Reductive Dechloramination: Finalized Study of KDF®85 Process Medium in Point-Of-Entry and Point-Of-Use Applications

Submitted By:

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Introduction

Monochloramine was widely used as a disinfectant in the 1930s. During World War II, due to ammonia shortages, its use was greatly reduced and it has never regained its past level of popularity [Kruithof, 1986]. This is due in part to the fact that chloramination generally requires contact times 100 times longer than chlorine to achieve the same deactivation of coliforms [Kruithof, 1986]. For these reasons the USEPA in 1979 recommended that chloramine not be used as a primary disinfectant [Kruithof, 1986]. At the end of this century chloramine use is again being reconsidered for many applications due to changes in the Clean Water Act requiring the limitation of chlorine disinfection by-products (DBPs), mainly trihalomethanes (THMs), formation during chlorination of drinking water. Chloramination produces substantially lower concentrations of THMs so this has once again become a viable alternative to the use of chlorine alone as a disinfectant.

The use of monochloramine as a primary disinfectant in a municipal water supply presents specific removal issues due to its low degradation rate. This means that the disinfectant will be persistent and have a long life within a municipal water supply. This has prompted KDF Fluid Treatment, Inc., (KDFFT) to investigate the use of its products, primarily KDF 85 process medium, as a reductant for monochloramine in potable water. The purpose of this study will be to establish the following operating parameters; volume of medium, flow rate, pH and backwash frequency.

Chloramination Reaction

Adding ammonia and chlorine to water produces monochloramine through the reaction:

$$NH_3 + HOCl \not\subset NH_2Cl + H_2O$$

Optimal production of monochloramine occurs at chlorine to ammonia ratios of 3:1 to 4:1 and in a pH range of 7 to 8 [Kruithof, J.C., 1986]. The reaction rate for the formation of monochloramine at the optimal pH is considerably high with 90 percent completion within one minute. At lower pH values and higher chlorine: ammonia ratios dichloramine and possibly trichloramine are formed which have been implicated as possible human carcinogens.

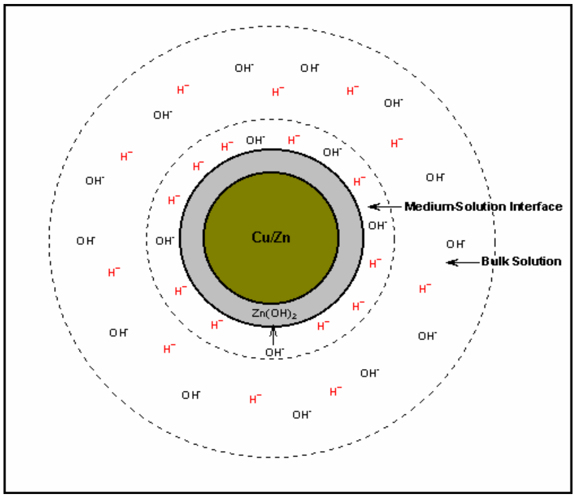
Reductive Dechloramination Mechanisms

The reactivity of the various forms of nitrogen appears to be controlled primarily by charge transfer kinetics associated with the change in oxidation state [Bard et.al, 1985]. This property of nitrogen has rendered normal thermodynamic predictions of reactivity invalid which is even further complicated by a relationship between pH and oxidation state [Bard et.al, 1985]. What this indicates is that dechloramination can not be simply defined by a redox reaction between the medium and the monochloramine present in solution. A driving force for the reaction may also have to be present.

As previously stated there is a relationship between pH and the various oxidation states of nitrogen compounds. Therefore it is theorized that by decreasing the bulk pH of the solution and increasing the acidity in the vacinity of the medium's surface monochloramine reduction could occur. Bulk pH can be decreased by the addition of an acid to the solution. However, this alone would not necessarily increase the acidity in the vacinity of the medium's surface. The presence of a metal ion that can be precipitated as a hydroxide can have this effect and zinc ions are generated by the medium. Zinc is amphotheric, meaning that it acts both as an acid and a base. In this instance it would be precipitated as a hydroxide that would then increase the activity of hydrogen ions (acidity) at the solution/medium interface.

