Cement & Concrete Composites 32 (2010) 479–485

Contents lists available at ScienceDirect

Cement & Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp

Biochemical attack on concrete in wastewater applications: A state of the art review

M. O'Connell, C. McNally [*], M.G. Richardson

School of Architecture, Landscape and Civil Engineering, University College Dublin, Newstead, Belfield, Dublin 4, Ireland

ARTICLE INFO

Article history:
Received 14 July 2009
Received in revised form 20 April 2010
Accepted 1 May 2010
Available online 7 May 2010

Keywords:
Sulfate attack
Sulfuric acid
Thiobacillus
Secondary cementitious materials
Performance specifications

ABSTRACT

The costs associated with the provision and maintenance of drinking water and wastewater infrastructure represents a significant financial demand worldwide. Maintenance costs are disproportionately high, indicating a lack of adequate durability. There remains a lack of consensus on degradation mechanisms, the performance of various cement types, the role of bacteria in the corrosion process associated with wastewater applications and testing methodologies. This paper presents a review of the literature, outlining the various research approaches undertaken in an effort to address this problem. The findings of these varying approaches are compared, and the different strategies employed are compiled and discussed. It is proposed that a key step in advancing the understanding of the associated deterioration mechanism is a combined approach that considers the interaction between biological and chemical processes. If this can be achieved then steps can be taken to establishing a performance-based approach for specifying concrete in these harsh service conditions.

1. Introduction

The provision of high quality water and wastewater infrastructure requires significant international expenditure on concrete with consequent expectations of lengthy service lives. For example in the US alone, it is estimated that annual investments of up to $20 billion and $21 billion is required to provide adequate infrastructure for drinking water and wastewater respectively [1]. It is also estimated that the annual operation and maintenance costs associated with drinking water and wastewater infrastructure to be in excess of $31 billion and $25 billion respectively. Against this backdrop, it is surprising to note that the corrosion of water and wastewater infrastructure has been a topic of debate for decades, with little consensus on the methods for designing and specifying this infrastructure to optimally meet the harsh environmental demands it will meet in service [2–7]. The majority of studies to date have focused on the deterioration of concrete in sewer systems and pipelines [5,8,9]. However little detailed research has been conducted into the effect of corrosion on the vital treatment facilities that are processing our wastewater. Concrete pipes in sewer systems tend to be an "off-the-shelf" product with little input by the specifier into specification of mix design. As a result the performance of the product is largely dependent on the manufacturer's mix design which is influenced by local factors. In treatment plants the concrete may be specified by the engineer, but a lack of in-depth research into the deterioration of these structures has meant little change in professional practice concerning concrete mix design.

Existing evidence has shown that corrosion is present in many concrete structures associated with water and wastewater treatment. The alarming fact is that some of these facilities are deteriorating significantly after less than a decade in service (Fig. 1). In this context it is clear that current design practices based on prescriptive approaches to concrete specification may not be appropriate to deal with the aggressive nature of wastewater, and in some cases, the treatment processes involved in drinking water purification [10]. Existing research findings are not yet influencing current construction practice. The lack of widely quoted 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. This will promote increased understanding of the deterioration mechanism and facilitate the introduction of a performance-based design approach.

2. Characterising the wastewater environment

The deterioration of sewer systems has long been a topic under considerable scrutiny and in the mid 1940s a comprehensive scientific evaluation was undertaken in an attempt to understand the corrosion process [11]. Current research has continued to focus on the deterioration of concrete sewer pipes and case studies have taken place throughout the world, including comprehensive

---

[*] Corresponding author. Tel.: +353 1 716 3202; fax: +353 1 716 3297.
E-mail address: ciaran.mcnally@ucd.ie (C. McNally).

0958-9465/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconcomp.2010.05.001

Fig. 1. Evidence of corrosion in grit removal tanks with gypsum and exposed aggregate visible above the water line in a wastewater treatment plant constructed in 2003.

reviews on current infrastructure [8]. In the latter, the condition of the sewer system in four cities in the Lebanon was evaluated whereby certain contributory factors in corrosion were outlined: Biological Oxygen Demand (BOD) levels, high sulfate and dissolved sulfide concentration, high temperatures, high H_2S gas concentration, high turbulence and long detention times, low dissolved oxygen levels, low water velocity and low wastewater pH. These and other criteria have been outlined in several publications, all of which detail the conditions leading to corrosion in sewer environments [4,5,12–14].

The contributory factors outlined above are not only limited to sewer piping – they are also found in wastewater treatment plants. Occurrences of concrete degradation in these structures have been recorded in a limited fashion in aeration tanks [15], in septic tanks and pumping stations [16] and the underside of concrete slabs and in primary influent channels [17]. The latter two sources both make reference to the fact that corrosion has been observed just above the waterline. This is significant in that prior experimental research [5,18] into understanding degradation of concrete in sewer pipes has proven that optimum corrosion levels also occur just above the waterline. Work carried out into determining depth profiles of sulfate ingress into concrete noted that core samples were taken from the walls surrounding the spiral pump of a sewage treatment plant as well as the concrete walls of a clarifier which has been damaged by sulfates originating from the sewage waters [19].

