CONFIDENTIAL TECHNICAL REPORT

PROFESSOR GRAEME GEORGE

Analysis of further Aquatherm pipe samples received from Jackson’s Landing Development, Pyrmont Sydney

to:

Aquatherm Australia Pty Ltd
Attention: Mr Bryce Christian
6F, 443 West Botany Street,
Rockdale NSW 2216 Australia
Executive Summary

(a) Aquatherm pipes and fittings from two buildings in the Jackson’s Landing, Pyrmont Development of Lend Lease (Distillery and Quarry) have been examined to determine the extent and possible cause of damage.

(b) The pipe from Distillery Unit 101 has been found to have been seriously eroded and has a weak degraded layer of PPR of ~0.5mm thickness. The structural thickness of the pipe has been lowered by ~9% and oxidation products are detected (by infrared analysis) to a depth of >1mm.

(c) The brown surface layer on the pipe interior is found to contain high levels of copper and the oxidation is believed to have arisen by copper catalysed auto-oxidation and rapid consumption of stabilizers in the pipe and fittings.

(d) The sample from Quarry was found to have very high levels of copper that were present not only in the main riser pipe but also in the sidearm pipe. The failures seen in both Distillery and Quarry buildings are linked to accelerated degradation of PP-R due to the aggressive environment of hot water combined with copper and possibly other pro-oxidants. The copper may have arisen from erosion of copper pipe in the recirculating ring main.

1. Background:

1.1 Samples of sectioned pipe and fittings from Distillery building, Jackson’s Landing, Pyrmont were supplied by Mr Bernd Emmert, Technical Manager, Aquatherm together with photographs to identify each. These are shown in Appendix 1. The pipe was identified by him as Aquatherm 25mm SDR 7.4 Faser composite pipe.

1.2 I was instructed by Mr Bryce Christian, General Manager, Aquatherm Australia, to undertake analysis of these samples and prepare a report on the likely cause of damage to the PP-R that has led to failure.
1.3 Analysis has also been made of a sample provided earlier from level 6, Quarry building, Jackson’s Landing. This is shown in Appendix 2, Fig. 2.12.

2 Analysis of samples

2.1 Figure 1.1 shows the bagged samples from Distillery Building, level 1, as sent by Aquatherm. Individual photographs of the samples before cutting are given in Figures 1.3 to 1.6. One sample had a rubber collar and clamp (Fig. 1.3) that was reported to have been fitted over the site of a leak. The samples that had been sectioned by cutting along the pipe length at my request are shown in Figures 1.2, 1.7, 1.8 and 1.9.

2.2 All sectioned samples were subjected to visual and microscopic examination to determine the nature of the damage. A previous study of samples from this site (my report of 5 April 2010) had identified that copper, a powerful pro-oxidant, was present on the surface of pipe removed from level 8, Distillery building (Appendix 5 of that report). To determine if copper is present at different locations in these samples a spot test was used in preference to the detailed analytical method which required a large area of sample.

2.3 The interior of the pipes were subjected to analysis using Quantofix \( \text{Cu}^+ / \text{Cu}^{2+} \) analytical strips. Further detail of these strips is available from the manufacturer: http://www.mn-net.com/Testpapers/QUANTOFIXteststrips/QUANTOFIXKupfer/tabid/10313/language/en-US/Default.aspx

The strips were dipped into a dilute solution of acetic acid (pH 3 to 4) for 1 second and then touched to the sample for 10 seconds. They were then read 20 seconds after removal and photographed along with the sample. The depth of purple colour developed indicated the amount of copper present as \( \text{Cu}^+ / \text{Cu}^{2+} \). It should be noted that the test is essentially qualitative in this application, but the depth of colour and its spatial development reflects the amount and location of copper ions on the solid sample. The mark left on the sample by the test procedure was apparent for many samples and is highlighted in the photographs.
2.4 Photographs are provided in Appendix 2 of the inner surfaces of the pipe and fittings and micrographs taken of the cracks and degraded material using a Zeiss Stereozoom microscope fitted with a Sony digital camera.

2.3 ATR-IR spectra were run of the PP-R material in the pipe and fittings. A Nicolet Nexus FTIR spectrometer fitted with a diamond ATR unit was used for all analyses and spectra were plotted using Nicolet Omni software. These studies were performed at QUT under my supervision by Dr Babak Radi who has a Masters degree and a PhD in polymer science. The spectra are given in Appendix 3.

3 Results and Discussion

Distillery samples

3.1 Figure 2.1 shows the interior of the sample from Distillery level 8 (apartment 802) that had been previously analysed in the Report of 15.4.10 as having 32.8 μg/cm² Cu. A test was made adjacent to the cracked welded in saddle (region circled in Fig 2.1) and it can be seen that the test strip shows an intense purple coloration. The depth of coloration is related to the concentration of copper present as either Cu⁺ or Cu²⁺.

