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EVALUATION OF FACTORS AFFECTING BULK CHLORINE DECAY KINETICS FOR THE ZAI WATER SUPPLY SYSTEM IN JORDAN. CASE STUDY

Chlorine decay behavior is significantly variable since it depends on the quality of water and the condition of a distribution system. The effect of various parameters on the bulk chlorine decay kinetics in water samples collected from the Zai water treatment plant in Jordan has been examined. These parameters are reaction time, temperature, TOC, and free chlorine dose. An empirical equation describing the abovementioned effects has been derived. The general trend of chlorine decay decreases upon time and can fairly be represented by first-order decay kinetics. An increase in the value of temperature and TOC parameters has proportional effects on the decay of bulk chlorine. However, the data show that the decay constants were found to be inversely proportional to the initial chlorine concentration. A general correlation for the calculation of bulk chlorine decay rate constant as a function of the parameters in question of this study has been proposed. Consequent predictions are in good agreement with the observed results in this study.

1. INTRODUCTION

Chlorine is predominately used for water treatment disinfection due to its aesthetic quality control, low cost, and broad range of effectiveness [1–5]. Because of its oxidizing potentials, minimum levels of chlorine residual must be maintained in the water distribution system to maintain both chemical and microbial quality of treated water [5–7]. Generally, most of chlorine used for disinfection is consumed in the oxidation process and

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a small fraction reacts to form disinfection by-products which are trihalomethanes, haloacetnitriles, chloroketones, chloroacetic acids, cyanogen chloride, chlorophenols [3–5, 8, 9]. The consumption of chlorine in the bulk aqueous phase is generally assumed that the chlorine decays by first order kinetics [10, 11]. The effect of bromide ions on shifting the reaction gradually from chlorinated trihalomethanes to brominated ones, as bromide acts like a substituting agent, was investigated in Jordan under specific disinfection conditions, such as reaction time, pH, and temperature [5].

Several models have been proposed and investigated to describe the chlorine decay kinetics and mechanism [12]. In addition to the aforementioned first order decay kinetics [6, 13], these models include: second order [13], power-law decay (*n*-th order) [11, 14], parallel first order [15], limited first-order decay, limited *n*th order. However, in all these models, only two variables, chlorine concentration and time, have been considered [16]. On other hand, mathematical predictive models for chlorine decay, as well as THMs formation in other models, based on empirical relationships have been investigated in the literature [2, 3]. Moreover, the empirical relationships of chlorine decay with some parameters were developed using different regressions methods [17].

For instance, a combined equation using various relationships can be developed to predict the chlorine decay over a range of conditions. Hallam et al. [18] described the relationship between the rate constant for chlorine decay and the initial chlorine concentration, temperature, total organic carbon (TOC) concentration and the number of times the water had been rechlorinated.

2. KINETIC MODEL

The decay rate of residual chlorine due to reactions with materials in the bulk aqueous phase is assumed to be in proportion of its concentration in the bulk phase. This may be expressed as:

$$\frac{dC}{dt} = -kC \tag{1}$$

where C is the chlorine concentration at the time t (mg/dm^3), k is the decay rate constant (day^{-1}), t is the time (day).

Equation (1) will be solved as:

$$C_{Cl}(t) = C_{Cl,\,0}\mathrm{e}^{-kt} \tag{2}$$

where, $C_{Cl}(t)$ is the free chlorine concentration (mg/dm^3) at time t, which is also called the chlorine residual, $C_{Cl,\,0}$ the free chlorine concentration (mg/dm^3) at time zero, which is the initial chlorine concentration, and k is the first-order rate coefficient (day^{-1}).

However, the first-order decay rate coefficient (k) is expressed in the present study as the decay due to the quality of the water itself, known as the bulk decay (k_b) [19]. The k_b is dependent on the water temperature [20], as well as, on the total organic carbon (TOC) content in water. Moreover, it has been reported that k_b is inversely proportional to the initial chlorine concentration [11]. Accordingly, the dependence of k_b on the temperature and TOC is expressed by the following equation [15]:

$$k_b = a \left(\frac{1}{C_{Cl,0}} \right) \left(TOC - b \right) \exp \left(-\frac{e}{T + 273} \right) \tag{3}$$

where, TOC is in the range of 1–3 mg/dm^3, and T is temperature expressed in °C. Constants a, b, and e can be estimated by the determination of k_b for various temperatures and other water quality conditions. The values of a, b and e probably depend on the characteristics of the organics in each water and therefore may vary spatially in the water distribution system [15]. However, care must be taken when statistically estimating the values of these three constants since they should not be extrapolated beyond the range of validity that temperature varies from 5 °C to 25 °C, and TOC ranges from 1 to 3 mg C/dm^3.

