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Performance of concrete incorporating GGBS in aggressive wastewater environments

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Abstract

Concrete is traditionally used as the main component of wastewater facilities. The sulfate and acidic environment presents significant challenges. Supplementary cementitious materials (SCM) such as GGBS are being used in increasing quantities in concrete and have been shown to provide concrete with increased durability in this particular environment. They have traditionally been used with CEM I, but in recent years a shift in concrete practice has led to the introduction of CEM II cements with reduced CO₂ footprint and obvious environmental and economic benefits. However, the change in cement chemistry associated with using CEM II and GGBS must also be accounted for in concrete specifications for aggressive environments. This has particular importance when concrete is exposed to elevated sulfate and sulfuric acid environments, such as that associated with water and wastewater treatment.

The performance of CEM II/A-L cements with varying amounts of GGBS was evaluated through a series of tests conducted to determine their durability characteristics in respect of sulfate attack and sulfuric acid attack. As a benchmark, samples were also tested using CEM I cement, CEM I with GGBS, and a sulfate resistant Portland cement. Results have shown that for all cases, the addition of GGBS resulted in considerable reductions in sulfate induced expansion relative to samples using CEM I or CEM II binders alone. A slight improvement in performance relative to sulphate resisting Portland cement (SRPC) binders was also observed. However in respect of the sulfuric acid environment the regime proved too harsh and ultimately resulted in the early failure of all samples. Some difference in performance was noted, but this was not considered noteworthy. The influence of pH and acid type was studied. The conclusions were that the concretes tested cannot adequately address the durability threat to all parts of wastewater infrastructure over a significant life span due to the extraordinarily harsh nature of this form of attack.

Keywords: GGBS; limestone cement; wastewater; sulfate; sulfuric acid

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1. Introduction

The provision of high quality wastewater infrastructure requires significant expenditure on concrete with consequent client expectations of lengthy maintenance-free service lives. For example in the US alone, it is estimated that an annual investment of up to \$21 billion is required for new wastewater infrastructure, but that annual operation and maintenance costs are in excess of \$25 billion [1]. A recent state of the art review [2] has highlighted the significant lack of consensus on the minimum satisfactory specification for this infrastructure to meet the harsh environmental demands on it over its service life. Research has tended to focus on the deterioration of concrete in sewer systems and pipelines [3, 4, 5]. In contrast, little detailed research has been conducted into the deterioration of concrete in treatment facilities for processing wastewater. The nature of sewer system components and concrete pipes is that they are commercially available products and the performance of the product is largely dependent on the manufacturer's mix design which is influenced by local factors and generic standards. In wastewater treatment plants the concrete needs to be specified by the engineer, but a lack of in-depth research into the deterioration of these structures has deprived engineers of the information they need to distinguish between zones of differing exposure to chemical actions and attack. This is supported by the number of existing concrete wastewater structures that are exhibiting excessive localised corrosion of surfaces after less than a decade in service [Fig. 1].

In this context it is clear that current specification practices based on prescriptive approaches using 'XA' exposure classes [6] may not be appropriate to fully describe the aggressive nature of wastewater at the interfaces with the air, and in some cases, this may also apply to treatment processes involved in drinking water purification [7]. Existing research findings are not yet influencing current construction practice. The absence of much research on durability design formulae illustrates that the deterioration mechanisms associated with this critical infrastructural application are not yet widely accepted or understood. This paper will assist in bridging this gap by considering the role of key parameters such as environmental conditions, the nature of the attack and the physical results of the attack on the concrete. It is hoped that this will promote increased understanding of the deterioration mechanism and facilitate the introduction of a performance-based design approach.

It was noted that there is little published research on the performance of GGBS and limestone cement combinations in aggressive sulfate environments. Such combinations are significant in some countries as the drift away from the dominance of CEM I becomes the norm. A comparative analysis was carried out using a modified ASTM C1012 sulfate exposure test to examine the behaviour of these combinations in concrete compared to sulfate-resisting Portland cement, which was used as a performance benchmark. This analysis indicated that the diffusion of sulfate ions may form a key part of the degradation

mechanism and that CEM II limestone cements may in fact possess an inherent sulfate resisting capability when compared with CEM I cements. Given that GGBS was known to possess similar resistance, the investigation examined if CEM II/A-L in combinations with levels of GGBS greater than 50% could equal or exceed the performance of sulfate resisting cement.

2. Experimental programme

Concrete mixes were tested to help determine the relative resistance of cementitious binders to the aggressive environments associated with wastewater treatment. The selected binders and their chemical composition are listed in Table 1. The limestone content of the CEM II/A-L was provided by the manufacturer and was 8%. The binder combinations selected for testing are listed in Table 2. Test methods selected to investigate the effect of accelerated exposure to wastewater environments were based on standard test methods where possible. However the nature of wastewater is such that the selection of test methods is not a straightforward task. Some of the chemical characteristics of domestic sewage are provided in Table 3 [8] but these parameters are very variable and dependent on factors such as nearby industries, type of industry, environmental conditions etc. It should be noted that sulfuric acid is generally not present in wastewater, but rather in the biofilm located above the water line where it is a product of the metabolic process of the Thiobacillus bacteria. Based on the nature of the wastewater induced deterioration, test methods were selected to assess the resistance of concrete to sulfate attack and sulfuric acid attack.