Evidence thus far has identified bacterial manifestation of the genus '*Thiobacillus*' as a major contributor to the deterioration process of concrete sewer pipelines [5,11]. The product of their metabolism results in sulfuric acid being formed which attacks the cementitious matrix of the concrete causing loss of strength and cohesion. *Thiobacillus* however, plays only a part of a much broader and complicated corrosion process. In the often anaerobic conditions which develop in raw sewage influent, sulfate-reducing bacteria convert sulfates into sulfides such as hydrogen sulfide (H_2S) gas. In favourable conditions this diffuses into the atmosphere and, in the presence of oxygen, is further reduced to elemental sulfur or partially reduced sulfur compounds. In turn, they provide the catalyst necessary for the aerobic *Thiobacillus* bacteria to begin producing sulfuric acid; a more detailed explanation of the corrosion process is presented in a subsequent section.

Sulfuric acid has been identified as a corrosive agent not only in corroding sewers but also in wastewater treatment plants [20,21]. An attack by sulfuric acid however is a combined acid–sulfate reaction with the hydrogen ion causing a dissolution effect, coupled with corrosive role played by the sulfate ion [2,22]. When sulfuric acid reacts with a cement matrix, the first step involves a reaction between the acid and the calcium hydroxide ($Ca(OH)_2$) forming calcium sulfate according to the following equation:

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O \tag{1}$$

This is subsequently hydrated to form gypsum ($CaSO_4{\cdot}2H_2O$), the appearance of which on the surface of concrete pipes takes the form of a white, mushy substance which has no cohesive properties and has, "the consistency of cottage cheese" [23]. In the continuing attack, the gypsum would react with the calcium aluminate hydrate (C_3A) to form ettringite, an expansive product:

$$3CaSO_4{\cdot}2H_2O + 3CaO{\cdot}Al_2O_3 + 26H_2O \rightarrow (CaO)_3{\cdot}(Al_2O_3){\cdot}(CaSO_4)_3{\cdot}32H_2O \tag{2}$$

According to Skalny et al. [22], the ettringite can be located in deeper sections of concrete as long as the pH is high enough for it to form and the gypsum can migrate into these regions. The evidence gathered by Davis et al. [23] in their analysis of piping, however, showed that little ettringite was discovered in the corroding front and that the thermodynamics of the conversion to gypsum may be so fast that ettringite is a short-lived intermediate.

From the evidence discussed above there seems to be a distinct relationship between the corrosion occurring in concrete sewers and that in wastewater treatment facilities. Common variables include environmental conditions, the nature of the attack and the physical results of the attack on the concrete. Mehta and Burrows [24] have discussed how a paradigm shift is required in concrete design, moving away from the traditional prescriptive approach to one that promotes a performance-based design. However for such an approach to succeed, it is imperative that the deterioration mechanism is fully understood. In this light it is necessary to account for the severe environments that wastewater infrastructures will encounter in service, and to take an in-depth look at the current state of research into sulfate and sulfuric acid corrosion in a wastewater environment.

3. Biodegradation aspects

3.1. Providing resistance to biochemical attack

When assessing the available scientific research, it is important to consider sulfate attack, sulfuric acid attack and how they are both relevant in determining the resistance of current concrete design specifications to such attacks as biogenic sulfuric acid (BSA) corrosion. As expected there is much conflicting data available on the subject, a scenario which is eloquently detailed in one practicing engineer's publication on the topic [6]. Also of interest is the performance of cements containing additions of ground granulated blast-furnace slag (GGBS) which, when mixed with Portland cement, has been proven to possess an inherent sulfate resisting capability [25,26]. GGBS is being used in increasing quantities in concrete practice today along with other secondary cementitious materials (SCMs) such as pulverised fuel ash (PFA). With the high CO_2 emissions associated with the production of Portland cement, these SCMs have the advantage of being by-products from other industrial processes and as such can help reduce the CO_2 footprint of a construction project. While concretes produced using these binders are more dense and durable in the long term, they are also prone to reduced early age strengths and require particular attention when curing [27–29].

In assessing experimental test methods previously used by researchers many contrasting opinions exist [4,30], including the proposed inadequacy of sulfate testing as a method to analyse biological corrosion in a wastewater environment while others stipulate simultaneous biological and chemical sulfuric acid testing as the only true methodology [4]. The participation of the sulfate ion in sulfuric acid (H_2SO_4) corrosion and that of residual sulfates present in wastewater (found in effluent from food and beverage industries [31]) cannot be ignored however. Reviewing in situ and simulated experimental test methods also provides a valuable insight into the aggressive nature of the environment that sewers and wastewater treatment plants are exposed to. This also helps to characterise the environmental conditions favourable to the initiation of biogenic sulfuric acid corrosion, allowing scope for investigating the role played by both sulfate-reducing and sulfur-oxidising bacteria.

3.2. Sulfate-reducing bacteria

Initiating the bacterial processes, sulfates present in the raw sewage in sewer system are converted into sulfides by sulfate-reducing anaerobic bacteria such as *Desulfovibrio* [4]. In partially filled sewers, anaerobic conditions can only occur in the slime layer on the walls of the pipe above the water line. Some of the essential environmental conditions necessary in the wastewater environment for these bacteria to function and grow are dissolved oxygen levels approaching zero and sufficient carbon and sulfate concentrations in the wastewater itself [32]. When this occurs they utilise the sulfates present in the wastewater to obtain the oxygen they require and in turn release sulfur ions [33]. According to research aimed at quantifying microbial-induced deterioration of concrete, the bacteria derive the energy required for the reduction of sulfate by the oxidation of organic compounds and H_2 [14]. In their assessment of Lebanon's sewer network, Ayoub et al. [8] claim that sulfate to sulfide reduction takes place when the bacteria derive their oxygen from dissolved oxygen and nitrates in the wastewater. They state however, that corrosion in Lebanon's sewers was not observed to have occurred in areas where dissolved oxygen levels were greater than zero. If sulfate-reducing bacteria require dissolved oxygen to induce the corrosion cycle, as they suggest, one must ask why is it that no corrosion was found where dissolved oxygen exists. Their own search of existing literature suggested that sulfide build-up could not occur with dissolved oxygen levels greater than 0.5 mg/l whereas Hewayde et al. [33] set a level of 0.1 mg/l above which corrosion will not occur.

