Chemical Permeation/Desorption in New and Chlorine Aged Polyethylene Pipes [Project #4138]

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OBJECTIVES:
The purpose of the project was to describe the fundamental processes that control new and aged polyethylene (PE) pipe and contaminant interactions by applying engineering and surface and bulk chemistry characterization techniques to evaluate pipe integrity and performance.

BACKGROUND:
PE water pipe has been and continues to be installed in buried and premise water distribution networks worldwide. Historically high density polyethylene (HDPE) pipe has been used in North America, while low, medium, and high density polyethylene are used around the globe. Although cross-linked polyethylene (PEX) materials have been used in premise plumbing applications for about a decade, it was not until 2007 that the American Water Works Association approved PEX pipe for buried service applications. With the abundance and expected growth of PE materials, it is critical that water industry personnel understand how PE materials perform when new and after they are aged and oxidized by contact with disinfected drinking water. The current literature suggests that mechanisms of oxidative degradation of polyethylene are similar for chlorine, chloramines, and chlorine dioxide. A particular concern is that increased regulatory and security emphasis on chemical contaminant fate in water distribution systems demands an understanding of how chemical contaminants interact with new and aged PE pipes. Unfortunately, little is known about contaminant interaction with aged PE pipes despite the fact that long-term disinfected water exposure is known to change surface, bulk, and mechanical properties of these materials. As a result, potable water distribution system designers, operators, regulators, and managers do not know if oxidation of new pipe caused by chlorination affects contaminant diffusion and desorption.

APPROACH:
To fill this knowledge-gap, experiments were performed to evaluate three PE materials—HDPE resin, HDPE water pipe, and medium density PEX A pipe—when new and after aging in chlorinated water. Principles and techniques from material science, chemistry, and civil and environmental engineering were applied. Specifically, PE materials were characterized by bulk oxidative resistance as measured by oxidation induction time (OIT), physical strength as measured by breakage, material density, and surface chemistry characteristics by infrared spectroscopy (IR). New PE materials were laboratory aged by immersion at atmospheric pressure in chlorinated water using 45 mg/L as Cl_2 with 50 mg/L as $CaCO_3$, pH 6.5, and at 37 ºC. The water was changed every three days over a 141 day aging period; these conditions provided a stable pH and

chlorine residual. The permeation and desorption of eight chemical contaminants were evaluated in the new and chlorine aged PEs. The contaminants were comprised of a group typical of drinking water contaminants or industrial chemicals: non-polar contaminants (methyl-t-butyl ether, chloroform, and toluene) and polar contaminants (acetonitrile, methyl ethyl ketone, 1-butanol, benzaldehyde, and benzyl alcohol). Sorption of pure contaminants was conducted for up to 104 days at room temperature to determine contaminant diffusivity and solubility in each new and aged PE material. Desorption of sorbed contaminants into air at room temperature was evaluated for greater than 100 days and desorption diffusivities calculated. Physical and chemical properties of the PE pipes and contaminants were assessed in relationship to diffusivity and solubility to determine if predictive trends could be found. The data matrix generated contained 3 PE materials x 8 chemical contaminants x 2 conditions (new and aged) x 2 parameters (solubility and diffusivity) for a total of 98 contaminant-polymer data pairs, in addition to a myriad of measured physical and chemical properties of the polymers and contaminants.

RESULTS/CONCLUSIONS:

There are several major outcomes of this research:

1. Properly functioning HDPE and poly (1–butene) (PB) pipes removed from a buried water distribution system had little oxidative resistance and exhibited signs of surface oxidation. These pipes had different exposure times and water qualities (disinfectant, pH, etc.). Interpreting field pipe surface chemistry and bulk characteristic data is complex since new versions of these materials are not available for comparison.
2. Standardized polymer accelerated aging methods using free available chlorine should be changed to be more realistic to drinking water conditions and account for changes in water chemistry and water sorption by polymers. Aging conditions with extreme temperatures and extreme chlorine concentrations should be avoided.
3. The one PEX pipe material evaluated was comprised of medium density PE. Contaminant diffusivity and solubility in this PEX was 2–4 times faster than in any HDPE pipe examined.
4. Exposing PE pipe to chlorinated water alters contaminant-material interaction with that material. PE pipe chlorine exposure and oxidation (1) increased polar contaminant diffusion into pipe during sorption and (2) decreased polar contaminant desorption from the pipe.
5. The application of polymer characterization techniques used in the material science and engineering industry was critical to execution of this research. Polymer properties, including density, characterization of surface and bulk properties, and mechanical strength should be determined in future polymer water pipe work because as shown in this research, polymer properties can help explain contaminant fate.

APPLICATIONS/RECOMMENDATIONS:

Utilities need to be aware that polyethylene pipes in distribution systems will age due to exposure to drinking water disinfectants and the resulting oxidation. PE pipes will sorb organic contaminants and the rate and amounts of sorption depends on the type of polyethylene (PE or PEX), the density (LPDE, MDPE, or HDPE), the pipe thickness, and the extent of oxidation of the polyethylene. The less dense the polyethylene material, the faster contaminants sorb. Nonpolar contaminants like toluene, chloroform, and methyl-t-butyl ether will permeate faster than polar contaminants like methyl ethyl ketone, or benzyl alcohol. Although the solubility of the sorbed contaminant will be similar in new and chlorine-aged pipes, pipe that are "aged" due to oxidation allow polar contaminants to permeate the pipe faster than if the pipe were new. The ability to desorb contaminants into air and remove them from PE distribution materials is also dependent on the density of the PE and the polarity of the contaminant. Contaminant desorption was slower from the more dense PE materials; nonpolar contaminants will desorb faster than polar contaminants.

Polyethylene pipes are comprised of organic chemicals whose properties and performance change due to reaction with oxidants and disinfectants used to treat drinking water. This research demonstrated that under chlorinated water conditions designed not to introduce micro- or macro- cracks to the polymer, the surface of the polyethylene became oxidized and allowed polar contaminants to permeate faster. If polar contaminants were introduced to an established and disinfected distribution system, faster removal of the contaminated water would be desirable to avoid contaminant uptake by the oxidized pipe. A similar strategy is expected for distribution systems exposed to chloramines and chlorine dioxide because the current literature suggests that mechanisms of oxidative degradation of polyethylene are similar for these oxidants although the rate of oxidation varies. Thus, any disinfectant could oxidize polyethylene distribution system materials and utilities should consider this when choosing alternative disinfectants for primary or secondary disinfection, or applying "super" disinfection for new or repaired water mains.

Assessing the permeability of pipe to organic contaminants should include testing both new and aged pipe. Accelerated aging methods for distribution system materials should be realistic in their simulation of distribution system conditions in terms of temperatures, typical high and low disinfectant doses, and stable water quality conditions. For chlorinated water, this research demonstrated that the following conditions produced a stable water quality that did not change over time: 45 or 250 mg/L as Cl_2 with 50 mg/L as $CaCO_3$ alkalinity concentration, initial pH 6.5, at 23 and 37 ºC, and water change frequency every 3 days. While utilities do not usually perform their own research regarding pipe aging conditions, they should carefully examine the American Society for Testing and Materials and National Sanitation Foundation accelerated aging and pipe testing protocols and consider suggesting revisions that incorporate monitoring of the water quality parameters of the aging solution and conditions more representative of potable water.

PARTICIPANTS:
Pasco County Utilities, City of New Port Richey, and Tampa Bay Water participated in this project.