2.1 Sulfate expansion tests

Mortar prisms of dimensions 285mm x 25mm x 25mm were prepared based on the mix designs specified in EN 196-1. Each mix contained 450g of binder, 1350g of CEN-Normensand (as per EN 196 Part 1) and 225g of water; this quantity was used to produce four prisms and reference studs were cast into the end of each prism to facilitate expansion measurements. The specimens were placed in a moist air cabinet at 20°C and demoulded after twenty-four hours. They were then placed in a water bath at 20°C and allowed to cure until twenty-eight days had elapsed. A modified ASTM C1012 standard was used to test the mortar prisms for change of length when exposed to a sulfate solution. The modification consisted of regular twenty-eight day expansion measurements for each mix for the duration of the investigation. The standard exposure solution used in this test method contains 50g of sodium sulfate (Na_2SO_4) per litre of distilled water. Each litre of the solution was prepared with 900ml of distilled water and mechanically stirred until fully dissolved. The solution was then topped up with distilled water until a volume of 1l was achieved. The specimens were stored in polyethylene containers which contained sufficient solution to cover the prisms by a

minimum of 5mm; this required 4.5 litres of solution which was in line with the ASTM requirements to utilise a volumetric ratio of 4.0 ± 0.5 between the solution and mortar prisms. The prisms were stored for a period in excess of one year and the solution was refreshed on a monthly basis. Length measurements were taken every four weeks. The readings consisted of taking an initial reference measurement for each prism and a standard reference bar prior to submersion in the sulfate solution then comparing them with readings of both the reference bar and mortar prism at the designated time intervals. The change of length of the prism from the initial reading was expressed as:

$$\Delta L = \frac{L_x - L_i}{L_g} \times 100 \quad (1)$$

where ΔL is the length change at age 'x' (%), L_x is the specimen comparator reading at age 'x' relative to that of an invar bar, L_i is the initial comparator reading of specimen relative to that of an invar bar and L_g is the nominal gauge length (250mm used). The percentage change of length of each prism was measured to an accuracy of 0.001% and the average of the four test specimens was recorded.

2.2 Sulfuric acid testing

A range of concrete samples were manufactured using the binder combinations listed in Table 2 and exposed to environmental conditions similar to those found in wastewater treatment plants. The focus in particular was the high levels of acidity associated with wastewater. The selected concrete mix involved a binder content of 360 kg/m^3 , and a water/binder ratio of 0.45. A predominantly limestone coarse and fine aggregate was used. The maximum aggregate size was 20mm and the coarse and fine aggregate contents were 1215 and 685 kg/m^3 respectively. This mix design was chosen to represent the minimum acceptable specified under exposure class 'XA3' of IS EN 206-1 [6], the standard relevant to the national location of the research project.

The concrete samples produced were immersed in a 1% sulfuric acid solution for six months and monitored for mass loss, expansion, visual appearance and compressive strength. The binder composition of the concrete mixes were as described in Table 2. Fourteen concrete cubes, of side 100mm, were cast for each mix using the binder combinations listed in Table 2. Four concrete prisms measuring 250mm x 75mm x 75mm were also cast for the purpose of monitoring expansion.

All of the samples were stored in a curing tank at 20°C for twenty-eight days at which time the compressive strength was determined by testing 2 cubes. The remaining 12 cubes were then divided into two sets of six; half of these remained under water in the curing tank

while the other half were subjected to immersion in a 1% sulfuric acid solution at $\text{pH}\approx 1.5$ for up to 168 days. This concentration is based on the work of Chang et al [9] who determined this concentration as providing the optimal balance between actual conditions and the need to accelerate the reaction processes to some degree. They did however emphasise the need to maintain awareness of the variable nature of the acid producing metabolic process which is sensitive to environmental conditions. The solution was monitored at 28 day intervals and the pH maintained at 1.5 by the addition of controlled amounts of sulfuric acid. The purpose of the division of the samples was to allow comparison between samples and accurate quantification of the effect of the sulfuric acid solution. The dimension of each cube was recorded at regular intervals; the samples were brushed with a wire brush every seven days under running water which resulted in a milky-white runoff. Brushing was ceased when the runoff colour reverted to clear water. All cubes were weighed every seven days for the first month and every twenty-eight days thereafter to record any mass loss or mass gain.

It should be noted that one objective of the experimental programme was to examine the effects of biogenic sulfuric acid deterioration on concrete, a biological phenomenon identified as the prime cause of wastewater infrastructure deterioration. As this is a difficult process to recreate within a reasonable experimental time frame it was decided to mimic the corrosive effect using purely chemical processes. Key to the biological deterioration process is the active biofilm layer only present in partially submerged concrete structures in wastewater facilities. Given that our experiments are purely chemical in nature with no bacteria and therefore no biofilm, it is therefore unnecessary to submit the test specimens to a partially submerged scenario.

2.3 X-ray diffraction analysis

Of particular interest in this study was the reaction (if any) between the various cementitious binders and the sulfate solution. At the end of sulfate testing the various mortar bars were crushed and ground in a mortar and pestle. The powder was then sieved and samples taken from the material passing a $125\mu\text{m}$ sieve. This preparation procedure was similar to that used by Chen & Jiang [10] who were assessing gypsum and ettringite formation in cementitious binders. They note that strongest reflections occur for ettringite and gypsum at 2θ angles of 9.08° and 11.59° respectively. As such, the powder samples were examined using a Siemens D500 diffractometer (XRD). The system was operated using a voltage of 40kV and a current of 30mA utilising $\text{Cu K}\alpha$ radiation. Measurements were taken between 2θ angles of 8 and 13 degrees with a resolution of 0.01 degrees. The duration per increment was 1 second.

3. Experimental results

3.1 Sulfate expansion tests

Comparator readings were taken for a 420-day period for all binder combinations and the results are presented in Fig. 2. Each of the samples was statistically analysed and the Q-test with a 90% confidence limit was used to identify outliers. The American Concrete Institute has published guidelines [11] for assessing the results produced from this expansion test, presented in Table 4, and it may be seen that all of the binders or combinations are satisfactory for “Moderate” exposure classes. Further analysis of the data however shows that the CEM I binder is not classified as suitable for “Severe” or “Very severe” exposure classes, while the CEM II/A-L and the sulfate resisting Portland cement are not suitable for “Very severe” exposure classes.

