

# ENVIRONMENTAL STRESS CRACKING OF POLYETHYLENE PIPES IN WATER DISTRIBUTION NETWORKS

J.P. Dear, N.S. Mason and M. Poulton  
Department of Mechanical Engineering  
Imperial College London  
South Kensington Campus, London, SW7 2AZ

## ABSTRACT

Water distribution networks are subject to both demanding operational and environmental stresses and these vary, for example, with the proximity of pipes to booster pumps, operating valves and other locations where the pipes are subjected to surge and other fluctuating stresses. Polyethylene water pipes are often used as they have good damage resistance to these stresses. A process that can shorten the life of polymer pipes is the removal of antioxidant from the material by chlorine present in the water. The result can be to reduce the life of the pipe by early exposure of weak features that can cause the pipe to fail. In assessing the average life of polymer water pipes, one need is failure data related to the loss of antioxidants for different concentrations of chlorine in the water. This study of the effects of chlorine in water pipes is part of researching the types and distribution of failures of a typical town's water distribution network.

## Introduction

To resist degradation, the polyethylene pipe material is saturated with antioxidants when it is produced. The antioxidants used depend upon the polyethylene supplier. It is important that a high degree of antioxidant is retained in the polyethylene during pipe manufacture. The retention of antioxidant during the in-service life of pipes is the main interest in this study. This is when the pipes are transporting pressurized chlorinated water. End of life failure of polyethylene pipes often starts with hairline axial cracks being generated on the pipe's inner surface that can be often the site of major failure. This study therefore focused on the degradation of the first 2 mm thickness of the pipe wall measured from the inner surface. Not specifically considered, in this study, is the loss of antioxidant from the outer surface of pipes or the effect of the ingress of aggressive agents via the outer surface of the pipe.

Antioxidants protect polymer chains from scission and other oxidizing effects. This is in the amorphous regions of the material because crystalline regions are resistant to oxygen penetration. A problem is that antioxidant agents in polyethylene continuously migrate to and are lost from the surface of the material. Unfortunately, flowing water aids this removal of antioxidant from the surface of the material resulting in a marked increase in the loss of antioxidant from the polymer. Also, the diffusivity of the antioxidant in the polymer is affected as the polymer absorbs water [1]. Studsvik Material AB [1-3] has studied the loss of antioxidants from polyethylene pipes filled with unchlorinated hot water. From these accelerated studies, it was estimated that polyethylene pipes could have a life, in water distribution systems, of about 50 years. However, this study did not obtain data related to the wide range of dynamic, static and environmental stresses to which water distribution systems can be subjected. Also, the presence of chlorine and other treatment agents in the water and the aggressive agents in the soil in which pipes are located was not researched. Of much interest, in this study, is to relate the findings of the early work by Studsvik to lifetimes that can be obtained from pressurized pipes particularly in this study with regards to the presence of chlorine in the water. The research method devised was to subject stressed and unstressed polyethylene pipes to chlorinated water until they failed or survived the test periods. After failure or at the end of test, the changes of properties of the polyethylene were studied. These evaluations included both different pressures and the degree of chlorine concentration in the water. The experiments were at high temperature to achieve accelerated degradation.

## Experimental

For the mechanical studies, polyethylene dumb-bell shaped specimens, of thickness 2 mm, were obtained from the inner wall of MDPE pipes as shown in Figure 1(a). These specimens conform to the standard shape required for mechanical tensile tests as specified in Type A test piece in BS 2782 Method 320A (1976). Several specimens were obtained from each section of pipe and these were used to obtain the average yield stress and elongation to failure of the material before and after exposure to

chlorinated water. All specimens were taken from along the axis of the pipe. For each study of pipe degradation, these specimens provided for consistent results (typical loading curve in Figure 1(b)). The rate of loading was  $25 \text{ mm min}^{-1}$ .

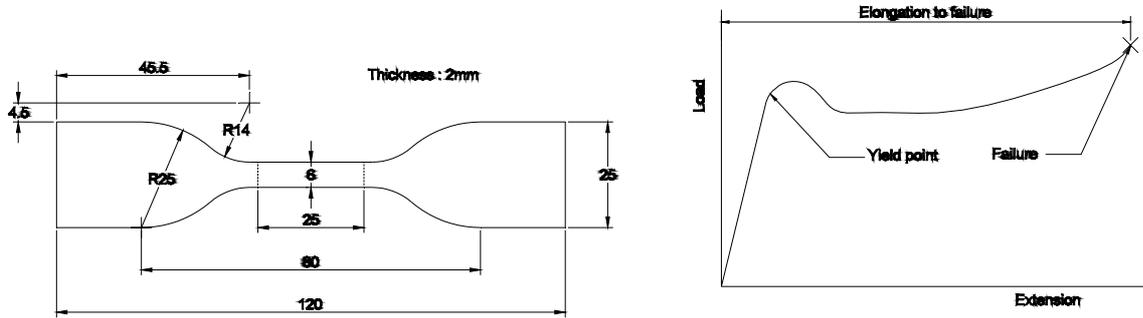


Figure 1. Tensile properties for MDPE: (a) Specimen shape, (b) Typical loading curve.

