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Oxidative Degradation of High Density Polyethylene Pipes from Exposure to Drinking Water Disinfectants

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EXECUTIVE SUMMARY

Since 2006, a number of peer reviewed studies have linked earlier observed polyethylene oxidation research to field failures of HDPE pipes in water disinfectant environments. Of particular interest are reports of premature polyethylene pipe failure in the presence of common chlorinated water disinfectants such as chlorine (hypo-chlorite), chlorine dioxide and chloramines. Studies in France by major water utilities (i.e. Suez Environnement and Veolia Environnement) have linked factors such as type of disinfectant, average service temperature, disinfectant concentration and pressure to HDPE pipe oxidation and failure. With a growing number of European studies documenting premature aging of HDPE of all types, the researchers of this study reviewed significant public work on the subject including laboratory and exhumed HDPE pipe studies from Europe and the US (Section I of this study) prior to completing a thorough forensic analysis of HDPE pipe from US water utilities (Section II of this study).

Findings from the literature review:

1) The finite supply of anti-oxidants (AO) included in the HDPE pipe formulation are consumed on the inner pipe surface both by being washed off that surface by flowing water and by chemical reaction with a continuous supply of oxidant in the form of water disinfectants continually flowing through the pipe. Additional AO in the bulk of the pipe wall is consumed as it migrates from the pipe core to the areas of reaction on the inner surfaces.

2) When the protective AO package is exhausted or depleted, the water disinfectant oxidants degrade the polymer at the pipe inner surface. This degradation is characterized by a reduced molecular weight and diminished mechanical properties of the polymer at that surface.

3) When degradation of the inner surface material is severe enough, the embrittled surface layer develops cracks which will propagate through the pipe wall, driven by internal pressure and other sources of pipe wall stress. The result of this process will be Stage III non-ductile failure of the HDPE pipe.

The oxidative embrittlement of HDPE pipe through exposure to water disinfectants is significant in that crack initiation in non-degraded pipe (non-chemical processes) may account for up to

90% of the total lifetime of a pipe. Therefore, overall HDPE service life could be dramatically reduced by inner pipe wall surface oxidation.

Fifty eight service-aged HDPE pipe samples were acquired from 13 utilities across the United States. These included an actual failure (leak) site in 23 cases. The samples were subjected to a variety of analytical techniques commonly used to assess oxidation in polyolefin piping (polybutylene, polyethylene and polypropylene). The techniques included:

1) Bend Back Tests – per *AWWA C906-07* – an optical examination of the inner surface to determine crazing or cracking that would be a sign of embrittlement. (57 samples)

2) Fourier Transform Infrared Spectroscopy (FTIR) – two FTIR techniques were utilized to measure the degree of oxidation on pipe samples. Carbonyl Index measurements were taken to assess the extent of polyethylene oxidation at various depths from the inner surface. (30 samples)

3) Oxidative Induction Time (OIT) – samples were subjected to OIT measurements per *ASTM D3895* to determine the amount of anti-oxidant remaining in the pipe samples after potable water service. Core and inner wall measurements were taken. (30 samples)

4) Ring Tensile Tests – a modified NOL-Ring Tensile Test was conducted on samples based on *ASTM D2290*. Elongation to break was measured to determine decreases that would indicate embrittled surfaces or degraded mechanical properties. (7 samples)

Significant oxidation was consistently found:

a) **Bend Back Tests** – 94.7% failure in samples tested.

b) **FTIR** – between 60%-73% of the samples exhibited carbonyl index measurements that indicate extreme or very high levels of oxidation.

c) **OIT** –OIT minutes (anti-oxidant content) from the pipe core were diminished by over 85% in 73.3% of the samples tested and by greater than 90% in 56.6% of the samples tested.

d) **Ring Tensile Tests** – Several field pipe samples did exhibit an apparent reduction in elongation and many of the samples exhibited a large scatter in the elongation values. Modified NOL Ring tests show reduced elongations of between 32% and 91% of the "virgin values".

The study illustrates that premature aging of pressurized HDPE pipe in the presence of water disinfectants needs to be addressed. Currently, no industry guidance is available for designers and owners who wish to incorporate design factors to account for varying service conditions such as service temperature, disinfectant type, disinfectant concentration, pressure, or resin grade. This study indicates that while the science of polyethylene oxidation is well understood and HDPE oxidation is observed in the field, more work is required to further the water industry's understanding of how service conditions exactly affect HDPE pipe service lifetimes in order for designers and owners to accurately forecast service life and set design factors for their specific service conditions.

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Impact of Polyethylene Pipe Oxidative Degradation on Pipeline Performance: A Literature Review – Section I

INTRODUCTION

Since its introduction in the 1950's, high density polyethylene (HDPE) pipe has been utilized in applications for the transport of water, either in the form of potable (drinking) water or in dilute aqueous solutions such as sewage or aqueous solutions in industrial processes. It was determined early on that establishment of a pressure rating and an estimate of expected service life for plastic pipes subjected to long term pressurization and in-ground burial was not a simple matter. The mechanical properties, such as strength and modulus, and physical characteristics like outside diameter and roundness when buried in the ground, are dependent upon the length of time that the pipe is under stress or deformation. As an example, creep is the time dependent deformation of an object under stress. Products manufactured from plastics exhibit creep under constant loads. An HDPE pipe at an applied stress of 800 psi, will creep after its initial deformation to the extent that the modulus of elasticity (equal to the applied stress divided by the total strain – "stiffness") will decrease from an initial value in the range of of 125,000 to 150,000 psi to a value of 55,000 psi in one hour at that level of stress [1].

The time dependent nature of the properties of polyethylene made it necessary to develop methods of material characterization that would account for these changes in properties. Experimental determination of the time dependent strength characteristics of the HDPE resin compounds from which pipes were going to be made were carried out over the years [2-8]. The results of such tests, when plotted as logarithm of stress versus logarithm of time to failure, clearly show the time dependent nature of the long term strength of polyethylene (see Figure 1).

Traditional laboratory testing of these time dependent strength properties created pipe failures exhibiting two different failure modes (see Figure 2). One mode, which occurred in relatively high stress, short time tests, had ductile pipe rupture occurring with ballooning of the pipe specimen and yielding of the HDPE material in the failure area [4]. This failure mode has become known as Stage I failure [9]. The second mode, which occurred at lower stresses and longer test times, exhibited very non-ductile, slit and pinhole failures [4]. This failure mode has become known as Stage II failure [9]. Note in the figure that the plot of Stage II failures on log(stress) vs. log(time) axes has a steeper slope than the plot of Stage I failures.

Protocols for this type of testing were developed many years ago and while the data analysis methods differ depending upon whether one is in Europe or North America, the end result, the allowable long term (i.e. for 50 years of service) level of stress in the pipe wall, is essentially the same [10–12]. However, these long term “strength” values of HDPE pipe materials are determined on pipes with no chemical or oxidative degradation associated with them.

OXIDATIVE DEGRADATION OF HDPE

It has long been known that HDPE materials are susceptible to oxidative degradation in certain environments. Wholesale oxidative degradation of HDPE leads to a reduction in the molecular weight of the polymer with a consequent loss of mechanical properties [13 - 15]. Oxidized HDPE material eventually can become so degraded that it will respond to an applied stress in a very brittle fashion with an elongation to break of only a few percent - as opposed to “new” HDPE pipe material in its normal form where the elongation to break can be from 600 – 1000%.

Technical publications have documented that oxidative degradation of polyethylene pipe can lead to premature failure of the pipe [16 – 20] and that HDPE pipe used in the transport of water or aqueous solutions is susceptible to oxidative degradation in that environment [21 – 26]. The steps that are normally taken to prevent oxidative degradation from occurring in HDPE materials include adding various chemical stabilizers, antioxidants (AO's) of various types, to the HDPE resin [27 - 33]. In this manner, a more oxidation resistant HDPE pipe compound is created through the combination of the base HDPE resin with an assortment of antioxidants and other additives. A typical HDPE pipe compound includes the base HDPE resin, carbon black added at 2 – 3 weight percent to protect the material against oxidative degradation from exposure to UV radiation, processing stabilizers (antioxidants to prevent oxidation during pipe extrusion at 350^{o} – 400^{o}F) and other antioxidants intended to provide protection against oxidation caused by long-term exposure to water containing dissolved air (oxygen) and other oxidative agents such as water disinfectants.

This process has proven to be successful in keeping premature oxidation from occurring. However, these antioxidants are consumed or “sacrificed” by a variety of processes. The chemical reactions that occur to inhibit oxidation alter the chemical structures of the antioxidants and eventually render them ineffective [23, 34 – 35]. In addition, the additives will migrate from throughout the HDPE pipe wall to the surfaces where oxygen or free radicals are most plentiful and oxidation will initially occur. This is a desirable characteristic of the antioxidants but if the pipe is conveying flowing water, some of the antioxidants at the surfaces will be washed away without ever reacting [36 – 49]. The antioxidants in the HDPE material are depleted by both of these mechanisms¸ until there is insufficient AO left to prevent oxidation of the pipe material [23, 41]. At this point the HDPE material at the surface in contact with the water begins to degrade and eventually deterioration of the polymer surface reaches the level at which fracture initiation will occur at stress levels that exist even in appropriately installed HDPE pressure pipe.

The polyethylene pipe industry has recognized for many years that oxidation-controlled failure of HDPE pipe does occur. The impact of this is depicted on the schematic creep-rupture curve in Figure 2. The two stages of mechanical failure manifested in pipe testing results as depicted in Figure 1 (Stage I and Stage II) are now joined by a third stage of oxidation-controlled failure (Stage III). Note that the line representing Stage III failure is very steep, indicating that once oxidation of the pipe material becomes the rate controlling step in pipe failure the level of stress in the pipe becomes much less of a factor in failure time – and pipe end-of-life occurs relatively quickly.

A rather severe example of the adverse effect that oxidative degradation can have on the performance of polyethylene piping is the experience with Celanese-Yardley water service pipe [21]. The Celanese Corporation was a manufacturer of polyethylene resin in the 1960's and 1970's. Celanese produced a pipe grade HDPE resin that had an unusually high molecular weight, called an ultrahigh molecular weight polyethylene (UHMWPE). High molecular weight is a necessary characteristic of HDPE pipe resins, because such resins possess much improved resistance to brittle fracture. Celanese owned a pipe extrusion company called Yardley which produced water service pipe from Celanese's UHMWPE polyethylene resin compound.

For certain commercial reasons, the Celanese UHMWPE resin was not compounded with antioxidants. Due to the very high molecular weight of the base resin, pipe produced from this resin had to be extruded at much higher temperatures than pipe from other HDPE resins. The net effect of the use of an unstabilized resin extruded at higher-than-normal temperatures was that the Yardley pipe became severely oxidized after only a few years in service. The Yardley water service lines became so severely degraded that lengths removed from service could be snapped like dry twigs when bent.

FAILURE MODE – SURFACE EMBRITTLEMENT

In the case of oxidatively induced pipe failure, it is not necessary for all of the material in the pipe wall to degrade, as was experienced with the Celanese-Yardley pipe. Previous work has shown that the long term performance of an HDPE pipe could be compromised when only a thin, 1 – 2 mil deep layer of material at the inner surface of the pipe had become sufficiently degraded [16, 17, 19, 20, 50]. Once a certain level of degradation of the inner surface material had occurred, fracture would commence in that brittle surface layer and the crack would subsequently grow through the entire pipe wall in fairly short order. It has been demonstrated that, in the earlier generations of HDPE pipe materials, the crack incubation time, that is the time for time-dependent viscoelastic processes (non-chemical) to initiate a crack in a non-degraded HDPE pipe, accounted for a significant portion (as much as 90%) of the total lifetime of the pipe [51, 52]. Surface embrittlement greatly reduces the crack incubation time by degrading the material at the pipe's inner surface and shortening the time necessary for a crack to start in that surface layer. Once the crack is formed in the degraded layer, crack growth proceeds in the normal manner. The difference between pipe having a degraded surface layer and pipe without degradation is that crack initiation occurs much faster in the degraded brittle surface layer than it does in an un-degraded surface layer. The time for the crack to propagate through the pipe wall remains essentially the same, but the 90% of normal pipe life that would be devoted to crack initiation in an un-degraded pipe is greatly shortened. Thus the overall pipe lifetime is shortened and premature leakage occurs.

ROLE OF TEMPERATURE

One environmental factor that has a significant effect on the performance of HDPE pipe is the pipe operating temperature. The long term strength of HDPE pipe is significantly reduced by elevating the operating temperature. Pressure ratings of HDPE pressure pipe of the type used in water service applications decreases significantly as operating temperatures increase from 23^{o}C (the temperature at which the ratings are established) to 60^{o}C [53, 54]. This de-rating occurs for pipe that is not degraded by oxidant attack. It does not account for the fact that oxidative degradation also occurs more rapidly as temperature rises, increasing reaction kinetics. Service temperature has a major effect upon the long term service life of HDPE pipe; both for the fact that the basic long term stress carrying capability diminishes and also for the fact that oxidation occurs more rapidly as temperature rises.

ANTIOXIDANT DEPLETION IN HDPE PIPE COMPOUNDS

In order for oxidation to occur in an HDPE material that has been compounded with appropriate antioxidants, the antioxidants must be in some way be deactivated or eliminated. There are multiple mechanisms by which this can occur, leaving the PE material unprotected. The first is that as the antioxidant chemicals perform their "sacrificial" job, they are converted into products that provide reduced and eventually no antioxidant protection. The reaction products are left behind in the HDPE, but they are no longer effective in inhibiting oxidative degradation of the material [23, 34 – 35]. A second is that some of the antioxidants will be washed off of the inside surface of the pipe by flowing water prior to ever performing the desired function [23, 37 – 50]. This second process was not initially recognized and much pipe "accelerated life" testing was performed with stagnant water in the test pipes. This research did not detect the "Stage III" failure mode and therefore painted an incomplete picture of HDPE pipe performance in service with water flowing inside the pipe. However, the impact of the second mechanism can be considerable; it has been stated that antioxidant deactivation from performing its intended function is insignificant compared to loss of antioxidant by migration into the environment inside the pipe [23].

The effect of the loss and/or deactivation of antioxidants in polyethylene water pipe compounds is important, because the greatest part of pipe lifetime in Stage III failures appears to be consumed in eliminating the antioxidant. In accelerated testing performed on pipe produced from an unstabilized PE resin (no antioxidants added), the pipe time-to-failure in the tests was less than 12% of that of pipe made from the same resin compounded with antioxidants [44]. That part of polyethylene water pipe lifetime that is taken up with elimination of the antioxidants is the longest aspect of the pipe's life. The fundamental resistance of the unstabilized PE to oxidative degradation is relatively short.

ANALYTICAL METHODS TO QUANTIFY OXIDATION AND ANTIOXIDANT CONTENT IN HDPE

A number of analytical methods have been developed through the years to identify and quantify the presence of oxidative degradation in HDPE pipes. Infrared spectroscopy was utilized as early as the 1950's as a technique by which oxidation could be identified in polyethylene materials [55 – 58]. When it became desirable to examine HDPE pipe for oxidative degradation, a parameter called the "carbonyl index" was created to quantify the extent of degradation [17, 19, 20, 41, 44]. The carbonyl index was defined as the intensity of the infrared absorption peak of a specific carbonyl moiety formed in the oxidation of HDPE material normalized by the intensity of a methylene absorption peak in the same spectrum. It was determined that there was a minimum carbonyl index required in only the first 50 microns or so of the inside surface of a pipe that was needed to embrittle that surface and produce premature failure in the pipe [19, 20]. Infrared spectroscopy continues to be utilized today to assess HDPE pipe materials for the presence of oxidation.

Optical microscopy can be used to make a visual determination of the onset of embrittlement of HDPE pipe surfaces (ASTM D2513). Generally, samples are bent back against the inner radius of a pipe and examined visually for patterns of cracking, crazing or other signs of embrittlement.

A common laboratory method used to determine the level of remaining antioxidant in HDPE samples is the determination of Oxidation Induction Time (OIT) through differential scanning calorimetry (DSC) per methods such as ASTM D3895 or ISO 11357-6. OIT levels are proportional to the concentration of antioxidant present in the polymer. They can be used to assess a polyolefin for the presence of antioxidant but cannot be used to determine long-term stability. Generally, a reduction in OIT values over the life of an HDPE pipe product indicates a consumption or elimination of antioxidant. When the antioxidant is gone, the HDPE material becomes susceptible to oxidative attack.

CURRENT SITUATION

There has been a renewed interest in the last decade in oxidative degradation of polyethylene water pipe and its role as a cause of premature pipe failure [25, 59 – 61, 64 - 67]. This has spawned a major amount of new research the effect of oxidation of polyethylene water pipe on long term performance and in the area of testing of polyethylene pipe for resistance to oxidation in the presence of water disinfectants and hydrostatic stress [59 – 67]. Disinfectants are added to drinking water to kill bacteria and make the water safe for human consumption. However, these disinfectants (e.g. chloramines, hypochlorous acid/hypochlorite salts, and chlorine dioxide) are themselves strong oxidizing agents that can degrade polyethylene. Recent testing has employed three of the most widely used disinfectants; chlorine dioxide, "chlorine" (hypochlorite) and chloramines in the test water conditions. Chlorine dioxide has been shown to be the most aggressive oxidizing agent with respect to polyethylene pipe while chloramines have appeared to be the least aggressive. However, similar effects have been observed in PE pipe carrying water disinfected with any of the three disinfectants. Testing with chlorine dioxide does not appear to introduce different oxidation mechanisms, only to speed up the processes that eventually occur with other disinfectants.

Improvements in catalyst and polymerization technologies in HDPE manufacturing have raised the long term tensile strengths of these materials by several percent. However, we must remember that the long term strength tests required by ASTM D2837 or ISO TR-9080 are performed on pipe specimens with no oxidative exposure or degradation. Even the latest HDPE pipe resins, called PE100's by the polyethylene pipe industry (also known as PE4710's in the US), have their long term performance capabilities reduced when they are tested with an oxidizing environment such as water containing a disinfectant chemical like sodium hypochlorite or chlorine dioxide, inside the pipe. Recent testing to evaluate pipe made from PE100 resin compounds for resistance to oxidation by water containing chlorine disinfectants has demonstrated that the long term performance of these newest HDPE materials is still compromised by oxidative degradation [59, 61].

There has been an effort in the last 10 years or so to create test methods directed at determining the effect that oxidative degradation has on polyethylene pipe lifetime [68 – 70]. These methods utilize standard elevated temperature hydrostatic pressure testing of polyethylene pipe with circulating hot, chlorinated water through the pipe test specimens. While these tests are conceptually sound, they suffer from a couple of problems. First, the tests are performed using hypochlorous acid/sodium hypochlorite as the oxidant. Testing with other disinfectants, e.g. chlorine dioxide or ozone, is not specified. Also, because users of the method do not desire to wait long periods of time for results, the test parameters in F2263 (the test method for non-crosslinked HDPE pipe) are not necessarily chosen to yield oxidation-controlled (Stage III) failures. Perhaps more important than these shortcomings in the test method is that as of yet, only crosslinked polyethylene (PEX) pipe standards like ASTM F876 require that testing be performed by one of these methods (F2023 is used for PEX testing). The requirements imposed on PEX pipe are really directed toward its performance in hot water plumbing systems rather than water distribution, since PEX pipe is not currently used in municipal water systems but only in household plumbing. Testing by these methods is not currently required in any PE pipe standards that apply to water distribution systems (i.e. AWWA C906). There is, therefore, no current requirement for evaluating the resistance of HDPE piping in the types of environments to which water distribution pipes are exposed. While an increasing number of recent research efforts on HDPE pipe failures as well as established science point to the potential for oxidative degradation as a cause for premature failure of HDPE pipes, the pipe industry does not provide appropriate design guidance in this area. Neither AWWA nor ASTM has addressed the issue of oxidative degradation in a manner useful to designers and owners of water pipelines.

The purpose of the current investigation is to assess recently excavated HDPE pipes for levels of oxidative degradation and whether oxidation of the pipe material is a significant contributing factor to recent HDPE water pipe failures. It is not known to what extent HDPE resin suppliers and pipe manufacturers have improved their antioxidant additive packages in order to forestall the onset of oxidative degradation and potentially extend the service life of HDPE water pipes. An assessment of recently excavated pipes, some associated with leaking water service lines and mains, should shed some light on recent (past 20 years) practices in the HDPE pipe industry and their effectiveness in eliminating HDPE oxidation as a potential life-limiting factor in polyethylene water pipe performance.

