The liquid manure storage facilities of a swine or dairy operation constitute a significant part of the agricultural building infrastructure investment. It is important that these facilities perform as expected and that they do so for the expected life of the operation. However, concrete in farm buildings is subjected to severe hydrogen sulphide (H₂S) and sulphate concentrations that result in the deterioration of reinforced concrete. This leads to premature deterioration of piers and floors, especially slatted floors. In some swine barns in Ontario a 50% loss of expected service life was reported when typical Portland cement concrete mixes were used. The results of this research will help find the most cost-effective solution for reducing concrete deterioration to a minimum and enhance the service life of reinforced concrete in livestock buildings, thus making better recommendations for durable structures in contact with manure.

In the present study 48 concrete cylindrical specimens, 100 mm in diameter and 100 mm in height, with a reinforcing steel bar in the centre were exposed to H₂S gas and sulphate solution, some for more than 3 years. One half of the specimens was partially immersed in sodium sulphate (20,000 ppm SO₄²⁻) and also subjected to H₂S gas (1,000 ppm H₂S). The second set was subjected to H₂S gas only. Each set consisted of 8 different treatments including Portland cement (PC) concrete with 0.4 and 0.5 W/CM ratios, PC concrete with 8% silica fume replacement, 25% fly ash and 35% slag of the total amount of cementing material and specimens made of PC concrete with combinations of silica fume and fly ash (6%, 25%), and silica fume and slag (6%, 25%). Finally one treatment was carried out with sulphate-resistant cement.

From the results it can be concluded that high-quality concrete with a low W/CM ratio and sulphate-resistant binder-like type 50 Portland cement (SR) is a simple and cost-effective method to produce durable reinforced concrete for livestock buildings. The sodium sulphate and H₂S form a more corrosive environment than the H₂S gas only.

1. Introduction

Reinforced concrete for the manure storage of a farm operation is often exposed to aggressive environmental conditions. Temporary storage of liquid manure underneath barn floors produces corrosive agents generated from aerobic and anaerobic fermentation, causing premature corrosion of reinforcement steel and degradation of the concrete. The rehabilitation of reinforced concrete structures due to corrosion of steel-reinforcing bars is quite expensive compared
with the use of more resistant concrete at the time of construction, as it is generally accepted that the quality of the concrete cover that protects the reinforcement is critical in limiting corrosion damage.

For Canadian climatic conditions, storage of manure for a period of 6 months, or even longer, is generally recommended, and in some provinces legislated, so that manure spreading can be avoided during winter. Before the manure can be removed from storage it usually has to be agitated, which causes the concentration of the various corrosive gases to increase drastically. Svennerstedt et al. (1999) reported that the concentrations of the gases measured directly after mixing of the slurry were extremely high. Methane (CH4) and carbon dioxide (CO2) concentrations increased to a level 2–3 times higher than the level before mixing took place. Hydrogen sulphide (H2S) concentration increased by a factor of 100–1000, whereas the NH3 concentration was 2–5 times lower. Of these, H2S is the most corrosive agent that leads to the rapid deterioration of concrete floors in barns. Frénay and Zilverberg (1993) and Idriss et al. (2001) reported that H2S dissolves in moisture films on the exposed concrete surface where it undergoes oxidation by aerobic bacteria to sulphuric acid (H2SO4) commonly referred to as biogenic H2SO4 attack. In addition, H2S attacks concrete directly by reacting with the calcium hydroxide in a set cement to form calcium bisulphide.

Different authors (Zhang et al., 1994; De Belie et al., 1997; Svennerstedt et al., 1999; Idriss, 2000; Jiang, 2002) have mentioned the presence of large amounts of lactic and acetic acid and aggressive ions like Cl\(^-\), SO\(4^{2-}\), Mg\(^{2+}\) and NH\(_4^+\). Table 1 shows the chemical composition of liquid, slurry and solid manure of fattening pigs (Svennerstedt et al., 1999).

Furthermore, the acidic nature of this environment may be a major factor in deterioration of floor slats, as the pH of the liquid manure varies between 5.3 and 6.9 (Zhang et al., 1994).