Studies of creep rupture by hydrostatic pressure were performed with chlorinated water, on MDPE pipes (diameter 90 mm with SDR 11 and SDR 17.6) using the WIS 4-32-03 standard [4]. The lengths of the pipe were 1 m and their ends were capped with electro-fusion seals as specified [4] by WIS 4-32-08. After these sealed pipes had been charged with the appropriate pressurized chlorinated water, they were immersed in water baths maintained at elevated temperature. The level of chlorine concentration of the water in the sealed pipes was monitored and maintained. These pressurized pipe experiments continued until the pipes failed or completed the test period. After failure, 2 mm thick dumb-bell specimens (Figure 1(a)) were taken from the inner wall of the pipe and these specimens were subjected to tensile tests to measure yield stress and elongation to failure.

For these studies, Energy Dispersive X-ray Analysis (EDAX) was used to determine the depth of penetration of chlorine into the inner wall of the polyethylene pipe. This was to perform an EDAX measurement at different depths from the inner wall surface of a cross-section of the pipe wall. The EDAX experimental data were confirmed by subjecting a number of specimens to Pyrolysis-Gas Chromatography (PGC) that revealed the concentration of chlorine at different through-thickness points in the specimen. This was by taking thin microtome wafers through the thickness of each pipe wall and subjecting each wafer to PGC.

Differential Scanning Calorimetry (DSC) to WIS 4-32-3 was used to determine the antioxidant loss by measuring the Oxidation Induction Time (OIT) at  $200 \text{ }^\circ\text{C}$  for samples subject to different ageing conditions. Taking thin microtome wafers through the thickness of each pipe wall and then subjecting the wafers to DSC determined the degree of depletion of the antioxidant through the thickness of the pipe wall. The initial OIT at  $200 \text{ }^\circ\text{C}$  for MDPE is ca. 70 minutes. It is important in these measurements to maintain good temperature control as explained by Billingham & Calvert [5].

For all experiments after chlorine exposure, Gel Permeation Chromatography (GPC) was performed by RAPRA Technology Limited to measure molecular mass distribution. The values of molecular mass are weight average molecular masses ( $M_w$ ).

## Results

The accelerated evaluations, to study the degradation of complete MDPE pipes (diameter 90 mm of SDR11 and SDR17.6), when pressurised with chlorinated water of different concentrations, were performed at  $80^\circ\text{C}$ . The chlorine concentration was varied from 500 to 120000  $\text{mg litre}^{-1}$  (changed every 672 hours (4 weeks)). Experiments were performed, using different hydraulic pressures, to give hoop stresses in the pipe wall of 2.7, 3.1 and 4.6 MPa as well as zero hoop stress. The pipes were then immersed into a large tank of unchlorinated water at  $80^\circ\text{C}$ . It is to be noted that at high temperatures, there can be changes in crystallinity and mechanical properties of the pipe material. This needs to be taken into account when relating the results obtained at high temperature to the working temperature of pipes. Also, to be noted, there are partial correlations, for example, between the effects of temperature, stress and chlorine concentration. In this study of MDPE pipes (28 samples), some pipes failed whilst others were removed without failure from the hot water tank at appropriate times.

For the pipes which failed, Figure 2(a) shows a plot of  $\log_{10}(\text{hoop stress})$  versus  $\log_{10}(\text{time to failure})$ . All of the failures for pipes, evaluated in this study, were of a macroscopically brittle nature. The *Reference* line shown on Figure 2(a) is, however, for both *Ductile* and *Brittle* failures in MDPE at  $80^\circ\text{C}$  when the water inside the pipe is not chlorinated. This reference line was based on the same conditions as originally employed by Gedde *et al.* [2]. *Ductile* failures exhibit drawn or yielded material about the failure site whereas *brittle* failures show little or no evidence of yielding and drawing and are mostly axial cracks. The *ductile* failure processes are mostly controlled by the viscoelasticity of the MDPE and hence the *ductile* failure line has a gradual slope. The brittle failure line, however, has a much sharper slope and shows that *brittle* failures occur at stress levels below those for *ductile* failures. As indicated by Figure 2(a), for the same hoop stress in the pipe wall, then, pipes will fail earlier for a higher chlorine concentration in the water.

For failures with chlorinated water at high temperature, there were no *ductile* failures only *brittle* failures. These brittle failures had the same stress versus time to failure gradient as those without chlorine in the water on the inside of the pipe. This is illustrated by a dotted line for 5000 mg litre<sup>-1</sup> at 80°C in Figure 2(a).

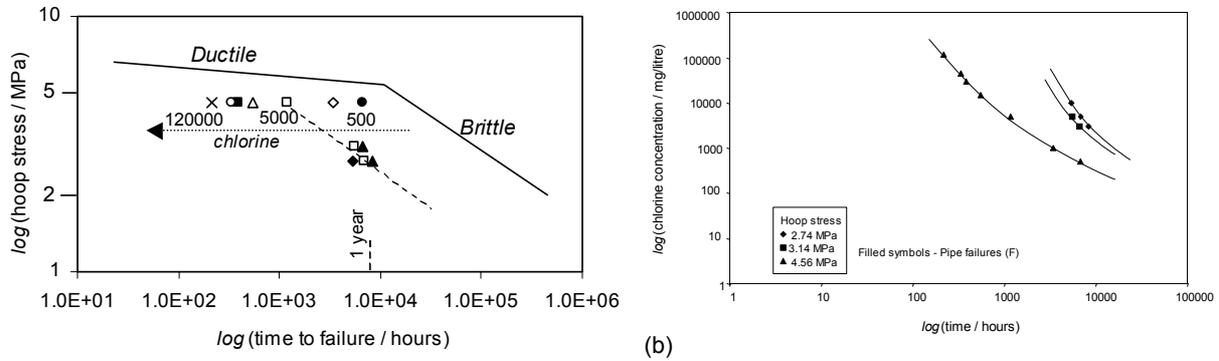


Figure 2. MDPE pipes when internally pressurized at 80°C (a): Hoop stress versus time to failure for chlorine concentrations in mg litre<sup>-1</sup>: 500 (●), 1000(◊), 3000(▲), 5000(◻), 10000(◆), 15000(△), 30000(■), 45000(○), 120000(X) - Reference line for *Ductile* and *Brittle* failures at 80°C when the pressurized water is not chlorinated, (b) Chlorine concentration versus time to failure for hoop stresses of 2.7, 3.1 and 4.6 MPa.

