

Corrosion of Reinforced Concrete Specimens Exposed to Hydrogen Sulfide and Sodium Sulfate

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ABSTRACT

Concrete in farm buildings is subjected to severe corrosion if manure is stored below slatted floors. Many chemicals associated with manure are identified as having a detrimental effect on concrete and the reinforcing steel embedded in the concrete. Of these, hydrogen sulfide is the most corrosive agent that leads to the rapid deterioration of concrete in barns. As well, manure has high concentrations of sulfates.

In the present study, 48 concrete cylinders, 100 mm diameter and 100 mm high, were made with Portland cement, and various combinations of slag, fly ash and silica fume. Each has a reinforcing steel bar embedded in it. 24 cylinders are half immersed in sodium sulfate (20,000 ppm SO_4^{2-}) and also subjected to hydrogen sulfide gas (1,000 ppm H_2S). The second set of 24 is subjected only to hydrogen sulfide gas. In each set, there are 8 different treatments.

The specimens results indicate that after 16 cycles (each cycle is about five weeks long) of testing over 28 months, specimens made with Portland cement (PC) concrete with a water-cementitious material (w/cm) ratio of 0.5 exhibited the least resistance to corrosion. All treatments containing silica fume, fly ash or slag, except the fly ash/silica fume combination, performed better thus far than PC concrete with 0.4 w/cm ratio. Also, it could be concluded further that concrete with sulfate resistant cement is more resistant to corrosion than type I Portland cement. Indeed, sulfate resistant cement concrete was one of the best performers in both sets of tests.

Keywords: Corrosion, concrete, fly ash, manure storage, silica fume, slag, sulphate, hydrogen sulphide

1. INTRODUCTION

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 sulfide and sulfate concentrations that result in the corrosion of reinforced concrete. This leads to premature deterioration of walls and floors, especially slatted floors, to the point of requiring replacement.

The Ontario Farmer of Sept. 11, 2001 reported the collapse of a hog barn in Innerkip, Ontario, on a calm August day, presumably as a result of corrosion of the supporting concrete piers inside the liquid manure tank. The upper parts of the piers, above the normal manure level, were so badly corroded that the reinforcement bars were exposed. The 12-year old structure collapsed killing 200 hogs and causing damage in excess of CAN\$ 0.7M. In some swine barns in Ontario a 50% loss of expected service life was reported, when regular concrete mixes, e.g. 25 Mpa PC concrete, were used. It is estimated that an average annual cost of depreciation on all structures is about \$250 million and about \$100 to 150 million is spent on repairs in Ontario. The results of this research will help find the most cost-effective solution for reducing concrete corrosion 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 order to improve the durability of concrete and the environmental protection under such severe agricultural aggressive conditions, some recent investigations have been made in an attempt to reduce the rate of deterioration by changing the concrete composition (De Belie et al. 1997; Idriss 2000; Jiang 2002). Idriss (2000) exposed small steel reinforced mortar specimens to hydrogen sulfite gas (1000 ppm) and found that steel corrosion started before serious corrosion of the mortar occurred. He found that silica fume replacement of the Portland cement was very effective in slowing steel corrosion.

In this study concrete made with various combinations of Portland cement, slag, fly ash and silica fume is subjected to hydrogen sulfide gas and sulfate solution. The broad long term objective of this study which was started by Idriss (2000) is to extend the lifespan of farm infrastructure, which is now drastically affected by corrosive environments, and to understand the mechanisms that are involved in this corrosion. The results of this research will help finding the most cost-effective solution for reducing concrete corrosion to a minimum and enhance the service life of reinforced concrete in livestock buildings, thus making it possible to make better recommendations for durable structures in contact with manure. The specific objectives of this paper are:

- i. To provide a progress report on the corrosion performance of eight different concrete mixes in the first stage of the present study, and
- ii. to draw preliminary conclusions regarding the corrosion resistance of these eight treatments under long-term exposure to hydrogen sulfide gas and sodium sulfate solution.

1. INTRODUCTION

The reason for the deterioration of concrete, even of high quality concrete, are the specific aggressive environmental conditions often occurring on and below floors in animal houses where manure is collected and stored below the floor. Table 1 shows the chemical composition of liquid, slurry and solid manure of fattening pigs (Svennerstedt *et al.* 1999).

Table 1. Chemical composition of fattening pig manure, in g/L (Svennerstedt *et al.* 1999)

Chemical Composition	Liquid manure	Slurry	Solid Manure
Ammonium (NH ₄ -N)	6.5	1.3 – 5.5	1.9
Phosphate (P ₂ O ₅)	0.9	3.6 – 6.6	9.0
K ₂ O	4.5	2.0 – 6.1	3.5
CaO	0.6	2.4 – 4.4	9.0
MgO	0.2	0.6 – 2.0	2.5
Cl ⁻	4.0	0.6 – 3.3	2.0
SO ₄ ²⁻	1.8	1.0 – 2.0	-
Acetic Acid	-	3.2 – 11.0	-

Table shows that the sulfate concentration of liquid manure and manure slurry is fairly high. CSA A 23.1 (1994) specifies the requirements for concretes subjected to high concentrations of SO₄²⁻. They are shown in Table 2.

