Journal of Hazardous Materials 500 (2025) 140437

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

A new experimental approach to chemical ageing in materials and piping for drinking water infrastructure exposed to chlorine dioxide

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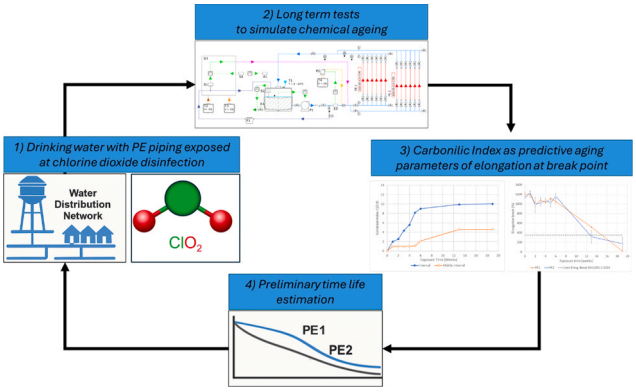
HIGHLIGHTS

- Accelerated aging of polyethylene pipes exposed to ClO_2 was investigated.
- Durability of PE materials in drinking water sector was evaluated.
- Correlation of macro/micro pipe traits after ClO_2 exposure was verified.
- Lifetime was estimated after chemical ageing at different temperatures.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Polyethylene pipes
Chlorine dioxide
Accelerated chemical ageing
Drinking water
Water distribution systems

ABSTRACT

The long-term durability of polyethylene (PE) pipes in water distribution networks is gaining importance due to updated European regulations on drinking water safety. This study investigates the accelerated ageing of two PE grades (PE1 and PE2) exposed to chlorine dioxide (ClO_2), a disinfectant known for its high efficacy and minimal formation of harmful by-products. Pilot-scale tests were conducted under realistic and dynamic conditions to evaluate chemical, microstructural, thermal, and mechanical degradation. The experimental approach introduces a novel preliminary ageing protocol, integrating both micro- and macro-scale characterization of materials exposed to ClO_2. Physicochemical analyses revealed a significant increase in the carbonyl index, particularly in PE1, which exhibited a higher oxidation rate (0.287 CI/CI_0/day) compared to PE2 (0.216 CI/CI_0/day). Crystallinity also increased by approximately + 4 % in PE1 and + 2 % in PE2. These changes were accompanied by a progressive decline in mechanical performance: between weeks 6 and 13, reductions in elongation at yield and ductility were observed. From week 12 onward, both materials failed to meet the mechanical conformity threshold defined by EN 12201–2:2024, with elongation at break falling below 350 %. Based on degradation kinetics, the estimated service life under real operating conditions was 18 years for PE1 and 23

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https://doi.org/10.1016/j.jhazmat.2025.140437
Received 4 August 2025; Received in revised form 30 October 2025; Accepted 8 November 2025
Available online 10 November 2025

years for PE2 at 40°C. The durability of PE1 and PE2 ranges from 19 to 60 years, depending on ClO_2 levels and temperature.

1. Introduction

Over the past four years, several new regulations have emerged in the drinking water sector. These include both direct measures related to water quality and emerging pollutants, as well as indirect measures linked to the implementation of Water Safety Plans. In this context, the latest European Drinking Water Directive (EU 2020/2184) introduced several innovative elements, including the adoption of safety standards based on WHO recommendations [1]. Among these, the directive promotes a risk-based approach that encompasses the entire water supply chain. It also includes provisions concerning the use of chemical substances and materials in contact with drinking water, such as treatment chemicals and filtration media.

Within this framework, the interaction between pipe materials, disinfectants, and water quality has become a central issue for chemical ageing. These interactions can have significant implications for the technical performance of water supply systems, particularly in terms of water leakage, service interruptions, and infrastructure lifespan.

Chlorine dioxide (ClO_2) is a powerful oxidant widely used for the inactivation of pathogens in drinking water. Its oxidative capacity and disinfection efficiency are significantly higher than those of other chlorine-based disinfectants, such as hypochlorite and free chlorine [2]. ClO_2 is particularly preferred in waters with high concentrations of organic matter including nitrogen derivatives, as it does not produce undesirable by-products such as trihalomethanes, haloacetic acids, or nitrosamines [3].

Typical average ClO_2 dosages in water distribution systems range from 0.2 to 2.0 mg/L, depending on the dosing method and application point [4]. Among the materials most commonly used in water pipelines, polyethylene (PE) is particularly sensitive to ClO_2 exposure. Chlorine dioxide is more aggressive toward plastic materials, including PE, than other chlorine-based disinfectants. It has been observed that PE pipes in water distribution systems may suffer from premature failure when exposed to ClO_2. The issue is particularly widespread considering that polyethylene pipeline systems have been used for drinking water supply since their introduction in the 1950s [5]. Chlorine dioxide initially attacks the standard antioxidants (typically phenolic compounds) and subsequently the polymer matrix of PE pipes, with greater aggressiveness than other disinfectants [6]. In fact, it has been reported that ClO_2 depletes antioxidants more than four times faster than chlorinated water [7].

One possible explanation for the aggressive degradation of polyethylene (PE) pipes by chlorine dioxide (ClO_2) is that ClO_2, being a dissolved gas, diffuses more rapidly into the polymer matrix than other disinfectants, thereby accelerating degradation reactions [8]. To mitigate this, phenol-based antioxidants are typically incorporated into PE during manufacturing to inhibit the reaction between ClO_2 and the polymer. However, some studies have hypothesized that the interaction between ClO_2 and these antioxidants may lead to the formation of reactive chlorine species, which can react even more rapidly with the polymer, ultimately negating the intended protective effect [9].

In general, numerous authors (e.g., [4,10]) have reported that the chemical and physical factors influencing pipe rupture and aging are closely linked to both material characteristics (e.g., polymer additives, surface morphology, crystallinity) and environmental conditions (e.g., temperature, atmospheric exposure, coatings, pressure). Although several manufacturers have developed new PE formulations with enhanced resistance to ClO_2, there is currently no harmonized or standardized method for testing and evaluating the performance of these materials in contact with ClO_2. A variety of accelerated ageing protocols have been proposed in the technical-scientific literature, each employing different test conditions, such as pressure, temperature, and ClO_2 concentration, which complicates the comparison of results across studies.

This study aims to address the current lack of normalized protocols for long-term testing of polyethylene (PE) pipes by proposing an innovative methodology derived from a critical review of recent literature [6,11]. As highlighted in these works, existing semi-realistic ageing techniques fail to reliably predict the service life of PE pipes under actual operating conditions. This paper addresses these gaps by presenting innovative experimental approaches designed to quantify the chemical accelerated ageing of PE pipes under semi-realistic and dynamic conditions in the presence of ClO_2. Furthermore, this paper seeks to identify the most relevant characterization parameters for in-service pipes, enabling a robust correlation between chemical micro-characteristics and mechanical macro-properties. This integrated approach is intended to support a more accurate determination of the real-world lifetime of PE pipes used in water distribution networks. The method and the results presented are entirely novel, stemming directly from the preliminary review analysis conducted by the authors [6].

