Achieving Simultaneous Total Organic Carbon Removal and Clarification Under Alkaline Conditions

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Growing populations often require municipalities to seek out alternative water sources for production of sufficient and safe potable water supplies. Surface water and groundwater are commonly used as the main source of drinking water supplies following process treatment. To meet the needs of an increasing population, municipalities have looked to combine both surface water and groundwater as a convenient way to provide the necessary volume and excess water supply for the future. Aquifer storage and recovery (ASR) systems are used as alternative water storage basins where excess treated water is injected into an underground geological basin for temporary storage until high-demand events occur. When accessing any of these typical water sources, process treatment is critical to ensure safe, potable water.

Clarification and softening are typically employed to meet the growing demands for drinking water and process water needs. Softening is most critical for customers who suffer from hard water sources containing two primary divalent ions: calcium and magnesium. Hard water can affect many aspects of drinking water, including corrosion problems (e.g., faucets and water heaters), dry skin, and unsightly spots on surfaces, which become nuisance problems for the customer and very costly for the utility over time. Municipalities impacted by hard water sources must implement a process treatment strategy that will address and minimize hard water effects. Various regions in the continental United States are more susceptible to hard water problems than others, particularly those utilizing groundwater or well water. Southwestern and Midwestern municipalities often experience these issues due to minerals that make up the geological sedimentary rock formations in the region from which water percolates, stripping and dissolving these mineral-laden formations that typically contain calcium and magnesium.

Not only are solids removal and hardness removal important; total organic carbon (TOC) can impact water treatment requirements, particularly with respect to disinfection byproducts (DBPs). Most TOC removal is accomplished under low pH conditions (below neutral pH) to achieve maximum removal via enhanced coagulation–flocculation treatment through surface area adsorption onto typical metal hydroxide floc. Experience has shown that natural organic matter (NOM) can play an important role in achieving efficient hardness removal or calcium carbonate precipitation and crystal growth. The NOM, such as humic or fulvic acids, can exert varying degrees of inhibitory effects on calcium carbonate precipitation (Williamson, 2010). Humic material consists of organic matter re-

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sulting from natural decay via microbial and oxidative decomposition of plant tissue, dead organisms, and complex organic molecules, including carboxylates, carbohydrates, proteins, lignins, lignans, phenolate groups, and fats that are found in water and soil (Elkins and Nelson, 2002). Process treatment methods, such as feeding ferric chloride prior to lime addition, granular activated carbon (GAC) pretreatment, or dual-stage treatment to remove a percentage of TOC, have proven successful in limiting NOM inhibitory effects, particularly with softening applications. The NOM inhibition of calcium carbonate precipitation has long been considered the responsible factor to limiting calcium carbonate precipitation and crystal growth; however, the physical and chemical properties associated with the multitude of molecular configurations (Figure 1) that constitute NOM can greatly dictate the ability to treat and limit calcium crystal inhibition (Elkins and Nelson, 2002).

The reported elementary composition of humic material generally consists of C (45-55 percent), H (3-6 percent), N (1-5 percent), O (30-45 percent), and S (0-1 percent). Humic material can also be divided into three distinct groups: humin, insoluble in water at all pH values; humic acid, insoluble at pH values less than 2, but soluble at higher pH; and fulvic acid, soluble in aqueous solutions over the entire range of pH (Elkin and Nelson, 2002). It is easily understandable why NOM inhibition is common in lime softening applications given this high affinity for solubility of humic and fulvic acids in the alkaline region (Williamson, 2010).

These highly active functional groups associated with humic and fulvic acids favor metal ion complexation, especially multivalent metals such as aluminum, calcium, iron, and magnesium (Elkin and Nelson, 2002). Humic sub-
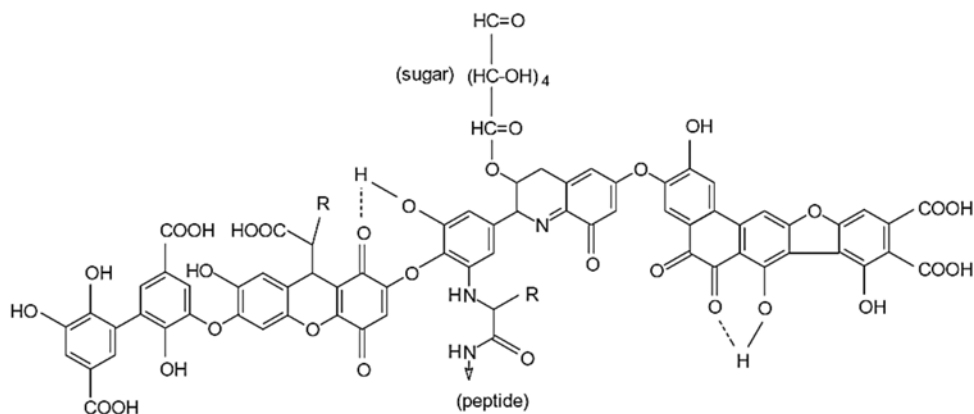

Figure 1. Model Structure of Humic Acid According to Stevenson (1982); R can be Alkyl, Aryl, or Aralkyl *(Source: Pena-Mendez et al., 2005)*

stances particularly will dissociate to a greater extent in the upper pH region (alkaline), making them more readily available to bind with free calcium. Moreover, free calcium can enhance the adsorption of anionic constituents onto the calcium carbonate crystal, thereby effectively reducing calcium carbonate precipitation (Liao and Randtke, 1986). The NOM can also form soluble complexes with free calcium through carboxylic acid moieties at neutral pH and with phenolic hydroxyl groups in the alkaline region. The formation of these dissolved NOM-calcium complexes can then affect calcite growth rate by (1) reducing the free calcium activity and degree of supersaturation, thereby decreasing calcite precipitation, and (2) by a change in the NOM molecular charge, resulting in surface adsorption onto the calcite crystal, thus interrupting calcite growth sites (Lin et al., 2005).