However, the results to date are identical to those observed in some of the research being carried out in Europe (59, 61). Results on HDPE pipe field failure specimens provided by water utility companies in the United States have yielded results similar to that shown in Photograph 3.

When subjected to a modification of the reverse bend back test of ASTM D2513 (59, 61), the inside surface of these pipes cracks extensively as seen in the photo. Thermal analysis of the inside surface layers reveal essentially no antioxidant left in that layer. Infrared spectroscopy of the first 0.002 inch layer inward from the inside surfaces of these samples confirms that the surface layers are oxidized. Full results of the laboratory examination of these field returns are published in Section II of this study.

It is hoped that this review of the technical literature combined with the field study of exhumed HDPE pipe can provide the water industry with an initial step toward building appropriate design standards that factor in oxidative degradation as a potential failure mode.

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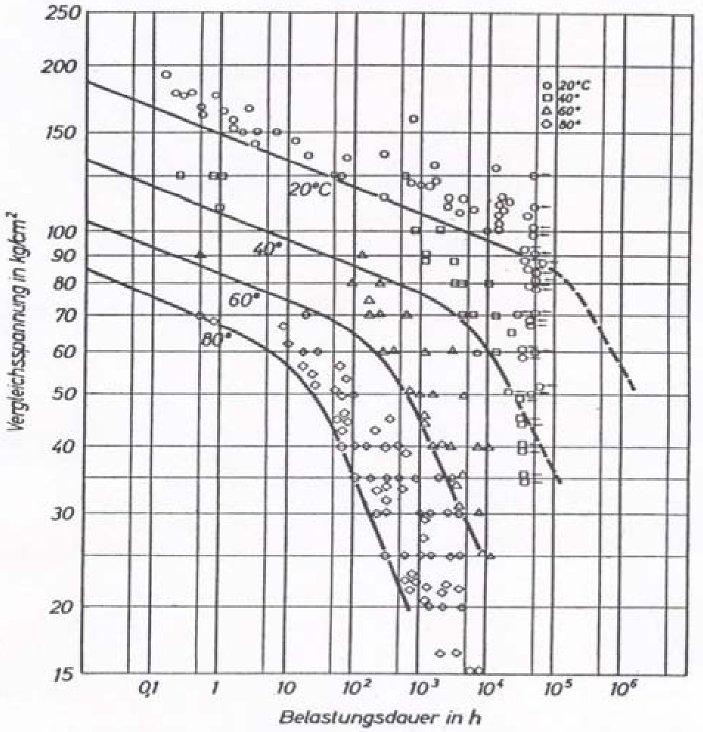


Fig. 6. Creep rupture strength curves (minimum values) of Ziegler polyethylene pipes for 20°, 40°, 60° and 80° C.

Figure 1: Pipe hoop stress vs. time to leak data for HDPE pipe (Ref. 3)

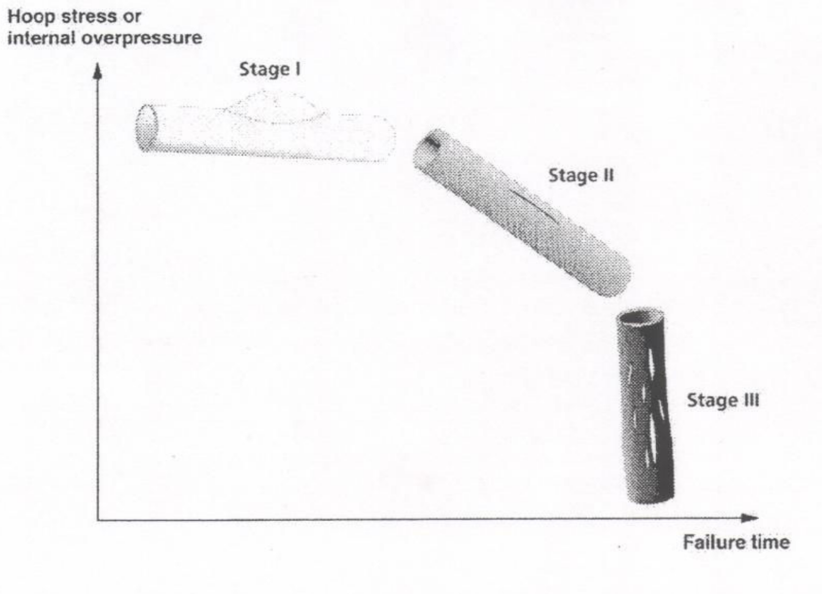
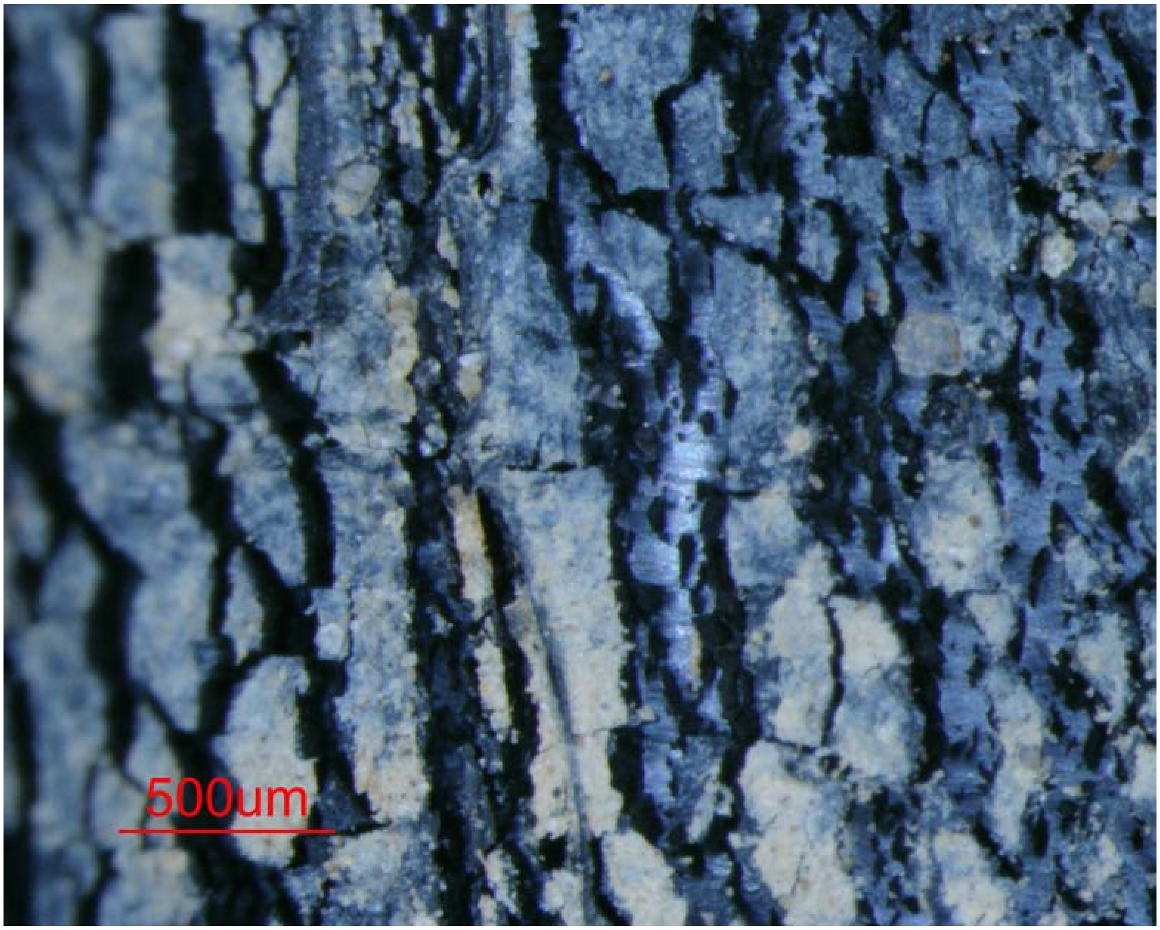


Figure 2: Three stages of creep rupture failure in HDPE pipe.



Photograph 3: Inside surface of in-service leaking HDPE pipe after reverse bend back test.

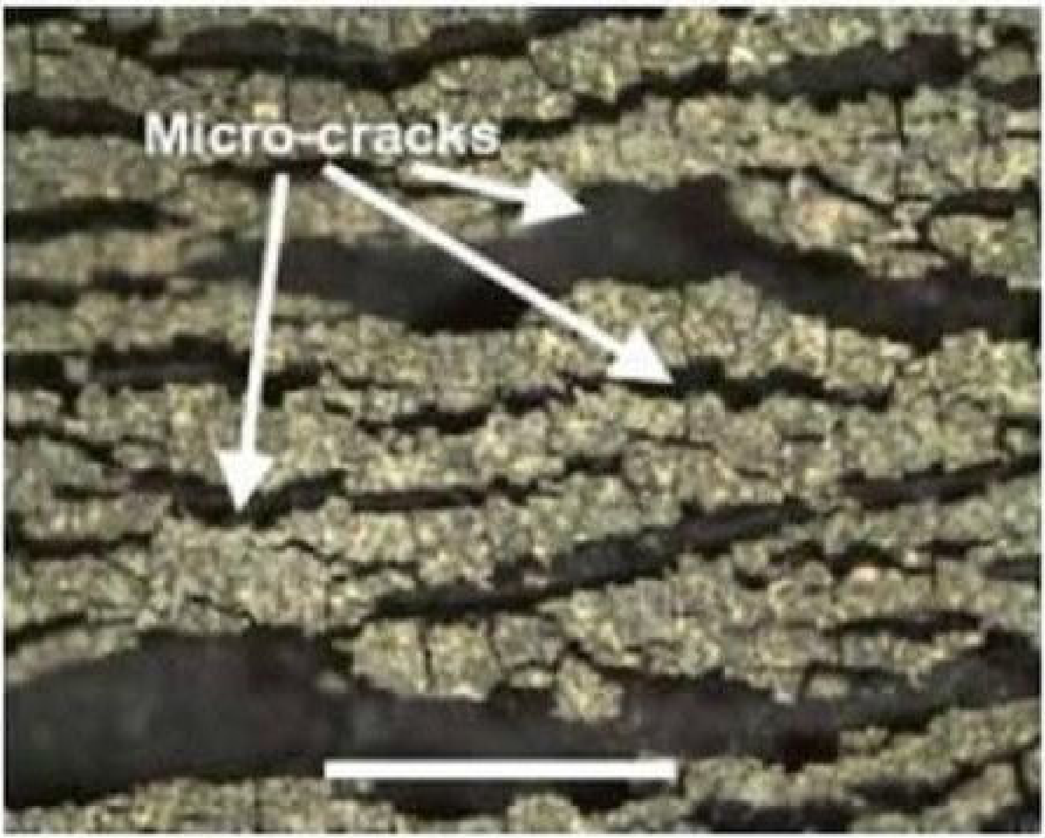


Figure 7: Typical micro-cracking after RBBT

Field sample N°1 (PE32).

Scale: bar = 1mm

Figure 4: Inside surface of field aged HDPE pipe after reverse bend back test from (Ref. 71)

CHARACTERIZATION OF OXIDATIVE DEGRADATION IN POLYETHYLENE PIPES REMOVED FROM WATER SERVICE – SECTION II

INTRODUCTION

Samples of polyethylene water pipe that failed in service were obtained from several water utilities across the United States. Pipes were obtained from many geographical areas and had been in service for various times prior to the failures. The extent of oxidation was characterized for these samples using micro-Fourier Transform Infrared spectroscopy (Micro-FTIR), oxidative induction time (OIT), bend back tests, ring tensile testing and an examination of the failure sites. Fifty-eight pipe samples were obtained from the following thirteen locations:

1. Laughlin, Nevada – 10 samples
2. Maui, Hawaii – 5 samples
3. West Maui Land, Hawaii – 4 samples
4. Lafayette, Louisiana – 1 sample
5. HB & TS Tennessee– 2 samples
6. Pomona, California – 1 sample
7. Visalia, California – 1 sample
8. HDOT in Hawaii – 1 sample
9. Bakersfield, California – 14 samples
10. Hamilton, Ohio – 15 samples
11. Henderson, Nevada – 2 samples
12. Virgin Valley, Nevada – 1 sample
13. Ocoee, Tennessee – 1 sample

Twenty-three of these samples included the failed section.

BACKGROUND

Polyethylene pipe has been used successfully for many decades in a variety of applications. High density polyethylene pipe has been used extensively in the gas distribution market and has also been used in potable water and sewer applications. It has been used to a lesser extent in water distribution, but has been used for over 40 years, mainly for water service lines (potable water lines 3” and less in diameter). Recent publications have brought forth evidence of premature failure of polyethylene water pipes, at least partially due to oxidative attack of the pipe inner surface by disinfecting chemicals that are added to the water. Oxidation of polyolefins exposed to chlorine, chloramine and chlorine dioxide environments has been known for many decades, as noted in other publications [1, 2]. Recently, there have been several utilities that have experienced failures in high density polyethylene pipes that have been in potable water service. While the failure of these pipes can be attributed in many cases to excessive in-service stresses, it is also clear that many of the pipes have been oxidized during service, leading to premature failure. This study characterizes the extent of oxidation in these pipes and its effect on the failure.

BEND BACK TESTS

Bend back tests were performed on the pipe samples per Section 5.7 of AWWA C906-07, *AWWA Standard for Polyethylene (PE) Pressure Pipe and Fittings*. The bend-back test evaluates the inside pipe surface for brittleness. The evaluation is made by observing the inside pipe surface for cracking or crazing under highly strained test conditions. Inside pipe surface brittleness, which may be the result of improper processing or material oxidation, can be detrimental to the long-term performance of the pipe. The presence of this condition in new PE pipe is cause for its rejection for use in water distribution systems. This test also is called out in ASTM D2513, Section A1.5.11.1.

Fifty-seven samples (57) were tested by this procedure and fifty-four (54) of them failed the test (94.7%). These results indicate that the inner surface of the pipes has been embrittled as a result of in-service operating conditions. The service times for these samples ranged from a little over one year to over 30 years. Similar to other recent studies, chlorine dioxide was found to be particularly potent in causing oxidation, as evidenced by the samples from Hamilton, Ohio [3]. These samples were in service the shortest time and yet still showed intense oxidation of the inner surface.

The failures in the bend back test correlated extremely well with the FTIR and DSC-OIT tests described below for a subset of the samples.

FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

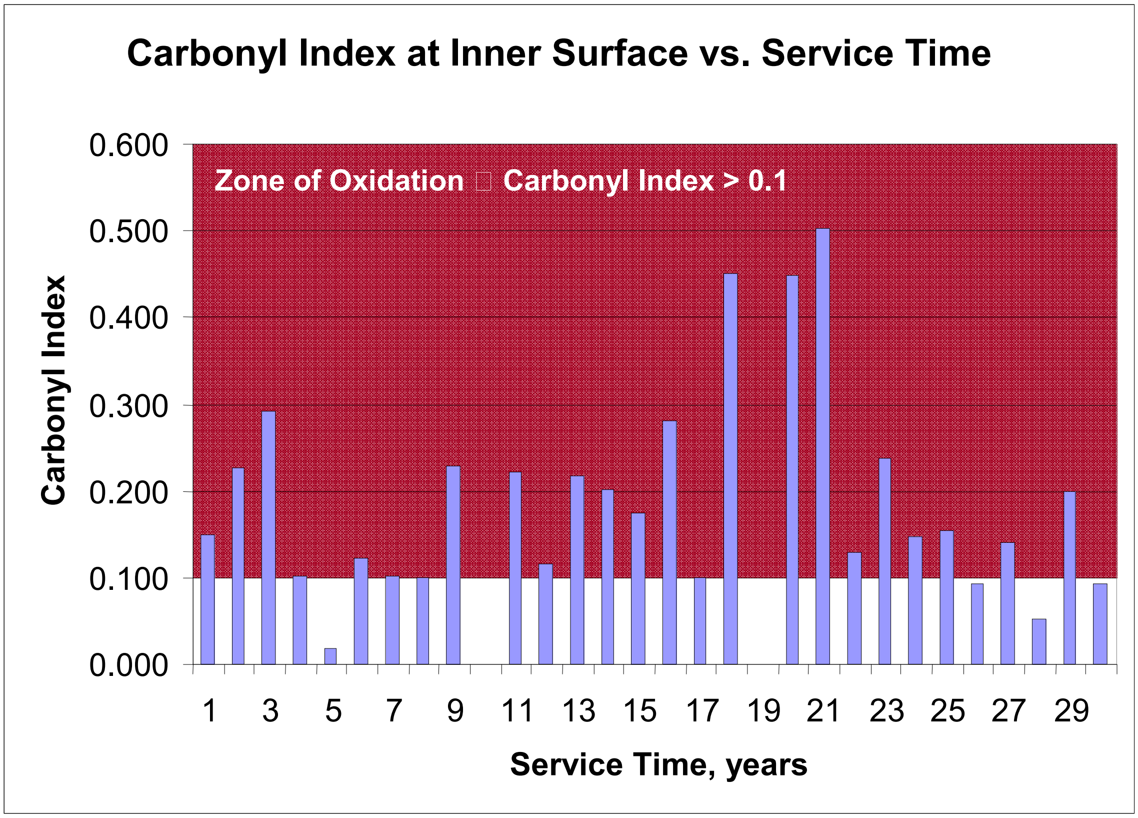
Micro-FTIR spectroscopy and ATR-FTIR spectroscopy were utilized to measure the degree of oxidation on twenty-nine of the HDPE pipe samples. Oxidation of HDPE results in the formation of carbonyl groups onto the HDPE molecules. These groups have characteristic infrared absorption frequencies. Among these groups, the strongest absorption peak is observed at about 1710 to 1720 cm^{-1}. Weaker peaks are seen at about 1735 and 1775 cm^{-1}. The stabilizer compounded into the HDPE has a carbonyl group with a characteristic infrared absorption peak at 1740 cm^{-1}. When oxidation occurs, a ketone carbonyl peak near 1710 cm^{-1} to 1720 cm^{-1} is formed, which progressively increases in intensity as the degree of polymer oxidation increases. The carbonyl index (C.I.) is defined as the ratio of this carbonyl absorbance to that of a polymer absorption band at 1465 cm^{-1}. The use of this ratio compensates for any differences in sample thickness and serves as an internal standard.

In the present study, the C.I. was profiled, using a Perkin Elmer Model Spectrum 100 FTIR instrument, equipped with an FTIR microscope accessory. The Micro-FTIR instrument allows one to focus the infrared beam at a precise location on the sample. The infrared spectra were recorded in two thousandths-of-an inch increments, using a 2 x 12 mil aperture, starting at the inner surface of the pipes.

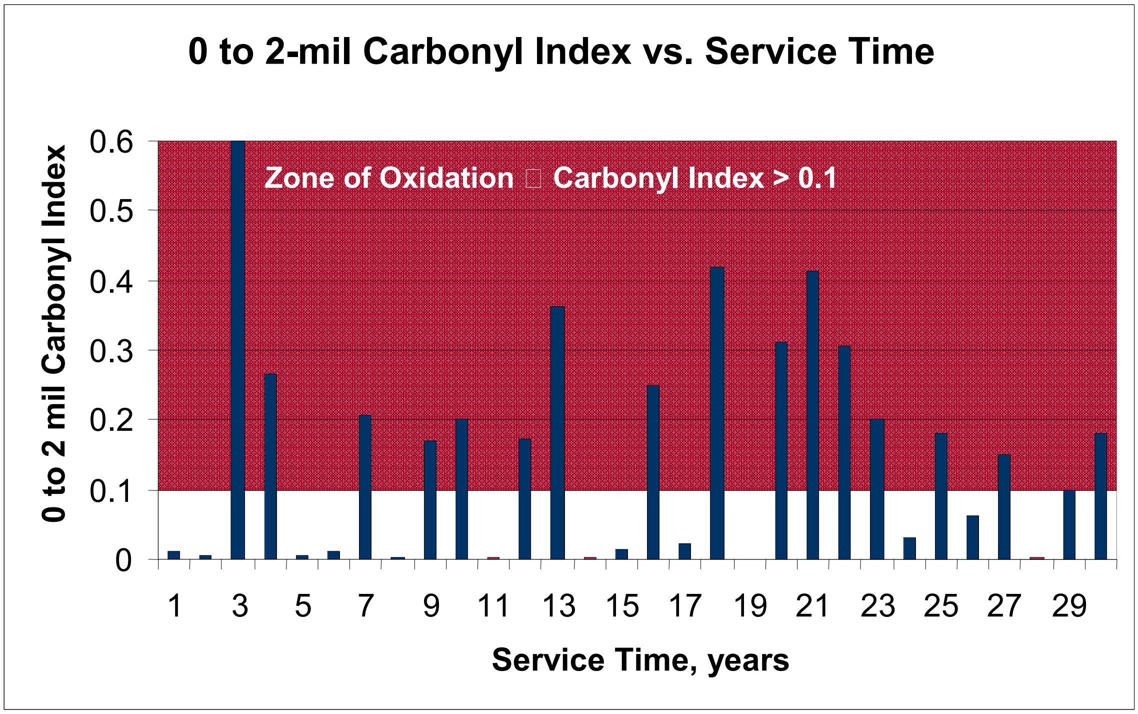
The samples consisted of microtomed cross-sections of the pipe wall, approximately 0.5 to 1 thousandth of an inch thick. The thickness of the microtomed specimens was sufficiently small so that all absorbance measurements were in the detector linear absorption range. In this case spectra were recorded in 2-mil increments from the inner surface until no oxidation was detected. A spectrum of the core was also obtained for each sample.

