

Deterioration of service reservoirs due to soft water attack

Rene Brueckner^{1*}, Graham Griffiths¹, Jed Hesling², Christopher Taylor², and Amber Telford¹

¹Mott MacDonald Ltd, UK

²Mott MacDonald Bentley, UK

Abstract. Service reservoirs in the UK designed in accordance with EN 206 have shown deterioration due to soft water attack, which is a form of mild acid attack, within one year of commissioning. The attack is represented by aggressive water transforming the surface into a soft paste fully depleted of calcium compounds. Overall, there are three distinct zones of deterioration which are characterised by full calcium depletion (Zone 1), carbonation (Zone 2) and portlandite depletion (Zone 3). The observation of this type of deterioration had initiated the requirement to investigate the type of attack and identify durable and practical concrete mixes to reduce the rate of deterioration as far as reasonably practical. The investigation comprised the production of concrete specimens based on the recommendations of EN 206 for XA3 exposure conditions and more stringent designs based on the limiting values for DC-4 in accordance with BS 8500 and BRE Special Digest 1. The specimens of 12 different mixes were investigated by immersing them in eight service reservoirs with different aggressiveness of hardness, alkalinity and Langelier Saturation Index. The paper discusses the findings of the field and laboratory investigation after one and seven years of immersion. It provides an indication of the most resistant mix designs, effects of the use of fly ash and ground granulated blastfurnace slag, and reliable water parameters that can be utilised to assess the risk and rate of attack.

1 Introduction

Deterioration of immersed concrete surfaces has been observed at several service reservoirs that have been constructed/refurbished during the last 20 to 25 years. The concrete elements have suffered from degradation that progresses from the surface inwards, resulting in an outer layer of soft paste due to aggressive dissolving by mildly acidic soft water.

In 2014, Phase 1 of the project commenced with the retrieval of core samples from some selected affected service reservoirs to assess the root cause of the deterioration [1]. Phase 2, which commenced in 2015, involved the installation of 84 concrete cubes comprising 12 concrete mixes inside eight service reservoirs (SRs). Fourteen of these cubes were removed 12 months after being submerged to provide initial recommendations for the most resistant concrete mixes and measures to mitigate the risk of deterioration [2].

In 2022 and 2023 (Phase 3), a further 35 cubes were removed and analysed using SEM/EDX. This paper summarises the results of the investigation into this second batch of cubes following seven years of immersion in water with varying degrees of aggressivity and provides conclusions and recommendations for all three phases.

The objectives of the investigation were to:

- Better understand the effects of the type of cement replacement and content,
- Assess the resistance of the concrete mixes based on the aggressiveness of the water,

- Estimate the rate of deterioration, i.e. loss of material and paste alterations,
- Verify/identify the most resistant but economic and practical concrete mixes,
- Establish any other factors that would help to protect the concrete against aggressive water.

2 Soft water attack

2.1 Mechanism

Most natural waters have acidities that fall into the pH range 4 to 8.5. Below pH 5, the acidity is usually due to the presence of humic acid, which is limited in aggression because calcium humate is almost insoluble in water, and this forms a protective layer on the concrete.

In general, concrete has excellent resistance to chemical attack, provided an appropriate mix is used. However, due to its high alkalinity, concrete containing Ordinary Portland Cement (OPC) is not particularly resistant against strong acids or compounds which can convert to acids. Natural pure water can attack concrete by dissolving calcium hydroxide and leaching lime. When natural waters that contain free carbon dioxide attack concrete, the aggressiveness and rate of attack are accelerated. In the presence of free carbon dioxide, the calcium hydroxide and the hardened cement paste are first carbonated and then dissolved, resulting in decalcification. The two attacking species are carbonic

* Corresponding author: rene.brueckner@mottmac.com

acid, H_2CO_3 , and calcium bicarbonate, $Ca(HCO_3)_2$. As calcium bicarbonate is soluble, it will be removed by the aggressive water, provided that sufficient carbonic acid is present to stabilise the bicarbonate formed. This results in an attack by carbonic acid of calcium carbonate, whether present due to the carbonation of calcium hydroxide or as limestone aggregate, and the hydrated cement phases. The end products of the attack are gelatinous forms of hydrated silica and alumina and iron hydroxides. In practice, most of the hydrated alumina and iron hydroxides are removed by the aggressive water, such that the only remaining product is gelatinous silica. Soft water attack causes the formation of soluble calcium bicarbonate, and its removal by the water is responsible for the degradation of concrete surfaces.