Table 2. Aggressiveness of solution to concrete, in mg/L

Exposure Class	Degree of exposure	SO ₄ ²⁻ concentration (mg/L)	Max. water-cementing material ratio	Portland cement type to be used
S-1	Very severe	>10,000	0.40	Type V
S-2	Severe	1,500 – 10,000	0.45	Type V
S-3	Moderate	150 – 1500	0.50	Type II, IV or V
	Negligible	<150		Type I

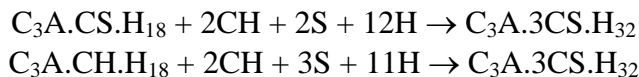
When manure is stored for long periods without agitation, it undergoes anaerobic decomposition during which manure gases are produced. Warm weather and poor ventilation can increase production of these gases. Liquid manure tanks therefore can hold toxic levels of gases, or lack of oxygen. Intermittent agitation of manure in a liquid storage results in a rapid increase in the release of manure gases (Brunet 2002). Agitation releases gases, like hydrogen sulfide, methane, carbon dioxide, and ammonia in large quantities. These gases are listed in Table 3 along with some of their characteristics (B. Svennersted 1999). H₂S can be oxidized to sulfuric acid; this process can be worsened considerably by bacterial action.

Table 3: Gases found above the slurry level, their concentrations and characteristics

Gas	Density	Conc. of non-fermented slurry (ppm)	Conc. of non-fermented slurry (ppm)	Recommended max. conc. (ppm)
Methane (CH ₄)	Lighter than air	200 – 23,000	550,000 – 700,000	500
Carbon dioxide (CO ₂)	Heavier than air	400 – 12,000	300,000 – 450,000	3000
Hydrogen sulfide (H ₂ S)	Heavier than air	1 – 2	50 – 10,000	0.5
Ammonia (NH ₃)	Lighter than air	37	4 – 100	20

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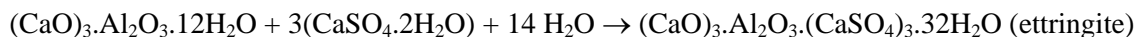
Mehta (1986) reported that calcium hydroxide and alumina-bearing phases of hydrated Portland cement are most vulnerable to attack by sulfate ions. On hydration, Portland cement with more than 5 percent potential C_3A will contain most of the alumina in the form of monosulfate hydrate, $C_3A.CS.H_{18}$. If the C_3A content of the cement is more than 8 percent, the hydration products will also contain $C_3A.CH.H_{18}$. In the presence of calcium hydroxide in Portland cement pastes both alumina-containing hydrates are converted to the high-sulfate form ettringite, $(C_3A.3CS.H_{32})$ when they come in contact with sulfate ions (Mehta 1986).



De Belie *et al.* (2002) support the argument that the sulfuric acid first reacts with the calcium hydroxide in the concrete to form gypsum. Gypsum is the primary reaction product of sulfate attack at high sulfate-ion concentrations (>8000 ppm SO_4^{2-}) (Santhanam *et al.* 2001).



Although gypsum is associated with an increase in volume by a factor of 1.2 to 2.2, the reaction between gypsum and tricalcium aluminate hydrate (C_3A) to form ettringite is much more detrimental.



The volume of ettringite mineral is much larger than the volume of the initial compounds. Thus the formation of ettringite is mainly responsible for the large volume expansion, which leads to increase in internal tensile stress and deterioration of the concrete matrix (De Belie *et al.* 2002).

Santhanam *et al.* (2001), reported that ettringite is not stable in low-lime environments when the pH falls below 11.5 – 12. At this low pH ettringite could decompose to form gypsum. Gypsum, which is a result of cation-exchange reactions, reduces the concrete stiffness and strength, followed by expansion, cracking, and eventual transformation of the material into a mushy or non-cohesive mass (De Belie *et al.* 2002). Vincke and Verstraete (2002) are of the opinion that due to these reactions, the solubility of the calcium compound changes from low to moderately or fairly soluble.

According to Svennersted *et al.* (1999), very high concentration of sulfate may build up within concrete structures which are only partially immersed, or are in contact on only one side, with sulfate water or soils. This is due to the continuing evaporation that will occur under such conditions. Thus, severe attack may occur even where the sulfate content is initially not high. This process is schematically presented in Figure 1. Concrete buried in soil, or completely immersed in water, is under static conditions where sulfate attack is confined to surfaces and therefore often of negligible severity.

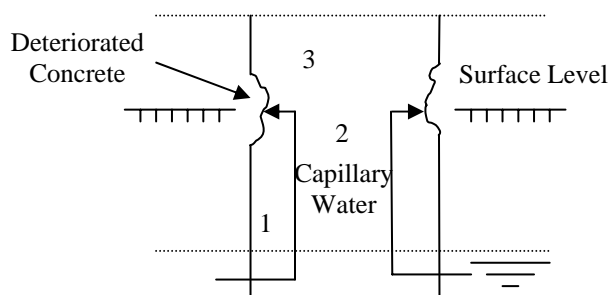


Figure 1. Deterioration of concrete by capillary transport of salts.

The process can be illustrated schematically by the following steps: 1. Continuous supply of dissolved salts, 2. Capillary transport, 3. Evaporation and crystallization.