ATR-FTIR was used to measure the C.I. right at the inner surface of the pipes using a Perkin Elmer Model Spectrum 100 FTIR instrument, equipped with a diamond ATR accessory. The sample is clamped against the diamond crystal and then analyzed. The depth of penetration for this method is very small, on the order of 5 microns, yielding another infrared spectra measurement of oxidation at the inner surface of the pipes.

The results at the inner surface measured by ATR-FTIR show that almost all of the samples have extreme oxidation, with C.I. values greater than 0.1. C.I. values of 0.1 and greater have been shown to correlate with embrittlement of polyethylene materials, leading to premature failures [1, 2]. In past experience in characterizing oxidation of polyolefins, C.I. values less than 0.02 were not considered as significantly oxidized.



The C.I. results for the first two thousandths of an inch of the inner surface also showed extensive oxidation, with 58.6% exhibiting average C.I. values greater than 0.1. Only 5 samples out of 29 exhibited average C.I. values over the first 2 thousandths of an inch that were comparable to that found in the core of the pipe, indicating little or no oxidation (C.I. < 0.010). The profile spectra reflect an average C.I. value over the 2-mil sample. Thus, for those samples having a very high inner surface C.I. and a very low value for the 0 to 2-mil increment, the depth of the oxidized layer was very thin, likely less than 1 thousandth of an inch deep.


0 to 2-mil Carbonyl Index vs. Service Time
Zone of Oxidation □ Carbonyl Index > 0.1
0 to 2 mil Carbonyl Index
0.6
0.5
0.4
0.3
0.2
0.1
0
1
3
5
7
9
11
13
15
17
19
21
23
25
27
29
Service Time, years

Sample	**Service Time, years**	**ATR Carbonyl Index**	**0-2 mil Carbonyl Index**
Virgin Valley Sample	6.00	0.102	0.265
Maui Sample	11.00	0.092	0.182
Makawao 1” Sample 1	13.01	0.116	0.174
Makawao 1.25” Sample 2	13.01	0.217	0.157
Central 1.25” Sample 3	17.07	0.202[1]	0.003
Kula 2” Sample 4	11.02	0.228	0.170
6”Ocoee TN	5.00	0.179	0.006
West Maui Land Sample 1	10.00	0.099	0.002
West Maui Land Sample 2	8.00	0.101	0.207
West Maui Land Sample 3	7.00	0.019	0.007
West Maui Land Sample 4	8.00	0.200[1]	0.100
Lafayette LA Location A	12.00	0.107	0.200
Lafayette LA Location B	12.00	0.087	0.118
HB&TS Driscopipe	25.04	0.503[1]	0.413
HB&TS Yardley	25.04	0.449[1]	0.310
Pomona CA	28.00	0.154	0.182
Laughlin NV 3711 Westcliff	25.2	0.128	0.306
Laughlin NV 1817 Oasis	22.10	0.450	0.420
Laughlin NV 1818 Oasis	22.00	0.280	0.250
Laughlin NV 3332 Colanda	25.50	0.238	0.449
HDOT Dillingham AF	7.00	0.150	0.012
CA Water Visalia 120	3.00	0.053	0.004
Bakersfield CA Sample 5 7708 N. Laurelglen Blvd.	31.03	0.085	0.061
Bakersfield CA Sample 6 12402 Woodson Bridge DR	7.09	0.081	0.012
Bakersfield CA Sample 10 3821 Ranier CT	19.61	0.174	0.014
Bakersfield CA Sample 11 5612 Anise CT	32.64	0.140	0.149
Bakersfield CA Sample 12 9900 Riverrock DR	26.12	0.147	0.032
Hamilton OH 128 Washington ST	5.78	0.291	0.830
Hamilton OH 1027 Tiffen	12.03	0.221	0.003
Henderson NV 354 Templeton	22.14	0.099[1]	0.024

[1] ESI ATR FTIR

Several samples exhibited oxidation to depths from 2 to 4 thousandths of an inch. Ten samples exhibited C.I. values greater than 0.02, five of which were greater than 0.1. Five samples exhibited C.I. values greater than 0.02 at depths from 4 to 6 thousandths of an inch and three samples exhibited oxidation at 6 to 8 thousandths of an inch deep. The deeper C.I. data is shown in the following table:

Sample	**Service Time, years**	2 - 4 mils	4 – 6 mils	6 – 8 mils
Virgin Valley Sample	**6.00**	**0.195**	**0.044**	**0.004**
Maui Sample	**11.00**	**0.073**	**0.009**	**0.002**
Makawao 1” Sample 1	**13.01**	**0.024**	**0.001**	**<0.001**
Makawao 1.25” Sample 2	**13.01**	**0.022**	**0.005**	**NA**
HB&TS Driscopipe	**25.04**	**0.267**	**0.174**	**0.047**
HB&TS Yardley	**25.04**	**0.224**	**0.023**	**0.027**
Laughlin NV 3711 Westcliff	**25.2**	**0.037**	**0.024**	**0.029**
Laughlin NV 3332 Colanda	**25.50**	**>0.200**	**>0.100**	**0.002**
Bakersfield CA Sample 11 5612	**32.64**	**0.149**	**<0.001**	**<0.001**
Bakersfield CA Sample 12 9900	**26.12**	**0.032**	**<0.001**	**<0.001**

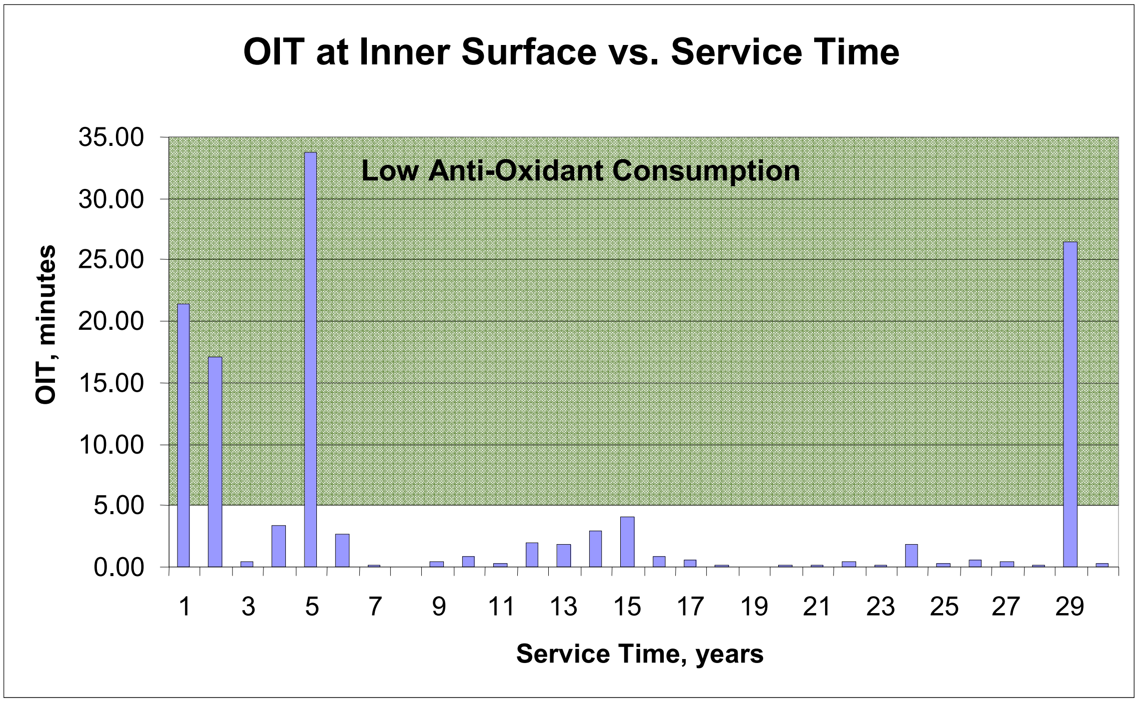
The data above clearly demonstrates that HDPE pipes can and do oxidize in water service when exposed to disinfectants such as chlorine, chloramine and chlorine dioxide. The extent of degradation varies with disinfectant type, with chlorine dioxide being the most aggressive. Higher ground/service temperatures and elevated stress also lead to increased oxidation of the pipes. Most of the pipe failures that have been investigated have been from warmer climates, some where the ground temperature may have been as high as 100 degrees F at times [4]. The oxidation reactions proceed at a much higher rate as the temperature increases. However, the Hamilton, Ohio samples demonstrate that in-service oxidation is not limited to warmer locales.

OXIDATIVE INDUCTION TIME (OIT)

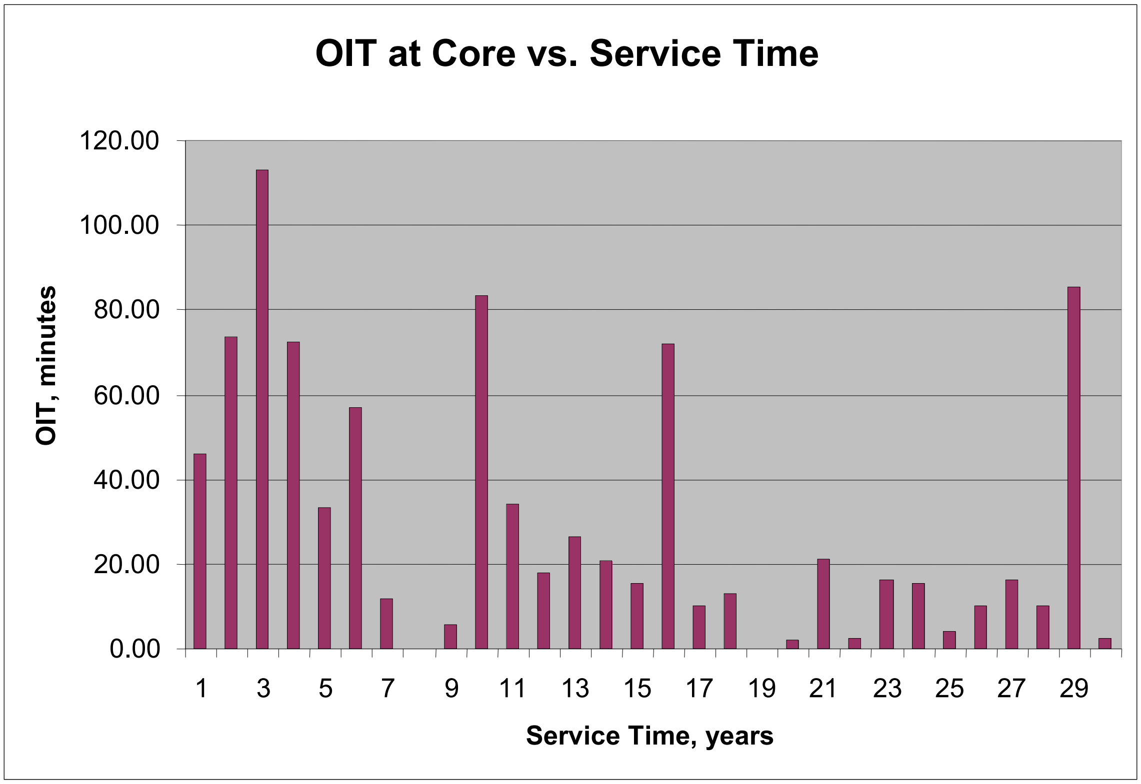
The oxidation induction time (OIT) was measured on thirty of the pipe samples at 200^{o}C per ASTM D3895, *Standard Test Method for Oxidative-Induction Time of Polyolefins by Differential Scanning Calorimetry*. This test is a relative measure of the amount of antioxidant still remaining in the pipe after extrusion and service. OIT was measured at both the inner surface and at the interior core of each pipe sample.

Most of the pipe samples tested exhibited very low OIT values at the inner surface, which correlates well with the FTIR and bend back test results. It is not uncommon for the inner surface OIT value to be low in polyolefin piping that has been exposed to an oxidizing environment for an extended period. The inner pipe wall surface can become oxidized even if there is anti-oxidant left in the core of the pipe since in some cases the reaction proceeds faster than the anti-oxidant can diffuse to the surface from the interior of the pipe.

One of the pipe samples, Sample 6, from Ocoee, TN exhibited a high inner surface OIT (17.06 minutes) while failing the bend back test and exhibiting a high carbonyl index by ATR-FTIR. This particular pipe is a 6-inch pipe with a thicker wall than most of the pipes included in the study. The core OIT is very high (73.6 minutes) and it is evident that the anti-oxidant migrated to the surface after the pipe was removed from service. This pipe exhibited cracking at several locations around the circumference of the pipe inner wall and had failed in service. The fracture surface for this sample is examined below in the Fracture Analysis section.



The core OIT values varied, depending on sample location and time in service. Many of the samples exhibited a dramatic depletion of the anti-oxidant level, even at the core.



The OIT data is shown in the following table:

Sample	Age - Yrs	OIT at I.S., min	% Reduction Core and I.S.	OIT at Core, min
Virgin Valley	6.00	3.37	95.4%	72.5
Initial Maui Sample	11.00	0.30	88.6%	2.63
Makawao 1" Sample 1	13.01	1.93	89.2%	17.79
Makawao 1.25" Sample 2	13.01	1.83	93.1%	26.36
Central 1.25" Sample 3	17.07	2.94	85.8%	20.69
Kula 2" Sample 4	11.02	0.48	91.8%	5.88
6"Ocoee TN	5.00	17.04	76.8%	73.60
West Maui Land Sample 1	10.00	7.8	47.7%	14.9
West Maui Land Sample 2	8.00	0.20	98.3%	11.80
West Maui Land Sample 3	7.00	33.8	-1.8%	33.20
West Maui Land Sample 4	8.00	0.20	98.1%	10.30
Lafayette LA Location A	12.00	0.90	99.2%	108.9
Lafayette LA Location B	12.00	0.8	99.0%	83.5
HB&TS Driscopipe	25.04	0.20	99.1%	21.10
HB&TS Yardley	25.04	0.20	89.5%	1.9
Pomona CA	28.00	0.30	92.7%	4.1
Laughlin NV 3711 Westcliff	25.2	0.40	83.3%	2.4
Laughlin NV 1817 Oasis	22.10	0.10	99.2%	13.2
Laughlin NV 1818 Oasis	22.00	0.80	98.9%	71.9
Laughlin NV 3332 Colanda	25.50	0.20	98.8%	16.1
HDOT Dillingham AF	7.00	21.40	53.6%	46.1
CA Water Visalia 120	3.00	26.40	69.1%	85.3
Bkrsfld CA Sample 5 7708	31.03	0.50	95.0%	10.1
Bkrsfld CA Sample 6 12402	7.09	2.70	95.3%	57.0
Bkrsfld CA Sample 10 3821	19.61	4.00	74.0%	15.4
Bkrsfld CA Sample 11 5612	32.64	0.40	97.5%	16.1
Bkrsfld CA Sample 12 9900	26.12	1.80	88.3%	15.4
Hamilton OH 128 Washington	5.78	0.40	99.6%	113.2
Hamilton OH 1027 Tiffen	12.03	0.30	99.1%	34.0
Henderson NV 354 Templeton	22.14	0.50	95.1%	10.2

RING TENSILE TESTS

Ring tensile tests were performed on several of the samples and tested according to ASTM D2290-04, *Standard Test Method for Apparent Hoop Tensile Strength of Plastic or Reinforced Plastic Pipe by Split Disc Method,* and by a modified NOL-Ring tensile test, as developed by Suez-Environnement Cirsee and Laboratoire National de Metrologie et D'Essai [5]. The modified version of the test is used to compare the elongation at break for samples that have been exposed to oxidative environments with the elongation at break for unexposed samples.

The main difference between the two tests is that the NOL test utilizes a 0.75-inch wide sample versus the 0.5-inch wide sample for ASTM D2290. The NOL test also tracks the elongation at break by assuming an initial gage length of 3 mm (0.125 inches).

The authors of the NOL test reported that unexposed polyethylene pipe specimens exhibit elongation at break values of greater than or equal to 1500 percent. Our testing with both the ASTM D2290 test and the NOL ring test did not show such high elongations for unexposed pipe, but slightly higher elongations were obtained for samples tested per the NOL ring test. Several field pipe samples did exhibit an apparent reduction in elongation and many of the samples exhibited a large scatter in the elongation values. A large variation in elongation at break typically occurs on materials with oxidized surfaces. Tensile strength is not very sensitive to degradation unless the degradation is very severe. Elongation to break measurements can be a good indicator of degradation, showing reductions in elongation as degradation proceeds. A standard tensile test should yield more consistent results than ring tensile tests for this, but the ring tensile is ideally suited for testing pipe samples.

Typical elongations at break for pipe grade polyethylene materials that are tested in standard tensile tests generally range from 500 to 1000 percent. We tested unused polyethylene pipe samples (HDPE and MDPE) using both test methods and obtained elongation at break values of 643 to 874 percent. The test data is shown in the following table:

Sample	Peak Stress, psi	Break Stress, psi	Approximate Elongation at Break, %
PE3408 pipe – ASTM D2290-04	3769	2740	643
PE3408 pipe – NOL Ring Test	3553	2519	874
MDPE pipe – ASTM D2290-04	3091	2109	493
MDPE pipe – NOL Ring Test	2831	1761	649

Seven of the pipe samples were initially tested by the ASTM D2290 method and some of these samples showed lower elongation at break values than for the unexposed samples tested above. Most of the samples exhibited a lot of scatter in the test results as well. A couple of the samples were re-tested per the NOL test protocol; HB & TS, TN Driscopipe and 3711 Westcliff Ave., Laughlin, NV. The data is shown in the following tables:

Sample	Test Method	Peak Stress, psi	Break Stress, psi	Approximate Elongation at Break, %
HB & TS, TN Driscopipe	ASTM D2290-04	3858	2767	617
HB & TS, TN Driscopipe	NOL Ring Test	3667	2806	796
5612 Anise CT, Bakersfield	ASTM D2290-04	3464	2686	709
3821 Ranier CT, Bakersfield	ASTM D2290-04	3787	2838	755
354 Templeton, Henderson, NV	ASTM D2290-04	3619	2210	524
128 Washington, Hamilton, OH	ASTM D2290-04	3567	2271	531
1027 Tiffen, Hamilton, OH	ASTM D2290-04	3844	2393	373
3711 Westcliff Ave., Laughlin, NV	ASTM D2290-04	3655	1960	352
3711 Westcliff Ave., Laughlin, NV	NOL Ring Test	3523	2546	283

FRACTURE SURFACE ANALYSIS

Twenty-three of the pipe samples included the failure location. The fracture surfaces of several of these samples were examined in order to determine the root cause of the failure.

3332 Calanda – from Laughlin, NV

This sample exhibited severe degradation of the inner surface with oxidation penetrating approximately 5 thousandths of an inch into the pipe. The pipe, which had been in service for 20.5 years, exhibits very brittle behavior that is clearly shown in the bend back test and the fracture surfaces. The sample is shown below in Figure 1, as received. The pipe has a longitudinal slit visible on the outer surface, approximately 0.5 inches long as shown in Figure 2.

The pipe was apparently squeezed off near the failure site. This may have occurred after the failure. The pipe has cracks at the leak site and opposite the leak, indicating that the pipe was squeezed, leading to some of the cracking (see Figures 3 through 5). The inner surface of the pipe exhibits “mud cracking”, which is typical of severely oxidized material. The material properties have been degraded to such an extent that stresses in all directions cause the material to crack. The depth of this degraded layer is approximately 5 mils thick, leading to multiple crack initiation sites and subsequent slow crack growth as seen in Figures 6 through 10.

