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Evaluation of coatings, mortars and mix design for protection of concrete against sulphur oxidising bacteria

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ABSTRACT

Deterioration of concrete in cooling tower basins by microbiologically influenced corrosion (MIC) is a concern in geothermal power plants. The effect of supplementary cementitious materials, epoxy coatings, latex-modified mortars and calcium aluminate cement mortar for protecting concrete from MIC was investigated. Laboratory exposure tests to a particular type of sulphur and iron oxidising bacteria, *Thiobacillus ferrooxidans*, were performed to rank candidate materials and these were followed by field exposure tests of the best materials in a cooling tower basin. It was determined that partial replacement of cement with 40% blast furnace slag or 5% to 10% silica fume improved resistance to MIC. A replacement level of 60% slag resulted in similar performance to concrete made with ordinary Portland or sulphate resistant cement. Epoxy- and styrene butadiene latex-modified mortars offered protection to concrete but still underwent a degree of attack. Epoxy coatings were found to be effective in protecting concrete. Calcium aluminate cement mortar showed excellent durability in laboratory and field tests.

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1. Introduction

Microbiological attack or microbiologically influenced corrosion (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 [1]. Such attack is typically caused by sulphur oxidising, nitrifying, iron or heterotrophic bacteria. Sulphur oxidising bacteria such as *Thiobacilli* (also known as *Acidithiobacilli*) genera produce sulphuric acid which is aggressive towards concrete. A common example of MIC of concrete occurs in sewer pipes [2]. Production of sulphuric acid on exposed surfaces in the sewer air space (crown) by sulphur oxidizing bacteria leads to softening and loss of cement paste. Degradation of concrete has also been attributed to MIC in other situations including outlet tunnels for artificial lakes [3] and water storage tanks [4].

Sulphur oxidising bacteria are aerobic and autotrophic. A variety of oxidation reactions can occur due to *Thiobacilli* and these are summarized by Videla [5]. Acidification of the environment by these bacteria results in corrosion of concrete. Sulphuric acid causes both sulphate and acid attack of concrete [6]. In general terms, sulphate ions react with free calcium hydroxide to produce hydrated calcium sulphate (gypsum). The calcium sulphate in turn 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.

MIC of concrete involving sulphur oxidising bacteria involves a progression of different species according to the precise pH conditions [3,7,8]. Initially, new concrete is highly alkaline and this is thought to prevent growth of bacteria. It is hypothesised that once carbonation of the surface occurs the pH then decreases and certain bacteria can become established. These bacteria further reduce pH, thereby enabling other bacteria that are more tolerant to more acidic environments to flourish. Systematic reduction of pH occurs with each new species. Recently, O'Connell et al. [8] have challenged the view that carbonation is required and proposed that pH reduction due to bacteria occurs in a thin moisture film on the concrete surface.

Prevention of MIC in sewer pipes includes control hydrogen sulphide concentration in the headspace by chemical treatment or spraying the crown with magnesium hydroxide to neutralize the acid generated by bacteria [9] and use of acid-resistant concrete or protective liners. Calcium aluminate cement mortars have been reported to provide resistance to sulphur oxidising bacteria and are used as liners to protect concrete in sewers [10–12].

Concrete cooling towers in geothermal plants are also subject to deterioration due to sulphur oxidising and nitrifying bacteria [13]. Pryfogle [14] undertook investigations of microbiological activity and species in geothermal cooling tower basins and cooling effluent from plants in California and Utah and identified several *Thiobacillus* species. Deterioration of other concrete structures due to *Thiobacillus* at the Larderello geothermal field [15] and has

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been implicated in attack of concrete culverts carrying cooling water and condensate from the Wairakei geothermal power plant [16].

Brookhaven National Laboratory was approached regarding severe deterioration of concrete in a cooling tower basin at a geothermal power plant in Indonesia. Whilst biocides can be used to control bacteria in cooling water, this represents an ongoing operational expense and concrete mix design or protective materials may be a more economic option for long-term defence against MIC. Subsequently, a research project was undertaken to determine: (a) means of protecting concrete from further deterioration; and (b) potential mix design modifications to reduce such MIC of concrete in new geothermal power plants. Approaches used for preventing deterioration in concrete sewers such as epoxy coatings, latex-modified mortars and calcium aluminate cements were explored for applicability to geothermal power plants. Calcium aluminate cements were selected based on previous reports of good resistance to MIC in sewers [10-12]. Addition of latex to mortars can increase resistance to acid [17] and was therefore of interest. The use of supplementary cementitious materials such as blast furnace slag and silica fume can improve durability of concrete [18] and of potential benefit in new construction of geothermal cooling towers.

The objective of this paper was to determine the effectiveness of changes in concrete mix design and protective materials for improving the resistance to MIC in geothermal cooling tower basins. The experimental research investigated one species of sulphur oxidising bacteria (*Thiobacillus ferrooxidans*). This particular type of bacterium is also iron oxidising. Field tests were performed in a cooling tower basin of a geothermal power plant in Indonesia. Initial results have been described previously by the author [19,20].

