Pulverised Fuel Ash and Preventing the Thaumasite Form of Sulfate Attack

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Abstract

Since its formation the UKQAA has been involved with numerous research projects looking at the thaumasite form of sulfate attack. These have investigated the effects of aggregate type, cement type, proportions of secondary materials such as pulverised fuel ash (PFA), oxidation conditions of pryritic clay, etc. The majority of this work has been carried out at 5C, the optimum temperature at which this deleterious reaction between sulfate and the cement hydration products occurs. The laboratory investigations at such low temperatures disadvantage pozzolanas such as PFA because of the sensitivity of the pozzolanic reaction to changes in temperature. Although laboratory findings are not reflected in concrete in real situations, they have resulted in a very conservative approach in specifications with regard to the use of PFA in situations where thaumasite may be a problem.

In order to address this issue, the UKQAA funded a three year laboratory programme commencing in August 2004 to investigate the effects of using an annual cyclic temperature profile as would be found 1m down into the soil. This was designed to replicate the true risks of thaumasite attack on concretes containing different proportions of ash. This paper will review the findings of the various projects carried out on the thaumasite form of sulfate attack and the one year results of the laboratory programme using temperature cycling.

Introduction

Thaumasite is a naturally occurring, though rare, mineral found in metamorphosed rocks that have undergone hydrothermal change, see figure 1. The formula is generally accepted as $CaSiO_3.CaCO_3.CaSO_4.15H_2O$ and its formation only occurs at lower temperatures. Bensted and Varma[1] in 1974 reported on the structure, properties and methods of detecting this mineral in detail. Because its structure is similar to that of carbonated ettringite many incidents of sulfate attack have probably been assigned to 'normal' sulfate attack rather than to thaumasite. However, ettringite formation results in expansion, whereas thaumasite destroys the cementing components, forming a soft, powdery material.

The first reported case of thaumasite in a concrete structure was in 1965[2]. However, by the mid 1980's it was recognised that thaumasite represented a potentially serious mechanism for sulfate attack on concrete and some cases of deterioration were being assigned to thaumasite.

Figure 1 – A specimen of naturally occurring thaumasite

Subsequently it was discovered, from the 1990's, in concrete structures around the world, though predominantly in the UK. During February 1998[3] bases for a bridge structure at Tredington-Ashchurch on the M5 motorway were found to be badly damaged by sulfate attack. The resulting white, soft material was diagnosed as thaumasite that had caused considerable reduction in the supporting columns' thicknesses by the loss of 70mm of concrete. Subsequently many other bridges in the M5 corridor have been found to have varying degrees of deterioration that have been considered to be due to the thaumasite form of sulfate attack. As a result a programme of investigation, strengthening and repairs was instigated on all the bridges in the M5 corridor.

The M5 Bridge problems all seemed to be associated with the presence of pyritic clays, known as the Lower Lias clay, which coincidently exists along most of the route of the motorway. These bridges were built in the mid 1960's and the concrete was found to be of high strength (60MPa); the aggregates were limestone and Portland cement had been used. The concrete mix design complied with the appropriate class sulfate based on the recommendations given at the time.

As thaumasite formation is not dependant on the presence of C_3A in the cement, even the traditional C_3A reduced cements known as 'Sulfate Resisting Portland Cement' (SRPC) are not immune. There were also examples of failures of SRPC based concrete, so as a result the thaumasite issue had the potential to be a major problem.

It could be seen from the M5 bridges and other cases that this could prove disastrous for the UK building stock if thaumasite attack was more commonplace than previously believed. As a result an extensive programme of research was funded by the UK government mainly with BRE. An expert group of researchers, specifiers, etc was convened and a report[4] summarising their deliberations, remedial measures and prevention was published in 1999. This was followed by a more detailed document being published by BRE, Special Digest 1[5] in 2001. Both of these documents advised on using lower water/cement ratio and higher minimum cement content concretes then ever before to resist the various classes of sulfates. In addition the method of assessing available sulfates was considerably improved, particularly in respect of the oxidation of pyrites found in some clay. BRE Special Digest 1 has been revised again in 2003[6] and in 2005[7], refining the requirements in response to ever greater understanding resulting from research.

UK Research into Thaumasite

Bensted and Varma had shown how to synthesize thaumasite, its structure, etc. Recreating the reactions in concrete in the laboratory required working at lower temperatures than the norm of 20C. The optimum temperature for the formation of thaumasite is 5C; however, it can form below 15C.