The Dutch standard NEN 5996 (Svennerstedt et al., 1999) established different levels of aggressiveness, depending on the pH and the concentration of SO\(4^{2-}\), Mg\(^{2+}\) and NH\(_4^+\), as shown in Table 2. The Canadian Standard CSA A23.1 (Canadian Standards Association, 2004) considers moderate exposure when concrete is in contact with water-soluble sulphate at 1000–2000 ppm and severe exposure when the solution has 2000–20,000 ppm SO\(4^{2-}\).

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>Liquid manure</th>
<th>Slurry</th>
<th>Solid manure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium (NH(_4^+))</td>
<td>6.5</td>
<td>1.3–5.5</td>
<td>1.9</td>
</tr>
<tr>
<td>Phosphate (P(_2)O(_5))</td>
<td>0.9</td>
<td>3.6–6.6</td>
<td>9.0</td>
</tr>
<tr>
<td>K(_2)O</td>
<td>4.5</td>
<td>2.0–6.1</td>
<td>3.5</td>
</tr>
<tr>
<td>CaO</td>
<td>0.6</td>
<td>2.4–4.4</td>
<td>9.0</td>
</tr>
<tr>
<td>MgO</td>
<td>0.2</td>
<td>0.6–2.0</td>
<td>2.5</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>4.0</td>
<td>0.6–3.3</td>
<td>2.0</td>
</tr>
<tr>
<td>SO(4^{2-})</td>
<td>1.8</td>
<td>1.0–2.0</td>
<td>–</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>–</td>
<td>3.2–11.0</td>
<td>–</td>
</tr>
</tbody>
</table>

**Table 2 – Aggressiveness of solution to concrete, NEN 5996 (concentrations in mg l\(^-1\))**

<table>
<thead>
<tr>
<th>Class</th>
<th>Slightly aggressive</th>
<th>Moderately aggressive</th>
<th>Highly aggressive</th>
<th>Very highly aggressive</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>&gt; 6.5</td>
<td>6.5–5.5</td>
<td>5.5–4.5</td>
<td>4.5–4.0</td>
</tr>
<tr>
<td>NH(_4^+)</td>
<td>15–30</td>
<td>30–60</td>
<td>60–100</td>
<td>&gt; 100</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>100–300</td>
<td>300–1500</td>
<td>1500–3000</td>
<td>&gt; 3000</td>
</tr>
<tr>
<td>SO(4^{2-})</td>
<td>200–600</td>
<td>600–3000</td>
<td>3000–6000</td>
<td>&gt; 6000</td>
</tr>
</tbody>
</table>
steel corrosion. Thus, this study looked at the comparable durability performance of eight different concrete mixes that are practical and cost-effective alternatives in the construction of livestock buildings and manure storage structures. Specimens were concrete cylinders, 100 mm in diameter by 100 mm in height, made of Portland cement, crushed limestone, sand and water, each with a 10 mm diameter by 90 mm length reinforcing steel bar embedded in the centre. They were cast in December 2000. In all mixes a superplasticiser (CATEXOL 1000 SP-MN) was used (625 ml per 100 kg of cementitious material) to increase concrete durability, improve workability and reduce bleeding. A further five larger replicates of each mix, 100 mm in diameter and 200 mm in height, were cast without a steel bar. Three were used for compressive strength determination at 28 days after curing in a 100% relative humidity environment. The other two were used for a deterioration test with H2SO4 and for a sorption test. The mix properties for all eight treatments are shown in Table 3.

One of the mixes was Normal Portland Cement type 10 (Canadian Standards Association (CSA) A3000, 1998) with water/cementitious material (W/CM) ratio of 0.5, which is considered as the most commonly used mix in farm building structures. Common wisdom is to lower the W/CM ratio to increase durability. The same cement type was used but with a W/CM ratio of 0.4, in order to study the influence of lowering W/CM ratio on the physical properties, permeability, durability and the overall quality of the concrete exposed to a sulphate and sulphide environment. However, lowering the W/CM ratio invariably means increasing the cement content of the mix, thereby increasing the tricalcium aluminate, 3CaO·Al2O3 (C3A), content of the hardened cement paste and thus decreasing the sulphate resistance. For the other six mixes, supplementary cementing materials, like slag, fly ash and silica fume, were added in order to reduce the Portland cement content. Supplementary cementing materials contribute to the properties of the hardened concrete through hydraulic or pozzolanic activity. They reduce the concrete permeability, decrease the cement content in the mix and decrease the W/CM ratio. They also, in general, improve the resistance of concrete to sulphate attack by lowering the overall content of tricalcium aluminate (C3A) in the mix.

