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The Use of Limestone in Portland Cements: Effect on Thaumasite Form of Sulfate Attack

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INTRODUCTION

This paper discusses the use of limestone as a component of portland cements, particularly in relation to the risk of sulfate attack due to thaumasite formation. This form of sulfate attack requires a source of carbonate ions, and concerns have been raised that the use of limestone in portland cement could increase the vulnerability of concrete to attack.

USE OF LIMESTONE IN PORTLAND CEMENT

The use of limestone as a component of portland cement is now common practice in Canada and Europe. In Europe limestone contents can be as high as 35%. Such practice is not permitted by standards governing cement manufacture in the U.S.A.; however, it is currently being proposed to allow up to 5% limestone in cements meeting ASTM C 150.

Use of Limestone in Canadian Portland Cements

After testing (unpublished data from CSA committee members) of both cement and concrete properties in the late 1970’s, to evaluate the influence of 5% limestone in portland cements, the 1977 version of CSA A5-M77 was amended in November 1980 to allow “a maximum of 5% addition of limestone” to normal portland cement (CSA Type 10, equivalent to ASTM Type I). Use of limestone at some plants started immediately. In the next revision to the standard, limestone was permitted in high-early strength cement (CSA Type 30, equivalent to ASTM Type III).

After 22 years of extensive use in the cold Canadian climate, which would tend to favor any potential thaumasite problems, there have been no cases of Thaumasite Sulfate Attack (TSA) related to the use of limestone in cement. In fact, the only reported case of TSA in Canada from concretes made since 1980 (Bickley, et al 1990) did not involve the use of cement with limestone, but rather a “sulfate-resisting” cement meeting CSA Type 50 and API Type G cement.

Limestone in European Cements

The use of limestone in portland cement was common and accepted practice in France in the 1980’s (Hawthorn, 1989), whereas even minor amounts of other constituents was not permitted by British Standards until 1991. A BRE Working Party was formed to examine the effect of
limestone on the performance of cement and concrete (Matthews, 1989). A comprehensive testing program was initiated by the members of the Working Party, to determine the effect of limestone at levels of 5% and 25% on the performance of concrete. A paper reporting the 5-year data (Matthews, 1994) concluded that the “… performance of cements containing 5% limestone is, overall, indistinguishable from that of OPC without additions, vindicating the decision to permit such additions under British Standards.”

In the European Standard, EN 197-1 *Cement – Part 1: Composition, specifications and conformity criteria for common cements*, all 27 common cement products defined are permitted to contain up to 5% of minor additional constituents (macs) which can be limestone. In addition to permitting limestone as a mac in other types of cement, EN 197-1 also covers portland-limestone cement, which may contain up to 20% limestone when designated as a CEM II/A cement or up to 35% limestone as a CEM II/B cement. It is not permitted to use limestone as a mac in portland-limestone cement.

The European Standard covering concrete, EN 206-1 *Concrete. Part 1: Specification, performance, production and conformity*, does not specify the types of cement that are permitted in various classes of chemical (sulfate) exposure. Instead, it simply refers to “sulfate-resisting cement,” which is intended to cover all cement types recognized as being sulfate resistant. However, there is as yet no European Standard for sulfate-resisting cements, as it has not been possible to achieve consensus among the member countries regarding the cement types to be included. This issue is therefore dealt with on a national basis. In the UK, blastfurnace cements, CEM III/B, with 66-80% slag, portland-fly ash cements, CEM II/B-V, with more than 25% fly ash, and pozzolanic cements, CEM IV/B, with no more than 40% fly ash, are all permitted in the most severe sulfate class, although fly ash cements are excluded in some situations where the magnesium ion concentration in the groundwater exceeds 1 g/L. The use of macs (≤ 5%) is permitted in the manufacture of all these cement types. Sulfate-resisting portland cement (SRPC) is also permitted in this exposure class. In the U.K. the governing standard for SRPC is BS 4027 (1996) *Specification for sulfate-resisting portland cement*, which does not permit any additional constituents. Portland-limestone cements (e.g. cements with more than 5% limestone) are only permitted for use in the lowest (i.e. most benign) sulfate exposure class in Europe and the U.K.

