A Bench Scale Study: Demonstrating Chloramine Disinfection Potential Using Liquid Ammonium Sulfate

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Stantec

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Agenda

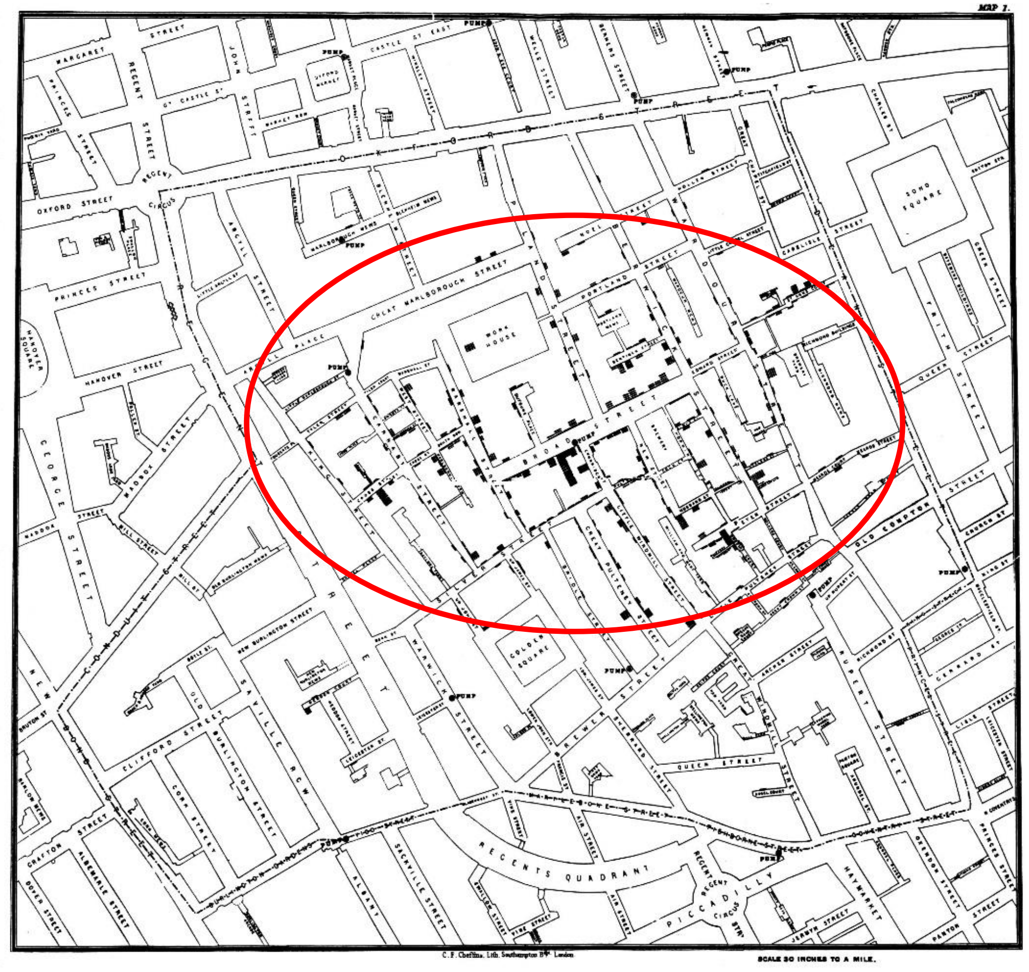
1. Introduction to Chloramination
2. Bench Scale Study Introduction
3. Bench Scale Study Calculations and Procedures
4. Bench Scale Study Results and Conclusions

1. Introduction to Chloramination

Disinfection

- Drinking water disinfection using chlorination began in Mid 1800's to reduce waterborne diseases

- Chlorination is the most used disinfectant in GCC countries and worldwide



John Snow's Cholera Outbreak Map of Soho London

Chlorine Chemistry

- Chlorine is used as a disinfectant either by gas or liquid form:

Chlorine Gas (Cl_2) *poisonous if released in the air*

$Cl_2 + H_2O$ ◊ $HOCl + H^+ + Cl^-$

Sodium Hypochlorite (NaOCl)