The attack by aggressive carbon dioxide, that can be classified as a mild acid attack, i.e., Soft Water Acid Attack, results in the formation of three characteristic affected zones, see Figure 1, that are affected by paste alterations above the sound cement paste / interior concrete, namely:

- Zone 1: outer porous zone.
- Zone 2: highly dense (carbonated) zone.
- Zone 3: inner porous zone.
- Zone 4: unaltered sound concrete.

The outer and inner zones are affected by decalcification and are represented by substantial porosity enhancement and calcium depletion (Zone 1) and Portlandite depletion resulting from leaching (Zone 3). The second zone (Zone 2) undergoes underwater carbonation, which forms a barrier against the attacking carbonic acid, as a result of moisture ingress containing dissolved carbon dioxide. The cement paste beyond Zone 3 is unaffected. The attack and depth of zones gradually progress inwards as material is dissolved and eroded at the outer surface of Zone 1.

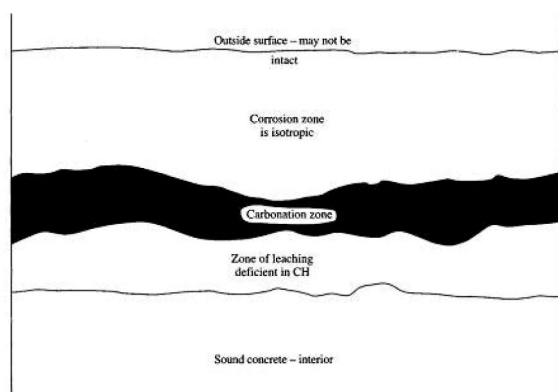


Fig. 1. Diagram illustrating the zones of acid attack [3].

2.2 Water characteristics

The Phase 1 and 2 investigations identified that the Langelier saturation index (L.S.I.), Ryznar stabilisation index (R.S.I.) and the alkalinity of the water provided the most reliable indicators with regard to the aggressiveness of the water and its potential to attack concrete. The aggressive carbon dioxide content and the total hardness of the water, which are generally accepted

indicators, were found to significantly underestimate the aggressiveness potential of the attacking water and to contradict the L.S.I., R.S.I., and alkalinity indicators. The total hardness at two service reservoirs could be categorised as hard, suggesting that the water is supersaturated with calcium carbonate, but as a result of the low alkalinity the L.S.I. and R.S.I. indices classified the water as dissolving. The dissolving properties were confirmed by the visual inspection of the concrete specimens submerged in the reservoirs.

The aggressive carbon dioxide content determined at the eight SRs in accordance with BS EN 13577 during Phase 2 indicated that the concrete should only be designed for the chemical exposure class of XA1 in accordance with the limiting values of Table 2 of BS EN 206. However, the submerged concrete specimens that conformed to the limiting values for XA2 and XA3, in BS EN 206, were found to be affected. The calcium carbonate precipitation potential (CCPP) indicator was also found not to fully align with the L.S.I., R.S.I., alkalinity and pH. The water aggressiveness classification is summarised in Table 1.

Table 1. Water aggressiveness classification [2, 4].

	L.S.I.	R.S.I.	CCPP	Aggressive CO ₂ [mg/L]	Alkalinity [mg CaCO ₃ /l]	Total Hardness [ppm CaCO ₃]
Scaling	>0	<6.2	>0	-	-	-
Non-aggressive	0	6.2 to 6.8	0 to -5	<15	>200	>280
Slightly aggressive Moderately aggressive	0 to -0.5	6.8 to 7.5	-5 to -10	15 to 40 (XA1) 40 to 100 (XA2)	100 to 200	-
Highly aggressive	-0.5 to -2.0	7.5 to 9.0	<10	100 to saturation (XA3)	50 to 100	-
Extremely aggressive	< -2.0	>9.0	<10	-	<50	-

2.3 Effect of type of aggregate

Siliceous (non-calcareous) aggregates, such as granite, basalt and dolerite, are not directly attacked by soft acidic water but are left standing proud of the corroded surface of the hardened cement paste when concrete is attacked, see Figure 2. As the attack progresses, smaller aggregates near the surface may become dislodged as the typical roughened degraded surface develops due to dissolution of the surrounding calcium-bearing cement paste. Further chemical and mechanical erosion results in larger pieces of aggregate falling out, leading to potential issues for the asset owner as aggregate enters the downstream system.