The quality of concrete, especially its low permeability, is the best protection against sulfate attack, as is the case with most corrosive agents. Adequate concrete thickness, low water/cementitious material ratio and proper compaction and curing of fresh concrete are among the important factors that contribute to low permeability. Portland cement containing less than 5 percent C_3A (Type V) is sufficiently sulfate resisting under moderate conditions of sulfate attack (i.e., when ettringite forming reactions are the only consideration). However, when high sulfate concentrations, of the order of 1500 mg/L or more, are involved, the Type V Portland cement may not be effective against the cation-exchange reactions involving gypsum formation. Under these conditions, experience has shown that cements potentially containing a little or no calcium hydroxide on hydration perform much better: These include high-alumina cements, Portland blast-furnace slag cements with more than 70 percent slag, and Portland pozzolan cements with at least 25 percent pozzolan (natural pozzolan, calcined clay or low-calcium fly ash) (Mehta 1986).

Another effective treatment is the use of silica fume. Due to reduced permeability, silica fume cement concrete provides excellent sulfate resistance. Recent research shows that ternary blends containing slag cement or fly ash, along with silica fume and Portland cement, can be effective for sulfate resistance concrete (Lafarge Canada Inc. 2001).

2. EXPERIMENTAL DESIGN

It is intended that the objectives of the research be attained by accelerated corrosion testing in the laboratory using concrete specimens subjected to hydrogen sulfide and sodium sulfate solution as the only corrosive agents. Acceleration is achieved by using much higher concentration than those experienced in the field, 1,000 ppm H_2S and 20,000 ppm SO_4^{2-} .

Eight treatments, which could reasonably be used in the construction of liquid manure tanks, floors and slats, are being examined for corrosion resistance. Concrete cylinders (100 mm diameter by 100 mm high) were made of Portland cement, limestone, sand and water, each with a 10 mm diameter by 90 mm long reinforcing steel bar embedded in the center. Six replicates for each treatment were made. In all treatments a superplasticizer (CATEXOL 1000 SP-MN) was used (625 mL/100 kg of cementitious material) to reduce the water requirements in concrete and attain the necessary workability without the use of excess water. Also an air-entraining admixture (CATEXOL A.E.260) was used in all treatments (50 mL/100 kg of cementitious

material) as is common in the field to increase concrete durability, improve workability and reduce bleeding. A further three larger replicates of each treatment, 100 mm diameter and 200 mm height, were cast without a steel bar for compressive strength determination at 28 days after curing in a 100% relative humidity environment. The mix proportions and materials used for all eight treatments are shown in Table 4.

The eight treatments are:

1. Portland Cement with water-cementitious material (w/cm) ratio 0.50 (PC50)
2. Portland cement with w/cm ratio 0.4 (PC40)
3. Sulfate resisting cement Type V (SR)
4. Slag cement (SC)
5. Fly ash cement (FAC)
6. Silica fume cement (SFC)
7. Silica fume and slag cement (SSFC)
8. Silica fume and fly ash cement (FASF)

Table 4. Mix Proportions for all Treatments

	PC50	PC40	SR	SC	SFC	FAC	SSFC	FASF
Cement type (ASTM C150)	I	I	V	I	I	I	I	I
Cement (kg/m ³ of concrete)	340	425	425	276.3	391	318.8	293.3	293.3
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
Fine aggregate (kg/m ³ of concrete)	691	616	616	616	616	616	616	616
Coarse aggregate (kg/m ³ of concrete)	850	850	850	850	850	850	850	850
Supplementary cementing material (% of cementitious material content)	---	---	---	35% slag	8% silica fume	25% fly ash	25% slag + 6% silica fume	25% fly ash + 6% silica fume

The top of all specimens, except those for the compressive strength tests, and the exposed ends of the steel bars were coated with an epoxy coating (TRU-GLAZE 4508 Chemical Resistant Epoxy Coating 4508-1000A and 4508-9999B with a ratio of 1:1) in order to prevent the diffusion of the corrosive ions through that surface.

For the corrosion study the 48 specimens are divided into two sets, each set having three replicates. Set I (i.e. 24 specimens) is tested partially (50%) immersed in sodium sulfate (20,000 ppm SO₄⁻²) and at the same time subjected to hydrogen sulfide gas (1,000 ppm H₂S) above the surface of the sodium sulfate solution (Figure 2). The sodium sulfate solution was replaced every other test cycle (every 10 weeks approximately), in order to keep it at the same concentration.

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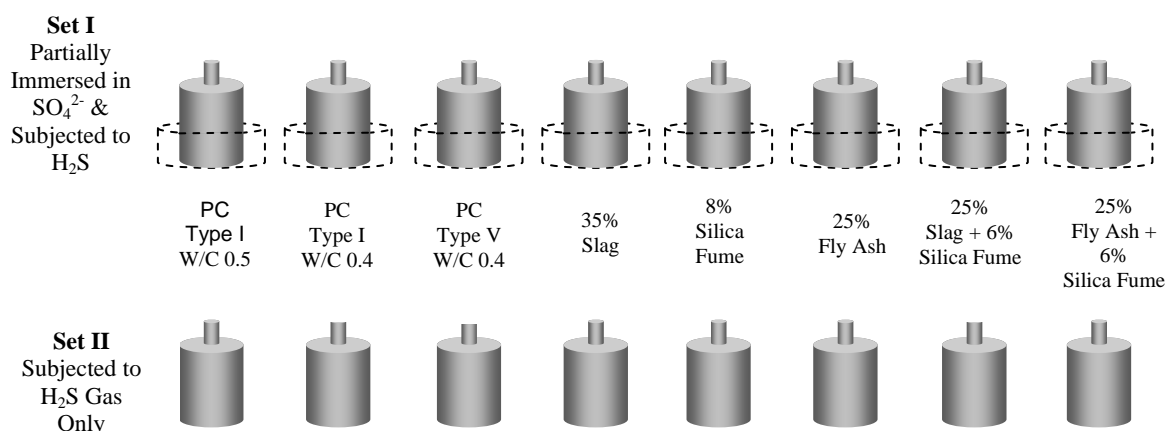