This is the basis of the hypothesized mechanism by which KDF 85 process medium reduces monochloramine. This occurs through a series of reactions, first free chlorine present in the water oxidizes the medium's surface (Steps 1-4). The hydroxide ion formed from the hypochlorite ion (OCl^-) is then used to from zinc hydroxide that concentrates hydrogen ions at the medium's surface (Steps 5-6). The hydrogen ions generated from the hypochlorous acid (HOCl) and concentrated at the medium's surface are then used in the reduction of monochloramine (Step 7). This mechanism is also illustrated in the drawing below right.

1. $Zn^0 \not\subset Zn^{+2} + 2e^-$
2. $OCl^- + H_2O \not\subset HOCl + OH^-$
3. $HClO + H^+ + 2e^- \not\subset Cl^- + H_2O$
4. $OCl^- + H_2O + 2e^- \not\subset Cl^- + 2OH^-$
5. $Zn^{+2} + OH^- \not\subset Zn(OH)^+$
6. $Zn(OH)^+ + OH^- \not\subset Zn(OH)_2$
7. $NH_2Cl + H^+ + 2e^- — NH_3 + Cl^-$



Another way by which galvanic reduction reactions can be facilitated and which is not illustrated by the above reactions is by increasing the cathodic surface area. KDF 85 process medium is an 85% copper 15% zinc alloy. In effect this means that 85% of the surface area is available for cathodic reactions. For this reason KDF 85 process medium was chosen as the primary reductant over that of KDF 55 process medium, a 50% copper 50% zinc alloy.

Monochloramine Reduction Mechanism Thermodynamics

Chemical reaction thermodynamics are a way of determining the feasibility of a reaction. A positive Gibbs free energy (ΔG^0_R) indicates non-spontaneity and a negative value spontaneity. From the example equations below, the free energy in both acidic and basic solutions is negative indicating that the reactions are feasible/spontaneous. However, free energy values are not indicative of reaction kinetics, speed of reaction. A more negative value does not necessarily indicate a faster reaction.

Reaction	**ΔG^0_R**
$Zn^0 \not\subset Zn^{+2} + 2e^-$	-147.16
$OCl^- + H_2O \not\subset HOCl + OH^-$	equilibrium at pH 7
$HClO + H^+ + 2e^- \not\subset Cl^- + H_2O$	-288.3343
$OCl^- + H_2O + 2e^- \not\subset Cl^- + 2OH^-$	-171.6643
$Zn^{+2} + OH^- \not\subset Zn(OH)^+$	-37.547
$Zn(OH)^+ + OH^- \not\subset Zn(OH)_2$	-54.587
$NH_2Cl + H^+ + 2e^-$ □ $NH_3 + Cl^-$	-262.68

	Zn^0/Zn^{+2}	**HOCl/OCl**	**$Zn(OH)^+$**	**OH^-/H_2O**	**$Zn(OH)_2$**	**NH_2Cl**	**H^+**	**NH_3**	**Cl^-**
ΔG^0_F (kj/mol)	0 -147.16	-79.32 -36.8	-342	-157.293 -237.178	-553.88	359.8277	0	322	-131.0563

[Bard, et.al., 1985]