The kinetics of chlorine decay in the bulk phase can be determined from conducting long term bottle tests (i.e., batch testing of samples held in dark bottles over increasing periods of time). Analytical kinetic models of free chlorine decay have been developed despite of the complexity of the reactions of chlorine with organic materials in water. The consumption of chlorine in water occurs through complex sequential and parallel reaction pathways with unknown rates [21].

However, to date; no authors reported on the analyses of factors affecting bulk chlorine decay kinetics on a real system such as for the Zai water supply system in Jordan, nor in the neighboring countries. Hence, the overall objective of this study was to investigate the effects of temperature, free chlorine dose, and TOC values of the Zai water on the bulk decay of free chlorine together with the development of functional relationships that can be used to enhance the durability of network models in Jordan. These relationships might be integrated to produce an equation capable of predicting decay rate constant values.

3. MATERIALS AND METHODS

Sampling site and sample conservation. The procedure adopted in this study was based on collecting 2 l samples from the effluent of the Zai water plant with water characteristics: pH 7.8, TOC 2.17 mg C/dm^3 and Br$^-$ concentration 52 µg/m^3. The samples were stored in the dark at certain constant temperature. For each measurement, a small 5 cm^3 sample was taken from the original large sample. The concentration of chlorine (Cl$_2$) was determined at specified conditions. In this part of the study, the measurements

were made at the laboratory scale for different combinations of Cl$_2$ concentration, contact time, TOC, and at increasing periods of times. pH was adjusted for each sample by the drop-wise addition of 0.1 M HCl or 0.1 M NaOH.

Effect of reaction time, temperature, TOC, and chlorine dose. The concentrations of Cl$_2$ were determined after the following reaction times: 0, 1.25, 5.25, 10.0, 18.0, 23.0, 29.25, and 49.25 h. The other parameters were fixed at: temperature 5 °C, pH 7.8, TOC 1.14 mg C/dm^3 and Br$^-$ concentration 42 µg/m^3. The study of the effect of temperature on the decay of Cl$_2$ was carried out at temperatures of 5, 14, 28, and 40 °C. The other parameters were fixed at: TOC 0.829 mg C/dm^3, pH 7.71, reaction time 3 h, and Br$^-$ concentration 50 µg/m^3. The residual Cl$_2$ was checked and changed for each sample by the drop-wise addition of standard Cl$_2$ solution prepared from 6% sodium hypochlorite solution.

The concentrations of Cl$_2$ were determined at the following conditions: temperature 14 °C, TOC 0.829 mg C/dm^3, pH 7.71, reaction time 1.5 h, and Br$^-$ concentration 50 µg/m^3, and at the following Cl$_2$ residuals values: 1.2, 1.75 and 2.88 mg/dm^3.

In order to study the effect of TOC different values in the lab, drops of influent water (with water characteristics: pH 7.8, TOC 2.17 mg C/dm^3 and Br$^-$ concentration 52 µg/m^3) were added to the effluent water to achieve the required TOC concentration for each final sample. The following TOC values: 1.33, 1.82, and 2.04 mg C/dm^3 were considered in this study. With these TOC levels, the concentrations of Cl$_2$ were determined for water samples under the following conditions: reaction time 2 h, temperature 15 °C and Br$^-$ concentration of 55 µg/m^3. In these experiments, there were very slight variations in pH and Cl$_2$ residuals for the three samples. These changes in pH are due to the presence of organic acids resulting in pH values of: 7.84, 8.01, 7.88. Rapid Cl$_2$ decay reaction resulted in different levels of Cl$_2$ (0.84, 0.7, 0.6 mg/dm^3). For those reasons an average pH of 7.91 and an average Cl$_2$ residual of 0.74 mg/dm^3 were taken for those samples.

