Application of First Order Kinetics for Modeling Chlorine Decay in Water Networks

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Abstract— Modeling chlorine residuals in water networks is quite complex, as decay rates depend on many factors. In this paper, first order chlorine decay reactions were used to simulate the water distribution network of Mtaileb-Rabieh in Lebanon. A set of water samples were analyzed for free residual chlorine. The experimental results showed that the value of the bulk decay rate is ($-8*10^{-5}$ min^{-1}). An extended period simulation was prepared using “Watercad” software. The hydraulic and water quality models were calibrated by adjusting Hazen-Williams coefficient and the pipe wall decay rate respectively. The results showed that pipe wall decay rate for 65-year-old cast iron and 20-year-old cement lined ductile iron pipes are (-0.5 day^{-1}) and (- 0.05 day^{-1}) respectively. As well, it was observed that 60% of the chlorine loss is due to pipe wall reaction, while 10% & 30% represent the bulk & tank reactions respectively.

Keywords— Residual chlorine, extended period simulation, pipe wall reaction, bulk decay, hydraulic modeling, water quality, calibration.

1 INTRODUCTION

In the past, many water suppliers thought that making a good hydraulic design is sufficient to supply consumers good water quality. Analyzing hydraulically a water distribution network is not sufficient to ensure that all consumers are getting good drinking water quality. Numerous factors affect water quality in the distribution system such as pipe material, diameter, presence of corrosion by-products and biofilm, water temperature, disinfectant residuals, and hydraulic conditions.

Water treatment has been practiced since a long time but with little understanding of the principles involved in the improvement of water quality. At these days, there is an increasing concern on the part of water utilities and regulatory agencies regarding potential water quality problems in drinking water distribution systems. Although considerable effort has been invested to assure good quality discharged out of the water treatment plant, the problem within the distribution system which might be a major factor in diffusing safe water to consumers, has received less attention. The quality of treated water leaving the treatment plant may deteriorate through complex physical, chemical and biological transformations that occur during its travel through the distribution system.

Drinking water must be free from organisms capable of causing diseases and from minerals and organic substances producing adverse physiological effects. Disinfection is a technique used to kill the microorganisms that cause diseases in water. It is used to destruct harmful and objectionable organisms in water. Drinking water has been disinfected since the beginning of the nineteenth century (Castro & Neves 2003). In the developed world the use of water supply disinfection as a public health measure has been responsible for a major reduction in people contracting illness from drinking water (Environmental Protection Agency 2011).

With more deep understanding to disinfection, several key factors such as kind and concentration of organisms to be destroyed, kind and concentration of disinfectant, contact time period, chemical characters and temperature of the water to be treated could potentially affect disinfection efficiency and level of treatment. The most common chemical disinfectant for water treatment, and the one that has historically made the greatest contribution to the prevention of waterborne disease worldwide, is chlorine (Environmental Protection Agency 2011).

Nowadays, the use of chlorine has become universal in the disinfection of water supplies. Chlorine is a strong oxidizing agent, it kills the bacteria and it may be applied to water to remove iron and manganese but it enhances the production of trihalomethane. Chlorine is used not only as a primary disinfectant in water treatment, but is also added to provide a disinfectant residual to preserve the water in distribution, where the chlorine is in contact with the water for much longer than during treatment (Environmental Protection Agency 2011). Free and total chlorine concentrations decreased with increasing residence time in the distribution system.

In this paper, a case study has been done to simulate free chlorine decay in water networks using “WaterCad” software. Hydraulic calibration of the “WaterCad” model followed by an extended period water quality calibration are performed in order to determine the pipe wall decay coefficient.

2 CHLORINE DECAY KINETICS

The modeling of chlorine residuals in water transmission and distribution systems is quite complex, as decay rates depend on many factors, water temperature,

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natural organic matter nature and concentration, reduced inorganic substances concentration, pH, initial chlorine concentration and hydrodynamic conditions (Monteiro et al. 2016). Clark et Haught (2005) supported the concept that the rate of free chlorine residual loss increased with velocity in unlined metallic pipe. Clark et al. (1986) showed how chlorine residuals could vary throughout the day at different locations in a distribution system depending on the flow path and residence time of the water reaching a location. Clark et al. (2010) confirmed that increased velocities in unlined pipes can result in increased losses in chlorine residual. Al-Jasser (2007) found that the effect of pipe age was most evident in cast iron pipes, whereas steel pipes were less affected. Hunt et Kroon (1991) noted that smaller pipes of the main transmission lines required larger decay rate constants to match observed chlorine levels better.