Burton[8] between 1975 and 1980 was probably one of the first researchers to see the deleterious effects of the thaumasite form of sulfate attack in a laboratory without knowing it. He had produced a series of concrete mixes containing Portland Cement (PC), Sulfate Resisting Portland Cement (SRPC) and various Pulverised Fuel Ash (PFA) blends. Samples from these concretes had been stored in tanks of magnesium or sodium sulfate solutions. After a period of five years many of the PC and SRPC samples had seriously degraded, however, the PFA blends had performed very well – see figure 2.

It transpired the storage tanks were not heated and went through the normal external temperature cycles over the period, including freezing. It is now believed these results demonstrate thaumasite attack occurred as the photographs show the same characteristics as found in recent work.

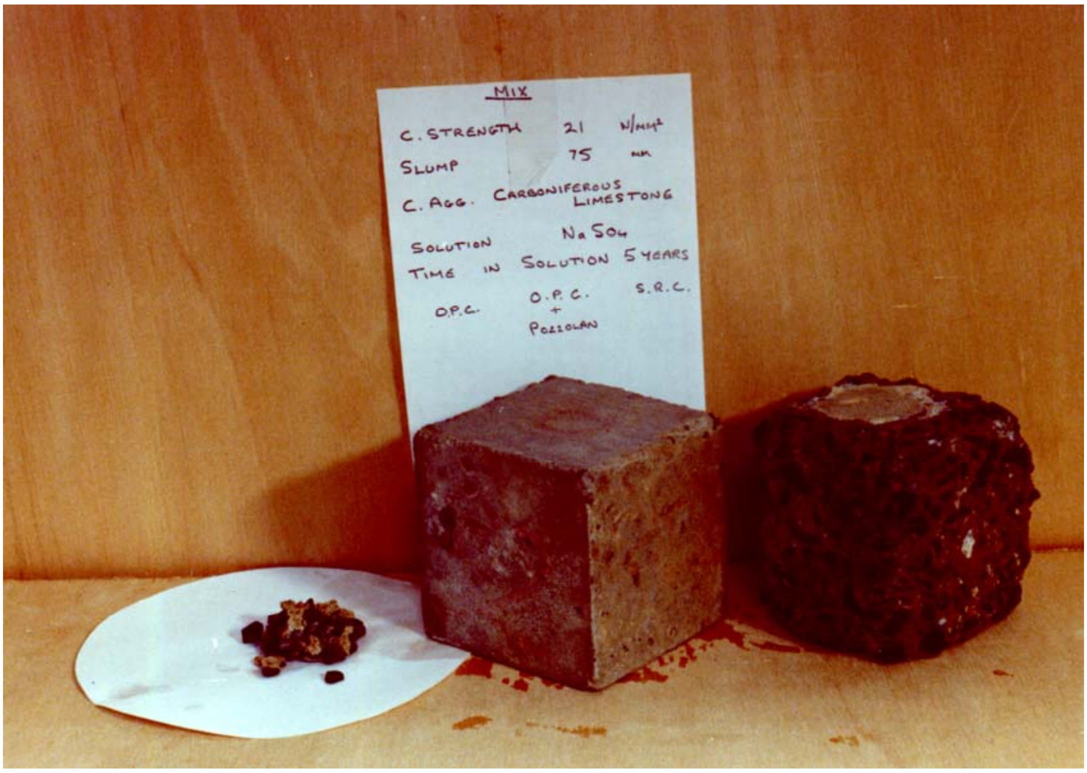


Figure 2 – In 1980 the deterioration of the PC (Left) and SRPC (right) mix could not be explained. However, the PFA blend (centre) performed well.

As a result of government funding, Crammond and Halliwell[9] of BRE carried out a considerable amount of work on the thaumasite issue during the mid 1990's, including investigating the M5 bridge problems, replicating the reactions in laboratory samples, etc. Further research was funded by the Ground Granulated Blastfurnace Slag industry and again Crammond & Halliwell[10] looked at various cementitious types in some detail and particularly the benefits of using GGBS. This work concluded that at higher blend ratios (70% GGBS) no deleterious attack occurred. They also concluded that the presence of carbonate aggregates was critical to the reaction occurring, Sulfate Resisting Portland Cement (SRPC), Portland cement and Portland/Pulverised Fuel Ash (PFA) blends all performed badly, the latter particularly badly at 25% PFA content.