Analyses. The DPD-colorimetric method was employed for residual chlorine measurement following Standard Methods 4500-Cl F [22]. The TOC analyzer employed was a DC-180 (3300) (Dorhman/Rosemount) with non dispersive infrared detector (NDIR). The pH was measured using an ORION 960 automatic system, with pH electrode (model No. 9172 BN). The bromide concentration in water samples was measured using an ion chromatograph (Model: DX-120, Dionex, USA) equipped with an IonPac AS14A analytical column and a conductivity detector (CD-20, Dionex).

4. RESULTS AND DISCUSSION

4.1. GENERAL CORRELATION

Based on the results of analyzing Cl$_2$ in the samples, in Fig. 1 plots of the observed decay in Cl$_2$ residual over time are shown. The behavior is seen to follow a first-order

kinetics. The first-order decay rate constant, k, is determined from the experimental data using best fit technique where reasonable fit is observed in Fig. 1. The best fit first-order decay rate constant for these data was calculated to be 0.53 day^{-1} (0.022083 h^{-1}). The experimental decay rate obtained in this study is very closely agreed with other studies where the k_b values were reported between 0.02–0.09 h^{-1} [20]. A bulk decay constant k_b of 0.55 day^{-1} was reported by Rossman [10]. Some researchers assumed a simple first--order Cl$_2$ decay reaction with bulk reaction rate coefficients ranging from 0.09 day^{-1} to 0.53 day^{-1} [13].
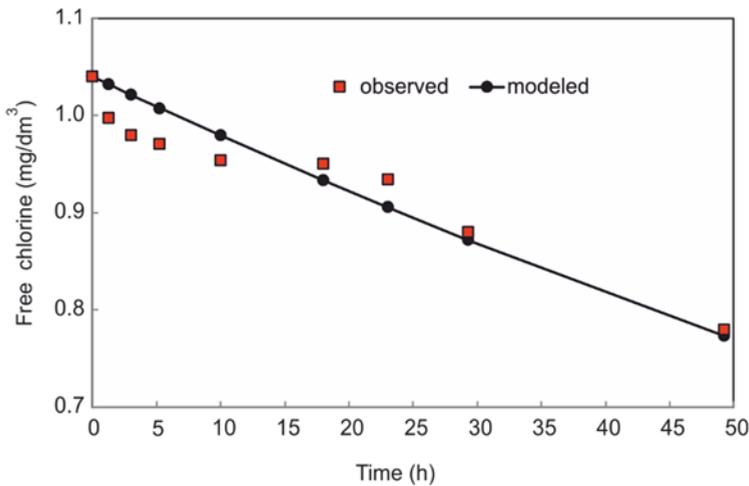

Fig. 1. Regression of Cl$_2$ decay kinetics for drinking water
at 5 °C, pH 7.8, TOC 1.14 mg C/dm^3, and [Br$^-$] 42 µg/m^3

4.2. REGRESSION MODEL

Equation (3) was rearranged and linearized to a multivariable linear fit. Accordingly, the Arrhenius equation was fitted to each set of tests by optimizing the values of a, b, and e to minimize the sum of the squared errors between modeled and observed k_b values. Accordingly, the values of $a = 4.977 \times 10^6$, $b = 0.6478173$, and $e = 5501.08$ °C were obtained. With $R^2 = 0.83$. Figure 2 shows the best fit regression between the modeled and observed k_b values. It is noticeable from the model and experimental results and under the conditions stated before that the free Cl$_2$ concentrations of the Zai treatment plant's drinking water decreases as the reaction time increases. The Cl$_2$ decay can fairly be represented by first-order decay kinetics as shown in Fig. 1 where good agreement between the experimental results and the model was achieved.

The general trend of Cl$_2$ decay decreases with time, as shown in Fig. 3, where dots represent the experimentally observed results and the curve represents the modeled results. It can be seen in Fig. 2 that the first-order model using k$_b$ values, calculated by Eq. (3),