In the field, concrete used for the construction of liquid manure handling or storage structures is subjected to both sulphide and sulphate. In some locations the concrete is submerged continuously, in other places the concrete is submerged some of the time and in some places the concrete is never exposed directly to the liquid manure. Field observations indicate that the partially immersed concrete structures deteriorate more severely than completely immersed ones. To reach the objectives of the research, a combination of laboratory research and numerical simulation was selected. The laboratory research consisted of accelerated deterioration testing of concrete specimens by subjecting them to H2S gas and a sulphate solution at high concentrations. One half of the specimens was partially immersed in sodium sulphate (20,000 ppm SO4 \(^2\)\(^-\)) and also subjected to H2S gas (1000 ppm H2S). This condition was chosen to simulate units of construction that are partially submerged in liquid manure. The second set was subjected to H2S gas only, a condition that may occur for concrete permanently above the manure. Each set consisted of the eight different mixes. Each mix in each set had three replicates. To keep the gas in the sealed Plexiglas test chamber at the required concentration a control circuit consisting of an H2S sensor, solenoid valves, flow meter, control program and a gas cylinder (1% H2S, and

| Table 3 – Mix Proportions and 28-day compressive cylinder strength of treatments |
|---------------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
|                                | PCS0a          | PC40b          | SRc            | SCd            | SFCe           | FACf           | SSFCg          | FASFh          |
| Cement type (CSA A3000, 1998)  | 10             | 10             | 50             | 10             | 10             | 10             | 10             | 10             |
| Portland cement (kg m\(^-3\) of concrete) | 340            | 425            | 425            | 276            | 391            | 319            | 293            | 293            |
| Cementing materials (kg m\(^-3\) of concrete) | 340            | 425            | 425            | 425            | 425            | 425            | 425            | 425            |
| Water (kg m\(^-3\) of concrete) | 170            | 170            | 170            | 170            | 170            | 170            | 170            | 170            |
| W/CM ratio                      | 0.5            | 0.4            | 0.4            | 0.4            | 0.4            | 0.4            | 0.4            | 0.4            |
| Addition, (% of cementing material content) | –              | –              | –              | 35%            | 8% Silica fume | 25% Fly Ash    | 25% Slag 6%    | 25% Fly Ash 6% |
| 28-day compressive strength (MPa) | 34.0           | 48.6           | 47.4           | 42.3           | 49.1           | 47.0           | 43.5           | 46.0           |

a PCS0, Portland cement (equivalent to CEM I) concrete with 0.5 W/CM ratio.
b PC40, Portland cement concrete with 0.4 W/CM ratio.
c SR, sulphate-resistant cement (equivalent to CEM III B) concrete.
d SC, Portland cement concrete with 35% slag replacement of the total amount of cementing material.
e SFC, Portland cement concrete with 8% silica fume replacement of the total amount of cementing material.
f FAC, Portland cement concrete with 25% fly ash of the total amount of cementing material.
g SSFC, Portland cement concrete with combinations of silica fume and fly ash (6%, 25%).
h FASF, Portland cement concrete with combinations of silica fume and slag (6%, 25%).
99% N₂) was used. The H₂S gas cylinder used for the test lasted 3 weeks, maintaining the concentration of the H₂S gas inside the chamber at 1000 ppm. One week was allowed to reduce the concentration of H₂S in the test chamber to a safe level (near 0 ppm) and a further week was used to carry out all tests on the concrete specimens. Thus, the gas cylinder was changed every 5 weeks, which was considered as a test cycle.