During this period of research, the mechanisms of the thaumasite form of attack in concrete were not clearly understood. It was suggested that the attack on the M5 bridge structures began as sulphuric acid attack, followed by ettringite, carbonation, etc. The principal was the pyrites from the Lower Lias clay oxidised when the clay was dug out in order to construct the bridge bases. This clay was exposed to the air for a period of ~6 months before being backfilled against the newly formed bridge structures. The theory was the sulphuric acid, formed from the oxidation process, caused the initial damage and thaumasite was only a secondary product formed thereafter. Another theory was that ettringite had to form first and thaumasite was a subsequent reaction product produced after the ettringite had caused the damage. Whatever was the process there did seem to be some inconsistencies in respect of PFA.

Byars, Cripps et al[11] from Sheffield University, between 2000 and 2003, looked more specifically at whether sulphuric acid attack was a precursor of thaumasite attack. They investigated the chemistry of the pyritic clays when exposed to oxidation, whether they could produce a significant amount of acid to dissolve the concrete. As it transpired, the natural carbonate within the pyritic clays was more than sufficient to neutralise oxidised pyrites, however, this did result in readily available carbonic acid. In addition they reproduced a range of concrete mixes in a variety of sulfate conditions held at 5C. The cementitious types were ranked in the following order (poorest first); Portland cement, Portland Limestone Cement (20% Limestone), Portland Fly ash (25% fly ash), Sulfate Resisting Portland Cement and Ground Granulated Blastfurnace Slag Cement (65% GGBS). However, a further test was carried out using a column made of the four main cement types using pyritic clay surrounding it in a pseudo real structure again held at 5C as shown in figure 3.

Figure 3 – Byars, Cripps et al, Sheffield University simulation of concrete exposed to pyritic clay

In this case the PLC suffered very quickly, deteriorating significantly after 6 months, whereas the other cementitious types were not damaged. It is interesting to note in these latter tests one surface of the concrete was coated with a simple bitumen coating. No attack occurred to this section of the specimens.

PFA and its resistance to thaumasite

The most comprehensive research project carried out between 2000 to 2003 by BRE[12]. This project looked at PC, SRPC, varying blends containing GGBS and PFA, including fly ash to EN450. Some of the conclusions were very interesting as follows:

1. The resistance to thaumasite attack did not depend on the aggregate carbonate content, either in the total or fine fraction of the aggregates.
2. There was no significant difference in performance of the concrete containing classified PFA to BS3892 Part 1 or EN450 fly ash.
3. Concretes containing 45% PFA/fly ash offered better resistance to thaumasite attack than 30% PFA/fly ash.

While the fly ash concretes at the UK norm of 30% PFA/fly ash blend ratio did not perform much better than PC or SRPC, it was clear from this work that the higher the proportion of fly ash the better the performance, e.g. 45% fly ash. Similarly at levels of 40% GGBS cementitious content there was also some deterioration. It is clear that there is a level of these secondary materials required in order to offer sufficient sulfate resistance.

Though the laboratory work showed fly ash at normal blend levels may have a problem, there was no evidence that problems were occurring with real fly ash concretes with 30% fly ash content in the ground. This had been confirmed by an extended site trial carried out at Shipston on Stour by BRE[13]. A failure of a house wall due to sulfate attack on the supporting concrete had occurred at Shipston. It had been possible to arrange an area near this house where test samples could be exposed to the same conditions. Samples included cast in situ concrete, laboratory prepared concrete cubes and masonry blocks. In 1998, 98 concrete samples were placed into the sulfate bearing soil and these were recovered after 3 years exposure to the sulfate bearing clay. Though there was evidence of thaumasite on the PC, Portland Limestone and SRPC concretes, BRE concluded that

> *"All concretes made with blended cements containing pfa, ggbs (including BRECEM), microsilica and metakaolin performed more or less satisfactorily irrespective of aggregate type".*

Though the PFA concrete used in this trial contained only 30% ash, less than the critical amount predicted from the laboratory work, the concrete had performed well. This result was confirmed by another BRE project[14] on precast concrete pipeline systems. A series of precast pipes were made with PC, SRPC, 30% fly ash and 65% GGBS concretes designed to resist design class DC 2 to 4. Core samples were taken of these pipes and kept in 5C sulfate solutions for 2 years. The pipe sections were buried in oxidised pyritic clay, beneath the groundwater level. The result was that no damage due to sulfate attack was found with either the laboratory or site specimens.