provides good description of Cl₂ decay. This is clear especially in the initial (rapid) stage at temperature 5 °C and 28 °C.
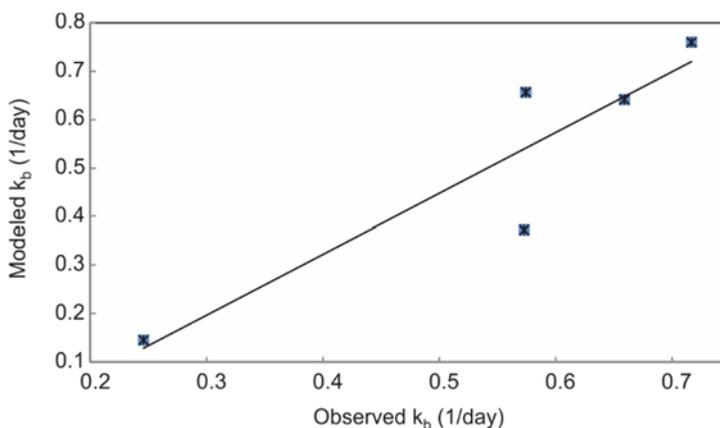

Fig. 2. Modeled and observed k_b values based on Eq. (3)
k_b modeled using Eq. (3) with the following constants:
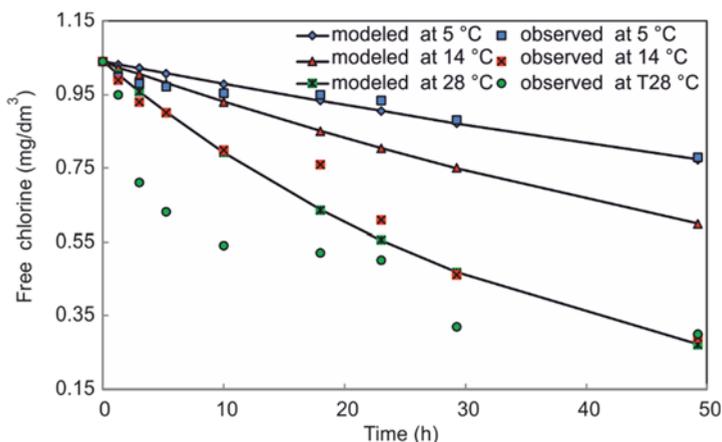$e = 5501.8$ °C, $a = 4.977\chi\times10^6$, $b = 0.6478173$, $R^2 = 0.8308$

Fig. 3. Regression of Cl₂ decay kinetics at various temperatures,
and at TOC 0.829 mg C/dm³, pH 7.71, reaction time 3 h, and [Br⁻] 50 μg/m³

Although, some shifts and deviations between the experimental and the modeled results are shown (Fig. 3), however, there is compatibility in the beginning and the end of this relationship. For instance, very good regression compatibility between the experimental and the modeled results was shown at temperature 14 °C. Generally speaking, most of chemical reactions kinetics increases with temperature. This can be mathematically expressed using the Arrhenius equation [23]. However, due to the limited data set and also for consistency, a linear regression was considered for all cases.
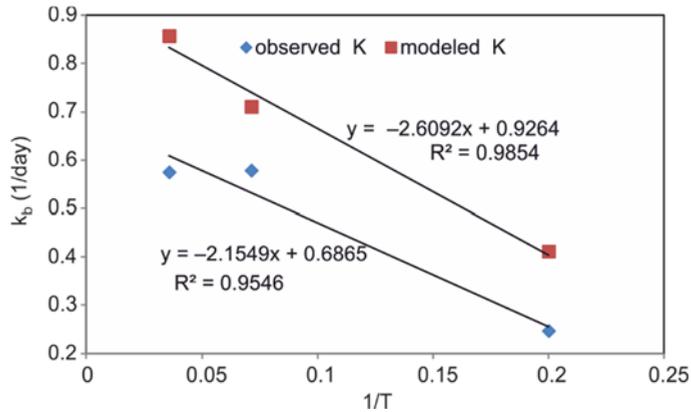
Fig. 4. Reaction rate constant of Cl_2 decay (k_b) as a function of temperature