A high-efficiency solids contact process treatment application can provide a viable physiochemical treatment approach to limit these effects and yield total hardness removal to within expected requirements. This study will address and demonstrate both successful removal of TOC and solids/turbidity and softening under alkaline conditions via high-rate solids contact clarification. This process treatment approach has long proven reliable through success in both the laboratory and full-scale applications.

Results

Growing populations throughout the U.S. are placing considerable demands on municipality water sources, forcing municipalities to look for additional or alternative sources to meet these rising demands. One Midwestern municipality looked at utilizing individual and various combinations of water sources, including surface water, groundwater, and ASR water produced from reclaimed wastewater following membrane filtration and aquifer injection, in order to address future expansion. Various blend ratios from each of these water sources would be utilized depending upon demand throughout the year. Representative samples collected from each of these three water sources were evaluated in the laboratory for softening and clarification utilizing calcium hydroxide, or hydrated lime, and ferric chloride, followed by a polymeric flocculant aid. The primary effluent treatment objectives defined for this treatability study included effluent turbidity below 2 nephelometric turbidity units (NTU), with a preferred goal of less than 1 NTU, according to the U.S. Environmental Protection Agency (EPA) Disinfectant/Disinfection Byproducts (D/DBP) Rule, and total hardness ranging from 125-135 mg/L as $CaCO_3$ with a preferred target of 120 mg/L as $CaCO_3$.

Table 1. Midwestern Municipality Raw Water Blend Ratios

Test #	Surface Water (SW)	Groundwater (GW)	ASR Water (ASR)
Test 1	100%	0%	0%
Test 2	0%	100%	0%
Test 3	0%	0%	100%
Test 4	50%	50%	0%
Test 5	50%	0%	50%
Test 6	0%	50%	50%
Test 7	0%	80%	20%
Test 8	33%	33%	33%

Table 2. Midwestern Municipality Raw Water Source Routine Characterization – Individual Raw Water Source and Blends

Analytical Parameter	Units	#1	#2	#3	#4	#5	#6	#7	#8
pH	s.u.	7.95	7.41	8.02	8.20	8.11	8.02	7.72	7.94
M-Alkalinity	mg/L CaCO₃	180	220	190	198	188	206	212	196
Total Suspended Solids	mg/L	11.1	1.2	<1.0	---	---	---	---	---
Turbidity	NTU	15.0	2.15	0.17	8.12	7.58	0.42	0.78	5.21
Whatman 2 Filtered (8µm) Turbidity	NTU	1.24	0.22	0.14	1.27	1.08	0.12	0.28	0.84
Total Organic Carbon	mg/L	5.02	1.00	5.05	2.89	4.88	3.15	1.76	3.52
D/DBP % TOC Removal Requirement	%	25%	NR	25%	15%	25%	15%	NR	15%
Dissolved Organic Carbon	mg/L	4.73	1.00	5.05	---	---	---	---	---
Total Hardness	mg/L CaCO₃	210	264	236	240	226	242	256	236
Calcium Hardness	mg/L CaCO₃	148	216	192	184	172	200	212	184
Magnesium Hardness	mg/L CaCO₃	62	48	44	56	54	42	44	52
Stoichiometric Lime Dosage	mg/L	176	241	185	207	183	214	229	200
Total Aluminum	mg/L	0.984	ND	ND	---	---	---	---	---
Soluble Aluminum	mg/L	0.011	ND	ND	---	---	---	---	---
Total Iron	mg/L	0.747	0.392	0.010	---	---	---	---	---
Soluble Iron	mg/L	ND	0.027	0.010	---	---	---	---	---
Soluble Iron Filtered On Site	mg/L	---	0.185	---	---	---	---	---	---
Total Manganese	mg/L	0.044	0.296	ND	0.112	---	0.112	0.214	0.079
Soluble Manganese	mg/L	ND	0.295	ND	0.088	---	0.110	0.207	0.079

Note: Refer to Table 1 for test condition makeup source
NR – Not required
ND – Nondetect below 0.010 mg/L

An aliquot from each water source was processed through a series of analytical procedures to characterize influent water quality. In addition to the individual water sources, various raw water blends were prepared in accordance to the plant's anticipated blend ratios. Blend ratios utilized for this treatability study are provided in Table 1, followed by pertinent analytical results in Table 2.

Based on the routine characterizations, required D/DBP TOC removal ranges from 15 to 25 percent, depending upon the raw water source as noted in Table 2 and outlined in the EPA D/DBP chart (Figure 2). Whatman 2-filtered turbidities suggested that charge neutralization (coagulant demand) would not be significantly impacted.

The laboratory treatability study was conducted based on a specific process treatment technology application and effluent water quality objective(s). The treatability study format included physical–chemical process treatment simulating high-rate solids contact such as SUEZ's Densadeg® Clarifier technology via standard-batch jar test procedures. Chemical injection was performed in systematic order utilizing a Phipps & Bird jar tester that included lime addition mixing at 1-00 revolutions per minute (rpm) for 13 minutes, followed by co-agulant addition for 2 minutes at 100 rpm, and flocculant aid addition for 0.5 minutes at 100 rpm. Afterwards, a 3-minute slow mix or flocculation was performed at 35 rpm, followed by

5-minute settling and collection of effluent parameters. Jar tests were performed on individual raw water sources, followed by the various blend ratios to evaluate the impact of switching periodically from the different water sources and what influence that may have on chemical dosing requirements and effluent water quality. Testing began initially with surface water and groundwater sources prior to receiving ASR due to availability of ASR from the site.

