PROTECTION OF CONCRETE IN COOLING TOWERS FROM MICROBIOLOGICALLY INFLUENCED CORROSION

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ABSTRACT

Concrete in cooling towers used in geothermal power plants is susceptible to microbiologically influenced corrosion (MIC). The resistance of different protective coatings, mortars and concrete mix proportions to sulphur oxidizing bacteria was investigated. The protective materials included three different epoxy coatings, epoxy-modified cement mortar, latex-modified mortar and calcium aluminate mortar. The influence of cement type, silica fume and blast furnace slag on concrete durability was examined. Laboratory screening tests were followed by field exposure tests in cooling tower basins. The epoxy coatings and calcium aluminate mortar gave the best performance. Partial replacement of cement with 5 to 10% silica fume or 40% blast furnace slag improved concrete resistance to MIC.

INTRODUCTION

Microbiologically influenced corrosion (MIC) of concrete can be induced by different bacteria. The two types of bacteria of major concern are sulphur oxidizing and nitrifying. Sulphur oxidizing bacteria such as *Thiobacillus thiooxidans* and *Thiobacillus ferrooxidans* produce sulphuric acid which is aggressive towards concrete. Sulphate ions react with free calcium hydroxide to produce hydrated calcium sulphate (gypsum). The calcium sulphate reacts with tricalcium aluminate hydrate to form calcium sulphoaluminate. Expansion associated with these reactions results in cracking and eventual disintegration of concrete. Sulphuric acid causes additional degradation by attacking calcium hydroxide and calcium silicate hydrates in concrete. Nitrifying bacteria (e.g., *Nitrosomonas* and *Nitrobacter*) can act to cause nitric acid degradation of concrete. *Nitrosomonas* oxidizes ammonia to nitrate and the presence of ammonia in cooling water stimulates its growth. *Nitrobacter* oxidizes nitrite to nitrate. Both of these nitrifying bacteria are capable of causing nitric acid degradation of concrete. Nitric acid reacts with calcium hydroxide to produce soluble calcium nitrate. As a result of acid attack, concrete loses its integrity.

MIC of concrete in cooling towers was identified as a frequent problem facing the geothermal industry in a survey of operation and maintenance-related materials needs (Allan, 1998). An example of this problem was given by Bacon et al. (1995). Corrosion was observed in the vapour zone of the Ohaaki natural draft tower. Both sulphur oxidizing and nitrifying bacteria were implicated. The concrete contained sulphate resistant cement and a pozzolanic material. Reduction of surface pH to 2 and corrosion up to a depth of 20 mm over six months occurred. Treatment of cooling water with biocides did not control corrosion above the water line and it was therefore necessary to install a spray gun to apply biocides directly to the vapour zone surfaces. Clevinger

(1992) discussed nitrogen chemistry in geothermal cooling tower water and the use of biocides to control microbiological activity.

The extent of degradation due to MIC can be reduced through the use of more durable materials. Acid-proof potassium silicate concrete and an epoxy coating were reported as being successful in resisting MIC due to sulphur oxidizing bacteria (Hall, 1989). Daczko et al. (1997) investigated use of admixtures in concrete for construction of sewer pipes and found that silica fume and an organic inhibitor reduced mass loss after 100 days of exposure to sulphuric acid. Calcium aluminate cement mortars have been reported to provide resistance to sulphur oxidizing bacteria and are used as liners to protect concrete in sewers (Scrivener et al., 1999; Sand et al., 1994). Work performed by Monteny et al. (2000) indicated that concrete containing blast furnace slag had less mass loss than plain or fly ash-modified concrete when exposed in sewer pipes.

