MICROBIALLY INDUCED DEGRADATION OF FIBRE REINFORCED PLASTIC (FRP) IN THE COOLING TOWER OF A GEOTHERMAL POWER STATION

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Keywords: *Cooling towers, FRP, sulfuric acid, corrosion, microbial degradation, sulfur oxidizing bacteria, geothermal*

ABSTRACT

Evaporative cooling water systems in geothermal power plants can pose several challenges for geothermal operators. The challenges of corrosion, deposition and biological control can be magnified in systems utilising direct contact condensers, due to the presence of hydrogen sulfide in the cooling water. Hydrogen sulfide provides an energy source for the growth of sulfur-oxidising bacteria, with the production of sulfuric acid as the main end-product. The sulfur oxidising bacteria can readily colonise such cooling towers, forming a biofilm on the large surface area provided by the tower's structure and fill material.

This paper describes a technical investigation, undertaken following discovery of wide-spread degradation of the Fibre Reinforced Plastic (FRP) structure of a geothermal cooling tower, after only 7 years' of service. The degraded FRP was found only in the top section of the tower, above the Drift Eliminator level. The subsequent investigation identified the cause of degradation as microbially-induced corrosion of the FRP material, due to the presence of sulfuric acid at about 1% concentration (pH 1). Several studies were conducted to understand the nature of the FRP degradation, its effect on the strength of the structural elements, and the extent of degradation over the tower's structure. Subsequent work considered a few possible ways to control bacterial growth and prevent the acid from accumulating. However, no suitable method could be found, with the decision taken to replace the affected FRP with new, acid-resistant FRP material. Because this type of degradation had not been previously reported, selection of new material required the development of an accelerated aging test. This test was extensively applied to FRP samples, covering a range of material formulations, allowing selection of suitable product for use in the tower's repair. This paper concludes with some observations about FRP formulations most suited to this type of cooling tower service.

1. INTRODUCTION

This paper reports on what appears to be a previously undescribed form of cooling tower structural corrosion. Identification of the cause showed the degradation mechanism to be unique to geothermal power stations which operate direct contact condensers.

Mercury operates a range of geothermal power stations, including flash plants, binary plants and combined flash-binary plants. The two large flash plants, which utilise condensing steam turbines in the power generation process, are the 138MW triple flash Nga Awa Purua (NAP) power plant and the 105MW double flash Kawerau (KAG) power plant.

Both the NAP and KAG plants utilise direct contact condensers and have a similar non condensable gas content and composition in their geothermal steam. As a result, a significant amount of hydrogen sulfide is dissolved in the cooling water while in the condenser. Hydrogen sulfide provides a readily metabolised energy source for the growth of sulfur oxidising bacteria (SOB) which colonise the tower, forming a biofilm on the large surface area provided by the tower's fill material. The SOB bacteria oxidise hydrogen sulfide to either elemental sulfur or completely to sulfate, in the form of sulfuric acid (Janssen et al. 1995; Jensen et al, 2011). The rate of bacterial activity and, hence, sulfuric acid production depends strongly on the cooling water temperature and the extent of biofilm growth, and is at its highest level during the warm months of summer (see Figure 1). Consequently, control of cooling water pH is required to avoid low pH induced damage to water-touched equipment.

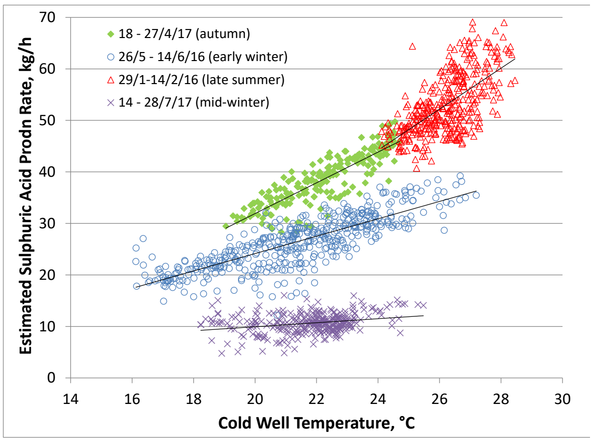

Figure 1: Estimated sulfuric acid production rate versus Cold Well temperature for different seasonal time periods (from Clark and Richardson, 2017)

Both the NAP and KAG cooling towers are of almost identical design and are constructed from FRP structural elements. The FRP degradation described in this paper has only been found in the NAP tower, despite the use of the same grade of FRP in both towers.