In relation to limestone aggregate (calcareous), the surface would be expected to be smoother under soft water attack, as the rate of attack would be expected to be similar for a good-quality aggregate, as also stated in Clause B2.2 of BRE Special Digest 1 [5].

The resistance of limestone aggregate to soft water attack also depends on its physical properties, such as water absorption, porosity and chemical composition, such as the presence of easily soluble chalk. The effect that a highly porous limestone can have on the surface is shown in Figure 3.



Fig. 2. Siliceous aggregate left standing proud.



Fig. 3. Dissolution of highly porous coarse calcareous aggregate and no effect on fine siliceous aggregate.

3 Methodology

84 concrete cube specimens using the 12 mix designs comprising OPC, 30% pulverized fuel ash (pfa), 50% and 70% ground granulated blastfurnace slag (ggbs) with cement contents ranging from 340 kg/m³ to 420 kg/m³, water-cement (w/c) ratios of 0.35 and 0.45 and siliceous aggregate, as represented in Table 2 were produced at an accredited laboratory. They were cured for 28 days and then delivered to the eight test sites and suspended into the service reservoirs using embedded stainless hooks to which chains were attached and fixed at access hatches. Additional cubes made with the 12 mixes were tested to determine the compressive strength at an age of 28 days.

During the Phase 2 investigation, 14 cubes were retrieved from the reservoirs after 1 year, and under Phase 3, 35 cubes were retrieved and examined after seven years. The 14 cubes at an age of 1 year were selected based on their level of visual deterioration and then issued for petrographic examination, comprising

four cubes from SR3, four from SR4 and six cubes from SR5 and SR6.

Table 2. Mix designs

Mix Ref	Water-Cement Ratio	Cement Content (kg/m ³)	Supplementary cementitious material (SCM)	28-day Compressive Strength (N/mm ²)
1	0.35	380	-	87.9
2	0.35	380	30% pfa	78.3
3	0.35	380	50% ggbs	80.5
4	0.45	380	-	66.5
5	0.45	380	30% pfa	53.9
6	0.45	380	50% ggbs	57.8
7	0.45	420	50% ggbs	59.1
8	0.45	360	70% ggbs	52.2
9	0.45	340	-	68.7
10	0.45	340	30% pfa	54.4
11	0.45	340	50% ggbs	60.9
12	0.45	360	50% ggbs	52.7

In phase 3, following retrieval of the cubes from the reservoirs after seven years, all were visually inspected, and the type and depth of deterioration were assessed using SEM/EDX for selected 35 cube specimens. The remaining cubes were placed back into the reservoirs.

4 Investigation Findings

4.1 Visual inspection

Deterioration of the condition of the cube specimens could be observed between 1 and 7 years when visually assessed on site and in the laboratory. Specimens that did not show any attack after one year either showed an onset of softening with some visible signs of paste loss, or softening had been clearly established when inspected on site after seven years. Brushing of the specimens enhanced the visible features of deterioration. The brushing led to the extent of aggregate particle exposure increasing from trace/minor to moderate and substantial loss of cement paste.

The stages of visual deterioration can be described as:

1. No deterioration.
2. No visible softening but potentially edging (minor attack of the surface seen under the microscope).
3. Occurrence of a soapy/gelatinous smooth layer that appeared to comprise mainly cement paste.
4. Occurrence of a soft layer with granular material containing fine aggregate.
5. Section loss, i.e., loss of coarse aggregate (this was not observed during Phase 3, but during inspections of similar structures affected over a longer time).

Table 3. Cubes submerged, mixes and reservoir water characteristics.