**SULFATE ATTACK**

**The Ettringite (Classical) form of Sulfate Attack**

The conventional form of sulfate attack, that occurs when concretes are exposed to ground waters or soils containing calcium, sodium and/or magnesium sulfates in solution, is reasonably well understood. All of these sulfates will react with C₃A, hydrated aluminates, or monosulfate (C₃A·CaSO₄·12H₂O) to form ettringite (C₃A·3CaSO₄·31H₂O), resulting in expansion and cracking of mature concrete. In addition, sodium sulfate will react with calcium hydroxide in the paste to form gypsum, which may cause damage in itself or react with monosulfate to form ettringite. Magnesium sulfates are far more aggressive to concrete since, in addition to attacking the aluminates, they will attack and decalcify the C-S-H matrix, forming gypsum, brucite, and hydrous silica. This results in loss of strength and softening of the affected areas.
Mitigation of these forms of sulfate attack is achieved by designing concrete with low permeability (i.e. low w/cm, well compacted and cured), and either limiting the amount of C₃A in the portland cement (i.e. Type II or V) or by use of an adequate cement replacement of tested pozzolans or slag (or by use of similar materials in the form of blended cements).

The Thaumasite form of Sulfate Attack (TSA)

Thaumasite is a calcium-silicate-sulfate-carbonate hydrate (CaSiO₃·CaCO₃·CaSO₄·15H₂O) that can form in concrete by reaction of the calcium-silicate hydrates (C-S-H) with sulfates in the presence of carbonate ions. The process only occurs in very wet environments and the rate of formation is increased at low temperatures. It should be noted that in all of the laboratory and field cases reported, the sulfates for this reaction come from external sources. The conversion of C-S-H into thaumasite results in a loss of binding material and hence the integrity of the concrete (or other cement-based material), however, the formation of thaumasite is not always damaging and a recent report from the Thaumasite Expert Group (1999) in the U.K. introduced the following terminology:

<table>
<thead>
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<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>TSA</td>
<td>Thaumasite form of Sulfate Attack</td>
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<tr>
<td>TF</td>
<td>Thaumasite Formation</td>
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</table>

TSA is a relatively rare form of sulfate attack and risk of its occurrence is thought to be negligible unless the following conditions are met (Thaumasite Expert Group, 1999):

- Presence of sulfates and/or sulfides in the ground,
- Presence of mobile groundwater,
- Presence of carbonate, generally in the concrete aggregates,
- Low temperatures (generally below 15°C).

However, Sims and Huntley (2002) recently presented a series of cases where TSA had occurred without all four of the above conditions being fully met, and other workers have provided evidence that TSA may occur in concrete containing siliceous aggregates where the source of the carbonate was the groundwater, and not the cement (French, 2000), while TF can occur in concrete stored at temperatures above 15°C (Brown and Hooton, 2002), and possibly even concrete with no access to external sulfate (Hartshorn and Sims, 1998). Also in some cases the source of carbonate has been identified as acidic, carbonate-bearing groundwaters (Hagelia et al, 2001). It has been argued (Crammond, 2002b) that the apparent scarcity of TSA is partly attributed to the following: (i) the conditions of most standardized sulfate resistance tests do not favor thaumasite formation, (ii) forensic examinations may have failed to detect TSA in deteriorated concrete, and (iii) buried concrete is rarely inspected. Rogers et al (1997) reported a
case of TSA in an old aqueduct, where previous investigations had wrongly attributed the deterioration to classical sulfate attack involving ettringite formation.