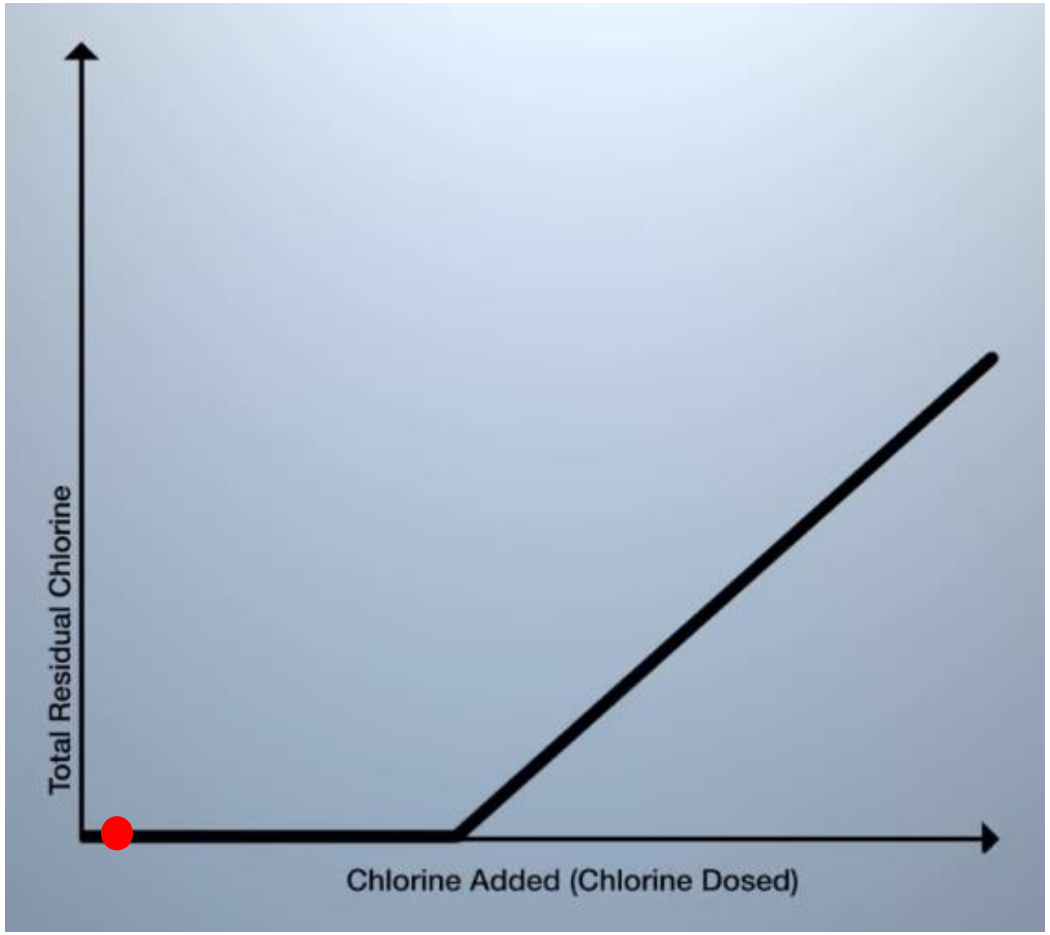
$NaOCl + H_2O$ ◊ $Na^+ + HOCl + OH^-$

- The two species formed by chlorine in water is hypochlorous acid (HOCl: above pH 7.5) and hypochlorite ion (OCl^- below pH 7.5)

$HOCl \leftrightarrow H^+ + OCl^-$

Chlorine “Breakpoint” Curve

- Chlorination curve describes what happens when chlorine added to water



Source: HACH

Chloramination Definition and Forms

- Chloramination is an alternative disinfection method, where a small quantity of ammonia is added to chlorinated water

- Chloramines are formed when free chlorine reacts with free ammonia present in the water forming:

  - Monochloramine (NH_2Cl) desired form
  - Dichloramine ($NHCl_2$)
  - Trichloramine (NCl_3)

Note:

- Monochloramine has high concentration and time (CT) value thus poor primary disinfectant
- However, high CT makes it ideal as a secondary disinfection in the distribution system

Chlorination Disadvantages and Advantages

- Chlorination Disadvantages:

1-Chlorination has the potential to react with natural organic matter and form chlorinated disinfectant by-products (DBPs) for **surface water sources**

θ DBPs have been shown to increase the risk of bladder cancer, among other health consequences

θ Main DBP’s include:

- Total trihalomethanes (TTHMs)
- Haloacetic acids (HAA5)
- Nitrosamines: N-Nitroso-dimethylamine (NDMA)

Chlorination Disadvantages and Advantages

- <u>Chlorination Advantages:</u>

1-It is recognized that chlorination will continue to be the most common disinfection process

- θ Enhanced removal of DBP precursors from raw water sources can be done by GAC and nanofiltration

Chloramination Disadvantages and Advantages

- Chloramination disadvantages:

  1- It is a poor oxidant and

  2- It is not effective for taste and odor control or for oxidation of iron and manganese

- Chloramination advantages:

  1- Eliminate the formation of chlorination by-products,

  2- Maintains long residual

  3- More economical than alternative disinfection methods (e.g. Ozone and UV disinfection)

1 Introduction to Chloramination

Chloramination Chemistry

- WTPs use chloramine compounds in the form of aqueous ammonia (**NH_4OH, AA**) and sodium hypochlorite (**NaOCl, SH**).

- Chloramines are frequently produced by adding ammonia to water containing free chlorine (ideal pH 8.4)

