**AVOIDING THE THAUMASITE FORM OF SULFATE ATTACK**

Thaumasite form of sulfate attack

M A HALLIWELL and N J CRAMMOND
Centre for Concrete Construction, Building Research Establishment, Watford, Hertfordshire, UK.

Durability of Building Materials and Components 8. (1999) *Edited by M.A. Lacasse and D.J. Vanier*. Institute for Research in Construction, Ottawa ON, K1A 0R6, Canada, pp. 139-148.


**Abstract**

Recent site and laboratory investigations carried out by BRE on problems of sulfate attack have shown that the mineral thaumasite has been responsible for the deterioration of concretes and mortars specifically designed to give good sulfate resistance. It has been shown that thaumasite may form if concretes containing commonly used limestone aggregates are exposed to sulfate solutions. Therefore, among other measures there is a need to establish a type of carbonate aggregate concrete which can resist this form of sulfate attack. Previous work carried out by BRE indicated that the use of blastfurnace slag cement could improve the resistance of carbonate aggregate concretes. In order to examine this possibility further sulfate resistance tests have been carried out at 5°C and 20°C on concretes containing various limestone aggregates. The main cementitious materials used with these aggregates were ordinary Portland cement (OPC), sulfate resisting Portland cement (SRPC), and an ordinary Portland cement blended with ground granulated blastfurnace slag (OPC/ggbs). This paper describes the one and two year results for these sulfate resistance tests. The results found that the ggbs performed satisfactorily with the good quality limestone aggregates; the concrete containing ggbs/Carboniferous limestone performed extremely well under the most aggressive conditions, and under the same aggressive conditions, the ggbs concretes did not perform satisfactorily when combined with the lower grade limestone aggregates. The SRPC concretes, stored in medium to strong magnesium sulfate solutions at 5°C, performed satisfactorily at 1 year with all grades of aggregate. However after two years, they have started to show unsatisfactory sulfate resistance with the magnesian limestone and lower grade calcareous limestone aggregate. This delay in deterioration of SRPC concretes has been seen in other sulfate resistance test work at BRE. The ggbs concretes containing good quality limestone aggregate continued to perform better than the equivalent OPC concretes.

Key words: Thaumasite, carbonate aggregate, sulfate attack, SRPC, GGBS.

# 1 Introduction

Recent evidence has been found to suggest that concretes containing commonly used limestone aggregate sometimes fail to perform satisfactorily when exposed to sulfate bearing groundwater (Crammond and Nixon, 1993, Crammond and Halliwell, 1995). This can be the case even when a sulfate-resisting Portland cement (SRPC) is used. The extent of this form of sulfate attack in the field is unknown. Preliminary site and laboratory investigations carried out by BRE (Crammond and Nixon, 1993, Crammond and Halliwell, 1995) on problems of sulfate attack have shown that the formation of the mineral thaumasite ($CaSiO_3.CaCO_3.CaSO_4.15H_2O$) has been responsible for the deterioration of these concretes.

From these studies it has been shown that the conditions favoured for thaumasite formation are cold wet environments, a source of calcium silicate, and a readily available source of carbonate and sulfate ions. The formation of thaumasite has a different effect on concretes and mortars compared with the classical form of attack in which ettringite is produced. The formation of thaumasite involves attack on the calcium silicate hydrate phase (CSH), which is the main binding agent in cements. Thaumasite formation is therefore accompanied by a reduction in the binding ability of the CSH phase resulting in a loss of strength and transformation of the concrete or mortar into a mushy incohesive mass.

Previous laboratory work carried out by BRE (Crammond and Halliwell, 1995) suggested that improved resistance against the thaumasite form of sulfate attack may be achieved by using a blended cement containing blastfurnace slag (ggbs) as the cementitious constituent. The work described in this paper explores the prospect of using ggbs cement as an effective sulfate-resisting cement in concretes containing limestone aggregate that are exposed to sulfate-bearing groundwater.