2. Material and methods

2.1. Experimental set-up according to the literature review

The subsequent review of the state of the art served as a foundation for defining the experimental plan and methods used. The ageing of polyethylene (PE) water pipes exposed to chlorine dioxide (ClO_2) is driven by a mechanochemical process involving: (a) oxidation of antioxidants and the polymer matrix, (b) crack initiation, and (c) crack propagation [12]. The total fracture time is determined by the degradation time of antioxidants at the inner pipe wall, followed by crack initiation and propagation phases. This failure mode is complex to quantify and highly sensitive to system operating conditions. Chlorite formation is influenced by several factors, including oxidizable substrates, initial ClO_2 concentration, temperature and pH [13]. Notably, a ClO_2 concentration of 0.15 mg/L reduces pipe lifespan to 10 years, compared to the 50-year design standard [7]. Ageing accelerates above 20 °C [14], while lower pressure and increased pipe thickness or diameter slow degradation [12,15]. Moreover, in real-world aqueducts, alternating cycles of water flow and stagnation can wash away protective materials and extend contact time, intensifying polymer degradation [7]. Once antioxidants at the polymer-solution interface are depleted, chain degradation begins. Micro-cracks formed under mechanical stress allow ClO_2 to penetrate and promote further crack growth—a phenomenon known as assisted crack growth. Phenolic antioxidants offer initial protection but react rapidly with ClO_2, generating radicals that accelerate polymer breakdown. Additionally, ClO_2 can permeate the PE matrix, leading to faster decomposition [7]. In summary, the priority parameters influencing PE ageing by ClO_2, ranked by importance, are: ClO_2 concentration, ClO_2^- concentration, ClO● concentration, water age/contact time, pressure and pipe thickness. According to this scenario, these main water parameters affecting PE ageing were considered to set up the experimental plan.

Regarding the piping test modalities, experimental trials under static conditions are more frequent in literature than those under dynamic situations, although the last ones are not representative of the operating conditions of the real aqueducts and do not consider the synergy between chemical and mechanical ageing. Therefore, dynamic tests that simulate real operation in the network are recommended [16]. The experimental conditions of the dynamic tests were critically discussed by the authors in Lancioni et al., [6] and are experimentally validated in

this study. Typical ClO_2 concentrations used in dynamic ageing tests range between 1 and 5 mg/L, with maximum pressures between 5 and 8 bar and temperatures from 40°C to 90°C [11]. A temperature of 40°C is the maximum measured in water supply systems [17] and the minimum tested in the literature during the dynamic accelerated tests. Lower test speeds (between 0.04 and 0.5 m/s) are more common than conventional operating speeds (1 m/s). In fact, the water velocity in the pipes influences the extension of the contact time (i.e. water age) between chlorine dioxide and chlorite with polyethylene. Furthermore, both mechanical and chemical characterization is essential for deeper understanding of the mechanisms of ageing by ClO_2 [11]. Moreover, from the analysis of the technical-scientific literature, the most used parameters for the chemical-mechanical characterization of PE are: Carbonyl Index (CI) through FTIR analysis, Oxidation Induction Time (OIT) and Degree of Crystallinity through DSC analysis, Qualitative SEM Analysis and Elongation at Break.

Based on these considerations, the experimental parameters were set and described as reported in the following paragraphs.

2.2. Preliminary characterization batch tests

In the first phase of the experimental activity, preliminary characterization tests were carried out on conventional pipe of polyethylene (PE1) in batch mode on 2 cm long specimens. The tests were executed in a thermostat bath at a controlled temperature of 40 °C with the main objective of making an initial approach to the definition of the macroscopic and microscopic properties of the material itself. The tests were carried out on PE1 with an exposure time of 21 and 42 days (in line with the dynamic tests subsequently carried out) at dioxide dosages of 5 and 10 mg/L. The initial test conditions are summarized in Table 1.

In addition, tests were carried out, at the same conditions, in the absence of PE pipes to evaluate the chlorine dioxide decay curve. Characterization of the test specimens was implemented at 0, 21 and 42 days, to identify several chemical and mechanical parameters. Specifically, Carbonyl Index (CI), ratio of the amplitudes of the spectrometric peaks of the carbonyl group and the starting polymer, was measured by FTIR experiments to determine the polymeric degradation of the material. Also, TGA experiments were used to quantify the thermal degradation curves and any volatile compounds due to the decomposition of the polymer with the purpose of showing the ageing index and the thermal stability. Oxidation Induction Time (OIT) at different depths and Degree of crystallinity were also determined, considering that OIT, usually, represents the consumption index of antioxidants. Visual analysis of qualitative status and cracks (micro/macro) on the material surface was defined by Scanned Electron Microscope and the percentage presence of chlorine in the polymeric material was detected by EDX. Finally, the tensile test for elongation at break (according to [18]) was developed to verify the mechanical proprieties.

2.3. Long term dynamic experimental tests

The objective of the dynamic tests is the development of normalized procedure specifically designed to investigate the effect of ClO_2 chemical attack. The tested pipes were new, the tests time was for some weeks and upon inspection after testing, showed no evidence of biofilm formation or biological layers. Therefore, the microbiological contribution was considered negligible. According to the parameters analyzed in the state of the art, Fig. 1 shows the P&ID (Piping and Instrumentation Diagram) of the experimental pilot used to perform continuous accelerated ageing tests on PE pipes in the presence of chlorine dioxide. The pilot plant is a prototype for studying ageing in a pressurized circuit under dynamic conditions with 12 pipe positions. The pilot thus makes it possible to replicate the ageing of PE pipes with different operating parameters, even up to pipe rupture. The parameters that can be set are: circuit pressure, circuit flow rate, continuous or batch operation, ClO_2 concentration and liquid temperature. The temperature was maintained by a heat exchanger R1.

Table 1
Initial setting conditions-Batch ageing tests.

PARAMETERS	TEST1	TEST 2	TEST 3	TEST 4
DN	20			
N°PE1 pipe	2			
Length of pipe (cm)	2			
ClO_2 dosage (mg/L)	5	10	5	10
P (bar)	Atmospheric pressure			
T (°C)	40			
Exposure time to ClO_2 (d)	21	21	42	42

The accelerated ageing test of PE pipes was performed through the pressurized test circuit. Water of aqueduct was used to support experimental replicability. Water was in contact only with the inner surface of the pipe as in the real aqueduct condition. Water and chlorine dioxide were circulated inside the pipes for 133 days, accelerating and simulating the oxidative mechanisms that occur in real aqueducts, at the testing conditions reported in Table 2. Middle test conditions from those referred in the state of the art, were preferred (T = 40°C, P = 6 bar, $[ClO_2]$ = 5 mg/L) to best replicate the chemical-mechanical ageing that occurs in real operative situations without an extreme enhancing of ClO_2 concentration, water pressure and temperature. Two different PE piping typologies were tested: PE1 and PE2. PE2 contains specific additives in the polymer mix to reduce oxidative processes.