Another puzzle was that it appears that aggregate type has little to do with the thaumasite form of attack in the later work, whereas it had been a definite feature in earlier laboratory work and the early cases of attack. However, the BRE and Sheffield projects carried out in 2000-2003 showed there was little evidence that aggregate type was having a significant bearing on the thaumasite reaction. It has subsequently been suggested that there are sufficient carbonate ions available from other sources, e.g. the sulfate bearing clay itself, acid groundwater and carbonation via the atmosphere.

Fly ash is a pozzolanic material – temperature dependency

A theory was postulated by the UKQAA to explain the apparent poor performance of 30% fly ash cementitious blends in the laboratory against its good site performance. As fly ash is pozzolanic the chemical reactions that form the additional hydration compounds are basically dormant at the temperatures that most of the research work was carried out at, e.g. at 5C. It would be perfectly logical that such materials are able to contribute to preventing sulfate attack in real temperature conditions as found in the UK. As suggested in the BRE project report, some work looking at the real ground temperatures may be useful and this work was instigated by the UKQAA in January 2003.

Figure 4 shows the measured ambient and ground temperatures found in the UK, in this example in North Wales. It is clear the temperature averages around 12C with only three winter months with 5C at 5cm below the ground surface being the norm. It is clear the use of 5C in the laboratory is very artificial and would probably accelerate deleterious reactions like thaumasite.

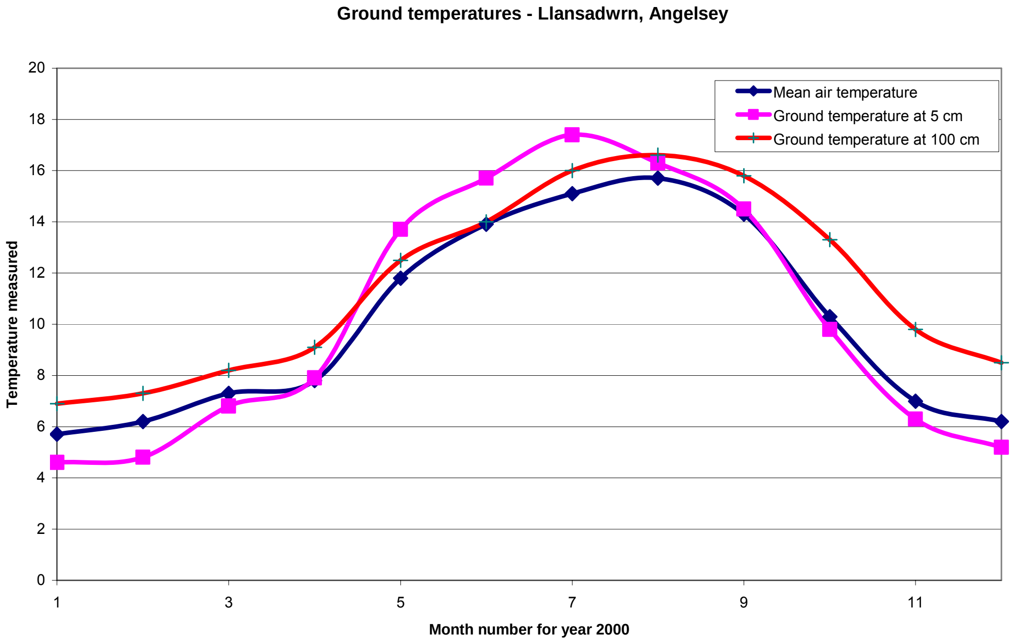


Figure 4 – Typical ambient and ground temperatures found in the UK

The proposal for the Temperature Cycling project was to prepare a series of concrete mixes containing Sulfate Resisting Portland Cement, as a control cement, and 30 and 50% fly ash cement blends using two differing sources of fly ash. These would contain limestone aggregates and use three differing temperature cycles would be adopted:

1. Fixed 12C,
2. A sinusoidal one yearly cycle ranging from 7C to 17C starting at 7C
3. A sinusoidal one year cycle starting at 17C

Two classes of sulfate attack, DC class 3 and 4 exposure were used for all the samples.

BRE were employed to look at this issue by the UKQAA commencing work in mid 2004 and the project is currently progressing. The concrete specimens were produced in the summer of 2004 and the three year exposure tests commenced. Test cubes for strength were taken and cured in the standard manner.