3.2 The purple coloration from the Distillery 802 sample may be contrasted with the lack of coloration when the test is performed on unused Aquatherm PP-R pipe as shown in Fig 2.2.

3.3 Figure 2.3 shows an overview of the interior of a PP-R elbow with two pipe sections welded to it. This is the sample shown in Fig 1.2 from Apartment 101, Distillery. Also shown in Fig 2.1 are three test strips after application to the pipe interiors: one at each end of the pipes and one from the pipe section with the darkest stain.

3.4 These sections are shown in more detail in Figs 2.2, 2.3 and 2.4 after contact with the test strips. Each section has tested positive for copper, but not uniformly, indicating differential deposition on the surface or loss of some of the copper salts in the degraded material as it flakes off. It can be seen that the darkest stained section of
the pipe (Fig 2.2) has the highest level of copper based on the depth and uniformity of purple coloration of the test strip.

3.5 Figs 2.5 and 2.6 show detail of the copper test on the two ends of the pipes attached to the elbow. It can be seen that even though there is no brown deposit, there are still localized regions of high copper concentration. Fig 2.6, in particular shows that the brown deposit (which flakes off as a crust) may be removed and the green PP-R below still shows the presence of copper in a small region, possibly where this outer layer has cracked.

3.6 The wall thickness of the PP-R pipe has been measured with and without the brown deposit. The values obtained (averaged across several regions) are:

Wall thickness (deposit on): 3.65 ± 0.10 mm
Wall thickness (deposit removed): 3.18 ± 0.15 mm.

Given that the wall thickness of Aquatherm 25mm SDR 7.4 Faser composite pipe is 3.5mm (Aquatherm catalogue, p126) the wall thickness in the regions where the deposit has been removed is reduced by ~ 9%. The flaky brown deposit is ~ 0.5 mm thick and is of a lower density than the PP-R since it has resulted in an apparent increase in the wall thickness of 0.15mm or 4%. This layer has no mechanical strength and flakes off when dry so the net effect is a reduction of 9% in structural thickness of the pipe wall.

3.7 Examination of the pipe shown in Fig 1.6 (from Distillery apartment 101) in more detail reveals the presence of fine longitudinal cracks as shown in Fig 2.7 within the circled region. Under the microscope (Fig 2.8) this can be seen to be ductile PP-R failure, where the white material is the outer skin of the polymer that has yielded under the pressure in the pipe as the wall thickness has reduced.

3.8 The interior of the pipe where the hairline cracking has occurred is shown in Fig 2.9 and it can be seen that there is a crack in the brown deposit. This corresponds to where there has been growth of a crack through the wall thickness leading ultimately to the failure seen in Fig 2.7 and 2.8.
3.9 A copper test strip is also shown in Fig 2.9 and it can be seen that the deposit has a uniformly high level of copper. Further analysis of the degraded layer has been performed by ATR-FTIR spectroscopy which is able to identify the extent of oxidation of PP-R. The results of this study are given in Appendix 3.

3.10 Figure 3.1 in Appendix 3 gives the infrared spectrum of the upper section of the brown deposit removed from the sample shown in Figures 1.7 and 2.9 (Aquatherm reference: DH_Level_1_Unit_101_030). A photograph of the section from where this was taken is shown in Figure 3.2 (circled).

3.11 The spectrum, Fig 3.1, is characteristic of oxidized PP-R. The signature bands for oxidation are circled and this can be compared with the spectrum from a section taken from the (cleaned) outer layer of the pipe. When in service this had been subjected to a slightly lower temperature than the interior, but had not been exposed to the circulating hot water and copper ions. This spectrum is shown in Fig 3.3 and only weak oxidation bands (circled) are apparent when compared to the circled region of Fig 3.1.

3.12 Spectrum Fig 3.4 was taken of the PP-R after the brown layer was scraped away (Fig 3.2). This shows that the polymer is as heavily oxidized under the brown deposit of thickness ~0.5mm (as noted in section 3.6) as it is on the pipe interior in contact with the water.

3.13 The oxidation was found to penetrate into the green PP-R a further ~1mm as may be seen from Fig 3.5 which is an expanded region of the spectrum over the oxidation (1850 to 1500 cm\(^{-1}\)) and reference band (1453 cm\(^{-1}\)) regions after successive layers are removed for analysis. Given that original oxidation layer is 0.5 mm this means that ~40% of the wall thickness may have some oxidation. It can be seen that slight oxidation is present even on the outer wall of the pipe.