The 10-cell cooling tower at NAP station is shown in Figure 2 with the location of the internal functional zones shown schematically in Figure 3. The volume of water within the system is about 6,500 m^3. Due to the rapid rate of water circulation between the condenser and the tower (27,000 t/h), this large volume of water is essentially fully mixed. The warm water from the condenser is distributed across the top of the Fill Pack layer. Consequently, with good pH control, the main cooling tower structure, below this level, is exposed to water at about pH 7 (range of pH 6 – 7.5).

The function of the tower's zones above the water distribution level are to minimize the characteristic "tower drift" – the mist formed by condensation, as the water-saturated exhaust air cools. Hence, the Drift Eliminator (DE) layer captures the large water aerosols and droplets, which fall back down the tower. The zone above the DE layer allows the mist-laden air to exit the tower through the large induced-draft fans on the roof, above each cell.

Figure 2: Cooling Tower at Nga Awa Purua Power Station (cells A to F run from left to right in photo)

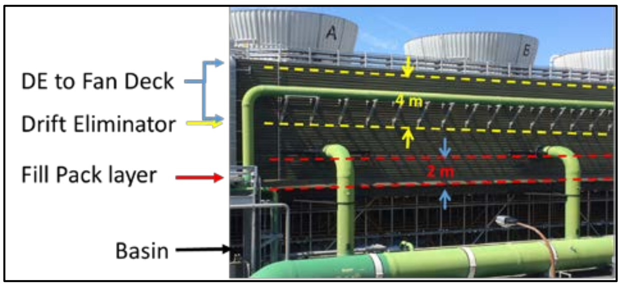

Figure 3: Schematic diagram of cooling tower in cross-section

2. DISCOVERY OF FRP DEGRADATION

The presence of obvious decay of the FRP structure was first observed during the station outage in November 2017 (7 years after the station was commissioned in 2010). Typical examples of damaged sections of FRP are shown in Figure 4. Significantly, this damage was almost entirely observed above the DE layer. Although some deterioration was noted below the DE and above the Fill Pack, this was limited and appeared to be propagating down from above.

While the areas of decay appeared widespread within the DE-to-Fan Deck zone, much of the FRP in this area appeared to be unaffected. Hence, the decayed areas were dispersed throughout the zone, although an underlying pattern became apparent. The worst affected areas were close to the walls (external and internal) of each cell, where continually moist conditions prevailed. In these areas a slimy biofilm layer was present, especially apparent on the horizontal surfaces of the girts and roof beams. FRP decay became less apparent, moving inwards towards the central fan well, where the structure appeared much dryer.

Some columns were removed for destructive testing and significant deposits of an unknown white substance were noted inside these columns. The texture of the fiberglass in the walls of the damaged columns and girts was described as “powdery”. The damage appeared to start from the inside of the columns and from drill holes in the girts and roof beams. Deformation of columns and girts were obvious physical indicators of severe deterioration. However, there were several, more subtle, symptoms of the decay process:

- White crystals (on surface or inside of drilled holes)
- White creamy residue on external surfaces
- Surface damage and cracking
- Delamination
- Split edges/corners
- Swelling/bulging
- Lines of dark discoloration
- Soft to press/dull noise on tapping

3. DETERMINING THE CAUSE AND EXTENT OF THE PROBLEM

3.1 Identifying the Cause of Degradation

Samples of the decayed FRP columns were sent for analysis in the US and locally at Scion. Microscopic analysis (SEM-EDS) of the damaged zones showed a high filler content – and reduced resin – compared to reference material. Delaminated sections demonstrated higher volatile content and lower resin content than intact areas (using Thermal Gravimetric Analysis). The white, debris material showed a high level of sulfur and subsequent chemical analysis confirmed it to be mainly calcium sulfate, although with elevated levels of aluminium, magnesium, and silica also present.

