The Effects of Chlorine Depletion of Antioxidants in Polyethylene

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Received: 19th September 2000; Accepted: 13th November 2000

SUMMARY
For many polyethylene products, their working life-span depends on retention by the material of its antioxidant. In dry air, when the working and environmental stresses remain within defined limits, the life-span of the material can be many decades. Immersed in water, for example, the diffusion and loss of antioxidant from the material’s surface can increase. Also, some types of aggressive agents, if in the water, can enter the material’s surface and migrate into the material to increase the depletion of the antioxidant population. Researched in this study, is the depletion of antioxidants in polyethylene when exposed to water containing different chlorine concentrations. This research relates to the world-wide use of polyethylene pipes in water treatment and distribution networks.

1. INTRODUCTION
Relative to many pipes, made of other materials, polyethylene pipes are lightweight and have a good degree of flexibility. The pipes can, therefore, be produced and installed in long lengths and this is without the need for expensive heavy handling equipment. The flexibility of the pipe reduces the number of joints needed for the pipeline to follow the contours of the land in which the pipes are to be buried. Also, after installation, the pipe will withstand well modest earth movements caused by the forces of nature and those produced by man. A particularly good feature is that polyethylene does not corrode. Hence the pipe’s inner surface remains smooth and the hydraulic performance is well maintained.

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 protection 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 hair-line axial cracks being generated on the pipe’s inner surface. This study, therefore, focuses on the degradation of the first 2 mm 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 oxidising effects. This is in the amorphous regions of the material because oxygen does not penetrate the crystalline regions. A problem is that antioxidant agents in polyethylene continuously migrate to and are lost from the surface of the material. Unfortunately, water is particularly good at removing antioxidant from the surface of the material with the result of increasing loss of antioxidant from the polymer. Also, the diffusivity of the antioxidant in the polymer becomes affected as the polymer absorbs water. Studsvik Material AB has studied these losses of antioxidants from polyethylene pipes filled with unchlorinated hot water. From these accelerated studies, it was estimated that polyethylene pipes would 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 life-times that can be obtained from
pressurized pipes, particularly with regard to the presence of chlorine in the water.

The research method devised was to subject polyethylene pipes to pressurized chlorinated water until they failed or survived the test period. After failure or at the end of the test, the changes of properties of 2 mm thick specimens from the inner wall 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.

2. EXPERIMENTAL PROCEDURES

Mechanical tensile studies

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. These specimens conform to the standard shape required for mechanical tensile tests as specified in the Type A test piece in BS 2782 Method 320A (1976). Several specimens were obtained from each section of pipe and 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 consistent results. A typical loading curve is shown in Figure 1 (the rate of loading was 25 mm min⁻¹).

Hydrostatic experiments

Studies of creep rupture by hydrostatic pressure were performed on MDPE pipes (diameter 90 mm with SDR 11 and SDR 17.6) using the WIS 4-32-03 standard⁴ (SDR is Standard Diameter Ratio = Pipe diameter / Wall thickness). The length of the pipes was 1 m and their ends were capped with electrofusion seals as specified⁴ 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 in the water in the sealed pipes was monitored and maintained. These pressurized pipe experiments continued until the pipes either failed or completed the test period. After failure, 2 mm thick dumb-bell specimens, which conformed with BS 2782 Method 320A (1976), were taken from the inner wall of the pipe, as shown in Figure 1, and these specimens were subjected to tensile tests to measure yield stress and elongation to failure.

Figure 1  The shape and dimensions of tensile specimens (thickness 2 mm) removed from the surface of the inner wall of the MDPE pipes: (a) Specimen dimensions (in mm), (b) Typical tensile loading curve (MDPE) showing yield point and elongation to failure

[Diagram of specimen dimensions and tensile loading curve]
Chlorine penetration

After each pressurized water study, 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 done by performing 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 achieved by taking thin microtome wafers through the thickness of each pipe wall and subjecting each wafer to PGC.

Antioxidant depletion

In the case of the pressurized sealed pipe chlorinated water studies, the degree of depletion of the antioxidant, through the thickness of the pipe wall, was determined by taking thin microtome wafers through the thickness of each pipe wall. These wafers were then subjected to a Differential Scanning Calorimetry (DSC) to WIS 4-32-3 to determine the antioxidant loss.

Molecular weight distribution

After exposure to pressurized chlorinated water, Gel Permeation Chromatography (GPC) was performed by Rapra Technology Limited to measure molecular weight distribution. The values of molecular mass are weight average molecular masses ($M_w$).

