

## LITERATURE REVIEW: EFFECT OF ClO<sub>2</sub> ON AGEING OF POLYMER MATERIALS AND RELATED TEST METHODS

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### SHORT SUMMARY

The lack of a fast, universally-accepted test method for chlorine-dioxide-disinfected water is hindering the development of improved plastic piping materials. A literature survey was performed to define the degradation process in which chlorine dioxide affects the ageing of polypropylene, and to describe and reflect on the different test methods stipulated by standards and developed by research institutes.

### KEYWORDS

*Oxidative degradation, Aging, Polypropylene, Chlorine Dioxide*

### ABSTRACT

*Chlorine dioxide (ClO<sub>2</sub>) is increasingly used in drinking water applications, due to its high efficiency as a disinfectant. However, it also attacks polyolefins more aggressively than hypochlorite (ClO<sup>-</sup>). This has led to premature failure of water pipes, especially at higher service temperatures.*

*To make polyolefins in general, and polypropylene specifically, more resistant to ClO<sub>2</sub>, it is imperative that the degradation mechanism is understood. Furthermore, these materials need to be tested in a rapid but functional manner to verify their resistance to the relevant failure mechanism as found in service. A literature survey was therefore carried out to define the degradation process and to describe and reflect on the different test methods stipulated by standards and developed by research institutes. It was concluded that it is imperative to ensure that the failure mode is not altered by accelerated ageing. Test methods should therefore use realistic concentrations and temperature conditions, which should be as close as possible to service conditions. This makes acceleration difficult. Flow, pH and oxidation reduction potential (ORP) must be monitored and controlled. Finally, the presence of an (applied) stress is crucial for the test to be representative of real service failures.*

*If pipe failure is the parameter used to characterize pipe performance, it is not realistic to expect results within a reasonable time. This means that another ranking criterion is required. A better understanding of the degradation mechanism of PP in ClO<sub>2</sub> and the influence of stress is necessary to find the best parameters to identify an early warning signal that can predict final pipe failure.*

## INTRODUCTION

Globally, water distribution networks are commonly disinfected using chlorination. Depending on national standards, various chlorine-containing compounds are used for this purpose. Chlorine dioxide ( $\text{ClO}_2$ ) is very efficient as a disinfectant, because it is a strong oxidizing agent capable of disinfecting water containing viruses and chlorine-resistant pathogens, and is especially popular for Legionella prevention. However, due to its strong oxidizing properties,  $\text{ClO}_2$  attacks polyolefins more aggressively than hypochlorite ( $\text{ClO}^-$ ). At the same time, polypropylene (PP) is becoming increasingly popular as a pipe material in the (domestic) water distribution sector, and in hot & cold systems as an alternative to other materials. Practical experience has demonstrated that a significant number of PP materials fail prematurely due to exposure to potable water containing  $\text{ClO}_2$ .

To make polyolefins in general, and PP specifically, more resistant to  $\text{ClO}_2$ , it is imperative to understand the failure mechanisms that arise when PP and  $\text{ClO}_2$  interact. Furthermore, these materials need to be tested in a rapid but functional manner to verify their resistance to the relevant failure mechanism as found in service. A literature survey was therefore carried out to define the degradation process and to describe and reflect on the different test methods stipulated by standards and developed by research institutes.

## POLYMER DEGRADATION

The macroscopic mechanism responsible for final pipe rupture when tested with water containing any of the three disinfectants chlorine, chloramines or chlorine dioxide is considered to be the same, i.e. depletion of stabilizer at the inner pipe surface, oxidation of the inner layer due to chain fracture, microcracking of the inner layer due to chemi-crystallization [1], crack propagation through the wall with oxidation in advance of the crack front and final rupture of the remaining pipe, ultimately resulting in pipe failure [2]. However, there is a difference in reactivity between the various disinfectants, which is also reflected in their disinfectant properties. Scientists have observed that chlorine dioxide attacks polyolefin (polyethylene, polypropylene and polybutylene) pipes [2-4] more aggressively than free chlorine or chloramine. One explanation for this could be the fact that chlorine dioxide is a dissolved gas, which diffuses into the polymer more readily. In addition, chlorine dioxide reacts easily with phenols. This is one of the advantages of chlorine dioxide as a disinfectant, but since the long-term stabilizers are usually hindered phenols, this will lead to a rapid reaction with the stabilizer. This makes the material susceptible to oxidative degradation.