Biswas et al. (1993) developed a model for chlorine decay within single pipes under steady state flow conditions that included both bulk flow reaction and radial diffusion, and subsequent pipe-wall reaction of chlorine. It is assumed that chlorine decays by first order kinetics with respect to chlorine as defined below:

$$\frac{dC}{dt} = -KC \qquad (1)$$

$$C = C_0 e^{(-Kt)} \qquad (2)$$

$$C = C_0 e^{-(Kb+Kw)t} \qquad (3)$$

Where
C = Chlorine Concentration at time t (mg/l)
C0 = Initial Chlorine Concentration (mg/l)
K = Overall Chlorine Decay Coefficient (days^{-1})
Kb = Bulk Decay Coefficient (days^{-1})
Kw = Wall Decay Coefficient (days^{-1})
t = Time in days

2.1 Bulk Decay

Bulk fluid reactions occur within the fluid volume and are a function of constituent concentrations, reaction rate and order, and concentrations of the formation products. The sign of the reaction coefficient signifies that a formation reaction (positive) or a decay reaction (negative) is occurring. The parameter used to express the rate of the reaction occurring within the bulk fluid is called the bulk reaction coefficient (K_b) which can be determined through the bottle test.

2.2 Wall Decay

The rate that disinfectant decays at the pipe wall depends on how quickly disinfectant is transported to the pipe wall and the speed of the reaction once it is there. Clark et al. (1993) reported that the wall decay coefficient (K_w) could exceed (K_b). Hua et al. (1999) examined three test pipes and found that K_w is only 10% of Kb. Rossman et al. (2001) reported that K_w value on the order of 3 day^{-1} was reasonable for cast and ductile iron pipes. A study by Doshi et al. (2003) suggested that with older unlined metal pipes, chlorine wall demand increases significantly with flowrate. Ahn et al. (2004) found that the wall decay of ductile iron pipes lined with cement mortar varies between 0.02 & 0.2 day^{-1}, while it varies between 0.1 & 0.7 day^{-1} for unlined grey cast iron pipes.

3 Materials & Methods

3.1 Network Description

The water network of Mtaileb-Rabieh region (347 hectares) in the Northern Suburb of Beirut in Lebanon was selected as a case study to simulate the free residual chlorine through comparing the field measurements to the calculated values using "WaterCad". The treated water is being supplied from Dbaye water treatment plant which serves the area under study in addition to two other areas not under this study. Dbaye water treatment plant treats about 75,000 m^3/day. The water pipes of the study area are made of cast iron and were installed in 1950. In 1995, the water authority has replaced most of the pipes (except the 600 mm diameter) by cement lined ductile iron pipes. The current water network model shown in Figure 1 consists of:

- A water treatment plant at Dbaye district including pump station 1 to pump water to Jal El Dib through a 600 mm diameter cast iron pipe with a length of 4,000 m installed in 1950.
- Pump station 2 at Jal El Dib to pump water to Lower Rabieh tank through a 300 mm diameter cement lined ductile iron pipe with a length of 3,735 m installed in 1995.
- Pump station 3 at Jal El Dib to pump water to Deir Al Salib through a 300 mm diameter cement lined ductile iron pipe with a length of 1,500 m installed in 1995.
- Pump station 4 at Lower Rabieh tank to pump water to Higher Rabieh tank through a 200 mm diameter cement lined ductile iron pipe with a length of 1,725 m installed in 1995.
- Pump station 5 at Lower Rabieh Tank to pump water to Mtaileb tank through a 300 mm diameter cement lined ductile iron pipe with a length of 1,900 m installed in 1995.
- Cement lined ductile iron distribution pipes (100 & 150 mm diameter) installed in 1995.