However, the data in Fig. 4 demonstrated the effect of temperature on the k_b values with the involvement of constant parameters (the initial chlorine concentration and TOC). It can be seen that the empirical Eq. (3) fits the experimental data very well, as it is shown in Fig. 4 which visually presents no systematic lack of fit. It was found that the decay constant of Cl_2 in the samples was linearly proportional to the temperature, as already reported in the literature [20].
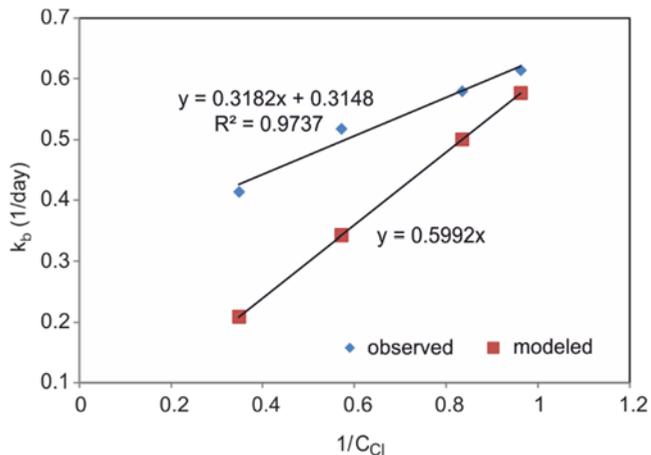

Fig. 5. Reaction rate constant of Cl_2 decay (k_b) as a function of C_{Cl}

As already reported in the previous studies, the decay constant is inversely proportional to the initial concentration of chlorine [15, 20]. In the present study, the kinetics of Cl_2 decay was investigated for each initial Cl_2 concentration, and it is found that the sample with the higher initial Cl_2 dose produces a lower decay rate, as shown in Fig. 5, and this has already been reported in previous studies [11, 20]. Figure 5 shows a very

good agreement in regression between the modeled results and the experimentally observed results.

The formation of DBPs is strongly dependent on the amount of naturally present humic substances (humic and fulvic acids), generally referred to as TOC [24]. Formation of the DBPs increases with increasing TOC in presence of free Cl_2 residuals [2, 4, 5]. Therefore, it is necessary to investigate the effect of TOC on Cl_2 decay in the present study. The results obtained showed that there is a certain positive correlation between the Cl_2 decay and TOC. For instance, Cl_2 decay increases with increasing TOC; this relation is shown in Fig. 6.
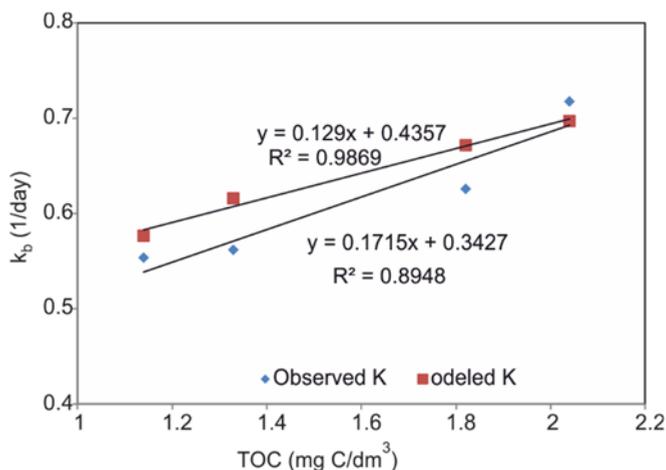

Fig. 6. Reaction rate constant of Cl_2 decay (k_b) as a function of TOC

5. CONCLUSION

• The chlorine decay in a real water system (the Zai water supply system) was well represented by the first-order kinetic model with consensus and accuracy between the proposed model results and experimental results.

• It was observed an increase of bulk chlorine with TOC and temperature, and a decrease with the initial chlorine dose. This was also theoretically validated using regression model which was linearized to a multivariable linear fit. High accuracy was obtained from the correlation proposed in this study where the experimental and predicted values of Cl_2 decay were very close.

REFERENCES

[1] KOWALSKA B., KOWALSKI D., MUSZ A., *Chlorine decay in water distribution systems*, Environ. Prot. Eng., 2006, 32 (2), 5.
[2] SAIDAN M., RAWAJFEH K., FAYYAD M., *Investigation of factors affecting THMs formation in drinking water*, Am. J. Environ. Eng., 2013, 3 (5), 207.

[3] DI CRISTO C., GIOVANNI ESPOSITO G., LEOPARDI A., *Modelling trihalomethanes formation in water supply systems*, Environ. Tech., 2013, 34 (1), 61.

[4] SAIDAN M., RAWAJFEH K., FAYYAD M., *Determination of trihalomethanes levels in a selected area of Amman's drinking water distribution system: case study*, Des. Water Treat., 2014, 54 (3), 642.