During the initial tower inspections, pH measurement of moisture in the areas showing the worst attack returned a pH of 1 in almost all areas tested. Small samples of this low pH water were collected and tested for sulfate concentration, returning values from 10 – 11 g/L. Sulfuric acid at this concentration is consistent with a pH of 1.

Fourier Transform-Infrared Spectroscopy (FTIR) analysis matched extracted resin material from the samples with one or more polyester resin types, which would be expected to be vulnerable to attack by strong acids.

Therefore, it became clear that the FRP had been under sustained attack by sulfuric acid, probably since the tower first started up 7 years earlier. This was a result of wide-spread colonization of the FRP by Sulfur Oxidising Bacteria. The presence of sulfuric acid at around 10 g/L (pH 1) is well beyond the range at which these SOB bacteria will normally grow. This conclusion further suggested that the acid was accumulating in and on the decaying FRP, because it was not being washed away. The lack of a “water wash effect” above the DE layer explains why acid attack was almost entirely restricted to this zone, since pH-controlled water can wash the structure below the DE level. The few areas of decay below the DE were attributed to sulfuric acid running down the inside of the columns all the way to the splice joint, which is just above the top of the Fill Pack. Clearly, water droplets falling from the DE could not wash the insides of the effected columns.

In summary, sulfuric acid attack appeared to have affected all or most of the FRP constituents:

- Dissolution of the calcium carbonate filler material, forming insoluble calcium sulfate, which was redeposited on the inside of columns and on horizontal surfaces of girts.
- Acid hydrolysis of the polyester resin, forming low molecular weight volatile degradation products.

Proceedings 42nd New Zealand Geothermal Workshop
24-26 November 2020
Waitangi, New Zealand
ISSN 2703-4275

- Acid attack on the glass fibres, suggesting the glass had a low resistance to strong acids.

The FRP structure below the DE layer has not suffered from any significant level of attack and has performed well under the expected conditions, with the cooling water pH controlled between about 6 and 7.5. Therefore, the FRP material was fit for this service, but was clearly not fit for service in the low pH zone above the DE.

Figure 4: Examples of FRP degradation in the tower zone above the Drift Eliminator layer

Determining the Extent of Damage

The next challenge was to determine the extent of the damage, so that an assessment could be made about the tower structure, pending decisions on remedial action and repair work.

The fact that the degradation was localised and not evenly spread across the DE-to-Fan Deck zone, made it difficult to estimate the impact on structural integrity. Modelling, to determine end of life, was considered but it was not possible to adequately characterise the properties and location of the damaged structural elements.

Non-destructive test methods, such as Ultrasonic Testing, were considered, but none could be successfully applied. Therefore, all 10 cells within the tower were visually surveyed, with columns and girts selected for inspection according to a sampling plan. The extent of decay of each FRP element was then rated using a semi-quantitative scoring method, based on the number of symptoms of decay that could be observed. This survey revealed that some cells were more damaged than others, with an apparent trend from Cell A (worst) to Cell F (least).

The use of core sampling of the FRP also proved useful to characterise the decay, as the following example illustrates. Core samples (16 mm diameter) were cut from 8 columns in Cell D, choosing a zone showing both decaying and apparently unaffected columns (see Figure 5). Cores were cut from each column at the top (just under the roof), middle, and bottom (just above the DE layer). The cores were visually examined, measured for core thickness, and then soaked in 2mL of deionised water and the resultant pH levels measured. The results are summarised in Table 1.

Two "reference cores" from Columns 1 and 4 were taken about 0.5m below the DE level and were found to be intact, with no evidence of decay and returned neutral pH values (see Fig. 6).

Figure 5: Columns in cell D selected for core sampling (the first 4 columns against the external (south) wall and the adjacent 4 in the second row)

The cores were examined to characterise the extent and nature of acid attack on these columns. Five of the 8 columns showed at least one core with significant degradation (thickness loss). The worst of the 8 columns (col. +3) had one core with 85% loss of wall thickness. Across all 8 columns, the average of the largest thickness losses measured was 34%. There was a trend in thickness loss from the top (least) to the bottom (most) of the effected columns, which is consistent with the idea that sulfuric acid can run down the inside of the columns. Visual examination of the degraded cores showed that some columns were being attacked from the inside, while others from the outside surface. The column which had the greatest level of degradation (col. +3) was being attacked entirely from the inside and looked apparently normal on the outer surface.