As with conventional sulfate attack, the rate of TSA can be slowed by producing low w/cm concrete with low-permeability properties, to reduce the rate of ingress by sulfate solutions. There is also evidence that use of pozzolans and slag may help, at least in as much as they contribute to lowering permeability. It is reported that ground-granulated blast-furnace slag as a partial cement replacement will help mitigate damage due to TSA, at least at 70 % replacement (Higgins, 2002; Higgins and Crammond, 2002). The use of 7 % metakaolin also appears to help (Smallwood et al, 2002). In all these cited cases, the carbonate source was from the aggregates.

**ROLE OF LIMESTONE AND TSA**

The recent discovery in the U.K. of severe deterioration in a number of buried concrete foundations containing carbonate aggregates has raised concerns about the effect of limestone in cement on the performance of concrete in sulfate environments. In these cases the concrete produced would have satisfied the prevailing recommendations for sulfate resistance at the time (e.g. BRE Digest 363 and BS 5328), but the deterioration was diagnosed as being the result of the thaumasite form of sulfate attack (TSA) rather than “classical” sulfate attack. The vulnerability of the concrete to TSA was ascribed to the presence of carbonate aggregate (Thaumasite Expert Group, 1999; Crammond, 2002a). However, in some of these cases, it must be noted that high levels of sulfates were not detected in the original undisturbed soils, but they did contain sulfides, which oxidised during the construction process to form sulfates. The role of carbonate in portland cement is discussed in greater detail below.

**Performance of “Limestone-Filled” Cements (more than 5% limestone)**

Part of the long-term study performed by the U.K. Working Group on limestone in cement included studies on sulfate resistance (Matthews, 1994). Concretes were produced with a range of portland cements, with C₃A contents ranging from 5.3% to 13.1% (by Bogue) and limestone contents of 0, 5 or 25%, and exposed to solutions of sodium sulfate (1.5% SO₃) or magnesium sulfate (0.35% and 1.5% SO₃) at 20°C (68°F). There was no consistent difference in the performance of concrete after 2 and 5 years with the limestone content of the portland cement, but as expected, a strong correlation was found between performance and the C₃A content of the cement. However, because of the poor performance exhibited by the cement with the highest C₃A and at a 25% limestone content, and the detection of thaumasite in most of the concretes produced with so-called “limestone-filled cements” (meaning more than 5% limestone), a recommendation was made that limestone-filled cements not be used beyond Class I sulfate conditions (i.e. when SO₄ content of groundwater exceeds 0.4 g/L or SO₄ content of a 2:1 water-soil extract exceeds 1.2 g/L). There is no such restriction on cements containing up to 5% limestone.

Later studies on concrete stored in sulfate solutions at 5°C (41°F) indicated little difference in the performance of concrete produced with high-C₃A (~ 10%) portland cement with and without 15% limestone (Barker and Hobbs, 1999). However, the mode of attack was different with
thaumasite and ettringite being the principle reaction products for the cements with and without limestone, respectively. Other workers have demonstrated that the presence of amounts of limestone in the range from 10% to 20% can change the dominant reaction product from ettringite to thaumasite (Borsoi et al, 2002; Justnes, 2002), but the impact of the limestone on physical deterioration in these studies is not clear.

The most recent work at the Building Research Establishment indicates that limestone-filled cements (typically containing much greater than 5% limestone) are the “least TSA-resistant binder types investigated” (Crammond, 2002b). These results are confirmed in laboratory studies conducted at Sheffield University in the UK (Hartshorn et al, 1999; 2001; 2002; Kakali et al, 2002; Torres et al, 2002).

**Performance of Portland Cements with 5% Limestone or Less**

A study conducted at the Building Research Establishment (BRE) concluded that 5% limestone had a marginal adverse impact on the sulfate resistance of mortars stored in cold Class 4 magnesium sulfate conditions (Halliwell et al, 1996). After much deliberation over the BRE data, the Thaumasite Expert Group (1999) concluded that “… this relatively low level of carbonate material will not adversely affect the PC’s performance in concretes containing either siliceous or carbonate aggregates”. It was pointed out that the use of 5% limestone in portland cement roughly translates into just 1% limestone by mass of aggregate even in a relatively cement-rich concrete mixture. Also, given that companies would have to target a lower addition rate to stay within the 5% proposed limit, the 1% by mass of aggregate value mentioned above would almost be halved.