Figure 2. Schematic of test set-up

The three replicates for each treatment are submerged in a separate container (Figure 3), and placed in the upper level of a two-storey test chamber. Set II (i.e. the remaining 24 specimens) is subjected to hydrogen sulfide gas and air (0.1% H_2S , 9.9% N_2 , 90% air) only in the lower level of the same chamber (Figure 2). To keep the gas in the sealed Plexiglas test chamber at the required concentration, a control circuit consisting of H_2S sensor, solenoid valves, flow meter, control program and a gas cylinder is used. The H_2S sensor is based on a semiconductor sensor manufactured by Gemini Detectors Inc., Texas. The sensing element is an indium oxide film whose resistance is determined by the reaction of oxygen adsorbed on the film surface with H_2S .



Figure 3. One Treatment of Set I

The hydrogen sulfide gas in one cylinder (1% H_2S , 99% N_2) lasts about 3 weeks, keeping the concentration of the H_2S inside the chamber at 1000 ppm (0.1%). After this the chamber is left closed for one more week in order to lower the gas concentration back to 0 ppm. Then all the different treatments are taken out of the chamber for the half-cell potential measurement, and thus they are subjected to air for another week. This test cycle is repeated approximately every five weeks.

A number of laboratory tests have been and will be conducted to evaluate the relative merit of each of the eight treatments in resisting corrosion from hydrogen sulfide gas and sulfates in solution.

Standard compression tests were conducted to evaluate the strength of the eight mixes after curing in a 100% moist environment, for 28 days. The results also provided an indication of the quality of the concrete. Compressive strength of the three 100 mm diameter by 200 mm high specimens were carried out for each treatment and averaged.

The pH of the eight solutions was measured every other test cycle using a potentiometric electrode in order to find out how the H_2S gas affects the acidity of the solutions, and the rate at which the concrete loses its alkalinity.

The electrochemical potential of reinforced concrete is a characteristic of the reinforcement steel/concrete interface, which reflects the ionic conduction between the bars and pore fluid of concrete. The half-cell potential, E_{corr} , is used to define the corrosion state of reinforcement bars. A copper-copper sulfate electrode (CSE) and a high impedance voltmeter were used to read E_{corr} . The half-cell potential measurement connection is shown in Figure 4. The first half-cell potential measurements were taken after three cycles of exposure to the corrosive environment. Six potential readings were taken every 20mm (at the air end, 20, 40, 60, 80, and 100 mm) along three meridians at 0° , 120° , and 240° , for a total of 18 readings per specimen (Figure 5). The mean of the 18 readings for each sample was calculated then the mean of the replicates for each treatment was used for monitoring corrosion of the steel and for comparison between the different treatments.

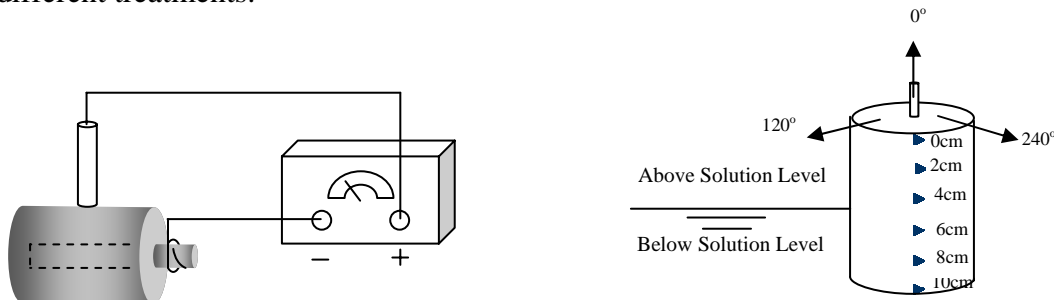


Figure 4. Half-Cell Potential Measurement. Figure 5. Potential Measurement Locations

Corrosion potential measurements provide an indication of the oxidizing power of the environment in which a specimen is exposed. It is important to remember, however, that potential is a thermodynamic quantity, and although it can be used to determine whether a reaction can occur spontaneously, it cannot be used to provide information about the rate of corrosion reactions.

At the end of this first stage of the project one of the three replicates will be removed from the exposure test and examined in detail for strength, composition and permeability. The exposure tests will be continued with two replicates for a further .. cycles in a second stage. Again, at the end of this second stage one replicate will be removed from the exposure tests and examined in

detail. Finally, the last of the three replicates will be exposed to the corrosive environment in a third stage until considerable concrete deterioration has taken place.