This sample has effectively reached the end of its life due to oxidative degradation. At this level of degradation, normal service stresses would lead to fracture, as happened in this case. The level of oxidation has been documented by FTIR, with C.I. values exceeding 0.1 through 5 mils, OIT values near zero at the inner surface and substantial reduction of anti-oxidant in the core.

Figure 1. 3332 Calanda sample, as received.

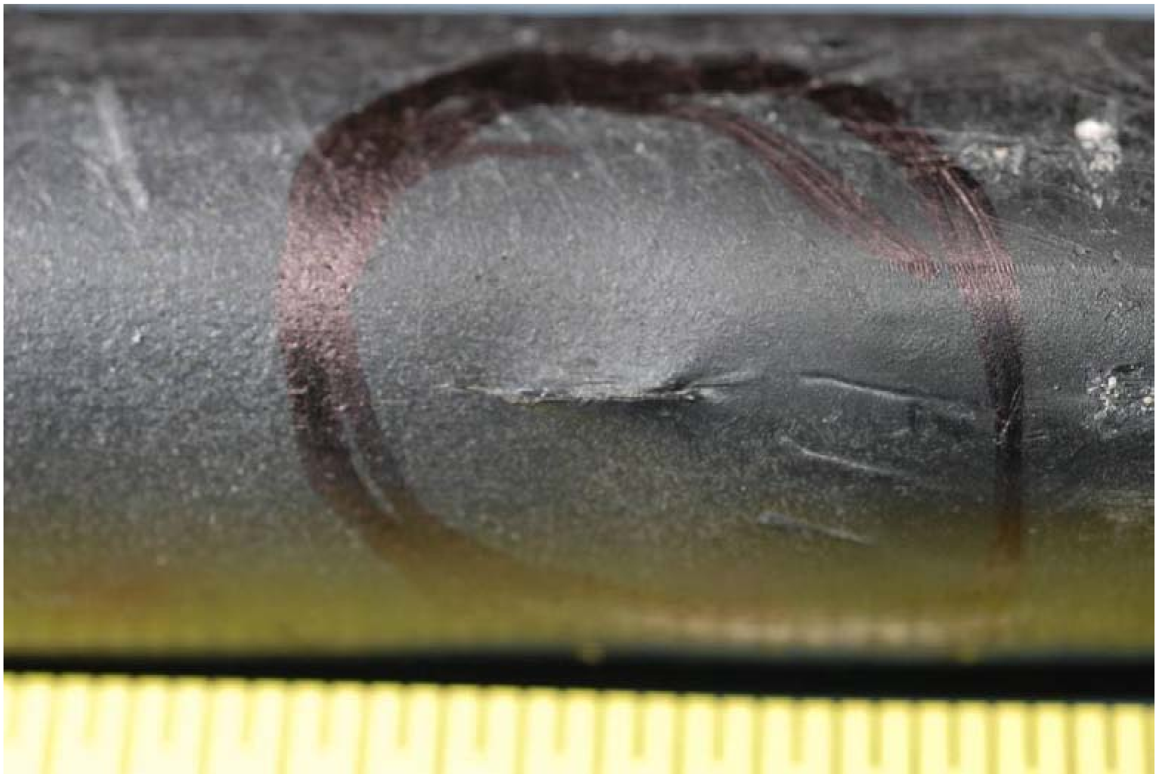


Figure 2. View of longitudinal slit on outer surface of sample.


Figure 3. Squeeze-off adjacent to failure location.

Figure 4. Inner surface view of fracture.

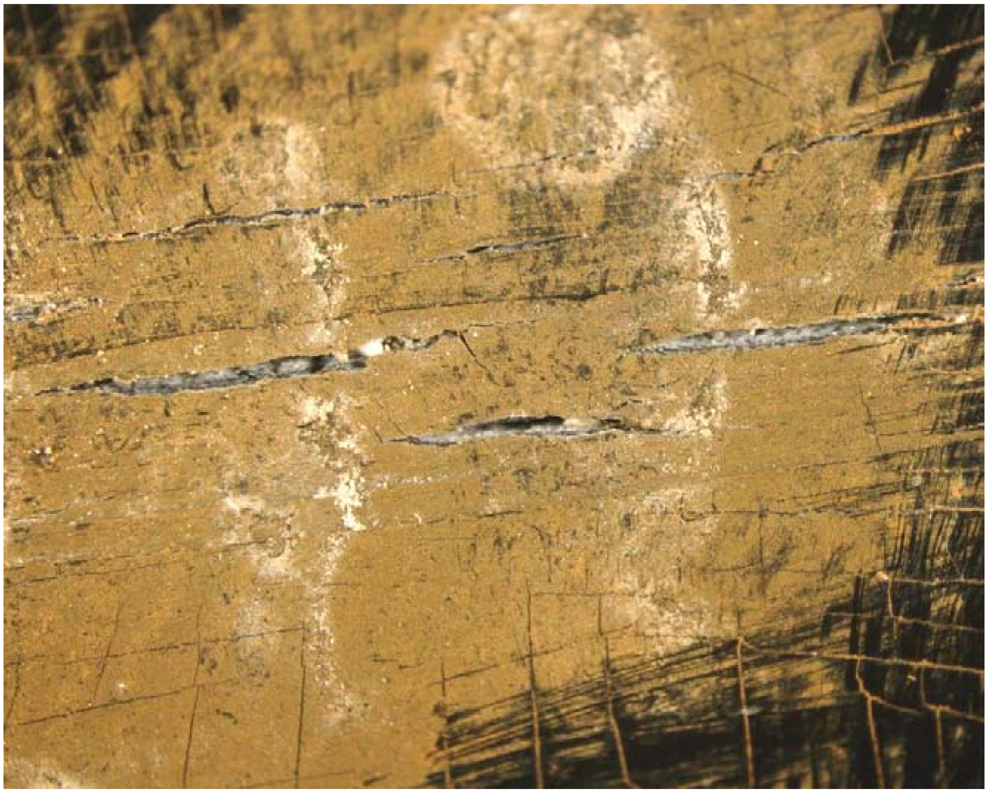


Figure 5. Partial crack opposite the leak site.

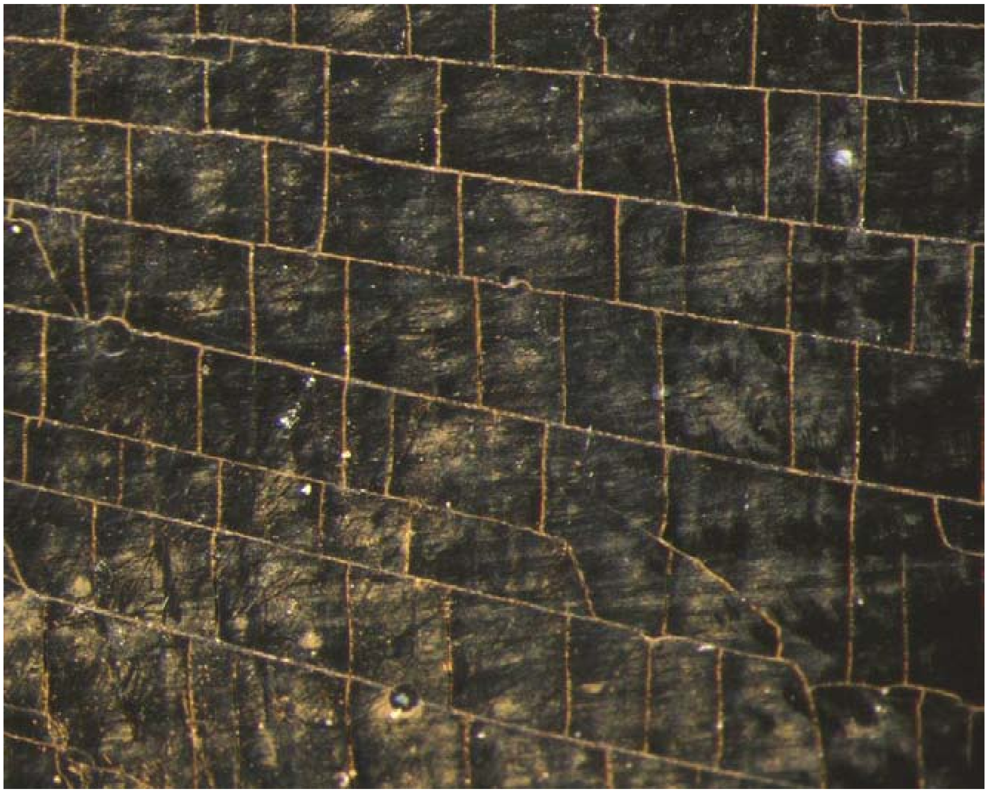


Figure 6. Multi-axial cracks on the inner surface away from the failure site.

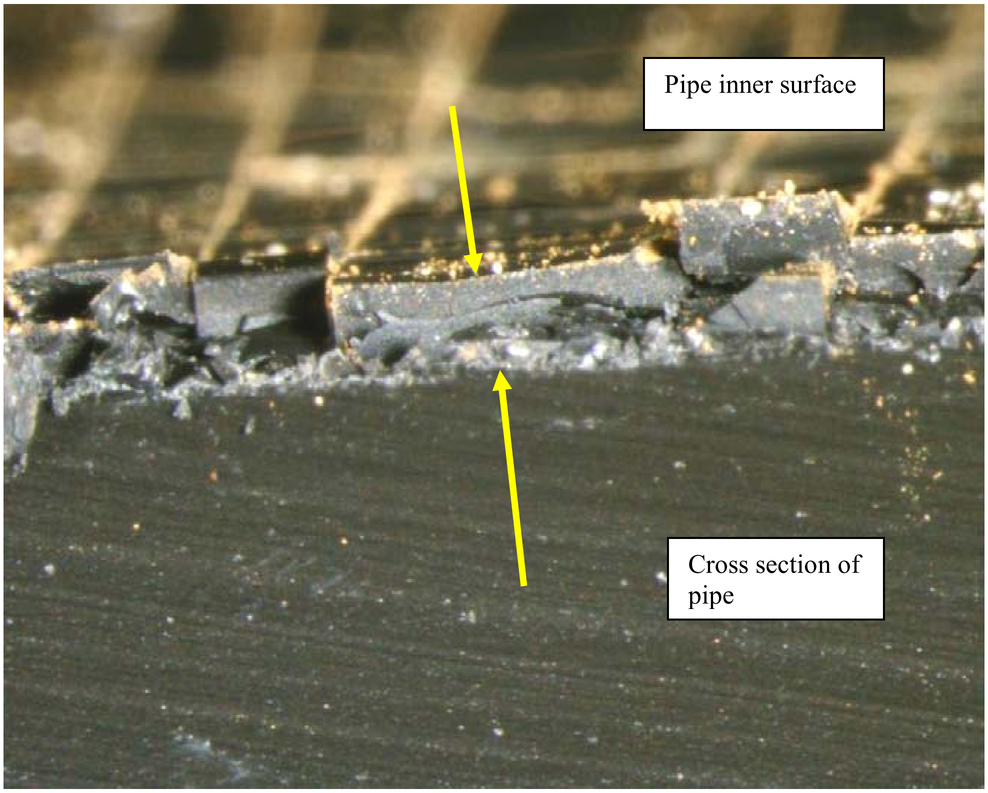


Figure 7. Thick degraded layer on inner surface of failed pipe.

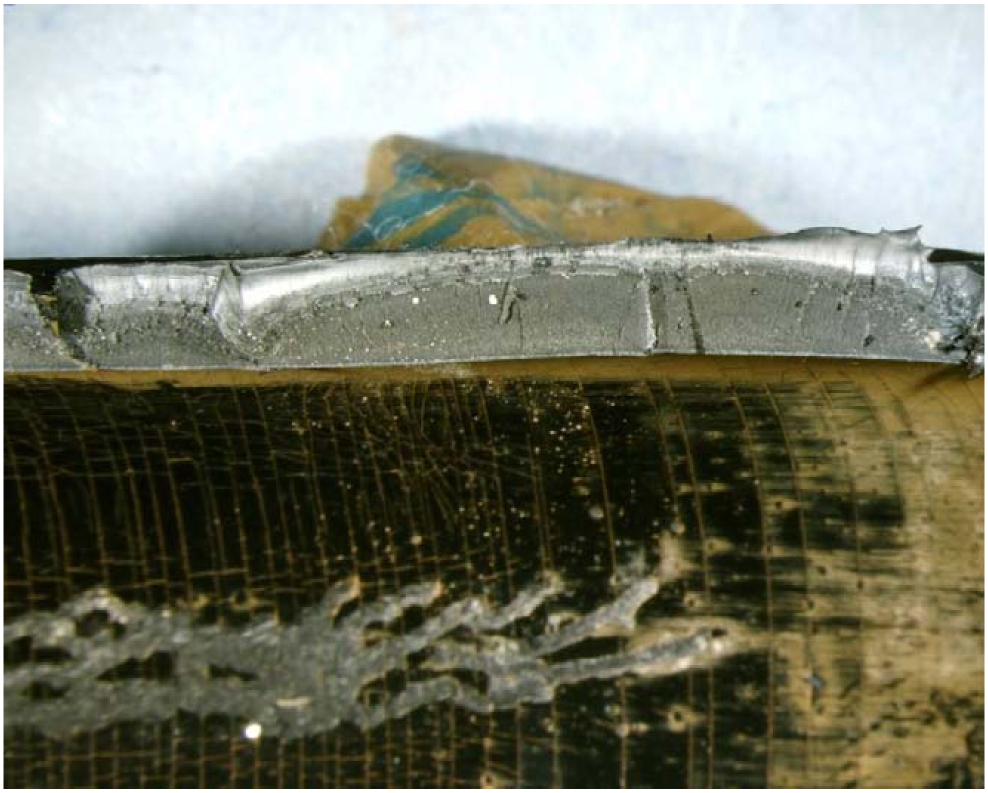


Figure 8. Fracture surface showing multiple initiation sites along the inner surface.

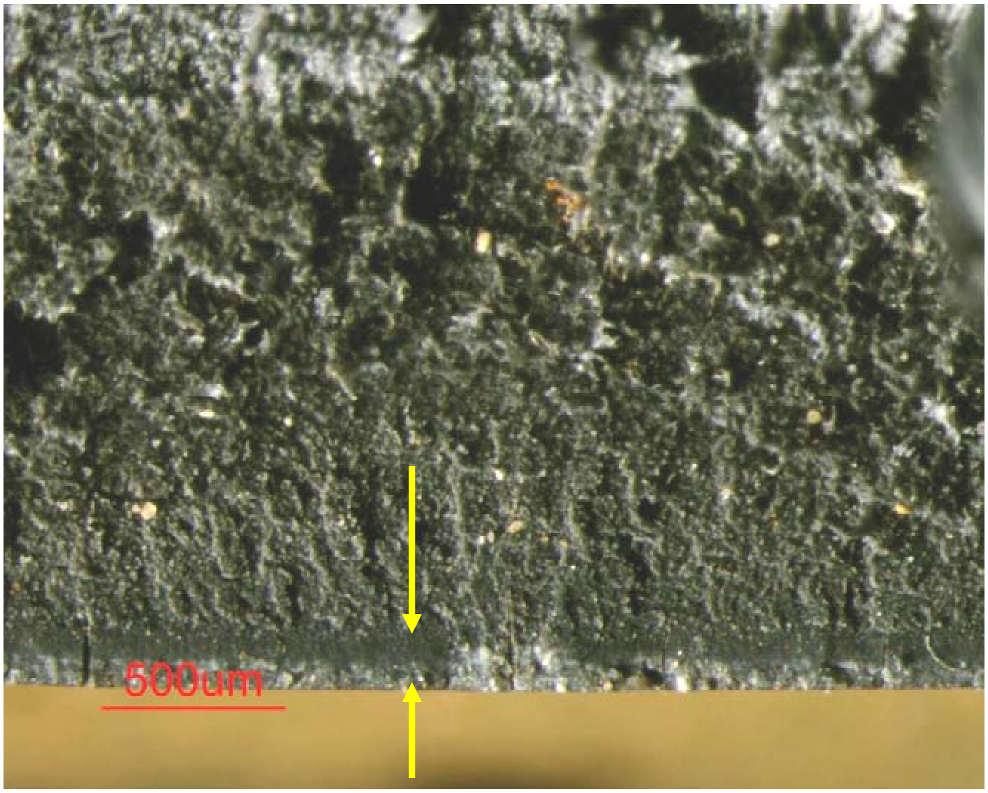


Figure 9. Close-up of a fracture origin showing degraded layer.

Figure 10. Fracture surface from an adjacent area showing brittle inner surface.

6" HDPE Pipe from Ocoee, TN

This pipe had failed after only 5 years in service, and exhibited cracking at various locations around the circumference. The sample is shown in Figures 11 and 12, as received. The sample was sectioned in order to examine the fracture surfaces. Figure 13 depicts the appearance of cracking on the pipe I.D. Figures 14 through 18 are photographs of the fracture surfaces. The large number of fracture origins and location at various locations around the circumference suggest that crack initiation was facilitated by the inner surface oxidation that was detected. These cracks then propagated through the pipe wall by a slow crack growth mechanism, driven by the in-service stresses.

Figure 11. Ocoee 6-inch HDPE pipe sample, as received.

Figure 12. Cracking of Ocoee sample on Pipe I.D.

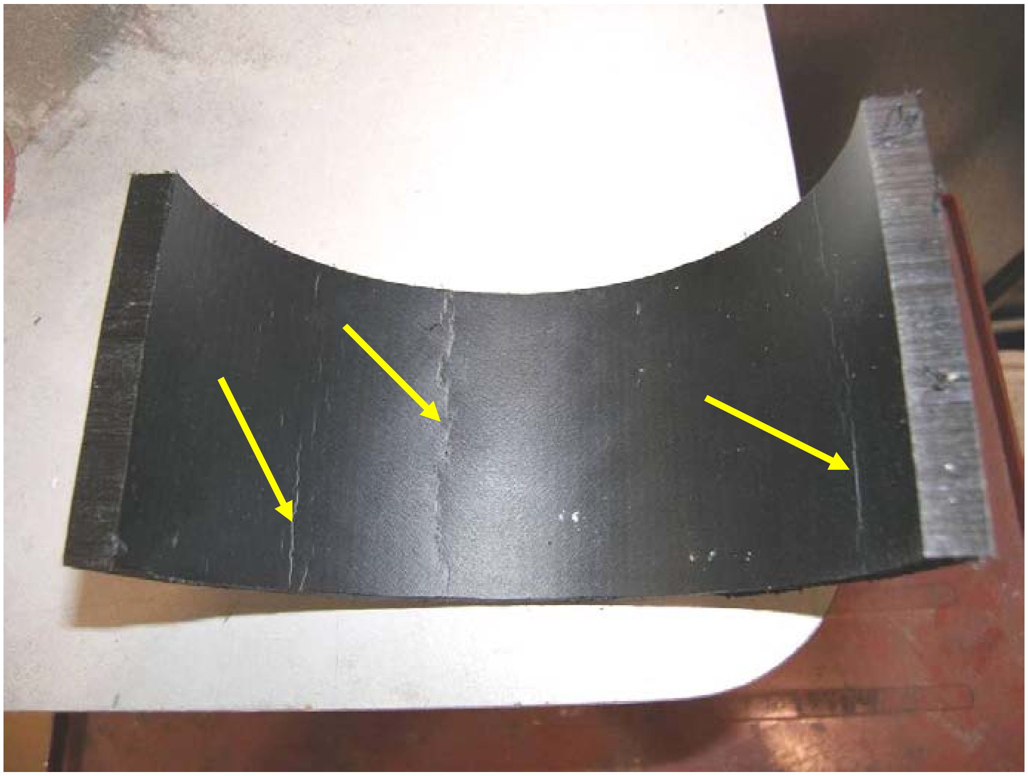


Figure 13. Cracking visible on the inner surface of the pipe I.D.