Test 1: Surface Water

Initial screening of the surface water source began with feeding lime dosages, ranging from 90 to 175 mg/L, followed by 20 mg/L of ferric chloride and 0.6 mg/L of a high-quality anionic emulsion flocculant aid (very high molecular weight, medium charge density). Sludge recycling was employed to simulate high-efficiency solids contact clarification where previously precipitated calcium carbonate crystals act to "seed" additional calcium carbonate precipitation in the reactor zone. When considering sto-

ichiometric calculations for lime consumption, the following reactions were taken into account:

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O \qquad (1)$$

$$Ca^{2+} + 2HCO^- + Ca(OH)^2 \rightarrow 2CaCO_3 + 2H_2O \qquad (2)$$
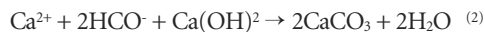
Because magnesium hardness removal is not required to meet the preferred total hardness objective of 120 mg/L as $CaCO_3$, theoretical stoichiometric calculations were based solely on raw water free carbon dioxide, calcium hardness, and bicarbonate alkalinity, according to Equations 1 and 2. The surface water raw water characterization determined that calcium hardness was 148 mg/L as $CaCO_3$ and total alkalinity was 180 mg/L as $CaCO_3$. Given that calcium hardness was less than the total alkalinity, calcium hardness can be considered entirely associated with carbonate hardness with no noncarbonate component; therefore, lime consumption would be influenced by the conversion of free carbon dioxide to carbonate alkalinity, and bicarbonate to carbonate

alkalinity, followed by calcium carbonate precipitation. Equation 1 establishes that for every 1 mg/L of free carbon dioxide present, 1.68 mg/L of lime is consumed; Equation 2 establishes that for every 1 mg/L of bicarbonate alkalinity present, 0.61 mg/L of lime will be consumed.

Based on estimated stoichiometric calculations when factoring in complete conversion of bicarbonate alkalinity, free carbon dioxide to carbonate, no magnesium precipitation, and an excess lime approach of 1.25, the final calculated lime dosage of 176 mg/L would likely be needed to achieve the preferred effluent total hardness objective of less than 120 mg/L as $CaCO_3$. This same procedure was applied to all succeeding water sources to determine stoichiometric lime dosing requirements.

According to jar test results (Figure 3), a lime dosage of 175 mg/L was able to yield total hardness removal below 120 mg/L as $CaCO_3$ and within good agreement of the stoichiometric calculation. Sludge recycling demonstrated that high-efficiency solids contact is able to improve chemical dosing requirements, in addition to including 20 mg/L of ferric chloride to achieve simultaneous TOC reduction in accordance to the EPA D/DBP Rule objective (25 percent removal for this water). Influent TOC was reduced from 5.02 mg/L to an effluent concentration of 3.78 mg/L, corresponding to a 24.7 percent reduction in TOC. Effluent turbidity was 0.48 NTU, well below the 1 NTU preferred objective.

Test 2: Groundwater

The groundwater source was evaluated feeding lime dosages ranging from 90 up to 240 mg/L, including sludge recycling, to zero in on the lime dosage needed to achieve the effluent total hardness objective. The estimated stoichiometric calculation suggests that a lime dosage of 241 mg/L would likely be needed to achieve the preferred effluent total hardness objective. Sludge recycling, along with 20 mg/L of ferric chloride, was evaluated to address mostly turbidity reduction (considering raw water TOC was well below 2 mg/L), thus requiring no further enhanced treatment. Laboratory results (Figure 4) demonstrated that a lime dosage of 240 mg/L was able to yield total hardness below 120 mg/L. In fact, there was some notable TOC reduction, although not required, and effluent turbidity below 1 NTU was achieved. Furthermore, sludge recycling (Figure 4) was shown to improve both total hardness and turbidity removal and demonstrates the benefits of high-efficiency solids contact clarification.

In addition to the main effluent objectives, it was noted that both total and soluble manganese (0.296 mg/L and 0.295 mg/L, respec-

Figure 2. U.S. Environmental Protection Agency Stage 1
Disinfectant and Disinfection Byproducts Rule

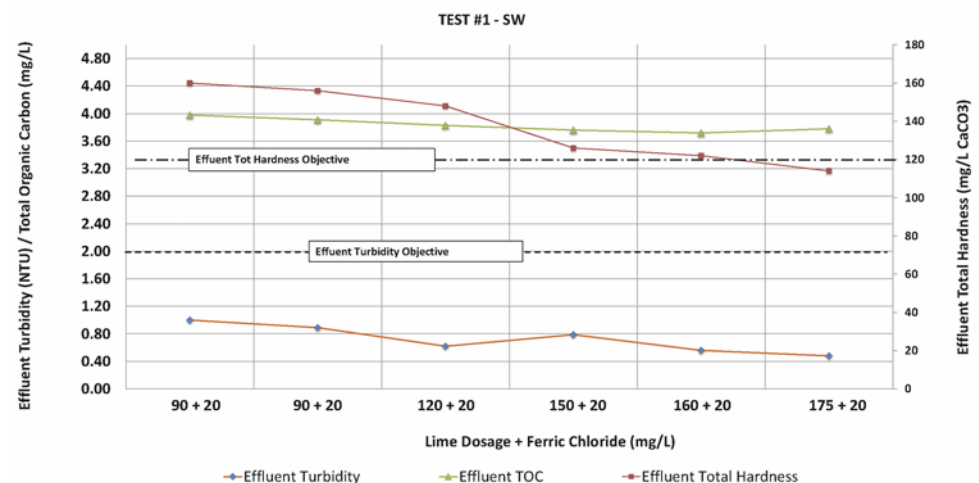| Required Removal of Total Organic Carbon by Enhanced Coagulation and Enhanced Softening for Subpart H Systems Using Conventional Treatment			
Source Water TOC (mg/L)	Source Water Alkalinity (mg/L as CaCO3)		
	0-60	> 60-120	> 120
> 2.0 to 4.0	35.0%	25.0%	15.0%
> 4.0 to 8.0	45.0%	35.0%	25.0%
> 8.0	50.0%	40.0%	30.0%

Figure 3. Test 1: Surface Water – Total Hardness, Total Organic Carbon, and Effluent Turbidity Relative to Lime and Ferric Chloride Dosage

tively) were above the EPA Secondary Drinking Water Regulations (SDWR) of 0.05 mg/L. Therefore, manganese was monitored during batch tests to determine if effluent residuals would fall below the EPA SDWR, given that manganese precipitation is favored under high pH conditions. Effluent test results were shown to achieve manganese reduction below 0.010 mg/L, thus satisfying the recommended manganese EPA SDWR of less than 0.05 mg/L.