3.1.1 X-ray diffraction

The results for the XRD scans are shown in Fig. 3 and are broadly in agreement with the results from the expansion tests. The most notable peaks correspond to the prisms manufactured using CEM I, and it can be seen that ettringite and gypsum have formed. The gypsum peak (11.59°) appears particularly strong. The prisms manufactured using CEM I with 70% GGBS show no obvious ettringite peak but a relatively broad gypsum peak. This would suggest that a poorly crystalline gypsum has been formed in this case. This is also the case for the prisms manufactured using CEM II/A-L. Both mixes containing CEM II/A-L and GGBS reacted very little and no obvious peaks can be seen, suggesting that no gypsum or ettringite has been formed. Finally, the prisms manufactured using SRPC has also reacted and formed both ettringite and gypsum.

3.1.2. Visual inspection

The mixes displayed notable differences with respect to visual deterioration, varying from corrosion and discoloration to cracking and warping, or a combination of both. The most deteriorated mixes were those that had suffered the strongest expansion (MD and MA including CEM I and CEM II respectively). Common to both was the formation of longitudinal cracks as the first form of physical deterioration. In the case of the CEM I mix (MD) these became visible at approximately 140 days exposure; for the CEM II/A-L mix (MA) the time was 286 days. With the latter however, this manifested initially in the form of the cracks being filled with a white substance, most likely gypsum.

Radial cracking was observed on one of the CEM II/A-L mix (MA) specimens along the boundary of the reference stud (Fig. 4). A further visual distinction between CEM II/A-L (MA) and CEM I (MD) was the presence of notable deposits of a white substance occurring in blotches at random intervals on one of the prisms which can also be seen in Fig. 4. These

deposits seemed to be an integral part of the paste and were not soft to touch, nor had they the ability to be removed by scratching the surface. Generally however, the appearance of white deposits was less locally concentrated than in Fig. 4 and consisted primarily of an intermittent speckled pattern throughout the prisms. This was applicable to all specimens and mixes after one year, except those containing 70% GGBS as a cement replacement. In these cases, the cracking of the mortar prisms appears to commence when approaching an expansion threshold of approximately 0.03%. This process then continues to progress, culminating in a total loss of cohesion; this is evidenced by the prism corners crumbling when touched. This extreme case has thus far only applied to the CEM I mix (MD) which displayed expansion levels 3 times higher than the next most expansive CEM II/A-L mix (MA) after one year.

The limestone cement/GGBS combinations (mixes MB and MC containing 50% and 70% GGBS respectively) demonstrated comparatively little expansion. The 50% mix (MB) has shown some minor discoloration but the 70% mix (MC) did not show any visual evidence of attack. The sulfate resisting cement specimens (SR) have been outperformed by all mortars containing GGBS either with CEM I or CEM II after one year. Visually the SRPC mix specimen began to exhibit the same common degradation phenomenon when the expansion level approached the 0.03% threshold, with cracking, some minor spalling and a white speckled appearance.

3.2 Sulfuric Acid Testing

3.2.1 *Scaling tests*

The measurement of a loss of mass over time of the concrete specimens immersed in a sulfuric acid environment was considered an acceptable means of assessing the performance of each mix as was previously used by Chang et al [9]. The results of the first technique, using a wire brush, are presented in Fig. 5. The results of this procedure indicated that there may be a slight increase in mass over the first twenty-eight days of exposure. The concrete made using a 100% CEM II-A/L binder showed the highest initial gain in mass relative to the five other mixes, although the amount was not regarded as noteworthy. After the initial gain in mass, the samples began losing material and this continued at a steady rate for the duration of the test. From the data in Fig. 5 it can be seen that the poorest performing mix corresponded to the SRPC, while the best performance corresponded to the mixes containing 70% GGBS; the difference however was not considered to be of note.

The test was repeated for a replicate series of samples, except this time without the use of a wire brush. Brushing had been included to mimic the abrasive behaviour associated with flowing water and will have an effect on the loss of material from the surface of the concrete. As expected, the recorded mass loss was reduced but the trends remained the

same, as illustrated in Fig. 6. Again the poorest performance corresponded to SRPC while those that contained 70% GGBS retained most mass. The results for these two tests at 168 days are summarised in Table 5. At first glance it may appear that the use of increased quantities of GGBS leads to an improvement in performance, but closer inspection of the data shows that this is not the case. For all binders the sulfuric acid exposure has resulted in severe degradation of the concrete and any distinction between binder performances is not relevant to expected concrete service life. This can be clearly seen from a typical before and after photo, such as that in Fig. 7.

3.2.2 Compressive strength

A number of concrete cubes were stored in sulfuric acid and the effect of this on compressive strength was recorded up to 168 days. The reduction in sample surface area is allowed for and the results for these tests are illustrated in Fig. 8 and it can be seen that in all cases the effect is to reduce the compressive strength of the concrete. After 28 days all samples possessed a compressive strength of 60 ± 5 MPa; after 168 days in a 1% sulfuric acid solution it can be seen that the compressive strength of all samples has dropped to approximately 25 MPa (a reduction of 62–70%). This is in agreement with the conclusions of the mass loss experiments described above, in that none of the samples possess the ability to resist the harsh exposure conditions.

3.2.3 Expansion tests

Expansion was recorded on concrete prisms for a period of 6 months but the results for this test were inconclusive. Little or no movement of the samples was recorded, suggesting that this methodology is not suitable for assessing resistance of concrete binders to sulfuric acid attack.