The degradation of polymers exposed to chlorine (as  $\text{HOCl}$ ) has been attributed to direct attack on the polymer by highly-reactive radicals (such as  $\text{OH}\cdot$  and  $\text{Cl}\cdot$ ), as described by Mitroka et al. [5] and Vu et al. [3]. For chlorine dioxide, on the other hand, there is some disagreement about whether chlorine dioxide can attack the polymer directly, or proceeds through species that arise when chlorine dioxide is reduced. Colin et al. [4] propose that it is only the initiation and one termination step that involve chlorine dioxide. The initiation is believed to be caused by hydrogen abstraction from the polymer (polyethylene), which leads to the radical chain reactions. While chlorine dioxide has an unpaired electron, others have reported that it is not reactive enough to abstract a hydrogen atom from a hydrocarbon [3,6]. Yu et al. [3] therefore propose that it is a strongly hydrogen-abstracting species such as  $\text{ClO}\cdot$  that will initiate the degradation of the polymer. How this is formed is not fully understood, but it has been suggested that it involves proton and electron transfer with a phenolic antioxidant.

One of the authors' own research indicates that  $\text{ClO}_2$  accelerates the auto-oxidation of the polymer [7]. Practical situations indicate that PP pipes show signs of failures when in

contact with ClO<sub>2</sub> solutions in a way that may be similar to Environmental Stress Cracking (ESC). It appears that the presence of an applied stress is crucial for the final rupture to occur. ESC is a common cause of unexpected brittle failure in thermoplastic polymers. The exposure of a polymer to an aggressive liquid tends to accelerate the crazing process, initiating crazes at stresses that are much lower than the stress that results in crazing in the absence of an aggressive liquid e.g. in air. The action of either a tensile stress (e.g. due to internal pipe pressure) or a corrosive liquid alone would not be sufficient to cause failure. However, with ESC, the initiation and growth of a crack is caused by the combined action of the stress and a corrosive environmental liquid.

It may be that both phenomena – oxidation and ESC – are jointly responsible for the degradation and thus the reduction in service life found for PP exposed to ClO<sub>2</sub>.

## **TEST METHODS**

At present, pipe manufacturers attempt to extend the time to failure by altering the polymer resin, additive package and/or wall thickness. However, since there is no fast and universally-accepted test method for chlorine-dioxide-disinfected water, the development of new material mixtures and compositions relies on a limited number of general testing standards and test methods developed by manufacturers and research institutes.

The lay-out of the methods often varies depending on whether they are designed for resin/additive testing or for pipe testing. Their validity as a means of properly ranking materials according to service life is often questionable due to the necessity of accelerating the testing.

The ASTM test methods F2023 [8] and F2263 [9] use only time to failure to characterize the pipe performance. This type of testing thus contributes very little knowledge about the degradation mechanism responsible for pipe failures. It also fails to give any indication as to whether the degradation mechanism is the same as occurs during real service conditions.

It is also important that testing the resistance of polymers to chlorinated disinfectants should not only characterize the mechanical properties, or only the chemical stability – both types of tests are essential [10].

## **Characterization**

In the first instance, characterization of the material by means of a visual inspection should not be neglected [11]. Rozental-Evesque et al. have identified eight degradation levels, ranging from whitening and crazing to micro-cracking and cracking after performing the reverse bend back test (RBBT), in accordance with ASTM D2513 [12] (this may also be carried out in accordance with AWWA C906-07 [13]). This is referred to as the “Overall Degradation Layer Index”, abbreviated to “ODL index” [14].

Scanning electron microscopy (SEM) can be used to investigate the fracture surface [15]. This can further increase the understanding of the failure mechanism, and can thus assist with classification.

One widely-used characterization tool is the Oxidation Induction Time (OIT). This is used in accordance with standards such as ISO 11357-6 [16] or ASTM D3895 [17] to determine the thermal oxidative resistance of polymeric materials. Various studies [13,14,18-22] have measured low OIT in pipes that have experienced premature brittle failure. The OIT can be seen as an effective tool, because a linear relationship exists between the concentration of phenolic antioxidant and the observed OIT. However, it does not necessarily reflect the specific

oxidative degradation of either the additives or the polymer itself induced by chlorinated disinfectants [23]. It is therefore possible that the OIT value decreases enormously under mild conditions, while the elongation at break shows almost no change [24], or that there is oxidation of the polymer even if there is still stabilizer present in the material [25]. In other papers, the Oxidation Onset Temperature (OOT) is used [15,26], to which the same warning applies.

Another widely-used tool is infrared spectroscopy (FTIR), since this can measure the formation of carbonylic oxidative products, which are one of the most common degradation products of polyolefins [13-15,18,26,27]. The Carbonyl Index (CI) is the ratio between a carbonyl peak and a typical peak of the polymer, referred to in standards such as DIN 53383-2 [28].