The final process in the initial stage of concrete deterioration involves the sulfur ions released by the bacteria. These in turn react with dissolved hydrogen in the wastewater to form an essential contributory product in the corrosion process, hydrogen sulfide (H_2S) [33]. The hydrogen sulfide initially formed is found in its dissolved liquid form but for this poorly soluble compound to contribute to the concrete deterioration process it must leave the wastewater and enter a gaseous phase. The normal pH of sewage is slightly acidic and in the range pH 5–6 but when this begins to lower in conjunction with turbulent water (often found in sewer pipes or associated with some wastewater treatment processes), the H_2S escapes and collects in the atmosphere above the water level [4,16,33]. A thin layer of moisture exists on the surface of the concrete pipe exposed to the atmosphere and it is into here the hydrogen sulfide is gas is dissolved. The condensate layer has a high pH attributed to the alkalinity of the concrete (which can have a pH of between 11 and 13). It also serves as the driving force behind the gas' dissolution. At high pH levels the hydrogen sulfide is separated into HS^- or S^{2-} ions which attract more H_2S into the moisture layer [14]. Research has also shown that the concentration of H_2S in the moisture film increases as the pH of the mortar lining of the concrete pipe decreases [13]. In the presence of oxygen the H_2S reacts to form elemental sulfur or partially oxidised sulfur species [4,9,14,21], which can sometimes be seen in the corrosion products deposited on the concrete surface [18].

3.3. Sulfur-oxidising bacteria

The formation of sulfur is perhaps the critical link in the chain of events leading to the corrosion of concrete in a wastewater environment. In microbiological experiments carried out in 1945 to investigate why sewer pipes were corroding, Parker [11] discovered five strains of the species *Thiobacillus* on the surface of concrete which oxidise sulfur, or some partially reduced form of sulfur, to form sulfuric acid. More recent research suggests some of the *Thiobacillus* strains involved in concrete corrosion as being *Thiobacillus thiooxidans*, *Thiobacillus intermedius*, *Thiobacillus perometabolis*, *Thiobacillus novellus*, *Thiobacillus thioparus*, *Thiobacillus neapolitanus* and *Thiobacillus versutus* all of which are known to oxidize and grow with reduced inorganic sulfur compounds [14,34]. Research has also identified iron-oxidising bacteria, such as *Thiobacillus ferrooxidans*, as being involved in the production of sulfuric acid in pyritic ground and in sewage treatment plants [35,36].

Bacteria of the genus *Thiobacillus* do not attach themselves to the surface of concrete under any conditions. Roberts et al. [14] state that the pH of the concrete has to be reduced to 9 and assuming sufficient moisture, nutrients and oxygen are present only then will the *Thiobacillus* bacteria colonise. Several theories for the lowering of the pH of the concrete to around 9 have been put forward, including the involvement of the dissociation process of hydrogen sulfide as discussed above. However the most widely assumed theory is that the pH will be lowered due to the effects of carbonation [13,14,23]. As a result of in situ tests conducted in a sewage system with high concentrations of hydrogen sulfide (>600 ppm) an alternative theory has been put forward into determining the conditions necessary for bacterial colonisation [7]. The authors claim that the generally accepted role of carbonation in lowering the pH of a concrete's surface does not hold for their experiments. Instead they theorise that in the thin moisture layer itself, the bacteria oxidise the hydrogen sulfide gas to form sulfuric acid, thereby reducing its pH. They further claim that the bacteria will grow in the layer even when the pH of the concrete itself ranges from pH 11–13. Parker [37] noted in his experimental observations however, that *Thiobacillus concretivorus* (as he termed the strain of *Thiobacillus* found to attack concrete) did not convert the hydrogen sulfide directly into sulfuric acid but only free sulfur or other forms of utilisable sulfur compounds including thiosulfate [38]. In characterising the strain *T. thiooxidans*, Waksman and Joffe [39] and Nica et al. [38] also stated that hydrogen sulfide and other sulfides are not used directly by the sulfur-oxidising organism.

In recognising the wide range of *Thiobacillus* strains that take part in sulfuric acid production, it must be noted that not all thrive in an identical environment. Some of these strains are categorised into 'acid-preferring' acidophilic sulfur-oxidising microorganisms (ASOM), such as *T. thiooxidans* and 'neutral-preferring' neutrophilic sulfur-oxidising microorganisms (NSOM), such as *T. intermedius* [14,38]. It is proposed that different strains of neutrophilic bacteria colonise the surface of the concrete as its pH depresses from approximately a value of 8 to around a value of 6 through their production of sulfuric acid [23]. It was also found that microbial succession is a surface phenomenon and that the ASOM move into the corroding concrete with the corroding layer whereas NSOM do not.