3.2.4 Visual inspection

For both the brushed and unbrushed experimental programmes the primary mechanism of deterioration was disintegration of the cement matrix along with some secondary spalling. There was no evidence of cracking at any point over the six month exposure period. The manifestation of the deterioration consisted of the formation on the surface of a soft white substance (most likely gypsum) that was soft to touch and easy to remove. This was visible after approximately one week of exposure to the acid and built up following each successive removal of loosely adhering corrosion products. Regular examination of the unbrushed concrete cubes also revealed the complete loss of cohesion of the surface layer of the cement matrix after twelve weeks.

4. Discussion

4.1 Sulfate resisting capabilities of limestone cements

The results have indicated that the CEM II limestone cement possess an inherent sulfate-resisting capability relative to CEM I cement. The recorded expansion readings are still relatively high but can be reduced further by the addition of 50% or 70% GGBS as a cement replacement. Existing research on the effect of limestone additions to cement has indicated wide-ranging consequences varying from beneficial to detrimental impacts on performance [12, 13]. Nonetheless a common conclusion seems to centre on an upper limit of limestone additions that provide an improved resistance and this seems to vary between 15% and 20% [14, 15]. Ramezani-pour et al [14] attribute this behaviour to the dilution of cement constituents; there is in effect less material present for the sulfate to react with. Irassar et al [15] suggest that the improved performance of CEM II is due to the reduced level of C_3A on the system and the level of calcium hydroxide (CH) in the hydrated cement paste.

There are clearly other issues regarding the reaction of limestone with both the cement paste and sulfate ions. Tsivilis et al [16] showed that a Portland limestone cement exhibited lower water permeability compared to ordinary Portland cement. This is in direct contrast with the findings of Pipilikaki et al [17] who discovered increased permeability associated with the use of limestone cements. Hornain et al [18] discovered that the addition of limestone resulted in reduced chloride diffusion coefficient. This is attributed to the influence of limestone on the tortuosity of the system. It should also be noted that the effective w/c ratio increases with the percentage of limestone used which can be attributed to its lack of pozzolanic properties.

Portland limestone cements suffer similar chemical reactions from a traditional sulfate attack as ordinary Portland cements resulting primarily in the formation of gypsum and ettringite. The formation of thaumasite may also be of concern given the high level of carbonate in the system. Gonzalez and Irassar [11] explained that during cement hydration carbonate ions from the limestone compete with sulfate ions from gypsum to react with aluminate ions from C_3A ; this results in the formation of monocarboaluminate, monosulfoaluminate and ettringite. Irassar et al. [19] suggest that the sequence of a sulfate attack begins with diffusion of sulfate ions, followed by calcium hydroxide leaching, ettringite formation, gypsum formation and depletion of CH. The latter stages involve the decalcification of C-S-H followed by thaumasite formation. These assumptions appear to be supported by the observed behaviour of the 100% CEM II binder. There was an initial low level expansion detected with very little visual deterioration which could indicate the onset of ettringite or early gypsum formation. As the attack progressed white deposits began forming on the exterior of each prism, followed by a lack of cohesion and spalling at the edges, possibly indicating the decalcification of the C-S-H phase. Irassar et al. [19] also describe

corrosion of edges and corners and attribute it to gypsum formation in parallel veins to the sulfate attack front. As apparent in Fig. 4, cracks/veins with a white deposit can be observed around the elapsed exposure time when the specimen began to shed some minor mortar particles.

4.2 Sulfate resisting capabilities of GGBS

It is clear that the adoption of a relatively high GGBS replacement rates for both CEM I and CEM II/A-L mortars has increased their resistance to a 5% sodium sulfate solution. The sulfate resisting capabilities of GGBS have been discussed on many occasions [20, 21] with much of the benefit being attributed to a denser matrix, decreased permeability and a reduction in calcium hydroxide present in the hydrated system [22, 23, 24]. Furthermore, with the formation of a secondary C-S-H phase attributable to the long-term hydration of the GGBS, much of the alumina in the system becomes 'locked up' in this product and is not available to form ettringite during a sulfate attack [25]. As discussed above, a visual inspection of the specimens manufactured using GGBS has found no evidence of a lack of cohesion from exposure to the sulfate solution. Researchers [26] have attempted to account for this effect in limestone cements and claim that an increase in GGBS content will also lead to an increase in the hydrated C-S-H in the system.

4.3 Understanding sulfuric acid deterioration

A critical assessment of scientific research into sulfuric acid attack on concrete has shown that this is not a widely discussed phenomenon. The literature review indicated that there seems to be some recognition of its role in wastewater facilities but little has been achieved in truly understanding the reaction and formulating a concrete specification to limit its effect. The dissolution effect of the hydrogen ion is, however, widely accepted as the probable cause of the extreme level of corrosion visible in acidic environments. In an attempt to further understand this type of aggressive environment comparisons are made against data collected by researchers in other acidic environments, not necessarily exclusively incorporating sulfuric acid. Secondly, there is an absence of a consistent approach to determining resistance to acid in the laboratory environment, invariably leading to further ambiguity in comparing research outputs. Developing a standardised approach to assessing performance in an acidic environment would therefore seem an appropriate first step to understanding the reaction.

4.3.1 Influence of pH and acid type

Pavlík and Uncík [27] carried out research on mortars suspended in small glass tubes and measured the advancing corrosion front at one end from acetic and nitric acid solutions. The

pH of the solutions was regulated at 2.8 and 0.7 respectively. The corrosion front had advanced approximately 7mm for acetic acid in one hundred and fifty days while nitric acid had already reached values between 12mm and 14mm in approximately one hundred and ten days. The authors' also investigated the effect of adding a supplementary cementitious material in the form of silica fume to test its behaviour in this environment concluding that no significant benefit was observed. The results of this investigation yielded the possible significance that pH plays in acidic environments. The sulfuric acid data presented in this paper has shown that following six months exposure to a pH of ≈ 1.5 the cubic dimension of the specimens had reduced by approximately 8mm for brushed specimens and 4mm for unbrushed specimens. In this case however, the cubes were attacked from all six sides and the testing was conducted on concrete and not mortar, as per [27].