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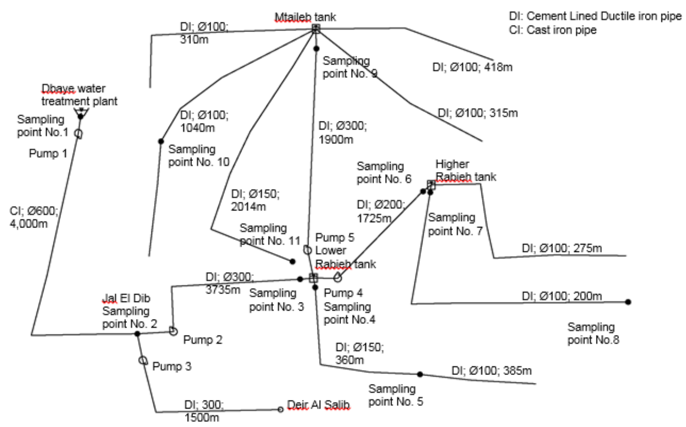

Fig. 1 Mtaileb-Rabieh water distribution network & water sampling locations

To assess the chlorine decay in the study area, field investigation was divided into two parts. The first part consists of reading the actual pressures where pressure gauges exist. These readings are used to calibrate the hydraulic model. The second part consists of collecting water samples and performing in-situ tests in order to measure the free residual chlorine and then determine the decay coefficients.

3.2 Water Demand Diurnal Pattern

After analyzing the flow readings, a 24 hour demand pattern shown in Figure 2 was prepared in order to simulate the hydraulic model.

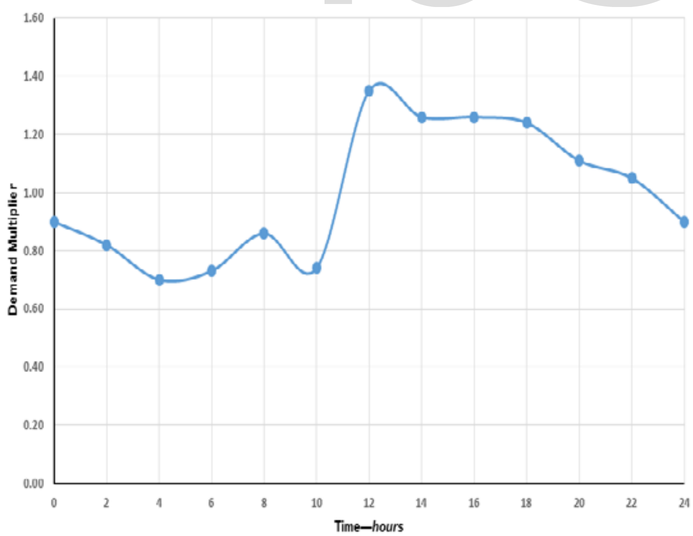

Fig. 2 Water Demand Diurnal Pattern

3.3 Sampling Points

Water samples are collected from several locations and analyzed in order to measure the free residual chlorine in the system. Sampling locations are selected taking into consideration the populated areas, existence of water facilities and sites accessibility. Some specific locations are not covered due to security reasons. Eleven sampling locations are selected as follows:

a- Seven sampling points at the water facilities (Dbaye treatment plant, Jal El Dib pumping station, inlet and outlet of lower Rabieh tank, inlet and outlet of higher Rabieh tank and inlet of Mtaileb tank).

b- Four sampling points within the distribution network as shown in Figure 1.

A total of 135 samples are collected from the water system. 16 samples from Dbaye water treatment plant and 119 samples are collected from various locations within the water network. Figure 3 shows the measured values of the free residual chlorine in the collected water samples from the identified sampling locations.