A research project was initiated at BNL to examine protective coatings and mortars and modification of concrete mix design through supplementary cementing materials to mitigate MIC of concrete. Laboratory and field exposure tests were performed on a range of different materials. These included epoxy coatings, latex-modified mortar, calcium aluminate mortar and concrete that was modified with either silica fume or ground granulated blast furnace slag. The laboratory tests involved exposure to one species of sulphur oxidizing bacteria (*Thiobacillus ferrooxidans*). In the field tests selected materials were exposed for eight months in cooling tower basins at a geothermal power plant in Indonesia. The field tests were conducted in collaboration with Unocal.

EXPERIMENTAL

Materials

The basic concrete mix design for the experimental research was similar to that used in a cooling tower basin of interest that had been experiencing MIC. Type V (sulphate resistant) cement was used to replicate that specified on the particular structure. Type I (ordinary) cement was also used as a baseline. The silica sand used conformed to ASTM C 33 and the coarse aggregate was siliceous stone with a nominal size of 9.5 mm. Both the fine and coarse aggregates were dried. Sodium naphthalene sulphonate superplasticizer was used to improve concrete workability. The target water/cement ratio was 0.40 and the target cement content was 350 kg/m^3. Several trial mixes were prepared to determine appropriate fine and coarse aggregate proportions for a medium slump concrete. Silica fume was used as a partial cement replacement at levels of 5 and 10% by mass. Ground granulated blast furnace slag was used at cement replacement levels of 40 and 60% by mass. Field tests were performed on plain Type I cement-based concrete and the two silica fume-modified mixes. The mix proportions of the different concretes evaluated are presented in Table 1. The associated 28 day compressive strengths are also given.

The concrete was cast into different specimens depending on the ultimate purpose. Eight compressive strength cylinders, 102 mm diameter and 204 mm high, were produced for each concrete mix. Beams, 76 mm x 104 mm x 406 mm, were cast for coating/mortar adhesion tests. Panels, 50 mm x 50 mm x 204 mm, were used for the laboratory and field exposure tests. All concrete specimens were cured in saturated lime water for 28 days. The panels to be coated were lightly sand blasted to remove laitance and roughen the surface. Panels that were coated with epoxies were first allowed to dry in air for 14 days prior to coating application. The mortars were applied to saturated surface dry substrates.

Table 1. Mix Proportions of Tested Concrete.

	Type I	Type V	5% Silica Fume	10% Silica Fume	40% Slag	60% Slag
Type I cement (kg/m^3)	348.4		340.0	322.2	208.3	138.7
Type V cement (kg/m^3)		348.9				
Silica Fume (kg/m^3)			17.9	35.8		
Blast Furnace Slag (kg/m^3)					138.9	208.0
Water (kg/m^3)	139.4	139.5	143.2	143.2	138.9	138.7
Fine aggregate (kg/m^3)	8243.6	824.7	846.1	846.1	820.6	819.5
Coarse aggregate (kg/m^3)	918.6	919.9	943.7	943.7	915.3	914.1
Superplasticizer (l/m^3)	3.49	3.49	3.58	3.58	3.47	3.47
Unit weight (kg/m^3)	2230	2233	2291	2258	2222	2219
28 day compressive strength (MPa)	40.9 ± 1.0	36.1 ± 1.0	45.0 ± 1.3	47.9 ± 0.8	50.8 ± 0.4	35.4 ± 1.8

The coatings and mortars selected for evaluation were two-component 100% solids epoxy coatings (Sikagard 62, Sika and Amercoat 351, Ameron), a two-component 66% solids epoxy coating (Amercoat 385, Ameron), a three-component water-based epoxy-modified cementitious mortar (Sikagard 75 EpoCem, Sika), latex-modified mortar that was formulated in-house and a commercial calcium aluminate mortar designed for use in sewers (SewperCoat, Lafarge). SewperCoat is a preblended material consisting of calcium aluminate cement and calcium aluminate fine aggregate.