The core pH values (measured after addition of 2 mL of DI water) were generally consistent with the amount of observed thickness loss. However, some cores returned quite low pH values, yet showed no significant loss in thickness. These observations suggested that the quality of the FRP was not consistent across the tower structure, such that some columns or beams were more susceptible to acid attack.

Figure 6: Photograph of intact, undamaged 16 mm cores, sampled below the Drift Eliminator level.

4. SEARCH FOR A METHOD TO SLOW OR STOP DEGRADATION

Since the degradation process was essentially limited to the structure above the DE layer, the investigation turned to possible ways to wash or biocide treat the structure.

Hence, small-scale trials were conducted to evaluate the efficacy of two approaches to stopping or slowing the activity of the SOB bacteria and, hence, rate of FRP attack:

1. "Deluge" water washing, and
2. Biocide treatment

Application was by manual spraying of either water or a 200 ppm solution of sodium hypochlorite onto the surfaces of individual ceiling beams in Cell D, chosen from an area that had consistently returned low pH measurements. The trials were carried out with two different volumes of each liquid (hence, 4 treatment runs in total)

The aim was to determine if the surface pH of these beams could be raised and maintained at a higher pH level. The treatments were applied to the right-hand half of each beam, with the left-hand side used as the reference or control zone. The pH of the biofilm layer of each beam was tested before spray application and about 30 minutes after the application was complete (Day 0 result). The pH levels were further tested during cell shutdowns on Days 1, 3, and 7

Results showed that none of the treatments provided a lasting effect on the surface pH and, hence, the activity of the sulfur oxidising bacteria on these beams. For 3 of the treatments applied on Day 0, the beam pH values had returned to 1 after just 1 day of operation. The 4th treatment (high volume hypochlorite) had a greater effect, with the beam returning to pH 1 after 3 days.

Based on this preliminary trial, it appeared that deluge spraying would not be effective in preventing on-going acid attack on the FRP structure. The results of the core testing work described above further supported this conclusion, since some of the columns were degrading from the inside. Clearly, a spray system would be ineffective at washing or neutralising acid being produced inside the FRP columns.

Since it appeared that slowing or halting the acid attack process could not be practically or effectively carried out, the decision was taken to repair the structure with an acid resistant FRP material.

Table 1: Core thicknesses and the pH values (measured after addition of 2 mL of DI water). Columns 1 – 4 refer to the first 4 columns against the south wall; columns +1 - +4 refer to the 4 adjacent columns, one row in to the tower). Low pH cores highlighted in red.

Core Location	**Column 1**	**Column 2**	**Column 3**	**Column 4**
Top	10 mm, pH 5	11 mm, pH 7	10 mm, pH 7	10 mm, pH 7
Middle	9 mm, pH 4	9 mm, pH 5.5	10 mm, pH 5	7 mm, pH 5
Bottom	8 mm, pH 6	10 mm, pH 5.5	9.5 mm, pH 6	5.5 mm, pH 1
Below Drift Eliminator	10 mm, pH 7			10 mm, pH 7

Core Location	**Column +1**	**Column +2**	**Column +3**	**Column +4**
Top	Not sampled	6 mm, pH 6	6.5 mm, pH 5	8.5 mm, pH 4
Middle	7 mm, pH 5.5	6 mm, pH 4.5	4 mm, pH 1	8.5 mm, pH 4
Bottom	4 mm, pH 5.5	7 mm, pH 4	1.5 mm, pH 1	Not sampled

5. DEVELOPMENT OF ACCELERATED AGING TEST

It became clear that an accelerated aging test was needed, to enable the testing of alternative FRP materials within a short time frame, since planning for the repair work was already underway. Industry specialist advice suggested that no standard test method, appropriate to this mode of degradation was available. Therefore, it was decided to develop and trial an in-house method that could provide meaningful test results, aiming for a test duration of a few weeks.

The key variables were acid concentration, temperature and time. Initial trials were run at 60°C with specimens immersed in either 5 or 10wt% sulfuric acid. As shown in Figure 7, the flexural strength of specimens cut from two different FRP profiles (7mm C-channel and 7mm box column) degraded only slightly faster in 10% acid, so 5% acid was selected for future work.