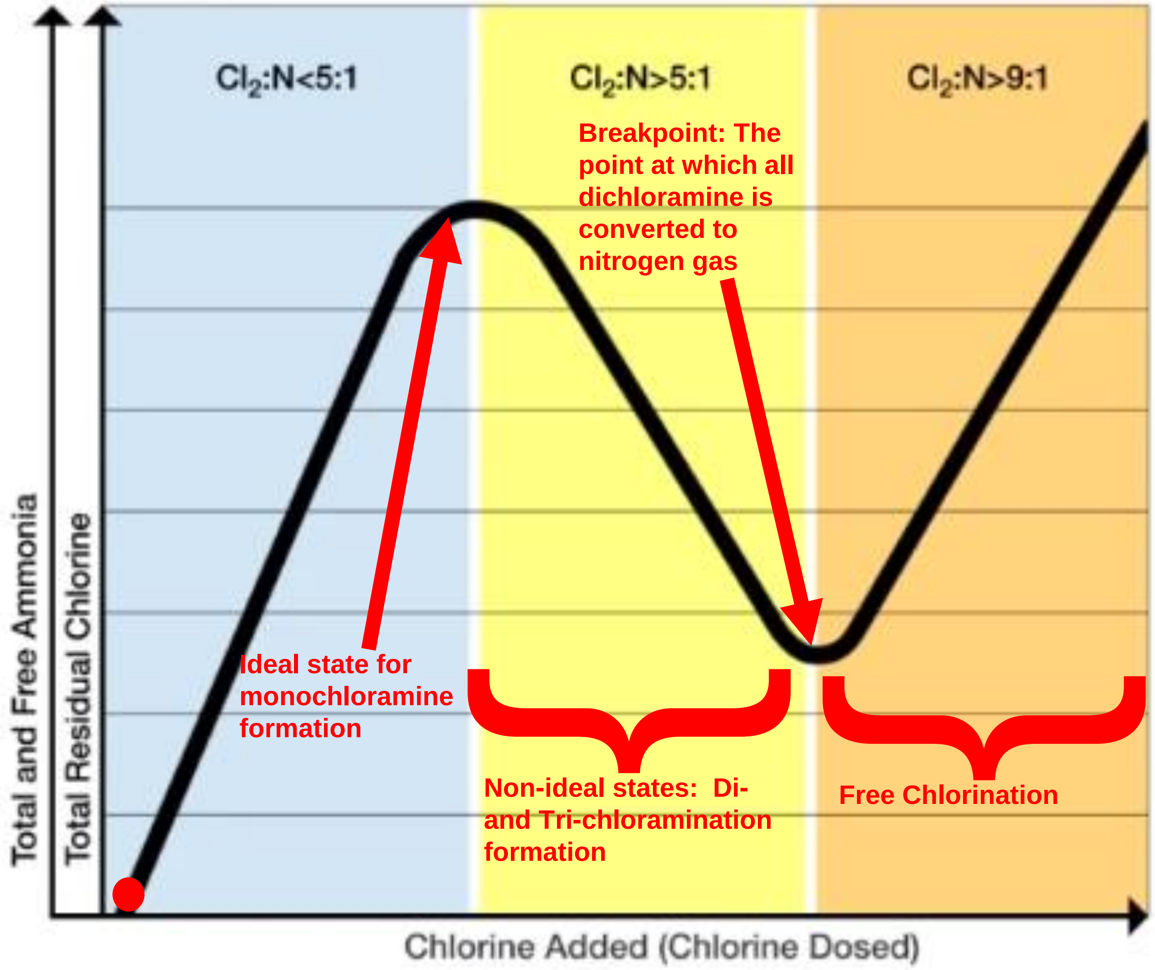
NH_3 + HOCl ◊ H_2O + NH_2Cl *(monochloramine)*

NH_2Cl + HOCl ◊ H_2O + $NHCl_2$ *(dichloramine)*

$NHCl_2$ + HOCl ◊ H_2O + NCl_3 *(trichloramine)*

Chloramination Curve

- Chloramination curve describes what happens when chlorine added with ammonia in water



Source: HACH

2. Bench Scale Study Introduction

The Client "EBMUD" Drivers for the Study

- EBMUD has a CSSIP to improve safety of all chemical process in WTP
- The use of AA has an **inherent risk** of ammonia vapor exposure to operators and to the general public in the vicinity
- Liquid ammonium sulfate (**$(NH_4)_2SO_4$, LAS**) is identified as a chemical substitute to AA
- Continued use of AA for chloramination will require several major safety and code upgrades at the client's WTPs
- Substitution of LAS for AA, reduces several safety, code, reporting, maintenance requirements and maintenance cost

