Chlorine decay and DBP formation under different flow regions in PVC and ductile iron pipes: Preliminary results on the role of flow velocity and radial mass transfer

Dr. Y. Jeffrey Yang, PE, D.WRE\textsuperscript{1}, Dr. Christopher A. Impellitteri\textsuperscript{1}, Dr. Robert M. Clark, PE\textsuperscript{2}, Roy C. Haught\textsuperscript{1}, Donald A. Schupp, PE\textsuperscript{3}, Srinivas Panguluri, PE\textsuperscript{3}, and E. Radha Krishnan, PE\textsuperscript{3}

1. U.S.EPA, National Risk Management Laboratory, Water Supply and Water Resources Division, Water Quality Management Branch, 26 W. Martin Luther King Dr., Cincinnati, Ohio 45268
2. Environmental Engineering Consultant, 9627 Lansford Dr., Cincinnati, Ohio 45242
3. Shaw Environmental and Infrastructure, Inc., 5050 Section Ave., Cincinnati, Ohio 45212

ABSTRACT

A systematic experimental study was conducted using a pilot-scale drinking water distribution system simulator to quantify the effect of hydrodynamics, total organic carbon (TOC), initial disinfectant levels, and pipe materials on chlorine decay and disinfection by-product (DBP) formation. The first phase of the experiments focused on the variables of flow rate and pipe materials and their effects on the formation of trihalomethanes (THMs), a primary category of DBPs in chlorinated drinking water. Different from previously reported bench-scale investigations, this experimental study was to determine chlorine decay and DBP formation kinetics under simulated field conditions and to contrast the effects of new PVC and aged ductile iron pipe materials. In this paper, we report the experimental findings on the rate of THM formation under stagnant, laminar, transitional and turbulent conditions, and further attempt to address the effects of the pipe materials on the reaction kinetics.

The results indicate that the second-order DBP formation model of Clark (1998) can sufficiently describe the variations in total trihalomethanes (TTHM) concentrations. The determined reaction constants are smaller under stagnant and turbulent flows in the new PVC pipes than the aged ductile iron pipe. The latter has a high rate of DBP formation accompanying by a rapid chlorine residual loss. It is suggested that these observed differences are a result of the mass-transfer enhanced wall demand in the aged ductile iron pipe. Implications for re-chlorination in the distribution network operations are discussed.

Key Words:

Disinfection by-product, trihalomethane formation, DBP formation kinetics, chlorination and re-chlorination, chlorine decay, distribution network
INTRODUCTION

Drinking water disinfection and disinfection-by-product (DBP) formation are two closely coupled processes affecting water quality at the consumer’s tap. Chlorine disinfectants are often used to control the growth of biological contaminants in a water distribution network; yet their reaction with organic matter results in DBP formation imposing health risk to consumers because of DBP’s toxicity. In network operation, how to balance the two competing and opposing objectives is of interest to water utilities and is also a system engineering challenge to the applied scientific research arena.

This paper, based on pilot-scale experiments conducted at the U.S. EPA’s Test and Evaluation (T&E) facility, is one of a series of publications to address the subject. On chlorine disinfection and DBP formation kinetics, extensive publications have addressed the formation mechanisms, laboratory experimental results, field observations and mathematical models (Rossman et al., 2001; Vasconcelos et al., 1996; Clark et al., 2001; Cowman and Singer, 1996; Clark and Sivaganesan, 2002; and references therein). However, kinetic studies in well-controlled and full-scale water pipe systems are scarce. In a flowing drinking water pipe, chlorine consumption in wall demand and bulk demand and the resulting DBP formation depend upon a set of intrinsically related controlling factors such as pipe materials (Rossman et al., 2001), disinfectant chemical properties (Hua and Reckow, 2007), total organic carbon (TOC) and compositions (White et al., 2003; Clark et al., 2001; Anastasia et al., 2003), and the hydrodynamic regimes of pipe flow (Clark and Haught, 2005; Clark et al., 2006). When these variables are systematically quantified, a predictive working model incorporating both wall demand and bulk demand can be improved to better simulate field conditions.