SR Reference	Number of Cubes Installed	Concrete Mixes	Alkalinity [mg/L CaCO ₃]	LSI	RSI	Aggressivity
SR1	8	Mixes 9 to 12	200	0	7.6	Non-/slightly aggressive
SR2	12	Mixes 3 to 8	132	-0.56	8.5	Moderately aggressive
SR3	16	Mixes 1 to 8	14	-2.5	13.0	Highly/extremely aggressive
SR4	16	Mixes 1 to 8	37	-1.2	10.8	Highly/extremely aggressive
SR5	8	Mixes 1 to 8	29	-1.05	11.0	Highly/extremely aggressive
SR6	8	Mixes 1 to 8	29	-	-	Highly/extremely aggressive
SR7	8	Mixes 9 to 12	125	-0.9	9.0	Moderately aggressive
SR8	8	Mixes 9 to 12	133	-1.1	9.6	Moderately aggressive

4.2 SEM/EDX Analysis

The SEM/EDX analyses of the cube specimens identified the chemical profiles for magnesium, phosphorus, sulphur and calcium below one of the cast sides of each specimen, i.e., a formed side. The chemical profiles were then used to determine the depth of chemical alteration of the paste, as shown in Figure 4. The results were analysed with regard to the following parameters:

- Calcium depletion depth and percentage depletion by mix.
- Calcium depletion varying with binder content.
- Calcium depletion varying with water-cement ratio.
- Rate of carbonation/calcium depletion.
- Effect of water characteristics.
- Effect of compressive strength on paste alteration.

4.2.1 Calcium depletion depth and percentage depletion

The results for average calcium depletion by depth and maximum percentage depletion with respective depth for the 12 mixes and three alkalinity ranges: alkalinity <100 mg/l (highly/extremely aggressive), 100 mg/l to 200 mg/l (moderately aggressive) and >200 mg/l (non-/slightly aggressive) is shown in Table 4.

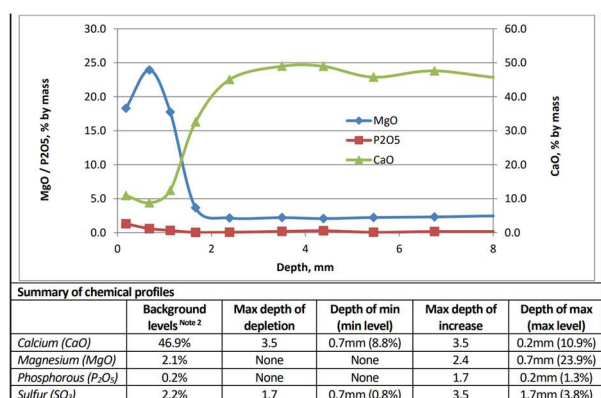


Fig. 4. Example of SEM/EDX line-scan data, SR3 – Mix 2.

The analysis of the specimens submerged for seven years in water with varying aggressivity showed that a decrease in water-cement ratio can reduce the depth of calcium leaching/depletion and the depth at which maximum percentage of calcium depletion occurs.

This was particularly evident when comparing the depth at maximum percentage depletion of mixes 1 to 6 in a highly/extremely aggressive environment (SR3, SR4, SR5, SR6). The 380 kg/m³ OPC mix showed a shift in maximum depletion from 0.5 mm to 0.2 mm when the w/c-ratio was reduced from 0.45 to 0.35 (mixes 4 and 1). A similar shift from 0.6 mm to 0.2 mm was observed for the 50% ggbs mixes (mixes 6 and 3). This shift was less evident in the 30% pfa mixes with w/c = 0.45 and 0.35 (mixes 5 and 2), but the maximum depth of calcium depletion decreased from 3.7 mm to 3.0 mm, respectively. In combination with the shift of the depth of maximum depletion towards the surface with the decrease in w/c-ratio, the percentage of maximum depletion increased, i.e., more calcium-bearing phases were dissolved. This indicates that there is a higher porosity in this smaller outer zone than in a wider zone with lower maximum percentage depletion. This shift is indicative of slowing down the reaction. As concrete is not acid resistant and calcium is dissolved in the presence of carbonic acid, the reaction cannot be stopped, but the rate can be reduced as far as reasonably possible. The slower the reaction can progress inwards, the more calcium will be dissolved in the affected zone. For the pfa mixes 2 and 5, the maximum percentage of depletion was slightly higher for w/c = 0.35 compared to the w/c = 0.45 mixes. However, as discussed above, there was a difference in the maximum depth of calcium depletion, which confirms the described mechanism.