From research in North America, the effect of using up to 5% limestone on conventional sulfate-resistant properties of portland cements has been shown not to be detrimental. Hooton (1990) tested a Type II cement with and without 2.6% limestone and found that, while both cements expanded less than the 6-month 0.10% limit in ASTM C 1012, the 2.6% limestone cement expanded less and had only half the expansion after one year. Taylor (1998) tested two Type V cements with and without 3% limestone using ASTM C 452 in two different labs. The results showed no significant difference in 14-day expansions due to the use of limestone. Equal to improved results were obtained when these same limestone levels in Type V cements were tested using ASTM C 1012 (Taylor, 2001).

Taylor (1998) also showed that there was no significant difference in C 452 tests when a Type II cement had 0, 2.5, 3.0, 3.5, or 5.0% limestone, with 14-day expansions of less than 0.03% in all cases. Later, Taylor (1999) found that the performance of these Type II cements using ASTM C 1012 was also unaffected.

Taylor (1998) also reported on concrete tests done by Matthews in the UK (Matthews 1994). The residual strengths of 100-mm concrete cubes were measured after 1, 2, and 5 years exposure in both sodium and magnesium sulfate solutions. In all exposures, after 5 years, the 5% limestone cement retained higher strengths than the control cement without limestone.
The use of limestone at levels of 2.75 and 5.50% were evaluated as part of PCA’s long-term test program to evaluate concrete performance in sulfate soils (Stark, 2002). The conclusion from this study was that “… limestone [in] Type I portland cement resulted in performance similar to the concrete mixture with no addition”. After 8 years the concretes with and without limestone all recorded a visual rating of 5 (worst rating) and the poor performance is attributed to the high C\textsubscript{3}A content (~ 13%) of the portland cement.

The most recent data published by a group of researchers at Sheffield University (Torres et al. 2002) concluded that even a small amount of limestone, just 5%, significantly impacted the performance of 8.5% C\textsubscript{3}A cement mortars exposed to a strong solution of 1.8% MgSO\textsubscript{4} at 5°C for 5 years. However, close reading of this report reveals that during the last year the storage condition was not maintained and the solution was permitted to evaporate exposing the mortar bars to concentrated solutions and atmospheric CO\textsubscript{2} as the bars slowly dried out. Prior to this, reports from the same group (e.g. Hartshorn et al. 2001; 2002) indicated that only small amounts of thaumasite were formed in the mortar with 5% limestone and engineering properties were not much affected. It is not clear to what extent the uncontrolled storage conditions influenced the performance of these mortars, but it is of interest that the control specimens (with no limestone) also deteriorated during this last year’s storage and that there was evidence of thaumasite (or ettringite-thaumasite solid solution) formation in these bars. Thomas et al (1993; 2002) reported evidence of deterioration due to TSA in mortar bars produced with CSA Type 50 sulfate-resisting cement (without limestone) when the bars were exposed to wet-dry cycling in sulfate solutions, the thaumasite forming in the carbonated surface layers of the mortar.

**SUMMARY**

Field experience with up to 5% limestone in portland cement in Canada and Europe for over 20 years has not produced any known cases where this has contributed to thaumasite sulfate attack. Based on the literature reviewed, there does not appear to be any significantly increased susceptibility to sulfate attack with respect to use of up to 5% limestone in portland cements. Research does exist concerning much higher levels of limestone (15 to 35%, or where the carbonate fines originate from the aggregate), where used in cold temperatures combined with wet and aggressive sulfate environments, that indicates more susceptibility to the thaumasite form of sulfate attack. Overall, the data available support the proposal to permit use of up to 5% limestone in portland cements.

**ACKNOWLEDGEMENTS**

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REFERENCES


