respectively. According to ASTM C595 any blended cement must have to contain a minimum of 70% of $CaCO_3$. To meet this requirement in some blended mixes the amount of calcitic and dolomitic filler have been adjusted with the control Type I/II cement.

The mixes where only calcitic limestone has been used to make the blended cements already meet the ASTM C595 requirement as both contain over 70% of $CaCO_3$. Besides this, some adjustments have been performed in mixtures where both dolomitic and calcitic limestone are being used. The final proportions taken from each filler are presented in Table 1 and Table 2.

Table 1: Weight % $CaCO_3$ based on QXRD test results

Ingredients	Control Type I/II cement	Calcitic limestone	Dolomitic limestone
Wt. % $CaCO_3$	91	95	9

Table 2: Fraction of limestone filler in different blended mixtures

Name of the blends	Original cement	Calcitic limestone	Dolomitic limestone	Overall % $CaCO_3$
M-I-10.5C-4.1D	Type I/II	6.1	4.1	70.22
M-V-10.5C-4.1D	Type V	10.5	4.1	70.83

Sample Calculation:

$((4.4\times 91)/14.6) + ((6.1\times 95)/14.6) + ((4.1\times 9)/14.6)$
= 27.42% (control Type I/II) + 40.34% (calcitic limestone) + 2.46% (dolomitic limestone)
= 70.22 % of $CaCO_3$

B.2 Magnesium sulfate concentration calculation

According to ASTM C1012, 50 gm of sodium sulfate powder needs to be added in 1000 ml of water to make 5% sodium sulfate solution. The percentage of SO_4 in $NaSO_4$ is calculated as 67.62 % which has a concentration of 33808 mg/L (based on the molar mass calculation for example, $NaSO_4$ has a molar mass of 142 g where SO_4 contains 96.02 g and Na contains the rest of the amount). Similarly, the total molar mass of $MgSO_4$ is 120.32 g, where, SO_4 contains 79.8% of total mass. To make the sulfate concentration exactly same as Na (50 g used in 1000 mL of water to make 33808 mg/L) 42.36 g of total $MgSO_4$ has been calculated.

The detailed calculations are shown below:

$Mg \times 1 = 24.30$ g
$SO_4 \times 1 = 96.02$ g, where S = 32.06 g and O = 15.99 g
Thus, $SO_4 = (32.06 \times 1) + (15.99 \times 4) = 96.02$ g
Total molar mass of $MgSO_4$ = 24.30 g + 96.02 g = 120.32 g
% SO_4= (96.02/120.32) = 79.8%

By iteration 42.36 g has been selected to make SO_4 concentration of 33808 mg/L in Mg SO_4 solution.
SO_4 concentration = (79.8/100) × 42.36 g = 33808 mg/L

Appendix C: Nebraska DOT Standard Specification for Highway Construction, Section 1004 – Portland Cement

SECTION 1004 -- PORTLAND CEMENT

1004.01 -- Description

1. Portland cement is the binder in concrete, locking the aggregate into a solid structure. It is manufactured from lime, silica, and alumina (with a small amount of plaster or Gypsum).

2. Equivalent alkali is defined as the sum of the Sodium Oxide (Na_20) and the Potassium Oxide (K_20) calculated as Equivalent Alkali $Na_20_e = Na_20 + 0.658\ K_20$).

3. Interground and Blended cements consist of uniform intergrinding and/or blending of Portland cement clinker, Slag cement, Pozzolan and/or Limestone.

1004.02 -- Material Characteristics

1. Type I, Type II and Type III Portland cement shall conform to the requirements in ASTM C 150 with the following additional requirements:

    a. Portland cement shall not contain more than 0.60% equivalent alkali.

2. Interground and Blended Cement shall conform to the requirements in ASTM C 595 with the following additional requirements:

    a. Interground/Blended cement (Type IP)

        (1) For Type IP(25) shall be composed of Class F fly ash or Class N pozzolan replacement at 25% - 2%.

        (2) For Type IP(20) shall be composed of Class F fly ash or Class N pozzolan replacement at 20% + 2%.

    b. Interground/Blended cement (Type IS)

        (1) For Slag Cement, the maximum replacement shall be 35% +5 when incorporated into the final Interground/Blended cement.

    c. Interground/Blended cement (Type IT)

        (1) For Supplemental Cementitious Materials (SCMs), Slag cement and Limestone, the maximum replacement by weight shall be 40%. The manufacturer has a production tolerance of + 2% from the proposed replacement.