Further data exists that explores the effect of pH on concrete degradation, although not always exclusively incorporating a pure acid solution. Some research [28] has focused on lactic/acetic acid at a pH of approximately 2 with sodium hydroxide additions yielding further buffered solutions of pH 3.8, 4.5 and 5.5. Testing incorporated CEM I, II and III concrete and showed that as the pH increased the mass loss decreased, although not proportionately. Their technique involved short wetting and drying cycles of eight days with brushing a key feature. CEM I particularly was not suited to any of the solutions while CEM II and CEM III concretes appeared to perform relatively better. It is interesting to note that the authors had some success in distinguishing between the performance of various concretes but the research described in this paper suggests that all of the cementitious binders are equally ill-equipped to meet the harsh testing environment.

Attiogbe & Rizkallai [29] conducted an experimental programme using 100mm x 12mm x 6mm prisms cut from concrete cylinders. The specimens were immersed in a controlled sulfuric acid solution of pH 1, oven-dried weighed and brushed at irregular intervals over a 10-week period. They observed a mass loss of approximately 12% for their ASTM type I ordinary Portland cement specimens; this is similar to the approximate 10% value achieved for the majority of samples reported above after eighty-four days exposure at a pH ≈ 1.5 . Research in [29] also noted that after the 10-week exposure period, their 6mm thick specimens had almost completely disintegrated indicating a surface corrosion rate broadly similar to that reported in this paper.

It is interesting to compare the results described in this paper with those of Pavia & Condren [22], DeBelie et al [28] and Attiogbe & Rizkallai [29]. The research described in [28] and [29] both used a form of wet/dry cycles yet produced clearly different results; this supports the notion that while pH is an important factor, so too is the type of acid. The testing above used similar acid and pH levels to [29] and received similar results. The testing in [22]

and [28] used similar pH values but differing acid types, resulting in significantly different results.

5. Conclusions

It was concluded in respect of sulfate attack that resistance of Portland cement binders is greatly enhanced by the use of high quantities of GGBS. Test results showed that GGBS combination produced a binder that was comparable to or outperformed the sulfate resistant Portland cement concrete. The CEM II-A/L limestone cement used in this research was noted to possess an inherent sulfate-resisting capability relative to CEM I Portland cement, which may be useful in 'Moderate' or 'Severe' environments.

The main deterioration mechanism in the sulfuric acid testing programme was found to be the formation of gypsum on the external surfaces of the concrete specimens, followed by surface delamination and some spalling. Expansion was not found to be an important parameter in sulfuric acid based degradation. The 1% sulfuric acid solution (pH≈1.5) represents the most severe conditions that the concrete will encounter in service and the rate of visual deterioration of a 1% solution of sulfuric acid attack greatly exceeded that of a 5% sodium sulfate solution. However in practice actual pH levels may vary according to time, temperature and bacterial activity.

When subjected to the sulfuric acid testing there was no noteworthy difference between the cements tested, although specimens containing GGBS outperformed all other mixes regardless of the cement type. It was evident that these concretes cannot adequately address the durability threat to all parts of wastewater infrastructure over a significant life span (e.g. 100 years) due to the extraordinarily harsh nature of this form of attack.

6. Acknowledgements

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7. References

- [1] Congressional Budget Office. Future Investment in Drinking and Wastewater Infrastructure. ISBN 0160512433, Congressional Budget Office, 2002.
- [2] O'Connell, M, McNally, C, Richardson, MG. Biochemical attack on concrete in wastewater applications: A state of the art review. *Cem Conc Comp* 2010; 32(7): 479-485.
- [3] Mori T, Nonaka T, Tazaki K, Koga M, Hikosaka Y, Noda S. Interactions of nutrients, moisture and pH on microbial corrosion of concrete sewer pipes. *Water Res* 1992; 26(1): 29-37.

- [4] Ayoub GM, Azar N, El Fadel M, Hamad B. Assessment of hydrogen sulfide corrosion of cementitious sewer pipes: a case study. *Urban Water J* 2004; 1(1): 39-53.
- [5] De Belie N, Monteny J, Beeldens A, Vincke E, Van Gemert D, Verstraete W. Experimental research and prediction of the effect of chemical and biogenic sulfuric acid on different types of commercially produced concrete sewer pipes. *Cem Concr Res* 2004; 34(12): 2223-2236.
- [6] National Standards Authority of Ireland. ISEN 206-1: Concrete - Part 1: Specification, performance, production and conformity. NSAI, 2002.
- [7] Kawamura S. Integrated design and operation of water treatment facilities. Wiley, 2000.
- [8] Metcalf, E, Reddy, H. Wastewater engineering: Treatment and reuse. New York, McGraw-Hill, 2003.
- [9] Chang ZT, Song XJ, Munn R, Marosszeky M. Using limestone aggregates and different cements for enhancing resistance of concrete to sulfuric acid attack. *Cem Concr Res* 2005; 35(8): 1486-1494.
- [10] Chen, JK, Jiang, MQ. Long-term evolution of delayed ettringite and gypsum in Portland cement mortars under sulfate erosion. *Con Build Mat* 2009; 23(2): 812-816.
- [11] American Concrete Institute. Building Code and Commentary, ACI Committee 318. ACI, 1995.
- [12] González, MA, Irassar, EF. Effect of limestone filler on the sulfate resistance of low C3A Portland cement. *Cem Conc Res* 1998; 28(11): 1655-1667.
- [13] Irassar, EF, González, M, Rahhal, V. Sulfate resistance of type V cements with limestone filler and Pozzolana. *Cem Conc Comp* 2000; 22(5), 361-368.
- [14] Ramezani-pour, AA, Ghasvand, E, Nickseresht, I, Mahdikhani, M, Moodi, F. Influence of various amounts of limestone powder on performance of Portland limestone cement concretes. *Cem Conc Comp* 2009; 31(10): 715-720.
- [15] Irassar, EF, Bonavetti, VL, Trezza, MA, González, MA Thumasite formation in limestone filler cements exposed to sodium sulphate solution at 20°C. *Cem Conc Comp* 2005; 27(1): 77-84.
- [16] Tsivilis, S, Tsantilas, J, Kakali, G, Chaniotakis, E, Sakellariou, A. The permeability of Portland limestone cement concrete. *Cem Conc Res* 2003; 33(9): 1465-1471.
- [17] Pipilikaki, P, Katsioti, M, Gallias, JL. Performance of limestone cement mortars in high sulfate environment. *Const Build Mat* 2009; 23(2): 1042-1049.
- [18] Hornain, H, Marchand, J, Duhot, V, Moranville-Regourd, M. Diffusion of chloride ions in limestone filler blended cement pastes and mortars. *Cem Conc Res* 1995; 25(8): 1667-1678.