The effect of low residual levels of chlorine in mains water would be expected to be small but for high chlorine concentrations (as used in water treatment plants), an early onset of brittle failure is to be expected. The relationship between chlorine concentration and the time to failure for the pipes that failed is shown in Figure 2(b) for hoop stresses of 2.7, 3.1 and 4.6 MPa at 80 °C. The most marked reduction in lifetime is produced by the combined effect of high stress and high chlorine concentration.

Infrared spectra of samples taken from the inner wall region were used to determine the relative absorbance of carbonyl bonds at 1745 cm<sup>-1</sup> and carbon-chlorine bonds at 600 cm<sup>-1</sup>, compared to the methylene group absorbance at 1450 cm<sup>-1</sup>, taken as an internal standard. The carbonyl groups indicate oxidation since they are oxidation products whilst the formation of carbon-chlorine bonds can be attributed to the reaction of chlorine with both the polymer and other organic molecules such as the antioxidants. Figure 3(a) is a plot of the relative absorbance of the carbonyl group against ageing time. This shows that the results fall in to three distinct areas. The four data-points in the bottom left-hand corner (low relative absorbance, short ageing time) relate to the pipes tested at very high chlorine concentrations. The data-points with 45 to 60% relative absorbance relate to the rest of the pipes that failed during the ageing process. The remaining data-points relate to the pipes that were removed before failure.

The results for the pipes removed without failure show a linear increase of the relative absorbance of carbonyl groups with time. The pipes that failed (excluding the specimens tested at very high chlorine concentration) reached a maximum relative absorbance at around 45% to 60% when they failed. There is evidence of the higher hoop stresses increasing the relative carbonyl absorbance for low chlorine concentrations. The 4.6 MPa data-points for chlorine concentrations of 500, 1000 and 5000 mg litre<sup>-1</sup> showed high carbonyl absorbance from 45 to 60% and also there was failure of these pipes. The oxidation process does however proceed without an applied hoop stress as shown by the results from the pipes that were not pressurised. The results for the very high chlorine concentration pipes seem to indicate that they did not fail because of oxidation, whilst it is likely that the higher levels of oxidation indicated by the carbonyl absorbance in the other failed pipes will lead to a reduction in mechanical properties possibly causing the failures.

Figure 3(b) is a plot of the relative absorbance of the carbon-chlorine bonds against ageing time. The results at first seem to replicate those of the carbonyl absorbance band. There is evidence of the higher hoop stresses increasing the relative carbon-chlorine absorbance for low chlorine concentrations. The 4.6 MPa data-points for chlorine concentrations of 500, 1000 and 5000 mg litre<sup>-1</sup> showed carbon-chlorine absorbance from 15 to 22 % and there was failure of these pipes. Also, the four pipes that failed with very high chlorine concentrations, did not exhibit much formation of carbon-chlorine bonds. The difference between the data-points with absorbance of 3% and the rest of the data-points is that the ones at 3% were not pressurised. This low absorbance could be attributed to the chlorine atoms reacting with the antioxidant and other organic molecules in the specimen rather than with the polymer when no stress is present. Since the failed pipes and those taken out both exhibit a limit on the formation of the carbon-chlorine bonds at around 20 to 23% relative absorbance, it is less likely that the formation of the carbon-chlorine bonds is a big factor in determining their failure. The cause of the limit on the formation of the carbon-chlorine bonds is also of interest, possible causes include:

- A limited amount of chlorine is available for reaction with the polymer.
- There is evidence of a limit of the solubility of chlorine in the polymer. The form of the chlorine in the polymer may be important. The chlorine may be in many different forms such as free chlorine or hypochlorite ions and only one of these forms may be reactive enough to form the bond.
- A limit on the number of sites that the chlorine can attack presents evidence that chlorine substitutes the hydrogen atom attached to a tertiary carbon atom. A tertiary carbon atom occurs at chain branches along the polymer backbone. The number of chain branches is limited and well controlled during manufacture of the polymer because of the effect of chain branching on the mechanical properties.