Parker [11] observed that the bacteria which he was cultivating survived to a pH of approximately 6.5 above which none was capable of growth. At these slightly acidic pH values the acidophilic sulfur-oxidising bacteria colonise and further depress the pH of the concrete surface to as low as 2 at which level the strain *T. thiooxidans* can be found thriving [18,40]. The optimum temperature at which the acid was produced in its highest quantities after 50 days was found to be 30 °C while Barbosa et al. [15] noted in their research that 'sulfide oxidation' by the strain *T. dentrificans* decreased at low temperature and was inhibited at 15.6 °C. Parker [11] also discovered that the rate of acid production in his bacteria increased with increasing nitrogen levels up to a concentration of 50 ppm, above which there appeared to be a slight inhibition.

3.4. Other acids and organisms

In a departure from the accepted role of the species *Thiobacillus* in lowering the surface pH of concrete from approximately 8 to 4, some authors have also attributed the initial reduction to that of fungus growth [5,41]. Mori et al. [5] found an unidentified green fungus which grew at high pH levels and was capable of reducing the pH to levels suitable for colonisation and growth of *T. thiooxidans*. Gu et al. [41] go further in their explanation and identified the fungus they observed as *Fusarium*. They claim that this has a more detrimental effect on the concrete that that of the neutrophilic bacteria *T. intermedius*. In their research they described the latter as being able to etch the surface of the concrete while the fungus *Fusarium* was able to penetrate the material. They also state that a wide range of acids are produced by fungi including acetic, oxalic and glucuronic acids. A further set of experiments [42] using mortar inoculated with bacteria including *T. intermedius* was conducted independently of Mori et al. [5]. In these experiments the deterioration of concrete was thought to be caused by the sulfuric acid produced by the bacteria; however the authors noted little gypsum and limited change in the sulfate ion concentration of the culture medium. They concluded that primary deterioration of the concrete was caused by carbonic and organic acids, which include acetic acid which are all metabolites produced by bacteria.

4. The role of biogenic sulfuric acid corrosion

4.1. Attack mechanisms

Only limited work has been carried out in assessing the performance of concrete mixes in a biological environment [4] a surprising fact considering several researchers have claimed that biogenic sulfuric acid corrosion found in wastewater systems is more severe than chemical sulfuric acid and sulfate attack [43,44]. This represents a key knowledge gap in the development of a material based performance specification. While research has identified gypsum, ettringite and even thaumasite as the end-product of the corrosion product the debate centres on the order of their formation, their quantities and specific effects on the cement matrix.

The corrosive nature of a sulfuric acid attack has been well documented from both in situ observations and chemical testing on concrete [4,5,22,30,45–47]. The dissolution effect of the hydrogen ion and the separate effect of the sulfate ion combine to create an aggressive set of chemical reactions, threatening the stability of a cement matrix. Debate exists however regarding the mechanisms behind chemical and biological sulfuric acid attacks, and resistance to the former does not necessarily result in resistance to the latter [4,9,48]. Explanations centre on the involvement of the sulfuric acid producing bacteria *Thiobacillus* where Monteny et al. [4] claim that it is the moist conditions in the gypsum corrosion front that constitute an excellent breeding ground for the bacteria to thrive. They then migrate into the concrete producing acid much closer to the corrosion front although Yamanka et al. [7] dispute this claiming it is the acid itself moving inward. In a chemical attack however, the poor penetration of sulfuric acid limits the effects of corrosion to the surface [49]. The acid must negotiate its way through this corrosion layer in order for the attack to continue. It is generally assumed that this results in less severe consequences relative to a biological attack, as the corroded surface acts as a barrier for further penetration. Hence regular brushing of loosely adhering particles may be important in any attempt to mimic biological activity with chemical testing [4,50].

4.2. Types of sulfuric acid attack

In 1945, C.D. Parker described a sulfuric acid attack on concrete sewers as producing a white putty-like deposit, moist, flaky and easily removed from the surface [11,37]. The calcium sulfate (gypsum) formed was a result of a reaction between the hydration products in the cement matrix and the sulfuric acid [22], as previously described in Eq. (1). Experimental and in situ analysis of both mortar and concrete has confirmed that gypsum formation is one of the primary corrosion mechanisms involved in the deterioration of the cement matrix leading to a loss of cohesion in cementitious calcium compounds [5,23,33,51]. The degradation of concrete foundations of an Italian building exposed to sewage waters however was attributed to the growth of gypsum crystals at the aggregate-paste interface causing a loss of strength [52]. The build-up of gypsum though can also act as a barrier to further penetration, slowing an attack [4,53] however it has also been claimed that the rougher surface area leads to a greater surface area to be attacked [18].

The relative resistance of various binder combinations to sulfuric acid attack has been discussed by some researchers. Experiments exposing 100 mm Portland cement concrete cubes with a binder of 35% ordinary Portland cement (OPC)/65% GGBS to an H_2SO_4 solution for 5 months, as described in BRE Digest 363 [54], reported higher performance than for binders of 100% sulfate resisting Portland cement (SRPC) or 75% OPC/25% PFA [47]. This improved performance of concrete in acidic conditions has been attributed to either lower porosity, lower levels of calcium hydroxide or both [4,45,48] while Saricimen et al. [16] determined that in a 3% flowing H_2SO_4 solution neither SRPC nor OPC showed any difference in resisting attack, a conclusion supported by [7]. Monteny et al. [43] suggest that a refined pore structure will increase the capillary action of the cement matrix and act as a mechanism for the aggressive solution to find its way deeper into the concrete.