FTIR can also lead to greater understanding of the consumption of stabilizer, since water absorption can be caused by the reaction products of the degraded stabilizer [25] and the oxidized polymer has also become much more polar.

For both OIT and FTIR, it can be useful to make a profile at varying depths to gain an understanding of the differences between surface degradation and bulk degradation [26,27,29].

Oxidation of polyolefins also affects the materials' short-term fracture mechanics [29,30]. It is therefore important to also test the mechanical properties of the materials. For mechanical testing, the most important characterizing parameter is often considered to be the elongation at break [11,14,27,31-33], principally because it reflects the embrittlement that can occur due to attack by the disinfectant. However, care must be taken, as the elongation at break can easily be influenced by pre-existing damage, and such influence is further amplified when chemical oxidation takes place [10].

Because it is not always possible or representative to test the mechanical properties of a pipe on tensile bars, Sanchez and Rozental-Evesque et al. developed the NOL ring test [11,13,14]. This was inspired by ASTM D 2290-04 [34] and adapted to small-diameter pipes (25 to 63 mm).

For this test, 20 mm wide rings are cut normal to the pipe axis with parallel sides. Two reduced areas are obtained by drilling two holes of 6.5 mm (0.26 in) in diameter, located where the minimum wall thickness is measured and diametrically opposite (i.e. at 180° from this point) respectively. The test specimen is subjected to a (hoop) circumferential stress using a ring tensile test (12.7 mm/min). The stress at break is similar to the circumferential pressure at failure for pipes subjected to pressure tests. The elongation rate here is taken as the ratio of the initial length (assumed to be 3 mm, which may be disputed) to the crosshead displacement. This leads to "NOL ring results" or an "NRR index". The first results showed that this test is a better indicator of degradation of the pipe material than a normal tensile test.

Nevertheless, this test method can lead to a relatively large amount of scatter in the final results. This may be due to preparation effects, since cutting can introduce small scratches that can initiate failure, but also because yielding on one side or both sides of the ring leads to a completely different elongation at break.

## **Simulation tests**

Now that the characterization is established, the pipe samples need to be exposed to chlorine disinfectants. Such exposure needs to accelerate degradation in respect of the environment in

the field, while preserving the same failure mechanism. This leads to many challenges and choices when selecting the test parameters, such as temperature, disinfectant concentration, sample shape/pipe dimensions, stress on the material, flow speed, pH of the fluid, the preferred failure time, etc. As such, many companies now rely on their own customized accelerated test method to check the performance of new materials. However, as Costa et al. have correctly observed: *“the lack of coherent and unambiguous accelerated test methods certainly obstructs the fast development of new materials and the validation of their improved performance against water disinfectant.”* [10]

Perhaps the simplest form of exposure is an immersion test. Samples of various shapes can be used, such as films [23], slices [25] or tensile test bars. The latter is prescribed by ISO 4433-1 [35]. The solution is generally refreshed every few days. However, because ClO<sub>2</sub> is sensitive to light and temperature, the concentration will decrease over time [29]. It is therefore very difficult to maintain a constant concentration of ClO<sub>2</sub>. Continuous monitoring and correction of the ClO<sub>2</sub> concentration are thus essential.

A second exposure method consists of using a vessel with a fresh ClO<sub>2</sub> flow, or a recirculating ClO<sub>2</sub> loop. In this case, a special dosing unit for ClO<sub>2</sub> is placed before the vessel, which contains the samples. By continuously monitoring the concentration, the ClO<sub>2</sub> can be dosed accordingly. From flow-through systems that use chlorine, we know that systems that continuously replenish the chlorine give significantly shorter times to failure than re-circulating systems without added chlorine [29].

There are many different setups in use. A short overview of five different test setups, including some test parameters, is given below:

1. **NOL Ring Creep Test.** This test is standardized in France by *XP T 54-986* and is used to age ring samples by submerging them in a thermostatically-controlled cell containing an aqueous solution of chlorine dioxide at 40°C, a hoop stress of 7 MPa and a concentration of 1 or 2 ppm ClO<sub>2</sub>. The solution renewal flow should be such that the chlorine dioxide solution does not deteriorate for the duration of the immersion. For example, a flow of 2 to 4 l/h is suitable for a cell with a volume of 5 l. The cell is fitted with stirring apparatus to homogenize the solution and make the chlorine dioxide attack uniform. The elongation at break is subsequently determined using the NOL ring test. [36,37]
2. **IRETI test method.** In this test, tensile test samples are placed without stress in an autoclave at 40°C with a ClO<sub>2</sub> concentration of 1-5 ppm, a circulation flow rate of 2.7 m<sup>3</sup>/h, an exchange rate with fresh water of 1 m<sup>3</sup>/day, an input pH value of 7.2, an input pressure of 2.5 bar and an exposure time typically between 30 and 90 days. The samples are subsequently tested using a tensile test in accordance with ISO 527 at 10 mm/min to determine the elongation at break. [36]
3. A similar setup as for the IRETI test method at LyondellBasell uses 60°C de-ionized water and a ClO<sub>2</sub> concentration of 20 ppm, a circulation flow of 1 m/s (~32 l/min) and a pH value of 6.5. It appears to be carried out at atmospheric pressure. Test specimens are exposed to the medium without any stress. [38]
4. PCCL has developed similar equipment [26,27]. The temperature may reach 60°C, and they use a 500 l/h recirculation flow rate. The ClO<sub>2</sub> concentration is max. 10 ppm (NaClO is max. 100 ppm). The pH is 6.8 and the oxidation reduction potential (ORP) is 650 mV. Unstressed blocks are exposed and thin films are cut for investigation. [15,31]
5. The test method of KTH uses a continuous supply of fresh water at 70°C containing chlorine dioxide (10 ppm at pH = 6.8) and unstressed PE tape of 0.3 mm thick. [10]

Of course, the method that is closest to practice is to expose pipes to chlorine dioxide. Two principle methods are available: the ASTM methods and the Accelerated Aging Bench of SUEZ, although other setups also exist, such as test facilities at Element (formerly Bodycote) [29], the Aliaxis R&D Center [19] and the Anjou Recherche Technical Center [39]. Only the first two are discussed below in more detail.

There are two ASTM test methods: F2023 for PEX [8] and F2263 for PE [9]. There is no test method for PP. ASTM F2389 (*Standard Specification for Pressure-rated Polypropylene (PP) Piping Systems*) simply refers to F2023 (PEX), therefore the suitability of the test parameters (e.g. the temperature) for this material is questionable.

Both ASTM methods are based on pressured pipes with flow and recirculation of the test fluid (> 0.04 m/s), while the pipes are submerged in hot water (temperature  $\geq 95^{\circ}\text{C}$ ).

The tests were originally designed for pressure testing with water, and were subsequently modified for chlorine (as HClO). However, it has been claimed that they are also valid for ClO<sub>2</sub> and chloramines. Test fluid prepared from reverse-osmosis (RO) or de-ionized (DI) water must have a pH in the range 6.5 to 8.0 and contain 2.5 ppm to 5 ppm (milligrams per liter) of free chlorine. The pH and free chlorine concentration combination must yield a minimum ORP of 825 mV for the test fluid. [8]

The time-to-failure is measured and an extrapolated time is calculated using ISO 9080 [40] and the Miner's Rule in accordance with ISO 13760 [41]. It is recognized that *"the extrapolated values only provide a relative indication of the resistance to the oxidative effects of hot, chlorinated water [...] The performance of a material or piping product under actual conditions of installation and use is dependent upon a number of factors including installation methods, use patterns, water quality, nature and magnitude of localized stresses, and other variables of an actual, operating hot-and-cold water distribution system that are not addressed in this test method."*

Nishimura et al. [42] state that *"the stress rupture test by circulating a 3 ppm aqueous solution of chlorine at elevated temperature is a suitable test method to evaluate the actual life of plastic pipes."*

SUEZ has prepared an accelerated-aging bench test [43]. The aging is performed under 6 bar of pressure, with a high level of disinfectant content (4 mg/l of chlorine or 1 mg/l of chlorine dioxide) at 40°C to accelerate the degradation mechanisms [44]. The pH value is 7.2 and the circulating flow is 200 l/h.

## **DISCUSSION**

Of the test methods described above, the ASTM test is the most widespread. However, there are many reports questioning the suitability of this method, both in terms of its accuracy in accelerating the degradation correctly, and also because it takes a very long time to generate results. The ASTM test method also requires pipes to be tested, which may be a drawback during resin and additive formulation testing.

Hassinen and Svedberg [45] have shown that using the ASTM F2023 test may result in Stage II rather than Stage III failure, and that a small change in the extrapolation stress will have a major impact on the predictions, due to the flat behavior of the regression lines. It is possible that estimations may end up being overly pessimistic or optimistic. Moreover, if the test temperature is too high, this can affect the material characteristics and performance. The

temperature acceleration factors between 115/105°C and 105/95°C must therefore be comparable. The study shows that not all materials are suited to testing at 115°C.