The latex-modified mortar comprised of Type I Portland cement, silica sand conforming to ASTM C 33, water and styrene butadiene copolymer latex with a solids content of 42% (Tylac 68014-00, Reichold Chemicals). The mix proportions of the mortar were 1 part cement, 3 parts sand, 0.3 parts latex and 0.262 parts water by mass. Prior to application of the mortar, a slurry coat of cement and latex was painted on the surface. The slurry bond coat consisted of 1 part cement to 0.45 parts latex by mass. The latex-modified mortar was protected from drying for three days by covering with plastic. The SewperCoat calcium aluminate mortar is available for either shotcrete or pumpable applications. In this project SewperCoat 2000 HS Regular was mixed with water at a water/solids ratio of 0.123 and trowel applied. The calcium aluminate mortar was cured for 14 days in lime water prior to any testing.

Thickness and Holiday Tests

The thickness of the epoxy coatings was measured non-destructively using a Positector 100-C1 ultrasonic thickness gauge. A minimum of 12 readings was taken per face of each panel. Thickness of the mortars was measured destructively. The epoxy coatings were tested for holidays (flaws) using an Elcometer 136 DC Portable Holiday Detector. The test voltage was set according to the coating thickness. Tests were performed in accordance with NACE RP0188-90.

Bond Strength Tests

Bond strengths of the coatings and mortars to the concrete substrate were measured using a Dyna Z15 pull-off tester. The materials were allowed to cure for 14 days prior to testing. The method used is given in ASTM D 4541. A 50 mm diameter aluminium dolly was glued to the coating/mortar surface at the desired location using 3M Scotch-Weld DP-100 epoxy adhesive. A tensile load was applied normal to the substrate at a constant rate until failure. The form of failure was noted (i.e., adhesive, cohesive, mixed). Six tests were performed per face of the concrete beams. For each material, two to four beams were tested. Residual bond strength tests were also performed on panels that were used in laboratory and field tests.

Laboratory Exposure Tests

Coated and uncoated concrete panels were used to assess the resistance to sulphur oxidizing bacteria. The panels were tested in an Atlas cell arrangement as described in ASTM C 868. Panels were clamped against a horizontally oriented open-ended glass cylinder with a diameter of 152 mm. The glass cylinder had ports for a thermometer, immersion heater, air bubbler and reflux condenser. Each cell was filled with 1.2 l of *T. ferrooxidans* medium described elsewhere (Allan, 1999; 2000). The average pH of the *T. ferrooxidans* medium at the start of the tests was 2.59 and the cell concentration was 10^5 to 10^6/ml. The medium temperature was maintained at 40^{o}C as this represented a typical value to which the coatings would be exposed. The temperature of the external concrete surface was 30.4^{o}C. Two replicate panels were tested per coating/mortar in addition to the uncoated concretes. The test duration was 60 days. At the conclusion of the tests the panels were examined for deterioration and bond strength tests were performed on the coatings/mortars. Uncoated concretes were visually assessed for degree of fine and coarse aggregate exposure as a result of MIC activity.

Field Exposure Tests

For the field tests three replicate specimens of uncoated plain, 5% and 10% silica fume-modified concrete and epoxy coated concrete were used. The three epoxies listed above were used and the panels were completely coated to prevent ingress beneath the coating from an unprotected edge. Calcium aluminate mortar was tested as solid panels due to difficulty in coating all sides of concrete panels with the mortar. The specimens were exposed in three different induced draft cooling tower basins at the same geothermal power plant in Indonesia. The water temperature was 38^{o}C. The water pH was typically between 7.8 and 8.0 and the total hardness typically <40 ppm as $CaCO_3$. The cooling water was treated with trichloroisocyanuric acid and sodium hypochlorite for microbial control and H_2S/NO_x abatement (Gallup, 1994) and sodium hydroxide. The specimens were exposed for eight months and shipped back to BNL. Post test analysis included visual inspection and adhesion tests on the epoxy coatings.