Chemical characterizations and analysis frequency are reported in Table 3, for macro and micro parameters to support the predictive characterization of PE ageing in contact with Chlorine Dioxide. For FTIR and DSC the different parameters were measured in 4 sections for each sample (s1 sample external wall -depth 3 mm; s2 sample intermediate wall-depth 2.5 mm; s3 sample intermediate wall-depth 1.25 mm; s4 internal wall sample-depth 0.5 mm). Moreover, OIT was assessed in 3 sections for each sample (s1 sample external wall -depth 3 mm; s3 sample intermediate wall-depth 1.25 mm; s4 internal wall sample-depth 0.5 mm). For EDX and SEM both interior and external walls of each sample were analyzed. Vibrational infrared FTIR spectroscopy allows the chemical oxidation process of the polymer to be followed by measuring the carbonyl index which is calculated as the ratio of the total signal areas between 1800 and 1500 cm^{-1} (relating to the stretching of carbonyls and carboxyls) to the total signal areas between 1500 and 1450 cm^{-1} (relating to the bending of methylene chain groups) of the FTIR spectrum acquired in attenuated total reflection (ATR) and converted to absorbance. The spectra were acquired with a SHIMADZU IR Affinity-1S instrument. The OIT200 index measures the time after which oxidation of polyethylene begins when the material sample has been heated to 200°C in an inert atmosphere at a rate of 20 K/min and then kept at a constant temperature under oxygen flow. The measurement is carried out through calorimetric measurements (DSC) by monitoring the enthalpy of oxidation of the sample over time. The OIT was calculated according to ISO 11357–6:2018 using the tangent method. Oxidation Induction Time is thus given by the time required to reach the first oxidation peak following the transition from inert atmosphere to oxygen. OIT is generally proportional to the presence of phenolic antioxidants in the sample. A reduction in OIT indicates depletion of the antioxidants in the PE pipes; if OIT is close to zero minutes, there is, therefore, complete depletion of the phenolic antioxidants in the polymer matrix. Microscopic characterization tests (FTIR and DSC) were performed along several points at different depths, from the inside to the outside of the pipe to study the oxidation of the material along the pipe section. Observation of tube sections using an SEM Scanning Electron Microscope with EDAX Microanalysis (ESEM) allows them to highlight, quantify and characterize the micro-cracks. The addition of EDX spectroscopy makes it possible to determine the presence of foreign C, H and O atoms that are naturally present in oxidized samples. In particular, the presence of chlorine due to the diffusion of ClO_2 or other chlorine compounds on the surface of the polymer matrix can be monitored.

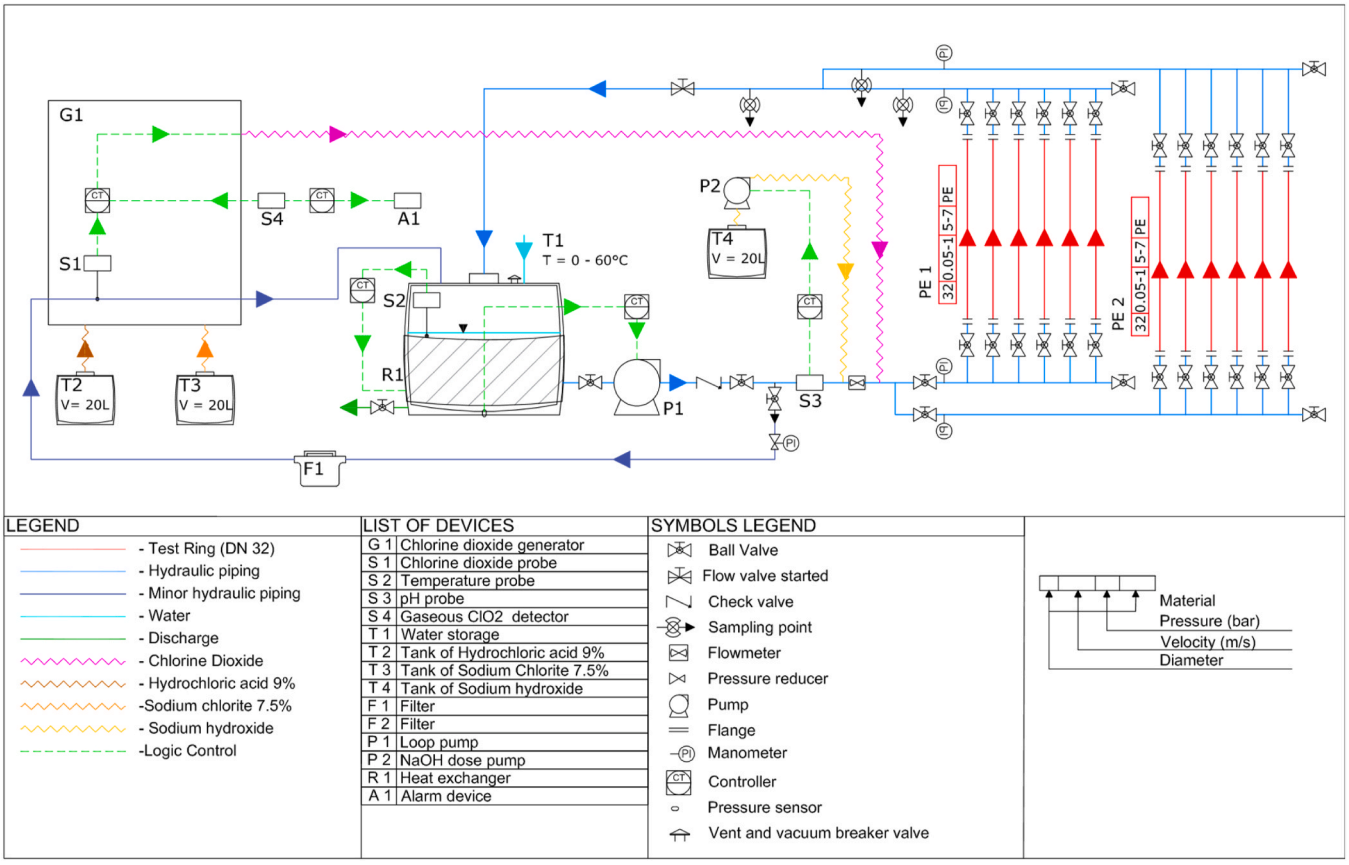


Fig. 1. P&ID Experimental Pilot.

Table 2
Initial setting conditions-Continuous ageing tests.

OPERATING PARAMETERS	TEST 1
Nominal diameter (DN) (mm)	32
Pipe thickness (mm)	3
No. PE1 pipes	6
No. PE2 pipes	6
Length of each pipe (cm)	100
ClO_2 dosage (mg/L)	5
Pressure (bar)	6
Water temperature (°C)	40
Circuit speed (m/s)	0.15
Pipe sampling	1 time every 7 days
Total test time	3192 h (133 d)

However, this analysis is only of qualitative value. Images were acquired with an EI Quanta 200 FEG instrument (FEI, Hillsboro, OR, USA) coupled to an energy dispersive X-ray spectrometer (EDAX Inc., Mahwah, NJ, USA). Determining the elongation at break of PE pipes makes it possible to characterize the changes in the elastic and plastic properties of the material as chemical and mechanical degradation proceeds. The elongation at break of PE pipes was determined according to the method described in [18] (Thermoplastic pipes - Determination of tensile properties). Three test samples were taken from each PE pipe subjected to a tensile test to derive an average elongation (%) representative of the pipes. Throughout the test period, chlorine dioxide within the circuit was monitored continuously, by probe, in order to keep the concentration constant throughout the duration of the test. In addition, chlorine dioxide by-products (i.e. chlorite and chlorate) were monitored discontinuously by analytical spectrophotometric method.