In the moderately aggressive environment (SR2), these features were less significant or could not be observed, as there was only mix 3 with w/c = 0.35. There were no specimens of mixes 1 and 2 that could be compared to their respective mix designs, but with w/c = 0.45. When assessing mixes 4 to 8 with w/c = 0.45, the highest percentage of calcium depletion and depth at maximum percentage was observed in mix 8 with 360 kg/m³ with 70% ggbs. An increase in cement content from 360 to 420 kg/m³ and reduction in ggbs content from 70% to 50% ggbs (mixes 8 and 7) resulted

Table 4. Maximum depth of calcium depletion, maximum percentage of calcium depletion with respective depth (at 7 years)

Mix Ref	Highly / extremely aggressive Alkalinity <100mg/l			Moderately aggressive Alkalinity 100 to 200mg/l			Non-/slightly aggressive Alkalinity >200mg/l		
	Max. Depth of Calcium Depletion	Max % of Calcium Depletion	Depth at Max %	Max. Depth of Calcium Depletion	Max % of Calcium Depletion	Depth at Max %	Max. Depth of Calcium Depletion	Max % of Calcium Depletion	Depth at max %
1	2.4mm	75.4%	0.2mm						
2	3.0mm	84.4%	0.5mm						
3	2.7mm	79.3%	0.2mm	2.0mm	51.9%	0.3mm			
4	3.7mm	61.6%	0.5mm	2.5mm	46.8%	0.4mm			
5	3.7mm	80.7%	0.5mm	5.7mm	46.7%	0.2mm			
6	2.4mm	64.7%	0.6mm	1.8mm	55.4%	0.1mm			
7	2.3mm	68.9%	0.7mm	3.2mm	38.8%	0.2mm			
8	2.4mm	64.1%	0.2mm	3.7mm	59.6%	0.5mm			
9							3.3mm	63.2%	0.6mm
10							1.7mm	25.2%	1.2mm
11							1.8mm	23.7%	0.4mm
12							1.4mm	36.6%	0.8mm

in the maximum percentage and depth at maximum percentage to be significantly decreased, i.e., indicating that a higher cement content is beneficial in this case. However, in the highly/extremely aggressive environment, this mix 8 performed well.

As the majority of mixes in medium and highly/extremely aggressive environments had a cement content of 380 kg/m³ and only one mix with 420 kg/m³, the cube study cannot provide conclusive remarks with regard to the effect of cement content. However, results obtained from core samples retrieved from a 16-year-old filter structure affected by soft water attack indicated that an increase in cement content can reduce the maximum depth of calcium depletion and, therefore, the rate of paste alteration. This is based on a C40/50 mix with w/c = 0.35 and 10% ggbs, but a difference of 80 kg/m³ in cement content (457 kg/m³ vs 537 kg/m³).

4.2.2 Rate of calcium depletion

The assessment of the effect of cement type on the resistance to soft water attack and, in turn, the rate of paste alteration showed that ggbs mixes perform better than OPC and pfa mixes.

This assessment is mainly based on the 50% ggbs mixes because the 70% ggbs mix (mix 8) appears to be an outlier that showed a significant decrease in rate after the 1-year data point (1.55 mm/year at 1 year to 0.14 mm/year from 1 to 7 years, i.e., a decrease of 91%). This outlier may also be attributed to an initial higher permeability of cements with ggbs or pfa, which decreases below comparable OPC mixes after a few months. This decrease in rate was not observed in the other mixes containing 50% ggbs (0.4 mm/year to 0.32 mm/year, 20%) or 30% pfa (0.7 mm/year to 0.45 mm/year, 36%).