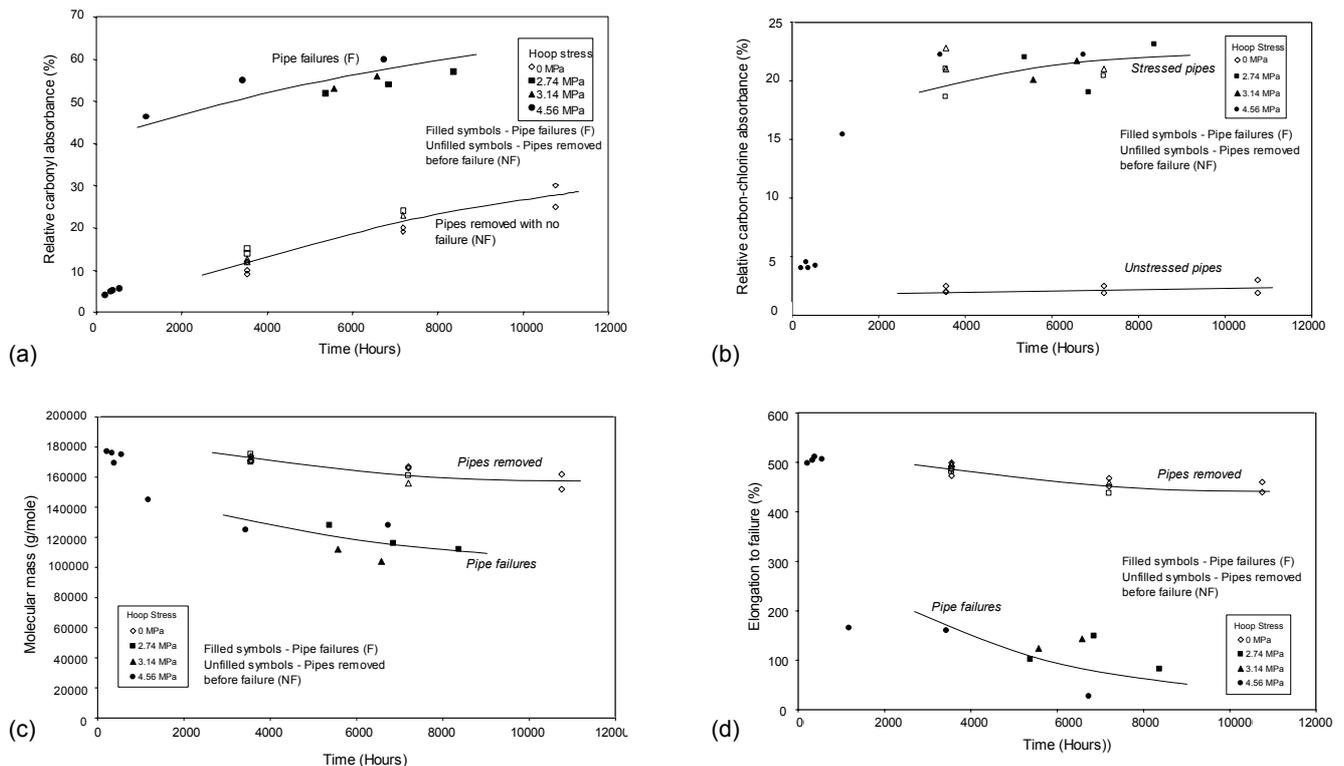


Figure 3. MDPE pipes internally pressurized with chlorinated water at 80°C: (a) Relative absorbance of carbonyl groups, (b) Relative absorbance of carbon-chlorine groups, (c) Molecular mass ( $M_w$ ), (d) Elongation to failure versus ageing time.

GPC was performed on samples scraped from the inner surface of the pipe. Figure 3(c) shows the weight average molecular mass against ageing time for the different hoop stresses used for all pipes. The trends in the results are very similar to those seen in the relative absorbance of the carbonyl groups. The four high chlorine concentration pipes again appear to differ from the other failed pipes with little, if any, reduction in molecular mass. There is a dramatic reduction of the molecular mass of the other failed pipes. The pipes that were taken out during the ageing process have seen a small reduction in molecular mass, proportional to the time aged. Again the effect of stress is not pronounced. It is evident from the results that the oxidation shown by the infrared spectra has markedly reduced the weight average molecular mass of the polymer in the pipes that failed. It is likely that they failed because the mechanical properties were greatly reduced by the reduction in molecular weight. Physical tests on specimens from the inner wall were then performed to determine whether the mechanical properties have been degraded.

Dumb-bell shaped specimens (as in Figure 1(a)) of 2 mm thickness were taken from the inner wall of the pipes subject to hot chlorinated water at 80°C. These specimens were tensile loaded to obtain elongation to failure and yield stress data. The elongation to failure results in Figure 3(d) mirror the relative absorbance of carbonyl bands and the molecular mass results. The high chlorine concentration pipes show little change in elongation to failure and yield stress. The pipes that have failed have a severely reduced elongation to failure and yield stress at the inner wall. The aged pipes that have been removed before failure show a small reduction in elongation to failure (and yield stress) over time. The reduction of ductility (and yield stress) in the failed pipes show the reduction in molecular mass has greatly embrittled the surface layer. This can be traced back through the results to the oxidation of the polymer shown by infrared spectroscopy in Figure 3(a).

Figure 4 shows examples of OIT profiles that were obtained for these aged pipes that failed. In these plots, the vertical dashed line shows the extent of the penetration of the chlorine as measured by EDAX. The upper horizontal dotted line relates to the