Table 3
Polyethylene characterization tests.

TEST	MEASURED PARAMETER	PURPOSE	FREQUENCY
FTIR	FTIR spectrum Carbonyl Index	Highlights polymeric degradation of PE Identification of ageing by-products from ClO_2	1/week until 42th days 1 time at 77th, 91st an 133rd days
DSC	Oxidation Induction Time	Phenolic antioxidant consumption index	1/week until 42th days 1 time at 91st an 133rd days
	Degree of crystallinity	Index of degradation, stiffening and possible fracture (ageing)	1/week until 42th days
SEM	Crack analysis	Qualitative material analysis	1/week until 42th days
EDX	Chlorine in the PE material	Chlorine dioxide diffusion within the polymer matrix	1/week until 42th days
TGA	Thermal analysis	Phenolic antioxidant consumption and index of material degradation	1/week until 42th days
Tensile test	Elongation at break	Index of Mechanical Properties of the Pipeline	1/week until 42th days 1 time at 91st an 133rd days

2.4. Temperature effect and carbonylic index

To study the temperature effect on the variation of the ageing tests, specific experimental activities were carried out to quantify or preliminarily estimate its contribution both on PE1 and on PE2. The tested temperatures were 40 °C (T0-Table 2), 30 °(T1) and 20°C (T2). The temperatures range was identified as representative of the conventional

real conditions of water supply systems where 40°C is the maximum upper limit value. The tests were conducted at the same conditions of Table 2 but maintaining constant temperature of 20°C and 30 °C for 3 weeks. The results in terms of CI values were compared with the initial continuous long test already described and completed at 40 °C.

3. Results

3.1. Batch tests results

As reported in Table 4, after 24 h of exposure between PE and ClO_2, there is a reduction of ΣCl (as sum of ClO_2, ClO_2^-, ClO_3^- expressed as Cl) around 18 %-19 % for the 5 mg/L and 10 mg/L solutions. At time zero, the solution contains a higher percentage of ClO_2 (53 %-54 %) than ClO_2^- (41 %-43 %). At the end of 24 h, there is a greater or comparable percentage of ClO_2^- (47 %-48 %) than ClO_2 (43 %-45 %), with a main speciation in chlorite compared to chlorate. In absence of piping, after 24 h at 5 mg/L, there is a 14 % reduction of ΣCl with 55 % of the content as chlorite. Also, for 10 mg/L, the ΣCl reduction is detected at 11 %, with a chlorine dioxide of 48 %, chlorite 47 % and chlorate 5 %. The percentage reduction of Cl in the controls is lower for both the chemical concentrations passing from 18 % to 19 % (with PE1 and PE2) to 14–11 % (Control). The overall balance between the two test sets, considering all forms and by-products of the dioxide, enhances that taking the batch tests with and without PE, a net reduction of ΣCl in the 24-hour was shown equal to5 % and 7 % respectively for 5 mg/L and 10 mg/L solutions. The estimated and preliminarily assessed reductions are probably due to the reaction of the chloride dioxide with the PE pipes.

Moreover, macro- and microscopic analytical characterizations were carried out after 21 and 42 days of exposure. It should be noted, however, that the batch tests are not significant for the real oxidative state of the pipes during their time life but could represent only the picture of the absolute behavior of the material and, therefore, cannot be considered predictive of the degradation phenomena. All the analytical data are included in Supplementary Material. Regarding the batch tests for the calculation of the Carbonyl Index, it can be pointed out that internal (In) and external (Out) walls show comparable CI values. Specifically, at the set dosage of 5 mgClO_2/L the following values were evaluated 0.34-Out and 0.38-In at 21st day and 0.38-Out and 0.37-In at 42nd day. Moreover, at the set dosage of 10 mgClO_2/L data of 0.37-Out and 0.35-In at 21st day and 0.42-Out and 0.42-In at 42nd day were observed. No oxidation products are observed inside the pipe. As the ClO_2 concentration and exposure time increases, the carbonyl index of the walls increases. About crystallinity percentages, it is possible to highlight significant increments in the degree of crystallinity for all the samples in contact with chlorine dioxide compared to the initial value. Specifically, at day 0, the crystallinity ranged between 55.44 % and 57.66 %. For samples exposed to 5 mg/L of ClO_2, the crystallinity ranged from 69.56 % to 79.64 % on day 21, and from 62.50 % to 82.06 % on day 42. At a higher dose of 10 mg/L ClO_2, the crystallinity ranged from 76.71 % to 79.64 % on day 21, and from 68.35 % to 75.00 % on day 42. Fewer crystalline fractions are evident for the intermediate samples than for the tube walls in direct contact with ClO_2. Increasing concentration and exposure time does not show clear and linear trends in the crystallinity value. The SEM analyses show extensive signs of degradation on the surface. For the Oxidation Induction Time (OIT), the tests enhance values of the aged samples always closer to zero. Therefore, after 21 days of exposure, the antioxidant (even along the entire thickness of the pipe) is completely consumed both at 5 mg/L and at 10 mg/L. The similarity of the data obtained indicates the severity of the batch test consisting of a strong oxidative stress that flattens the evidence for this type of characterization. In conclusion, from batch tests for the most representative chemical parameters to be considered for verifying the state of degradation and the level of ageing of Polyethylene in contact with Chlorine, could be in order of priority: carbonyl index; oxidation induction time and degree of crystallinity.

3.2. Continuous tests results

The main microstructural parameters related to crystallinity percentages and Oxidation Induction Time (OIT) are summarized in Fig. 2. For both pipes, the crystallinity percentage increases after one week of ageing compared to the initial (time zero) values. Crystallinity generally decreases progressively from the inner to the outer surface of the pipe, with the outer surface showing values close to those at time zero. The absolute crystallinity values of PE2 are consistently lower than those of PE1. PE1 exhibits a significant increase in crystallinity (+4 %) after just one week of accelerated ageing. In contrast, PE2 shows a 2 % increase only starting from the third week of testing.

For both PE1 and PE2, after one week of ageing, the crystallinity of the inner surface exceeds that of the unaged pipe. The crystallinity percentage decreases gradually from the inner to the outer surface, where it approaches the initial value.

OIT tests conducted at 200 °C reveal a partial depletion of antioxidants on the inner surface of PE1 after the first week of ageing, due to contact with chlorine dioxide. The OIT value of the inner wall reaches a minimum of 2 min in the second week of exposure. The intermediate and outer sections show no significant antioxidant depletion.

For PE2, partial antioxidant depletion on the inner wall is observed after two weeks of ageing. The OIT value reaches its minimum (5 min) in the third week. As with PE1, the intermediate and outer sections of PE2 are unaffected by oxidation.

Scanning Electron Microscopy (SEM) images were acquired for both PE1 and PE2, focusing on the inner surfaces in direct contact with chlorine dioxide during accelerated ageing, as well as the outer surfaces. In PE1, microfractures appear on the inner surface after the third week of ageing (Supplementary Material). In PE2, sporadic microfractures are observed after 14 days of ageing (Supplementary Material). No microfractures are detected on the outer surfaces of either PE1 or PE2 (Supplementary Material).