Figure 1 Experimental setup for testing and examination of chlorine decay and DBP formation in field conditions. A) Experimental setup at U.S.EPA T&E facility. \( t^* \) and \( t_0 \) are the starting times for the tank and the pipe units, respectively; B) Schematic showing the chlorine decay and DBP formation in response to bulk demand (reaction) and wall demand under the flow regimes; and C) Schematic to illustrate the three principal factors (in axes) examined in the pipe loops (PL#4 and PL#5). In the comparative studies, TOC and reactant compositions were maintained as a constant.
network conditions and to assist field applications.

The EPA study aims at determining chlorine decay and DBP formation and their quantitative relationships with three principal control variables: initial chlorine level, pipe materials, and flow regions within the pipe. The investigation is based on the use of a pilot-scale distribution system simulator designed to simulate water distribution under stagnant, laminar and turbulent conditions. In this paper, we report the investigation results on the relationship among DBP formation kinetics, pipe flow hydrodynamics, and pipe materials. The relationships on chlorine decay kinetics and modeling results will be presented elsewhere.

**EXPERIMENTS**

To better simulate field operations, the experiments are focused on isolation and quantification of flow hydrodynamics and pipe materials in DBP formation kinetics. Figure 1a shows a schematic of the experimental setup. The pilot-scale drinking water distribution simulator used for the tests has an unlined ductile iron and a PVC pipe loop, each measuring 22.9 meters in length. The new PVC pipe has a measured nominal diameter of 14.5 cm (Panguluri et al., 2007). The aged ductile iron pipe has heavy scale buildup and biofilm formation inside the pipe of an estimated 15.2-cm nominal diameter. In each experiment, the de-chlorinated Cincinnati tap water was re-chlorinated using sodium hypochlorite in a well-mixed 9463-L steel storage tank (Figure 1). The finished water (pH~8) was adjusted to a 4 mg/L total organic compound (TOC) concentration by the addition of Biohume® humic acid at time $t_0$. At time $t_0$, the water circulation in the pipe loop continued at a constant flow rate for 36 hours during which period water samples were collected through a sampling port and analyzed for concentrations of free and total chlorines, trihalomethanes (THMs) and haloacetic acids (HAAs). Individual THM and HAA compounds were quantified using extraction techniques followed by GC-ECD.

**Experimental Conditions**

Table 1 shows the experimental conditions for 10 sets of experiments on chlorine decay and DBP formation. Initial concentrations of humic acid in the storage tank remained at 4 mg/L. This TOC level is higher than that in finished water from a regular water treatment plant, and represents a worst-case scenario. In the experiments, initial free chlorine concentration in the 9463-L tank ranged from 1.9-5.1 mg/L and the concentration decreased by ~2 mg/L during the transferring and filling of the 420-L pipe loops (Figure 1). We noted the difficulty in controlling the initial free chlorine concentration in the pipe during these pilot-scale studies.

Flow rate and pipe materials are the two variables under systematic examination in this study with the objective to define their relationships with chlorine decay and DBP formation (Figure 1b and 1c). Flow rates in the testing were 6.31, 0.63, 0.38, and 0.19 L/sec, corresponding to a Reynolds number ($Re$) of 51500, 5100, 3100, and 1500 covering the full range of turbulent, transitional and laminar flows in field conditions. In addition, a stagnant flow condition ($Q=0$ L/sec) was also tested. Under these controlled experimental conditions, the variations in chlorine decay and DBP formation kinetics were quantified for the aged ductile iron and the new PVC pipes that offer two contrasting wall demand conditions.
Chlorine Decay and DBP Formation