3. RESULTS

The accelerated evaluations, to study the degradation of complete MDPE pipes (diameter 90 mm of SDR11 and SDR 17.6), when pressurized with chlorinated water of different concentrations, were performed at 80°C. The chlorine concentration was varied from 500 to 120000 mg litre$^{-1}$ (changed every 672 hours (4 weeks)). Three groups of experiments were performed, using different hydraulic pressures, that produced hoop stresses in the pipe wall of 2.7, 3.1 and 4.6 MN m$^{-2}$. The pressurized pipes were immersed in a large tank of unchlorinated water at 80°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. Table 1 summarises the results from this study of MDPE pipes (28 samples) showing the ageing time and whether the pipes failed (F) or were removed without failure (NF) from the hot water tank at the stated time.

For the pipes which failed (F), Figure 2 shows a plot of Log$_{10}$ (hoop stress) versus Log$_{10}$ (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 is, however, for both ductile and brittle failures in MDPE at 80°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 show 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, for the same hoop stress in the pipe wall, pipes will fail earlier for a higher chlorine concentration in the water.

It was to be expected that the brittle failure lines, related to the pressurized chlorinated water, would have the same slope as the brittle failure line for unchlorinated water. This was verified by subjecting pipes to different pressures of chlorinated water (5000 mg litre$^{-1}$ at 80°C) and drawing a dotted line through these brittle failure points (see Figure 2). The dotted line was parallel to the brittle failure line for the pressurized unchlorinated water.

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 a hoop stress of 4.6 MN m$^{-2}$ at 80°C is shown in Figure 3. Each plot point is coded using a different symbol for each chlorine concentration as in Figure 2.

After subjecting the sealed pressurized pipes to different concentrations of hot chlorinated water at 80°C dumb-bell shaped specimens (BS 2782: Method 320A-Type A dimensions, see Figure 1) of 2 mm thickness were taken from the pipe’s inner wall. These specimens were tensile loaded to obtain yield
Table 1 Summary of the results from the ageing study of MDPE pipes (diameter 90 mm of SDR 11 and SDR 17.6) showing hoop stress, chlorine concentration, ageing time and whether the pipes failed (F) or were removed without failure (NF) from the hot water tank at the stated time.

<table>
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<th>Chlorine conc. (mg litre⁻¹)</th>
<th>Time (hours)</th>
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Figure 2 Plot of Log₁₀ (hoop stress) versus Log₁₀ (time to failure) for the MDPE pipes which failed when internally pressurized with chlorinated water at 80°C for the following concentrations in mg litre⁻¹: 500 (●), 1000(○), 3000(▲), 5000(□), 10000(●), 15000(△), 30000(■), 45000(●), 120000(X). A reference line is shown for ductile and brittle failures at 80°C when the pressurized water inside the pipe is not chlorinated.

Figure 3 Plot of chlorine concentration versus Log₁₀(time to failure) for the MDPE pipes which failed when internally pressurized (hoop stress of 4.6 MN m⁻²) with chlorinated water at 80°C for the following concentrations in mg litre⁻¹: 500(●), 1000(○), 5000(□), 10000(●), 15000(△), 30000(■), 45000(●), 120000(X).
stress and elongation to failure data. For those pipes subjected to hot chlorinated water and a hoop stress of 4.6 MN m⁻², Figure 4(a) is a plot of the yield stress of the aged pipe material versus time to failure. Each plot point is coded using a different symbol for each chlorine concentration. Before exposure, the yield stress of the MDPE is just above 20 MN m⁻². For high chlorine concentrations, greater than 15000 mg litre⁻¹, the time to failure of the pipe is less than 1000 hours but the yield stress of the aged specimen is little affected. However, for chlorine concentrations of 5000 mg litre⁻¹ or less, the time to failure is longer and there is a marked reduction in the yield stress of the aged specimen. Figure 4(b) shows the related effect on the elongation to failure, measured for the specimens aged by exposure to hot chlorinated water. Figure 4(c) shows the molecular mass \( M_w \), measured using GPC, for the aged specimens plotted against time to failure. This reveals that \( M_w \) reduces with the longer exposure time to the hot chlorinated water. The reduction in \( M_w \) by chain scission would occur mostly in the amorphous material and relates to the concentration of chlorine, oxygen and the level of stress in the working pipe. In the following, an explanation is provided for the initial slow rate of change of the material properties with ageing shown in Figure 4.