It is also proposed that a reference blank sample using no chlorine (0 ppm) with the same circulation conditions be performed to allow the effect of chlorine to be measured, rather than a combination of chlorine, dissolved oxygen and flow.

One of the authors' own research [25] has shown that, during exposure to high temperatures, stabilizer consumption takes place both at the surface and in the bulk, causing a physical loss rather than stabilizer consumption due to penetrating ClO<sub>2</sub>. It is concluded: *"when using temperatures higher than around 70°C (for PP), the physical loss of stabilizer is much higher than in service conditions of around 50°C."*

Chung et al. [22] have suggested that the ASTM F2263 test methodology is capable of replicating the mechanisms of field aging under accelerated conditions. They have also attempted to accelerate failure using a notch at the inner surface [46]. For the two materials studied, the relationship appears to be similar to a direct correlation between the % notch depth and the reduction in failure time. For example, with a notch of approximately 40% of the wall thickness, the time to failure is also reduced by approximately 40%.

A clear downside is that the tests are extremely lengthy (1-3 years depending on the polyethylene pipe lifetime) [31]. Nevertheless, the test results from these long-term tests give a reasonable indication of the performance of any material. [10]

Since a wide range of test methods exist, the authors endorse calls for a fast and reliable test method to determine the resistance of polyolefins to chlorine dioxide, without altering the failure mechanism. This is especially true for polypropylene, although most research focuses on polyethylene. It is understood that the development of another new test method is challenging, but if laboratories make small adjustments to their test methods, at least some increase in alignment is possible.

It is therefore proposed that the following test parameters be considered and reported:

- **Concentration.** Due to the unstable nature of chlorine dioxide, it is very important to control the concentration of the aqueous solution accurately. A recirculating or flow-through system is required, and proper monitoring and adjustment is a crucial part of any experiment. [26]
- **Flow.** The flow should be controlled and registered. Many different flows are given in the literature [8,31,36,38,43]. This means that it is necessary to report not only the volume per time unit, since this is dependent on the volume of the vessel used, but also the rate at which the solution passes the samples.
- **pH and ORP.** Although little research has focused on the effect of pH or oxidation reduction potential (ORP) on polyolefins while exposed to ClO<sub>2</sub>, it is important to monitor and register this to allow comparison with other studies. It is important to note that the specific ORP/pH/chlorine relationship is dependent on specific water quality [8].
- **Temperature.** The temperature must remain within reasonable limits that are comparable to practice. As mentioned above, the physical loss of antioxidants is very dependent on temperature, and should not be confused with chemical and oxidative attack by ClO<sub>2</sub>, which has different temperature dependence. If the temperatures used are too high, it is possible that Stage II failure will result, rather than Stage III. Moreover, this may change the material characteristics, such as crystallinity, and performance [45]. In addition, Chung et al. [47] have found a temperature discontinuity in chlorine

dioxide testing of PE pipe. This means that a non-Arrhenius temperature relationship is observed, which means that it does not appear to be possible to conduct extrapolations based on the Arrhenius temperature relationship.

- **Pressure and stress.** As mentioned above, it appears that the presence of an (applied) stress is crucial for final rupture to occur. For example, PE responds differently to different pressures when exposed to ClO<sub>2</sub> [31]. Testing samples without any stress is therefore not realistic. Due to the possible effect of crystallinity, preference should be given to pipes or to ring-shaped samples prepared directly from pipe.

## CONCLUSIONS

Pipe manufacturers attempt to extend the time to failure of their products by altering the polymer resin, additive package and/or wall thickness. However, the development of new material mixtures and compositions relies on a few general testing standards and test methods developed by manufacturers and research institutes. Various test setups use loops, in which pipe samples are exposed to hypochlorite or ClO<sub>2</sub>, or loops containing (stressed) rings or other small samples. Other tests lack continuous refreshment of the solution and are only based on immersion. Many parameters can be monitored during the various tests, and even more characterization tests are possible afterwards. However, the lack of a rapid, universally-accepted test method is hindering the development of new piping materials.

When developing such a test method, it is imperative that the failure mode is not altered by accelerated ageing. Test methods should therefore use realistic concentrations and temperature conditions, which should be as close as possible to real service conditions. This makes acceleration difficult. Flow, pH and ORP must be monitored and controlled. Finally, the presence of an (applied) stress is crucial for the test to be representative of real service failures.

Using pipe failure as the parameter for characterizing the pipe performance within a reasonable time frame is not realistic, and as such some other ranking criterion is required. A better understanding of the degradation mechanism of PP in ClO<sub>2</sub> and the influence of stress is necessary to find the best parameters to identify an early warning signal that can predict final pipe failure.

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