3. RESULTS AND DISCUSSION

3.1 Compressive Strength Test

Table 5 shows the mean 28-day compressive strength of the three concrete specimens for the eight treatments, including the standard deviation. The compressive strength of 34 MPa for the PC50 treatment, the only treatment with a w/cm ratio of 0.5, is considerably lower than the strength of the other seven treatments. Also, the results for SC and SSFC treatments (i.e. slag cement and silica fume and slag cement) show that incorporating slag in the cement reduces its compressive strength. The rest of the treatments had compressive strengths ranging from 46 to 49 MPa with silica fume cement concrete providing the highest value.

Table 5. Mean 28-day compressive strength in Mpa for the eight treatments

Treatment	PC50	PC40	SR	SC	SFC	FAC	SSFC	FASF
w/cm ratio	0.5	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Compressive strength	34.0	48.6	47.4	42.3	49.1	47.0	43.5	46.0
S.D.	12.7	22.5	43.1	15.3	10.7	32.5	13.8	32.2

3.2 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 three months, then each two cycles when the solution was changed to bring the SO₄²⁻ concentration back up to its original concentration of 20,000 ppm. The different pH measurements are shown in Table 6, the increases in pH from the initial value of 6.64 to the final value are shown in Figure 6. 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 sulfate solution. After the 5th test cycle the pH increased significantly less as the concrete started to lose its alkalinity.

Table 6. pH measurement for the eight treatments.

Time	PC50	PC40	SR	SC	SFC	FAC	SSFC	FASF
1 st test cycle	12.01	11.87	12.09	11.45	12.09	12.2	11.86	11.85
2 nd test cycle	10.99	10.64	11.49	10.64	11.46	11.57	11.27	11.43
3 rd test cycle	11.2	11	10.9	10.7	10.7	11	10.4	10.7
5 th test cycle	9.02	9.83	9.35	9.05	8.85	9.7	8.95	9.4
7 th test cycle	8.75	9.07	8.85	8.5	8.8	9	8.5	8.5
9 th test cycle	9.4	9.13	8.99	8.3	8.77	8.7	8.5	8.3

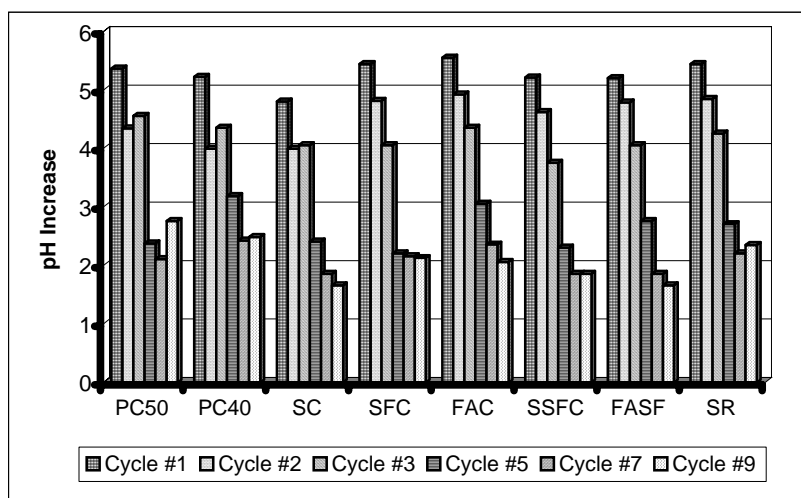


Figure 6. pH increase from initial value of 6.64 for the eight treatments.

A control solution of Na_2SO_4 solution (20000 ppm SO_4^{2-}) having a pH of 6.64, was placed in the experimental box and exposed to 1000 ppm H_2S for one cycle (one month). The resulting pH was 5.44. This decrease in the pH is due to the reaction: Hydrogen Sulfide + Oxygen \rightarrow Sulfuric Acid.

3.3 Electrochemical Potential Measurement

So far the potential measurements for the different treatments have been taken fourteen times since the start of the experiment. The means of the 54 readings (18 readings per specimen, 3 replicates) are plotted in Figure 7 for the 8 treatments exposed to hydrogen sulfide and half submerged in sulfate solution. Figure 8 presents the results for the 8 treatments exposed to hydrogen sulfide only. The means are also presented in Tables A1 and A2 together with the respective standard deviations