The specimens were exposed to the corrosive environment in the test chamber in May 2001 at the age of 6 months. The first potential readings were carried out in October 2001 after 5 months of uninterrupted exposure. This was considered the start of test cycle 1. The test was terminated for one of the three replicates at the age of 26 months at which time 11 cycles of exposure had been experienced. The second replicates were taken from the test chamber at the age of 32 months after having received 15 cycles of exposure to the corrosive agents. The final replicates were taken out after 23 cycles; they were exposed to the corrosive environment for a total of almost 3 years. The age of the concrete then was 41 months.

The sodium sulphate solutions in which the specimens were half submerged were replenished every other test cycle because the presence of the concrete and the effect of H₂S changed the concentration of the solution. They were analysed and their pH's measured to follow the leaching of the alkalis from the concrete paste and the effect of H₂S gas on the solution acidity and SO₄²⁻ concentration.

The actual damage to the concrete was measured using the volume loss of the concrete at the end of the test period. The deterioration of concrete is either caused by a direct chemical reaction of the corrosive agents with the concrete at its surface, or by reactions below the surface after diffusion of the corrosive gases or liquids into the concrete.

To try to measure the extent of the latter, the total sulphur profile was determined across the concrete cover thickness. Three 10 mm thick discs were cut from the samples that were subjected to the H₂S gas and the sulphate solution: one at mid-height, a second 10mm above mid-height and a third 10mm below mid-height. All discs were then cut again to obtain samples approximately 1000 mm² in size at different depths below the cylindrical surface (0-0.6, 0.6-1.9, 1.9-3.2, and 3.2-4.5 cm) as shown in Fig. 1. The samples were cut by a low-speed diamond cutter and then pulverised.

For the purpose of comparing with a real-life case, samples were taken from the barn that collapsed in Innerkip in 2001 and were analysed for total sulphur. Two samples were taken from the outer surface of a beam, which were subjected to the gas only, and another two samples were taken out of the outer surface of a pier, which were exposed to wet and dry cycles depending on the manure level. Unfortunately, there is little information available on the quality of concrete used in the construction of the collapsed barn in 1989. Tests carried out after the collapse indicated that the concrete in the precast piers was Portland cement concrete with an approximate cement content of 500 kg m⁻³.

Finally, the mineralogy of the concrete was studied using a powder X-ray test to confirm the nature of the chemical reactions that took place. The test was carried out for three concrete mixtures: PC40 as control, and SR and SFC, which were the two best-performing mixes. The samples were taken from the last set of replicates for both corrosive environment exposures, which makes a total of 6 samples. For the ones that were partially submerged in the sulphate solutions, the samples tested were taken from above the solution level, where the sulphur concentration was higher than below the solution level. Samples that were taken from the collapsed barn in Innerkip in 2001 were also tested. One sample was taken from the beam surface and another from the outer surface of a pier. These samples were used to confirm that the laboratory results were similar to those that occurred in a field situation where a pig barn collapsed due to deterioration of the concrete structure.

After completion of the sulphide/sulphate deterioration tests, a small H₂SO₄ deterioration experiment was carried out on 25 mm thick by 100 mm diameter discs positioned on the flat. Specimens of PC50, PC40, SR, SC, SFC and SSFC were tested. No mixes containing fly ash were included because they performed poorly in the earlier deterioration tests. The top of the discs was the top surface of the cylinders from which they were cut; the cut surface was on the bottom. Three times per week 2 cm³ of 7% (by volume) H₂SO₄ was dripped slowly on the surface of the discs. After every 10 applications (about 3 weeks) the discs were washed, scrubbed to remove loose material,
dried in an oven for 1 week and weighed. The weight losses were used as a comparative measure of deterioration. This experiment was terminated after 150 applications.

3. Results

3.1. Compressive strength

The 28-day compressive strengths were determined for all treatments, and the average of the compressive strengths of the three test cylinders is shown in Table 3. The average strength of the PC50 treatment, the only treatment with a W/CM ratio of 0.5, was 34 MPa at 28 days, considerably lower than that of the other seven concrete mixes with a W/CM ratio of 0.4. An increase in strength is generally obtained as the W/CM ratio is reduced.