# 2 Concrete mixes

This work examined the performance of a series of concrete mixes designed for good sulfate resistance as specified in Digest 363 (BRE 1996). The mixes contain various carbonate-containing aggregates together with a range of cement types as follows:

- **Cement Types**. The cements used were: PC (7.2%$C_3A$), SRPC (0% $C_3A$), 30% PC with 70% ggbs of normal (12%) alumina content, 30% PC with 70% ggbs of high (17%) alumina content and BRECEM (50% calcium aluminate cement (CAC) and 50% ggbs). Halliwell and Crammond, 1997 gives a complete list of the chemical analyses of the cementitious materials.
- **Aggregates.** The aggregates used in this study were split into two main groups. Firstly, good quality aggregates normally used in concretes. These were; (i) Thames Valley Flint, (ii) a mixture of crushed Carboniferous limestone coarse and Jurassic limestone fine aggregate to produce an all-carbonate aggregate concrete and (iii) a mixture of Thames Valley flint coarse

and crushed Carboniferous limestone fine aggregate is needed produce an aggregate with carbonate only in the fine fraction. Secondly, two further aggregate combinations were included. These were materials which would not normally be used in concrete because of their high absorptivity and/or low strength and these were: (i) a mixture of poor quality magnesian carbonate as coarse and fine aggregate and (ii) a mixture of inferior oolitic limestone as coarse and fine aggregate. A complete list of the physical properties of the aggregates are given in Halliwell and Crammond, 1997.

### 2.1 Concrete mix designs

All mixes were designed to have a free water/cement ratio of 0.50, which is the maximum for Class 3 sulfate conditions in accordance with BRE Digest 363 (BRE, 1996). For the 'core' mixes made with the normal concreting aggregates, the cementitious content was fixed at 350 $kg/m^3$. In order to achieve a compactable concrete with a w/c of 0.50 for the mixes made with the low-quality aggregates, it was necessary to increase the cementitious content to 400 $kg/m^3$ and use a water-reducing admixture. Even with these adjustments, the inferior oolitic mixes were of low workability.

Details of the compositions of the mixes, their compacting factors and 28-day strengths are provided in reference 6. For the six 'core' mixes, triplicate specimens were exposed in each test condition, requiring 75 cubes per mix. For the eleven smaller mixes, duplicate specimens were used for each test condition with some of the test permutations being omitted, requiring only 36 cubes per mix. The total programme involved nearly a thousand cubes.

## 3 Experimental procedures

### 3.1 Preparation and storage of specimens

All concretes were vibrated into 100mm cube moulds and stored for 24 hours under damp hessian and polythene sheet, before being de-moulded and numbered. The cubes were then cured for a further 27 days at 20°C, either in water or in air at 65% relative humidity. For both air and water storage, the cubes were stacked three high. Some of the cubes stored in water stuck together and had to be prised apart. Immediately after curing, the cubes were transferred into containers containing the test solutions. Five concentrations of solution were used:

- Solution 'E': magnesium sulfate, of strength 1.8% as $SO_4$
- Solution 'C': magnesium sulfate, of strength 0.42% as $SO_4$
- Solution 'M': magnesium sulfate, of strength 0.14% as $SO_4$
- Solution 'I': sodium sulfate, of strength 1.8% as $SO_4$
- Tap water

Each container held four cubes, spaced apart in a single layer, and submerged in approximately 3.5 litres of solution. The 'control' cubes, which contained no carbonate aggregate, were kept separate from cubes containing carbonate aggregate.

To simulate the static conditions characteristic of a clay soil on site, some of the solutions were never changed. In other containers the solutions were emptied and replaced with fresh solutions every 3 months, to simulate a mobile groundwater. A further variable in the test conditions was temperature; specimens were tested in solutions maintained at 5°C and at 20°C.

### 3.2 Visual and photographic assessment

After approximately one and two years, the cubes were visually assessed and photographs were taken of specimens that showed evidence of attack.

### 3.3 Wear rating

'Wear rating' is a measure of the attack on the corners of a cube and was measured after approximately one and two years. Previous experience at BRE (Harrison, 1985) has found it to be a useful measurement on specimens subject to conventional sulfate attack, because here the initial damage is predominantly cracking or erosion of the corners. Measurements are made on the struck face and the opposite face of the cubes. On each of these faces two diagonal measurements are made of the distance from the edge of one corner damage to the edge of the diagonally opposite corner damage. Knowing the corresponding length on an undamaged cube, the wear rating of a cube is calculated as: *"the sum of the loss in millimetres of the four measured diagonals, divided by 8"* ( Harrison 1985), i.e. the average depth of erosion or damage for one corner (in millimetres).