In general, the decrease in rate between the first year and the period between year 1 to 7 is 12-17% for mixes with w/c=0.35 (mixes 2 and 3) and 34 to 46% for mixes with w/c=0.45 (mixes 4, 5, 6), see Table 5. The 70% ggbs mix (mix 8) showed a decrease in rate by 91%, which is unlikely to be realistic and is considered an outlier; see also Figure 5. The decrease in rates of the w/c = 0.35 mixes (mixes 2 to 3) currently appears to suggest that the rate of attack is unlikely to show substantial flattening in the future, and as long as free dissolved carbon dioxide is available to form carbonic acid the reaction will proceed in the presence of flowing water. The differences in rate decrease between the w/c = 0.35 (mixes 2 and 3) and w/c = 0.45 mixes (mixes 4, 5, 6) indicated an initial higher resistance of mixes with lower w/c-ratios. The first-year rate differences of the mixes within each w/c-ratio group confirm the initial higher permeability of cements with ggbs or pfa compared to OPC mixes. The unlikely substantial reduction in a decrease of the rate of attack was also confirmed in a structure where data after 8 and 16 years was available, and the rate appeared to be constant, resulting in a linear rate of paste alteration. Based on these observations, it is suggested to assume a constant rate of attack after the first year resulting in paste alteration using the data between 1 and 7 years, unless additional data points can be obtained in the future. Apart from the results of mixes 5, 7 and 8, there is a decrease in rate from (see Table 5):

- highly/extremely aggressive (0.32 to 0.49 mm/year) to
- the medium aggressive environment (0.26 to 0.36mm/year).

The highly/aggressive rates are based on the period between years 1 to 7, and the medium aggressive rates are between years 0 and 7, i.e. the medium aggressive rates are more conservative, and a reduction factor of 2

to 8% to account for an initial higher rate during year 1 could be applied to the 50% ggbs mixes. The identified rates were confirmed by field data, where well-compacted C40/50 concrete showed average paste alteration rates of between 0.3 to 0.4 mm/year. Higher rates, of 0.8 to 1.1 mm/year, were identified in low-quality or low-strength concrete and around crack locations.

Table 5. Calcium depletion rates [mm/year].

Mix	Highly/extremely aggressive				Moderately aggressive
	Rate 0 to 1 year	Rate 0 to 7 years	Rate 1 to 7 years	Decrease (versus 1 to 7 years)	Rate 0 to 7 years
1		0.34			
2	0.50	0.43	0.42	17%/3%	
3	0.43	0.39	0.38	12%/2%	0.29
4	0.75	0.53	0.49	34%/7%	0.36
5	0.87	0.53	0.47	46%/11%	0.81
6	0.50	0.34	0.32	37%/8%	0.26
7		0.33			0.46
8	1.55	0.34	0.14	91%/59%	0.53

Note: Data were not available for all mixes at 1 and 7 years.

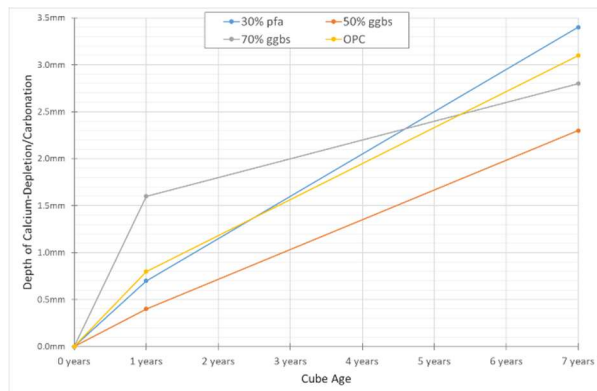


Fig. 5. Depth of calcium depletion/carbonation versus time.

To estimate the rate of paste alteration, the maximum depth of calcium depletion was used, but to assess the time until corrosion of reinforcement occurs, the depth at which the pH of the pore solution drops below 10.5 needed to be identified. This depth was found to correlate with the location, with approximately 35% of residual calcium oxide in the cement paste. This is at approximately 70% of depth compared to maximum calcium depletion. The 35% limit was identified from the data from this research, and this was also confirmed by the results presented by Rosenqvist et al [6]. Thus, a reduction factor of about 30% can be applied to the rates of paste alteration used to estimate the rate until corrosion of reinforcement is likely to occur. This resulted in the evaluation of:

- Rates of 0.22 to 0.34 mm/year for the onset of corrosion of in highly/extremely aggressive environments, and
- Rates of 0.32 to 0.49 mm/year in highly/extremely aggressive environments for paste alteration depths.

In the medium aggressive environment, rates of 0.18 to 0.37 mm/year may be expected for the onset of corrosion. In a non- or slightly aggressive environment, that factor is likely to be even greater as leaching may still occur or not be applicable at all where scaling occurs. However, further work is required to verify this high-level assessment.