- [19] Irassar EF, Bonavetti VL, González M. Microstructural study of sulfate attack on ordinary and limestone Portland cements at ambient temperature. *Cem Concr Res* 2003; 33(1): 31-41.
- [20] Building Research Establishment. BRE special digest 1: Concrete in aggressive ground. Part 1: Assessing the aggressive chemical environment. 2nd ed. BRE, 2003.
- [21] Higgins, DD, Crammond, NJ. Resistance of concrete containing GGBS to the thaumasite form of sulfate attack. *Cem Conc Comp* 2003; 25(8): 921-929.
- [22] Pavía, S, Condren, E. Study of the durability of OPC versus GGBS concrete on exposure to silage effluent. *J Mat Civil Eng* 2008; 20(4): 313-320.
- [23] Al-Dulaijan, SU, Maslehuddin, M, Al-Zahrani, MM, Sharif, AM, Shameem, M, Ibrahim, M. Sulfate resistance of plain and blended cements exposed to varying concentrations of sodium sulfate. *Cem Conc Comp* 2003; 25(4): 429-437.
- [24] Osborne, GJ. Durability of Portland blast-furnace slag cement concrete. *Cem Conc Comp* 1999; 21(1): 11-21.
- [25] Gollop, RS, Taylor, HFW. Microstructural and microanalytical studies of sulfate attack: Comparison of different slag blends. *Cem Conc Res* 1996; 26(7): 1029-1044.
- [26] Brown, PW, Taylor, HFW. The role of ettringite in external sulfate attack. In: Marchand, J, Skalny, J (Eds.) *Proceedings, Seminar on sulfate attack mechanisms*, Quebec, Canada, 1999.
- [27] Pavlik, V, Uncik, S. The rate of corrosion of hardened cement pastes and mortars with additive of silica fume in acids. *Cem Conc Res* 1997; 27(11): 1731-1745.
- [28] De Belie, N, Verselder, HJ, De Blaere, B, Van Nieuwenburg, D, Verschoore, R. Influence of the cement type on the resistance of concrete to feed acids. *Cem Conc Res* 1996; 26(11): 1717-1725.
- [29] Attiogbe, EK, Rizkallai, SH. Response of concrete to sulfuric acid attack. *ACI Mat J* 1988; 85(6): 481-488.

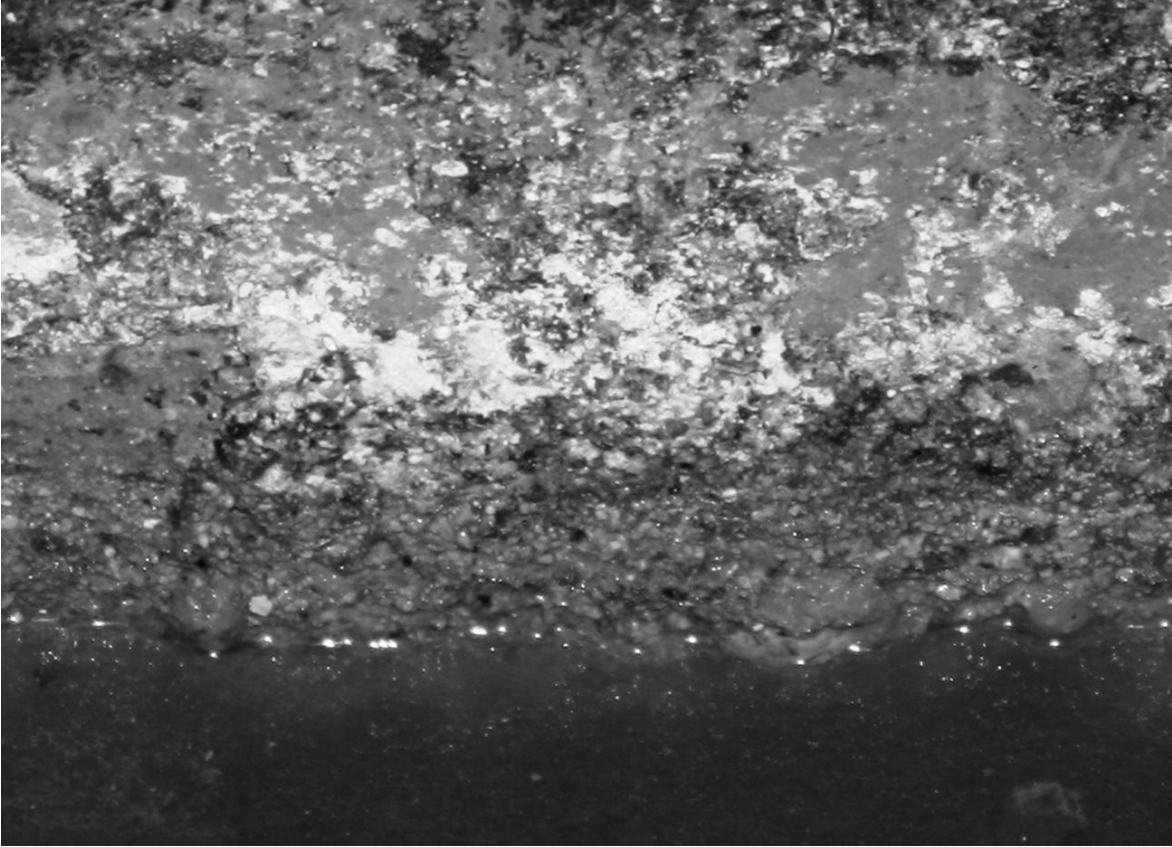


Fig. 1. Example of concrete corrosion at the typical water level in an 8 year old wastewater tank