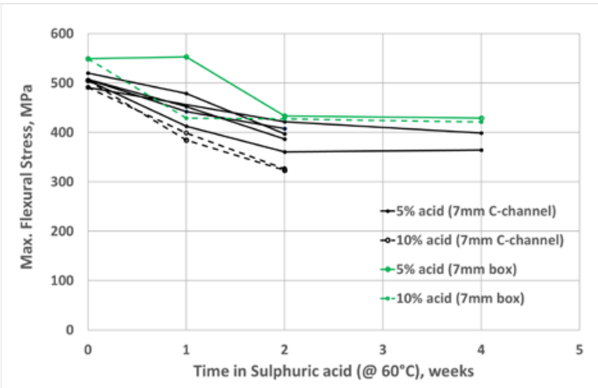

Figure 7: Comparison of the effects of 5% and 10% sulfuric acid on FRP sample flexural strength during accelerated aging tests at 60°C (results for 7mm C-channel and 7mm box sections of a vinyl ester product)

Further trials (results not shown) established that adequate differentiation of FRP samples could be obtained within about 4 weeks, when comparing a range of FRP materials. Therefore, 60°C and 5% acid were judged adequate for future trial work. Further details of the accelerated aging and flexural strength testing procedures, including specimen preparation, are given in Appendix 1.

6. SEARCH FOR AN IMPROVED FRP MATERIAL

For economic reasons, the search for superior FRP material, able to withstand the highly acidic conditions, focused on commodity pultrusion products. Custom-made product formulations manufactured in small production runs were expected to be cost prohibitive. Therefore, the sourcing of product samples for testing focused on a small number of well-known manufacturers.

It was clear from the initial analytical work on the failure mode, that the polyester resin used in the tower's FRP was not suitable for the acidic conditions. Specialist advice suggested that vinyl ester resins would be more acid resistant, and so several vinyl ester products were selected for comparative testing. It was also apparent that the calcium carbonate filler material in the original FRP was reacting with sulfuric acid and apparently playing a role in the failure of the material. Therefore, one set of trials was conducted with FRP produced in trial volumes, with two different fillers – the commonly used calcium carbonate and a clay product.

To illustrate typical results from the comparative testing, Figures 8 and 9 show the flexural bending strength and modulus results for one set of trials. It was immediately clear that the vinyl ester products were much more resistant than

Proceedings 42nd New Zealand Geothermal Workshop
24-26 November 2020
Waitangi, New Zealand
ISSN 2703-4275

the original polyester material. This is further illustrated in Figure 10, which shows photographs of the original polyester material before and after 2 weeks incubation in acid, showing severe delamination of the test specimens.

All three vinyl ester products performed well under the test conditions, which were typically run to 8 weeks and showed similar rates of loss in flexural strength and stiffness. Some tests were extended to 16 and 32 weeks, to provide confirmation of the trends observed at the shorter times. However, there were some clear differences between the products, mainly in terms of stiffness (modulus).

The comparison of filler materials (calcium carbonate versus clay) in Product C proved useful. Surprisingly, the calcium carbonate filled material had superior strength and stiffness, although the differences were modest and both formulations were quite resistant to acid attack. Therefore, it was considered that properly made vinyl ester material containing calcium carbonate could perform well under the acidic test conditions.