Based on the results regarding mix design parameters, 50% ggbs mixes performed better than OPC and 30% pfa mixes. Research undertaken by the University of Dundee concluded that the optimum ggbs content is 55% and for pfa mixes 25% [7]. The adoption of 55% ggbs content agrees with the findings of this research, which recommends 50% ggbs.

There is also an improvement in resistance to soft water attack when reducing the water-cement ratio as far as reasonably practical. In the case of this study, mixes with a w/c-ratio of 0.35 performed better than with a w/c-ratio of 0.45. The study did not provide any conclusive data on the influence of the cement content, but data from structures in the field indicated that a higher cement content is beneficial. The cement content should be chosen in combination with the w/c-ratio, as a minimum amount of cementitious material needs to be present to make the mix workable, and also heat of hydration aspects need to be considered.

4.2.3 Effect of compressive strength on paste alteration

An assessment of the effects of purely compressive strength, independent of mix design, indicated that higher strength results in shallower depth at maximum percentage depletion. There were, however, no trends that showed a decrease in both maximum depletion depth or percentage of maximum depletion for all or within each aggressivity range.

4.2.4 Effect of water characteristics

Alkalinity and Langelier Saturation Index (LSI) were identified to be the most reliable parameters for predicting aggressivity. A trend of decreasing maximum depth of calcium depletion with increasing alkalinity/LSI could be identified for the 50% ggbs and 30% pfa mixes but not for OPC and 70% ggbs, see Figure 6. The aggressivity was not found to alter the conclusions for the most resistant concrete mix designs containing 50% ggbs. The aggressivity will only have an effect on the rate of paste alteration and onset of corrosion.

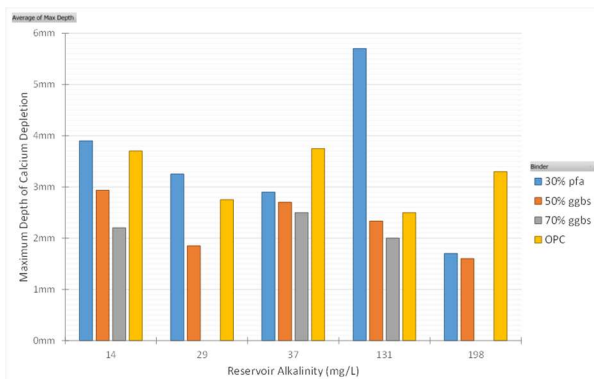


Fig. 6. Calcium depletion depth compared by binder content/type and reservoir alkalinity

4.2.5 Comparison to field cases

Data from core samples obtained by the authors from structures exposed to soft water confirmed the cube observations from this study, with the resistance increasing with decreasing water-cement ratio and increasing cement content. There was, however, no clear indication about the effect of cement type. The benefits of an increased strength due to a reduction in w/c-ratio with the same cement type was confirmed from investigations at a structure that suffered from construction quality issues that affected the concrete strength.

5 Conclusions and recommendations

5.1 Conclusions

The 7-year study resulted in the following conclusions:

- Deterioration of all cube samples, independent of mix design, could be visually observed between 1 and 7 years, and the early stages of deterioration are visibly observable: 1. Edging of the surface; 2. Occurrence of soapy/gelatinous smooth layer; 3. Soft layer with granular material; and 4. Section loss.
- The roughness of the affected concrete surface is dependent on aggregate type and quality of calcareous aggregate. High-quality calcareous aggregate, with low absorption and porosity, is likely to undergo a similar rate of deterioration as the cement paste, whereas inert siliceous aggregate would become projecting and low-quality calcareous aggregate would disintegrate at a faster rate than the paste, creating holes in the surface. All deterioration will result in fine materials accumulating on the reservoir floor, with more coarse material in the case of siliceous aggregate.
- Ggbs mixes generally performed better than the OPC or pfa mixes, in this order, when assessing visually or using SEM/EDX analysis.
- A water-cement ratio of 0.35 has a positive effect on reducing the depth of calcium leaching/depletion, and the location of maximum percentage of calcium depletion moves closer to the surface, in comparison

to mixes with a w/c of 0.45. This also indicates that a densification of the surface, such as that achieved by using Controlled Permeability Formwork (CPF), will initially slow down attack.