Based on the EDX analysis, all samples in direct contact with chlorine dioxide (i.e., the internal surface of the pipe) exhibit the presence of surface deposits. These deposits are primarily composed of Cl, Na, Mg, and Al, with smaller amounts of Si, Fe, Ni, Co, and Zn. These elements are likely associated with the characteristics of the water used during the

Table 4
Batch tests results of PE exposure to ClO_2.

Set ClO_2 Concentration	Pipe	Time	ClO_2	ClO_2^-	ClO_3^-	∑Cl	Cl Reduction
mg/l			mgCl/L	mgCl/L	mgCl/L	mgCl/L	%
5	-	0	4.5 ± 0.2	4.3 ± 0.1	0.30 ± 0.1	9.1 ± 0.4	14 ± 0.5 %
		24	3.2 ± 0.1	4.3 ± 0.1	0.4 ± 0.2	7.8 ± 0.4	
	PE1	0	4.03 ± 0.87	3.22 ± 0.57	0.35 ± 0.23	7.6 ± 1.24	19 ± 8 %
		24	2.75 ± 0.65	2.90 ± 0.67	0.51 ± 0.23	6.2 ± 1.16	
10	-	0	7.0 ± 0.2	5.1 ± 0.1	0.40 ± 0.1	12.5 ± 0.4	11 ± 0.5 %
		24	5.4 ± 0.1	5.3 ± 0.1	0.5 ± 0.2	11.1 ± 0.4	
	PE1	0	6.57 ± 1.71	4.84 ± 1.07	0.62 ± 0.58	12.03 ± 2.94	18 ± 8 %
		24	4.21 ± 1.43	4.63 ± 1.04	0.82 ± 0.47	9.65 ± 2.33	

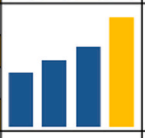
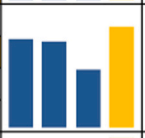
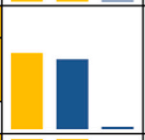
Sample	Depth	Cristallinity %		Trend Cristallinity (%)		Depth (mm)	OIT (min)		Trend OIT (%)	
days		PE1	PE2	PE1	PE2		PE1	PE2	PE1	PE2
0		69.1	67.6				>60	>60		
7	external	71.8	64.7			external	>60	>60		
	middle ext.	71.6	68.1			intermediate	>60	>60		
	middle int.	74.4	67.5							
	internal	73.6	69.4			internal	36.9	>60		
14	external	69.6	63.5			external	>60	>60		
	middle ext.	71.0	69.2			intermediate	>60	>60		
	middle int.	72.6	67.3							
	internal	76.2	69.2			internal	2.4	39		
21	external	73.6	64.3			external	>60	>60		
	middle ext.	73.4	71.8			intermediate	>60	>60		
	middle int.	70.0	70.8							
	internal	75.2	70.4			internal	1.4	5.9		
28	external	73.0	64.3			external	38.6	>60		
	middle ext.	74.8	70.2			intermediate	35.9	>60		
	middle int.	73.8	73.2							
	internal	77.0	74.6			internal	1.9	4.9		
35	external	65.5	63.1			external	>60	>60		
	middle ext.	65.3	71.0			intermediate	>60	>60		
	middle int.	70.8	70.2							
	internal	77.2	75.2			internal	2.4	4.4		
42	external	65.3	70.0			external	>60	>60		
	middle ext.	70.0	74.0			intermediate	>60	>60		
	middle int.	72.0	72.6							
	internal	76.8	74.8			internal	2.4	5.4		

Fig. 2. Cristallinity percentages and OIT trends for PE1 and PE2 in continuous ageing test (orange color is used for indicating maximum value of the crystallinity and OIT).

experimental tests (see EDX profile in the Supplementary Material).

For both PE1 and PE2 samples, no significant changes were observed in the thermogravimetric degradation profiles of the polymers. In all cases, thermal decomposition occurred at 390 ± 5 °C, with a total mass loss of 97 ± 2 % at 500 °C. No partial mass losses were detected prior to decomposition. The thermogravimetric analysis was discontinued after week 6 (see TGA profile in the Supplementary Material).

Regarding the Carbonyl Index (CI), Fig. 3 presents the CI evolution for PE1 (Fig. 3a) and PE2 (Fig. 3b) as a function of exposure time and for each analyzed section. After the first week of ageing, an increase in the CI was observed on the internal wall of both pipe types. As exposure time progressed, the CI continued to rise. The CI values for the internal sections of PE1 and PE2 remained nearly unchanged and comparable up to week 3 for PE1 and up to week 5 for PE2, indicating a slower oxidation rate in the latter.

The variation in CI relative to the initial value (CI_0) over time is shown in Fig. 3c for PE1 and Fig. 3d for PE2. The rate of CI increase was higher for PE1 (0.287 CI/CI_0/day) compared to PE2 (0.216 CI/CI_0/day), with the inflection point occurring earlier in PE1 (week 4) than in PE2 (week 6).

Tensile tests were conducted on both PE1 and PE2 samples. For both aged and reference specimens, the stress–strain curves up to the sixth week exhibit the typical behavior of plastic materials, characterized by an initial elastic region followed by a plastic deformation phase after yielding, culminating in fracture at a stress level higher than the yield stress—indicative of a work-hardening phenomenon.

No significant changes were observed in the elastic region for either PE1 or PE2 up to week 6 (Fig. 4). However, between weeks 6 and 13 (Fig. 4b and c), a reduction in elongation at yield becomes evident. A similar trend is observed in the plastic deformation phase, with a progressive decline in ductility as ageing progresses beyond the sixth week.

Between approximately weeks 12 and 15, both materials exhibit a loss of mechanical conformity in terms of elongation at break, falling below the threshold defined by EN 12201–2:2024, which requires an elongation at break greater than 350 %.

3.3. *Temperature effect on carbonylic index*

As shown in Fig. 5.a and 5.b, there is a noticeable difference in the variation trends of CI values at 40 °C compared to those at 20 °C and 30 °C. The data collected at 20 °C and 30 °C are closely aligned, indicating similar degradation behavior at these lower temperatures. In contrast, the response at 40 °C is significantly more pronounced, suggesting a faster degradation process. This implies that the material's response to environmental stress, as measured by the Carbonylic Index, accelerates with increasing temperature. Notably, at 40 °C, the CI value doubles within just two weeks of testing, underscoring the substantial impact of elevated temperature on the degradation rate.

4. Discussion

4.1. *Long term ageing and key characterization parameters*

The comparison between the results obtained from the long-term ageing test and those reported in the technical-scientific literature is presented in Table 5. In several instances, direct comparison proves challenging due to the differing conditions and configurations of the accelerated ageing tests described in the literature, which often diverge from those simulated in this pilot plant. Notably, many studies omit critical details regarding the tested pipes, such as length, diameter, antioxidant content, and section characteristics.