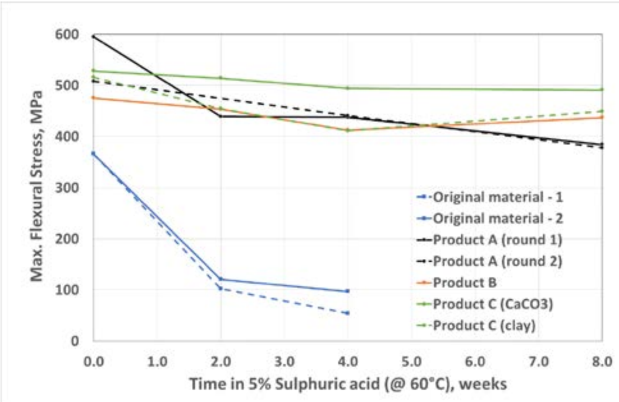

Figure 8: Time-course of Flexural Stress changes during accelerated aging tests

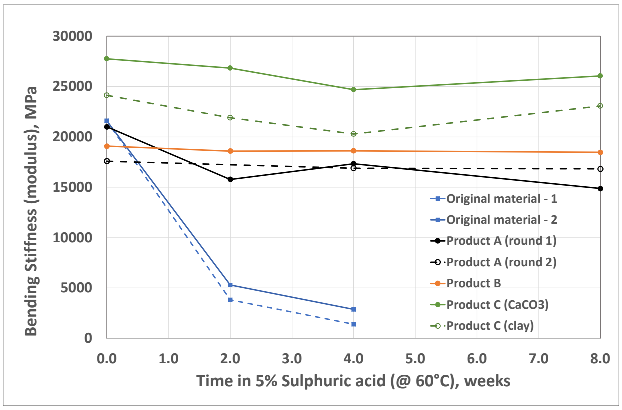

Figure 9: Time-course of Flexural Stiffness changes during accelerated aging test

Product A was eventually selected for the rebuild. The final use of the accelerated aging test was to conduct QA testing of samples from the manufactured batches of each of the FRP profiles required for the rebuild. Clearly, it was important to ensure that each manufactured batch performed similarly to the samples previously used for selection purposes. This QA acceptance was required prior to the product being shipped, in order to meet the rebuild timeline.

Inevitably, the QA testing did find some anomalies, requiring the manufacturer to supply additional samples for retesting. All the product batches were eventually cleared for supply.

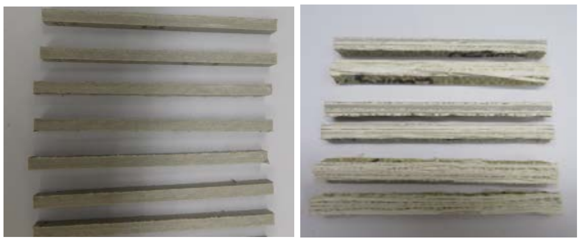

Figure 10: Photographs of test specimens cut from samples of the original tower FRP, before (left) and after (right) two weeks incubation in acid. Note severe delamination.

7. REBUILD PLAN AND EXECUTION

The rebuild plan for the tower's upper section considered the following;

- Expected life
- Cost
- Construction mode

Since the polyester FRP material below the Drift Eliminator was still in good condition with no significant issues noted, it was decided to only repair the zone at and above the Drift Eliminator. With that in mind it was determined that a 20-year life for the new material would be acceptable. This, in turn, opened a wide range of options from the accelerated tested products. However, when cost was considered the choice was reduced to two of the vinyl ester materials.

Mercury considered multiple contract options for the rebuild:

- Fixed cost
- Time and Materials (Vendor purchased)
- Time and Materials (Mercury purchased)

Following economic considerations, it was determined to go with Time and Materials, with the vendor purchasing on Mercury's behalf.

The final decision for vendor selection considered construction method, health & safety and cost. Two construction methods were considered:

- Stick by Stick build
- Modular Construction

Both stick build and modular construction had advantages and disadvantages, especially around health and safety. The safety risks around heavy lifting and time of exposure were considered in decision making.

When taking the above into consideration, it was determined that both Expected Life and Construction Method were of equal importance in decision making. Ultimately, it was Cost that was the decider.

Repairs began mid-2019 and are expected to be complete early 2021. Due to cooling constraints, the project needs to go on hold during the summer periods to maintain production availability. The modular mode of construction was chosen, where each cell is divided up into four individual modules which are lifted in and interlocked in place. Due to cable trays and the Non-Condensable Gas (NCG) line, the first two bents need to be completed in a stick by stick approach. The time frame for a cell to be rebuilt has been between 3-4 weeks, with the old modules removed and the new installed over a two-day period.

9. CONCLUSIONS

This study underlines the importance of understanding microbial behavior in the cooling water systems of geothermal power stations which operate direct contact condensers. While Sulfur Oxidising Bacteria were active throughout the cooling tower, the very low pH conditions found in the zone above the Drift Eliminator was due to the absence of any effective water washing mechanism in this zone.

