

A kinetic model for predicting the oxidative degradation of additive free polyethylene in bleach desinfected water



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ABSTRACT

The chemical interactions between additive free PE and bleach were investigated by FTIR spectrophotometry and viscosimetry in molten state after immersion (for a maximum duration of one hundred days) in bleach solutions maintained at a temperature of 60 °C, a free chlorine concentration of 100 ppm, and a pH = 4, 5 or 7. It was found that the polymer undergoes a severe oxidation from the earliest days of exposure in a superficial layer of about 50–100 μm thick, almost independent of the pH value. In this layer, oxidation leads to the formation and accumulation of various carbonyl products (mostly ketones and carboxylic acids) but also, after about 2–3 weeks of exposure, to a dramatic decrease in the average molar mass due to the large predominance of chain scissions over crosslinking. It was also found that the oxidation rate is maximum at pH = 5, and of the same order of magnitude at pH = 4 and 7. Based on the equilibrium diagram giving access to the relative predominance of the three main chemical species as a function of the pH value of the bleach solution, it was assumed that oxidation is initiated by radical species coming firstly from hypochlorous acid (ClOH) and secondarily from chlorine (Cl₂), given that hypochlorite ions (ClO⁻) are totally insoluble into the PE matrix. In addition, for explaining the surprisingly large value of the oxidized layer thickness despite the high reactivity of the involved radicals, it was assumed that ClOH and Cl₂ do not decompose into radicals in the water phase, but migrate deeply into the PE matrix prior to dissociating into Cl· and HO· radicals and then, initiating a radical chain oxidation. The validity of the kinetic model derived from this scenario was successfully checked by comparing the numerical simulations with all the experimental data collected in this study. This model predicts the general trends of the oxidation kinetics and its dependence on the pH value, but also gives access to the transport properties of the chlorinated disinfectants and their radical species, and the rate constants of the radical attack.

1. Introduction

Steel pipes (with or without polymeric coating) are traditionally used for tertiary cooling circuits in nuclear power plants. Water is commonly disinfected by chlorinated reagents in order to control the microbiological growth and limit the deposit and development of shellfish and seaweed that might clog the circuit input. However, steel is sensitive to corrosion and water disinfectants are relatively strong oxidizers susceptible to accelerate corrosion. Therefore, in recent years, the nuclear industry has launched heavy testing campaigns for qualifying polymeric materials for this type of application, in particular polyethylene (PE), in view of using them in replacement of steel.

PE pipes are currently used for conveying drinking water under a pressure of a few bars since the early 1970s. There is an abundant

literature on results of isobaric and isothermal ageing tests in pure distilled water at temperatures higher than typically 40 °C (see for instance references [1–3]). The construction of a single master curve by using adequate Arrhenius shift factors [2] allows extrapolating these results up to ambient temperature and thus, demonstrating that pipes perish always by brittle fracture with lifetimes exceeding typically 50 years in the domain of water pressures of practical interest.

In the past half century, considerable research efforts were accomplished for optimizing the polymer structure, at both macromolecular and morphological scales [4–10], but also the processing conditions [11] in view of improving the pipe durability. In the last two decades however, it was discovered that the water disinfectants do not only destroy the organic substances in water by oxidizing processes (among which radical processes play a key role), but also consume the

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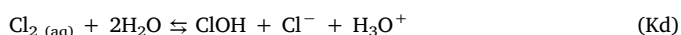
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stabilizing function of phenolic antioxidants and initiate a radical chain oxidation of the polymer matrix in the inner wall of pipes, thus leading to a significant reduction of the pipe lifetime. These deleterious effects are especially pronounced when chlorine dioxide is used as a disinfectant [12–14], but measurable effects were also evidenced in the case of chlorine and bleach [15–21].

The chemistry of water disinfection is relatively well known. Both radical and ionic species (for instance, ClO^- in the case of chlorine and bleach) have a strong oxidizing power. However, PE acts as a selective absorber because highly polar species such as ions are totally insoluble into this non-polar matrix. This characteristic was first discovered by Ravens [22] in the case of the poly(ethylene terephthalate) (PET) hydrolysis. PE is part of the less polar polymers: its dipolar moment is zero and its dielectric permittivity is 2.3 [23]. In contrast, radicals are more or less soluble into PE depending on their solubility parameter. As a result, three distinct scenarios can be considered for explaining the chemical attack of both phenolic antioxidants and PE matrix:

- S1) The disinfectant is itself a free radical in ground state which can migrate into PE. This is the case of chlorine dioxide (ClO_2) [12,13];
- S2) The disinfectant generates radicals in water, then these latter migrate into PE;
- S3) The disinfectant itself, or a non-dissociated molecule formed from this disinfectant in water, migrates deeply into PE where it dissociates into radicals.