RESULTS AND DISCUSSION

Quality Control Tests

Table 2 gives the coating/mortar thicknesses of the panels used in the laboratory and field tests. The spark tests on the beams with epoxy coatings revealed that all were free from holidays except Amercoat 351. It was observed during application of this coating that holidays were associated with small (< 1 mm diameter) air voids in the concrete substrate. Effort was made to cover these defects with the second coat. However, the second coating did not completely bridge the small holidays. All panels used in the *T. ferrooxidans* exposure tests were holiday free.

Table 2. Thickness of coatings/mortars used in laboratory and field exposure tests.

Coating/Mortar	Laboratory Panel Thickness (μm)	Field Panel Thickness (μm)
Amercoat 351	353 ± 121	575 ± 75
Amercoat 385	346 ± 95	412 ± 81
Sikagard 62	472 ± 62	636 ± 98
Sikagard EpoCem 75	2020 ± 210	-
Latex-modified	2950 ± 370	-
SewperCoat	3130 ± 360	-

Laboratory Exposure Tests

Considerable biofilm developed on all of the uncoated concrete panels in the immersed zone. When the film was washed off it was revealed that extensive etching of the cement paste in Type I and Type V cement concrete surfaces in the immersed zone had occurred to expose coarse and fine aggregate. Etching was also evident in the vapour zone and was less severe. Deterioration was visually more severe for the Type V cement concrete. The silica fume-modified mixes were lightly etched to expose fine aggregate in the immersed zone and the extent of attack was visually similar for the 5% and 10% cement replacement levels. The concrete mix containing 40% blast furnace slag exhibited light etching in the immersed zone and had similar degree of attack to the silica fume-modified concretes. Increasing the slag content to 60% replacement of cement decreased the resistance to attack by *T. ferrooxidans.* The 60% slag concrete underwent extensive etching in the liquid zone and slight etching in the vapour zone. The degree of attack was visually similar to the Type I and Type V cement concretes. Long-term field testing of slag-modified concrete is recommended for more detailed and realistic evaluation.

The epoxy-coated panels were free of any biofilm. Some of the coatings changed colour and showed brown stains attributed to iron salts in the *T. ferrooxidans* medium. Small blisters, 1 to 2 mm in diameter, appeared in the immersed zone for Amercoat 351. No blisters were observed for the other coatings.

All of the mortars had biofilm growth in the immersed zone. The Sikagard 75 EpoCem epoxy-modified mortar exhibited etching beneath the biofilm and this was also evident to a lesser extent in the vapour zone. The degree of etching was not as great as that observed on uncoated concrete. The observations for the latex-modified mortar were similar to those for the epoxy-modified mortar. The calcium aluminate mortar exhibited the best resistance of all the mortars tested with minimal etching.

Field Exposure Tests

The uncoated concretes all experienced deterioration from exposure in the cooling tower basins. The most severe attack was observed on the plain Type I cement concrete. Extensive etching occurred to reveal coarse and fine aggregate. Partial replacement of cement with silica fume improved the durability. Attack of the silica fume-modified concretes also occurred but was not as advanced as that for the plain concrete. Fine aggregate and small amounts of coarse aggregate were exposed on the silica fume-modified concretes. The 10% silica fume mix had the best performance of the tested concretes. Figures 1 and 2 compare the surfaces of the plain and 10% silica fume concretes after the field tests. The degree of attack on all of the field tested uncoated concrete specimens was greater than that in the laboratory tests. This is probably due to the longer exposure period plus the possibility of other bacteria involved in the MIC process. The field rankings of the materials were similar to those obtained from exposure to sulphur oxidizing bacteria in the Atlas cell arrangement. *(Insert Figures 1 and 2)*

The epoxy coated panels gave excellent durability in the field tests except for one specimen of Sikagard 62. This particular specimen exhibited blistering between coats. The reason for this was not clear and may have been an anomaly from coating application. The calcium aluminate mortar showed negligible attack and appears to be highly suitable for protecting concrete from MIC.