[5] SAIDAN M., MERIC S., RAWAJFEH K., AL-WESHAH R., AL-ZUBI S., *Effect of bromide and other factors on brominated trihalomethanes formation in treated water supply in Jordan*, Des. Water Treat., 2016, 57 (33), 15304–15313.

[6] CLARK R.M., ADAMS J.Q., SETHI V., SIVAGANESAN M., *Control of microbial contaminants and disinfect ion by-products for drinking water in the US: cost and performance*, J. Water Supply. Res. Tech. (Aqua), 1998, 47 (6), 255.

[7] CHOWDHURY S., HUSAIN T., *Evaluation of drinking water treatment technology. An entropy-based fuzzy application*, J. Environ. Eng., 2006, 132 (10), 1264.

[8] EL-KHORDAGUI H.K., MANCY K.H., *Formation of trihalomethanes during disinfection of drinking water*, Water Qual. Bull. Environ. Canada, 1983, 8 (1), 37.

[9] CLARK R.M., LYKINS W.M., BLOCK J.C., WYMER L.J., REASONER D.J., *Water quality changes in a simulated distribution system*, J. Water Supply Res. and Tech. Aqua, 1994, 43 (6), 263.

[10] ROSSMAN L.A., CLARK R.M., GRAYMAN W.M., *Modeling chlorine residuals in drinking-water distribution-systems*, J. Environ. Eng., 1994, 120 (4), 803.

[11] POWELL J.C., WEST J.R., HALLAM N.B., FORSTER C.F., SIMMS J., *Performance of various kinetic models for chlorine decay*, J. Water Res. Plan. Manage., 2000, 126 (1), 13.

[12] VIEIRA P., COELHO S.T., LOUREIRO D., *Accounting for the influence of initial chlorine concentration, TOC, iron and temperature when modeling chlorine decay in water supply*, J. Water Supply. Res. Technol. (Aqua), 2004, 53 (7), 453.

[13] BOCCELLI D.L., TRYBY M.E., UBER J.G., SUMMERS R.S., *A reactive species model for chlorine decay and THM formation under rechlorination conditions*, Water Res., 2003, 37, 2654.

[14] JADAS-HECART A., EL MOHER A., STITOU M., BOUILLOT P., LEGUBE B., *The chlorine demand of a treated water*, Water Res., 1992, 26 (8), 1073 (in French).

[15] POWELL J.C., HALLAM N.B., WEST J.R., FORSTER C F., SIMMS J., *Factors which control bulk chlorine decay rates*, Wat. Res., 2000, 34 (1), 117.

[16] KOHPAEI A.J., SATHASIVAN A., *Chlorine decay prediction in bulk water using the parallel second order model: An analytical solution development*, Chemical Eng. J., 2011, 171, 232.

[17] GOLFINOPOULOS S.K., XILOURGIDIS K., KOSTOPOULOU N., LEKKAS T.D., *Use of a multiple regression model for predicting trihalomethane formation*, Water Res., 1998, 32, 2821.

[18] HALLAM N.B., HUA F., WEST J.R., FORSTER C.F., SIMMS J., *Bulk decay of chlorine in water distribution systems*, J. Water Res. Plan. Manage., 2003, 129, 78.

[19] CLARK R.M., GRAYMAN W.M., GOODRICH J.A., DEININGER R.A., SKOV K., *Measuring and modeling chlorine propagation in water distribution systems*, J. Water Res. Plan. Manage., 1994, 120, 871.

[20] HUA F., WESTI J.R., BARKER R.A., FORSTER C.F., *Modelling of chlorine decay in municipal water supplies*, Water Res., 1999, 33 (2), 2735.

[21] KAVANAUGH M.C., *An empirical kinetic model of THM formation. Applications to meet the proposed THMs standard*, J. AWWA, 1980, 72, 578.

[22] *Standard methods for the examination of water and wastewater*, American Public Health Association, American Water Works Association, and Water Environment Federation, Washington 1995, 19.

[23] SAWYER C.N., *Chemistry for environmental engineering*, McGraw-Hill, New York 1994.

[24] VASCONCELOS J.J., BOULOS P.F., GRAYMAN W.M., *Characterization and modeling of chlorine in distribution systems*, AWWA Res. Formation, Denver 1996.