- Based on field data, an increase in cement content is likely to increase the resistance of the concrete to soft water attack.
- The average rate of calcium depletion with time is lowest, on average, for GGBS mixes. OPC and PFA mixes have higher rates of calcium depletion, and all rates are also highly influenced by w/c-ratio.
- The rate of deterioration decreased by 12 to 17% between years 1 and 7 compared with the first year for mixes with w/c = 0.35. For w/c = 0.45 mixes, this reduction is approximately 34 to 46%. This indicates a significant initial higher permeability of the cement paste within the first year, which is lower in w/c = 0.35 mixes compared to w/c = 0.45 mixes, i.e. lower w/c-ratios and / or CPF are beneficial. Based on a field case with an age of 16 years, it is likely that the rate will be nearly constant over time, and a substantial ‘flattening’ of the curve is unlikely.
- Paste alteration rates ranged from 0.32 to 0.49mm/year in highly/extremely aggressive environments and 0.26 to 0.46 mm/year in medium aggressive environments. The lower rates were observed for Mix 6 specimens, i.e. w/c = 0.45 and 380 kg/m³ with 50% ggbs.
- The rate to initiation of corrosion is approximately 70% of the paste alteration rate and represents a residual calcium oxide content in the cement paste where corrosion is likely to occur.
- Rates calculated based on average field data confirmed the rates established in this study.
- There is no apparent trend between depth of paste alteration and compressive strength, i.e. resistance is mainly based on the mix design: w/c-ratio and cement type.
- An increased strength, however, shifts the depth of maximum percentage of calcium depletion towards the surface.
- Alkalinity is seen as the defining metric of water aggressiveness, with reservoir water having an alkalinity of less than 100 mg/L showing a higher percentage of calcium depletion in all mixes, compared to those higher than 100 mg/L.
- The rate of paste alteration reduces with reducing aggressiveness.
- Paste alteration/leaching will also occur in non-/slightly aggressive environments as long as the concrete is exposed to moisture, but alterations will not affect the protective layer at the reinforcement.
- Paste alteration is not equal to loss of cross-section. The rate of section loss is conservatively assessed as

0.1 mm/year, which means that for a 100-year design life, a sacrificial cover of 10 mm should be added to the minimum cover required to provide bond.

- Concretes with Portland limestone cement were not investigated, but the presence of limestone powder may accelerate deterioration as pores will be formed when attacked, i.e. porosity will increase. Based on literature, limestone powder in excess of a maximum amount, approximately 15%, will result in an acceleration of concrete deterioration that is not limited to soft water attack [8].

5.2 Recommendations

The recommendations of the study are as follows:

- Water-cement ratio: Use concrete mixes with water-cement ratios as low as practical, i.e., as close as possible to 0.4 or lower, and a maximum of 0.45. (It is acknowledged that mixes with w/c of 0.35 are not practical in the UK).
- Cement content: Minimum 380 kg/m³ (note: to achieve a w/c of 0.4, a cement content in the region of 420 kg/m³ will be required for workability; further, higher cement contents appear to provide better resistance but will introduce early-age thermal cracking and sustainability issues).
- Cement type: Ggbs is the preferred cement replacement at a percentage of 50 to 55%, i.e. CEM III/A. Cement combinations with limestone filler need to be carefully assessed, and the overall limestone content within the cement combination should be kept as low as possible.
- Concrete compressive strength: Minimum grade of C40/50.
- Use of a high-quality limestone aggregate: Low absorption (<1.5%) and low porosity. If limestone sources have higher absorption, then siliceous aggregate with a low coefficient of thermal expansion, i.e., granite (10.5×10^{-6}), basalt (10.5×10^{-6}) or dolerite (10×10^{-6}) may be considered.
- The use of controlled permeability formwork (CPF) is beneficial to reduce the rate of attack in the outer cover zone, and effective curing is highly important.
- The use of waterproofing admixtures, such as those based on crystalline technology, may provide additional resistance, to be further investigated.
- The concrete cover design should consider the actual material loss when determining the minimum cover for reinforcement bond strength.
- The rate of paste alteration should inform the design for concrete cover against corrosion.

The authors would like to thank Yorkshire Water, Scottish Water and Wessex Water for allowing access to their facilities

to store the cube samples and/or retrieve cores for analysis and providing water quality data.

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