### 3.4 XRD studies

Any interesting surface deposit or deterioration product was removed and analysed using X-ray diffraction, (XRD). The samples were allowed to dry naturally and were then finely ground for qualitative XRD using a Siemens D500 automated diffractometer.

## 4 Presentation of results

A combination of wear rating values (as shown in Table 1) and visual assessment (photographs shown in Figure 1) gave a very good indication of the degree of sulfate attack in the cubes under test. Little deterioration was detected at 20°C and consequently this paper only reviews the 5°C data. All wear rating tables and photographs are presented in Halliwell and Crammond 1997.

### 4.1 Assessment of sulfate-resisting properties using the wear rating results

It has been shown that normal production, demoulding and handling of cubes produces 'wear rating' values due to imperfect cubes of between 1 and 3 with a mean of 2 (Harrison, 1985). Harrison differentiated between the wear ratings obtained from the struck face and the opposite face. He detected greater attack at the corners of the struck face and deduced that wear rating values of greater than 5 (2+3) in the first year could be taken as an indication of the onset of sulfate attack. Hence values between 2 and 5 for the struck face would indicate satisfactory resistance to sulfate attack.

In the present study, the general impression was that the wear rating values measured for the struck face and the opposite face were similar. The opposite face was therefore treated as being just as susceptible to attack as the struck face and Harrison's performance criteria have been adopted as follows:

**one year criteria**
values > 5 imply poor sulfate resistance
values ≤ 5 imply satisfactory sulfate resistance
values ≤ 2 imply good sulfate resistance

**two year criteria**
values > 8 imply poor sulfate resistance
values ≤ 8 imply satisfactory sulfate resistance
values ≤ 4 imply good sulfate resistance

## 5 Discussion of the results from the sulfate resistance tests

The main finding from the 2 year cube assessment data was that concretes made with BRECEM performed the best, followed by those containing ggbs and SRPC cements with the OPC concretes showing the worst performance. It is important to note that at 1 year the SRPC concretes made with poor quality limestone aggregates were performing well, but after 2 years they had developed an unsatisfactory wear rating.

Two other important findings were that the sulfate resistance of the concrete specimens continued to be much reduced at 5°C and, at this lower temperature, it was predominantly concretes containing limestone-bearing aggregate which deteriorated.

Concrete cubes containing good quality carbonate aggregates performed well at 5°C when used in combination with all cement types except OPC. No concretes performed satisfactorily when they contained the poorer quality aggregates. At 1 year it was found that the SRPC was performing well with the poor quality aggregates, but at 2 years this was found not to be the case.

The ggbs concrete has performed particularly well when made with Carboniferous coarse and Jurassic fines. This combination performed better than the equivalent SRPC concretes, as shown in Figure 1 and Table 1. In this study, the most aggressive solution was found to be the strong magnesium sulfate solution, followed by the strong sodium sulfate solution. The medium magnesium sulfate solution gave some deterioration but only really with the concretes that had performed very poorly in the stronger solutions. One exception is the poor performance of the SRPC concretes after 2 years exposure to solution C at 5°C compared with their satisfactory performance after one year. No significant sulfate attack was found in the very weak magnesium sulfate solution. On the whole the solutions that were changed every three months caused more deterioration and attack than those that were left unchanged.

The effect of air-curing the concretes was to enhance significantly the sulfate resistance of all the concretes. Even the poorest quality concrete subjected to the most aggressive environment benefited from this form of curing. However, in the case of OPC concrete containing Carboniferous limestone coarse aggregate the performance of the air-cured specimens deteriorated greatly between one and two years (see Figure 2). This was due to preferential attack on their 'stuck faces' (see later section).