The results for the two treatments with slag cement (SC and SSFC) are both about 10% lower than the other treatments with a W/CM ratio of 0.4, which indicates that incorporating slag into the cement reduces its 28-day compressive strength. This confirms the well-known slowing effect of slag on the strength gain (Svennerstedt et al., 1999). The rest of the treatments had compressive strengths ranging from 46 to 49 MPa with the silica fume concrete providing the highest value, indicating excellent quality concrete. Silica fume is less affected by the pozzolanic reaction-slowing effect (Kosmatka et al., 1995). They also stated that the strength development of concrete with fly ash is similar to Portland cement concrete. This was observed for the two treatments carried out with fly ash (FAC and FASF).

3.2. The pH measurement

The pH of the Na₂SO₄ solution before placing the concrete specimens in it (20,000 ppm SO₄²⁻) was 6.64. The pH was measured at the end of every test cycle for the first 3 months, and then after two cycles before the solution was changed to bring the SO₄²⁻ concentration back to its original concentration of 20,000 ppm. The increases in pH from the initial value of 6.64 to the final value are shown in Fig. 2.

It may be noted that the pH changed rapidly from neutral (~7) to basic (~12) in the first few months due to the leaching of the alkalis from the concrete into the sulphate solution. Santhanam et al. (2001) reported the same observation. After the 5th test cycle the pH increased significantly less as the concrete near the surface started to lose its alkalinity. The most common dissolution of paste components is portlandite, Ca(OH)₂, due to its high solubility. This process increases the permeability of concrete and has a direct influence on the mechanical properties of cement-based material. This was confirmed by the fact that the tensile strength for all the treatments started to drop off, especially after the 15th test cycle. Another reason for the decrease in pH is the reaction of H₂S with oxygen to form H₂SO₄.

3.3. Solution analysis

The sulphate solutions in which half of the specimens were submerged were analysed chemically after the 2nd, 6th, 12th and 18th cycle. The main ions that were detected in the analysis were sulphate, calcium, sodium and chloride.

3.3.1. Sulphate

Sulphate concentrations after the 2nd, 6th, 12th and 18th cycle are shown in Fig. 3 for the eight mixes. It is evident, from Fig. 3, that after test cycle 2 the sulphate concentrations
increased up to five times from the initial value of 20,000 ppm and that they varied widely from 58,240 to 131,340 ppm. However, after cycles 6 and 12 the sulphate concentrations were fairly uniform at about twice the initial value. The concentration after the 18th cycle varied from about 3 to 4 times the original concentration.

The main reason for the sulphate concentration increase is the following reaction: \( \text{H}_2\text{S}+2\text{O}_2 \rightarrow \text{H}_2\text{SO}_4 \). At the beginning of the test the concrete was sound and had a good-quality concrete cover. Thus, the consumption of \( \text{SO}_4^{2-}/\text{C}_0 \) ions present in the original solution, or that formed according to the above reaction, was slow, which led to the large increase in the sulphate concentrations in the different solutions. As the \( \text{SO}_4^{2-} \) ions started to migrate into the concrete and react with aluminium-bearing species present in the concrete paste and the \( \text{Ca}^{2+} \) ions supplied by the dissolution of the portlandite, the \( \text{SO}_4^{2-} \) ions concentration in the different solutions decreased, due to their consumption after the 6th cycle. The \( \text{SO}_4^{2-}/\text{C}_0 \) concentrations in all the solutions increased again after the 18th cycle, where the rate of the reaction diminishes as the reaction products accumulate. During and Hicks (1991) reported that the removal of soluble materials like \( \text{Ca} (\text{OH})_2 \) increases the permeability and the rate of deterioration. But the attack might become self-inhibiting in that an insoluble ettringite is deposited, thus decreasing permeability by blocking the pores.