At the time of writing this paper the 1 year results are available and have proven most interesting. Firstly it is clear temperature cycling has not had a significant effect on the performance of the resulting concrete. There is no difference between beginning curing at 17C or 7C followed by a temperature cycle or using a fixed 12C throughout the test period. Secondly, 30% fly ash concrete remains prone to thaumasite attack in DC 3 and 4 conditions, however 50% fly ash blends have performed very well, at least as well as SRPC in Class DC 4 conditions and better than SRPC in Class DC 3 conditions.

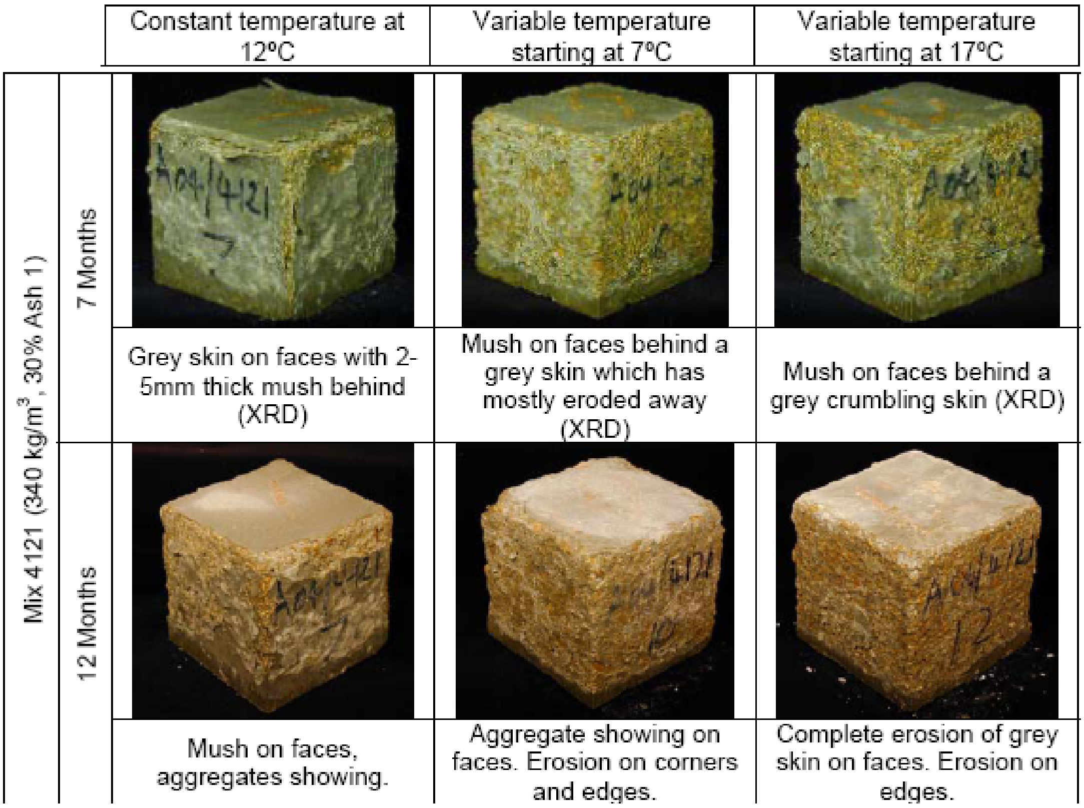


Figure 5 – Concrete specimens from the Temperature cycling project. At 30% ash content, significant damage takes place at 1 year

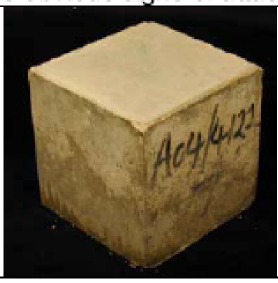
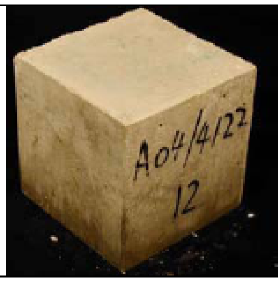
Mix	Age	Constant temperature at 12°C	Variable temperature starting at 7°C	Variable temperature starting at 17°C
Mix 4122 (340 kg/m^3, 50% Ash 1)	7 Months			
		Slight wear on corners but no obvious signs of attack	No signs of attack	No signs of attack
	12 Months			
		Slight wear on corners but no obvious signs of attack.	General good condition except slight damage to one edge and one air void filled with white mush.	Good condition all over, slight edge damage to one top edge.