There have been extensive studies and a wealth of literature on chlorine decay and DBP formation in drinking water pipes (Rossman et al., 2001; Biswas et al., 1993; Clark, 1998; Clark and Sivaganesan; 2002; Boccelli et al., 2003; Anastasia et al., 2003; Hua and Reckow, 2007). In a conceptual physical model, chlorine as an oxidant in drinking water reacts with TOC in bulk demand to form THMs and HAAs. It is also simultaneously transferred to pipe walls and consumed in reaction by wall demand with pipe materials and biofilms. These two processes are given by:

\[
\frac{\partial c_A}{\partial t} = \bar{u}_x \frac{\partial c_A}{\partial x} + \frac{1}{Pe_L} \left( \frac{\partial^2 c_A}{\partial x^2} \right) - k_b c_A - \frac{2k_{mt}}{a} (c_A - c_{A,w})
\]

\[
\frac{\partial c_A}{\partial t} = -k_b c_A \cdot c_B , \text{ and } \frac{\partial c_B}{\partial t} = -k_b c_A \cdot c_B
\]

where, \(c_A\) is chlorine concentration; \(c_B\) is the concentration of TOC and other chlorine scavengers, collected as bulk demand. \(c_{A,w}\) is chlorine concentration at pipe wall; \(k_b\) and \(k_B\) are, respectively, the bulk decay and TOC-chlorine reaction (DBP generation) kinetic constant; \(k_{mt}\) is the mass transfer coefficient; and \(t\) is time for \(t_o\) in Eqs.1-2 or \(t_o^*\) in Eq.2. Physical representations of \(t_o\) and \(t_o^*\) are shown in Figure 1a. Other hydrodynamic parameters are: \(\bar{u}_x\) - averaged water velocity across the pipe section along axial distance (x); \(Pe_L\) - longitudinal Péclet number.

The chlorine transport governing equation (Eq.1) has been discussed extensively in the literature and analytical solutions have been published for chlorine decay and transport in water pipes (Biswas et al., 1993; Rossman, 2002 and references therein). Clark and Haught (2005) developed a mass transfer limited chlorine model and compared it with others in Rossman et al. (1994) and Biswas et al. (1993). Further chlorine modeling and discussions for chlorine experimental results will be presented elsewhere. Based on Eq.2 and further assuming negligible competition for chlorine from wall demand and other bulk demand compared to the introduced TOC, the DBP formation follows second-order kinetics. Rewritten from Clark (1998):

\[
\frac{c_{\text{DBP}}}{c_A^0} = T - \frac{T(1-R)}{1-R \cdot e^{-ut}} + \frac{c_{\text{DBP}}^0}{c_A^0}
\]

where, \(c_{\text{DBP}}\) and \(c_{\text{DBP}}^0\) are DBP concentration at time \(t\) and the initial concentration at \(t_o\) or \(t_o^*\); \(c_A^0\) is initial chlorine concentration. \(u\) is the reaction rate constant. \(R\) and \(T\) are dimensionless parameters. Based on Eq.3, the ratio \(\frac{c_{\text{DBP}}}{c_A^0}\) is non-linearly related to the rate constant.

Based on this relationship, water samples collected from the pipe loop at designated time intervals were analyzed for free and total chlorine, THMs (CHCl₃, CHBrCl₂, CHBrCl₂, and CHBr₃), HAAs (CMCAA, MBAA, DCAA, TCAA, BCAA, BDCAA, BDAA, CDBAA, and
TBAA, pH, turbidity, and total organic carbon (TOC). In this paper, experimental results for the total THMs (TTHM) are discussed.

RESULTS AND DISCUSSIONS

In comparative studies at equivalent flow and other experimental conditions, the newly constructed PVC pipe in loop #5 and the ductile iron counterpart in loop #4 have shown different rates of chlorine consumption and THM formations. This difference is further explored in relation to the Reynolds number in the pipe.

Chlorine consumption and THM formation

Figure 2 shows an example of differential response in chlorine decay and THM formation between the aged ductile iron and the new PVC pipes. At the turbulent flow condition (Q=0.63 L/sec, Re=5100), the free chlorine decayed rapidly to depletion within 3 hours and 7 hours, for the ductile iron and PVC pipe respectively, after which the THM formation continued and reached a pseudo-steady state concentration.