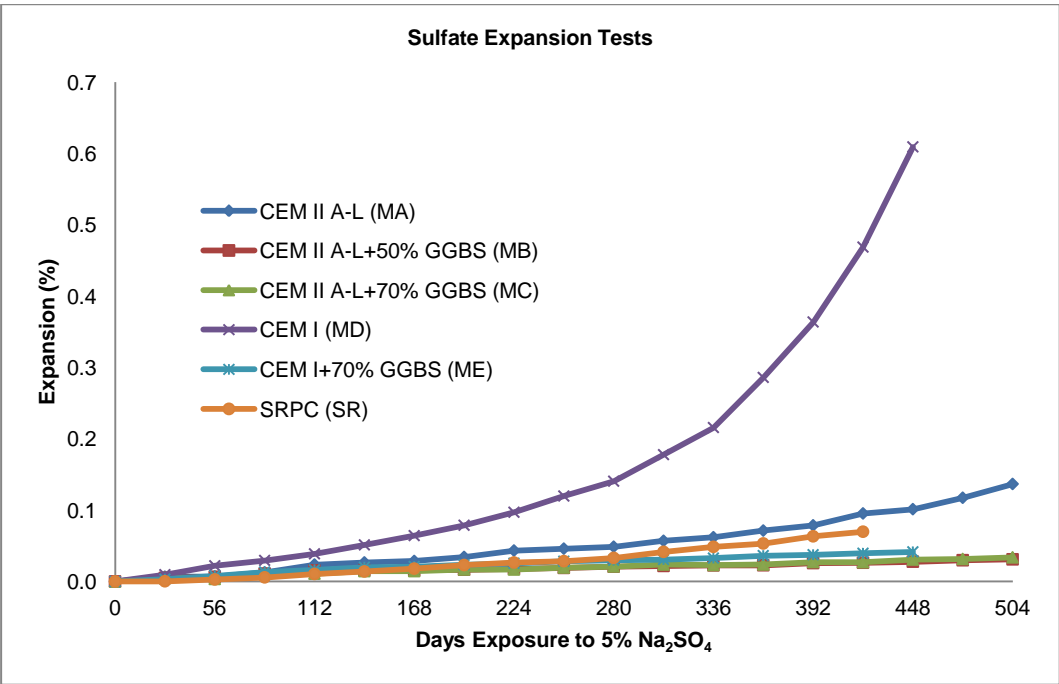


Fig. 2. Results of sulfate expansion tests

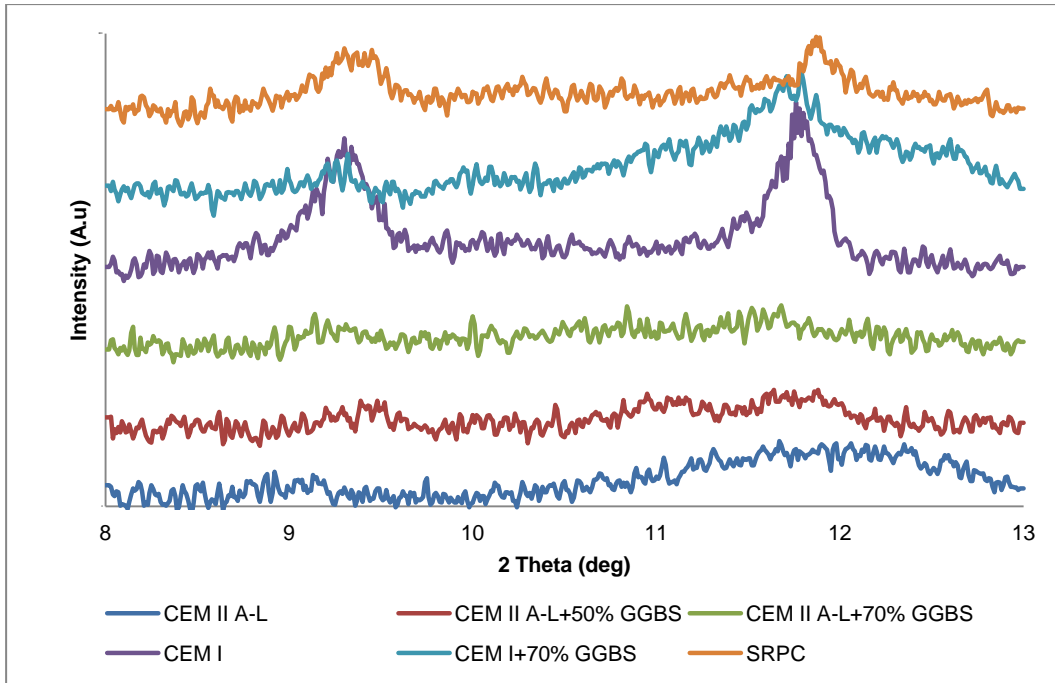


Fig. 3. Results of XRD analysis of mortar samples to determine ettringite or gypsum formation