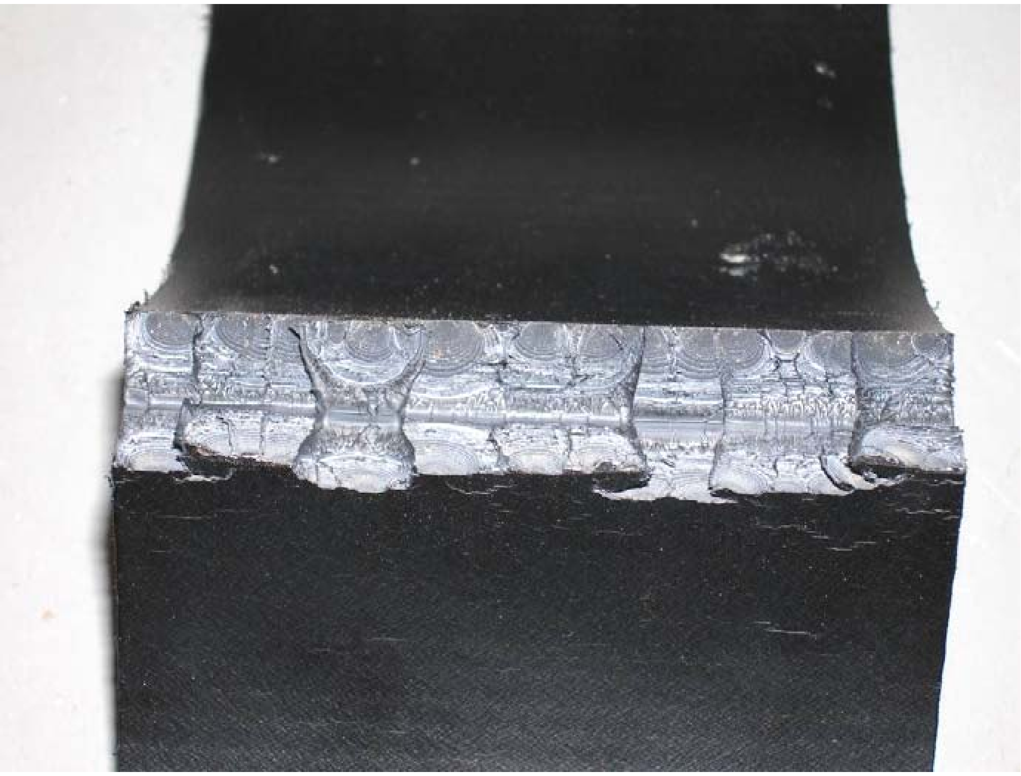


Figure 14. Exposing the fracture surface - Ocoee sample.

Figure 15. A portion of the fracture surface showing multiple fracture origins and slow crack growth.

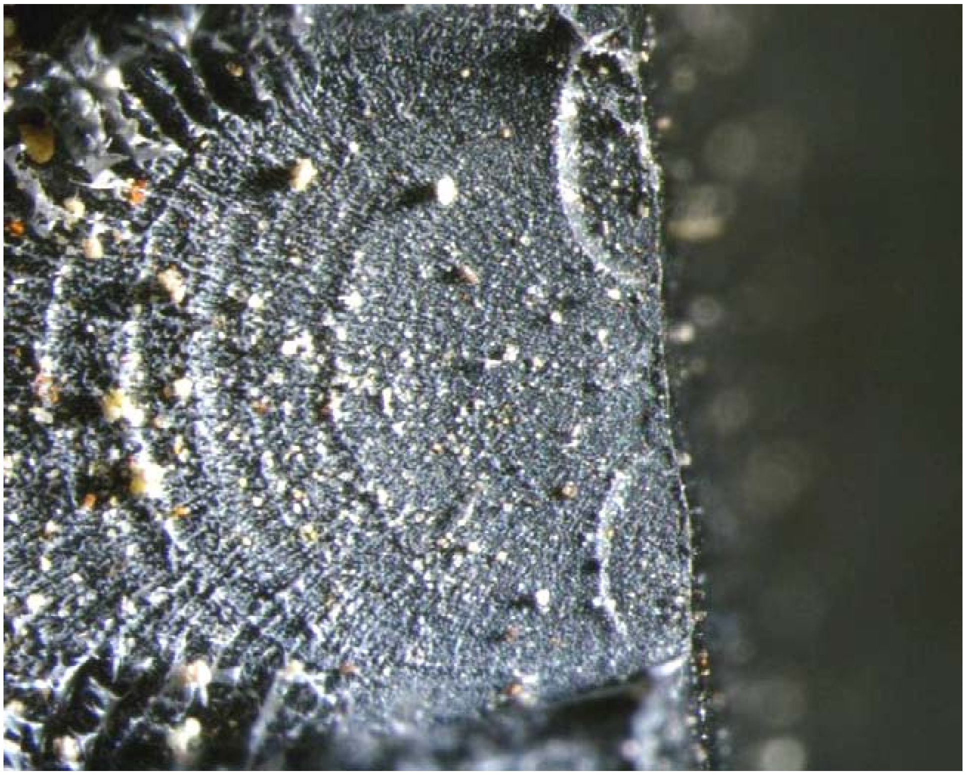


Figure 16. Close-up of fracture surface showing slow crack growth progression.

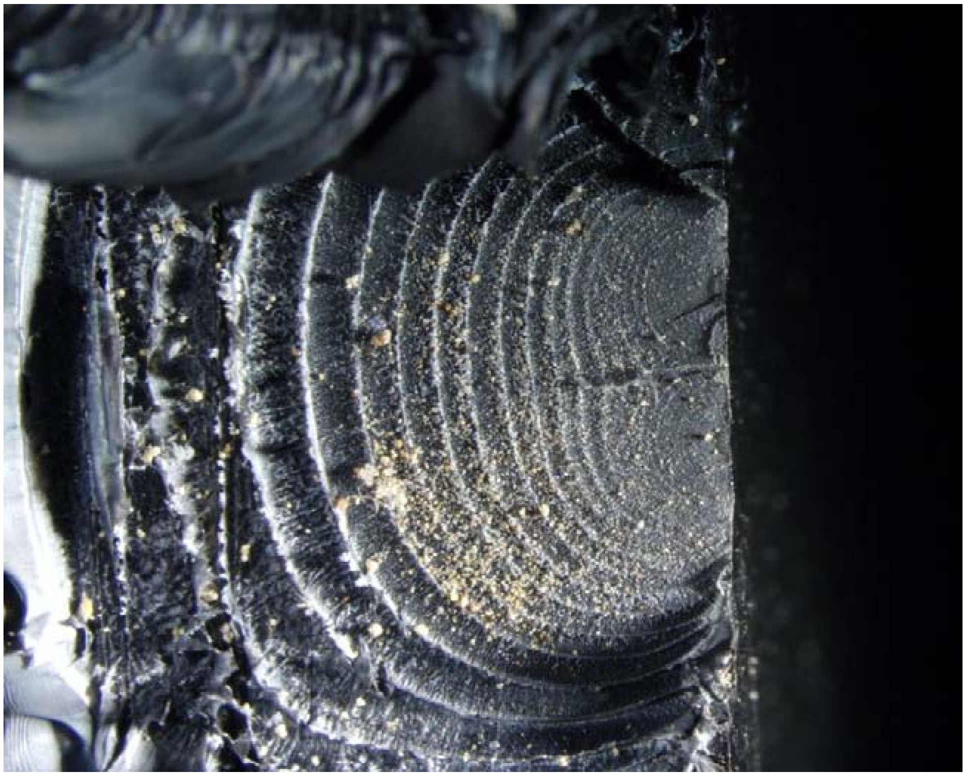


Figure 17. Adjacent fracture origin area.

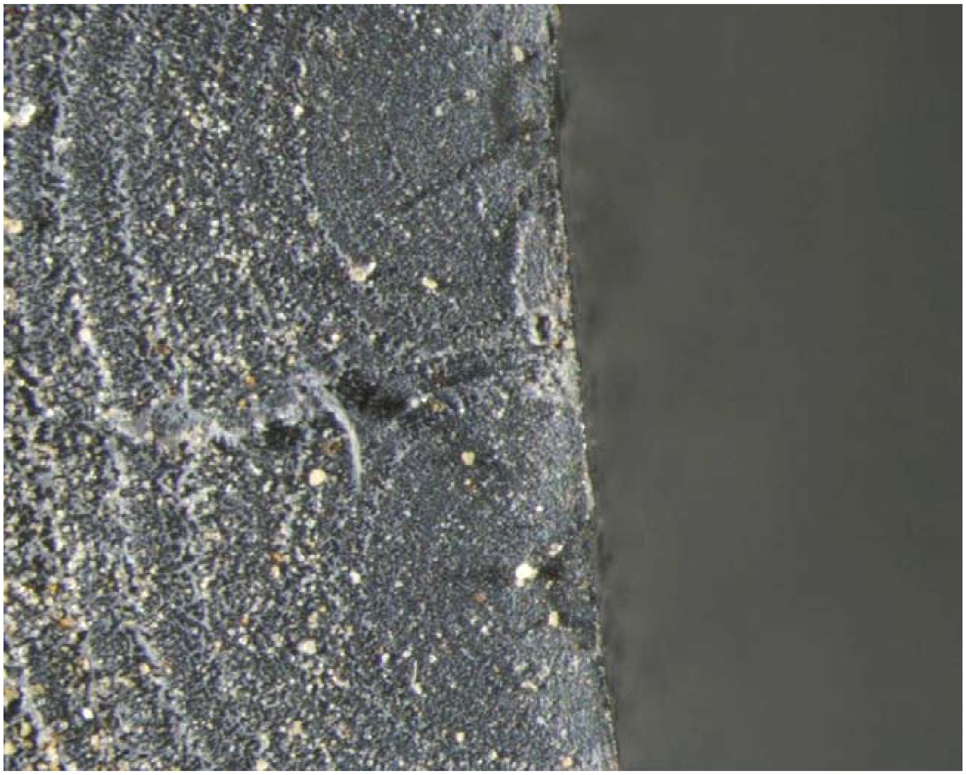


Figure 18. Close-up of fracture origins.

Failed samples from Bakersfield

Five samples from Bakersfield, CA included the failed area in the sections that were provided, ranging in age from 5 to over 30 years. Several of these samples appeared to have failed due to rock impingement and exhibited eroded surfaces where the fracture surface was partially destroyed. These samples all exhibited slow crack growth failures initiating from the inner surface. The fracture origins were right at the inner surface where oxidation was found. The pipes exhibited multiple fracture origins and brittle initiation, as shown in Figures 19 through 28.

Failed Samples from Hamilton, OH

The samples from Hamilton, Ohio all exhibited intense oxidation at the inner surface. These samples failed after service times of from 1 to 12 years. This oxidation was limited to the first 2 mils, but did lead to crack initiation and failure in many instances. The Hamilton, Ohio location was the only one where chlorine dioxide was used as a water disinfectant.

Figures 29 through 37 depict various views of the pipe failure locations. Several of these samples appear to have failed due to rock impingement and exhibited eroded surfaces where the fracture surface was destroyed. Many of the samples exhibited fractures with multiple fracture origins with brittle initiation at the inner surface, followed by slow crack growth propagation through the pipe wall thickness. The oxidation in these samples was a significant factor in the shortened lives of these samples along with what, in some cases, appears to have been overstressing.

Figure 19. Longitudinal fracture from 5612 Anise CT, Bakersfield, CA .

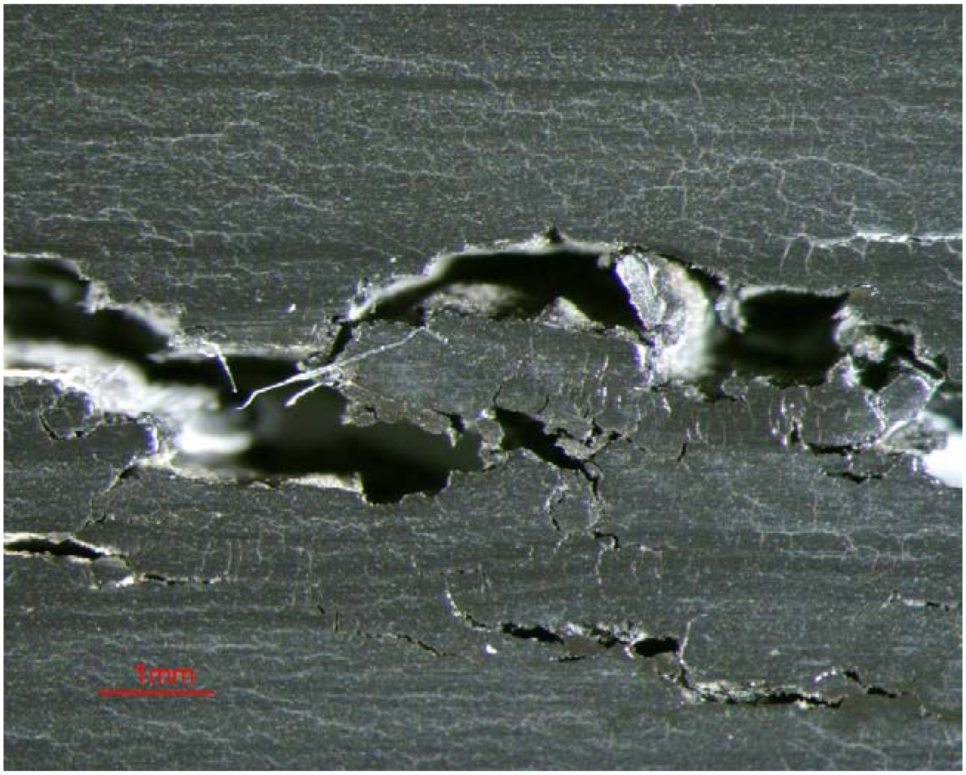


Figure 20. Inner surface view of fracture – 5612 Anise CT, Bakersfield, CA.

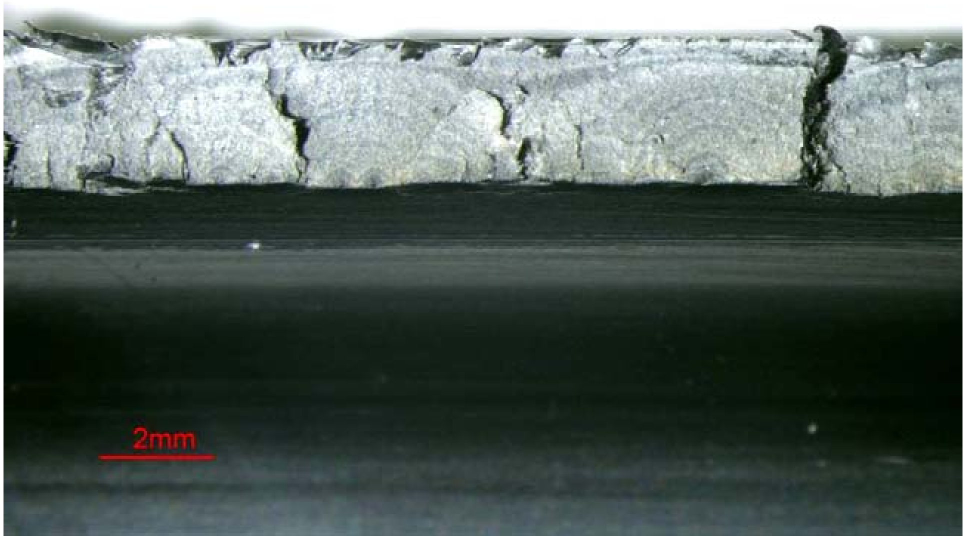


Figure 21. Fracture surface from 5612 Anise CT with multiple origins at I.D.

Figure 22. Bakersfield failure sample.

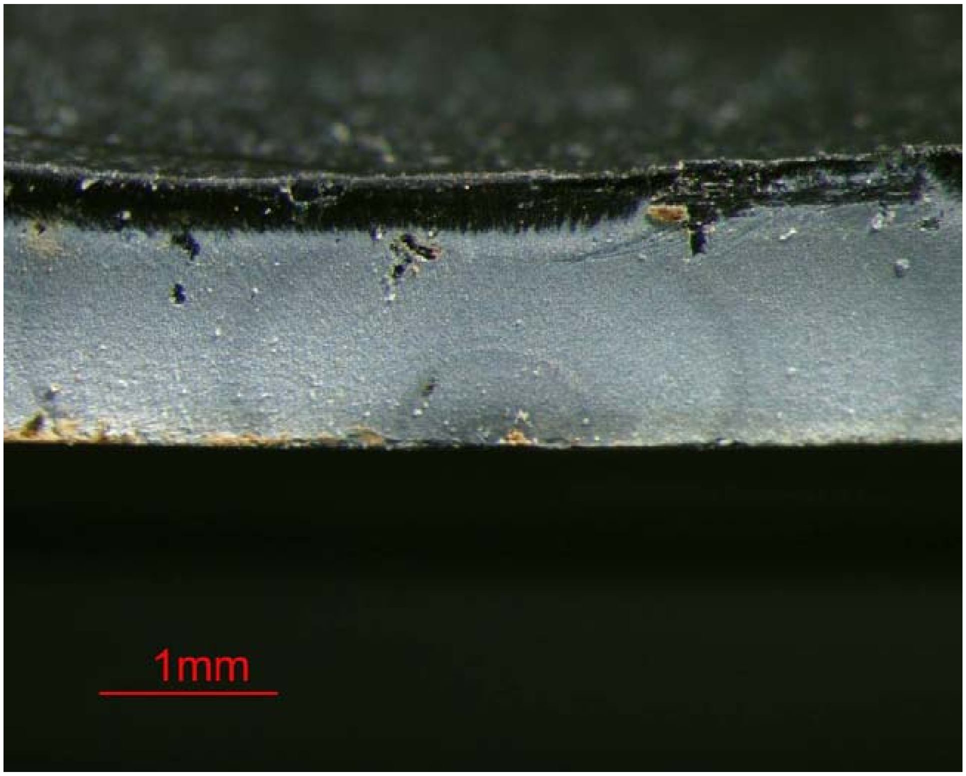


Figure 23. Apparent rock impingement fracture surface from Figure 22.

Figure 24. Failure at a squeeze-off – Bakersfield.

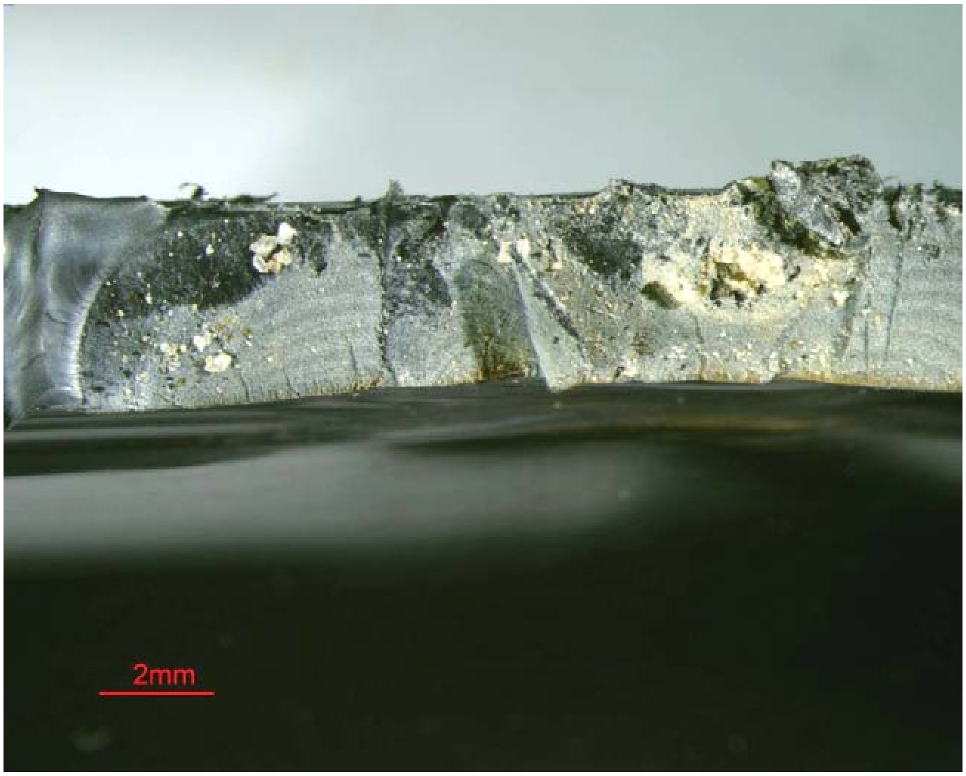


Figure 25. Multiple fracture origins along I.D. at squeeze-off location.

Figure 26. Failure location with outer surface deformation – Bakersfield sample.