        (2) For Limestone cement, the replacement range shall be from 5.1% to 10.0% when incorporated into the final Interground/Blended cement.

    d. No additional SCMs, Slag cement and Limestone will be added at the batch plant.

1004.03 -- Procedures

1. The Contractor shall provide adequate protection for the Portland and Interground/Blended cement against dampness.

    a. Portland and Interground/Blended cement shall be hauled or stored in railroad cars, dry bulk trailers or in suitable moisture-proof buildings.

    b. The use of tarpaulins for the protection of the Portland and Interground/Blended cement will not be allowed.

2. No Portland and Interground/Blended cement which has become caked or lumpy shall be used.

3. Portland and Interground/Blended cement which has been spilled shall not be used.

4. Accepted Portland and Interground/Blended cement which has been held in storage at the concrete mix plant more than 90 days shall be retested.

5. Portland and Interground/Blended cement coming directly from the manufacturer shall not be used until its temperature is 150°F or less.

6. Portland cement having false set when tested in accordance with ASTM C 150 will not be used.

1004.04 -- Acceptance Requirements

1. Portland and Interground/Blended cements shall be on the Department's Approved Products List (APL).

2. The Contractor shall submit any new Portland and Interground/Blended cements to the Engineer to be approved for the APL with the following:

a. Material source information:

(1) Mill Location

(2) Type of Portland and Interground/Blended cements

(3) Grinding Period

(4) Associated Manufacture Product Name

(5) Provide source and type of each SCMs and/or Slag Cement used for final product.

(i) The Department will allow the use of ASTM C 1697.

(a) When two or more SCMs and/or Slag Cement are pre-blended, the Contractor shall report chemical composition analysis of the final blend.

(b) The final blend shall be reported as per ASTM C 1697, Paragraph 4.

(6) Portland cement shall conform to ASTM C 150.

(7) Interground/blended cements shall conform to ASTM C 595.

(8) Provide total cementitious materials replacement per ASTM C 595.

(9) Report test results per ASTM C 1567 at 28-days.

3. Alkali Silica Reaction Requirements and Testing:

a. Interground/Blended cement shall be tested according to the provisions of ASTM C 1567.

(1) The mortar bars shall be composed of Type IP, IS or IT Interground/blended cement and sand and gravel from an approved Platte River Valley-Saunders County source.

(i) When Elkhorn River-Madison County source or an out of state aggregate source is being used on a project, the Elkhorn River or an out of state aggregate source shall be used in lieu of the Platte River Valley-Saunders County source.

(ii) When Contractor proposes a change of aggregate source, then the new aggregate source shall be tested by ASTM C 1567.

(2) The mortar bars for the ASTM C 1567 shall not exceed 0.10% expansion at 28 days.

4. Portland and Interground/Blended cements will be placed on the Department's Approved Products List based on the conformance with the Department's Acceptance Policy for Portland and Interground/Blended Cements.

1004.05 -- Sampling and Testing Requirements

1. All Portland and Interground/Blended cements shall be sampled and tested at the rate described in the Department's Materials Sampling Guide.

a. The Department will inform the Contractor when a sample is required.

b. A sample shall be taken by a Contractor's Certified Portland Cement Sampler and must be under the supervision of Department certified personnel.

c. The sample shall be taken at the plant from a bulk shipment of a rail car, dry bulk trailer, batch plant silo or from the line between the bulk truck and the silo. Upon sampling, the Department will take immediate custody of the sample.

2. Noncompliant material shall be tested in accordance with ASTM C 1567 and in accordance with Section 1004.04, Paragraph 3.a. (1).