2. Experimental

2.1. Materials

The control concrete mix design for the experimental research was similar to that used in a cooling tower of interest that had been experiencing MIC. ASTM C 150 Type V (sulphate resistant) cement was used to replicate the cement specified on the cooling tower basin. Concrete with Type I (ordinary Portland) cement was investigated for comparison. The silica sand used conformed to ASTM C 33 and the coarse aggregate was siliceous stone with a nominal maximum size of 9.5 mm. Both the fine and coarse aggregates were oven dried prior to use. Sodium naphthalene sulphonate superplasticizer was used to improve concrete workability. Supplementary cementitious materials (silica fume and ground granulated blast furnace slag) were investigated for potential improvement in resistance to MIC. Silica fume (SF) conforming to ASTM C 1240 was used as a partial cement replacement at levels of 5 and 10% by mass. ASTM C 989 Grade 120 ground granulated blast furnace slag (BFS) 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 water/cementitious material ratio was kept constant at 0.40. Several trial mixes were prepared to determine appropriate fine and coarse aggregate proportions for a medium slump (\sim 80 mm) concrete. The mix proportions of the concrete used in the MIC studies are presented in Table 1.

The concrete was mixed in a laboratory pan mixer located in a walk-in fume hood. The coarse and fine aggregates were first dry blended for 1 min. Cement and any silica fume or slag were then added and dry blended for a further minute.

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Mix proportions of tested concrete.

Two thirds of the water–superplasticizer mix was added and mixing continued for another minute. The remaining water and superplasticizer were then added and the total mixing time was 5 min. This procedure had been modified from ASTM C 192 to improve workability for concrete prepared with the type of mixer used. Concrete was cast and consolidated in accordance with ASTM C 192 and vibrated on a vibrating table until large bubbles (>10 mm diameter) ceased to appear on the top surface. Unit weight (density) of the freshly mixed concrete was measured following ASTM C 138. All concrete specimens were demoulded after 24 h and cured in saturated lime water at 23 °C for 28 days.

Eight cylinders, 102 mm diameter and 204 mm high, were produced per mix design for compressive strength tests. Panels were cast for testing the coating/mortar resistance to *T. ferrooxidans*. The panels were 204 mm high, 204 mm long and 50 mm thick.

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 cement mortar designed for use in sewers (SewperCoat[®], Lafarge). Sewper-Coat[®] is a preblended material consisting of calcium aluminate cement and calcium aluminate fine aggregate (Alag[®]).

Concrete specimens that were to be epoxy coated were dried in air at 23 °C for 14 days after the 28 day curing period. The specimens were then lightly sand blasted to remove laitance and roughen the surface. The coatings were applied by brush since the specimens were relatively small and two coats were applied. In the case of the mortars, the concrete specimens were sand blasted and then soaked in water to produce a saturated surface dry condition prior to trowel application of the mortar.

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. The polymer/cement ratio was 12.6%. A slurry coat of cement and latex was painted on the concrete surface before application of the mortar. The slurry bond coat consisted of 1 part cement to 0.45 parts latex by mass. After trowel application of the latex-modified mortar the specimens were covered in plastic sheet for 3 days and then allowed to dry in air. The same curing procedure was used for the Sikagard 75 EpoCem[®] epoxy-modified cementitious mortar.

SewperCoat 2000 HS Regular[®] mortar was mixed with water at a water/solids ratio of 0.123 and trowel applied on the concrete specimens. The calcium aluminate cement mortar was cured for 14 days in lime water prior to any testing.

2.2. Compressive strength

Compressive strength tests were performed to characterise the concrete. Specimens for compressive strength measurements were capped and tested in accordance with ASTM C 39 using a Forney compression tester.

2.3. Coefficient of permeability

The coefficient of permeability (hydraulic conductivity) of different concrete mixes was measured as an indicator of quality and resistance to water ingress. Tests were performed under saturated conditions in a flexible wall triaxial cell permeameter on cylindrical specimens 102 mm diameter and 90 mm long. The permeant was de-aired tap water at room temperature. The applied pressure gradient was 207 kPa over the length of the specimen. The confining pressure applied to seal a latex membrane to the side surface of the concrete specimen was 414 kPa. The experimental set-up followed that given in ASTM D 5084. Tests commenced after a curing period of 28 days. The specimens were vacuum saturated with de-aired water prior to measurement. Volumetric flow rates in and out of the specimens were monitored and measurements commenced when equilibrium was reached after approximately 24–48 h. The test duration after achievement of equal flow rates was 48–72 h.

	Туре І	Type V	5% SF	10% SF	40% BFS	60% BFS
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)	824.6	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 or density (kg/m ³)	2230	2233	2291	2258	2222	2219
Superplasticizer (1/m ³) Unit weight or density (kg/m ³)	3.49 2230	3.49 2233	943.7 3.58 2291	943.7 3.58 2258	3.47 2222	3.47 2219

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