antioxidant level prior to ageing of the pipe and the lower solid line shows the antioxidant profile after ageing. Figure 4(a) relates to a pressurized pipe, with a hoop stress of 4.6 MPa and aged with a chlorine concentration of 120000 mg litre<sup>-1</sup>, which failed after 216 hours. Figure 4(b) relates to a pressurized pipe, with a hoop stress of 4.6 MPa and aged with a chlorine concentration of 15000 mg litre<sup>-1</sup>, which failed after 552 hours. For both cases, there is a sharp loss of antioxidant from the inner wall of the pipe and the diffusion of antioxidant to the inner wall has increased. This loss of antioxidant via the inner wall surface is much greater than the loss via the outer wall surface that is only exposed to unchlorinated water. Initially, a substantial proportion of the antioxidants diffusing to and lost from the wall surfaces will be the more mobile antioxidants. Figures 4(c) and 4(d) relate to two examples of OIT profiles for aged pipe samples that failed after longer times. Figure 4(c) relates to a pressurized pipe, with a hoop stress of 4.6 MN m<sup>-2</sup> and aged with a chlorine concentration of 5000 mg litre<sup>-1</sup>, which failed after 1176 hours. Figure 4(d) relates to a pressurized pipe, with a hoop stress of 4.6 MN m<sup>-2</sup> and aged with a chlorine concentration of 1000 mg litre<sup>-1</sup>, which failed after 3432 hours. For both cases, the consumption of antioxidant is much more marked. In particular, Figure 4(d) shows that the penetration of the chlorine is nearly halfway through the thickness of the pipe wall and the antioxidant depletion is considerable both behind and ahead of the chlorine front.

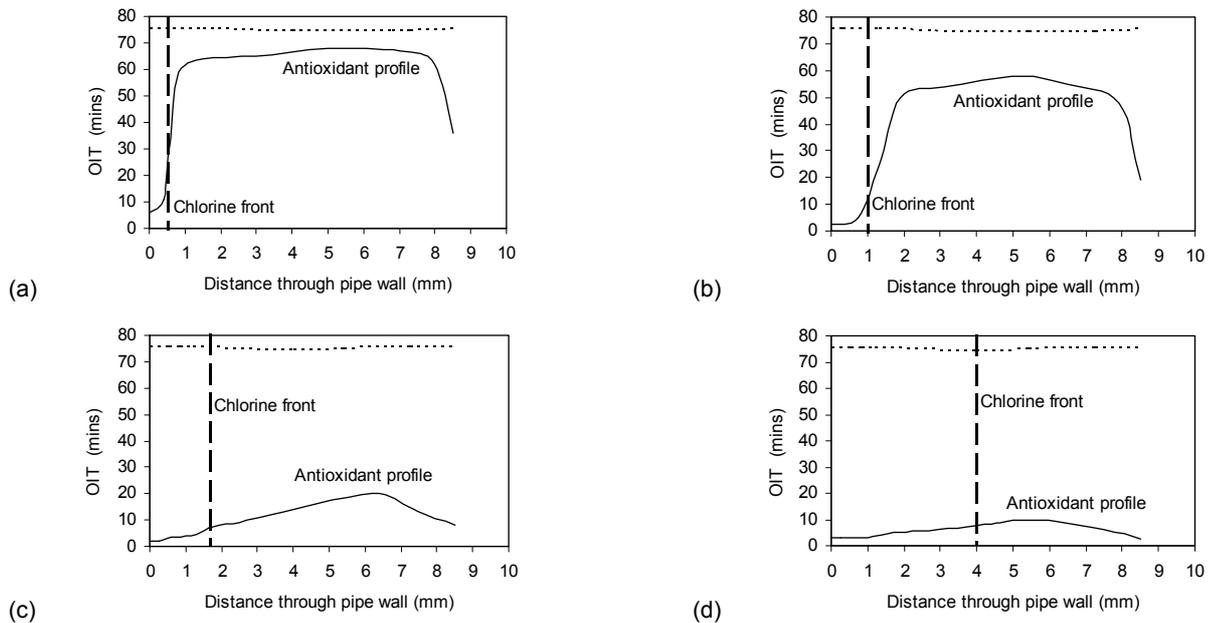


Figure 4. Antioxidant concentration by OIT versus distance from inner wall for failures of aged MDPE pipes (hoop stress 4.6 MPa) with vertical dashed line showing penetration of chlorine by EDAX: (a) Time to failure 216 hours, (b) Time to failure 552 hours, (c) Time to failure 1176 hours, (d) Time to failure 3432 hours.

Figure 3 showed that there is little change in the material properties of the 2 mm thick specimens removed from the inner wall of the aged pipes for times to failure of the pipes less than 500 hours. This is explained in Figure 4, which shows that it is not until the chlorine penetration zone has gone beyond the first 1 mm of the wall thickness (50% of the 2 mm specimen thickness) that the material properties start to fall dramatically. This is when the chlorine and oxygen has had time to affect the material properties of at least 50% of the 2 mm specimen thickness.

The extent of penetration by chlorine and the corresponding loss of antioxidant via the inner wall surface for the MDPE were observed. This is for all the pipe failures and chlorine concentrations varying from 500 to 120000 mg litre<sup>-1</sup>. The results show that the depth of penetration ( $s$ ) into the MDPE by the chlorine followed a relationship of the form:

$$s \cong \sqrt{D_{Cl}t} \quad (1)$$

where penetration depth is  $s$  and time of exposure is  $t$ . It was found that the diffusion coefficient obtained for chlorine,  $D_{Cl}$ , varies with hoop stress. For a hoop stress of 4.6 MPa, the diffusion coefficient,  $D_{Cl}$ , was  $\sim 0.003$  for a depth,  $s$ , in mm and time of exposure,  $t$ , in hours.