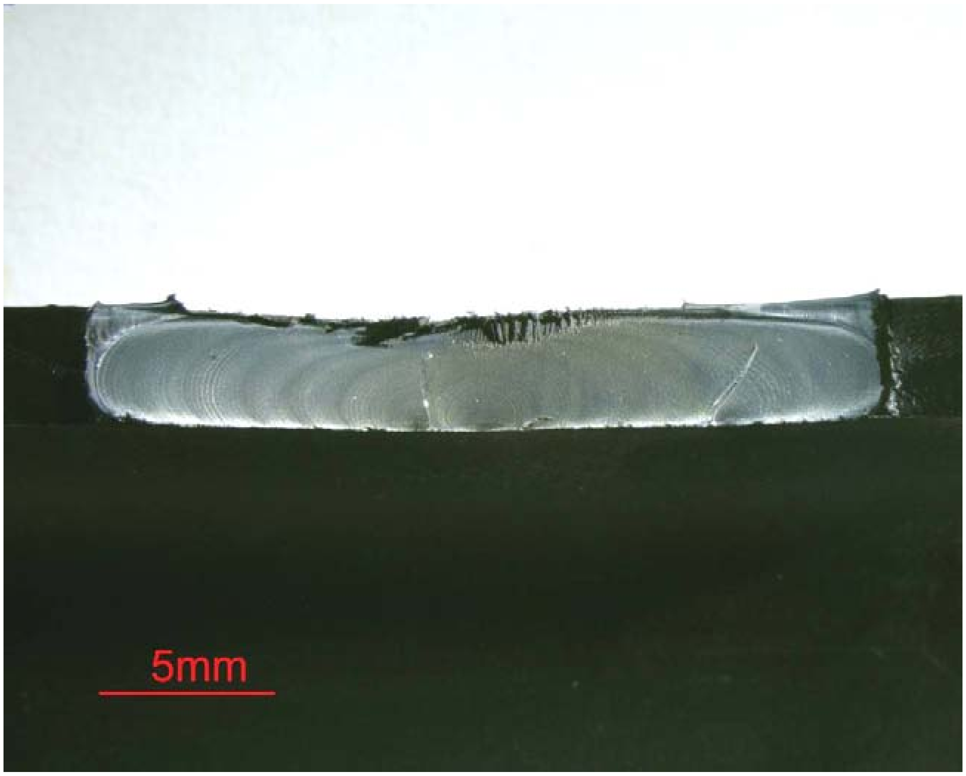


Figure 27. Overall fracture surface from Figure 26 – Bakersfield sample.

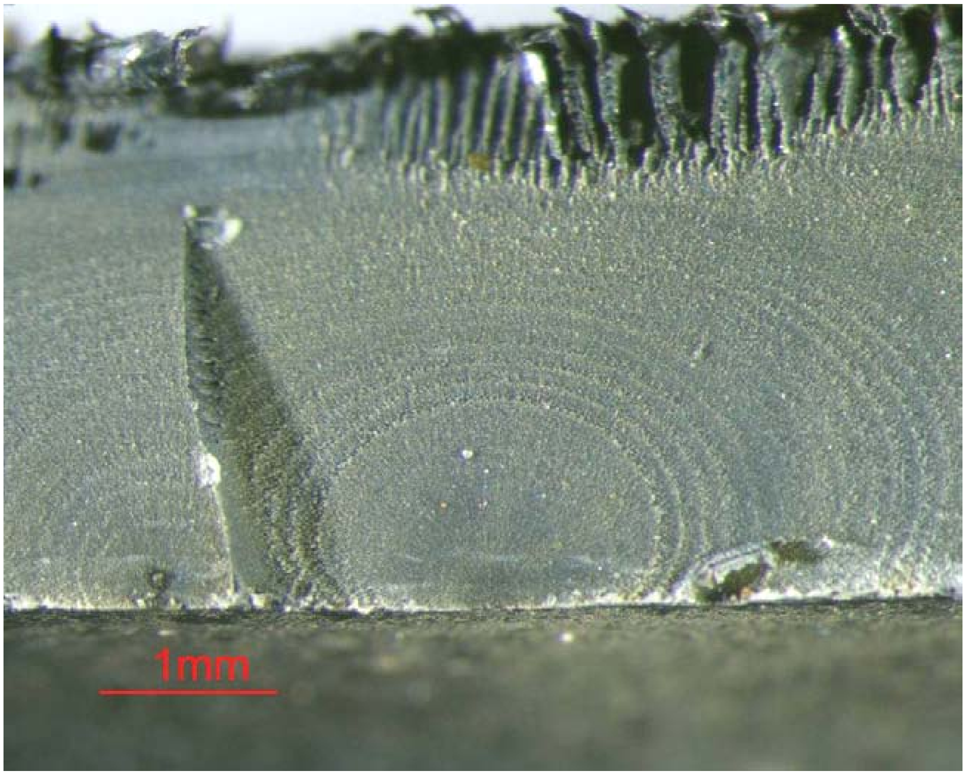


Figure 28. Close-up of fracture origins from Figure 27 – Bakersfield sample.

Figure 29. Hamilton, OH sample with longitudinal split.

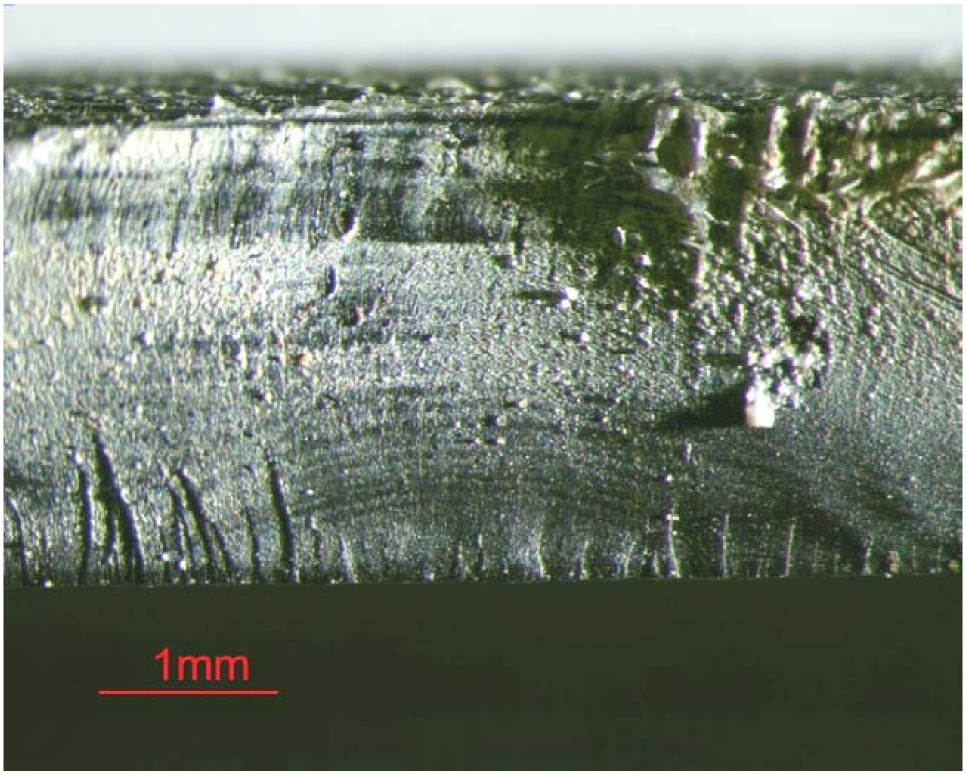


Figure 30. Fracture surface from Hamilton, OH sample from Figure 22 showing brittle fracture initiation along the oxidized inner pipe wall.

Figure 31. Second Hamilton, OH sample with longitudinal split.

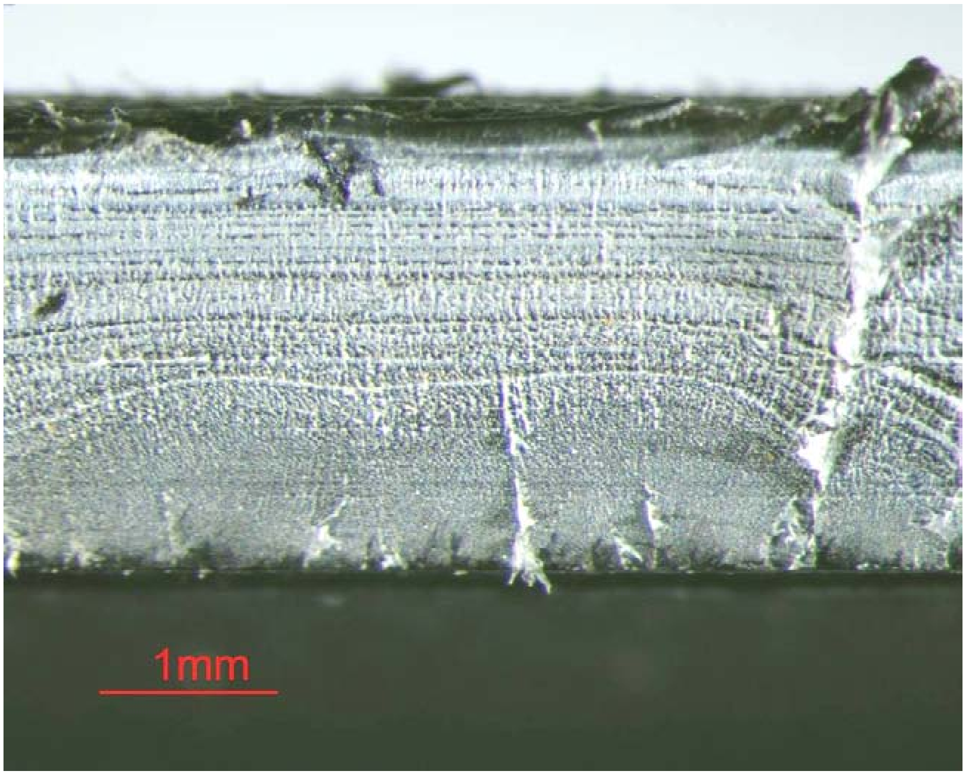


Figure 32. Fracture surface from sample in Figure 24.

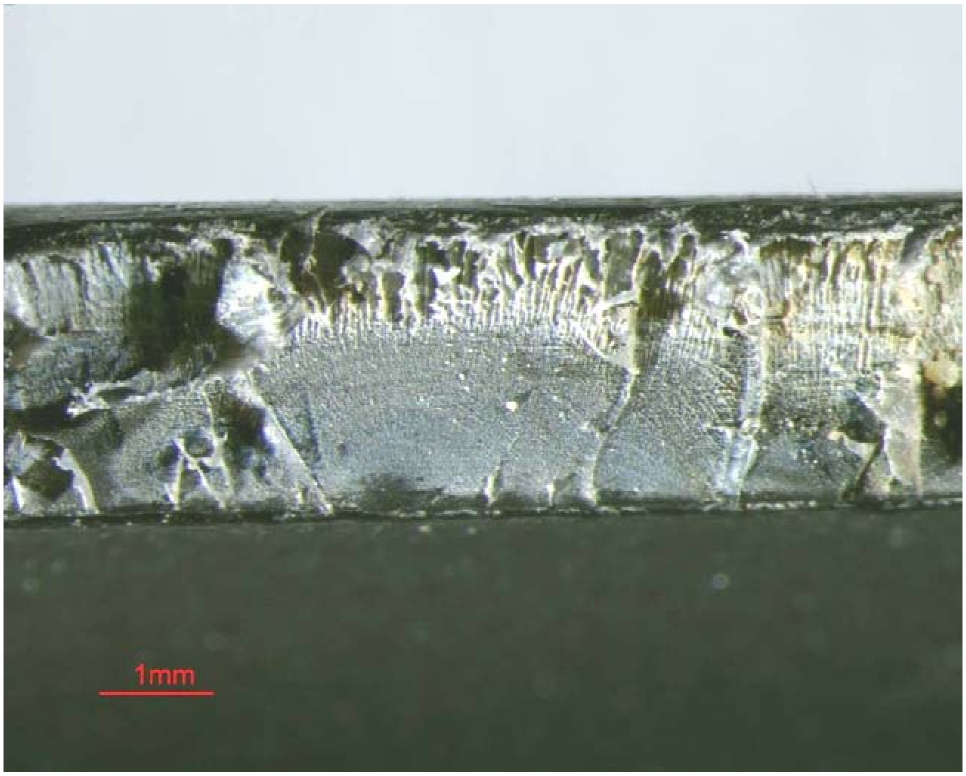


Figure 33. Fracture surface from additional Hamilton, OH sample.

Figure 34. Failure area from Hamilton, OH showing deformation of outer surface.

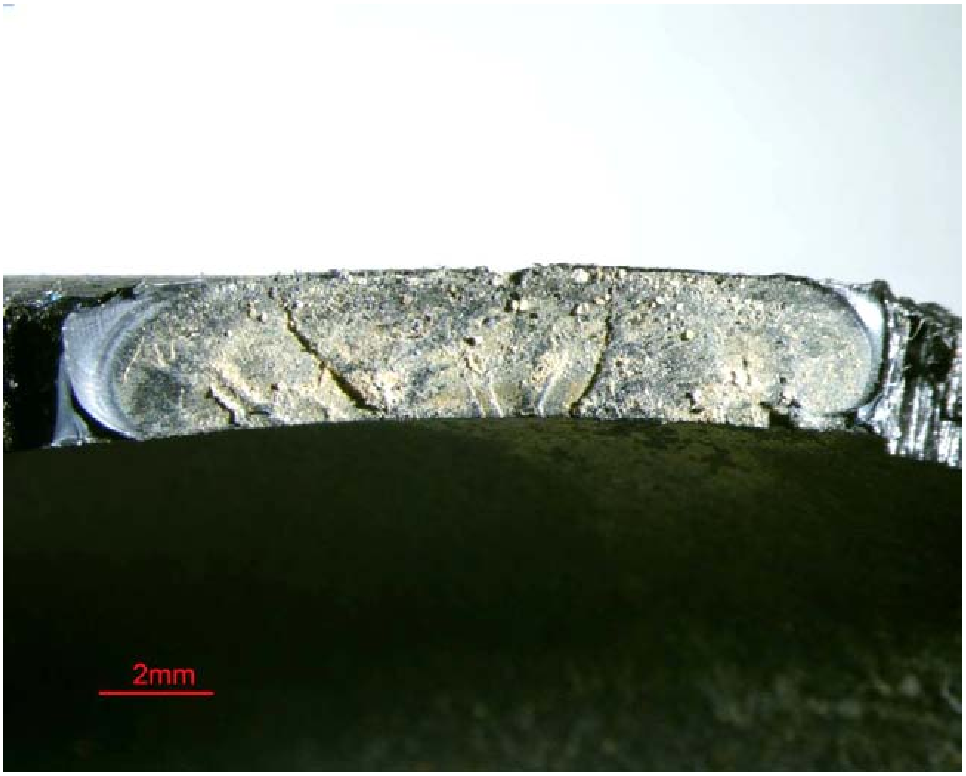


Figure 35. Fracture surface from Figure 27.

Figure 36. Failure at fitting – Hamilton, OH sample.

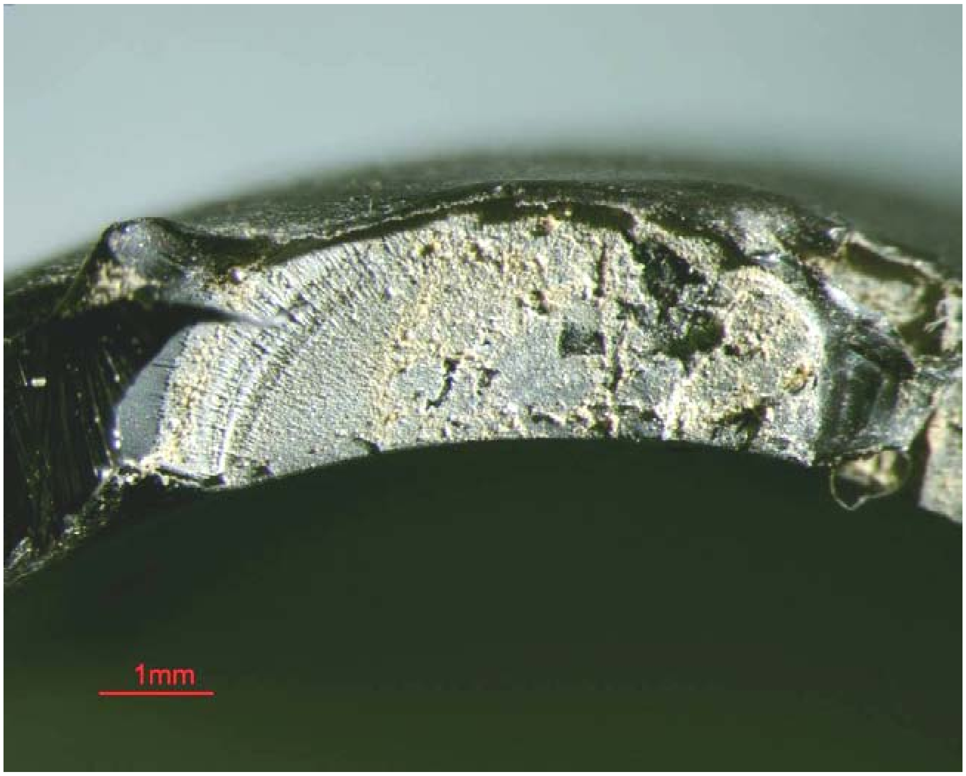


Figure 37. Fracture surface from Figure 29 showing slow crack growth failure due to bending at fitting.

CONCLUSIONS

The data clearly show that the chlorine-based disinfectant chemicals commonly used in potable water systems degrade the inside wall surface of polyethylene pipes. Most of the failed pipes have been from areas with warmer ground temperatures. The increased temperature alone would affect the lifetime of the pipe, even without oxidation of the inner surface.

It has historically been estimated that crack initiation time comprises approximately 90 percent of the pipe’s lifetime. The degraded inner surface of the pipes can greatly shorten the crack initiation time. Thus, oxidation of the pipe’s inner surface leads to premature failures. The percentage of lifetime that the crack initiation time comprises likely varies for different polyethylene materials, but there has been little data showing what that percentage might be. One thing that has been shown in oxidation studies is that even the newer grades of polyethylene are subject to oxidation [6]. More data needs to be generated in order to gauge how actual pipe lifetime is affected by varying factors such as type of water disinfectant, service temperature and pressure.

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3. X. Colin, et al., "Aging of Polyethylene Pipes Transporting Drinking Water Disinfected by Chlorine Dioxide. Part II – Lifetime Prediction", Polymer Engineering and Science, (2009)

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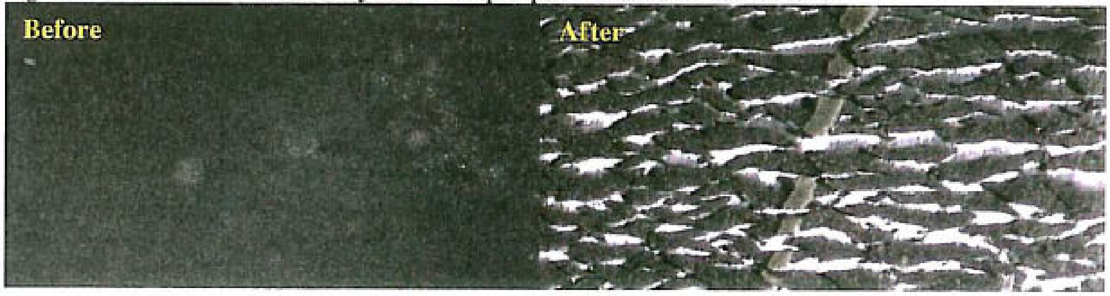
5. M. Rozental, et al., "The NOL Ring Test an Improved Tool for Characterising the Mechanical Degradation of Non-failed Polyethylene Pipe House Connections, paper presented at *Plastic Pipes XIV*, Budapest, Hungary, Session 3B, September 23, 2008.

6. M. Rozental, et al., "A reliable bench testing for benchmarking oxidation resistance of polyethylene in disinfected water environments," paper presented at *Plastic Pipes XIV*, Budapest, Hungary, Session 3B, September 23, 2008.