3.3.2. Calcium

The calcium concentrations found in the different solutions increased dramatically after cycle 12 and at the same time the sulphate concentrations decreased. Gypsum formation is due to the following reaction: \( \text{Ca}^{2+}/\text{SO}_4^{2-}+2\text{H}_2\text{O} \rightarrow \text{CaSO}_4\cdot2\text{H}_2\text{O} \) and the solubility product, \( K_{sp} \), of gypsum, which is a constant, can be calculated by

\[
K_{sp} = \frac{[\text{Ca}^{2+}][\text{SO}_4^{2-}]}{[\text{CaSO}_4]} = 2.4 \times 10^{-5}.
\]

The activity of \( \text{CaSO}_4 \) is 1 since it is a solid. The ionic product of the different treatments after the 2nd, 6th, 12th and 18th cycle was calculated, using the concentrations of sulphate and calcium. The ionic product was calculated to find the saturation condition of the different solutions, indicating whether a precipitate would be formed on the specimen outer surface or not. The results of the ionic products are presented in Table 4.

The ionic product of most of the solutions is below the \( K_{sp} \) value but not far from super-saturation. In some cases the ionic product was greater than the \( K_{sp} \) of gypsum, which indicates that the supersaturated solution exists and a precipitate, in this case gypsum, would form in order to lower the ionic concentration until the ionic product is once again equal to \( K_{sp} \). For all specimens that were half submerged in the sulphate solution, it was observed that a...
white precipitate had formed on the outer surface. In most treatments the ionic product was highest after the 12th cycle, when the sulphate concentration was at its lowest value. This indicates that the sulphate was consumed in forming the precipitate, as the ionic product pushes the equilibrium equation towards building gypsum.

3.3.3. Chloride
Chloride concentrations are shown in Fig. 4. The high concentrations, up to 3000 ppm, result from the fact that the chloride-binding capacity of cement decreases rapidly with increasing sulphate contents. Csizmadia et al. (2000) reported that there is a competition between sulphates and chlorides to react with C₃A and this is won by the sulphates, with a simultaneous increase of the Cl⁻ concentration in the pore solution. It is obvious from Fig. 4 that the most porous concrete, PC50, has the highest chloride concentrations. A higher W/CM ratio results in a smaller amount of bound chloride.

3.4. Concrete volume loss
The results of the volume loss measurements after the 23rd test cycle (after 32 months of exposure) are presented in Fig. 5. All concrete specimens exposed to sulphate solution and H₂S gas showed higher volume loss than those exposed to H₂S gas only. Most of the concrete loss occurred above the solution level. The evaporation of water from a concrete surface that contains a large amount of alkali sulphates causes crystallisation of salts, which in turn generates a disruptive pressure. This is in good agreement with the field observations of the deterioration of precast columns in a manure tank below a swine barn in Innerkip, Ontario, that collapsed as a result of this deterioration in August 2001. The upper third of the columns were badly eroded to expose the steel completely; the bottom half of the columns, the part fully submerged in the liquid manure most of the year, was in excellent shape (Fig. 6).

The half-submerged PC50 specimen, with the highest W/CM ratio (0.5) and cement content of 340 kg m⁻³, performed significantly better in terms of concrete volume loss than the PC40 specimen, which has a W/CM ratio of 0.4 and a cement content of 425 kg m⁻³. The low-to moderate cementitious material content of the former resulted in less available paste.
to attack. Lenehan and O’Kiely (1999) found that an optimum performance of concrete in a sulphate environment involves a mix with a low W/CM ratio and acceptable cement content. They reported that a cement content of 350 kg m\(^{-3}\) might represent an optimum.

The least volume loss was recorded for the SR treatment although it had a high cement content of 425 kg m\(^{-3}\). However, the sulphate-resisting cement (type 50) had only 2% C\(_3\)A available in the cement paste to be attacked whereas the type 10 Portland cement had 9.8%. This shows the importance of lowering the amount of C\(_3\)A in the long-term durability of concrete exposed to a sulphate environment. The decrease of the total amount of C\(_3\)A in the concrete mix can also be achieved by the replacement of ordinary (type 10) Portland cement with supplementary cementing materials.

3.5. **Total sulphur analysis**

In all cases the sulphur concentration was the highest near the surface of the cylindrical specimens confirming that external sulphate attack proceeds by the inward movement of a degradation front. This was also found by Gollop and Taylor (1992), and Wang (1994). Skalny et al. (2002) also concluded that the sulphate-cement paste degradation is initiated at the surface of the material, moving gradually inwards as the process continues.