Monochloramine Reduction Mechanism Kinetics

The reduction mechanism becomes confusing at this point as a number of separate but connected reactions with their own rates are occurring. First there is the group of reactions where free chlorine is reduced followed by the formation of zinc hydroxide that increases the hydrogen ion activity at medium's surface. Secondly there is the actual reduction of monochloramine using the hydrogen ions generated by hypochlorous acid reduction and accumulated at the medium's surface. This is confused even more since kinetics of reactions with more than one step have what is known as a rate determining step. This step is significantly slower than the other steps in a reaction mechanism and therefore determines the overall rate of reaction [Oxtoby, D.W., 1990]. For all practical purposes the last reaction where, monochloramine is converted to ammonia and chloride ions, can be considered the rate determining step. This would lead to a rate expression of:

$$\text{Rate} = K[NH_2Cl]\,[H^+]$$

Another way to express kinetics of a reaction is the observed rate or a change in concentration over a change in time:

$$\text{Observed Rate} = \Delta C/dt$$

For this study fixed beds of medium where used, so time in this instance will be actual contact time between the monochloramine and the medium bed. This changes the above rate expression to:

$$\text{Rate} = \Delta C/\text{contact time} = [\text{Final conc.} - \text{Initial conc.}] / \text{contact time} \quad (\text{ppm/sec})$$

Methodology

This study was conducted in two phases, point-of-entry (POE) and point-of-use (POU) applications, to determine the feasibility of the use of the medium to treat potable water.

Test System Designs

KDFFT has a challenge water delivery system, Appendix II, that complies with ANSI/NSF 42-1996 standards. This system is composed of two 500-gallon storage tanks that feed a 1-inch PVC test line via a ¾-hp pump attached to a bladder tank. Challenge water, analysis Appendix II, was created by mixing the laboratories well water with 130-mL of sodium hypochlorite solution 12.5% and 30-mL of ammonium hydroxide 29% NH_3. Because hydrogen ions are essential for the reduction to occur the pH of the challenge water was adjusted to seven by the injection of a 29% nitric acid solution. An equivalent solution of sodium hydroxide was injected to keep the pH above 6.5. Both solutions were automatically injected using an electrode controlled pumping system.

Phase I POE

Flow Rate: 4 gpm
Influent pH: 6.50 – 7.50
Influent Pressure: 30 - 40 psi
Reactor Diameter: 8-inches
Medium Configuration: 0.25 cubic feet (42 pounds), 9-inch bed
Contact Time: 28.2 seconds

Phase II POU

Flow Rate: 0.50 gpm
Influent pH: 6.50 – 7.50
Influent Pressure: 30 - 40 psi
Reactor Diameter: 2.75 inches
Medium Configuration: 0.0241 cubic feet (4 pounds), 7-inch bed
Contact Time: 21.6 seconds

Testing Protocols

Phase I POE

A full-scale point-of-entry pilot was used to determine effective life of the medium and to establish backwash frequencies. Challenge water was fed to an 8-inch diameter vessel containing 42-pounds of KDF 85 process medium at the flow rates of 4.00 gpm at an approximate pH of 7. The filter was first run for 3-minutes to flush the systems then initial influent and effluent samples were grabbed and analyzed immediately for monochloramine and free ammonia. After the first grab sampling frequency was every 1000 gallons (two tanks) Note: this is reported at 3000-gallon interval in the Data section for simplicity but all statistical calculations were performed using the entire data set.

Phase II POU

A full-scale point-of-use pilot was used to determine the practicality of using the medium in this type of application. Also this test gives some indication as to an effective life of the medium without backwashing and copper and zinc dissolution from the medium. Challenge water was fed to a 2.75-inch diameter cartridge filter containing 7-pounds of KDF 85 process medium at the flow rates of 0.50 gpm at an approximate pH of 7. The filter was first run for 3-minutes to flush the systems then initial influent and effluent samples were grabbed and analyzed immediately for monochloramine and free ammonia. After the first grab sampling frequency was every 500 gallons (one tank).

Analytical Methods

Monochloramine and free ammonia concentrations were determined using HACH Method 10045, salicylate method, using a HACH DR 2000 spectrophotometer at a wavelength of 655 nm [HACH Company, 1997].

