



City of Ripon, California
Proposition 50 Project
ID No. P50-3910007-055



City of Ripon, California
Proposition 50 Project

Integrated Nitrate and Arsenic Treatment Demonstration

FINAL REPORT

ID No. P50-3910007-055
February 2010



Table of Contents

0.0 Executive Summary 1

 0.1 Phase A Investigation 1

 0.2 Phase A and Phase B Media Change 2

 0.3 Phase B Investigation..... 2

 0.4 Hydraulic Loading Rate Small-Scale Column Testing..... 3

 0.5 Summary of Investigation..... 3

1.0 Introduction..... 4

 1.1 Site Background..... 5

 1.2 Arsenic Treatment..... 6

 1.3 Nitrate Treatment..... 6

 1.4 Summary of Previous SMI-III® Research..... 8

 1.4.1 Nitrate Removal 9

 1.4.2 Empty Bed Contact Time..... 10

 1.4.3 pH Effects 11

 1.4.4 Solids Precipitation..... 12

 1.4.5 Influent Nitrate Concentration 13

 1.4.6 Nitrogen Balance 13

 1.4.7 Soluble Iron..... 14

 1.4.8 Particle Size 15

 1.4.9 Iron to Nitrate Ratio..... 15

 1.4.10 Metals Treatment 16

2.0 Pilot System Description..... 16

 2.1 SMI-III® Equipment 16

 2.2 Coagulation/Filtration Equipment 17

 2.3 Chemical Feed Systems 17

 2.4 Online Instrumentation 18

 2.5 Sampling/Monitoring Locations 20

3.0 Pilot Study Objectives..... 20

4.0 Phase A Investigation 21

 4.1 Test Plan..... 21

 4.2 Water Quality Results..... 23

 4.2.1 Comparison of Online and Grab Sample Nitrate Results 23

 4.2.2 Nitrate Removal 26

 4.2.3 Nitrogen Balance 28

 4.2.4 Iron Release 33

 4.2.5 Iron Removal 34

 4.2.6 Arsenic Removal..... 36

 4.2.7 Co-Contaminant Removal 36

 4.2.8 Oxidation Reduction Potential..... 37

 4.2.9 Calcium Carbonate Deposition..... 38

 4.3 Operational Results..... 39

 4.3.1 Effects of Fluff Cycle..... 39



4.3.2	SMI-III [®] Reactor Differential Pressure	40
4.3.3	Media Consumption.....	41
4.4	Phase A Investigation Summary.....	42
5.0	SMI-III [®] Media Size Small-Scale Column Investigation.....	42
5.1	Experimental Set-up.....	43
5.2	Experimental Schedule	45
5.3	Experimental Results	47
5.3.1	Nitrate Removal.....	47
5.3.2	Nitrite Production.....	48
5.3.3	Ammonia Production.....	49
5.3.4	Nitrogen Removal.....	50
5.3.5	Iron Release	51
5.4	SMI-III [®] Media Size Small-Scale Column Investigation Summary	52
6.0	Phase B Investigation.....	52
6.1	Additional Data Analysis.....	53
6.2	New SMI-III [®] (NF-3) Media Development.....	57
6.3	Phase B Test Plan.....	58
6.4	Phase B Test Conditions.....	62
6.5	SMI-III [®] Media Change Out and Startup	62
6.6	Water Quality Results.....	65
6.6.1	Nitrate Removal.....	65
6.6.2	Nitrite Production.....	67
6.6.3	Ammonia Production.....	68
6.6.4	Nitrogen Removal.....	69
6.6.5	Total Nitrogen and Total Dissolved Nitrogen	73
6.6.6	Iron Release	75
6.6.7	Arsenic Removal.....	77
6.6.8	Co-contaminant Removal	78
6.6.9	Total Trihalomethane Formation	79
6.7	Operational Results.....	79
6.7.1	Flow Rate.....	79
6.7.2	pH.....	80
6.8	Media Characterization.....	80
6.9	Residual Management.....	82
6.10	Phase B Operational Cost	83
6.11	Phase B Investigation Summary	83
7.0	Hydraulic Loading Rate Small-Scale Column Testing.....	84
7.1	Background.....	84
7.2	Results.....	85
7.2.1	Nitrate Concentrations	85
7.2.2	Nitrite Concentrations.....	87
7.2.3	Ammonia Concentrations	87
7.2.4	Hydraulic Loading Rate and Nitrate Reduction.....	89
7.2.5	Determination of Nitrate Reduction Rate Constant.....	90
7.3	Summary	93
8.0	References.....	94