Only at the outer surface were the total sulphur concentrations of the specimens exposed to H\(_2\)S higher (mean 13.0 g sulphur per kg dry material) than those exposed to sodium sulphate and H\(_2\)S (mean 7.7 g kg\(^{-1}\) above the liquid level, 6.0 g kg\(^{-1}\) below), but the inner locations had lower concentrations (mean 3.0 g kg\(^{-1}\) adjacent to the steel). A contributing factor no doubt was the fact that the specimens exposed to H\(_2\)S only were dry. As Skalny et al. (2002) pointed out, without water no mechanism of deterioration can proceed.

This is in good agreement with the total sulphur content of the samples that were taken from the barn that collapsed in Innerkip. The samples that were taken from the outer surface of a beam supporting the floor above the manure storage, which was subjected to the gas only, had higher sulphur concentrations than those samples that were taken from the outer surface of a pier, which were exposed to wet and dry cycles depending on the manure level (see Table 5).

In general, the concentrations of sulphur in the specimens that were exposed to sodium sulphate and H\(_2\)S were higher above the water level than on the part below the liquid level. The mechanisms of deterioration involve the penetration of sulphate solutions either by simple diffusion or by capillary suction. When pore water evaporates from above-ground surface or solution level, the sulphate concentration becomes sufficiently high to cause crystallisation, which may be accompanied by volume expansion.

3.6. **Powder X-ray diffraction of the concrete paste**

The powder samples used for the X-ray diffraction test were taken from the outer surface of the PC40, SR and SFC...
treatments in both sets. For the partially submerged specimens the powder samples were taken from above the solution level where the total sulphur concentration was higher. The diffraction patterns for the three concrete mixtures for both corrosive environment exposures indicated the presence of gypsum. In all six samples that were tested no ettringite was found. The two samples that were taken from the collapsed barn in Innerkip in 2001 showed that gypsum had formed on the beam surface and on the outer surface of the pier. Biczok (1967) found that the mechanism of sodium sulphate attack changes with concentration of the solution. At low concentrations (<1000 ppm SO$_4^{2-}$) the main product is ettringite, while at high concentrations (>8000 ppm SO$_4^{2-}$), like those experienced in the laboratory experiments, gypsum is the primary product. In the intermediate range (1000–8000 ppm SO$_4^{2-}$), which was probably the case in the collapsed barn, both gypsum and ettringite are formed. But since ettringite is not stable when the pH falls below 11.5–12, gypsum forms near the surface and a limited formation of ettringite may take place at a depth where a high enough pH value is still maintained (Santhanam et al., 2001; Skalny et al., 2002).

3.7. Sulphuric acid deterioration

The mass loss results from the H$_2$SO$_4$ deterioration tests are shown in Fig. 7 versus the number of applications. After 150 applications of H$_2$SO$_4$ over a period of approximately 1 year the PC50 experienced the greatest loss in mass of 8.2% of the original dry mass. The 5 specimens with a W/CM ratio of 0.4 had losses ranging from 5.8% to 6.8%. The least amount of mass loss (5.8%) was experienced by the sulphate-resistant cement specimen, SR. These results are not conclusive because of the limited number of specimens. What is evident from visual observation of the specimens is that the lime-stone aggregate helps to reduce concrete deterioration from cement paste loss only and breakdown of the concrete structure. The limestone aggregate has an enormous capacity for neutralising acid. After a year of testing no pieces of coarse aggregate had become dislodged. Fig. 8 shows the PC50, SR, SC and SFC specimens after 150 acid applications. The pictures clearly show the greater deterioration of the PC50 specimen compared to the other three.

4. Conclusion

The sulphate-resisting cement mix (SR) with only 2% C$_3$A had the least volume loss (0.1%) whereas the type 10 Portland cement lost 9.8% in the combined sulphate/sulphide deterioration test. This confirms the importance of lowering the amount of C$_3$A for concrete exposed to a sulphate environment, such as manure structures. The SR mix also performed best in the limited H$_2$SO$_4$ deterioration test with a mass loss of 5.8% after 150 applications of H$_2$SO$_4$.