Fig. 4. Radial cracking around the reference studs (left) and white blotches appearing on the surface of the prism (right)

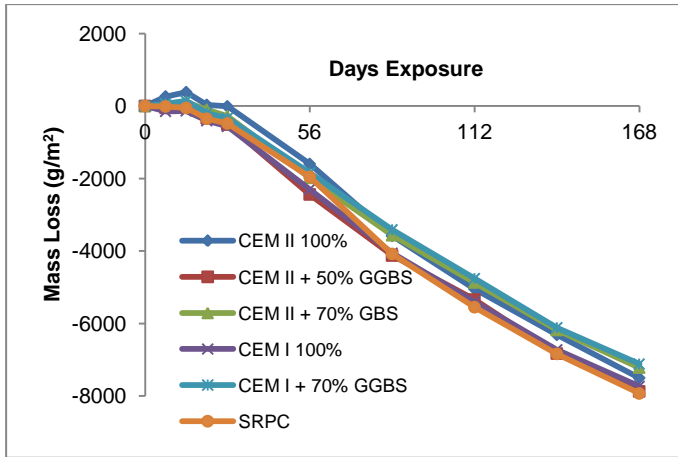


Fig. 5. Mass loss of samples after sulfuric acid exposure (with brushing)

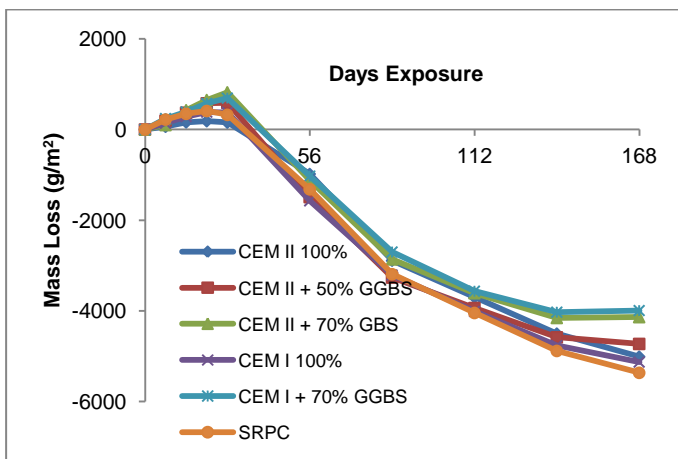


Fig. 6. Mass loss of samples after sulfuric acid exposure (without brushing)



Fig. 7. Effect of acid exposure on cube samples (cube shown corresponds to 100% CEM I)

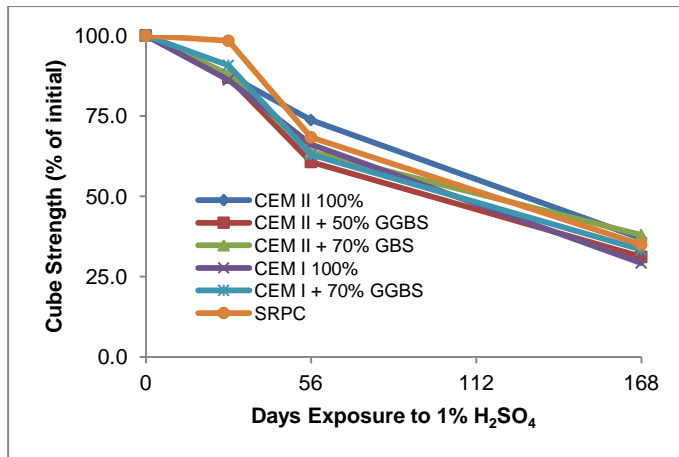


Fig. 8. Influence of period of acid exposure on compressive strength

Table 1 Chemical composition of cementitious binders

Chemical Composition (% mass)	Binder Type			
	CEM I	CEM II/A-L	GGBS	SRPC
SiO ₂	20.8	19.8	35.1	21.3
Al ₂ O ₃	4.8	4.8	12.4	3.5
Fe ₂ O ₃	2.7	3.1	0.6	4.1
CaO	64.3	62.8	40.6	63.3
MgO	0.7	1.9	8.6	2.1
Mn ₃ O ₄	0.1	0.2	0.4	0.1
Na ₂ O	0.1	0.2	0.3	0.2
K ₂ O	0.7	0.6	0.4	0.6

Table 2 Binder combinations chosen for testing

Mix Designation	Binder Composition
MA	100% CEM II/A-L
MB	50% CEM II/A-L; 50% GGBS
MC	30% CEM II/A-L; 70% GGBS
MD	100% CEM I
ME	30% CEM I; 70% GGBS
SR	100% SRPC

Table 3 Composition of typical domestic sewage [8]

Concentration	Weak	Medium	Strong
BOD ₅ (mg/l)	110	220	400
Sulfate (mg/l)	20	30	50
pH	7.0 – 7.8		

Table 4 ACI performance guidelines for concrete exposed to sulfate when tested according to ASTM C1012 [11]

Exposure Level	Exposure Class	Dissolved sulfate in water (ppm)	Max Expansion When Tested Using ASTM C1012 (%)		
			At 6 months	At 12 months	At 18 months
Moderate	S1	$150 \leq \text{SO}_4^{2-} \leq 1500$ (Seawater)	0.10		
Severe	S2	$1500 \leq \text{SO}_4^{2-} \leq 10000$	0.05	0.10	
Very severe	S3	>10000			0.05

Table 5 Reduction of mass loss from concrete samples relative to SRPC binder after 168 days

Sulfuric Acid Testing	Reduction in Mass Loss Relative to SRPC	
	Brushed Samples	Unbrushed Samples
MA	5.4%	6.6%
MB	0.7%	11.9%
MC	9.0%	22.9%
MD	2.5%	4.4%
ME	10.2%	25.6%
SR	0.0%	0.0%