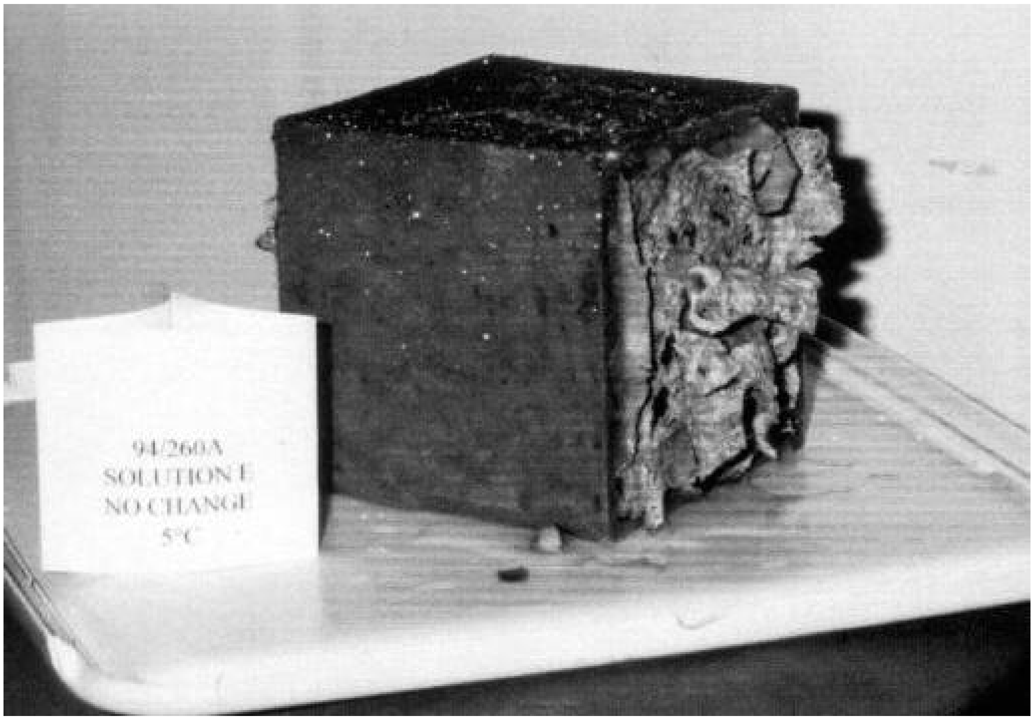

**Fig. 2: Air cured OPC/Carboniferous limestone cube stored in solution E at 5°C. The effect of the stuck faces during curing is clearly illustrated**

After the one-year assessment some of the results disagreed with data obtained from a previous study (Crammond and Halliwell, 1995,1996). The two main differences were that:-

1. Concrete mixes containing SRPC and Magnesian limestone deteriorated in the earlier work but performed well in the present investigation.
2. Concrete mixes containing SRPC and either Carboniferous limestone or Jurassic limestone were showing definite signs of wear after one-year of exposure in the first programme of work but performed satisfactorily after 14 months exposure in the current study.

However, after two years it has become apparent that the present work does agree with the earlier studies. Firstly, concrete mixes containing SRPC and Magnesian limestone have now deteriorated to unsatisfactory levels. Secondly the SRPC concretes made with Carboniferous limestone are now showing signs of deterioration.

The reason for these differences could be the slight variations in composition between the two SRPCs and the two Magnesian limestones used in the two studies. It is known that different SRPCs, for example, may remain dormant for different lengths of time before the onset of attack. The SRPC used in this work contains a slightly lower $C_3A$ content compared with that used in the previous work (Crammond and Halliwell 1995) which may have provided an improved sulfate resistance.

Inferior oolitic limestone was not included as one of the aggregates examined in the first programme of work. The poor performance of OPC concretes containing the inferior oolitic limestone in the present study was expected but the poor performance of the equivalent cubes containing ggbs was not.

Thaumasite was found by X-ray diffraction studies to be the main reaction product in the concretes that had deteriorated at the lower storage temperature of 5ºC.

During the curing of many of the samples, some of the cubes stacked on top of each other became bonded together. Many of these faces which were 'stuck' to each other had to be prised apart before immersion in the sulfate solutions. Some of the concretes were air-cured after demoulding for a period of 28 days and subsequently placed in sulfate solutions. The effect of the cubes being 'stuck' during curing was dramatically shown in these air-cured mixes**.** Figure 2 shows the effect of an OPC concrete with Carboniferous aggregate stored in the most aggressive environment (solution E, strong $MgSO_4$ , at 5°C). No significant corner wear was recorded on this cube after one year exposure, but where the faces had 'stuck' together, they had literally burst open. After 2 years storage in solution E, the wear rating values of this particular cube had increased to a unsatisfactory level. The reason for this mode of attack appeared to be that, as a result of these cube faces being stuck together during curing, calcium hydroxide from the hydrating cement would not have been carbonated during air-curing or leached during water-curing. Consequently this retained calcium hydroxide has been readily available for reaction with sulfate ions.