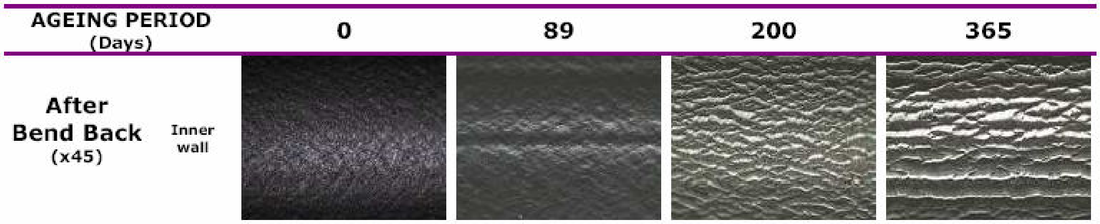
Appendix A: Guide to HDPE Oxidation Analytics

Reverse Bend Back Test – Optical Microscopy is used to determine embrittlement and cracking of inner surface of pipe after the pipe sample has been "bent back" or "inside-out". Chemically or oxidatively embrittled surfaces are evident in this "before and after" bend-back test of HDPE subjected to oxidation in the laboratory (Chung 2007). Note that the inner surface of the HDPE pipe prior to bend back may not appear to be degraded.

Figure 6: Inner surface of laboratory failure samples prior to and after reverse bend



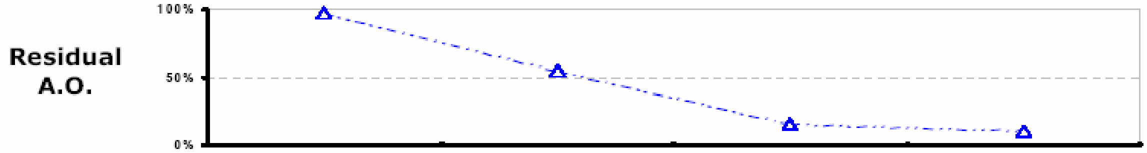
Chung, JANA ANTEC 2007



Rozental – Suez 2008

Laboratory oxidized HDPE subjected to bend-back after accelerated conditions from 0-365 days

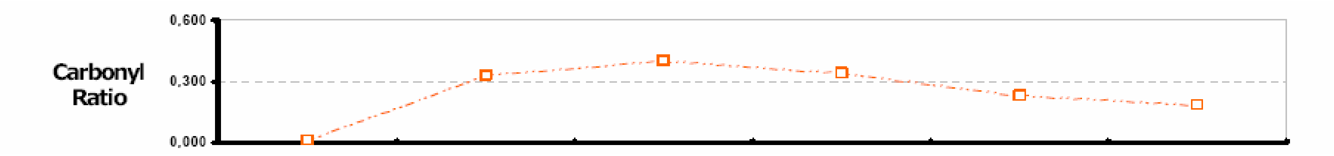
OIT (Oxidation Induction Time) - A differential scanning calorimeter (DSC) is used to determine the OIT of the polymer sample. OIT represents the polymer's relative resistance to oxidation – by representing a material's antioxidant content. Appreciable oxidation usually does not occur until embedded antioxidant is depleted. Low OIT values indicate that the polymer is vulnerable to oxidation and surface changes have already started to occur or are about to occur. New HDPE OIT values usually range from 75 minutes to 120 minutes. OIT values of less than or equal to 5 minutes represent high levels of consumption and attack (Rozental – 2008).



Rozental -Suez 2008

OIT (AO – antioxidant) of HDPE pipe decreasing from 0-365 days in chlorine water disinfectant oxidation study

FTIR Bond Indices (ATR and Transmission) – Fourier Transform Infrared spectroscopy is a technique used to identify chemical changes in the structure of the polyethylene pipe. Oxidation of polyethylene leaves behind reaction species in the pipe wall – such as vinyl groups, chlorine groups and carbonyl groups where they should not exist on non-degraded HDPE. ATR (Attenuated Total Reflectance) and Transmission FTIR's are two spectroscopy methods used in the study to identify carbonyl groups (depicted as a CI – or carbonyl index). CI's of greater than 0.05 were claimed to be indicative of moderate oxidative degradation and greater than 0.10 termed "highly degraded" by a recent Suez Environnement study and by previous ESI polyolefin oxidation work.

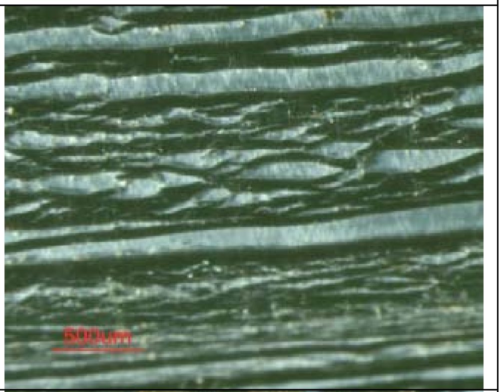
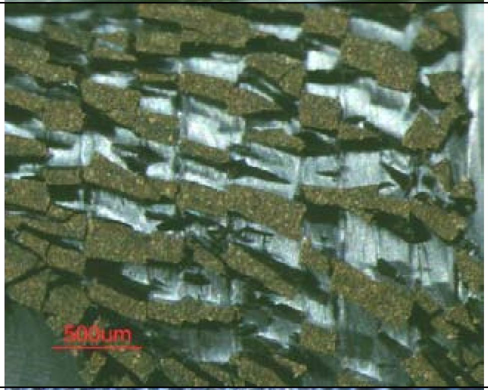
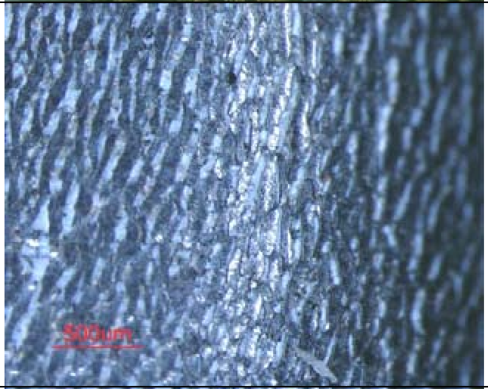
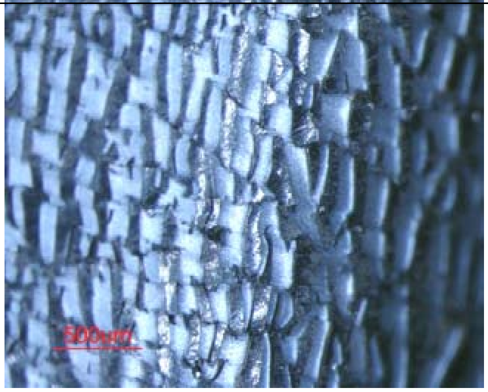


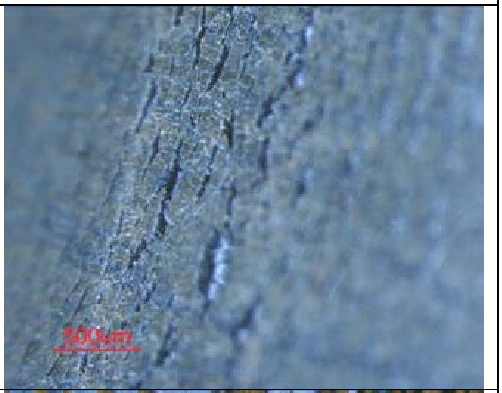
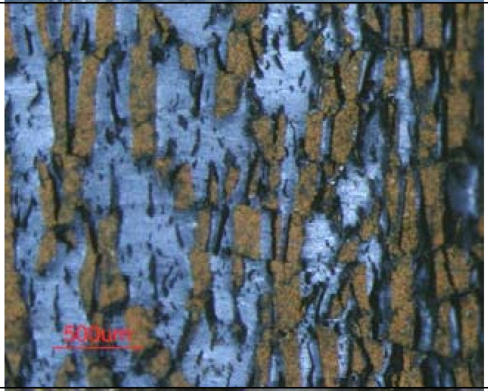
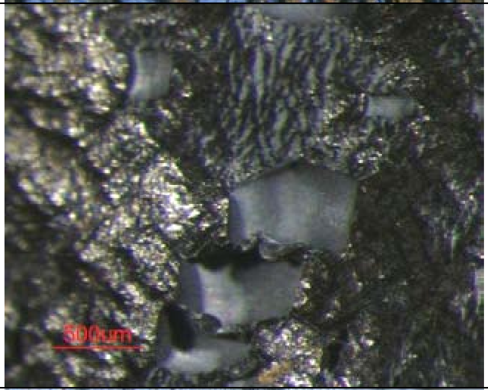
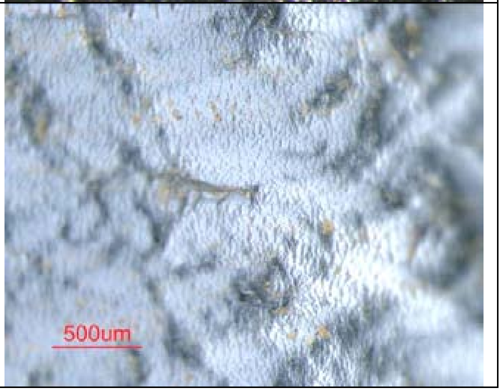
Rozental -Suez 2008

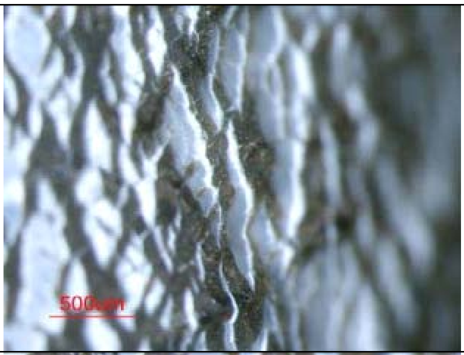
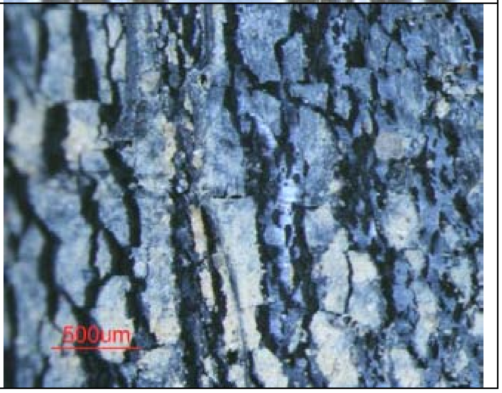
Carbonyl Index of HDPE pipe increasing from 0-365 days in chlorine dioxide oxidation study

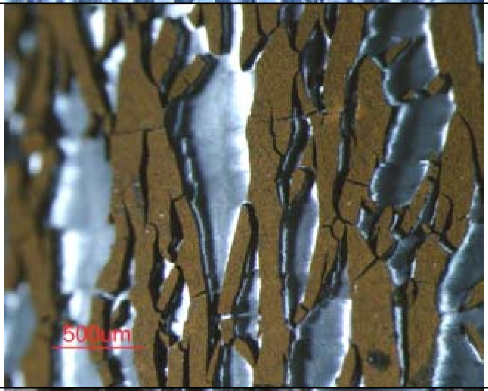
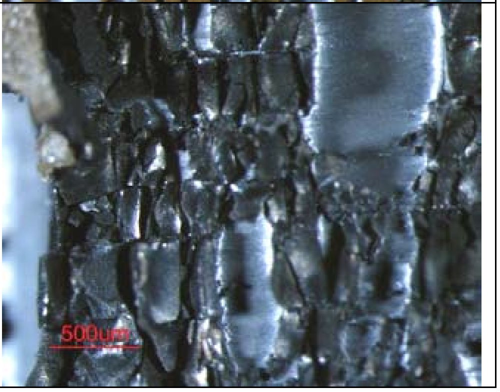
Appendix B: HDPE Pipe Oxidation Sample Summary

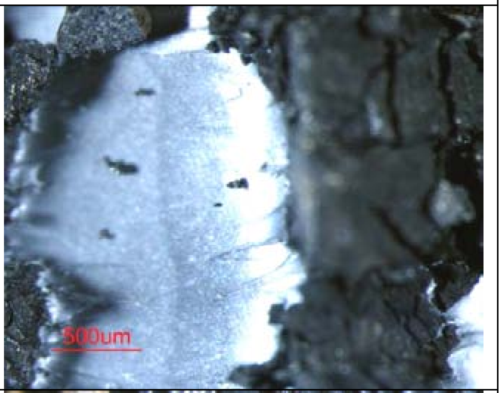
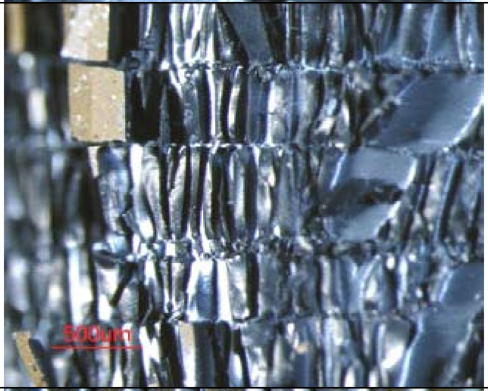
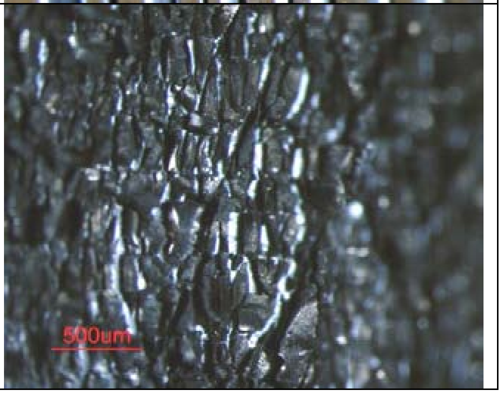
🟥 Highly Degraded 🟨 Moderately Degraded 🟩 Low/No Degradation

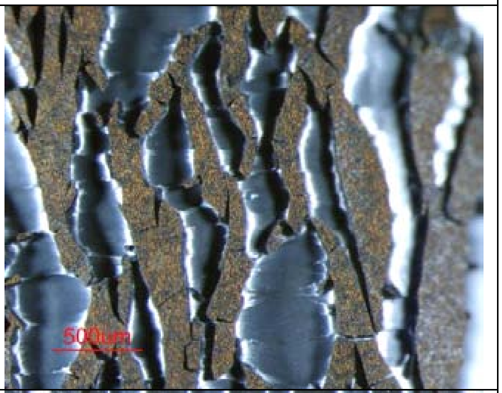
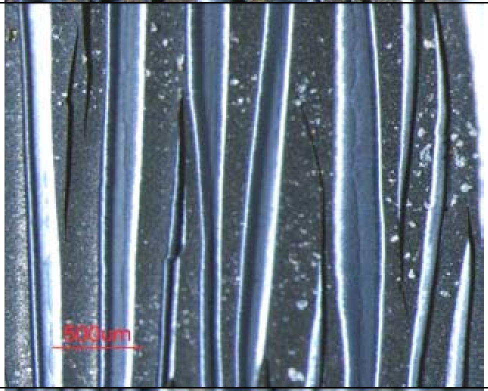
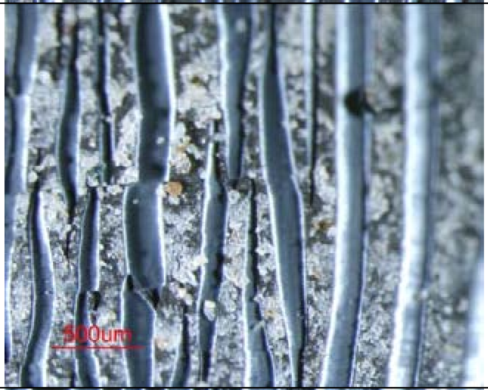
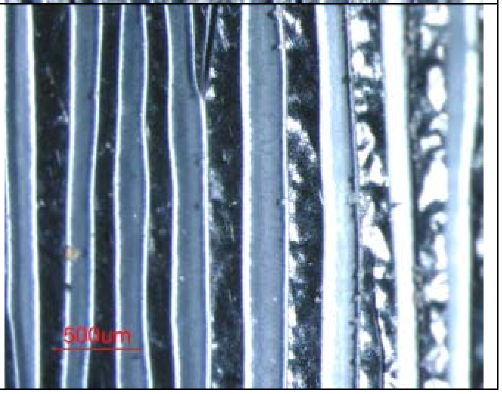
Sample	Service Time, years	Bend Back Test Result
Virgin Valley NV 1” SDR9 Mfg- Vanguard OIT: 3.37 🟥 CI (ATR): 0.102 🟥 CI (T): 0.265 🟥	6.00	
Maui HI 1” Nominal, 0.28” wall Mfg – Driscopipe OIT: 0.30 min 🟥 CI (ATR) : 0.092 🟨 CI (T) : 0.182 🟥	11.00	
Makawao Maui HI- 1” Sample 1 1” DR9 Mfg - Driscopipe OIT: 1.93 🟥 CI (ATR): 0.116 🟥 CI (T): 0.174 🟥	13.01	
Makawao Maui HI - 1.25” Sample 2 1.25” DR9 Mfg – Driscopipe OIT: 1.83 🟥 CI (ATR): 0.217 🟥 CI (T): 0.157 🟥	13.01	

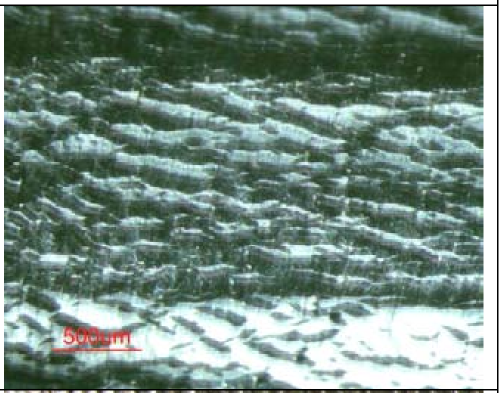
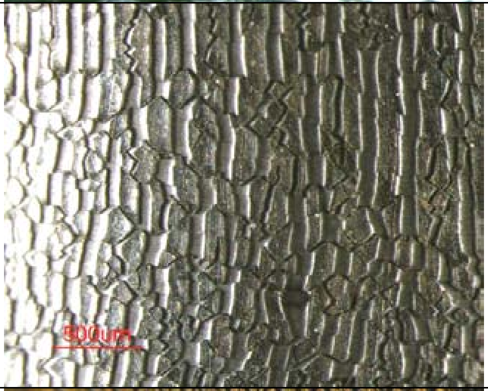
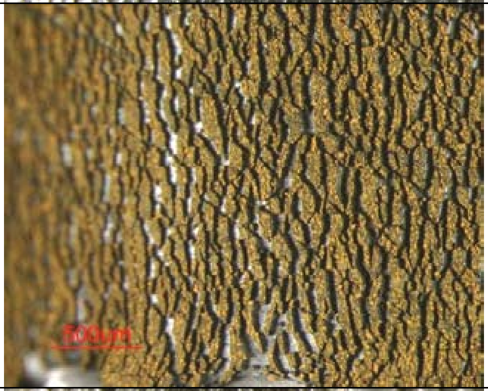
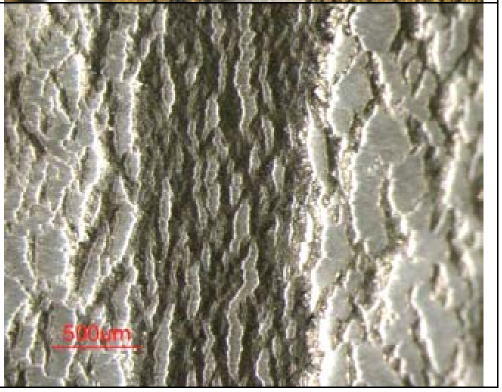
Sample	**Service Time, years**	**Bend Back Test Result**
Central Maui HI – Sample 3 1.25” DR9 Mfg – Driscopipe OIT: 2.94 🟥 CI (ATR): 0.202 🟥 CI (T): 0.003 🟩	17.07	
Kula Maui HI - 2” Sample 4 2” DR9 Mfg – Driscopipe OIT: 0.48 🟥 CI (ATR): 0.228 🟥 CI (T): 0.170 🟥	11.02	
Ocoee TN 6” DR17 Mfg – Polypipe OIT: 17.04 🟨 CI (ATR): 0.179 🟥 CI (T): 0.006 🟩	5.00	
West Maui Land – Maui HI 4” DR13.5 Mfg – Plexco OIT: 7.8 🟨 CI (ATR): 0.099 🟨 CI (T): 0.002 🟩	10.00	