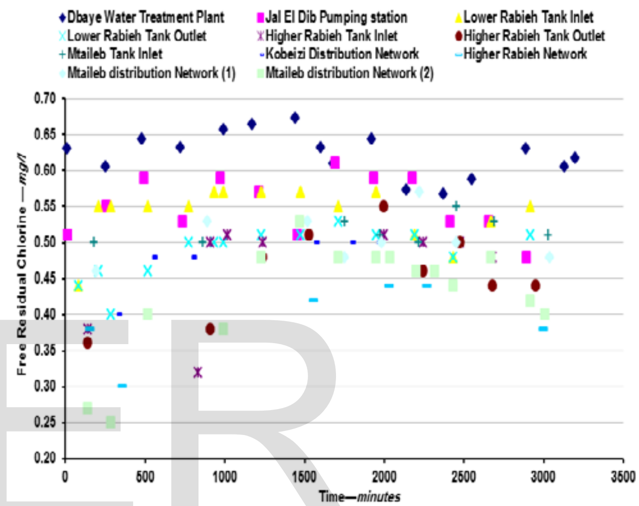

Fig. 3 Free residual chlorine measurements

3.4 Bulk Decay Coefficient (K_B)

Chlorine bulk decay coefficient was be determined using a simple experimental procedure called a bottle test. The first order decay equation was used as a good fit to determine the decay of free chlorine.

Chlorine decay was studied in 100 ml amber glass bottles according to Powell et al. (2000) bottle tests. The bottles were treated with 10 mg/l free chlorine in Milli-Q water to remove any chlorine demand. In order to determine the bulk decay, steps procedure indicated by Walski et al. (2001) were followed. Sixteen water samples were collected from Dbaye treatment plant sampling point. The bottles were stored in an incubator in order to be placed at constant temperature. The chlorine concentration of the first bottle was measured and the time was noted as the start time. Samples were tested every half hour for the first two hours in order to determine if it is a fast or slow reaction, then every two, four and six hours. The duration of the bottle test was 32 hours. All chlorine measurements were analyzed for the N,N-diethyl-p-phenylenediamine (DPD) colorimetric method (APHA 2005). The constituent concentrations are charted along the Y-axis in log scale, and the time is charted along the X-axis. Figure 4 shows the test data and the best fit straight line. The slope of the line for the data presented in Figure 4, (-8*10-5 min^{-1}), is the bulk reaction coefficient with a regression coefficient (R^2=0.9457).

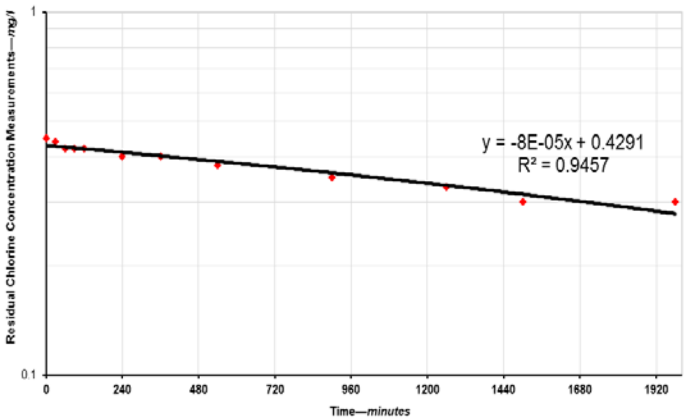

Fig. 4 Chlorine bulk decay rate

3.5 Wall Decay Coefficient (K_W)

Since the wall decay coefficient depends on the actual conditions of the pipe such as material, age, diameter, roughness, biofilm formation and water temperature, it is difficult to measure it in laboratory. As the network consists of 65 year old cast iron pipes and 20 year old cement lined ductile iron pipes, several values of K_w were assumed as follows:

- (-0.5, -1, -1.5) for cast iron pipes.
- (-0.02, -0.05, -0.1) for cement lined ductile iron pipes.

In order to determine the wall decay coefficient, several scenarios were performed using the "WaterCad" software until the values of the free residual chlorine from the model are close to the measured concentrations at different sampling locations.

4 Results & Discussions

4.1 Hydraulic Modeling

Characteristics of the existing water network such as pipes sizes, materials and construction dates along with the survey data about the network layout and operation obtained from field were input into the "WaterCad" software. A hydraulic model of the water distribution network is prepared followed by a hydraulic calibration. A 24 h extended period simulation was performed to compute flows, pressures and velocities in all pipes.