East Bay Municipal Utility District
EBMUD

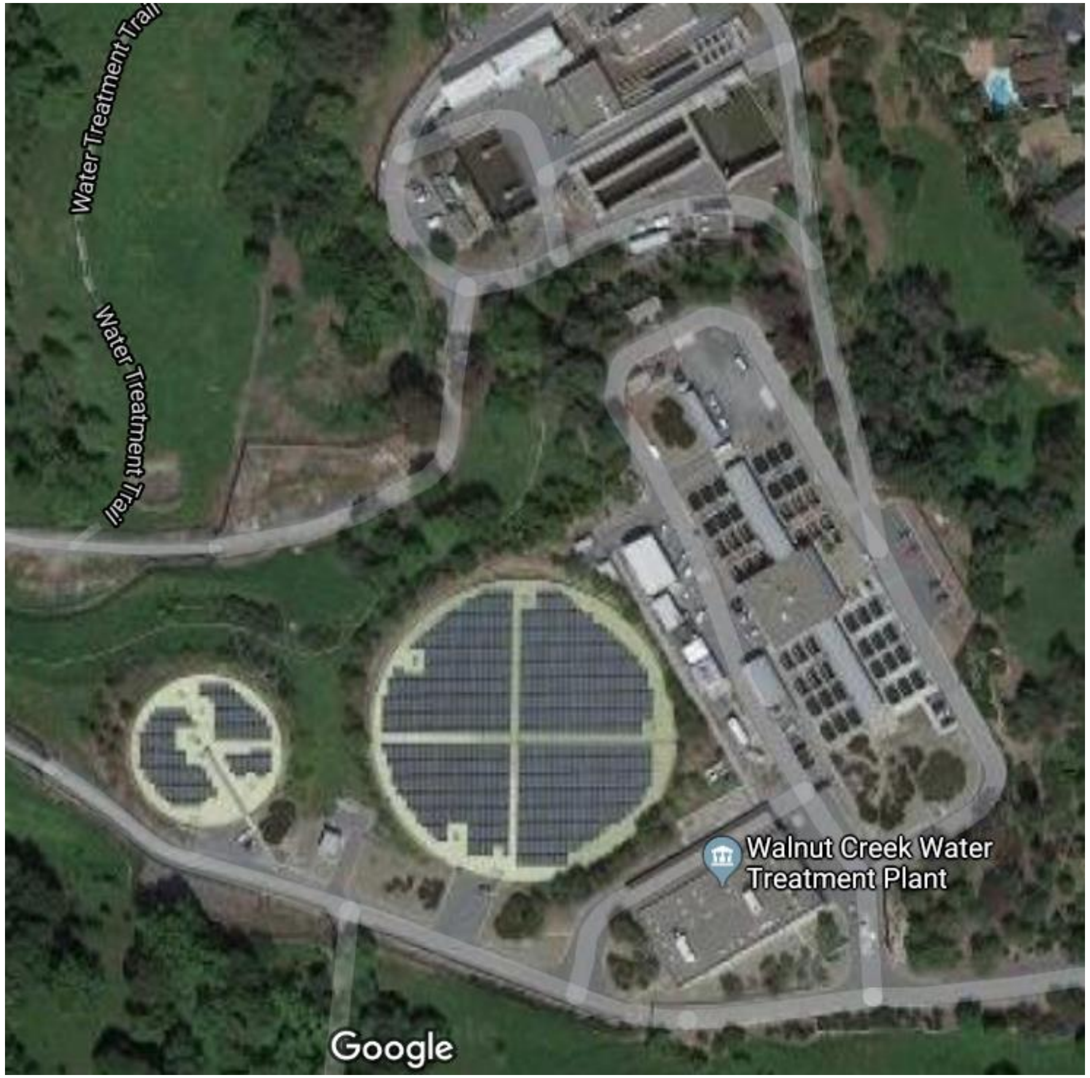
Chemical Properties: AA versus LAS

Property	Aqueous Ammonia (Ammonium Hydroxide), AA	Liquid Ammonium Sulfate, LAS
Formula	$NH_4(OH)$	$(NH_4)_2SO_4$
Concentration	19-20%	38-40%
Density	992.7 g/L	1,222.2 g/L
Available Ammonia	185.7 g NH_3/ L AA solution	121 g NH_3/ L LAS solution
pH	11.6	3.0-5.0
Volatility	High vapor pressure (32.5 kPa @ 21 C) Off-gassing of ammonia vapors	Non-volatile, stable, does not off-gas (1.8 kPA)
Odor	Strong	No odor

2 Bench Scale Study Introduction

Walnut Creek WTP in California, USA

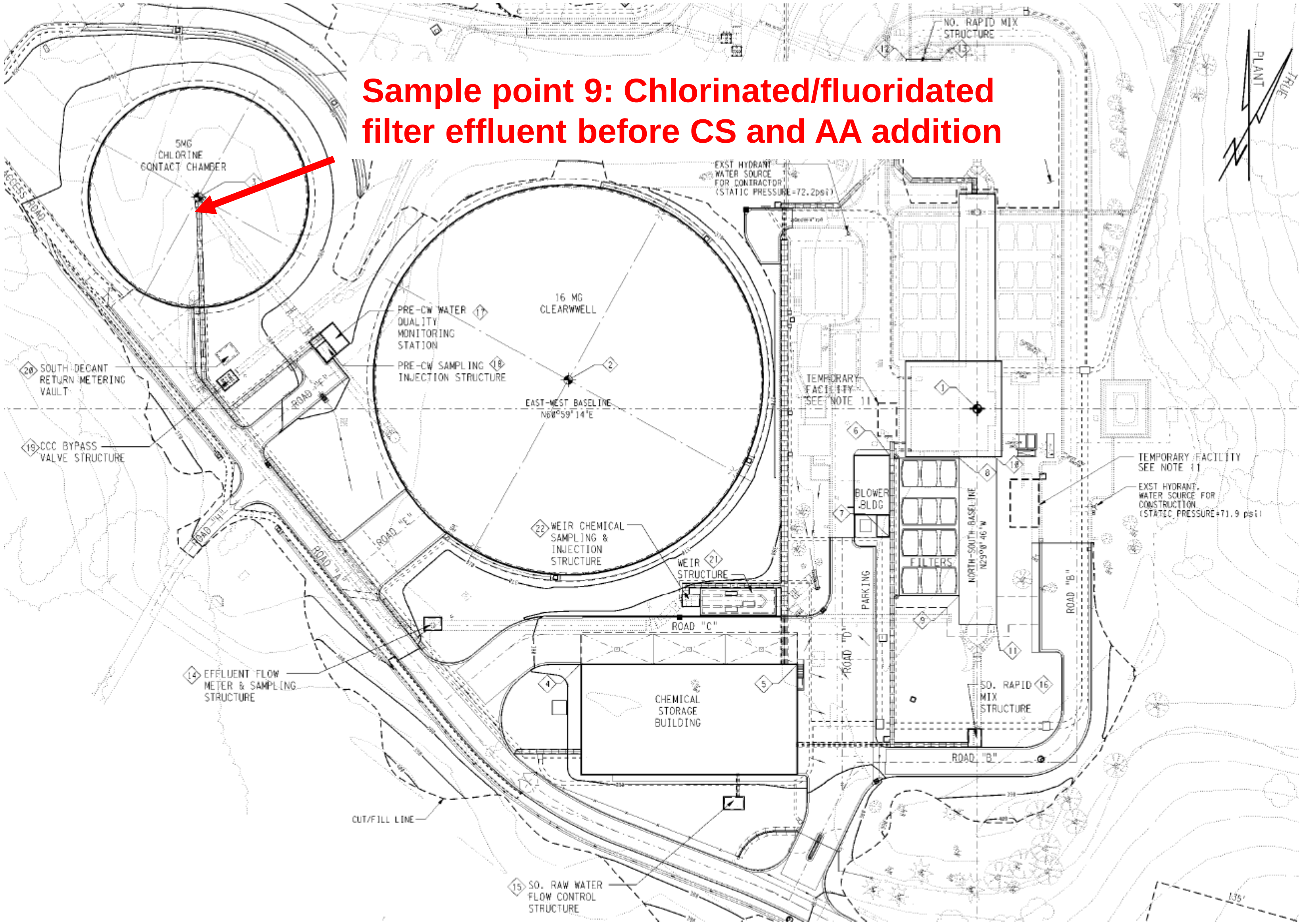
- Walnut Creek WTP has a treatment capacity of 115 MGD (435,322.4 m^3/d)
- The water source is Pardee Reservoir in the Sierra
- The treatment process utilizes direct filtration – skips flocculation phase and coagulation occurs in-line prior to rapid mix