Polyester resin based FRP appears unsuitable for duty in this zone, while vinyl ester material was found to be much more durable under the accelerated aging test conditions. However, the variable nature of the observed attack indicates that some of the original FRP material was more resistant to acid than the degraded material, suggestive of product variability. Therefore, when sourcing FRP, QA testing of representative samples from each manufactured batch is recommended using some type of sulfuric acid specific aging test.

ACKNOWLEDGEMENTS

The authors would like to thank Mercury NZ Limited for allowing publication of this work.

REFERENCES

1. Clark, T A and Richardson, I (2017) In: Proceedings NZ Geothermal Workshop 2017, 22-24 November 2017, Rotorua, New Zealand.

2. Janssen, A J, Slyster, R, van der Kaa, C, Jochemsen, A. (1995) Biological sulfide oxidation in a fed-batch reactor. ***Biotechnology and Bioengineering***, Vol. 47.

3. Jensen, H.S., Lens, P.N., Nielsen, J.L., Bester, K., Nielsen, A.H., Hvitved-Jaconsen, T., Vollersten, J. (2011). Growth kinetics of hydrogen sulfide oxidising bacteria in corroded concrete from sewers. ***Journal of Hazardous Materials***, Vol. 189(3): 685-691.

APPENDIX 1: ACCELERATED AGING AND FLEXURAL TESTING METHODS

A1.1 Accelerated Aging

The flexural specimens for aging, were water jet cut to dimensions 142 x 10 x 6.5mm or 192 x 20 x 9mm, depending on the source material thickness as per ASTM D790 Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials. Water jet cutting was used in preference to saw cutting because it produced a superior surface finish. Cut samples were visually inspected and any samples which had been cut roughly, included large notches or other such defects, either as a result of the water jet cutting or manufacturing defects were excluded from testing. Photographs were taken of sample groups before and after mechanical testing to monitor this.

These samples were soaked in 5% sulfuric acid solution at 60 °C for up to 16 weeks. Each set of 5 samples was soaked in an individual 900 mL (6.5 mm samples material) or 2.5 L jar (9 mm sample material) to ensure thorough effectiveness of the acid. Samples were taken after 1, 2, 4, 8 and 16 weeks of testing. Following removal from the acid, they were rinsed thoroughly (three times) in distilled water to remove any residual acid. They were then gently blotted dry and conditioned at 23±1°C and 50±2% of relative humidity for at least 40 hours prior to testing.

A1.2 Flexural Testing

This was done in accordance with the standard conditions specified in ASTM D618 Standard Practice for Conditioning Plastics for Testing. The flexural testing was performed in accordance with ASTM D790 using an Instron Universal Testing Machine 5566 equipped with 3-point bending apparatus and a 10 kN load cell, see Figures A1 and A2. Depending on the sample thickness, the crosshead speed was set at 2.77 mm/min (for 6.5 mm thickness) or 3.78 mm/min (for 9 mm thickness), the support span was 104 mm or 144 mm respectively (to ensure a 16:1 length to depth ratio), the radius of the supports and loading nose was 7.5 mm and five specimens were tested from each sample per time period.

Figure A1: Flexural testing set-up.

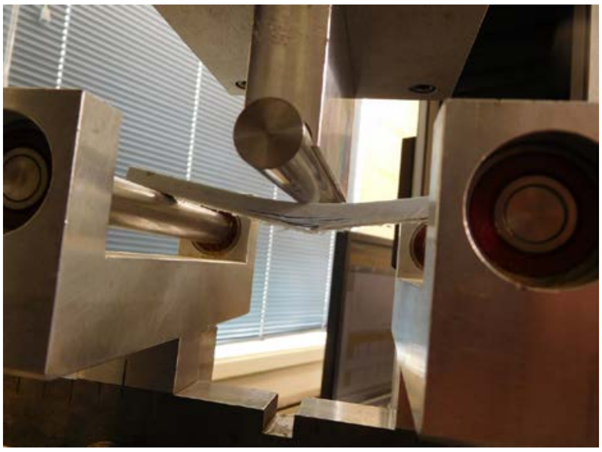

Figure A2: Flexural testing showing normal fracture mode of a well-performing FRP sample.

ISSN 2703-4275