Despite these limitations, the time required for the Oxidation

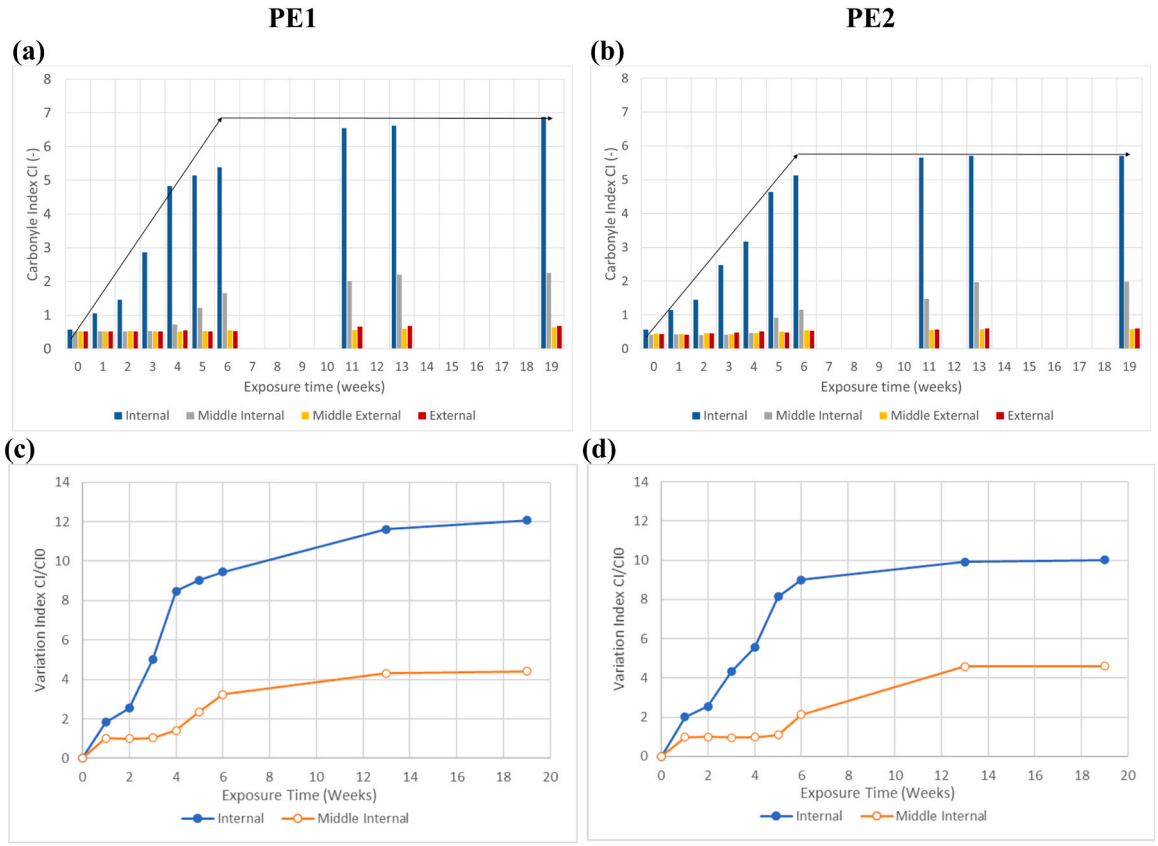


Fig. 3. Carbonyl Index (absolute values panels (a) and (b)) and variation of CI relative to the initial value (panels (c) and (d)) for PE1 (panels (a) and (c)) and PE2 (panels (b) and (d)) in continuous aging tests.

Induction Time (OIT) of the internal wall to reach zero in this study aligns well with literature values, which range from 11 to 60 days. Furthermore, the observed increase in crystallinity during the ageing process—7 % for PE1 and 9 % for PE2—is consistent with findings reported by other authors (e.g., 5 % by [9]; 8 % by [8]). Lastly, although the final increase in the Carbonylic Index (CI) is more moderate, the values recorded for PE1 and PE2 remain within the same order of magnitude as those reported by Bredács et al., [23].

To determine which of the applied characterization techniques most effectively represent and quantify the oxidation of polyethylene (PE) in contact with chlorine dioxide (ClO_2) over time, a correlation matrix was developed. This matrix includes the quantitative parameters measured for both PE1 and PE2, considering the amount of chlorine dioxide (g ClO_2) to which the pipes were exposed. Fig. 6 presents the correlation matrices for the internal section of the pipes. Comparable results were observed for the intermediate and external sections, as detailed in the Supplementary Material.

Each cell in the matrix displays the Spearman Correlation Coefficient, which ranges from −1 (indicating a strong inverse correlation) to 1 (indicating a strong direct correlation). Red stars denote the p-value, indicating the statistical significance of the correlation. The most interesting correlations are highlighted within the red rectangle. The statistical significance increases with the number of stars, with a p-value > 0.05 considered statistically significant.

Analysis of the correlation matrices for both PE1 and PE2 indicates that the Carbonyl Index (CI) exhibits the strongest and most consistent correlation with the amount of chlorine dioxide (ClO_2) and its by-products (ClO_2^- and ClO_3^-) in contact with the pipe surfaces. Additionally, the percentage of crystallinity also shows a high correlation with ClO_2 exposure, reinforcing its relevance as an indicator of oxidative degradation.

Based on these findings, the most representative parameters for quantifying and critically assessing the oxidation of PE pipes in contact with chlorine dioxide are, in order of significance: 1) Carbonyl Index (CI); 2) Percentage of Crystallinity; 3) Oxidation Induction Time (OIT).

These parameters corroborate the results obtained during batch tests, while also emphasizing the Carbonyl Index as a particularly effective and innovative metric for predicting oxidative phenomena. The CI not only varied significantly during chemical exposure but also showed a clear correlation with the loss of mechanical properties, as evidenced by the Elongation at Break values.

Importantly, a critical exposure period was identified between 85 and 105 days, during which a marked change in the CI was observed. This suggests that the CI can serve as a predictive parameter for the chemical ageing of PE pipes, offering a practical and expedient tool for monitoring material degradation in real-world applications.

4.2. Long term chemical ageing and time life of real water supply

In the experimental setup, a higher daily dosage of disinfectants was applied compared to typical levels used in conventional water distribution systems. The accelerated exposure allowed for the observation of signs of mechanical degradation in shorter time. By comparing the total disinfectant load administered during the test to the cumulative exposure expected over years of real-world operation, an approximate estimation of the system's service life under standard conditions was derived. In fact, to better contextualize the experimental results within real-world water supply networks, typical chlorine dioxide (ClO_2) dosing rates for distribution pipes—ranging from 0.2 to 0.7 g ClO_2/day—were considered, based on an average assumed flow rate of 0.12 L/s and a specific dose of 0.07 mg ClO_2/L. These values were compared to the dosing applied in the pilot-scale tests (55.2 g ClO_2/day) to estimate the equivalent real-time ageing effects.