Noteworthy in Figure 2 is the timing and concentration relationships between free chlorine residual loss and THM formation. After the depletion of free chlorine residual at t=3 hours, the THM concentration in loop #4 reached a pseudo-steady state concentration of 67.8 μg/L in the next 6 hours. The rate of THM formation in loop #5 is comparable with that in loop #4 before complete residual loss at t=3 hours (Figure 2). In subsequent time period, the two loops became different. Because of lower wall demand in the new PVC pipe, the chlorine residual remained present at t<7 hours. After complete residual loss, the THM concentration continued to rise asymptotically to a pseudo-steady state concentration of approximately 105 μg/L.
These observations indicate the dominant role of chlorine presence in the THM formation in a drinking water pipe. Because of this dependence, the THM formation and chlorine decay is a function of two interrelated processes: the chlorine-TOC reaction in the bulk phase, and the chlorine consumption at the wall (Figure 1b). For chlorine, the two competing processes are represented in the Eqs.1 and 2. If this is true for water pipes, it follows that both Eq.1 and 2 need to be solved simultaneously to obtain the time-dependent THM concentrations. Because chlorine wall consumption is flow-dependent in Eq.1 (Clark and Haught, 2005; Clark et al., 2006), the THM formation becomes dependant upon the hydrodynamic properties in pipe flow.

**THM Formation in Pipe Flows**

Based on Eq.2, Clark (1998) laid the mathematical foundation for subsequent work (Clark and Sivaganesan, 2002; Boccelli et al., 2003; Warton et al., 2006) for modeling and calculation of THM formation in a drinking water pipe. The analytical solution of governing Eq.2 is given in Eq.3 (Clark, 1998), and can be applied to the experimental results on THM formation. Figure 3 shows the experimental results for loop #4 and loop #5, and the non-linear regression results based on Eq.3. Under all flow conditions ($Re = 0 – 51500$), the experimental results are sufficiently described by the second-order DBP formation kinetics.
A detailed analysis also indicates the differences between two pipe materials in THM formation kinetics and their variation with the Reynolds number ($Re$). In the aged ductile iron pipe in loop #4, free chlorine residual decreased rapidly and DBP concentrations reached an asymptotic level within 7-10 hours (Figure 3). The pseudo-steady state condition, as described earlier in Figure 2, is the result of complete loss of free chlorine residual in the water. In water distribution network operations, re-chlorination is generally applied to compensate the excessive loss of chlorine residual to control biological contaminants. Boccelli et al. (2003) described the DBP formation in re-chlorination process. In the experiments at loop #4, the aged ductile iron pipes can lose all chlorine residual within 10 hours. For many parts of a distribution network, water age is often more than 24-hours and re-chlorination is required. The re-chlorination, however, is likely to further increase the DBP levels. For example, the asymptotic TTHM level was 60-75 μg/L in the experiments of aged ductile iron pipe loop. The initial free chlorine level was ~2.0 mg/L comparable to that of finished water but the TOC level (4 mg/L) was relatively high. Nonetheless, the observed 60-75 μg/L TTHM concentration is only 5-20 μg/L below the U.S. drinking water standard 80 μg/L. In the Stage I DBPR (63 FR69390 at 69396), EPA reduced the existing MCL for TTHM from 0.10 mg/L to 0.080 mg/L (63 FR 69390 at 69396). Therefore, it may be necessary to optimize the re-chlorination operation to minimize THM formation during the re-chlorination process.

Secondly, DBP formation rate is different in new PVC pipes. This difference is largely due to the low chlorine loss and longer duration of chlorine present in the experiments under turbulent flow conditions. When the free chlorine residual is consumed, the DBP concentration subsequently reached an asymptotic level around 80-100 μg/L (Figure 3). For the PVC pipe under turbulent conditions, this occurred with a water age >20 hours in the experiment.