Bond Strengths

The results of bond strength tests on the concrete panels subjected to laboratory and field exposure are given in Table 3. The mean and standard deviation are reported. The results for the field exposed Sikagard 62 coating that underwent degradation are not included in the table. The bond strength of this specimen was 1.7 ± 0.5 MPa. Coating and mortar bond strengths on unexposed beams have been reported previously (Allan, 1999; 2000).

Table 3. Bond Strengths for Panels used in Laboratory and Field Exposure Tests

Coating/Mortar	Bond Strength (MPa)			
	Unexposed	Laboratory: Immersed	Laboratory: Vapour	Field
Amercoat 351	3.1 ± 0.3	3.6 ± 1.2	3.8 ± 1.5	3.4 ± 0.9
Amercoat 385	2.9 ± 0.5	2.9 ± 1.6	3.9 ± 0.2	3.5 ± 0.5
Sikagard 62	3.5 ± 0.1	4.0 ± 0.3	3.9 ± 0.8	3.2 ± 0.7
Sikagard EpoCem 75	2.5 ± 0.5	2.8 ± 0.3	3.1 ± 0.5	-
Latex-modified	3.3 ± 0.4	3.2 ± 0.4	3.5 ± 0.3	-
SewperCoat	2.2 ± 0.3	2.6 ± 0.3	3.2 ± 0.3	-

Bond strengths between 1.4 and 2.1 MPa are generally considered acceptable for coatings on concrete and cohesive failure within the concrete substrate is preferred to adhesive failure at the coating/concrete interface. The tested materials met these criteria except for one field exposed Sikagard 62 specimen and one Amercoat 385 specimen that both exhibited some degree of interfacial failure. None of the coatings subjected to laboratory exposure showed a statistically significant reduction of bond strength. The Amercoat 385 and Sikagard 62 coatings had higher bond strengths in the vapour zones compared with the unexposed zones at the 5% significance level. However, the number of samples tested was small and no definitive conclusions can be drawn. Other than one of the Sikagard 62 specimens, none of the field exposed specimens lost bond strength.

CONCLUSIONS

Different supplementary cementing materials, protective coatings and mortars were evaluated for suitability in preventing MIC in concrete cooling tower structures. An Atlas cell arrangement allowed the resistance of different materials to sulphur oxidizing bacteria, *T. ferrooxidans*, at elevated temperature to be compared under laboratory conditions. Field exposure tests of selected materials were also performed. Plain concrete based on either Type I or Type V cement was prone to severe attack manifested as surface etching of cement paste. It was determined that use of 5 to 10% silica fume as a partial cement replacement in concrete improved resistance to MIC, but did not eliminate attack. Concrete having 40% cement replacement with blast furnace slag had better durability than plain concrete. Epoxy- and latex-modified mortars underwent some deterioration. Epoxy coatings and calcium aluminate mortars exhibited durability and retained bond strength under the test conditions and appear suitable for protecting concrete from MIC.

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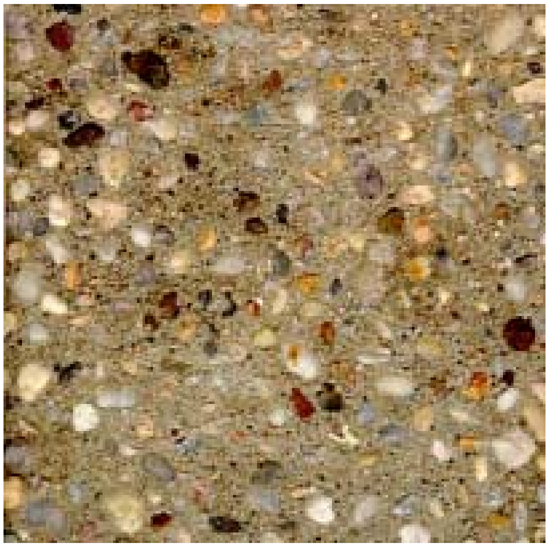

Figure 1. Surface of plain concrete after field exposure.

Figure 2. Surface of 10% silica fume concrete after field exposure.