3.14 Carbonyl index (the ratio of the oxidation band at 1712 cm\(^{-1}\) to the PP-R peak at 1453 cm\(^{-1}\)) is a widely accepted measure of oxidation. This is initially high at 0.32 (highly degraded polymer) and decreases to 0.07 after the 4\(^{th}\) layer is removed as shown in Figure 3.5. The lowest value is 0.017 at a depth of ~1mm.
3.15 The surface of the polymer underlying the brown oxidized layer and weakly attached powder is roughened by the oxidation and it appears that the brittle crack has propagated into this weakly oxidized layer resulting eventually in a ductile failure. The crack propagation has most likely been driven by the fluctuations in water pressure until the wall has been penetrated leading to the ductile yielding along the hairline crack as seen in Figure 2.8.

3.16 A further sample provided (D101-3) shown in Fig 1.8 was also examined. The interior was found to be stained brown and there was evidence for a growing longitudinal crack as seen in Fig 1.7. When the cut sample with the crack was flexed the crack grew to the pipe surface as shown in Fig 2.10. There is great similarity to the failure seen in sample D101-2 in Figs 2.7 to 2.9.

3.17 Fig 2.11 shows the interior of the pipe D101-3 after testing for copper using the Quantofix test strips. It is seen that the staining is positive for Cu but less uniform than from D101-2 and is lower where the degraded layer has been removed (right edge of pipe in Fig 2.11).

*Quarry sample*

3.18 A samples removed from the Quarry building level 6 on 27/11/08 is shown in Fig 2.12. The section was removed due to a leak in a weld-in saddle as circled in the photograph. To determine the extent to which this sample may have been exposed to copper ions, a survey was carried out on the pipe without sectioning by using the copper test strips.

3.19 The pipe in the sidearm was still glossy and had no obvious signs of oxidation as shown in Figs 2.13 and 2.14. However, the surface of the pipe had a fine brown film on the glossy surface and it can be seen from the intense purple colour that this tested strongly for copper.

3.20 Examination of the two ends of the riser pipe showed that there was evidence for oxidation of the pipe as there was a powdered layer forming. Figs 2.14 and 2.14 show
the copper test strips in the locations where the test was made and it can be seen that they also show a strong positive test for copper ions.

3.21 The presence of high levels of copper in the section from level 6 of Quarry is strong support for copper-catalysed oxidation of the PP-R. The copper may have arisen from erosion of copper pipe in the recirculating ring main.

4. Declaration

9.1 This report is based only on a limited examination of the samples shown in the photograph in Appendix 1 and 2.

9.2 I am an expert in the performance and failure of polymers and composite materials and my qualifications and experience are described in my attached short CV (Appendix 4).

Graeme George AM, 24 October, 2011
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APPENDIX 1: Photographs of samples from Distillery Hill as identified, sectioned and photographed by Aquatherm and studied in this report.

Fig 1.1: Bagged samples as sent to QUT. DH_Level_1_Unit_101_035

Fig 1.2: Pipe and elbow cut section: DH_Level_1_Unit_101_020
Fig 1.3: Sample with identified leak (under collar). DH_Level_1_Unit_101_022

Fig 1.4: 25mm faser pipe. DH_Level_1_Unit_101_023
Fig 1.5: 25mm return pipe. DH_Level_1_Unit_101_024

Fig 1.6: Pipe in Fig 1.3 after removal of clamp to show point of leak (circled). DH_Level_1_Unit_101_029
Fig 1.7: Interior of leaking pipe after removal of clamp and sectioning. DH_Level_1_Unit_101_030

Fig 1.8: Pipe section after sectioning. DH_Level_1_Unit_101_033
Fig 1.9: Return line after sectioning. DH_Level_1_Unit_101_034
APPENDIX 2: Photographs and micrographs of sections from Pyrmont apartments

Fig 2.1: Interior of pipe section from Unit 802, Distillery Hill showing area analysed (circled) and positive copper test strip. The opposite end of this section had been previously analysed as having 32.8μg/cm² copper (Appendix 5, Report of 15.4.10).

Fig 2.2: Test on unused Aquatherm PP-R pipe showing no copper is present.
Fig 2.3: Overview of elbow and pipe sample from Fig 1.2 with copper test strips

Fig 2.4: Detail of Fig 2.3 showing brown deposit and test strip with positive identification of copper. Circle indicates region analysed.
Fig 2.5: Detail of Fig 2.3 showing copper test from region circled.

Fig 2.6: Detail of Fig 2.3 showing copper test from region circled.
Fig 2.7: Detail of Fig 1.6 showing hairline crack in pipe (arrowed).

Fig 2.8: Higher magnification view of hairline crack in Fig 2.7
Fig 2.9: Interior of sample in Fig 1.7 with positive copper test from region circled.