Figure 6 – Concrete specimens from the Temperature cycling project. Using 50% fly ash performs well

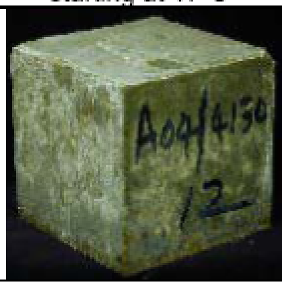
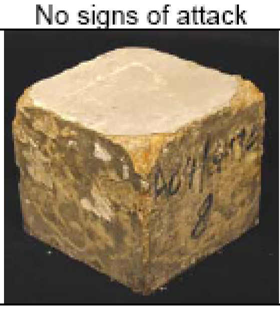
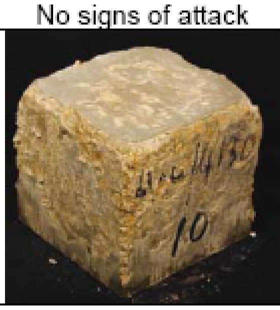
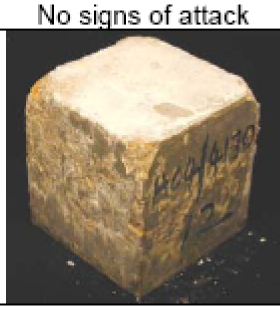
Mix	Age	Constant temperature at 12°C	Variable temperature starting at 7°C	Variable temperature starting at 17°C
Mix 4130 (380 kg/m^3, SRPC)	7 Months			
		No signs of attack	No signs of attack	No signs of attack
	12 Months			
		Erosion of corners and edges. White mush on faces.	White mush on faces behind grey skin. Erosion of corners and edges. (XRD)	White mush on faces. Erosion of corners and edges (XRD).

Figure 7 – Concrete specimens from the Temperature cycling project. SRPC performs well at 7 months, but begins to deteriorate at 1 year.

The Conclusions from the various Research Projects

There are many apparent inconsistencies in the results from the projects carried out over the last 10 years, particularly in respect of fly ash concrete. The questions posed are:

1. Concrete containing <40% fly ash as part of the cementitious content does appear to be more prone to thaumasite attack. However, concrete typically containing 30% fly ash has been widely used in the UK for sulfate resistance and yet there are no examples of deterioration due to thaumasite to our knowledge.
2. Increasing the fly ash content ≥36% seems to considerably enhance the resistance to thaumasite. Why? Is this simply a dilution effect?
3. Fly ash is a pozzolanic material and the reactions are temperature dependant. From the 12 months results of the recent BRE project, why do the temperature conditions the fly ash concretes are exposed to appear to have no significant effect on performance? This applies even when the initial curing starts at 17C – above the temperature that thaumasite can form.
4. The presence of carbonate aggregate was originally felt to be critical for the thaumasite reaction to occur. It is now believed that there are sufficient carbonates available from other sources to permit the reaction. Is this supported by examples in real concretes?
5. As both the specification of concrete and the method of assessing sulfate conditions in the ground have been improved in the various versions of BRE Special Digest 1, is there a danger that a large element of over specification for concrete has resulted? It would appear a simple bitumen coating is able to prevent attack and it's really only an issue with oxidised pyritic clay.

Conclusions in respect of fly ash

While there are many questions raised by the various research projects it is clear that fly ash is able to resist the thaumasite form of sulfate attack. The issues are:

1. For best performance of fly ash concrete in higher levels of sulfate exposure (DC 3 and 4), ≥36% of fly ash of the cementitious content is required.
2. There are inconsistencies in the performance of fly ash concrete in thaumasite laboratory work that need explanation:
    a. Such laboratory trials do not seem to reflect the real insitu ability of fly ash concretes to resist thaumasite attack.
    b. The effects of temperature in relation to thaumasite do not correlate with the normal understanding of the pozzolanic reactions.
3. The insitu performance of fly ash concrete in real sulfate conditions is considerably better, for some reason, than implied by the accepted specifications implies.

While in recent times the problem of the thaumasite form of sulfate attack has been of less prominence, the above issues do need resolving in order we have a complete understanding of how fly ash and sulfate attack relate.

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