Pressure measurement was used as one of the hydraulic calibration methods (Ormsbee 1986). The hydraulic model was calibrated by adjusting Hazen-Williams coefficient (C-factor). The pipes were classified into two groups according to their material & installation date as follows:

- Group 1: 600 mm cast iron pipes installed in 1950.
- Group 2: 100 to 300 mm cement lined ductile iron pipes installed in 1995.

Several hydraulic extended period simulation scenarios were performed using "WaterCad" software covering all possible alternatives for the assumed Hazen-Williams coefficient "C" for both groups 1 & 2 as shown in Table 1 below:

Table 1 Hydraulic Model Scenarios

		Scenario								
		1	2	3	4	5	6	7	8	9
C value for Group 1	65	x	x	x						
	70				x	x	x			
	75							x	x	x
C value for Group 2	125	x			x			x		
	130		X			x			x	
	135			x			x			x

Hydraulic calibration was done by calculating the squared relative difference and the mean square error (MSE) between the calculated and measured pressures at 10 existing pressure gauge stations. Then, the average mean square error was calculated for each scenario. The optimum "C" value was selected from the scenario that resulted in the least average mean square error. Scenario No. 2 having a C value of 65 for cast iron pipes & 130 for cement lined ductile iron pipes has the least average mean square error as shown in Table 2.

Table 2 Mean Squared Error for the Hydraulic Scenarios

Scenario	1	2	3	4	5	6	7	8	9
MSE	0.24	0.21	0.30	0.24	0.24	0.29	0.33	0.26	0.31

4.2 Water Quality Modeling

After performing the hydraulic analysis, an extended period water quality analysis was performed based on chlorine constituent. This analysis will help to reveal the values of wall reaction rates for all pipes and estimate the amount of the chlorine losses in the water distribution network. The value of the bulk decay constant K_b (–8x10^{-5} min^{-1}) obtained from the bottle test was assigned to all pipes and tanks. The only remaining parameter to be specified in the chlorine decay model was the wall decay constant K_w. Several values of K_w were assumed as follows:

- (-0.5, -1, -1.5) for group 1.
- (-0.02, -0.05, -0.1) for group 2.

Several extended period simulation scenarios were performed using "WaterCad" software covering all possible alternatives for the assumed Kw for both group 1 & 2 as shown in Table 3 below.

Table 3 Water Quality Model Scenarios

		Scenario								
		1	2	3	4	5	6	7	8	9
K_w for Group 1	-0.5	X	X	x						
	-1				x	x	x			

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	-1.5							x	x	x
K_w for Group 2	-0.02	X			x			x		
	-0.05		X			x			x	
	-0.1			x			x			x

Calibration of the water quality model was done by calculating the squared relative difference and the mean square error (MSE) between the measured and calculated free chlorine residual concentrations at each sampling point for all the scenarios. Then, the average mean square error is calculated for each scenario. The optimum K_w value was selected from the scenario that resulted in the least average mean square error. It was found that scenario No. 2 having a K_w of (-0.5) for cast iron pipes & (-0.05) for cement lined ductile iron pipes had the least average mean square error as shown in Table 4.

Table 4 Mean Squared Error for the Water Quality Scenarios

Scenario	1	2	3	4	5
MSE	0.0045	0.0018	0.012	0.063	0.022
Scenario	6	7	8	9	
MSE	0.052	0.0086	0.0034	0.0057	

For wall reaction coefficient K_w of (-0.5 day^{-1}) for the pipeline from Dbaye treatment plant to Jal El Dib pumping station and wall reaction coefficient Kw of (-0.05 day^{-1}) for all other pipes, the model free residual chlorine values are close to the field measurements. The value of the wall reaction Kw for the pipeline from Dbaye treatment plant to Jal El Dib pumping station is greater than the value of the wall reaction Kw for the remaining pipes. This is mainly due to pipe age (65 years old) for cast iron pipe while all cement lined ductile iron are 20 years old.

After determining the values of the bulk and wall decay rate, the total chlorine loss in the system due to the reactions in the tanks, bulk flow and pipe wall reaction were calculated. Figure 5 shows the free chlorine loss versus time for the entire network. It is clear that the system itself, due to pipe wall demand utilizes a significant chlorine demand. The repeating pattern of increasing or decreasing the chlorine loss is due to the residence time of the water in the tanks. The chlorine loss due to tank reaction is proportional to the residence time of the water in the tank.