Figure 5 shows two examples of OIT (oxidation induction times) profiles, which were obtained for aged pipes that failed in a relatively short time. Figure 5(a) relates to a pressurized pipe, with a hoop stress of 4.6 MN m⁻² and aged with a chlorine concentration of 120000 mg litre⁻¹, which failed after 216 hours (sample number 25). Figure 5(b) relates to a pressurized pipe, with a hoop stress of 4.6 MN m⁻² and aged with a chlorine concentration of 15000 mg litre⁻¹, which failed after 552 hours (sample number 28). In both plots, the vertical shaded region shows the extent of the penetration of the chlorine as measured by the EDAX. The upper dotted line relates to the antioxidant level prior to ageing of the pipe and the lower solid line shows the antioxidant profile after ageing. 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.

For comparison, Figure 6 shows two examples of OIT profiles for aged pipe samples that failed after longer times. Figure 6(a) relates to a pressurized pipe, with a hoop stress of 4.6 MN m⁻² and aged with a chlorine concentration of 5000 mg litre⁻¹, which failed after 1176 hours (sample number 16). Figure 6(b) relates to a pressurized pipe, with a hoop stress of 4.6 MN m⁻² and aged with a chlorine concentration of 1000 mg/litre⁻¹, which failed after 3432 hours (sample number 15). For both cases, the consumption of
antioxidant is much more marked. In particular, Figure 6(b) 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 shows 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 Figures 5 and 6 which show 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 as shown in Figures 5 and 6. This is for all the pipe failures at a hoop stress of 4.6 MN m^{-2} for chlorine concentrations varying from 120000 to 500 mg litre^{-1}. Figure 7 shows a plot of depth of penetration into MDPE by the chlorine versus exposure time for this failure data. The results show that the depth of penetration (s) into the MDPE by the chlorine followed a relationship of the form:

\[ s \propto \sqrt{Dt} \]  

(1)

where the diffusion coefficient, D, varies with hoop stress but was ~0.003 for a depth, s, in mm and time of exposure, t, in hours. There was not a strong dependence of chlorine concentration on the depth of penetration. However, the depletion of antioxidant behind the chlorine front was very much greater for higher chlorine concentrations.

Using optical aids, small axial cracks (less than 1 mm in length) can be seen on the inner surface of pipes
Figure 7 Chlorine penetration from inner wall of pipe versus time to failure for aged MDPE pipes at a hoop stress of 4.6 MN m⁻² with chlorinated water at 80°C for concentrations in mg litre⁻¹: 500 (●), 1000(◊), 5000(△), 15000(Δ), 30000(■), 45000(○), 120000(X).

Figure 8 Electron micro-graph showing axial cracks in the embrittled inner surface of an MDPE pipe that had been subjected to pressurized chlorinated water at 80°C. From left-hand edge to right-hand edge of image is 3.5 mm

Figure 9 Electron micro-graph of a slow crack growth fracture surface through the MDPE pipe wall. Top of main picture (A) relates to the inner pipe surface from which a thumb-nail shaped crack has grown. Higher magnification pictures (B and C) show close-up detail of the initiation site for the slow crack growth. The two other pictures (D and E) show close up detail of changing fracture surface texture. From top edge to bottom edge of main picture (A) is 6 mm.
that had been subjected to ageing experiments using hot chlorinated water at 80°C. Figure 8 is an electron micrograph showing the axial cracks in the embrittled inner surface of an aged pipe that had been exposed to pressurized hot chlorinated water. These small cracks in the MDPE pipe provide many sites from which a slow crack can grow. Figure 9 shows an electron micrograph of a slow crack growth fracture surface through the thickness of the pipe wall. The top of the micro-graph relates to the inner pipe surface from which a thumb-nail shaped slow crack has grown.

4. MODELLING

The 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\(^5\) 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\(^5\) 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 the following study, the Studsvik AB model\(^5\) was used together with a model for the diffusion of chlorine into MDPE. In this case, there was water at both the free surfaces so that the gradient of the diffusion coefficient, if it existed, would be small. Also, in this case, as the chlorine diffused into the MDPE pipe it would dominate the loss of antioxidant from the material. This joint 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 eight 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:

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

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

where \(C_A(r,t)\) and \(C_{Cl}(r,t)\) are concentrations, \(D_A(r)\) and \(D_{Cl}(r)\) are diffusion coefficients and \(R_A(r,t)\) and \(R_{Cl}(r,t)\) are reaction terms for antioxidant (A) and chlorine (Cl) respectively.