In experiments to assess commercially available piping, De Belie et al. [9] prepared non-standard cylindrical specimens of concrete with CEM I and CEM III high sulfate resisting cement and exposed them to a 0.5% H_2SO_4 solution in alternating wet/dry cycles. They concluded the limestone aggregate, acting as a sacrificial medium to reduce the rate of acid attack, played a more crucial role against attack that the cement type. The sulfate resisting cements also performed better than the blast-furnace slag cements, an observation similarly supported by other experimental results [29] (conducting experiments with 60% GGBS cylinders in a 1% H_2SO_4 for 168 days). This is however contradicted by research from Monteny et al. [4] who performed experiments in 1–5% H_2SO_4 solutions. However it is noteworthy that the significance of the role played by the limestone aggregate has been emphasised [25,29].

Ettringite is a crystalline compound and its formation can be observed in the process of cement hydration (primary ettringite) and in the effects of an external sulfate attack (secondary ettringite). Some of the reactions associated with its formation involve calcium aluminates, such as C_3A, and gypsum but may also incorporate an external sulfate attack on the calcium aluminate hydrates and monosulfate hydrate phases [4,54]. According to Skalny et al. [22] under sulfuric acid attack only limited amounts of ettringite will form in deeper sections of the concrete as long as the pH is high enough to maintain its stability and enough of the gypsum formed in the initial stages of attack can move into the concrete. This assessment concurs with other researchers who have also stated ettringite's inability to survive in an acidic environment [44] and even in alkaline environments with pH's as high as 10.6 [49]. In contrast, Monteny et al. [4] stress in their assessments the importance of ettringite and its more devastating effect on concrete than gypsum, while its formation from a sulfuric acid attack was also documented by others assessing the influence of fungi on concrete corrosion [42] and simulated biogenic sulfuric acid corrosion [5].

It is noteworthy that the presence of such key compounds such as gypsum and ettringite is accepted as being a function of mix design and the binder combinations used. However the notion of using this material design to control the presence of these expansive compounds is not at this stage well developed.

4.3. Influence of the sulfate ion

As an attack by sulfuric acid is a combined acid–sulfate reaction, many researchers have deemed it prudent to assess concrete susceptibility in standard sulfate testing solutions including sodium sulfate (Na_2SO_4), magnesium sulfate ($MgSO_4$) or a combination of both. The validity of this method to assess attack in a wastewater environment has however drawn some uncertainty based on discrepancies in chemical and biological tests [4].

Sodium and magnesium-based sulfate solutions have substantially different effects on concrete. With the former, calcium hydroxide primarily undergoes decomposition to gypsum and subsequently ettringite. When there is an insufficient source of calcium for the reaction to continue only then will the solution begin to attack the C–S–H phase [22,51]. Magnesium solutions attack all phases simultaneously in the cement matrix preferring calcium hydroxide first followed by the calcium–silicate–hydrate (C–S–H) phase to obtain its reactive calcium. The products from a magnesium sulfate reaction include gypsum, ettringite, a magnesium–silicate–hydrate (which lacks cohesive properties) and the mineral form of magnesium hydroxide, brucite [55].

In sodium sulfate, ettringite can be associated mainly with the reaction between the AFm monosulfate phase and the sulfate ions migrating into the concrete. At low concentrations of sulfate solutions (<1000 mg SO_4^{2-}/l) ettringite will be the primary cause of deterioration [4] whereas at higher concentrations (>8000 mg SO_4^{2-}/l) gypsum will dominate in a sulfate attack [56]. It is important, therefore, to use a concentration of sulfates that accurately represents the corrosion mechanism in the desired environment.

In magnesium sulfate solutions the deterioration mechanism is primarily a result of the loss of cohesion and disintegration with the formation of gypsum and magnesium hydroxide [4,22]. The saturated solution pH of magnesium hydroxide is approximately 10.5 and consequently this causes the destabilisation of ettringite. As a result the circumstances favourable in the formation of ettringite from a magnesium sulfate attack are significantly impeded [57]. Skalny et al. [22] do note however that a limited amount may form when the pH remains high enough in the concrete for a sufficient period of time while research on slag cements [58] attributed ettringite formation as substantially contributing to the damage produced by $MgSO_4$ solutions.

Gollop and Taylor [51,58] concluded in their analysis that the resistance of GGBS concretes to attack by sulfates increases with decreasing levels of Al_2O_3. Lower levels of C_3A were noted by other researchers [16,29] in reducing the harmful effects of exposure to sodium sulfate. In using cement pastes in their analysis however, Gollop and Taylor neglected the effects of the aggregate-paste interface previously considered important in analysing a sulfate/sulfuric acid attack [49,59–61]. Their addition of increasing levels of GGBS up to a level of 92% increased resistance to attack by sodium sulfate solutions but had the opposite effect when exposed to magnesium sulfate. In an assessment of 150 mm × 75 mm reinforced concrete cylinder specimens exposed to a 2.1% SO_4^{2-} sulfate solution, Al-Amoudi [61] indicated that for a 60% GGBS replacement level, deterioration in the mixed magnesium/sodium based solution was considered significant. It was concluded that GGBS mixes fared poorest when compared to other cement replacement materials including silica fume (10% replacement) and fly ash (20% replacement). In assessing results from a study by the BRE [25,46], Osborne [29] also came to similar conclusions regarding the effects of magnesium and sodium sulfate solutions and the use of high percentages of GGBS as a cement replacement. The TEG one-year review [62] also noted the benefit of a 70% GGBS replacement level with limestone cement and good quality carbonate aggregate against conventional forms of sulfate attack.