List of Tables

Table 1-1	Summary of wells for the City of Ripon as of 2006.....	5
Table 2-1	Design parameters for the SMI-III [®] reactor and coagulation/filtration equipment.....	17
Table 2-2	Manufacturer and model information for online analyzers.....	18
Table 2-3	Sample port descriptions	20
Table 4-1	Summary of Phase A test conditions.....	22
Table 4-2	Phase A sampling and monitoring schedule.....	23
Table 4-3	Minimum and maximum nitrate reduction for each Phase A test condition.....	27
Table 4-4	Phase A nitrogen removal based on the summation of nitrogen species at S1 and S4.....	31
Table 4-5	Phase A total nitrogen and total dissolved nitrogen removal results.....	33
Table 4-6	Arsenic results at the Raw Water (S1) and Finished Water (S4) locations.....	36
Table 4-7	Summary of Phase A paired sample results for chromium, uranium, and vanadium.....	37
Table 5-1	SMI-III [®] media size small-scale column investigation design parameters.....	44
Table 5-2	SMI-III [®] media size small-scale column investigation sample location descriptions.....	46
Table 5-3	SMI-III [®] media size small-scale column investigation sampling and monitoring schedule.....	47
Table 6-1	Summary of proposed Phase B test conditions	60
Table 6-2	Summary of Phase B laboratory samples.....	61
Table 6-3	Additional parameters to be analyzed during Phase B.....	61
Table 6-4	Phase B testing schedule	62
Table 6-5	Physical parameters of the original and modified SMI-III [®]	63
Table 6-6	Summary of Phase B nitrate results.....	66
Table 6-7	Summary of Phase B nitrite results	67
Table 6-8	Summary of Phase B ammonia results.....	68
Table 6-9	Summary of summed nitrogenous species from the S1, S3, and S4 sample locations.....	73
Table 6-10	Summary of total nitrogen and total dissolved nitrogen	74
Table 6-11	Summary of iron results for the S3 and S4 sample location	77
Table 6-12	Summary of paired sample results from Phase A and Phase B for chromium, uranium, and vanadium.....	79
Table 6-13	CalWET results for the Phase A and Phase B SMI-III [®] media.....	81
Table 6-14	TCLP results for the Phase A and Phase B SMI-III [®] media	82
Table 6-15	Conceptual production costs.....	83
Table 7-1	Design Characteristics of the Columns used in the HLR Investigation	85



List of Figures

Figure 1-1 Conceptual schematic of an integrated SMI-III[®]/coagulation/filtration treatment system 8

Figure 2-1 Conceptual diagram of the integrated nitrate and arsenic treatment system with sample locations..... 19

Figure 4-1 Comparison of the S2 untreated water lab and Hach online nitrate results 24

Figure 4-2 Comparison of the S4 finished water lab and Hach online nitrate results 25

Figure 4-3 Percent difference results between paired lab and Hach online nitrate results 26

Figure 4-4 Phase A raw (S1) and finished (S4) water nitrate concentrations..... 27

Figure 4-5 Phase A nitrogen species from S1 and S4 for an EBCT of 30 minutes 29

Figure 4-6 Phase A nitrogen species from S1 and S4 for an EBCT of 20 minutes 30

Figure 4-7 Phase A nitrogen species from S1 and S4 for an EBCT of 15 minutes 30

Figure 4-8 Averaged total nitrogen results for each Phase A test condition 32

Figure 4-9 Averaged total dissolved nitrogen results for each Phase A test condition 32

Figure 4-10 Average total iron release for each Phase A test condition..... 34

Figure 4-11 Phase A total and dissolved iron at the S4 location 35

Figure 4-12 Phase A oxidation reduction potential monitored at the S3 location 37

Figure 4-13 Calcium concentrations during Phase A testing..... 38

Figure 4-14 pH, ORP, and nitrate concentration of the SMI treated water (S3) 39

Figure 4-15 Box and whisker plot of the differential pressure across the SMI-III[®] reactor..... 41

Figure 5-1 SMI-III[®] media size small-scale column investigation schematic..... 44

Figure 5-2 SMI-III[®] media size small-scale column investigation photographs..... 45

Figure 5-3 SMI-III[®] media size small-scale column investigation nitrate results 48

Figure 5-4 SMI-III[®] media size small-scale column investigation nitrite results..... 49

Figure 5-5 SMI-III[®] media size small-scale column investigation ammonia results 50

Figure 5-6 SMI-III[®] media size small-scale column investigation total nitrogen results..... 51

Figure 5-7 SMI-III[®] media size small-scale column investigation total iron results..... 52