The flux boundary conditions controlling the loss of antioxidant at the inner and outer surfaces of the pipe are of the form\(^3\):

\[
D_A \frac{\partial C_A}{\partial r} = \alpha_1 C_A \quad \text{for } r = a \tag{6}
\]

\[
D_A \frac{\partial C_A}{\partial r} = \alpha_2 C_A \quad \text{for } r = b \tag{7}
\]

where \(D_{0,A}, D_{0,Cl}, \lambda_A, \lambda_{Cl}\) are constants, \(b\) is the outer radius and \(a\) is the inner radius of the pipe.

The diffusion coefficients for antioxidant and chlorine, \(D_A(r)\) and \(D_{Cl}(r)\) are of the form\(^5\):

\[
D_A(r) = D_{0,A} \left[ 1 + \lambda_A \frac{b - r}{b - a} \right] \tag{4}
\]

\[
D_{Cl}(r) = D_{0,Cl} \left[ 1 + \lambda_{Cl} \frac{b - r}{b - a} \right] \tag{5}
\]

where \(D_{0,A}, D_{0,Cl}, \lambda_A, \lambda_{Cl}\) are constants, \(b\) is the outer radius and \(a\) is the inner radius of the pipe.

\[
C_A(r,t=0) = C_{0,A} \quad \text{for } a < r < b \tag{8}
\]

\[
C_{Cl}(r=a,t) = C_{0,Cl} \quad \text{for } t > 0 \tag{9}
\]
where $C_{0,A}$ is the initial antioxidant concentration and $C_{0,Cl}$ is the chlorine concentration of the inner surface pipe material.

In this study, the reaction terms, $R_A(r,t)$ and $R_{Cl}(r,t)$, are of the form:

$$R_A(r,t) = k_{A,Cl}C_A(r,t)C_{Cl}(r,t) + k_A C_A(r,t)$$  \hspace{1cm} (10)

$$R_{Cl}(r,t) = k_{A,Cl}C_A(r,t)C_{Cl}(r,t)$$  \hspace{1cm} (11)

where $k_{A,Cl}$ is the rate constant for the reaction between chlorine and antioxidant and $k_A$ is the rate constant for consumption of antioxidant by other oxidation processes. For the following simulation, the $k_A$-term is very small so as to make only minor changes in antioxidant concentration compared to the changes in antioxidant concentration produced by reactions between chlorine and antioxidant ($k_{A,Cl}$-term) and diffusion processes.

Equations (1) and (2) were solved numerically for the above conditions with parameters ($D_0 A$, $D_0 Cl$, $A$, $D_{0,Cl}$, $A$, $D_{0,Cl}$, $k_{A,Cl}$, $k_A$, $\alpha_1$, $\alpha_2$) selected to achieve data comparable with the experimental results. Figure 10 shows in sequence the eight 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.

5. DISCUSSION

As a preliminary to this research, MDPE pipes that had failed in water distribution networks were examined. Those that had suffered brittle failure had a multitude of very short, fine axial cracks about the failure site. It was possible to simulate this brittle failure process using accelerated life evaluation methods to study the effect of chlorine in the water.

The fine axial brittle cracks were attributed to the changes in the physical properties of the inner surface of the pipe material and these included a reduction of yield stress, elongation to failure and molecular mass. Overall, the changes lead to an embrittlement of the inner surface of the material, resulting in stress increases on the inner surface, producing craze-like axial cracks. These brittle failure processes, produced in the accelerated life evaluations, started at weak points generated in the inner surface that had been produced by more concentrated embrittlement attack. Mostly, the concentrated attack was at inherent weak points on the inner surface of the material where small conglomeration of catalyst residue and pigment had gathered during the manufacturing process. This is in the amorphous material where chain scission and other degradation processes occur.