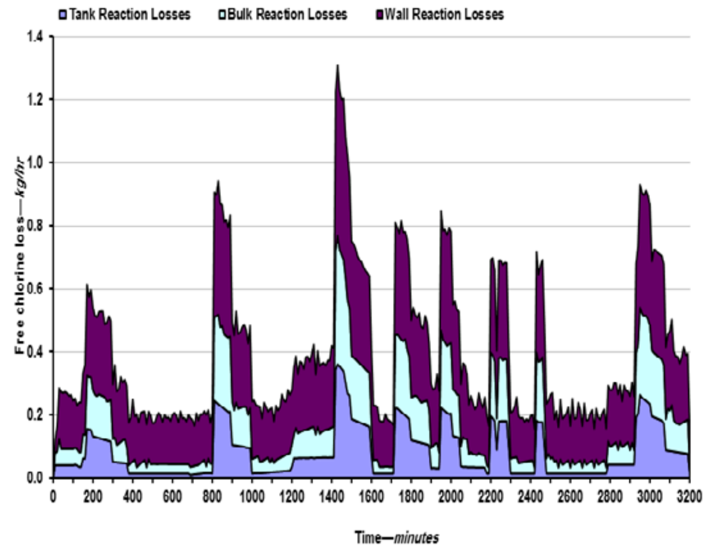

Fig. 5 Predicted free chlorine loss rates

It can be concluded that a cleaning or replacement program for the pipes will be more effective than changing tank operation in reducing the overall chlorine loss in this system. The high level of decay within pipes might be more serious than long residence times in tanks. These losses imply that the pipes are old especially the pipeline connecting Dbaye treatment plant to Jal El Dib pumping station. Figure 6 represents the percentage of chlorine loss due to bulk, pipe wall and tank reactions (60% loss at the wall, 10 % in the bulk flow, and 30 % in the tank).

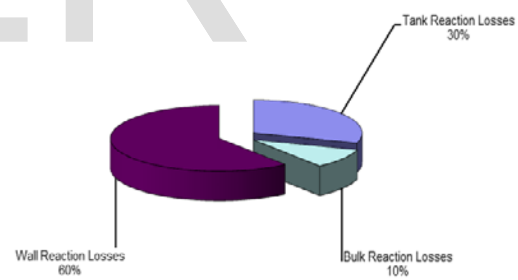

Fig. 6 Chlorine Losses

5 Summary & Conclusions

Chlorination is one of the most efficient methods to have potable water free from organisms capable of causing diseases and organic materials that affect its taste and odor. There is an increased interest among international regulatory agencies and water utilities in the factors that result in chlorine propagation and deterioration between the treatment plant and the consumer's tap. Having a calibrated hydraulic & water quality model is a necessity. In this study, a simulation of the existing water network of Mtaileb-Rabieh in Lebanon for the determination of the free residual chlorine concentrations, bulk and pipe wall decay rates was prepared. Field measurements showed that consumers are receiving a good water quality with respect to chlorine concentration. The laboratory experiments resulted in a value of (-8*10-5 min^{-1}) for the bulk decay rate. A hydraulic model of the water network was prepared followed by a hydraulic calibration.

For the determination of the pipe wall reaction rates, an extended water quality period simulation for chlorine concentration was performed using "WaterCad" software. The results showed that pipe wall demand varies between pipe materials and age. The pipe wall decay rate for 65 year old cast iron and 20 year old cement lined ductile iron pipes are (-0.5 day^{-1}) & (- 0.05 day^{-1}) respectively. For the study area, the free chlorine loss rate due to reactions in tanks, bulk flow and pipe wall are 30%, 10% and 60% respectively. It can be concluded that replacing the 65 year old cast iron pipe by a new cement lined ductile iron pipe could reduce the chlorine losses and therefore reducing the chlorine dose at the source. Future works to be focused on the correlation between the pipe roughness coefficients, flow rate, water temperature and the pipe wall decay rate.

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