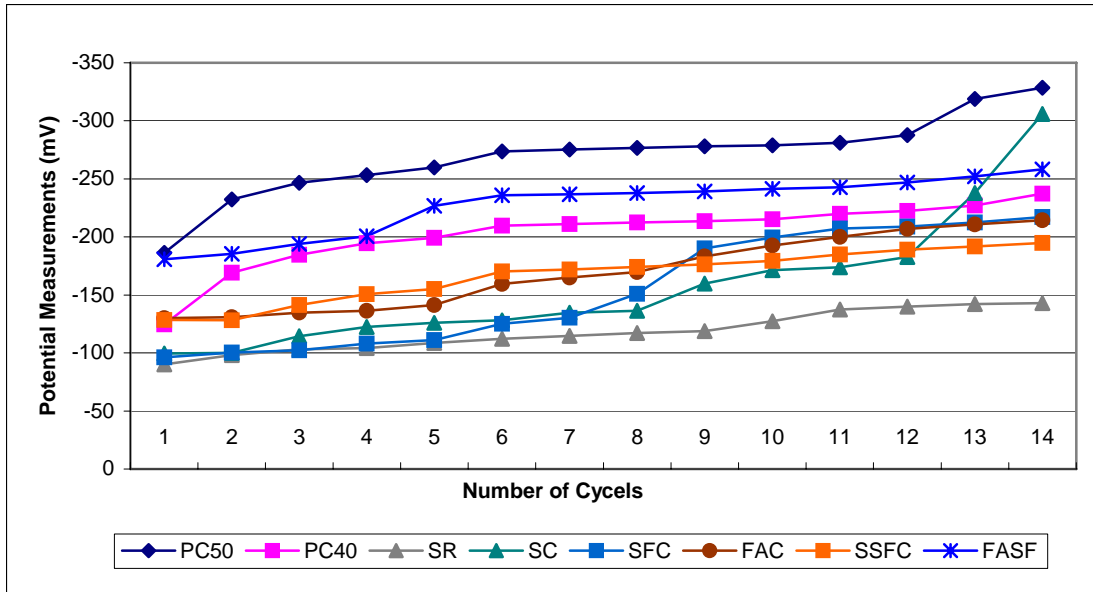


Figure 7. Potential measurement of the samples that are half submerged in sulfate solution and exposed to hydrogen sulfide gas.

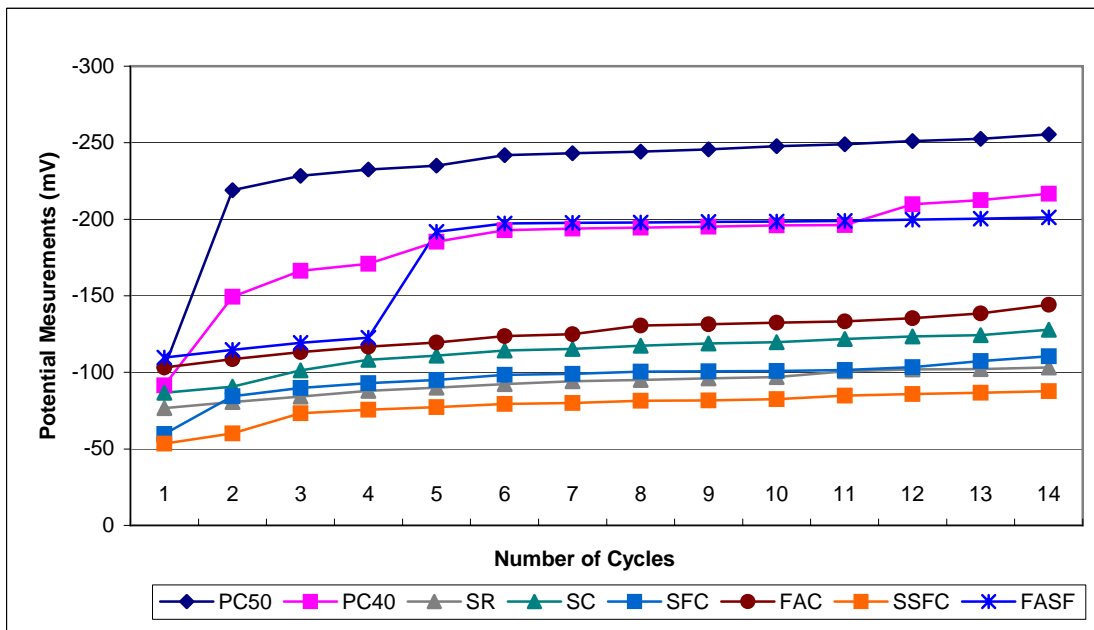


Figure 8. Potential measurement of the samples that are exposed to hydrogen sulfide gas only.

Some observations can be made from the results in Figures 7 and 8. In examining the curves it should be noted that the closer the potentials are to -350 mV the greater the probability of active steel corrosion is. Treatment PC50 already stands out as the worst performer. After 14 cycles of exposure the risk of corrosion of the steel is in the 50% range. So far all treatments containing silica fume, fly ash or slag, except FASF, perform better than PC40. Also, there is an indication

that sulfate resistant cement (SR) is more resistant than type I Portland cement. Treatment FASF, concrete containing fly ash and silica fume, stands out at this stage as performing worse than plain PC concrete with the same w/cm ratio.

The steel embedded in those specimens that are exposed to SO_4^{2-} as well as H_2S corrodes faster than those exposed to H_2S only. All treatments indicate this consistently through higher negative potentials. In the specimens that were exposed to H_2S only, the potential was fairly uniform over the surface of the cylinders as indicated by the low SD's in Table A2. This was not the case with those half submerged in the Na_2SO_4 . The negative potentials above the surface are greater than those below in all treatments, especially in the first 10 cycles (see Table A1). This indicates that the effect on the upper part of the specimen is more severe than on the part below the liquid level. This effect may be increased permeability of the concrete or greater corrosion activity of the steel. A detailed examination of the specimens after the exposure tests will determine which.

Visual inspection of the specimens after 16 cycles showed considerable change in colour of the concrete to a very dark gray. For the specimens that were partially submerged in sulfate some degradation of the smooth concrete surface was evident at the water line. However, no other deterioration of the concrete could be detected at this stage.