It is also worth noting that soluble iron (0.185 mg/L) measured in the groundwater source submitted appears to make up nearly 50 percent of the total iron (0.392 mg/L) fraction based on analysis of a separate acid-preserved sample collected onsite at the time of sample collection. Although slightly above the EPA SDWR of 0.3 mg/L in the total fraction, routine characterization upon arrival demonstrated that iron was relatively easily oxidized to 0.027 mg/L in the soluble fraction during transport and suggested that no further chemical treatment was necessary; however, the mere presence of soluble iron may indicate the need to monitor iron levels to determine if additional process treatment is warranted for the groundwater source.

Test 3: Aquifer Storage and Recovery

The ASR water source, received a few weeks later, was evaluated feeding lime dosages ranging from 180 to 260 mg/L, followed by 20 mg/L

of ferric chloride and 0.6 mg/L of flocculant aid. The estimated stoichiometric calculation suggests that a lime dosage of 185 mg/L was needed. Test results (Figure 5) demonstrated that a slightly higher lime dosage of 260 mg/L was necessary to yield total hardness of less than 120 mg/L as $CaCO_3$ and simultaneous TOC reduction in accordance to the EPA D/DBP Rule objective (25 percent removal for this water). Influent TOC was reduced from 5.05 mg/L to an effluent concentration of 4.15 mg/L, corresponding to a 17.8 percent reduction in TOC. There was some difficulty with meeting the less than 1 NTU objective once the effluent total hardness was met. Further testing was repeated adjusting the coagulant dosage to 40 mg/L, along with solids recycling, which resulted in improved TOC reduction of 26.7 percent (3.70 mg/L) and effluent turbidity less than 1 NTU, while maintaining total hardness.

Test results were summarized in Table 3 to compare chemical dosing requirements and effluent water quality. It's interesting to point out that stoichiometric dosing requirements were within reasonable agreement of the actual lime dosage fed. The TOC removal under alkaline conditions was also achievable and demonstrates that high-efficiency solids contact is an effective technology for meeting both total hardness and TOC reduction in a single-stage treatment design.

Blend ratios were evaluated, given that the municipality would potentially utilize a combination of the three water sources based on demand. Blend ratios of 50:50, 80:20, and 33:33:33 were among the test conditions evaluated, as outlined in Table 1.

Test 4: 50 Percent Surface Water/50 Percent Groundwater Blend

A 50:50 blend of surface water and groundwater was prepared and evaluated feeding lime dosages ranging from 160 to 220 mg/L, followed by 20 mg/L of ferric chloride and 0.6 mg/L of flocculant aid. The estimated stoichiometric calculation suggests a lime dosage of 207 mg/L would likely be required to meet the preferred effluent total hardness objective. Laboratory test results (Figure 6) demonstrated that 200 mg/L of lime was capable of yielding total hardness of less than 120 mg/L as $CaCO_3$ and 24.9 percent TOC removal (corresponding to an effluent concentration of 2.17 mg/L), which falls easily within the 15 percent removal requirement based on the EPA D/DBP Rule; however, effluent turbidity (1.33 NTU) was limited to above the preferred less than 1 NTU effluent turbidity objective. Although below the less than 2 NTU target objective, sludge recycling simulating solids contact would have demonstrated the ef-
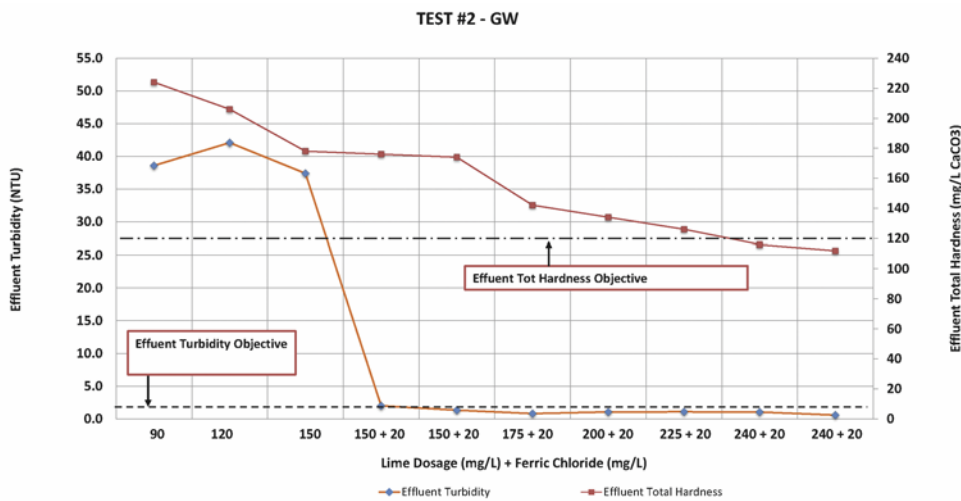