If normal Portland cement is used then the restriction on both the maximum W/CM ratio and on maximum C$_3$A is
advisable; hence, a maximum Portland cement content is extremely important. The results showed that the half-submerged PC50 specimen (0.5 W/CM ratio and of 340 kg m\(^{-3}\) cement content) had 1.8% less volume loss than PC40 specimen (0.4 W/CM ratio and 425 kg m\(^{-3}\) cement content). Low-to-moderate cementing material content (around 350 kg m\(^{-3}\)) results in less available paste to be attacked. This means that mixes in critical areas will require superplasticisers in order to maintain a low W/CM ratio (say 0.45) with a cementing material content of 350 kg m\(^{-3}\).

All concrete specimens exposed to sulphate solution and H\(_2\)S gas showed 0.1–2.4% higher volume loss than those exposed to H\(_2\)S gas only. Most of the concrete loss for the former set was located above the solution level. This is in good agreement with the field observations. Water evaporates from the concrete surface that contains a high amount of alkali sulphates causing yet higher concentrations of sulphates and crystallisation of salts, which in turn generates a disruptive pressure.

The chloride-binding capacity of cement decreases due to the presence of sulphate in the solution. The finding that PC50 had the highest chloride concentrations points out that lowering the W/CM ratio is beneficial in reducing the risk of concrete deterioration.

The ionic product of calcium and sulphate of most of the solutions is not far from the solubility product \(K_{sp}\) of gypsum. Also the powder X-ray diffraction pattern showed the presence of gypsum in PC40, SR and SFC specimens, after the 23 cycles of exposure to both environments.

The sulphur concentration was the highest near the surface of the cylindrical specimens. This confirms the fact that an external sulphate attack usually proceeds by the inward movement of a degradation front. Also the sulphur concentrations at the outer surface of the specimens that were exposed to H\(_2\)S only were higher than those exposed to sodium sulphate and H\(_2\)S, because the latter were continuously kept in the solution, which provides a path to the penetration of the ions. This confirms that the diffusion rate through saturated concrete is much faster than in dry concrete. Specimens exposed to sodium sulphate and H\(_2\)S had higher sulphur concentrations above the liquid level than below; this is again due to the capillary suction and the evaporation of water from the concrete surface above the level of the solution.

**Acknowledgements**

The authors acknowledge the financial support from the Natural Sciences and Engineering Research Council of Canada and the Ontario Region of the Cement Association of Canada for the research work that is reported in this paper. In addition, Lafarge Canada Inc. The authors thank for all their technical assistance and the materials they provided for this project.

**References**


Canadian Standards Association (2004). Concrete Materials and Methods of Concrete Construction. CSA Standard A23.1-04, Toronto, ON


Csizmadia J; Balázs G; Tamás F D (2000). Chloride ion binding capacity of tritracalcium aluminoferriate. Periodoly Polytechnica Series—Civil Engineering, 44, 135–150

De Belie N; De Coster V; Nieuwenburg V (1997). Use of fly ash or silica fume to increase the resistance of concrete to feed acids. Magazine of Concrete Research, 49(181), 337–344


Kosmatka S H; Panarese W C; Gissing K D; MacLeod N F (1995). Design and Control Mixtures, 6th Canadian edn. Canadian Portland Cement Association, Ottawa

Lenehan J; O’Kieley P O (1999). Evaluation of mix specification and PFA as a cement replacer in concretes used in silage storage structures. Irish Agriculture and Food Development Authority, TEAGASC, Grange Research Center, Dunsang (<http://www.teagasc.ie>)


Skalny J; Marchand J; Odler I (2002). Sulfate Attack on Concrete. Spon Press

Svennerstedt B; De Belie N; Braam C R; Lenehan J J; Richardson M; Snock B (1999). Durability of building materials and components in agricultural environment. Report 119, Department of Agricultural Biosystems and Technology, Swedish University of Agricultural Sciences, Sweden