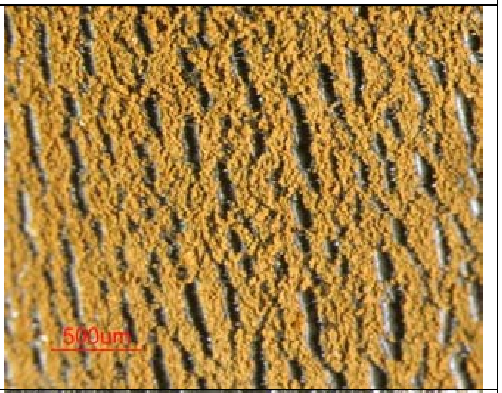
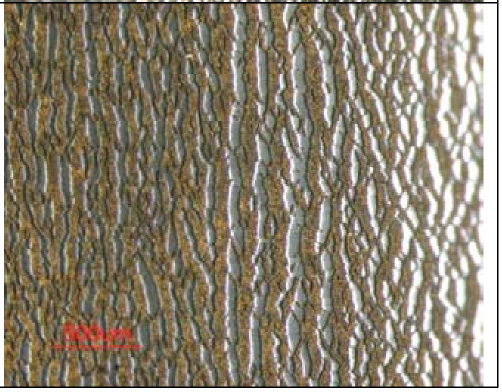
Sample	**Service Time, years**	**Bend Back Test Result**
West Maui Land Sample 2 6” DR11 Mfg – Plexco OIT: 0.20 🟥 CI (ATR):0.101 🟥 CI (T): 0.207 🟥	8.00	
West Maui Land #3 6’’ DR9 Mfg – Polypipe OIT: 33.8 🟩 CI (ATR): 0.019 🟩 CI (T): 0.007 🟩	7.00	NA – Sample too small
West Maui Land Sample 4 6’’ DR9 Mfg – Plexco OIT: 0.20 🟥 CI (ATR): 0.200 🟥 CI (T): 0.100 🟥	8.00	
Lafayette LA 6” Mfg – ? OIT: 0.90 🟥 CI (ATR): 0.107 🟥 CI (T): 0.200 🟥	12.00	
HB&TS ¾” DR9 Mfg – Driscopipe OIT: 0.20 🟥 CI (ATR): 0.503 🟥 CI (T): 0.413 🟥	25.04	

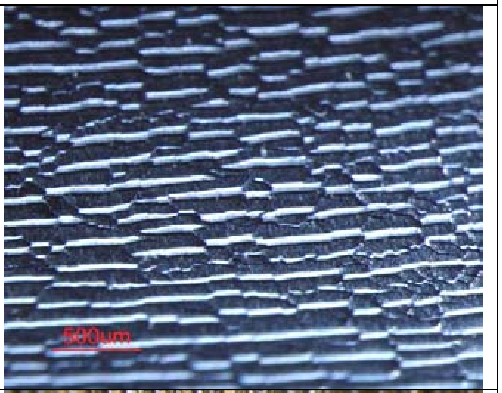
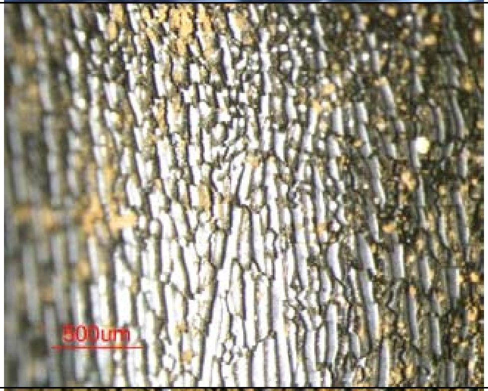
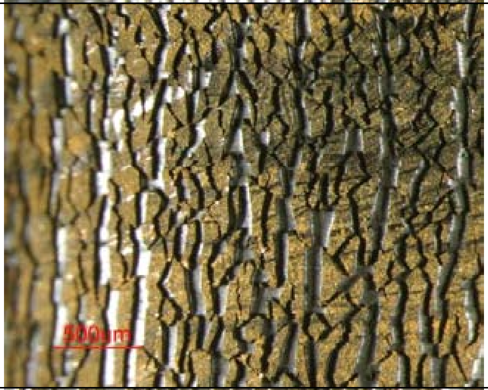
Sample	**Service Time, years**	**Bend Back Test Result**
HB&TS ¾” DR9 Mfg – Yardley OIT: 0.20 🟥 CI (ATR): 0.449 🟥 CI (T): 0.310 🟥	25.04	
Pomona CA ¾” Mfg – Orangeburg OIT: 0.30 🟥 CI (ATR): 0.154 🟥 CI (T): 0.182 🟥	28.00	
Laughlin NV 3711 Westcliff 1” Mfg – UNK OIT: 0.40 🟥 CI (ATR):0.128 🟥 CI (T): 0.306 🟥	25.2	
Laughlin NV 1817 Oasis 1” Mfg – UNK OIT: 0.10 🟥 CI (ATR): 0.450 🟥 CI (T): 0.420 🟥	22.10	

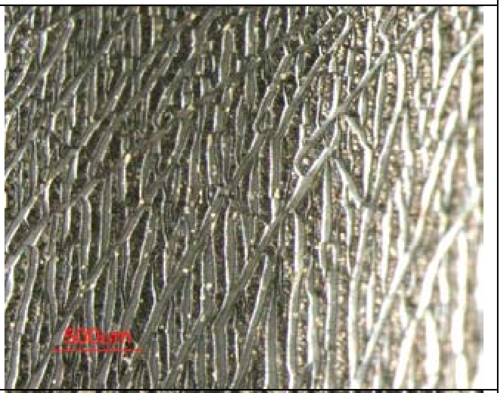
Sample	**Service Time, years**	**Bend Back Test Result**
Laughlin NV 1818 Oasis 1” Mfg – UNK OIT: 0.80 🟥 CI (ATR): 0.280 🟥 CI (T): 0.250 🟥	22.00	
Laughlin NV 3332 Calanda 1” Mfg – UNK OIT: 0.20 🟥 CI (ATR): 0.238 🟥 CI (T): 0.449 🟥	25.50	
Laughlin, NV 2142 Pebble Creek 1” Mfg – UNK OIT: CI (ATR): CI (T):	22.00	
Laughlin, NV 2189 High Dunes 1” Mfg – UNK OIT: CI (ATR): CI (T):	21.92	

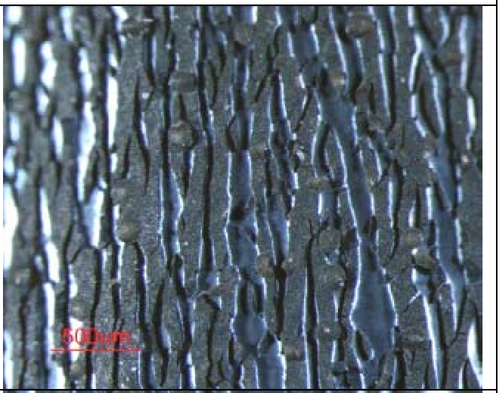
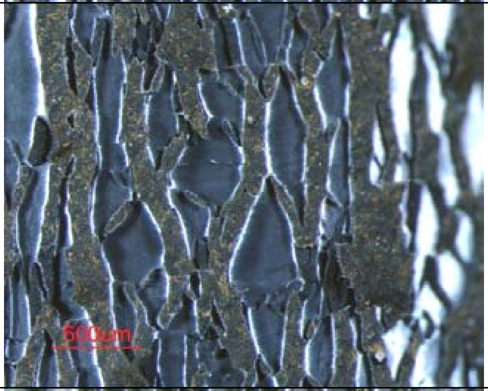
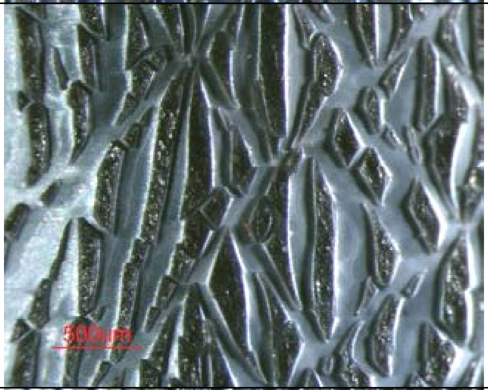
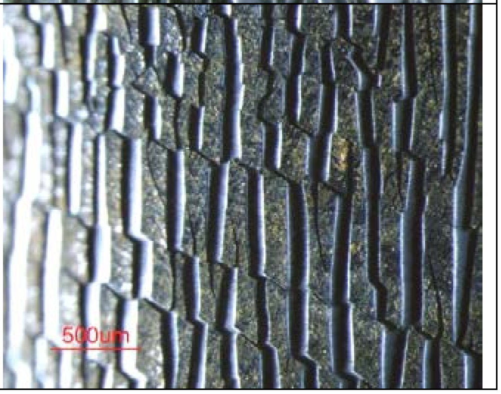
Sample	**Service Time, years**	**Bend Back Test Result**
Laughlin, NV 3659 Catalina Dr. 1” Mfg – UNK OIT: CI (ATR): CI (T):	25.25	
Laughlin, NV 2160 Pebble Creek, Section 1 1” Mfg – UNK OIT: CI (ATR): CI (T):	21.92	
Laughlin, NV 2160 Pebble Creek, Section 2 1” Mfg – UNK OIT: CI (ATR): CI (T):	21.92	
Laughlin, NV 1818 Oasis. Pt. 2 1’’ Mfg – UNK OIT: CI (ATR): CI (T):	22.00	

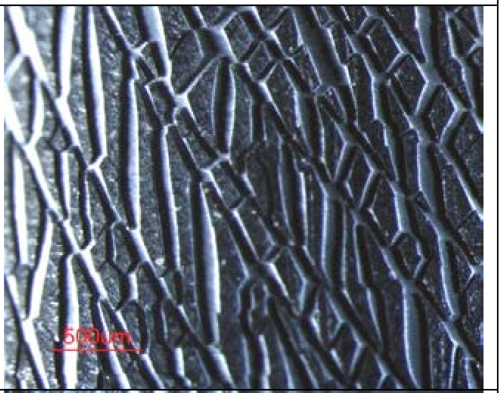
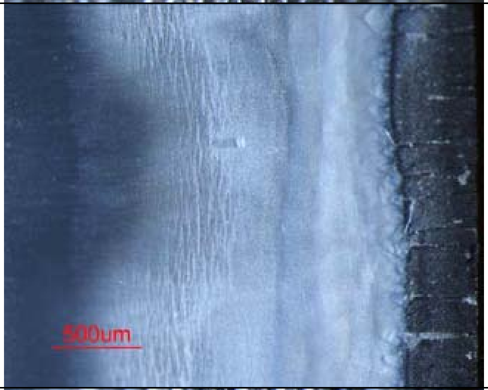
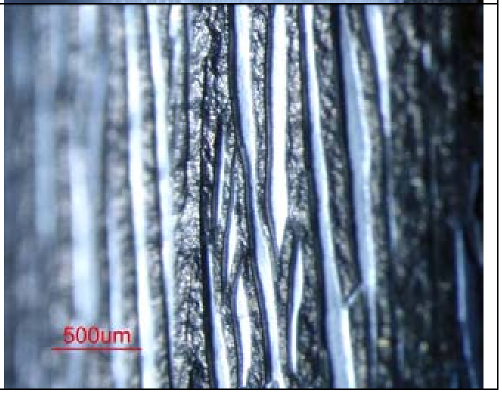
Sample	Service Time, years	Bend Back Test Result
Bakersfield, CA Sample 1-10310 Barnes 1” DR9 Mfg – Wesflex OIT: CI (ATR): CI (T):	7.60	
Bakersfield, CA Sample 2 - 6908 Natchitoches Way 1” PE 3406 Mfg – Orangeburg OIT: CI (ATR): CI (T):	28.43	
Bakersfield, CA Sample 3 - 3024, 3100 Whitley Dr ¾” DR9 PE 3406 Mfg – Driscopipe OIT: CI (ATR): CI (T):	31.35	
Bakersfield, CA Sample 4 - 320 Sonoma Vine Ct. 1” DR9 PE 3408 Mfg – Wesflex OIT: CI (ATR): CI (T):	5.45	

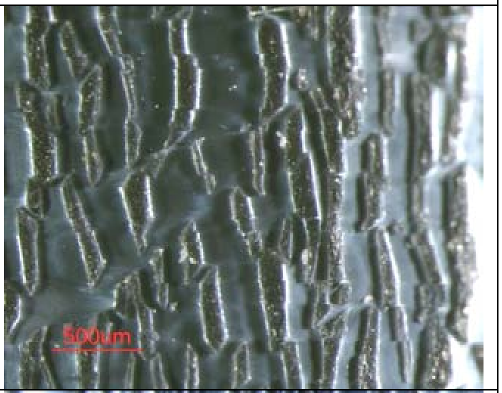
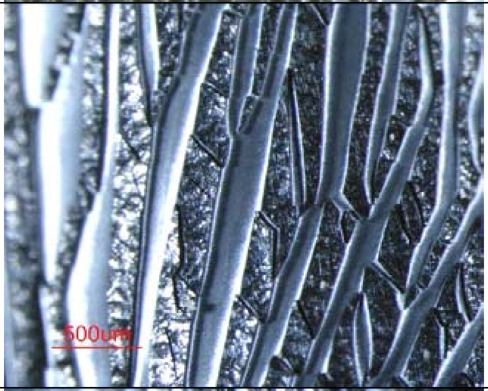
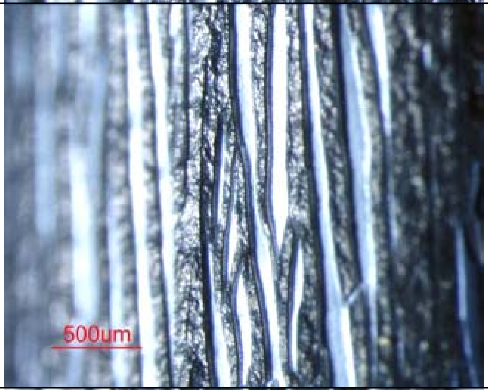
Sample	Service Time, years	Bend Back Test Result
Bakersfield CA Sample 5 – 7708 N. Laurelglen Blvd. 1” Mfg – UNK OIT: 0.50 🟥 CI (ATR): 0.085 🟨 CI (T): 0.061 🟨	31.03	
Bakersfield CA Sample 6 – 12402 Woodson Bridge Dr 1” DR9 PE 3408 Mfg – Wesflex OIT: 2.70 🟥 CI (ATR): 0.081🟨 CI (T): 0.012 🟩	7.09	
Bakersfield, CA Sample 7- 11710 Clarion River Dr. 1” DR9 PE 3408 Mfg – Wesflex OIT: CI (ATR): CI (T):	9.67	
Bakersfield, CA Sample 8 - 13501 Morocco Ave. 1” Mfg – Wesflex OIT: CI (ATR): CI (T):	17.94	

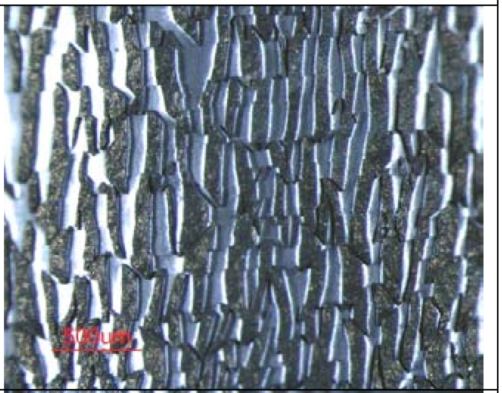
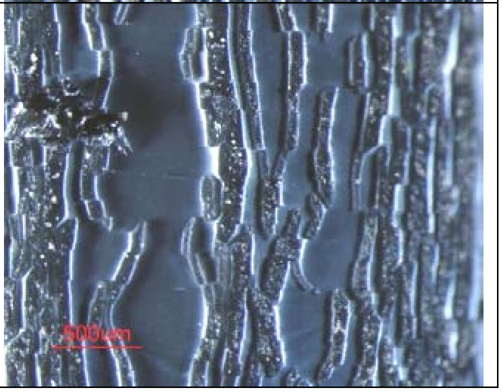
Sample	**Service Time, years**	**Bend Back Test Result**
Bakersfield, CA Sample 9 - 14400 San Esteban Ave. 1” Mfg – UNK OIT: CI (ATR): CI (T):	24.63	
Bakersfield CA Sample 10 – 3821 Ranier CT 1” Mfg – Wesflex OIT: 4.00 🟥 CI (ATR): 0.174 🟥 CI (T): 0.014 🟩	19.61	
Bakersfield CA Sample 11 – 5612 Anise CT ¾” Mfg – UNK OIT: 0.40 🟥 CI (ATR): 0.140 🟥 CI (T): 0.149 🟥	32.64	
Bakersfield, CA Sample 12 - 9900 Riverrock Dr. 1” Mfg – UNK OIT: 1.80 🟥 CI (ATR): 0.147 🟥 CI (T): 0.032 🟩	26.12	

Sample	Service Time, years	Bend Back Test Result
Bakersfield, CA Sample 13 - 1102 Hilaire Blaise Dr. 1” DR9 Mfg – Wesflex OIT: CI (ATR): CI (T):	9.86	
Bakersfield, CA Sample 14 - 901 Mohawk St. #66 1” Mfg – UNK OIT: CI (ATR): CI (T):	28.59	
HDOT Dillingham AF 8” IPS Mfg – ? OIT: 21.40 🟩 CI (ATR): 0.150 🟥 CI (T): 0.012 🟩	7.00	
CA Water Service Visalia 120 14” IPS Mfg – JMM OIT: 26.40 🟩 CI (ATR): 0.053 🟨 CI (T):0.004 🟩	3.00	

Sample	Service Time, years	Bend Back Test Result
Henderson, NV 119 St. Alban ¾” Mfg – Wesflex OIT: CI (ATR): CI (T):	23.14	
Henderson, NV 354 Templeton ¾” Mfg – Wesflex OIT: 0.50 🟥 CI (ATR): 0.099 🟨 CI (T): 0.024 🟩	22.14	
Hamilton, OH 10 Carlton ¾” DR9 Mfg – Moore Blue Diamond OIT: CI (ATR): CI (T):	1.98	
Hamilton, OH 1024 Tiffen ¾” DR9 PE 3408 Mfg – Driscopipe OIT: CI (ATR): CI (T):	11.97	

Sample	**Service Time, years**	**Bend Back Test Result**
Hamilton, OH 1027 Tiffen ¾” DR9 PE 3408 Mfg – Driscopipe OIT: 0.30 🟥 CI (ATR): 0.221 🟥 CI (T): 0.003 🟩	12.03	
Hamilton, OH 627 Hayes ¾” DR9 Mfg – UNK OIT: CI (ATR): CI (T):	11.32	
Hamilton, OH 4055 Pembroke ¾” Mfg – Moore Blue Diamond OIT: CI (ATR): CI (T):	2.31	
Hamilton, OH 24 Carlton ¾” DR9 Mfg – Moore Blue Diamond OIT: CI (ATR): CI (T):	1.40	

Sample	Service Time, years	Bend Back Test Result
Hamilton, OH #1 Unknown-C.O.H. ¾” DR9 Mfg – Moore Blue Diamond OIT: CI (ATR): CI (T):	NA	
Hamilton, OH 112 Tari Ct. ¾” DR9 Mfg – Driscopipe OIT: CI (ATR): CI (T):	6.48	
Hamilton, OH 24 Carlton 7/31/2007 ¾” DR9 Mfg – Moore Blue Diamond OIT: CI (ATR): CI (T):	1.16	
Hamilton, OH #2 Unknown-C.O.H. ¾” DR9 Mfg – Moore Blue Diamond OIT: CI (ATR): CI (T):	1.29	

Sample	**Service Time, years**	**Bend Back Test Result**
Hamilton, OH 128 Washington St. ¾" DR9 Mfg – Aqua-Jet OIT: 0.40 🟥 CI (ATR): 0.291 🟥 CI (T): 0.830 🟥	5.78	
Hamilton, OH 627 Hayes ¾" DR9 Mfg – Organgeburg OIT: CI (ATR): CI (T):	1.31	
Hamilton, OH 121 Beckett ¾" DR9 Mfg – Aqua-Jet OIT: CI (ATR): CI (T):	5.80	
Hamilton, OH 4117 Bedford ¾" DR9 Mfg – Moore Blue Diamond OIT: CI (ATR): CI (T):	3.00	

Sample	**Service Time, years**	**Bend Back Test Result**
Hamilton, OH 3425 Benninghoffen ¾” DR9 Mfg – Orangeburg OIT: CI (ATR): CI (T):	11.39