**Reaction Rate and Flow Regions**

The reaction rate ($u$) in Eq.3 is a function of chlorine-TOC reaction kinetic constant ($k$), initial chlorine concentration ($C_o^c$), and the reaction stoichiometric constant ($a, b$). Rewritten from Clark (1998) and Boccelli et al. (2003),

$$u = \frac{C_o^c R k}{(1 - R)} \quad \text{and} \quad R = \frac{a \cdot C_o^c b}{b \cdot C_A^o}$$

or

$$k = \frac{R}{C_o^c (1 - R)} u$$

In deriving Eq.3 for THM generation, it is assumed (Boccelli et al., 2003) that observed chlorine residual loss equals to THM formation adjusted by the reaction stoichiometric constants. This assumption applies for bottle experiments with negligible wall demand. In Eq.4, the reaction constant is dependent upon only the initial concentrations of the reactants and on the reaction properties in THM formation.

However, when the wall demand becomes important relative to the THM-forming reactions in the bulk, free chlorine residual is consumed in two simultaneously-occurring
processes (Figure 1b) as given in both Eq.1 and 2. The reaction constant \((u)\) solved from Eq.3 contains the effect of wall demand. Mathematically, the larger the wall demand, the greater is the apparent reaction constant. In the pilot-scale pipe loop experiment, the intrinsic relationship is shown in Figure 4 where the experimentally determined reaction constants are plotted against Reynolds number representing the stagnant, laminar, transitional and turbulent flows. The reaction constant for the new PVC pipe falls into a narrow range except for the experiment at \(Re=1500\). A large difference is shown for the aged ductile iron pipe at turbulent and stagnant flows. Under the stagnant flow and turbulent flow conditions \((Re>4100)\), the aged ductile iron pipe is found to have a higher rate of chlorine decay and DBP formation (Figure 3) and larger reaction rate constants (Figure 4) than the PVC counterparts.

The apparent difference at turbulent flow is largely a result of mass transfer enhanced wall demand. This is consistent with the rapid chlorine decay shown in Figure 2 for the \(Re=5100\) experiments. Clark et al. (2006) discussed the mass transfer enhancement in chlorine decay, and attributed it to the observed dependency of chlorine decay on flow properties. Conversely, the flow-related differences between the two pipes diminish in the stagnant flow experiments. The water in the pipes is equivalent to that in the storage tank typical of a batch reaction process. Consequently the influence of flow-related mass transfer becomes negligible. This leads to the similar time-series DBP formation curves between the ductile iron pipe and the steel storage tanks (Figure 3). It also follows that due to its greater wall demand, the aged ductile iron pipe has a greater apparent reaction constant than the new PVC pipe (Figure 4).

Obviously, the relationships among the apparent reaction constant, wall demand and flow properties will be benefitted from further quantitative modeling assessments.

**SUMMARY**

The chlorine decay and DBP formation experiments were conducted using a pilot-scale pipe loop device under controlled flow conditions similar to those of field network operations.
Tested conditions included stagnant, laminar and transitional, and turbulent flows (Re=0 – 51500). Major findings are:

- Compared to the aged ductile iron pipe, the new PVC pipe has lower chlorine decay rates and lower apparent reaction constants in THM formation under turbulent and stagnant flow conditions. The difference is the largest at fully turbulent flow conditions, likely as a result of flow-assisted chlorine mass transfer toward pipe walls. Under stagnant flow, the ductile iron pipe and the steel storage tank behave similarly with higher chlorine decay rate and higher apparent THM formation rate than the new PVC pipe.

- In a flowing water pipe, chlorine residual loss occurred in competition between wall demand and bulk phase reaction. The reaction between TOC (or organic matter) and chlorine in the bulk results in DBP formation. When chlorine residual is depleted, THM formation continues and reaches an asymptotic level within 7-10 hours. Re-chlorination as required to protect drinking water from biological contaminants, will further increase the THM formation. The operation optimization is necessary to assure TTHM concentration below the 80 μg/L standard set forth in the U.S. EPA drinking water regulations (63 FR 69390 at 69396). Further studies on the optimization of re-chlorination practice are needed.

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