Data

Table 1.1 Phase I POE

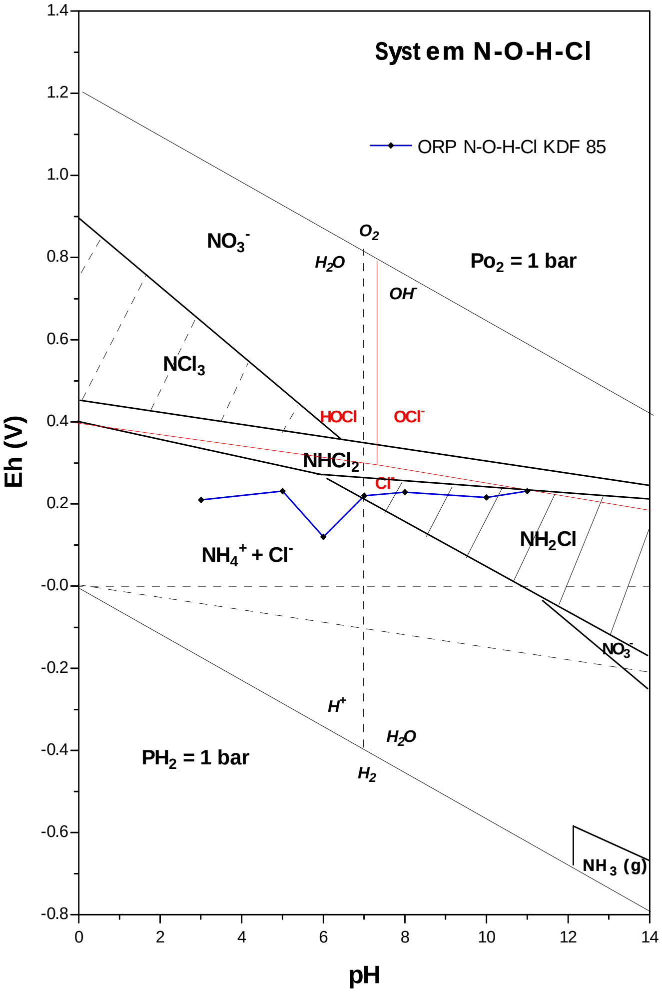
	Influent		Effluent		
Gallons	**NH_2Cl**	**NH_3**	**NH_2Cl**	**%**	**NH_3**
0	1.29	0.11	0.02	98	0.52
3000	0.60	0.30	0.02	97	0.17
4000	0.87	0.22	ND	>99	0.28
5000	0.48	0.22	ND	>99	0.28
6000	0.69	0.57	ND	>99	0.15
7000	0.42	1.08	ND	>99	1.38
8000	0.75	0.81	ND	>99	0.27
9000	0.85	1.10	ND	>99	0.51
10,000	4.60	4.50	0.05	99	0.21
11,000	0.21	0.81	0.04	80	0.13
13,000	0.31	0.50	0.03	90	0.54
15,000	0.16		0.02	88	
17,000	0.37		0.02	95	
19,000	1.13		0.13	88	
24,000	0.51		0.14	72	
25,000	0.95	0.15	0.45	53	0.30
26,000	0.77	0.13	ND	>99	0.19
27,000	0.54	0.45	ND	>99	0.19
32,000	0.68	ND	ND	>99	0.10

Table 1.2 Phase II POU

	Influent		Effluent		
Gallons	**NH_2Cl**	**NH_3**	**NH_2Cl**	**%**	**NH_3**
0	0.98	0.44	0.03	97	0.13
2000	1.02	0.16	0.07	93	0.32
4000	0.80	0.07	ND	>99	0.08
6000	0.86	0.22	0.32	63	ND
8000	0.94	0.08	0.04	96	0.08
10,000	0.74	0.13	ND	>99	0.07
12,000	0.96	0.14	0.08	92	0.17
14,000	0.87	0.11	0.09	90	0.07
16,000	0.50	0.12	0.01	99	ND
18,000	0.88	0.08	0.15	83	0.25
20,000	0.60	0.14	0.09	85	0.22
22,000	0.98	0.01	0.12	88	0.41
24,000	1.10	0.08	0.13	88	0.15