4.4. Simulation of the biological corrosion process

In a simulated wet/dry 17-day attack cycle Vincke et al. [21] exposed 2 × 2 × 5 cm specimens of concrete to a biological sulfur solution containing *Thiobacilli* bacteria following an incubation period in an H_2S environment. After a total of 51 days and three cycles, the specimens made with a CEM I Portland cement and CEM III blast-furnace slag cement were analysed in terms of weight loss. Results indicated that both mixes performed similarly. De Belie et al. [9] used an almost identical process to the above [21], using specimens that were 80 mm diameter and 15 mm deep, which were subjected to a fourth cycle of 17 days. In their experiments they observed the sulfate ion concentration of their solution to increase from 2 g/l to 4 g/l which the authors cite as evidence for the production of sulfuric acid by the sulfur-oxidising bacteria. The results of their experiments concluded that Portland cement performed better than CEM III blast-furnace slag cement. In this instance they theorise that owing to the greater surface area of CEM III the bacteria are able to colonise the surface of the cement more rapidly than the Portland cement.

Further investigation has revealed other methods of modelling biological corrosion in the wastewater environment. A simulation chamber was developed by researchers in Hamburg, described by Monteny et al. [4], which allowed the corrosion process to be modelled at eight times the in situ level could be reached through the optimisation of the corrosive environment. Test blocks of 60 × 11 × 7 cm were immersed in 10 cm of water at 30 °C and sprayed with *Thiobacilli* bacteria. H_2S gas at 10 ppmv was pumped into the chamber and acted as a substrate for the bacteria. The number of bacteria on the surface of the specimens was counted and it was found that the rate of corrosion was dependent on the levels of *T. thiooxidans* detected.

Experimental work was also carried out into the corrosion mechanism involved in the deterioration of concrete constructing a simulated sewer pipe 20 m long and a diameter of 15 cm [5]. Test specimens of mortar bars 4 × 4 × 16 cm were made with the bottom half of these bars placed in sewage and exposed to H_2S gas not exceeding 300 ppm. Identical mortar bars were placed half submersed into a sewage medium, an autotrophic basal growth culture medium without thiosulfate and distilled water. These were inoculated every two weeks with *T. thiooxidans*. Corrosion just above the waterline was observed on bars in the sewage and autotrophic basal media. Those in water remained unaffected while the sewage samples displayed the greatest corrosion rate. The authors concluded that based on these results the bacteria required a supply of moisture and nutrients to initiate the corrosion process while the corrosion products formed were determined to be gypsum and secondary ettringite. As with the issue of sulfuric acid attack, the possibility of restricting the formation of corrosion products through appropriate mix design is not developed.

5. Conclusions

Three research foci were evident in the study of sulfate/sulfuric acid effects on concrete. These are:

- Studies of the biological processes behind the corrosion of wastewater infrastructure, with particular reference to the role of sulfate-reducing and sulfur-oxidising bacteria.
- Studies of the chemical effects of sulfates and sulfuric acid on concrete mixes.
- Laboratory-based research methodologies, especially those incorporating the biological effect on concrete.

Chemical tests alone do not fully represent the microbial effects on concrete, although they may help in assessing the types of damage that can occur. Some researchers have carried out full-scale laboratory analysis, but it is worth noting that the equipment necessary to adequately mimic in situ conditions is invariably complicated, cumbersome and custom built [4,63]. The realisation of resources required to undertake such research continues to be an obstacle to addressing this topic. The use of such complex research apparatus in routine performance-based specification is impractical.

Although there exists significant quantities of data on the topics of sulfate, sulfuric acid and biogenic corrosion of concrete, little has been achieved in the way of formulating an accepted mathematical model of deterioration that incorporates agreed parameters of significance. This represents a significant knowledge gap and acts as a technical barrier towards using material design as a means of controlling corrosion due to biochemical attack. This continues to inhibit the design of durable concrete wastewater infrastructure and has significant implications for public expenditure in this area. The need to consider the interaction of biological and chemical processes may hold the key to achieving greater progress and allow practitioners to use concrete mix design as a means of delivering intended service lives.

Acknowledgements

The authors gratefully acknowledge the financial support provided by Enterprise Ireland Innovation Partnership Project IP/2008/540 and Ecocem Ireland.

References

[1] Congressional budget office. future investment in drinking and wastewater infrastructure. ISBN 0160512433, Congressional Budget Office; 2002.

[2] Attiogbe EK, Rizkalla SH. Response of concrete to sulfuric acid attack. ACI Mater J 1988;84(6):481–8.

[3] Beeldens A, Monteny J, Vincke E, De Belie N, Van Gemert D, Taerwe L, et al. Resistance to biogenic sulfuric acid corrosion of polymer-modified mortars. Cem Concr Compos 2001;23(1):47–56.

[4] Monteny J, Vincke E, Beeldens A, De Belie N, Taerwe L, Van Gemert D, et al. Chemical, microbiological, and in situ test methods for biogenic sulfuric acid corrosion of concrete. Cem Concr Res 2000;30(4):623–34.

[5] 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.