Figure 4. Test 2: Groundwater – Total Hardness, Total Organic Carbon, and Effluent Turbidity Relative to Lime and Ferric Chloride Dosage
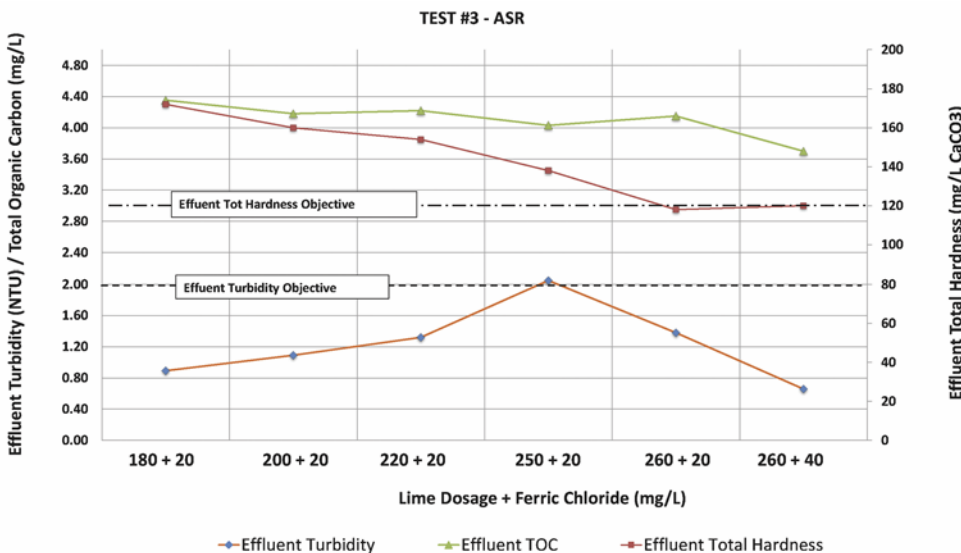

Figure 5. Test 4: Aquifer Storage and Recovery – Total Hardness, Total Organic Carbon, and Effluent Turbidity Relative to Lime and Ferric Chloride Dosage

fectiveness of high-efficiency solids contact, resulting in improved turbidity removal as seen during Test 2 given sufficient water availability.

Manganese was also monitored based on the level of soluble manganese originally measured in the groundwater source. Test results continued to show that operating under high pH conditions was suitable for achieving soluble manganese concentrations well below the EPA SDWR.

Test 5: 50 Percent Surface Water/50 Percent Aquifer Storage and Recovery Blend

A 50:50 blend of surface water and ASR was prepared and evaluated feeding lime dosages ranging from 200 to 240 mg/L, followed by 20 mg/L of ferric chloride and 0.6 mg/L of flocculant aid. The estimated stoichiometric calculation suggests that a lime dosage of 183 mg/L would likely be required to meet the preferred effluent total hardness objective. Test results (Figure 7) showed that a lime dosage of 200 mg/L was capable of yielding total hardness of less than 120 mg/L as $CaCO_3$ and simultaneous TOC reduction from an initial raw water blend concentration of 5.04 mg/L to an effluent TOC concentration of 3.95 mg/L (a 19.1 percent reduction), falling below the EPA D/DBP Rule of 25 percent TOC removal for this water source. Therefore, testing was repeated with a 40 mg/L dose of ferric chloride (and no sludge recycling) and resulted in improved TOC removal of 28.1 percent (3.50 mg/L) and effluent turbidity less than 1 NTU, while still maintaining the preferred target effluent total hardness objective.

Test 6: 50 Percent Groundwater/50 Percent Aquifer Storage Recovery Blend

A 50:50 blend of groundwater and ASR was prepared and evaluated feeding lime dosages ranging from 240 to 260 mg/L, followed by 20 mg/L of ferric chloride and 0.6 mg/L of Nalco 7768 polymer. The estimated stoichiometric calculation suggests that a lime dosage of 214 mg/L would likely be required to meet the preferred effluent total hardness objective. Laboratory test results (Figure 8) demonstrated that a lime dosage of 240 mg/L was capable of yielding total hardness of less than 120 mg/L as $CaCO_3$ and 28.9 percent TOC removal (corresponding to 2.24 mg/L in the effluent), which is well above the EPA D/DBP Rule of 15 percent removal.

Effluent turbidity was initially limited to 2.02 NTU; however, solids recycling was able to demonstrate improved effluent turbidity removal down to 1.05 NTU. Furthermore, continual sludge recycling up to optimal design conditions will provide the added benefit of high-efficiency solids clarification. Manganese continued to be monitored and was shown to be well below the

Table 3. Surface Water, Groundwater, and Aquifer Storage Recovery Chemical Treatment Summary