Discussion of Results

This study has provided evidence to support the hypothesized reduction mechanisms. A simplified way of illustrating the reduction mechanism taking place was to generate a stability diagram (Eh-pH) for free chlorine and chloramines, graph right. This diagram shows the theoretical stability lines of the individual species, both reduced and oxidized, at various pH and potentials. An ORP line generated for KDF 85 process medium has been placed onto this diagram indicating the expected effluent potential over the pH range. This line shows that the ORP of water treated by KDF process medium would be below that at which the oxidants chlorine and chloramine are stable. The lower potential generated forces a reverse reaction producing the reduction by-products ammonium and chloride. The actual measured ORP from this test as indicated on the graph falls within an acceptable distance from this line.



For POE applications the medium is rated at approximately 15 gpm/ft^3 and a minimum bed height of 10-inches is recommended. This information can be used to configure a treatment application. For example, at an influent flow rate of 10-gpm 0.625 ft^3 of medium would be required (application flow rate ÷ 15 gpm/ft^3). If a 10-inch bed is to be maintained then a vessel diameter of 12-inches would be required (solved from the volume equation: 0.625 ft^3 = $\pi r^2 h$). This configuration would give the 0.03 ppm/sec reaction rate up to 1-ppm of influent monochloramine. To get the required contact time at higher concentrations of monochloramine the volume of medium would theoretically have to be increased accordingly. For example doubling the concentration doubles the required contact time, 2-ppm increases the contact time to 66 seconds, so logically the volume of medium would have to be doubled. This scenario would only hold true if the observed reaction rate as a function of concentration of monochloramine were linear. From the limited amount of data from these tests it appears that the rate is not linear up to 2-ppm but flattens out somewhere above 1-ppm. Therefore, for all practical purposes as the influent monochloramine concentrations of municipal waters will be in the 2-ppm range the rating of 15 gpm/ft^3 will be used.

As to backwash frequencies for the medium, the tests indicate that the medium provided sufficient reductions up to 10,000-gallons. However, loading rates of iron were not included in this test and iron loading will influence actual gallons in any application. For this reason the recommended backwash frequency of once a day for KDF 85 process medium in iron applications will be recommended. It must be stressed here that actual results, as to backwash frequency and monochloramine reduction efficiency, will vary depending upon the water quality. The recommendations made in this report are general based upon results with one water type.