Studsvik Material AB1-3 showed that pressurized, unchlorinated water at 80°C, removed antioxidant from the inner surface of pipes more rapidly than air at the outer pipe surface. For the study of the effect of chlorine in the water, the findings by Studsvik AB are used as a reference (Figure 2). Several effects of chlorine were found that increased the deterioration of polyethylene water pipes. One was chlorine’s ability to penetrate polyethylene in the amorphous regions that resulted in the depletion of the antioxidant. A related effect was the diffusion of the antioxidants towards the depletion zone produced by the advancing chlorine, notably increased. The result was that ahead of the advancing chlorine front, the antioxidant loss in the bulk of the polyethylene was increased, and dramatically so by the time the chlorine front had reached a third of the way through the pipe wall (Figures 5 and 6). This chlorine effect was small for low chlorine concentrations but then rapidly increased for higher chlorine concentrations, as indicated by the marked reduction of time to brittle failure of the inner surface material (Figure 3). The data shown in Figure 3 is for one hoop stress level but it can be seen from Figure 2 that hoop stress (water pressure) has an effect. This is partially due to the increase in the rate of penetration of chlorine (and oxygen) into the wall of the pipe at the higher stress levels. Also, the higher stressing of the inner wall advanced the generation of fine axial cracks and the development of the final brittle failure.

For pipes in pressurized water distribution systems, a sufficient thickness of pipe is used to minimize the risk of early ductile failures and therefore, brittle failures have the main life-determining effect. This is if the installed pipes are not subjected to damage by
Figure 10  Eight recorded concentration profiles from the model simulation obtained by numerical solution of coupled Equations (1) and (2). Normalised antioxidant concentration ($C_A/C_{0,A}$ - symbol ◦) and normalised chlorine concentration ($C_{Cl}/C_{0,Cl}$ - symbol Δ) are shown across the thickness of the pipe wall (from $r = a$ to $r = b$ for a pipe of diameter 90 mm and SDR 11).
The Effects of Chlorine Depletion of Antioxidants in Polyethylene

excessive water hammering or by earth movements, naturally occurring and man-made. When water pipes are buried under busy streets of roads and towns along with many other services, the risk of damaging disturbance can be high. The findings of this study relate to brittle failures of water pipes that have not been damaged by natural or man-made disturbances.

The onset of brittle failure starts on the inner wall of the pressurized water pipe and it is the degradation of the first 2 mm of the inner wall that is of most interest. All the studies of physical properties of the pipe materials used in this research relate to the first 2 mm of the inner pipe wall. It is the inherent weak points in the first 2 mm of the inner pipe wall that are likely to be the initiation sites of brittle failures. All 2 mm thick test specimens were obtained from the inner wall of pipes and shaped to conform with BS 2782 Method 320A (1976).

Directly relating accelerated life failures to those that occur in working pipes is difficult because of the practical problems of monitoring the deterioration of working pipes. Some water companies, however, have selected installation sites specifically to provide for monitoring degradations and other network failures. This includes joints, valves and other components used in the network. These installation sites are also most useful for assessing components of new design. There remains, however, the point that water pipes are installed in a very wide variety of soil conditions, some of which are subject to industrial contamination. It follows that the actual life of pipes can vary greatly. Also, quoted life predictions can vary considerably depending on whether the average life, minimum life or some other qualification is being used.

Slow crack growth in MDPE follows a relationship of the form:

\[ \frac{da}{dt} = A_c K^n \]  

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

\[ t_p = \frac{1}{A_c (Y\sigma)^n a_{n/2}} \cdot \frac{2}{(n-2)} \left[ \frac{1}{a_{i}^{n/2-1}} - \frac{1}{a_{f}^{n/2-1}} \right] \]  

where \( a_{i} \) is the initial crack length and \( a_{f} \) is the final crack length (wall thickness). Equation (13) shows \( t_p \sim \sigma^{-n} \) and \( \log_{10}(\sigma) \sim -(1/n) \log_{10}(t_p) \). For MDPE, \( A_c \sim 10^{-7} \) and \( n = 4 \) (see Ref. 8) for \( da/\)dt in m s\(^{-1} \) and \( K \) in MN m\(^{-3/2} \) giving a slope of \( \sim 0.25 \) for the brittle failure line as observed in Figure 2. For chlorinated or other water pressurized pipes, equation (13) can also be used to predict the initial defect size. This is when slow crack growth determines the time to failure.

To illustrate this effect, the following determines the size of defect, from equation (13), for different levels of chlorination of water at 80\(^{\circ} \)C:

- Using the reference line (unchlorinated water) in Figure 2, the time to brittle failure would be 23000 hours for a hoop stress in the pipe wall of 4.6 MN m\(^{-2} \). For this brittle failure, Equation (13) gives an initial defect size close to 20 \( \mu m \). Particulate matter (catalyst residue or colouring agents) can result in faults of 20 \( \mu m \) in size on or near the inner surface of the pipe.
- Using the dotted line (chlorinated water of 5000 mg litre\(^{-1} \)) in Figure 2, the time to brittle failure would be 1176 hours for a hoop stress in the pipe wall of 4.6 MN m\(^{-2} \). For this brittle failure, Equation (13) gives an initial defect size of 340 \( \mu m \). This explains the much shorter time to brittle failure due to the presence of chlorine.