| Parameter	Test 1 Surface	Test 2 Ground	Test 3 ASR
Influent Water Quality			
pH	7.95	7.41	8.02
M-Alkalinity (mg/L CaCO₃)	180	220	190
Turbidity (NTU)	15.0	2.15	0.17
TSS (mg/L)	11.1	1.2	<1.0
TOC (mg/L)	5.02	1.00	5.05
DDBP Requirement	*25%*	*Not Required*	*25%*
Total Hardness (mg/L CaCO₃)	210	264	236
Chemical Treatment Conditions			
Stoichiometric Lime (mg/L)	*176*	*241*	*185*
Lime (mg/L)	175	240	260
Ferric Chloride (mg/L)	20	20	40
Flocculant Aid (mg/L)	0.6	0.6	0.6
Effluent Water Quality			
Softening pH	10.05	9.66	10.45
Final pH	8.69	8.59	9.44
P-Alkalinity (mg/L CaCO₃)	2	6	22
M-Alkalinity (mg/L CaCO₃)	66	56	58
Total Manganese (mg/L)	---	<0.010	---
Soluble Manganese (mg/L)	---	<0.010	---
Turbidity (NTU)	0.48	0.57	0.66
Whatman 2 Turbidity (NTU)	0.25	0.43	0.15
TOC (mg/L)	3.78	<0.80	3.70
% TOC Removal	*24.7*	*26.0*	*26.7*
Total Hardness (mg/L CaCO₃)	114	112	120
TSS - Sludge Solids (mg/L)	343	446	423
TSS - Calculated Sludge Solids (mg/L)	322	474	461
Ratio of Calculated Solids to Measured Solids	0.9	1.1	1.1
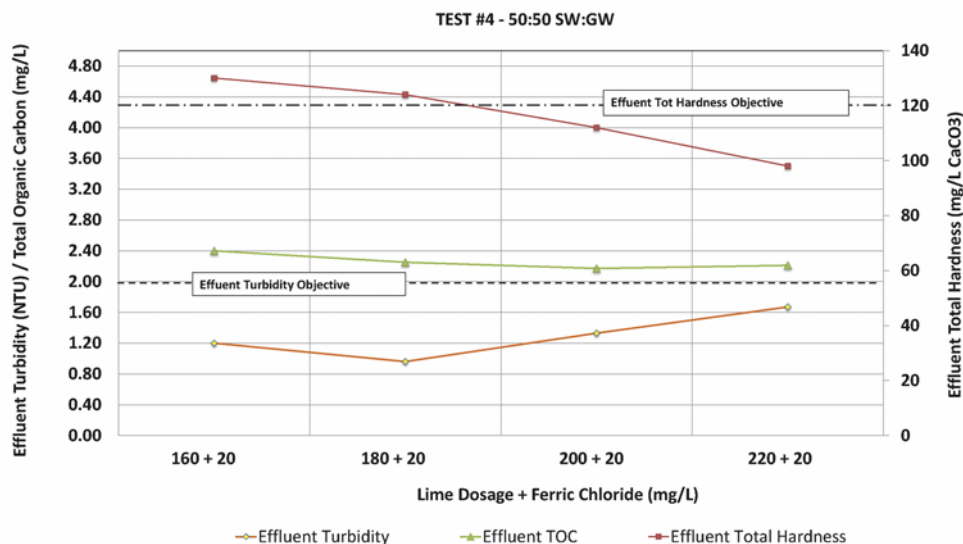
Figure 6. Test 4: 50:50 Groundwater/Surface Water – Total Hardness, Total Organic Carbon, and Effluent Turbidity Relative to Lime and Ferric Chloride Dosage
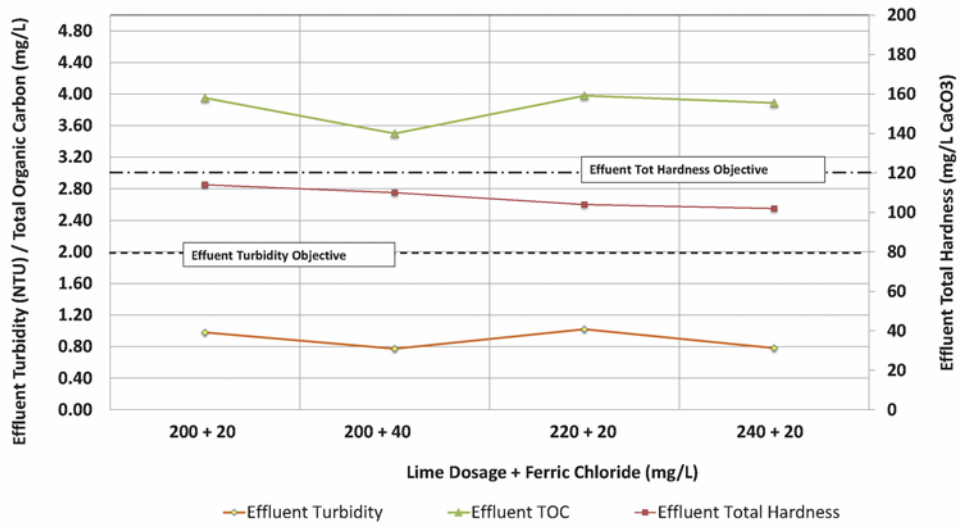
Figure 7. Test 5: 50:50 Aquifer Storage Recovery/Surface Water – Total Hardness, Total Organic Carbon, and Effluent Turbidity Relative to Lime and Ferric Chloride Dosage

Figure 8. Test 6: 50:50 Groundwater/Aquifer Storage and Recovery – Total Hardness, Total Organic Carbon, and Effluent Turbidity Relative to Lime and Ferric Chloride Dosage
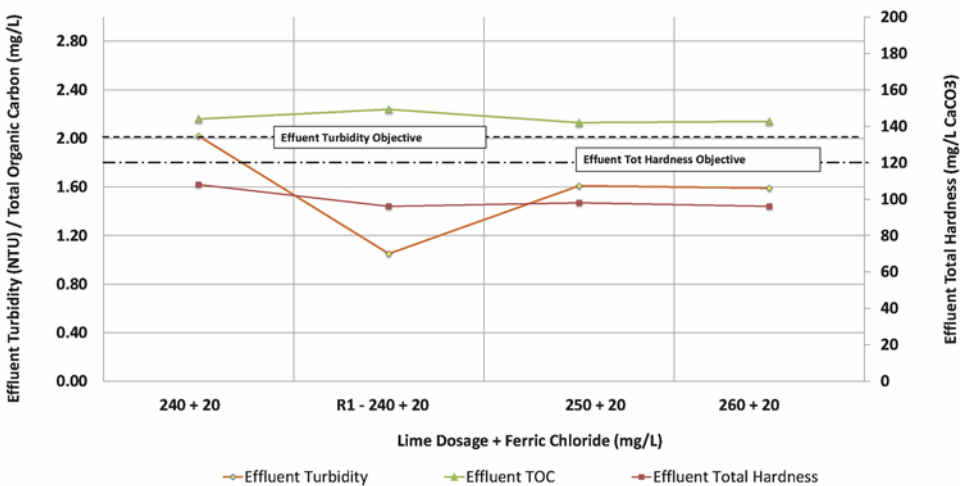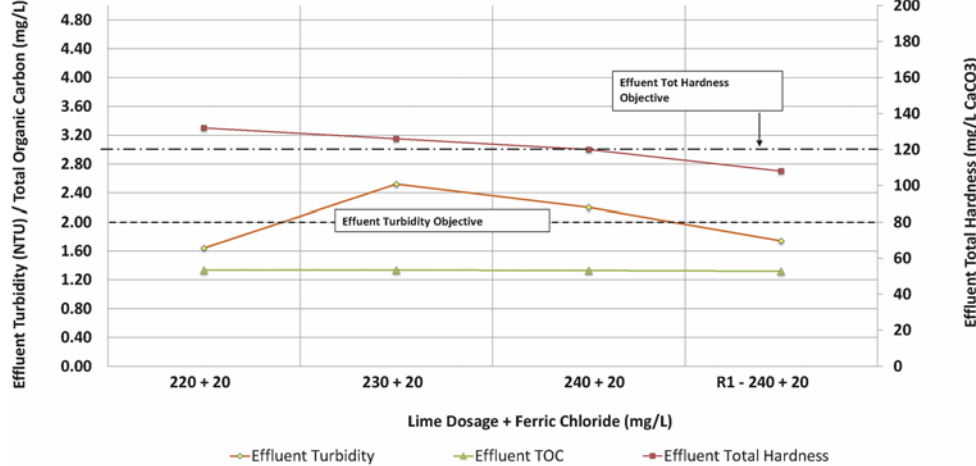