## 6 Conclusions

- Ggbs concretes performed well when made with the good quality carbonate aggregates. Apart from the equivalent BRECEM concrete the mix containing ggbs and Carboniferous limestone was the best performing concrete under the most aggressive environment (solution E at 5ºC). Ggbs concretes performed less satisfactorily when they contained the lower grade inferior oolitic and Magnesian limestone aggregates.
- The SRPC concretes made with the poor quality limestones performed satisfactorily up to one year but by two years were deteriorating significantly. SRPC concretes performed satisfactorily with both the good quality limestones and flint aggregates at one year, but were showing early signs of deterioration at 2 years with the good quality limestones.
- Deterioration was much more noticeable in the concrete cubes stored at 5°C than those stored at 20°C and at the lower temperature, thaumasite was identified by XRD studies to be the main reaction product formed.
- As expected, OPC concretes were the least resistant against sulfates. The worst sulfate resistance was found with OPC concretes exposed to strong magnesium sulfate solutions. Those containing carbonate-bearing aggregates had severely

eroded whereas those containing flint aggregate had remained intact but had expanded significantly.

- All the BRECEM concretes performed perfectly in every environment.
- Most air-cured concretes performed extremely well, even concretes made with OPC and Inferior Oolitic limestone stored at 5°C. Problems only arose when excess erosion occurred at ‘stuck faces’ which had not therefore been exposed to the air.
- Storage in the strong magnesium sulfate solution produced the greatest degree of sulfate attack followed by storage in the strong sodium sulfate solution.
- In general immersion in solutions that were changed every three months resulted in more deterioration and attack compared with those that were left unchanged.

## 7 Acknowledgements

The work described has been carried out under the Partners in Technology scheme, and was jointly funded by the Department of the Environment, Transport and the regions (DETR) and the Cementitious Slag Manufacturers Association (CSMA).

## 8 References

Building Research Establishment Digest 363, ‘Sulfate and acid resistance of concrete in the ground’, new edition 1996.

Crammond N.J. and Nixon P.J. (1993) ‘Deterioration of concrete foundation piles as a result of thaumasite formation’, *6th Int. Conf. on Durability of Building Materials*, Japan, pp 295-305.

Crammond N.J. and Halliwell M.A.(1995) ‘ The thaumasite form of sulfate attack in concretes containing a source of carbonate ions - a microstructural overview’. *2nd Symp. Advances in Conc. Tech,* ACI SP154-19.

Crammond N.J. and Halliwell M.A.(1995) Resistance of sulfate resisting concretes containing commonly used limestone aggregates to laboratory prepared sulfate solutions, BRE report.

Crammond N.J. and Halliwell M.A.(1996) ‘Assessment of the conditions required for the thaumasite form of sulfate attack’. To be published in proceedings of Materials Research Society fall meeting, Boston.

Halliwell M.A. and N J Crammond. (1997)‘Final report of the partners in technology programme on avoiding the thaumasite form of sulphate attack’. BRE report CR 118/97.

Harrison W.H.(1985) ‘Sulfate resistance of buried concrete. The third report on a long-term investigation at Northwick Park and on similar concretes in sulfate solutions at BRE’, BRE Report 164.