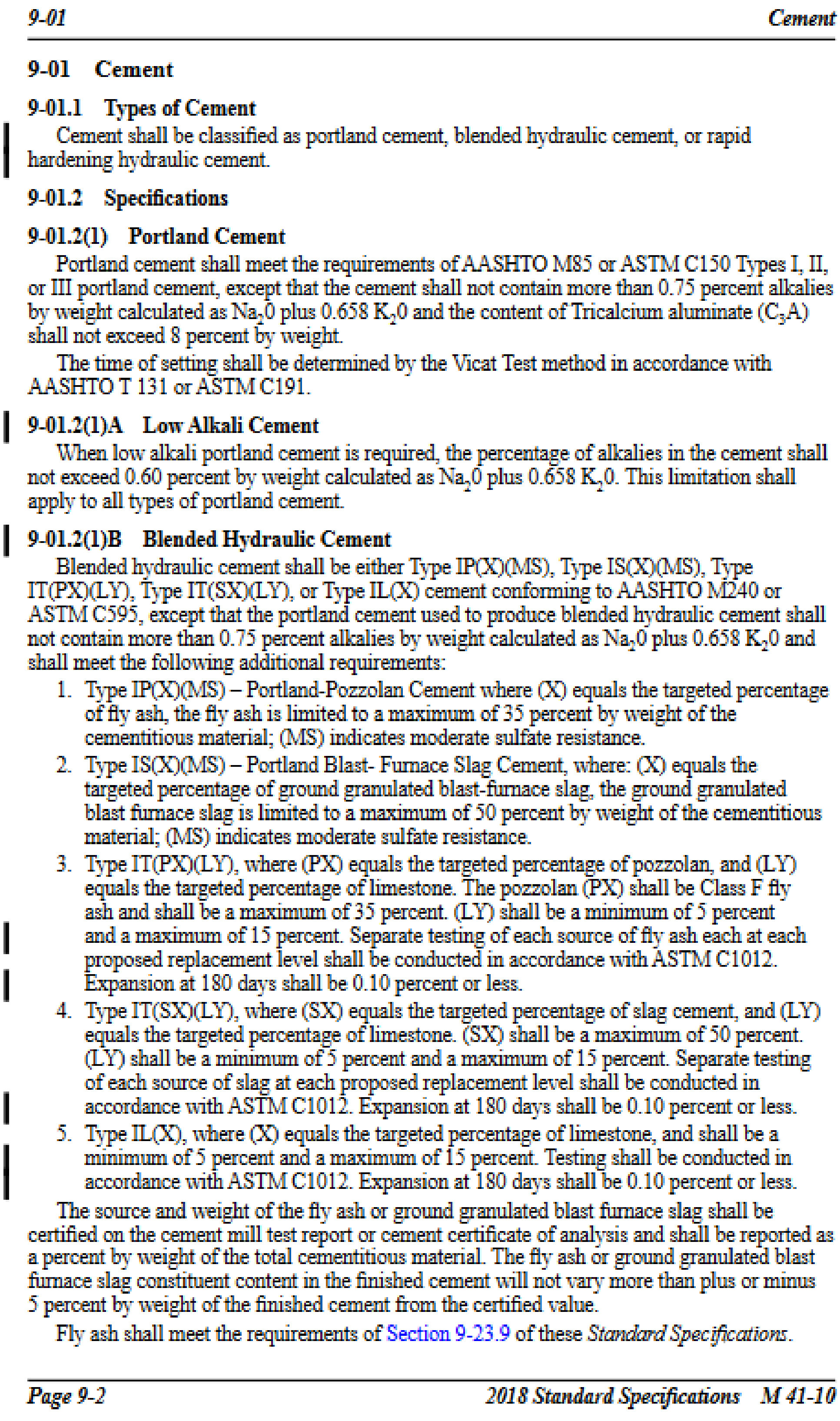
a. The mortar bars for the ASTM C 1567 shall not exceed 0.10% expansion at 28 days.

b. If the expansion is greater than 0.10% at 28 days, then the Interground/Blended cement shall be subject to removal, 40% pay and/or removal from the Department's APL in accordance with Department's Acceptance Policy on Portland and Interground/Blended Cements.

3. Noncompliant material from the mill, terminal or project will be temporarily removed from the Approved Products List pending further investigation.

4. If the noncompliant Portland or Interground/Blended cement is removed from the Department's Approved Products List, all shipments from the supplier will be held until the investigation of the failing samples have been completed by the Department's Materials and Research Division.

Appendix D: Washington State DOT Standard Specifications, 9-01 – Cement



9-01 *Cement*

9-01 Cement

9-01.1 Types of Cement

Cement shall be classified as portland cement, blended hydraulic cement, or rapid hardening hydraulic cement.

9-01.2 Specifications

9-01.2(1) Portland Cement

Portland cement shall meet the requirements of AASHTO M85 or ASTM C150 Types I, II, or III portland cement, except that the cement shall not contain more than 0.75 percent alkalies by weight calculated as Na$_2$0 plus 0.658 K$_2$0 and the content of Tricalcium aluminate (C$_3$A) shall not exceed 8 percent by weight.

The time of setting shall be determined by the Vicat Test method in accordance with AASHTO T 131 or ASTM C191.