Figure 6-1 Phase A nitrogen removal as a function of pH 54

Figure 6-2 Phase A nitrogen removal as a function of EBCT 54

Figure 6-3 Change in nitrate versus change in nitrogen as a function of pH..... 56

Figure 6-4 Change in nitrate versus change in nitrogen as a function of EBCT 56

Figure 6-5 Results of side-by-side column testing of SMI-III and SMI-III(NF3) with alternative acid feeds..... 58

Figure 6-6 Service flow lateral before cleaning for Phase B 64

Figure 6-7 Photographs of SMI reactor vessel failure and media loss 65

Figure 6-8 Phase B nitrate data 66

Figure 6-9 Phase B nitrite data..... 68

Figure 6-10 Phase B ammonia data 69

Figure 6-11 Raw water (S1) total nitrogen versus post SMI (S3) total nitrogen..... 70

Figure 6-12 Raw water (S1) total nitrogen versus finished water (S4) total nitrogen..... 71

Figure 6-13 Post SMI (S3) total nitrogen versus finished water (S4) total nitrogen 72

Figure 6-14 Total nitrogen and total dissolved nitrogen at the S1 and S4 sample locations..... 74



Figure 6-15 Comparison of the summed, total, and total dissolved nitrogen analysis at the S1 and S4 sample locations during Phase B testing.....75

Figure 6-16 Total and dissolved iron results at the S3 and S4 locations76

Figure 6-17 Arsenic at the S1 and S4 sample locations.....78

Figure 6-18 Box and whisker plot of Phase B pH80

Figure 7-1 Nitrate results for the raw water and each column.....86

Figure 7-2 Delta nitrate (Nitrate_{Raw} - Nitrate_{Column}) for each column.....87

Figure 7-3 Ammonia results for each column88

Figure 7-4 Ammonia concentration versus delta nitrate.....89

Figure 7-5 Nitrate removal as a function of hydraulic loading rate for each the columns90

Figure 7-6 Nitrate reduction plotted versus temperature91

Figure 7-7 Rate constant *k* (mg-N/L-min) plotted versus temperature.....92

Figure 7-8 Predicted nitrate reduction plotted versus actual nitrate reduction93



0.0 Executive Summary

The City of Ripon (City), in conjunction with Damon S. Williams Associates (DSWA), has conducted a pilot-scale investigation of an integrated nitrate and arsenic treatment system. This City of Ripon Integrated Nitrate and Arsenic Treatment Demonstration has been approved for California Proposition 50 funding under Chapter 6b.

The integrated pilot system implements chemical reduction of nitrate with SMI-III[®] followed by coagulation/filtration for arsenic removal. SMI-III[®] is a patented, iron-based granular media that has been commercially developed for the removal of nitrate, co-contaminants including uranium, vanadium and chromium, and other compounds from water. It is foreseen that the greatest benefit of this technology is that it does not produce a costly brine stream as do the currently accepted nitrate removal technologies of ion exchange and reverse osmosis.

The pilot investigation was comprised of two discrete phases: Phase A and Phase B. The goal of Phase A was to define the operational conditions that could consistently demonstrate the ability of the integrated treatment system to achieve treated nitrate and arsenic goals of 36 mg/L and 8 µg/L, respectively, under dynamic operational conditions and economically-realistic operating conditions. Last, additional small-scale column testing was conducted to determine the effect of hydraulic loading rate on nitrate reduction.

0.1 Phase A Investigation

The primary purpose of the Phase A investigation was to identify the operational conditions (EBCT and pH) where nitrate reduction was maximized. These conditions were found to be an EBCT of 30 minutes and a pH of 6.0. The maximum nitrate reduction observed for these conditions was 18 mg/L as nitrate. These results demonstrate the viability of the SMI-III[®] media to reduce nitrate. Given that the average raw water nitrate concentration during the Phase A study was greater than 60 mg/L as nitrate, these conditions did not result in finished water nitrate concentrations that meet the project goal of 36 mg/L as nitrate. The treatment system was successful in removing arsenic. All finished water arsenic sample results during Phase A testing were below the laboratory detection limit of 2 µg/L. Last, the Phase A results demonstrated the operational viability of the integrated SMI-III[®] and coagulation/filtration process. The pilot



system operated reliably without any hydraulic challenges that have been previously encountered with SMI-III[®] media pilot testing.