Under the test conditions (84–105 days at 40 °C), the observed loss of

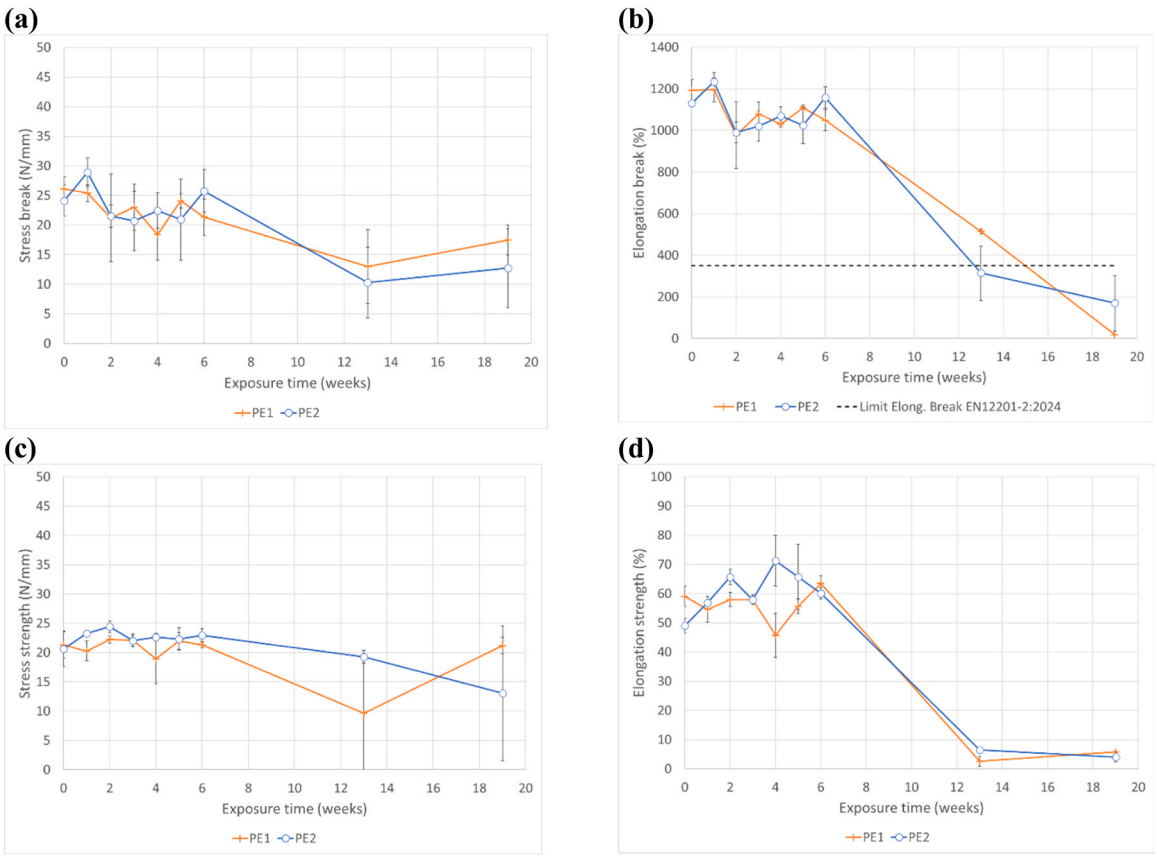


Fig. 4. Tensile tests for PE1 and PE2 in continuous aging tests: stress and elongation at break point (panel (a) and (b)) and at strength point (panel (c) and (d)).

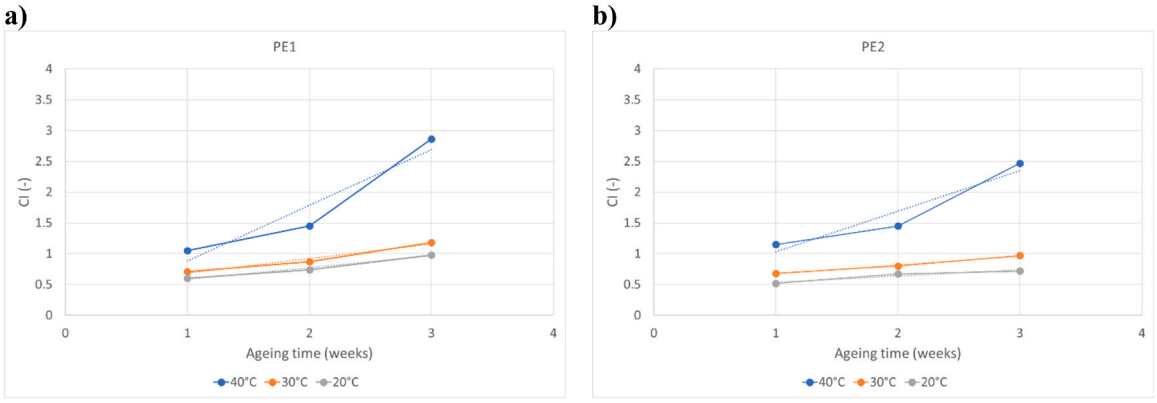


Fig. 5. Carbonylic index at different temperatures for PE1 (a) and PE2 (b); dotted lines represent data linear interpolation.

elongation properties due to chemical ageing corresponds to an estimated real-time service life of approximately 18 years for PE1 and 23 years for PE2, assuming a ClO_2 dose of 0.7 g/day. The detailed lifetime calculation is provided in the supplementary material.

Assuming a conservative, linear growth trend of the Carbonyl Index (CI) which remains to be fully validated the critical exposure period for tests conducted at 20 °C and 30 °C is projected to occur at 180 days for PE1, corresponding to approximately 40 years of real-time exposure (at 0.7 g ClO_2/day) and at 280 days for PE2, corresponding to approximately 60 years of real-time exposure (at the 50th percentile dose of 0.7 g ClO_2/day). The results obtained are preliminary and based on a conservative linear growth trend extrapolated from short-term accelerated aging data at conventional aqueduct temperature between 20 °c and 40 °C. Future projections require further validation. This should be achieved through long-term data collected at multiple temperatures and supported by more robust kinetic models, not necessarily linear (es. preliminary Arrhenius-type model) especially considering that the degradation dynamics occur at the solid–liquid interface. Moreover, these projections should be corroborated with field data, particularly through the analysis of pipe samples that have failed in service after varying operational durations.

5. Conclusions

This study provides a thorough evaluation of chemical degradation in polyethylene (PE) pipes exposed to chlorine dioxide (ClO_2) under both batch and continuous ageing conditions. For degradability testing, continuous ageing experiments remain the most reliable and

Table 5
Comparison of results with scientific and technical literature.

Reference	ClO_2	P	T	V	Trial time	OIT *	Ageing time **	Cristallinity		CI	
								Initial	Final	Initial	Final
	mg/L	bar	°C	m/s	d	min	d	%	%	-	-
[9]	4	7	90	7	66	50	21	50	55	-	-
[8]	1	5	70	0.5	56	-	-	46	54	-	-
[19]	1	5	-	-	42	-	37	-	-	-	-
[20]	5	2.5	40	1.8	365	50	60	-	-	-	-
[21]	70	1	40	-	167	110	11	-	-	-	-
[22]	1	n.a.	70	-	5	-	-	-	-	0	30
This Study PE1	5	6	40	0.15	133	60	14	70	77	0.5	14
This Study PE2						60	21	64	75	0.6	10

*OIT initial value (time 0) at internal section
**Ageing time corresponding OIT minimum value (OIT = 0 min)