4. SUMMARY AND CONCLUSIONS

Corrosion tests of 48 concrete specimens are being carried out using hydrogen sulfide gas and a sodium sulfate solution. One half of the specimens is partially immersed in the sodium sulfate (20,000 ppm SO_4^{2-}) and also subjected to hydrogen sulfide gas (1,000 ppm H_2S). The other is subjected to hydrogen sulfide gas only. Each set consists 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 cementitious 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 is made with sulfate resistant cement.

After 16 cycles of testing over about 28 months the electrochemical potential results indicate that the PC concrete with 0.5 w/cm ratio is the least corrosion resistant, as might be expected. All treatments containing silica fume, fly ash or slag, except FASF, performed better thus far than PC40. Also, there is an indication that sulfate resistant cement (SR) is more resistant than type I Portland cement. Indeed, sulfate resistant cement concrete was one of the best performers in both sets of tests. The corrosion activity in the reinforcing steel of all treatments as indicated by the electrochemical potentials is greater for the specimens that were partially submerged in sulfate solution and exposed to H_2S gas than for those exposed to H_2S gas only.

After 16 cycles visual inspection of the specimens showed considerable discolouration of the concrete, to a very dark gray colour. For the specimens that were partially submerged in sulfate some degradation of the smooth concrete surface was evident at the water line. However, no other deterioration of the concrete could be detected at this stage.

5. ACKNOWLEDGEMENT

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6. REFERENCES

- ASTM C 150. 2002. Standard specification for Portland cement. American Society for Testing and Materials, Philadelphia, PA.
- Brunet, L. 2002. Rural Environment Engineer, Farmstead Planning, Health and Safety Specialist, OMAF. Hazardous Gases. <http://www.gov.on.ca/OMAFRA/english/engineer/facts/99-001.htm>
- Canadian Standards Association. 1994. Concrete materials and methods of concrete construction, CAN3-A23.1-94 and CAN3-A23.2-94, Canadian Standards Association, Toronto, ON.
- De Belie, N., De Coster, V., Van Nieuwenburg, D. 1997. Use of fly ash or silica fume to increase the resistance of concrete to feed acids, Magazine of Concrete Research, 49:181
- De Belie, N., Monteny, J., and Vincke, E. 2002. The effect of chemical and biogenic sulfuric acid on the different types of concrete for sewer pipes, Proc. IVth Int. Symposium for Concrete for a Sustainable Agriculture - Agro-, Aqua and Community Applications, Ghent, Belgium.
- Frénay J. W., Zilverberg H. 1993. Durability of concrete in agricultural environment, IMAG-DLO Report 93-17, IMAG –DLO, Wageningen, Netherland.
- Idriss, A.F. 2000. Corrosive effect of hydrogen sulfide on cement mortar. Ph.D thesis, School of Engineering, University of Guelph, Guelph, ON, Canada.
- Jiang, S. 2002. Use of blast furnace slag cement for the durability of precast concrete in agricultural application. Proc. IVth Int. Symposium for Concrete for a Sustainable Agriculture - Agro-, Aqua and Community Applications, Ghent, Belgium.
- Kosmatka, S.H., Panarese, W.C., Allen, G.E., Cumming, S. 1991. Design and control of Concrete Mixtures, 5th Ed. Canadian Portland Cement Association, Ottawa
- Lafarge Canada Inc. 2001. Publication No 16.
- Mehta, P.K. 1986. Concrete structures, properties, and materials”, Prentice-Hall, Inc., Englewood Clifffes, New Jersey.
- Santhanam, M., Mesnashi, D.C., and Olek, J. 2001. Sulfate attack research-whither now?, Cement and Concrete Research, Vol. 31, pp. 8845-851.
- 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, Swedish University of Agricultural Sciences Department of Agricultural Biosystems and Technology; Sweden.
- Vincke, E., and Verstraete, W. 2002. Concrete and microorganisms: friend or enemy? Proceeding of the 11th International Symposium (Concrete for a Sustainable Agricultural Agro-, Aqua- and Community Application), Ghent, Belgium.

Zhang, H., Prince D., Xin, H., Harmon, J.D. 1994. Production and emission dynamics of manure gas in nursery swine rooms with shallow pits”, Presented at the December 13-16 1994 ASAE International Winter meeting. Paper No.944541.

Appendix A

Table A1 presents the means and standard deviations of the 54 electrochemical potential measurements (18 readings per specimen, 3 replicates) for the 8 treatments exposed to hydrogen sulfide and half submerged in sulfate solution. Table A2 presents the same results for the 8 treatments exposed to hydrogen sulfide only.

Table A1: The mean potential measurements of all 54 readings for each treatment that is half submerged in SO_4^{2-} solution and exposed to H_2S .