The 340 \( \mu m \) defect, for the start of the slow crack growth process, could result from the embrittlement of the pipe’s inner surface as the chlorine deprives this surface of its antioxidant and oxidation of the polymer molecules occurs. It can be seen from Equation (1), as measured by EDAX studies, that after only 100 hours, the chlorine front would be expected to have penetrated about 0.5 mm into the pipe wall producing embrittlement and thus providing for the formation of defects up to this size. It is to be noted, however, that the higher the chlorine concentration the greater will be the tendency for environmental stress cracking to be a significant part of the failure process.

With the study of degradation of in-service polyethylene distribution pipes, there are many environmental and other factors that can determine their end-of-life failure. For laboratory experimental studies, the degradation processes in polyethylene pipe material can be related to well-defined conditions and specific ageing processes. A difficulty with
laboratory studies is to monitor the stage by stage effect of different deterioration processes. This is, for example, the diffusion of chlorine, from chlorinated water, into the pipe material and the related loss of antioxidant with the increasing presence of chlorine. To obtain these data, destructive measurement methods are needed, so many repeated experiments for different degradation times are required. Care is needed in bringing together these fragmented studies to obtain a full life cycle of degradation processes. A great help is a model able to simulate full life cycle degradation processes that can also provide these data at frequent degradation intervals. The model was devised to simulate the effects of chlorine, from chlorinated water, on MDPE pipe material. This relates to the reduction and changing distribution of the antioxidants in the material to the diffusion of chlorine into the material via the pipe’s inner surface. The simulation included unchlorinated water at the outer surface of the pipe so that the effect of chlorinated water could be compared with that of unchlorinated water. The results from the model showed that after an early stage when there was an enhanced diffusion of antioxidants into the chlorinated water together with reaction loss of antioxidants in the chlorinated zone of the MDPE, the reaction loss then became the dominant effect of the chlorine. The stronger the concentration of the chlorine, then, the more quickly the reaction loss of antioxidants being dominated by chlorine reaction processes will occur. This modelling data relates well to Figure 3, showing the effect of increased chlorine concentration in the water inside MDPE pipes. It is to be noted that failures often start in the first 2 mm of the inner wall of a pipe material and the onset of these failures can be evident in the early life cycle of a pipe and this can affect the results of experimental studies. In the case of the modelling, the onset of failure and the effect this could have on the loss of antioxidants from the first 2 mm of the inner wall are not considered in this paper.

6. CONCLUSIONS

In this short paper, it was not possible to include details of all the related studies on the effects of pressurised, chlorinated water in water treatment plants and distribution networks. The research presented does, however, report on a number of the main study objectives. Below are some key findings and observations:

- It was found that the lifetime of an MDPE pipe could largely be determined by the formation of a brittle layer on the inner pipe wall. The presence of chlorine in the water accelerates this embrittlement process. This is due to oxidation, accelerated by chlorine diffusing through the wall and consuming the antioxidant. This results in cracks and other flaws being produced in the embrittled inner wall from which slow cracks can grow. This embrittlement, related to the penetration of chlorine, varies from very severe in pipes employed in water treatment plants to very much less severe in water distribution pipes.

- For polyethylene pipes, used in water treatment plants, where the chlorine concentration can be as high as 3000 mg litre
  - 1, the life of these pipes is expected to be less than 10 years.

- It has been demonstrated that high levels of chlorine in water can much greatly the expected lifetime of 50 years of polyethylene pipes but the effects of low levels of residual chlorine in water, leaving the treatment plants, are small. However, the spread of end-of-life of working pipes in the distribution network is likely to be considerable for several reasons.

- Earlier failures (below 50 years) are to be expected if the water distribution pipes are subjected to water hammer and other pressure transients which can occur near booster pumps, operating valves and other control equipment.

- Extended life (above 50 years) can be expected from water distribution pipes that are not disturbed and are located in well-drained soil not containing, for example, aggressive industrial chemicals.

- Not to be overlooked is that pipes may need replacement due to damage from natural ground movements and third party activities.

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.

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