Figure 9. Test 7: 80:20 Groundwater/Aquifer Storage and Recovery – Total Hardness, Total Organic Carbon, and Effluent Turbidity Relative to Lime and Ferric Chloride Dosage

EPA secondary maximum contaminant levels (SMCL) when operating under high pH conditions that favor partial lime softening.

Test 7: 80 Percent Groundwater/20 Percent Aquifer Storage and Recovery Blend

An 80:20 blend of groundwater and ASR was prepared and evaluated feeding lime dosages ranging from 220 to 240 mg/L, followed by 20 mg/L of ferric chloride and 0.6 mg/L of flocculant aid. The estimated stoichiometric calculation suggests a lime dosage of 229 mg/L. Laboratory results (Figure 9) demonstrated that a lime dosage of 240 mg/L was capable of yielding total hardness of less than 120 mg/L as $CaCO_3$ and simultaneous TOC reduction of 25 percent following one recycle. Furthermore, TOC removal was not necessary, given that the influent concentration was initially below 2 mg/L in accordance to the EPA D/DBP Rule.

Once again, it was seen that effluent turbidity was initially limited to 2.20 NTU in the effluent and applying a single recycle was shown to improve effluent turbidity removal down to 1.74 NTU. Continual solids recycling up to optimal design conditions will likely provide the additional benefit of high-efficiency solids clarification. Also, manganese was shown to be well below the EPA SMCL when operating under high pH conditions that favor partial lime softening.

Test 8: 33 Percent Surface Water/33 Percent Groundwater/33 Percent Aquifer Storage and Recovery Blend

A final blend including all three water sources (33:33:33 blend ratio) was prepared and evaluated feeding lime dosages ranging from 190 to 210 mg/L, followed by 20 mg/L of ferric chloride and 0.6 mg/L of flocculant aid. The estimated stoichiometric calculation suggests that a lime dosage of 200 mg/L would likely meet the required effluent total hardness objective. Laboratory test results (Figure 10) demonstrated that a lime dosage of 210 mg/L was capable of yielding total hardness of less than 120 mg/L as $CaCO_3$ and 20.5 percent TOC reduction (corresponding to 2.80 mg/L in the effluent) and well above the EPA D/DBP Rule of 15 percent removal of 20.5 percent, with an effluent turbidity of 0.79 NTU. Manganese was also well below the EPA SMCL when operating under high pH conditions.

Summarizing test results in Table 4 from both individual and blend sources, it is easy to see that solids contact is an effective means for meeting simultaneous total hardness, TOC, and turbidity objectives under alkaline conditions. Theoretical sludge solids were also calculated and measured to confirm solids production for each given water source to estimate solids han-

dling. In fact, one particular benefit with a high-rate solids contact clarifier, such as the Densadeg Clarifier, is its sludge thickening capability that helps to eliminate the need for additional sludge handling equipment, such as a thickener.

Much of the literature research has focused on inhibition of calcium carbonate crystal development and growth by NOM or humic substances (TOC surrogate) through surface binding onto the calcium crystal surface, causing minimal to no crystal growth. What was evident from this laboratory testing is that TOC inhibition was minimized or not even realized, based on the excellent removal efficiencies that were seen and despite treating the individual sources or blends.

Lastly, settling tests were limited to water availability and performed only with the groundwater source feeding 240 mg/L of lime, followed by 20 mg/L ferric chloride and 0.6 mg/L of flocculant aid to evaluate sludge settling performance.
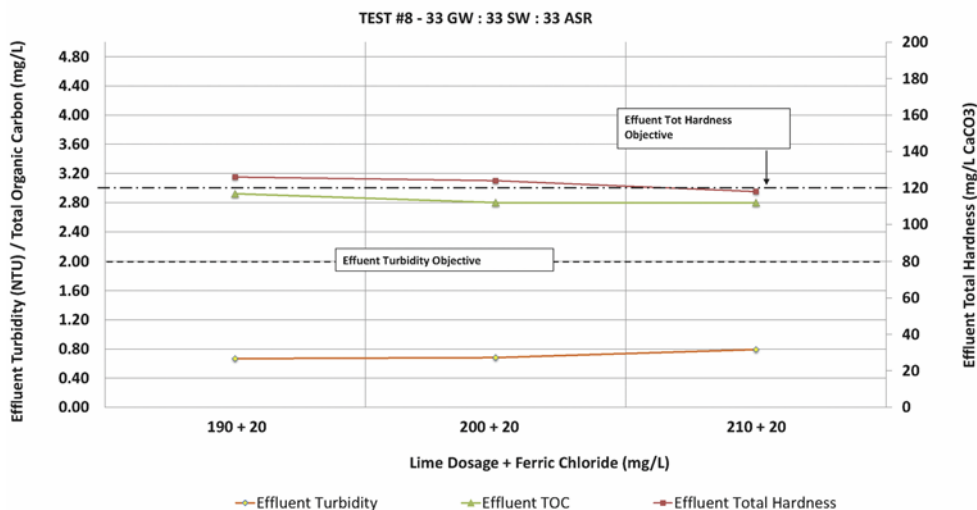
Figure 10. Test 8: 33 Groundwater/33 Surface Water/33 Aquifer Storage and Recovery – Total Hardness, Total Organic Carbon, and Effluent Turbidity Relative to Lime and Ferric Chloride Dosage