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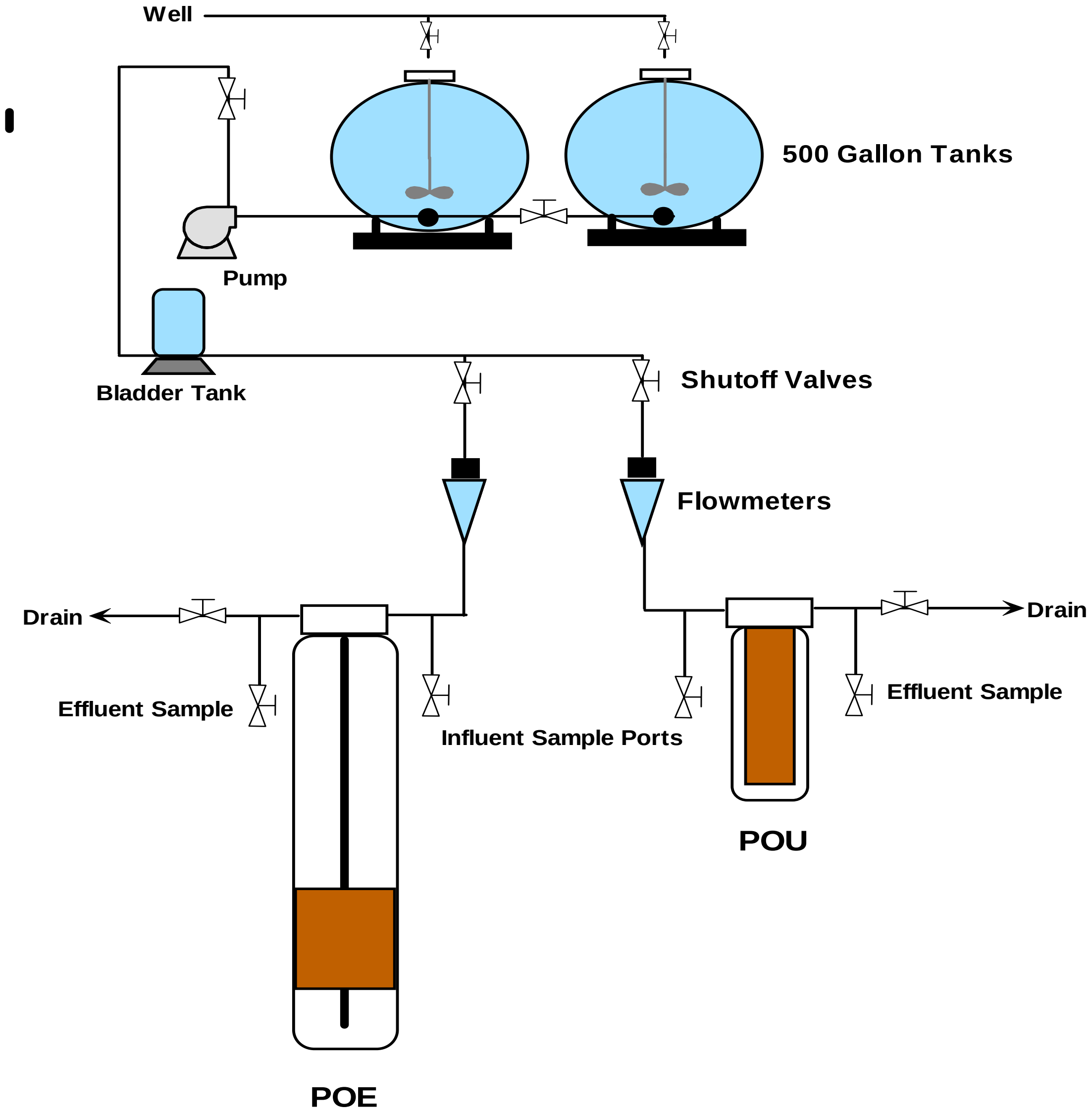
Appendix I

Test Apparatus Schematic



Appendix II

Challenge Water Analysis

Parameter	Method	Results	Units
pH	SM 18th 4500 B	7.00	pH units
Conductivity	SM 18th 2510 B	695	μS/cm
TDS	SM 18th 2510 B	350	mg/l Total
Total Alkalinity	SM 18th 2320 B	300	mg/l as
Total Hardness	SM 18th 2340 C	390	mg/l as
Calcium	SM 18th 3500 Ca D	100	mg/l Ionic
Magnesium	Calculated	54	mg/l Ionic
Sodium	ISE Method	3.97	mg/l Ionic
Potassium	HACH Method 8049	2.35	mg/l ionic
Iron, Total	HACH Method 8008	0.24	mg/l Ionic
Copper, Dissolved	SM 18th 3500 Cu B	ND	mg/l Ionic
Zinc, Dissolved	SM 18th 3500 Zn B	0.01	mg/l Ionic
Sulfate	HACH Method 8051	46	mg/l Ionic
Nitrate	HACH Method 8171	0.60	mg/l Ionic
Orthophosphate	SM 18th 4500 P E	0.05	mg/l Ionic
Chloride	SM 18th 4500 Cl^- B	50	mg/l Ionic
Silica	HACH Method 8185	10.1	mg/l Ionic
Chlorine, Free	SM 18th 4500 Cl G	NA	mg/l ionic
Chlorine, Total	SM 18th 4500 Cl G	NA	mg/l Ionic
Monochloramine	HACH Method 10045	~0.50	mg/l Ionic
Ammonia, Free	HACH Method 10045	~0.30	mg/l