Fig 2.10: Exterior of pipe in Fig 1.8 showing incipient cracking where interior cracks are seen. (DH_Level_1_Unit_101_033)
Fig 2.11: Interior of pipe (Fig 1.8 and 2.10) showing cracks and copper test strips.

Fig 2.12: Pipe and welded saddle from level 6 Quarry with leaking region circled.
Fig 2.13: Interior of sidearm from Fig 2.12 with positive copper test from pipe.

Fig 2.14: Detail of Fig 2.13 showing sidearm pipe interior is undamaged and glossy except for brown deposit
Fig 2.15: Copper test on slightly oxidised interior of main riser pipe (ie. to left of Fig 2.13). The region tested is apparent from the mark remaining on the pipe deposit.

Fig 2.16: Positive copper test from opposite end of main riser pipe from Fig 2.13
Appendix 3: ATR-FTIR spectra of material removed from failed pipe

Fig 3.1: Brown layer from pipe interior (D-101-2) Aquatherm reference: DH_Level_1_Unit_101. Oxidation bands are circled.

Fig 3.2: Region of surface (circled) after removal of brown layer for analysis.
Fig 3.3: Section taken from exterior of pipe D-101-2 showing only weak oxidation as indicated by the circled bands compared with the same region of Fig 3.2.

Fig 3.4: Spectrum from green powder under brown deposit i.e. as circled in Fig 3.2. Oxidation bands are apparent and are circled.
Fig 3.5: Spectra over a narrow range (1400 to 1850 cm\(^{-1}\)) from successive layers of PP-R after removal of the powdery degraded layer (shown in Figs 3.1 to 3.4). Spectra are normalized to the PP-R band at 1453 cm\(^{-1}\) and show a progressive reduction in oxidation (in the direction of the arrow) as the layers are removed. The last spectrum is from the exterior of the pipe (ie. lowest oxidation).
APPENDIX 4: SHORT CV Professor Graeme A. George

Date of Birth: 30 November 1944
Current Positions: Professor Emeritus of Polymer Science, QUT; Professorial Fellow, the University of Queensland
Qualifications: BSc(Hons) 1967; PhD 1971. (University of Queensland)

PREVIOUS APPOINTMENTS:

1997-2005 Dean, Faculty of Science, Queensland University of Technology (QUT)
1997 Director of Research and Postgraduate Studies, Faculty of Science, QUT
1993-1996 Professor of Chemistry and Head, School of Chemistry, QUT
1989-1992 Senior Lecturer in Physical Chemistry, The University of Queensland
1983-1988 Senior Lecturer in Physical Chemistry, Queensland Institute of Technology
1979-1983 Principal Research Scientist and Head – Polymer Research Group, Materials Research Laboratory (MRL), Melbourne
1978-1979 Senior Research Scientist, (MRL)
1970-1978 Research Scientist, (MRL)

PROFESSIONAL BODIES AND AWARDS:

Member, Order of Australia (AM) 2007
Polymer Medal, Royal Australian Chemical Institute, 2006
Medal of Département du Rhône, France, 2004
Honorary Medal, Polymer Institute, Slovak Academy of Sciences, 2003
President, Royal Australian Chemical Institute (RACI), 1999
Citation for Outstanding Research, RACI Polymer Division, 1997
Applied Research Medal, (the D H Solomon Award), RACI, 1994
Pacific Polymer Federation – Australian Councillor (1993-8)
Editorial Boards:
Polymer Degradation and Stability (UK)
Polymer International (UK) (Associate Editor) (1993-2010)
Polymers for Advanced Technologies (USA) (1996-2011)
High Performance Polymers (UK) (1989-2001)
Progress in Polymer Science (USA) (1997-2007)
Journal of Macromolecular Science (USA) (2000-05)
Chairman, RACI Polymer Division, 1992-93
Fellow, Royal Australian Chemical Institute, 1987

RESEARCH AND CONSULTANCY

Professor Graeme George has had 30 years experience in studying the properties and performance of polymers (plastics, rubbers, textiles and composite materials), particularly when used in hostile environments. He presently leads a research group of postgraduate students and postdoctoral fellows at both QUT and the University of Queensland investigating the development and application of novel sensitive spectroscopic techniques to study polymerization, structure and performance of thermoplastic and thermosetting polymers. This research has produced over 200 refereed journal articles, book chapters and conference presentations at an international level. Professor George has been an expert witness in the field of polymer analysis, performance and failure to the District, Coroner and Supreme Courts in Queensland and New South Wales as well as an expert and Referee for the NSW Supreme Court. He has also been a consultant to over 80 companies, government departments and professional bodies in the field of polymer science. He has been engaged as an expert in the area of failure of industrial polymers, geomembranes and composite materials.