Using optical aids, small axial cracks (less than 1 mm in length) can be seen on the inner surface of pipes that had been subjected to ageing experiments using hot chlorinated water at 80°C. Figure 5(a) is an electron micrograph showing the axial cracks in the embrittled inner surface of an aged pipe that had been exposed to pressurised hot chlorinated water. These small cracks in the MDPE pipe provide many sites from which a slow crack can grow. Figure 5(b) shows an electron micrograph of a

slow crack growth fracture surface through the thickness of the pipe wall. The top of the main micrograph relates to the inner pipe surface from which a thumbnail shaped slow crack has grown. Additional high magnification views show the initial defect site (top) and the slow crack growth (bottom).

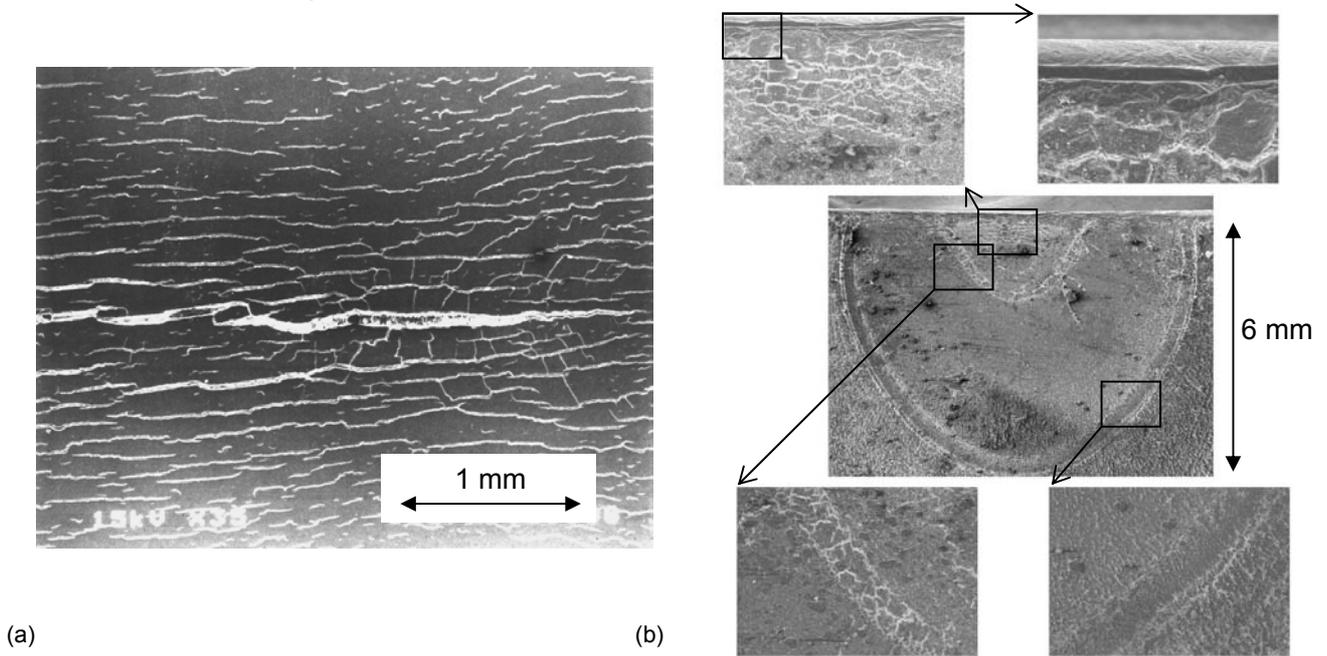


Figure 5. Electron micrographs of failure site in MDPE pipe subjected to pressurized chlorinated water at 80°C: (a) Axial cracks in the embrittled inner pipe surface, (b) Slow crack growth fracture surface through the pipe wall with inset high magnification views.

### Modelling

Experimental studies have shown that the higher the concentration of chlorine diffusing into the inner surface of the MDPE pipe, the more dominant is its effect on the resultant degradation of the MDPE. For low chlorine concentration levels, then the degradation of the first 2 mm of the inner surface of the pipe could be a combination of two effects. One is the enhanced diffusion of the antioxidants in the MDPE into the chlorinated water. The other is the increased reaction loss of antioxidant in the chlorine diffusion zone as it advances into MDPE from the inner pipe surface. To study these factors further, a model has been constructed to simulate the diffusion and reaction losses. This is from the initial condition when the MDPE pipe material is saturated with antioxidants to the final condition when there is very little antioxidant left in the MDPE. Studsvik Material AB presented a diffusion model [6] to simulate the migration of antioxidants to and lost from the free surfaces of MDPE pipe. This was when the water in the pipe was not chlorinated and the outside of the pipe was surrounded by air. With water on one surface and air on the other, the Studsvik AB model [6] uses a substantial variation of the diffusion coefficient across the wall of the pipe. Also, this model provided for reaction loss processes for antioxidants in the MDPE. For this study, the Studsvik AB model was adapted to include chlorine diffusion, the reaction between chlorine and antioxidant and the resulting loss of antioxidant from the material. The modelling was for a thick-walled pipe containing pressurized chlorinated water and immersed in a large water bath. The temperature was constant for both the chlorinated water in the pipe and the water outside the pipe that was not chlorinated. At each of the simulated stages of the chlorine penetration into the MDPE from the inner pipe surface, output from the model was obtained. This is to record the changing concentration profiles of chlorine and antioxidant through the thickness of the pipe wall. For the model, the equations for antioxidant and chlorine diffusion in terms of radial distance ( $r$ ) and time ( $t$ ) are as follows:

$$\frac{\partial C_A(r,t)}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left[ r D_A(r) \frac{\partial C_A(r,t)}{\partial r} \right] - R_A(r,t) \quad (2)$$