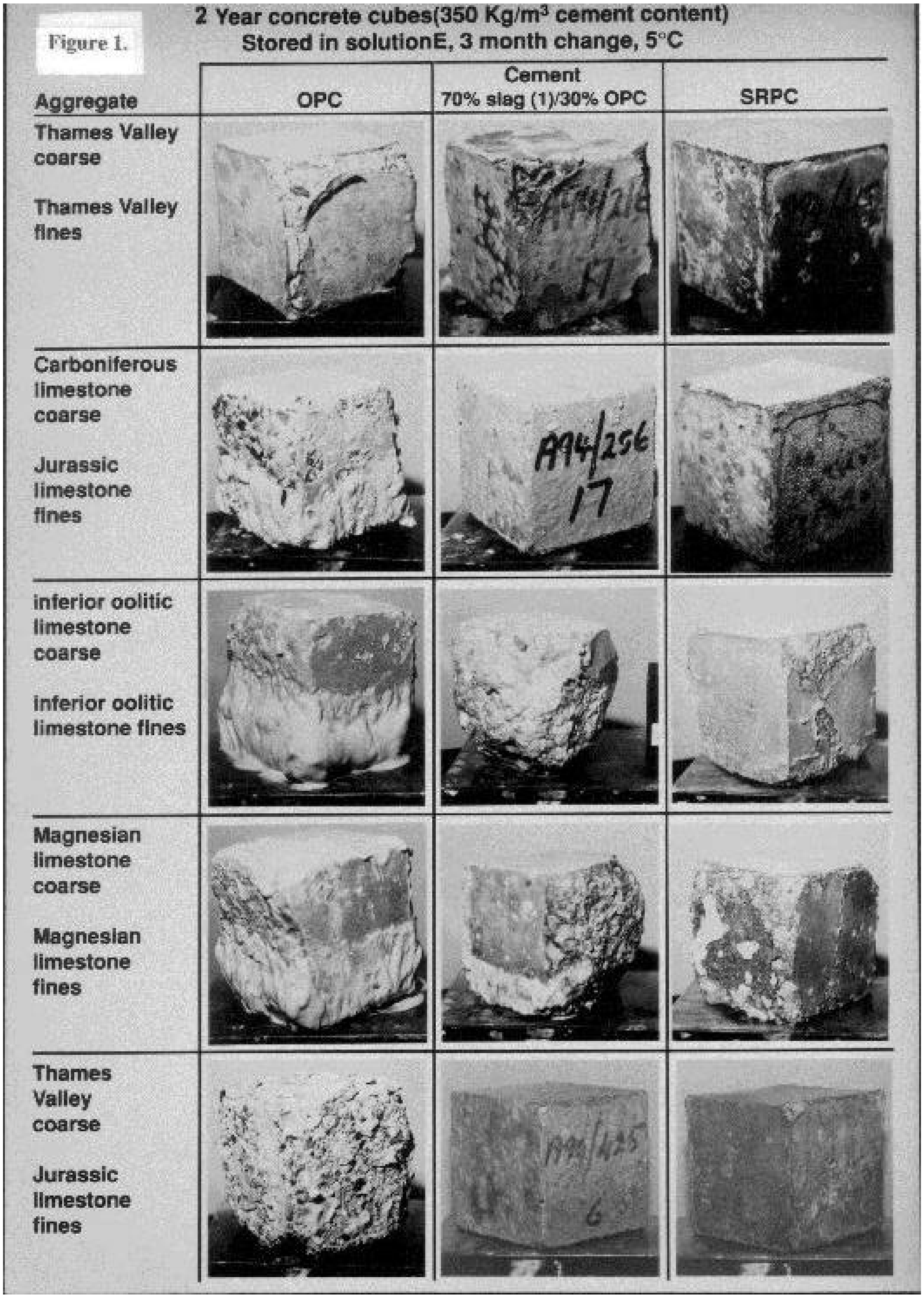


**Fig. 1: Sulfate attack in the cubes under test**

**Table 1: Wear rating for 100mm cubes after two years storage in sulphate solutions at 5°C**

| Cement Type | Cement Content kg/m3 | Aggregate type | | Sulphate solution type | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 1.8% SO4 MgSO4 | | 1.8% SO4 Na2SO4 | | 0.42% SO4 MgSO4 | | 0.14% SO4 MgSO4 | |
| | | Coarse | Fines | change 3M | no change | change 3M | no change | change 3M | no change | change 3M | no change |
| OPC | 350 | Thames flint | | **11.0** | **10.0** | **13.0** | **12.0** | **9.0** | *1.0* | *0.5* | *0.0* |
| OPC | 350 | Carbonif Lst | Jurassic Lst | **18.0** | **10.0** | **8.0** | 5.0 | **9.0** | *4.0* | *3.0* | *0.0* |
| OPC | 400 | Inferior Oolitic Limestone | | **18.0** | **13.0** | **10.0** | *1.5* | **10.0** | *3.0* | *2.0* | *0.0* |
| OPC | 400 | Magnesian limestone | | **13.0** | **8.0** | **11.0** | *3.0* | **8.0** | *2.0* | *4.0* | *0.0* |
| OPC | 350 | Flint | Carbonif Lst | **17.0** | **9.0** | **8.0** | *3.5* | **8.0** | *2.0* | *4.0* | *0.0* |
| SLAG/OPC | 350 | Thames flint | | **14.0** | *3.5* | **10.0** | *0.0* | 5.5 | *0.0* | *0.0* | *0.0* |
| SLAG/OPC | 350 | Carbonif Lst | Jurassic Lst | *3.5* | *3.5* | *0.5* | *0.0* | *0.0* | *0.0* | *0.0* | *0.0* |
| SLAG/OPC | 400 | Inferior Oolitic Limestone | | **29.0** | **10.0** | **24.0** | **9.0** | **15.0** | *0.0* | *0.0* | *0.0* |
| SLAG/OPC | 400 | Magnesian limestone | | **15.0** | 6.0 | **13.0** | 4.0 | **11.0** | *1.0* | *0.0* | *0.0* |
| SLAG/OPC | 350 | Flint | Carbonif Lst | *2.5* | *0.0* | *1.0* | *0.0* | *0.0* | *0.0* | *0.0* | *0.0* |