East Bay Municipal Utility District
EBMUD

2 Bench Scale Study Introduction

Walnut Creek WTP Process



Objectives of the Bench Scale Study

1. Determine and verify the dose of SH to LAS and caustic soda (CS) to LAS, in order to:

(a) achieve a chlorine to ammonia ratio (Cl_2:N) of at **least 4.7** but not **exceeding 4.9** which is the optimal ratio for monochloramine formation

(b) increase the **pH** of the effluent treated water to **9.2** for corrosion control in the distribution system

Objectives of the Bench Scale Study

2. Compare DBP formation for AA/SH and LAS/SH to the maximum contaminant level (MCL) allowed

3. Compare the rate of chloramine decay when using AA/SH vs. LAS/SH to ensure a lasting chloramine residual is maintained

3. Bench Scale Study Calculations and Procedures

AA, LAS and CS Concentrations

- Below summarizes stock solution concentrations used and calculated

Chemical	**Units**	**AA**		**LAS**	**CS**
Formula	--	NH_4OH	NH_3	$(NH_4)_2SO_4$	NaOH
Molecular Weight	g/mol	35.04	17.031	132.14	40.1
% of Product	--		19%	40%	50%
Specific Gravity/Relative Density	--	0.9		1.23	1.53
Stock Concentration	mg/L		170,684	491,090	761,090
Stock Concentration – N	mg/L		140,307	104,060	N/A
Dilution (mL Stock to mL Water)	--		100	100	1000
Diluted Concentration	mg/L		1,403.07	1,040.60	761.09
	mg/mL		1.40	1.04	0.76

NH_4-N Dose Calculation

- The testing does of ammonia in the form of AA and LAS is determined from the free-chlorine concentration measured in the tested water to satisfy the (Cl_2:N) ratio desired

- Example of NH_4-N dose calculation:

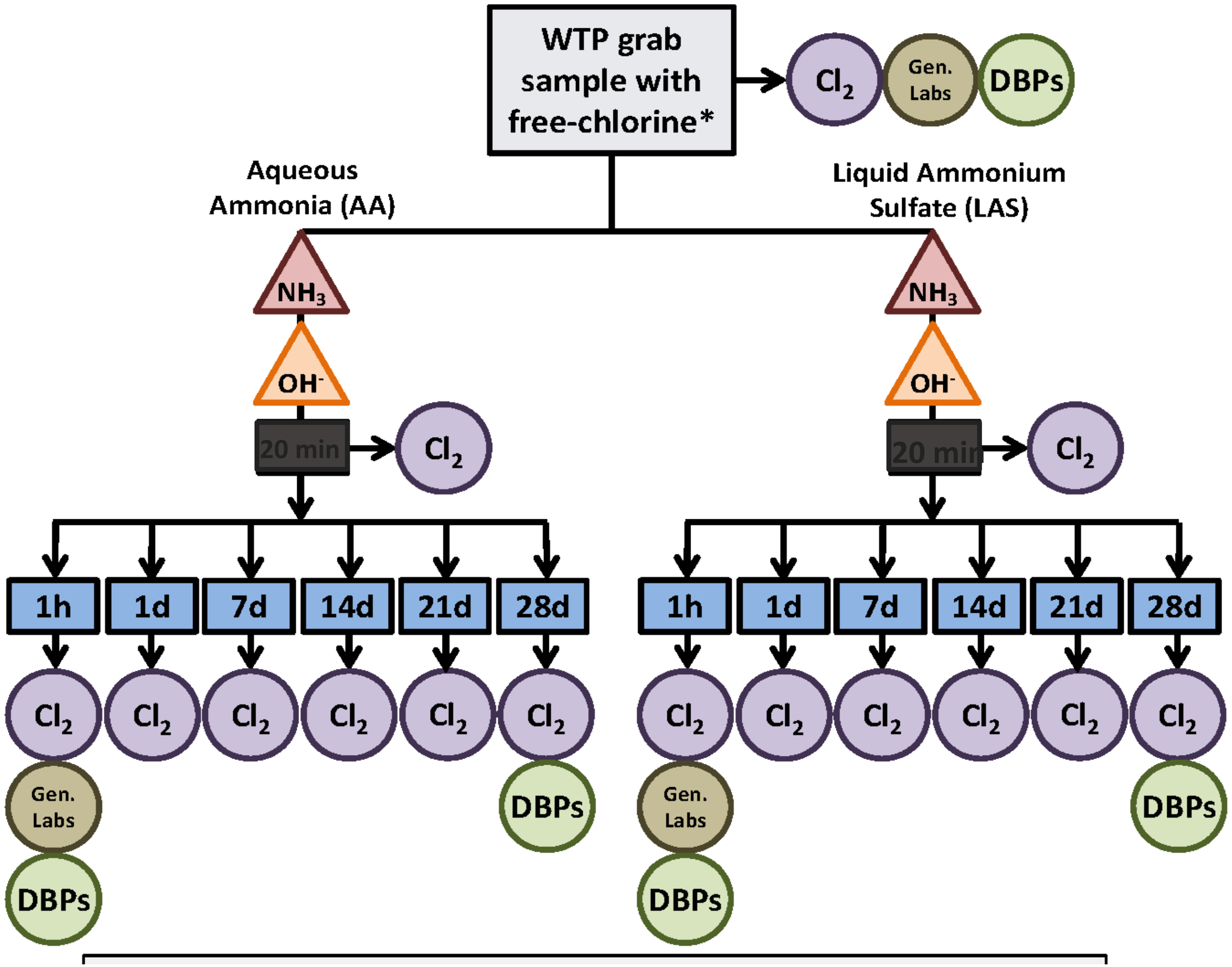
Free chlorine residual (mg/L)	2.61
Time of measurement	9:08
Desired ratio (Cl_2:NH_4-N)	4.8
NH_4-N dose (mg/L)	0.544

Measured from sample point

Calculated from ratio desired

- LAS and AA are calculated according to the NH_4-N dose in the red box

Testing Procedures



Legend

Cl_2	Perform analysis at WTP Lab: pH, temperature, total chlorine, monochloramine, free ammonia, turbidity
Gen. Labs	Collect sample for lab analysis for alkalinity, conductivity, TDS, calcium, anions (Cl, SO_4, NO_2, NO_3), TOC, TKN.
DBPs	Collect sample for lab analysis for TTHMs, HAA5, and nitrosamines
NH_3	Dose ammonia (either AA or LAS) to reach a Cl_2:NH_3 between 4.7-4.9. Mix well.
OH^-	Adjust final with caustic to pH: • 9.2 for inline filter plants • 8.5 for conventional plants
28d	Total hold time after ammonia addition in minutes (m), hours (h), or days (d)

Testing Procedures – Dose Determination and Data Sheet

- A sample dose determination for AA and data sheet while testing is shown below:

AA and LAS Concentration Determination **(Cl_2:N)**

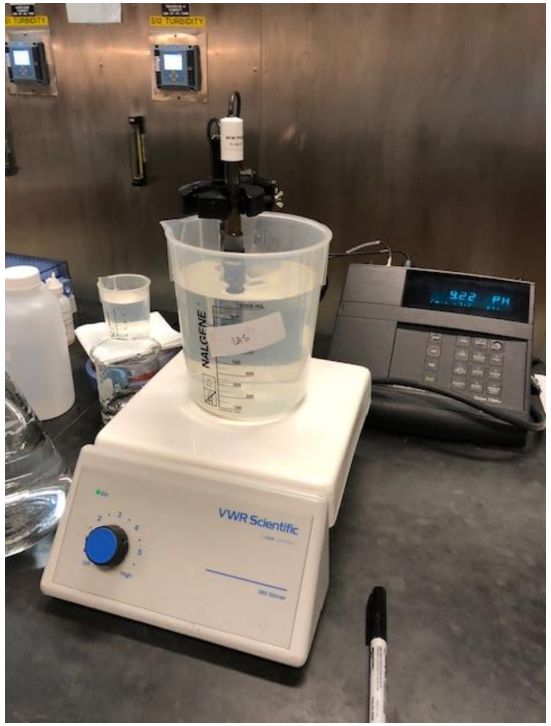
CS Concentration Determination **(pH)**

LAS/AA + CS Dose Determination			
Working volume (L)	1	1	1
Chemical	AA	LAS	CS (AA)
diluted stock concentration - N mg/mL	1.40	1.04	0.76
volume to add per L mL/L	0.39	0.52	
volume to add per 1L of sample (mL)	0.39	0.52	3.94
concentration (mg/L)	0.544	0.544	< to be determined by titration