The identification of the reactive species and the determination of their respective concentration in the PE matrix remain an open issue, especially in the case of chlorine and bleach for which the two last scenarios S2 and S3 are conceivable. It is now well known that bleach solutions contain three main chemical species whose the relative proportions depend essentially on the pH value [24], as shown for instance at 25 °C in Fig. 1. These latter can be determined from the kinetic analysis of the two following chemical equilibria:



It comes:

$$\%_{\text{Cl}_2} = \frac{100 \times 10^{-\text{pH}+\text{pK}_d}}{1 + 10^{-\text{pH}+\text{pK}_d} + 10^{\text{pH}-\text{pK}_a}} \quad (1)$$

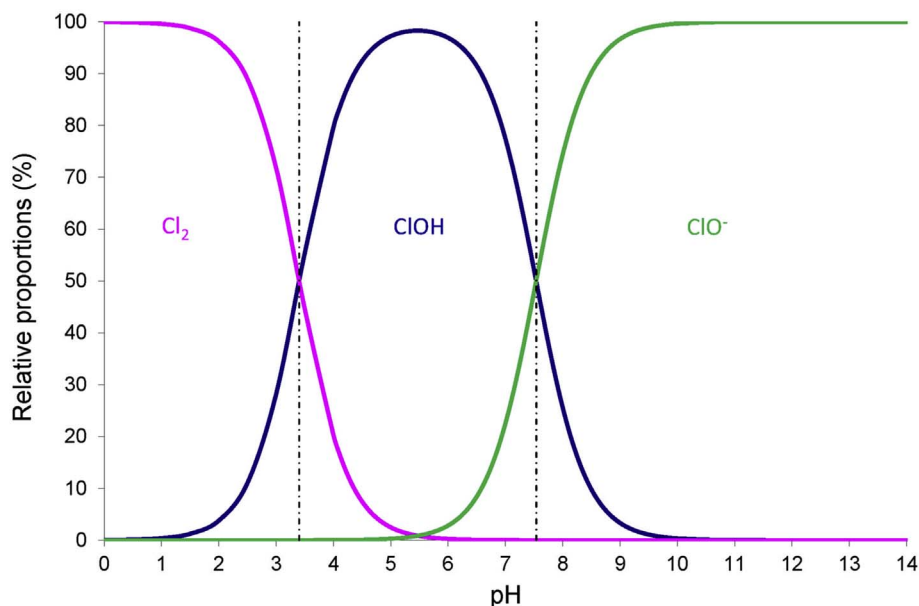


Fig. 1. Chemical composition of a bleach solution in function of the pH value at 25 °C.

$$\%_{\text{ClOH}} = \frac{100}{1 + 10^{-\text{pH}+\text{pK}_d} + 10^{\text{pH}-\text{pK}_a}} \quad (2)$$

$$\%_{\text{ClO}^-} = \frac{100 \times 10^{\text{pH}-\text{pK}_a}}{1 + 10^{-\text{pH}+\text{pK}_d} + 10^{\text{pH}-\text{pK}_a}} \quad (3)$$

The temperature dependence of the equilibrium constants K_d and K_a was reported in the literature [25,26]. Typically between 0 and 45 °C, it can be written:

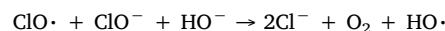
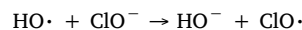
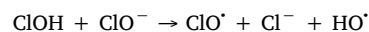
$$\text{pK}_d = \frac{982.798}{T^2} - \frac{5.485.7}{T} + 10.7484 \quad (4)$$

$$\text{pK}_a = \frac{3000}{T} - 10.0686 + 0.0253 T \quad (5)$$

Since K_d and K_a are very slowly decreasing functions of temperature, the chemical composition of bleach is almost insensitive to temperature. In fact, the chemical equilibria are very slightly shifted towards lower pH values when increasing the temperature. It can be thus concluded that chlorine (Cl_2), hypochlorous acid (ClOH) and hypochlorite ion (ClO^-) predominate respectively in highly acidic ($\text{pH} < 3$), weakly acidic ($3 < \text{pH} < 7.5$) and basic media ($\text{pH} > 7.5$), whatever the temperature. Moreover, the maximum yield of ClOH is reached at $\text{pH} = 5$.

Based on these observations, it is thus possible to select carefully pH conditions for identifying what chemical species are responsible for the polymer degradation, but also for deciding between the two possible scenarios S2 and S3.

According to Holst [27], when they coexist (at $\text{pH} = 7.5 \pm 1.5$), ClOH and ClO^- would generate ClO^\bullet and HO^\bullet radicals in water:



Thus, scenario S2 could be considered. This scenario was supported by some authors who effectively found a maximum degradation rate at $\text{pH} = 7$ for polyether-based polyurethane fibers [28], or at $\text{pH} = 8$ for polysulfone membranes [29–31].

On the contrary, for other authors [18,20,32,33], Cl_2 and ClOH could directly dissociate into Cl^\bullet and HO^\bullet radicals (presumably within the PE matrix) because $\text{Cl}-\text{Cl}$ and $\text{Cl}-\text{O}$ bonds are characterized by a very low dissociation energy (of respectively 242 and 247 kJ mol^{-1} [34]):

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