9-01.2(1)A Low Alkali Cement

When low alkali portland cement is required, the percentage of alkalies in the cement shall not exceed 0.60 percent by weight calculated as Na$_2$0 plus 0.658 K$_2$0. This limitation shall apply to all types of portland cement.

9-01.2(1)B Blended Hydraulic Cement

Blended hydraulic cement shall be either Type IP(X)(MS), Type IS(X)(MS), Type IT(PX)(LY), Type IT(SX)(LY), or Type IL(X) cement conforming to AASHTO M240 or ASTM C595, except that the portland cement used to produce blended hydraulic cement shall not contain more than 0.75 percent alkalies by weight calculated as Na$_2$0 plus 0.658 K$_2$0 and shall meet the following additional requirements:

1. Type IP(X)(MS) – Portland-Pozzolan Cement where (X) equals the targeted percentage of fly ash, the fly ash is limited to a maximum of 35 percent by weight of the cementitious material; (MS) indicates moderate sulfate resistance.
2. Type IS(X)(MS) – Portland Blast- Furnace Slag Cement, where: (X) equals the targeted percentage of ground granulated blast-furnace slag, the ground granulated blast furnace slag is limited to a maximum of 50 percent by weight of the cementitious material; (MS) indicates moderate sulfate resistance.
3. Type IT(PX)(LY), where (PX) equals the targeted percentage of pozzolan, and (LY) equals the targeted percentage of limestone. The pozzolan (PX) shall be Class F fly ash and shall be a maximum of 35 percent. (LY) shall be a minimum of 5 percent and a maximum of 15 percent. Separate testing of each source of fly ash each at each proposed replacement level shall be conducted in accordance with ASTM C1012. Expansion at 180 days shall be 0.10 percent or less.
4. Type IT(SX)(LY), where (SX) equals the targeted percentage of slag cement, and (LY) equals the targeted percentage of limestone. (SX) shall be a maximum of 50 percent. (LY) shall be a minimum of 5 percent and a maximum of 15 percent. Separate testing of each source of slag at each proposed replacement level shall be conducted in accordance with ASTM C1012. Expansion at 180 days shall be 0.10 percent or less.
5. Type IL(X), where (X) equals the targeted percentage of limestone, and shall be a minimum of 5 percent and a maximum of 15 percent. Testing shall be conducted in accordance with ASTM C1012. Expansion at 180 days shall be 0.10 percent or less.

The source and weight of the fly ash or ground granulated blast furnace slag shall be certified on the cement mill test report or cement certificate of analysis and shall be reported as a percent by weight of the total cementitious material. The fly ash or ground granulated blast furnace slag constituent content in the finished cement will not vary more than plus or minus 5 percent by weight of the finished cement from the certified value.

Fly ash shall meet the requirements of Section 9-23.9 of these *Standard Specifications*.

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Ground granulated blast furnace slag shall meet the requirements of Section 9-23.10 of these *Standard Specifications*.

Limestone shall meet the requirements of AASHTO M240 or ASTM C595.

9-01.2(2) Rapid Hardening Hydraulic Cement

Rapid hardening hydraulic cement shall meet the requirements of ASTM C 1600.

9-01.3 Tests and Acceptance

Cement may be accepted by the Engineer based on the cement mill test report number or cement certificate of analysis number indicating full conformance to the Specifications. All shipments of the cement to the Contractor or concrete supplier shall identify the applicable cement mill test report number or cement certificate of analysis number and shall be provided by the Contractor or concrete supplier with all concrete deliveries.

Cement producers/suppliers that certify portland cement or blended hydraulic cement shall participate in the Cement Acceptance Program as described in WSDOT Standard Practice QC 1. Rapid hardening hydraulic cement producers/suppliers are not required to participate in WSDOT Standard Practice QC 1.

Each mixing facility or plant utilizing portland cement shall be equipped with a suitable means or device for obtaining a representative sample of the cement. The device shall enable the sample to be readily taken in proximity to the cement weigh hopper and from a container or conveyor holding only cement.

Cement may be tested using samples taken at the job site by the Engineer for submission to the State Materials Laboratory for testing.

9-01.4 Storage on the Work Site

At the request of the Engineer, the Contractor shall provide test data to show that cement stored on site for longer than 60 days meets the requirements of Section 9-01. Tests shall be conducted on samples taken from the site in the presence of the Engineer. Test results that meet the requirements of Section 9-01 shall be valid for 60 days from the date of sampling, after which the Engineer may require further testing.