	Trial 1			Trial 2		
	mL AA added	mL CS added	pH	mL AA added	mL CS added	pH
AA + CS Titrations	0.39	0	8.37	0.39	0	8.34
		1	8.77		3.3	9.22
		1	9		0.2	9.23
		0.5	9.08			
		0.2	9.11			
		0.2	9.14			
		0.2	9.17			
		0.2	9.2			
		3.3	9.2		3.5	9.23
AA concentration (mg/L)	0.544			0.544		
actual CS concentration (mg/L)	2.50			2.65		

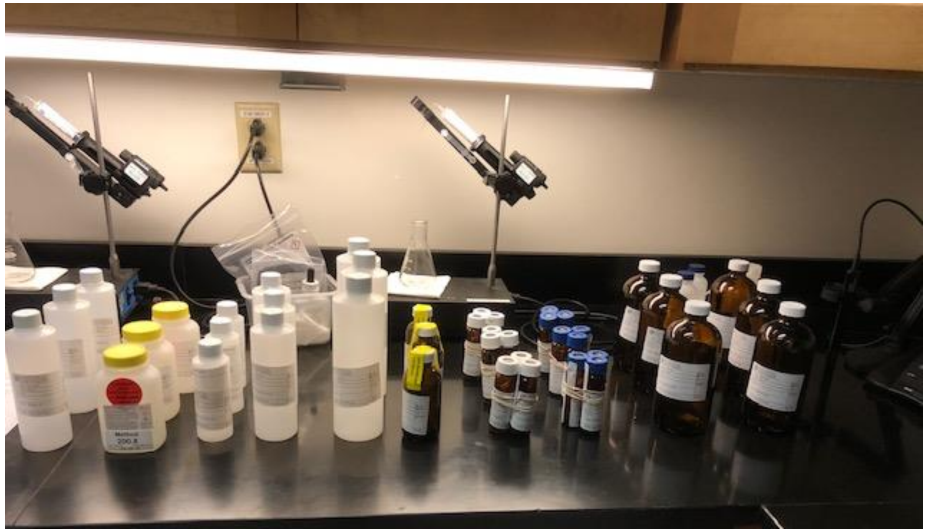
3 Bench Scale Study Calculations and Procedures

Testing Procedures – Photos



CS concentration determination of LAS sample

Spigots containing LAS/CS and AA/CS samples prior to lab analysis



Outside lab analysis samples

4. Bench Scale Study Results and Conclusions

4 Bench Scale Study Results and Conclusions

Test Results

- **Objective 1:** (a) achieve a **Cl_2:N** of at least **4.7 but not exceeding 4.9**
- (b) **pH** of the effluent treated water to **9.2**. Achieved based on Data below

AA+CS	**0m**	**20m**	**1h**	**1d**	**7d**	**14d**	**21d**	**28d**
Date	4/11/2018	4/11/2018	4/11/2018	4/12/2018	4/18/2018	4/25/2018	5/2/2018	5/9/2018
Time	15:05	15:25	16:05	15:17	11:01	15:02	8:22	8:34
Location	WCWTP	WCWTP	WCWTP	PP	PP	PP	PP	PP
pH		9.23	9.25	9.34	9.26	9.24	9.21	9.24
Temperature (deg C)		16.5	16.8	14.9	14.4	14.8	15.2	15.2
Total Chlorine (mg/L)		2.63	2.6	2.48	2.33	2.2	2.14	2.08
Monochloramine (mg/L N)		0.56	0.57	0.51	0.471	0.446	0.434	0.402
Free ammonia as (mg/L N)		0	0	0	0.02	0	0.01	0.04
Total ammonia		0.56	0.57	0.51	0.491	0.446	0.444	0.442
Turbidity (NTU)		0.046	0.045	NA	0.053	0.04	0.043	0.039
Cl_2:N Ratio		4.70	4.56	4.86	4.75	4.93	4.82	4.71

LAS+CS	**0m**	**20m**	**1h**	**1d**	**7d**	**14d**	**21d**	**28d**
Date	4/11/2018	4/11/2018	4/11/2018	4/12/2018	4/18/2018	4/25/2018	5/2/2018	5/9/2018
Time	15:00	15:20	16:00	15:05	10:51	14:35	8:03	8:24
Location	WCWTP	WCWTP	WCWTP	PP	PP	PP	PP	PP
pH		9.1	9.11	9.13	9.13	9.04	9.04	9.05
Temperature (deg C)		17	17.4	15.3	14.6	15	15.2	15.2
Total Chlorine (mg/L)		2.5	2.51	2.49	2.2	2.19	2.18	2.08
Monochloramine (mg/L N)		0.53	0.54	0.503	0.474	0.447	0.44	0.401
Free ammonia as (mg/L N)		0	0	0.02	0.04	0	0.01	0.05
Total ammonia		0.53	0.54	0.523	0.514	0.447	0.45	0.451
Turbidity (NTU)		0.047	0.047	NA	0.052	0.04	0.045	0.043
Cl_2:N Ratio		4.72	4.65	4.76	4.28	4.90	4.84	4.61