[6] Neville A. The confused world of sulfate attack on concrete. Cem Concr Res 2004;34(8):1275–96.

[7] Yamanaka T, Aso I, Togashi S, Tanigawa M, Shoji K, Watanabe T, et al. Corrosion by bacteria of concrete in sewerage systems and inhibitory effects of formates on their growth. Water Res 2002;36(10):2636–42.

[8] 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.

[9] 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):2223–36.

[10] Kawamura S. Integrated design and operation of water treatment facilities. Wiley; 2000.

[11] Parker CD. The isolation of a species of bacterium associated with the corrosion of concrete exposed to atmospheres containing hydrogen sulfide. Aust J Exp Biol Med Sci 1945;23:81–90.

[12] Fan CY, Field R, Pisano WC, Barsanti J, Joyce JJ, Sorenson H. Sewer and tank flushing for sediment, corrosion, and pollution control. J Water Res Pl 2001;127(3):194–6.

[13] Jana D, Lewis RA. Acid attack in a concrete sewer pipe – a petrographic and chemical investigation. In: Proceedings of 27th international conference on cement microscopy. Victoria, Canada; 2005.

[14] Roberts DJ, Nica D, Zuo G, Davis JL. Quantifying microbially induced deterioration of concrete: initial studies. Int Biodeter Biodegr 2002;49(4):227–34.

[15] Barbosa VL, Burgess JE, Darke K, Stuetz RM. Activated sludge biotreatment of sulphurous waste emissions. Rev Env Sci Biotech 2002;1(4):345–62.

[16] Saricimen H, Shameem M, Barry MS, Ibrahim M, Abbasi TA. Durability of proprietary cementitious materials for use in wastewater transport systems. Cem Concr Compos 2003;25(4):421–7.

[17] Stufflebean J. Report on bids and award of contract for the San José/Santa Clara water pollution control plant, FY 2007/2008 CIP, east primary influent channel repair project. San José, California; 2007.

[18] Vollertsen J, Nielsen AH, Jensen HS, Wium-Andersen T, Hvitved-Jacobsen T. Corrosion of concrete sewers – the kinetics of hydrogen sulfide oxidation. Sci Total Environ 2008;394(1):162–70.

[19] Weritz F, Taffe A, Schaurich D, Wilsch G. Detailed depth profiles of sulfate ingress into concrete measured with laser induced breakdown spectroscopy. Constr Build Mater 2009;23(1):275–83.

[20] Idriss AF, Negi SC, Jofriet JC, Hayward GL. Corrosion of steel reinforcement in mortar specimens exposed to hydrogen sulfide, part 1: impressed voltage and electrochemical potential tests. J Agr Eng Res 2001;79(3):223–30.

[21] Vincke E, Verstichel S, Monteny J, Verstraete W. A new test procedure for biogenic sulfuric acid corrosion of concrete. Biodegradation 1999;10(6):421–8.

[22] Skalny J, Marchand J, Odler I. Sulfate attack on concrete. London: Spon Press; 2002.

[23] Davis JL, Nica D, Shields K, Roberts DJ. Analysis of concrete from corroded sewer pipe. Int Biodeter Biodegr 1998;42(1):75–84.

[24] Mehta PK, Burrows RW. Building durable structures in the 21st century. Concr Int 2001;23(3):57–63.

[25] Building Research Establishment. BRE special digest 1, concrete in aggressive ground: part 1: assessing the aggressive chemical environment, 2nd ed.; 2003.

[26] Higgins DD. Increased sulfate resistance of GGBS concrete in the presence of carbonate. Cem Concr Compos 2003;25(8):913–9.

[27] Chidiac SE, Panesar DK. Evolution of mechanical properties of concrete containing ground granulated blast furnace slag and effects on the scaling resistance test at 28 days. Cem Concr Compos 2008;30(2):63–71.

[28] McNally C, Richardson MG, Evans C, Callanan T. Determination of chloride diffusion coefficients for use with performance-based specifications. In: Dhir RK, Newlands MD, Whyte A, editors. Proceedings of 6th international congress global construction: ultimate concrete opportunities; application of codes, designs and regulations. Dundee; 2005. p. 321–7.

[29] Osborne GJ. Durability of Portland blast-furnace slag cement concrete. Cem Concr Compos 1999;21(1):11–21.

[30] 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):1486–94.

[31] Percheron G, Bernet N, Moletta R. Start-up of anaerobic digestion of sulfate wastewater. Bioresour Technol 1997;61(1):21–7.

[32] Mohan SV, Rao NC, Prasad KK, Sarma PN. Bioaugmentation of an anaerobic sequencing batch biofilm reactor (AnSBBR) with immobilized sulphate reducing bacteria (SRB) for the treatment of sulphate bearing chemical wastewater. Process Biochem 2005;40(8):2849–57.

[33] Hewayde E, Nehdi M, Allouche E, Nakhla G. Effect of geopolymer cement on microstructure, compressive strength and sulfuric acid resistance of concrete. Mag Concr Res 2006;58(5):321–31.

[34] Emtiazi G, Habibi MH, Setareh M. Isolation of some new sulphur bacteria from activated sludge. J Appl Microbiol 1990;69(6):864–70.

[35] Longworth TI. Contribution of construction activity to aggressive ground conditions causing the thaumasite form of sulfate attack to concrete in pyritic ground. Cem Concr Compos 2003;25(8):1005–13.