Cycle no.	PC50	PC40	SR	SC	SFC	FAC	SSFC	FASF
3	-186.4	-124.5	-90.1	-99.4	-96.3	-130.1	-128.4	-180.9
S.D.	22.8	42.8	15.1	22.8	11.8	11.6	6.0	8.4
4	-232.3	-169.1	-98.2	-100.1	-100.2	-130.8	-128.2	-185.4
S.D.	27.9	52.0	14.6	22.8	7.9	12.6	7.5	8.3
5	-246.7	-184.6	-103	-114.3	-102.3	-134.7	-141.3	-194
S.D.	23.6	41.6	16.7	15.8	7.3	14.3	8.1	5.1
6	-253.4	-194.6	-104.4	-122.5	-108	-136.4	-150.8	-200.7
S.D.	22.4	37.1	16.1	14.4	4.8	15.1	8.3	3.8
7	-260	-199.2	-108.5	-126	-111	-141.4	-155.1	-226.7
S.D.	19.1	36.3	19.0	12.9	4.3	13.0	7.3	9.9
8	-273.7	-209.7	-112.3	-128.2	-125	-159.7	-170.4	-235.8
S.D.	13.1	33.9	20.1	12.2	8.9	14.4	6.8	6.4
9	-275.2	-211.2	-114.7	-134.7	-130.4	-165	-171.9	-236.7
S.D.	12.8	33.9	21.3	15.4	6.1	12.5	7.6	6.7
10	-276.8	-212.5	-117.2	-136.4	-150.9	-169.9	-174.2	-237.9
S.D.	12.7	33.4	20.2	16.2	8.6	11.4	7.6	6.5
11	-278.1	-213.6	-118.8	-159.9	-190.2	-183.3	-176.3	-239.3
S.D.	12.8	32.8	21.2	13.1	2.4	9.0	8.0	6.8
12	-278.8	-215.2	-127.2	-171.3	-199.4	-192.6	-179.5	-241.3
S.D.	12.6	31.1	22.6	11.0	6.6	8.2	7.5	7.0
13	-281.2	-219.9	-137.4	-173.8	-207.3	-200.1	-184.9	-242.8
S.D.	13.8	24.7	23.9	11.6	1.5	9.7	8.9	7.7
14	-287.6	-222.3	-140.1	-182.6	-208.9	-206.9	-189	-242.8
S.D.	14.3	22.7	22.7	14.1	2.9	8.2	6.1	6.5
15	-318.9	-227.2	-142.1	-237.8	-212.4	-210.8	-191.7	-252.3
S.D.	10.8	21.3	21.5	7.9	2.7	9.1	2.8	4.0
16	-328.6	-237.3	-143.1	-305.8	-217.1	-214.5	-194.9	-258.3
S.D.	8.4	11.5	21.8	10.6	2.3	8.8	2.1	2.1

V. Assaad, J. Jofriet, S. Negi, and G. Hayward. “Corrosion of Reinforced Concrete Specimens Exposed to Hydrogen Sulfide and Sodium Sulfate”. Agricultural Engineering International: the CIGR Ejournal. Vol.VII. Manuscript BC 03 013. April, 2005.

Table A2: The mean potential measurements of all 54 readings for each treatment that is exposed to H₂S.

Cycle no.	PC50	PC40	SR	SC	SFC	FAC	SSFC	FASF
3	-103.3	-91.4	-76.6	-86.8	-59.8	-103.1	-53.4	-109.6
S.D.	6.5	5.0	1.3	8.7	20.9	7.7	3.5	4.2
4	-219	-149.4	-80.7	-90.7	-84.4	-108.7	-60.2	-114.7
S.D.	11.0	17.0	4.1	7.6	8.5	8.0	2.4	4.3
5	-228.4	-166.2	-84.2	-101.3	-89.8	-113.2	-73.4	-119.3
S.D.	10.8	25.0	5.6	6.5	3.9	8.0	5.2	2.6
6	-232.6	-170.8	-88.0	-108.3	-93.0	-116.8	-75.7	-122.7
S.D.	12.7	24.6	5.5	11.9	2.7	9.5	6.9	1.9
7	-235	-185.3	-90.1	-111	-95.0	-119.6	-77.3	-191.8
S.D.	13.1	13.3	5.9	11.3	2.9	8.3	6.2	4.3
8	-241.9	-192.9	-92.4	-114.3	-98.5	-123.7	-79.4	-197.3
S.D.	13.5	16.6	7.0	10.5	1.6	6.6	6.7	2.2
9	-243.1	-193.8	-94.2	-115.3	-99.1	-124.9	-80	-197.7
S.D.	14.2	15.8	5.6	10.8	2.1	6.7	6.4	2.2
10	-244.3	-194.5	-95.1	-117.5	-100.5	-130.5	-81.4	-197.9
S.D.	13.3	15.3	5.2	11.2	1.5	5.7	5.5	2.4
11	-245.7	-195.2	-96.2	-118.9	-100.7	-131.5	-81.7	-198.2
S.D.	12.2	15.8	4.6	10.3	1.3	5.9	5.5	2.1
12	-247.7	-195.9	-97	-119.8	-101	-132.5	-82.5	-198.5
S.D.	10.3	15.6	4.8	9.6	1.0	5.9	5.2	2.0
13	-249.1	-196.2	-100.6	-121.9	-101.6	-133.3	-84.8	-198.8
S.D.	10.1	15.4	4.0	9.3	0.9	5.7	4.5	1.7
14	-251.1	-209.7	-101.9	-123.4	-103.4	-135.3	-85.9	-199.7
S.D.	10.7	8.9	3.8	9.4	1.3	5.9	4.2	2.3
15	-252.6	-212.4	-102.2	-124.4	-107.4	-138.6	-86.6	-200.4
S.D.	11.6	6.2	4.0	10.3	1.6	5.4	3.8	2.9
16	-255.6	-216.7	-103.2	-127.8	-110.6	-144.2	-87.7	-201.1
S.D.	11.9	4.5	4.3	11.6	1.1	6.0	3.4	3.4