Test Results

- **Objective 2:** Compare DBP formation for AA/SH and LAS/SH

Analysis	Unit	Control Sample	AA &SH 1 Hour Sample	AA &SH 28 Days Sample	LAS &SH 1 Hour Sample	LAS &SH 28 Days Sample	Federal MCL
Testing Date		4/11/2018	4/11/2018	5/9/2018	4/11/2018	5/9/2018	
Total Haloacetic Acids (HAA5)	ug/L	24	23	39	23	38	60
Nitrosamines: N-Nitroso-dimethylamine (NDMA)	ug/L	ND	ND	0.007	ND	0.008	No MCL
Total Trihalomethanes (TTHM)	ug/L	34	28	37	33	36	80

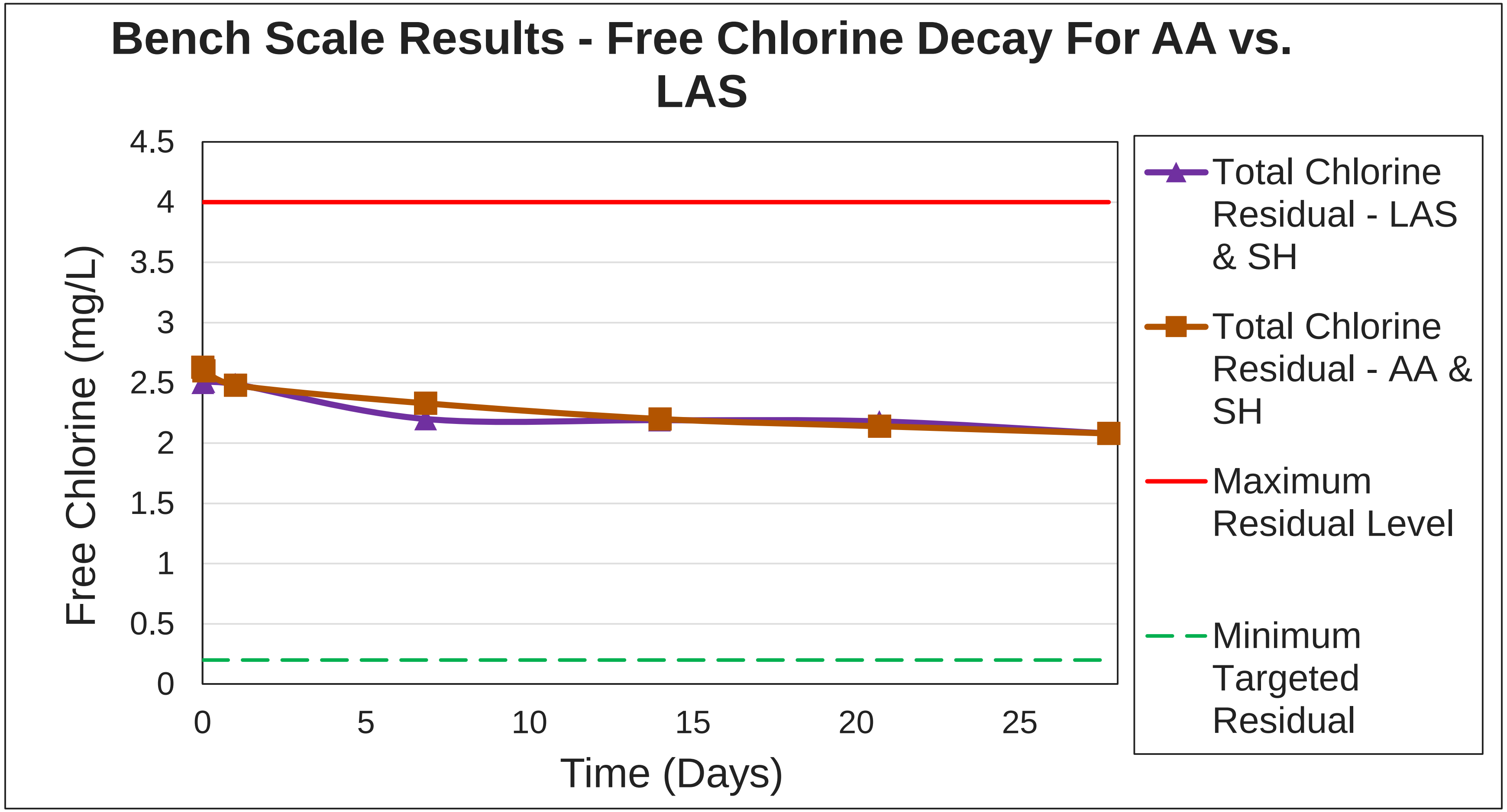
Abbreviation

ND = Nondetectable

4 Bench Scale Study Results and Conclusions

Test Results

- **Objective 3:** Compare the rate of chloramine decay when using AA/SH versus LAS/SH



4 Bench Scale Study Results and Conclusions

Conclusions

- Chloramination is an effective alternative of chlorination because:
  1. it reduces DBPs formed in drinking water
  2. It maintains a lasting free-chlorine residual in the distribution network

- Chloramination using LAS has no effect on residual decay rates or DBP formation and is safe to store and handle by WTP operators

- EBMUD decided to keep AA systems due to high initial capital cost of replacing current system

- Future studies should be conducted to observe temperature effects of using LAS versus AA for chloramination

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