Table 4. Individual and Blend Ratio Chemical Treatment Summary

Parameter	Test 1 Surface	Test 2 Ground	Test 3 ASR	Test 4 50/50 Grd/Surf	Test 5 50/50 ASR/Surf	Test 6 50/50 Grd/ASR	Test 7 80/20 Grd/ASR	Test 8 33/33/33 ASR/Surf/Grd
Influent Water Quality								
pH	7.95	7.41	8.02	8.20	8.11	8.02	7.72	7.94
M-Alkalinity (mg/L CaCO₃)	180	220	190	198	188	206	212	196
Turbidity (NTU)	**15.0**	**2.15**	**0.17**	**8.12**	**7.58**	**0.42**	**0.78**	**5.21**
Whatman 2 Turbidity (NTU)	1.24	0.22	0.14	1.27	1.08	0.12	0.28	0.84
TSS (mg/L)	11.1	1.2	<1.0	---	---	---	---	---
Theoretical Turbidity (NTU)	---	---	---	*8.58*	*7.58*	*1.16*	*1.75*	*5.77*
TOC (mg/L)	**5.02**	**1.00**	**5.05**	**2.89**	**4.88**	**3.15**	**1.76**	**3.52**
DDBP Requirement	*25%*	*Not Required*	*25%*	*15%*	*25%*	*15%*	*Not Required*	*15%*
DOC (mg/L)	4.73	1.00	5.05	---	---	---	---	---
Theoretical TOC (mg/L)	---	---	---	*3.01*	*5.04*	*3.02*	*1.81*	*3.69*
Total Hardness (mg/L CaCO₃)	**210**	**264**	**236**	**240**	**226**	**242**	**256**	**236**
Ca Hardness (mg/L CaCO₃)	148	216	192	184	172	200	212	184
Mg Hardness (mg/L CaCO₃)	61.8	47.8	44	56	54	42	44	52
Theoretical Total Hardness (mg/L CaCO₃)	---	---	---	*237*	*223*	*250*	*258*	*237*
Chemical Treatment Regime								
Stoichiometric Lime (mg/L)	*176*	*241*	*185*	*207*	*183*	*214*	*229*	*200*
Lime (mg/L)	175	240	260	200	200	240	240	210
Ferric Chloride (mg/L)	20	20	40	20	40	20	20	20
Flocculant Aid (mg/L)	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Effluent Water Quality								
Softening pH	10.05	9.66	10.45	10.14	10.28	10.15	9.99	10.56
Final pH	8.69	8.59	9.44	8.14	8.67	9.41	8.51	8.17
P-Alkalinity (mg/L CaCO₃)	2	6	22	0	4	12	4	0
M-Alkalinity (mg/L CaCO₃)	66	56	58	56	40	36	74	62
Total Manganese (mg/L)	---	<0.010	---	<0.010	---	<0.010	<0.010	0.011
Soluble Manganese (mg/L	---	<0.010	---	<0.010	---	<0.010	<0.010	0.010
Turbidity (NTU)	**0.48**	**0.57**	**0.66**	**1.33**	**0.77**	**1.05**	**1.74**	**0.79**
Whatman 2 Turbidity (NTU)	0.25	0.43	0.15	0.19	0.21	0.22	0.23	0.21
TOC (mg/L)	**3.78**	**<0.80**	**3.70**	**2.17**	**3.50**	**2.16**	**1.32**	**2.80**
% TOC Removal	*24.7*	*26.0*	*26.7*	*24.9*	*28.1*	*31.4*	*25.0*	*20.5*
Total Hardness (mg/L CaCO₃)	**114**	**112**	**120**	**112**	**110**	**96**	**108**	**118**
Ca Hardness (mg/L CaCO₃)	62	66	80	66	60	56	64	66
Mg Hardness (mg/L CaCO₃)	52	46	40	46	50	40	44	52
TSS - Sludge Solids (mg/L)	343	446	423	380	393	397	433	363
TSS - Calculated Sludge Solids (mg/L)	322	474	461	388	376	468	472	402
Ratio	0.9	1.1	1.1	1.0	1.0	1.2	1.1	1.1

Laboratory settling test results demonstrated that at nearly maximum reactor solids concentrations of 18,400 mg/L, a calculated rise rate of 6.5 gpm/ft² was achieved and would suggest that this is an excellent application for the high-rate solids contact clarification designed at standard rise rates. It should be noted that laboratory-calculated rise rates based on batch jar tests are not indicative of actual clarifier performance, but merely estimate the impact of solids concentrations on floc settling rate performance under specified chemical treatment conditions. Batch jar tests cannot duplicate the dynamic processes seen in pilot or full-scale systems, such as shear rates and sludge thickening performance.

Conclusions

The key findings from the treatability study demonstrated that effluent turbidity below 2 NTU and mostly below 1 NTU were achievable. Total hardness removal was reduced to within acceptable effluent concentrations ranging within the 125-135 mg/L as $CaCO_3$, and even below the 120 mg/L objective. Simultaneous removal of both total hardness and TOC was achievable with a ferric chloride dosage ranging from 20 to 40 mg/L in conjunction with a high-quality, NSF-approved flocculant aid, thus demonstrating the benefits of high-efficiency solids contact process treatment. Furthermore, solids contact helps to manage chemical dosing requirements, given the high-efficiency and enhanced treatment provided by calcium carbonate seeding and enhanced TOC adsorption onto metal hydroxide surfaces.

Controlled use of flocculant aid and coagulant injection points will also provide benefits in achieving optimal TOC removal efficiencies throughout the year under softening conditions. Laboratory settling rates suggest that sludge solids are ideal for such a single-stage process treatment application. When summarizing these results, it's shown that high-rate, high-efficiency solids contact clarification can provide municipalities a viable option and level of performance that can translate into capital-expenditure and operating-expense cost savings benefits, including minimal equipment needs, lower chemical costs, and higher yields with regard to sludge solids concentrations.

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