[36] Maeda T, Negishi A, Komoto H, Oshima Y, Kamimura K, Sugio T. Isolation of iron-oxidizing bacteria from corroded concretes of sewage treatment plants. J Biosci Bioeng 1999;88(3):300–5.

[37] Parker CD. The function of *Thiobacillus concretivorus* (nov. spec.) in the corrosion of concrete exposed to atmospheres containing hydrogen sulfide. Aust J Exp Biol Med Sci 1945;23:91–8.

[38] Nica D, Davis JL, Kirby L, Zuo G, Roberts DJ. Isolation and characterization of microorganisms involved in the biodeterioration of concrete in sewers. Int Biodeter Biodegr 2000;46(1):61–8.

[39] Waksman SA, Joffe JS. Microorganisms concerned in the oxidation of sulfur in the soil II. *Thiobacillus thiooxidans*, a new sulfur-oxidizing organism isolated from the soil. J Bacteriol 1922;7:239–56.

[40] Jin SM, Yan WM, Wang ZN. Transfer of IncP plasmids to extremely acidophilic *Thiobacillus thiooxidans*. Appl Environ Microbiol 1992;58(1):429–30.

[41] Gu JD, Ford TE, Berke NS, Mitchell R. Biodeterioration of concrete by the fungus Fusarium. Int Biodeter Biodegr 1998;41(2):101–9.

[42] Tazawa EI, Morinaga T, Kawai K. Deterioration of concrete derived from metabolites of microorganisms. In: Proceedings 3rd CANMET/ACI international conference durability of concrete. American Concrete Institute. Nice, France; 1994. p. 1087–97.

[43] Monteny J, De Belie N, Vincke E, Verstraete W, Taerwe L. Chemical and microbiological tests to simulate sulfuric acid corrosion of polymer-modified concrete. Cem Concr Res 2001;31(9):1359–65.

[44] Thomson G. Corrosion and rehabilitation of concrete access/inspection chambers. In: Proceedings of 63rd annual water industry engineers and operators' conference. Brauer College, Warrnambool, Australia; 2000. p. 28–35.

[45] Bassuoni MT, Nehdi ML. Resistance of self-consolidating concrete to sulfuric acid attack with consecutive pH reduction. Cem Concr Res 2007;37(7):1070–84.

[46] Building Research Establishment. BRE special digest 1, concrete in aggressive ground. Part 2: specifying the concrete and additional protective measures, 2nd ed.; 2003.

[47] Hill J, Byars EA, Sharp JH, Lynsdale CJ, Cripps JC, Zhou Q. An experimental study of combined acid and sulfate attack of concrete. Cem Concr Compos 2003;25(8):997–1003.

[48] Vincke E, Wanseele EV, Monteny J, Beeldens A, Belie ND, Taerwe L, et al. Influence of polymer addition on biogenic sulfuric acid attack of concrete. Int Biodeter Biodegr 2002;49(4):283–92.

[49] Allahverdi A, Skvara F. Acidic corrosion of hydrated cement based materials. Part 2 – kinetics of the phenomenon and mathematical models. Ceram–Silikáty 2000;44(4):152–60.

[50] De Belie N. Evaluation of methods for testing concrete degradation in aggressive solutions. In: Proceedings of workshop on performance of cement-based materials in aggressive aqueous environments – characterisation, modelling, test methods and engineering aspects. RILEM Publications SARL; 2008. p. 79–90.

[51] Gollop RS, Taylor HFW. Microstructural and microanalytical studies of sulfate attack. IV. Reactions of a slag cement paste with sodium and magnesium sulfate solutions. Cem Concr Res 1996;26(7):1013–28.

[52] Tulliani JM, Montanaro L, Negro A, Collepardi M. Sulfate attack of concrete building foundations induced by sewage waters. Cem Concr Res 2002;32(6):843–9.

[53] Rendell F, Jauberthie R. The deterioration of mortar in sulphate environments. Constr Build Mater 1999;13(6):321–7.

[54] Building Research Establishment. BRE digest 363, sulfate and acid resistance of concrete in the ground, 2nd ed.; 1991.

[55] Collepardi MA. State-of-the-art review on delayed ettringite attack on concrete. Cem Concr Compos 2003;25(4):401–7.

[56] Hekal EE, Kishar E, Mostafa H. Magnesium sulfate attack on hardened blended cement pastes under different circumstances. Cem Concr Res 2002;32(9):1421–7.

[57] Santhanam M, Cohen MD, Olek J. Sulfate attack research – whither now? Cem Concr Res 2001;31(6):845–51.

[58] Gollop RS, Taylor HFW. Microstructural and microanalytical studies of sulfate attack. V. Comparison of different slag blends. Cem Concr Res 1996;26(7):1029–44.

[59] 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.

[60] Pavía S, Condren E. Study of the durability of OPC versus GGBS concrete on exposure to silage effluent. J Mater Civil Eng 2008;20(4):313–20.

[61] Al-Amoudi OSB. Performance of 15 reinforced concrete mixtures in magnesium–sodium sulphate environments. Constr Build Mater 1995;9(3):149–58.

[62] Clark LA. Thaumasite expert group one-year review. London: Department of the Environment, Transport and the Regions; 2000.

[63] De Muynck W, De Belie N, Verstraete W. Effectiveness of admixtures, surface treatments and antimicrobial compounds against biogenic sulfuric acid corrosion of concrete. Cem Concr Compos 2009;31(3):163–70.