$$\frac{\partial C_{Cl}(r,t)}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left[ r D_{Cl}(r) \frac{\partial C_{Cl}(r,t)}{\partial r} \right] - R_{Cl}(r,t) \quad (3)$$

where  $C_A(r,t)$  and  $C_C(r,t)$  are concentrations,  $D_A(r)$  and  $D_C(r)$  are diffusion coefficients and  $R_A(r,t)$  and  $R_C(r,t)$  are reaction terms for antioxidant(A) and chlorine(C) respectively. Eqs. (2) and (3) were solved numerically for the above experimental conditions. Figure 6 shows in sequence four-recorded concentration profiles from the model simulation. The first concentration profile is before there is any penetration of chlorine and the pipe is fully saturated with antioxidant through the thickness. At the second concentration profile, the effect of the loss of antioxidants from the MDPE pipe relates to two effects. One is the diffusion loss from both inner and outer free surfaces and the other is the reaction loss. The main reaction loss, in this simulation, relates to the presence of chlorine that has diffused into the MDPE. This is particularly so in later concentration profiles where it can be seen that the reaction loss of antioxidant in the chlorine diffusion zone becomes dominant. The overall effect is that the antioxidant is increasingly confined to the outer half of the simulated MDPE material and eventually is dramatically reduced.

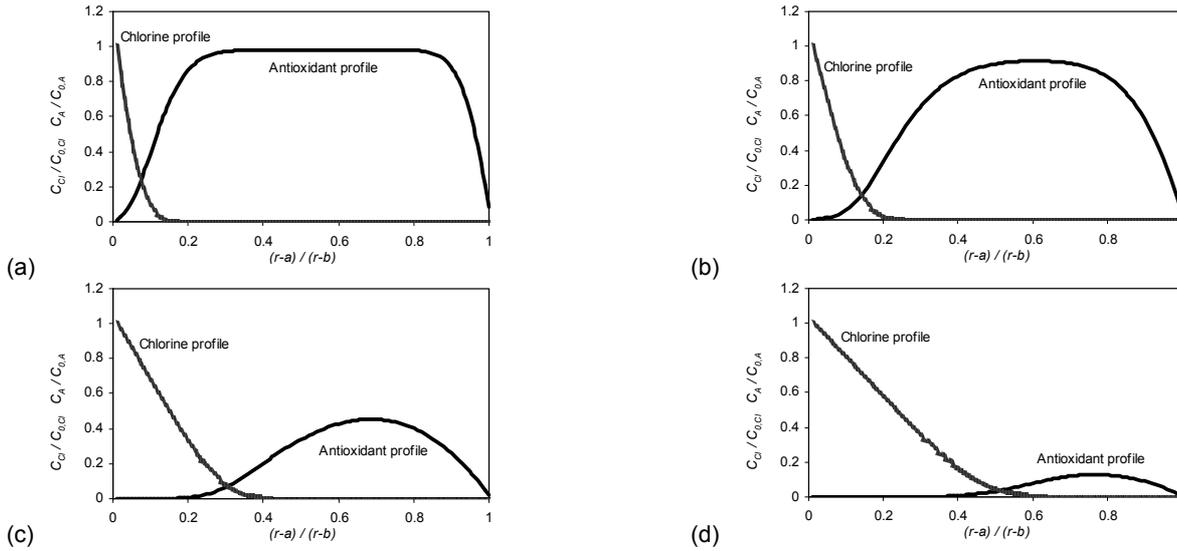


Figure 6. Antioxidant and chlorine concentration profiles for increasing exposure time.

When chlorine is present, the failures of the pipes are brittle in nature and Figures 2 and 5 indicate that slow crack growth is a dominant failure mode. Slow crack growth in MDPE [7,8] follows a relationship of the form:

$$\frac{da}{dt} = A_c K^n \quad (4)$$

where  $da/dt$  is the crack velocity and  $K (=Y\sigma(\pi a)^{1/2})$  is the stress intensity factor ( $Y$  is geometry factor,  $\sigma$  is applied stress and  $a$  is crack length). By integration, it can be shown that the time for a slow crack to propagate is given by:

$$t_p = \frac{1}{A_c(Y\sigma)^n \pi^{n/2}} \cdot \frac{2}{(n-2)} \left[ \frac{1}{a_i^{n/2-1}} - \frac{1}{a_f^{n/2-1}} \right] \quad (5)$$

where  $a_i$  and  $a_f$  are the initial and final crack length. From Eq. (5),  $t_p \sim \sigma^{-n}$  &  $\text{Log}_{10}(\sigma) \sim - (1/n) \cdot \text{Log}_{10}(t_p)$ . For MDPE,  $A_c \sim 10^{-7}$  and  $n$  is 4 for  $da/dt$  in  $\text{m s}^{-1}$  and  $K$  in  $\text{MPa m}^{1/2}$  [9] giving a slope of  $\sim 0.25$  for the *Brittle* failure line as observed in Figure 2(a).

Eq. (5) can be used to predict the initial defect size when slow crack growth determines the time to failure. The solid *Reference Line (unchlorinated water)* in Fig. 2(a), gives a time to brittle failure of 23000 hours for a hoop stress in the pipe of 4.6 MPa. For this brittle failure, Eq. (5) gives an initial defect size close to 20  $\mu\text{m}$ . Particulate matter (catalyst residue or colouring agents) can result in faults of 20  $\mu\text{m}$  in size on or near the inner surface of the pipe.