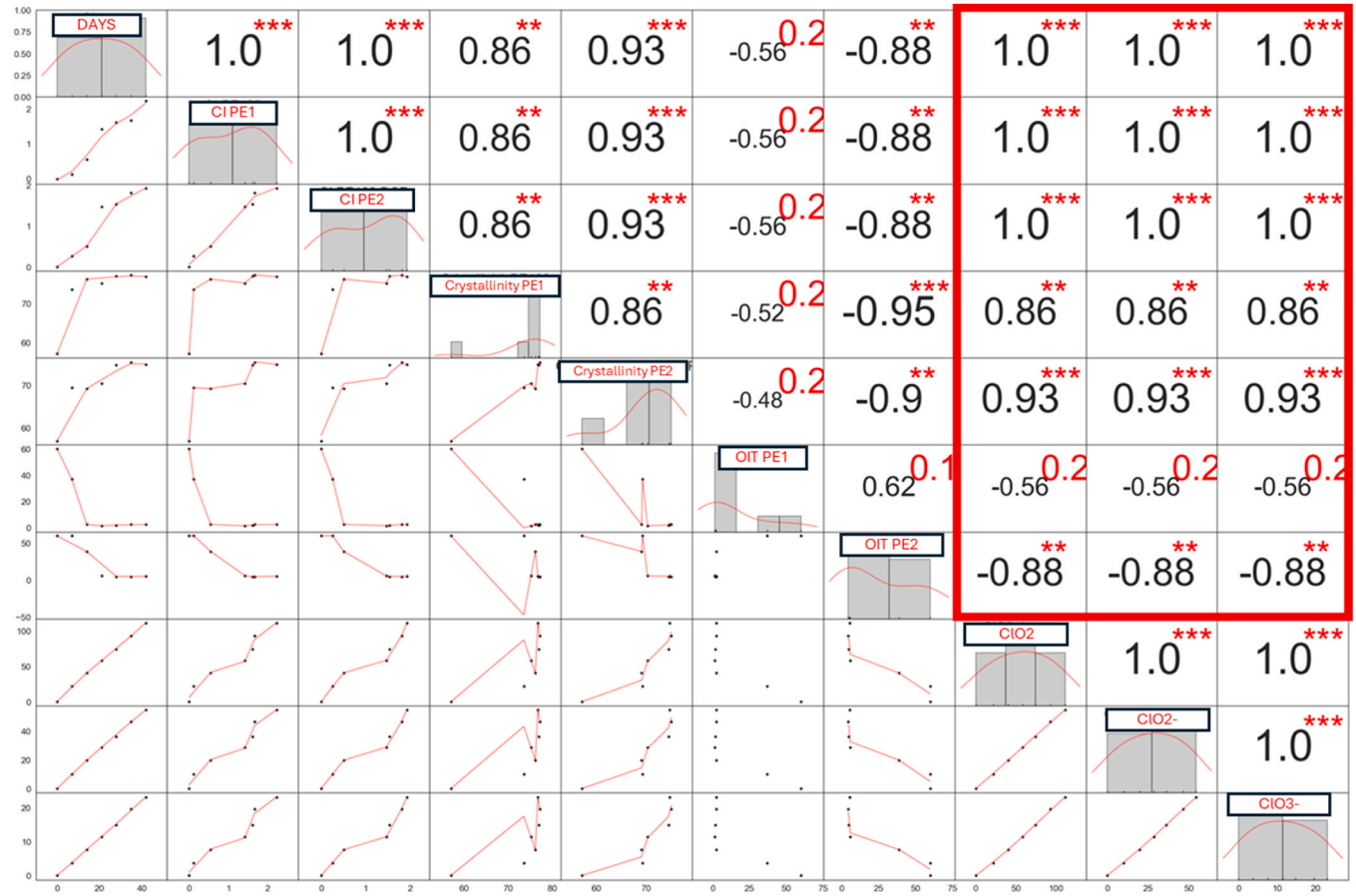


Fig. 6. Correlation Matrix Operative Ageing conditions and Characterization Parameters.

representative approach.

Overall, the study identifies the Carbonyl Index, Oxidation Induction Time and crystallinity as the most representative parameters for evaluating the degradation state of PE in contact with ClO_2. These findings underscore the need for normalized testing protocols and predictive models to assess the long-term performance of polymeric materials in disinfected water systems. Moreover, the results demonstrate that ClO_2 induces significant oxidative degradation, particularly on the internal surfaces of the pipes, as evidenced by the progressive increase in Carbonyl Index (CI), crystallinity and the depletion of antioxidants (OIT). Among the tested materials, PE1 exhibited a faster degradation rate than PE2, with earlier inflection points in both CI and mechanical performance loss. CI proved to be the most sensitive and predictive metric, correlating strongly with ClO_2 exposure and mechanical decline, particularly in elongation at break. Temperature was found to be a critical factor, with degradation accelerating significantly at 40 °C, compared to 20 °C and 30 °C. Extrapolated to real-world conditions, the estimated service life of PE1 and PE2 ranges from 19 to 60 years, depending on ClO_2 levels and temperature. These projections, while promising, require validation through long-term field data and post-failure pipe analyses.

Correlation matrix analysis confirmed the reliability of CI, crystallinity, and OIT as indicators of oxidative ageing. A critical exposure window (85–105 days at 40 °C) was identified, marking intensified degradation and suggesting a predictive threshold for failure. Overall, the findings underscore the importance of standardized ageing protocols and support the use of CI as a practical tool for monitoring the long-term performance of PE pipes in disinfected water distribution systems.

Exogenous factors, such as water hammer, pressure cycling, and flow rate fluctuations, could further accelerate chemical degradation under real-world pipe installation conditions. These aspects should be further quantified and verified in specific cases through field validation in future studies.

Environmental implications

The study highlights the growing environmental importance of evaluating polyethylene (PE) pipe durability in water distribution networks, particularly as chlorine dioxide (ClO_2) gains preference for its lower ecological impact and reduced formation of harmful by-products. By replicating real-world ageing conditions, the research provides valuable insights into the long-term behavior of PE materials, helping to mitigate risks of water loss, contamination, and compromised drinking water quality. A key innovation is the adoption of a normalized approach for chemical ageing quantification also by using the Carbonyl Index as a predictive indicator of polymer degradation. This method enables proactive maintenance planning and aligns with European regulatory frameworks aimed at building safer, more sustainable water infrastructure.

CRediT authorship contribution statement

Francesco Fatone: Funding acquisition, Conceptualization. **Anna Laura Eusebi:** Writing – review & editing, Writing – original draft, Validation, Supervision, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization. **Luciano Soldini:** Writing – original draft, Validation, Supervision, Methodology, Conceptualization. **Giovanna Darvini:** Writing – original draft, Validation, Supervision, Methodology, Conceptualization. **Michele Mattioli:** Investigation, Data curation. **Vieri Fusi:** Investigation, Data curation. **Luca Giorgi:** Investigation, Data curation. **Marco Parlapiano:** Validation, Investigation. **Nicola Lancioni:** Validation, Methodology, Investigation, Data curation. **Massimiliano Sgroi:** Writing – original draft, Investigation, Data curation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

Centraltubi S.p.A. and Marche Multiservizi S.p.A. staff and DISPEA_Paderni_Prog24 of Department of Pure and Applied Sciences are kindly acknowledged for the support.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2025.140437.

Data availability

No data was used for the research described in the article.

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