| SRPC | 350 | Thames flint | | *4.0* | *2.0* | 7.0 | *1.5* | *2.5* | *0.0* | *0.0* | *0.0* |
| SRPC | 350 | Carbonif Lst | Jurassic Lst | **9.0** | 6.5 | 5.5 | *0.0* | **8.0** | *0.0* | *4.0* | *0.0* |
| SRPC | 400 | Inferior Oolitic Limestone | | **12.0** | *2.5* | *4.0* | *0.0* | **9.0** | *0.0* | *0.0* | *0.0* |
| SRPC | 400 | Magnesian limestone | | **12.0** | *3.0* | *4.5* | *1.0* | **10.0** | *0.0* | *4.5* | *0.0* |
| SRPC | 350 | Flint | Carbonif Lst | *2.5* | *3.5* | *3.0* | *1.5* | *1.5* | *3.0* | *0.5* | *0.0* |
| SLAG(2)/OPC | 350 | Thames flint | | **25.0** | **13.0** | *5.0* | *3.0* | **13.0** | *0.0* | *1.5* | *0.0* |
| SLAG(2)/OPC | 350 | Carbonif Lst | Jurassic Lst | 7.0 | *1.5* | *1.0* | *0.0* | *0.0* | *0.0* | *1.5* | *0.0* |
| BRECEM | 350 | Thames flint | | *0.0* | *0.0* | *0.0* | *0.0* | *0.0* | *0.0* | *0.0* | *0.0* |
| BRECEM | 350 | Carbonif Lst | Jurassic Lst | *0.0* | *0.0* | *0.0* | *0.0* | *0.0* | *0.0* | *0.0* | *0.0* |
| **Air cured** | | | | | | | | | | | |
| OPC | 350 | Thames flint | | *1.5* | *2.0* | *1.0* | *0.0* | - | - | *1.0* | *0.0* |
| OPC | 350 | Carbonif Lst | Jurassic Lst | **14.0** | **11.5** | 6.0 | *3.0* | - | - | *2.0* | *0.0* |
| SLAG/OPC | 350 | Thames flint | | *0.0* | *0.0* | *0.0* | *0.0* | - | - | *0.0* | *0.0* |
| SLAG/OPC | 350 | Carbonif Lst | Jurassic Lst | *0.0* | *0.0* | *0.0* | *0.0* | - | - | *0.0* | *0.0* |
| SRPC | 350 | Thames flint | | 5.5 | *2.0* | *4.5* | *3.0* | - | - | *0.0* | *0.0* |
| SRPC | 350 | Carbonif Lst | Jurassic Lst | *0.0* | *3.0* | *3.5* | *0.0* | - | - | *0.0* | *0.0* |

values > 8 imply poor sulphate resistance **(bold)**    values < 8 implying satisfactory sulphate resistance