From the *dotted line (chlorinated water of 5000 mg litre<sup>-1</sup>)* in Figure 2(a), the time to brittle failure would be 1176 hours for a hoop stress in the pipe wall of 4.6 MPa. For this brittle failure, Eq. (5) gives an initial much larger defect size of 340  $\mu\text{m}$ .

Assuming this slow crack growth model with the time to failure equal to the crack propagation time gives an initial defect size as shown in Figure 7. Superimposed on this plot are the depths of chlorine penetration in 1/10 of the time to failure and in the time to failure as given by Eq. 1 which was determined by the EDAX studies. This gives an indication of the extent of polyethylene material affected by the chlorine advance. Once the material is deprived of its antioxidant, then, chlorine and other oxidising agents search out weaknesses in the material and an initial defect is formed.

From Figure 7, the depth of chlorine penetration in 1/10 of the lifetime is ca. 0.5 mm for a hoop stress of 4.6 MPa and a chlorine concentration of 5000 mg litre<sup>-1</sup>. This penetration and concentration of chlorine is sufficient to produce a 340 µm initial defect for the start of the slow crack growth process. This would result from the embrittlement of the pipe's inner surface as the chlorine deprives this surface material of its antioxidant and oxidation of the polymer molecules subsequently occurs. Therefore, for chlorine concentrations up to 5000 mg litre<sup>-1</sup>, the chlorine enhances the size and formation of the initial defect responsible for the slow crack growth. The subsequent slow crack growth is less affected by the presence of chlorine. However, for higher chlorine concentrations above 5000 mg litre<sup>-1</sup>, there is a greater tendency for a combined environmental stress cracking failure process where chlorine and stress have a synergistic effect for the whole crack growth process.

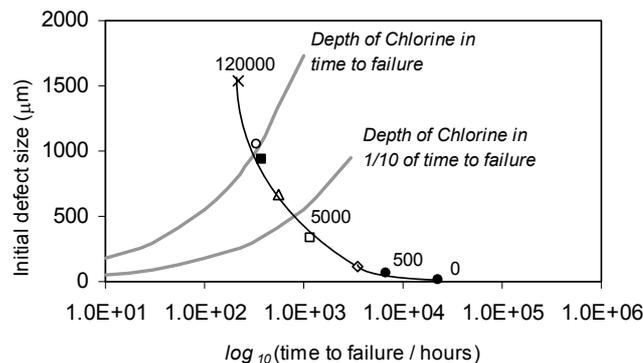


Figure 7. Initial defect size calculated from Eq. 5 for the slow crack growth model, for hoop stress of 4.6 MPa, with curves showing depth of penetration of chlorine superimposed for 1/10 life and the full life of pipe.

### Conclusions

This research has shown that up to 5,000 mg litre<sup>-1</sup>, chlorine accelerates the initiation of slow crack growth (SCG) by:

- Chlorine being absorbed in the polymer, diffusing and consuming antioxidant.
- Oxidation of the polymer chains occurring leading to a reduction of molecular mass through chain scission.
- Reduction in tensile properties leading to a brittle layer forming and as the pipe expands due to creep; the brittle layer cracks and so provides an initiation site for SCG.

Above 5,000 mg litre<sup>-1</sup>, the chlorine results in the pipes failing very rapidly due to environmental stress cracking.

### Acknowledgments

To the staff of the Water Research Centre (WRc) and Anglian Water Services, in particular: Drs Gerald Jones, Jon Morris, Robin Peck and Graham Kemp. To EPSRC and DTI for their joint support of a Postgraduate Training Partnership.

### References

1. Viebke, J. and Gedde, U.W., "Antioxidant diffusion in polyethylene hot-water pipes", *Polymer Engineering and Science*, **37**(5): 896-911 (1997).
2. Gedde, U.W., Viebke, J., Leijstrom, H. and Iwarson, M., "Long-term properties of hot water polyolefin pipes – a review", *Polymer Engineering and Science*, **34**(24): 1773-1787 (1994).
3. Karlsson, K., Smith, G.D. and Gedde, U.W., "Molecular structure, morphology and antioxidant consumption in medium density polyethylene pipes in hot water applications", *Polymer Engineering and Science*, 1992, **32**(10): 649-657 (1992).
4. Water Industry Standard, "Specification for blue polyethylene (PE) pressure pipe for cold potable water (nominal sizes 90 mm to 1000 mm for underground protected use)", WIS 4-32-03 & WIS 4-32-08, May (1987).
5. Billingham, N.C. and Calvert, P.C., "The physical chemistry of oxidation and stabilisation of polyolefins", in *Developments in Polymer Stabilisation* (G. Scott, Ed.), Applied Science, London (1980).
6. Smith, G.D., Karlsson, K. and Gedde, U.W., "Modelling of antioxidant loss from polyolefins in hot-water applications I: Model and application to medium density polyethylene pipes", *Polymer Engineering and Science*, **32**(10): 658-667 (1992).
7. Williams, J.G., *Fracture Mechanics of Polymers*, Ellis Horwood, Chichester (1984).
8. Gray, A., Mallinson, J.N. and Price, J.B., "Fracture behaviour of polyethylene pipes", *Plastics and Rubber Processing and Applications*, **1** (1): 51-53 (1981).
9. Mason, N.S., PhD Thesis *The asset lives of plastic pipes - technical and economic factors affecting the in-service life of polymer pipes in the water industry*, University of London (1998).