0.2 Phase A and Phase B Media Change

During the course of the Phase A investigation, SMI-Inc. changed contract manufacturers. The new contract manufacturer produces a smaller sieve size SMI-III[®] media and altered the media sulfur modification process. Preliminary laboratory experiments indicated the media provided by the new contract manufacturer had a greater propensity for nitrate reduction than media from the previous contract manufacturer. The media used in the Phase A portion of the experiment was replaced with new media from the new contract manufacturer before the start of Phase B testing.

0.3 Phase B Investigation

Phase B testing continued to build on the knowledge gained during Phase A testing. Although the nitrate water quality goal of less than 36 mg/L was not achieved, two sample events produced water that were below the nitrate MCL of 45 mg/L. The average nitrate reduction during Phase B was 12 mg/L as nitrate. The degree of nitrate reduction does not appear to change with raw water nitrate concentrations. Although the removal was not substantial enough to meet the project goals for the Ripon Well 12 water, the SMI-III[®] technology may prove to be viable for systems with source water nitrate concentrations at or slightly above the nitrate MCL. With respect to arsenic removal, the system continued to effectively reduce arsenic concentrations. The instances where arsenic was detected in finished water samples can likely be attributed to challenges with the chlorine feed system or extended filter run lengths leading to iron breakthrough in the filters.

Operationally, Phase B testing identified the SMI-III[®] media as being much more operationally robust than previously anticipated. The media did not lose any discernable hydraulic or reductive capacity as a result of the tank failure, atmospheric exposure, storage and reloading. This finding, although unintentional, is very important as it shows the SMI-III[®] media can withstand service interruptions without detrimental effects.



0.4 Hydraulic Loading Rate Small-Scale Column Testing

The investigation of hydraulic loading rate (HLR) confirmed that nitrate reduction via SMI-III[®] is independent of the HLR. Future SMI-III[®] treatment systems can be designed without restriction of the reactor vessel dimensions. Future reactor vessels can be adapted to existing site constraints without being limited to height:width ratios that would exist if nitrate reduction were to depend on HLR.

The results of this investigation also highlighted the effect of temperature on the nitrate reduction reaction and developed a cursory tool to predict the amount of nitrate reduction that can be accomplished at a given temperature, 30 minute EBCT, and a pH of 6.0. This tool can be used to assist in the design of future installations as an appropriate EBCT could be determined based on the raw water nitrate concentration and the temperature range of the source water.

0.5 Summary of Investigation

Through this investigation, SMI-III[®] has proved to be an effective technology for the reduction of nitrate. While the finished water quality goals were not consistently achieved, the technology did show the capacity to reduce nitrate to levels below the nitrate MCL. In waters where the source water nitrate concentrations exceed more than 25 mg/L above the 45 mg/L as nitrate MCL, SMI-III[®] may not be an appropriate nitrate control technology. However, the process may provide an effective nitrate control technology for source waters with nitrate concentrations closer to the 45 mg/L as nitrate MCL. This technology may also be appropriate in areas with naturally high groundwater temperatures given the positive correlation between water temperature and nitrate reduction as demonstrated in the hydraulic loading rate investigation.



1.0 Introduction

The City of Ripon (City), in conjunction with Damon S. Williams Associates (DSWA), has conducted a pilot-scale investigation of an integrated nitrate and arsenic treatment system. This City of Ripon Integrated Nitrate and Arsenic Treatment Demonstration has been approved for California Proposition 50 funding under Chapter 6b.

Increasing nitrate and arsenic concentrations in City's groundwater have forced the City to take critical wells out of its drinking water supply. The City is proactively addressing these challenges in order to continue delivering an adequate supply of high quality drinking water that meets all drinking water standards. This project has built on bench- and pilot-scale efforts utilizing SMI-III[®] granular media to remove nitrate and coagulation/filtration to remove arsenic as the first pilot-scale testing of this integrated treatment system.

The SMI-III[®] treatment process may have the potential to solve nitrate problems for many communities in California, which like Ripon, do not have the means to dispose of high strength brine solutions that are a byproduct of more commonly utilized nitrate removal technologies (e.g., ion exchange, reverse osmosis). Although several bench-scale studies have demonstrated the potential application of SMI-III[®] for nitrate removal, several key operational and design issues need further evaluation and it is imperative to evaluate the effectiveness of integrating SMI-III[®] with a typical arsenic coagulation/filtration system for the combined removal of nitrate, arsenic, and other trace metals.

The integrated pilot system implements chemical reduction of nitrate with SMI-III[®] followed by coagulation/filtration for arsenic removal. SMI-III[®] is a patented, iron-based granular media that has been commercially developed for the removal of nitrate, metals, and other compounds from water. It is certified by NSF International for use in drinking water treatment. SMI-III[®] may offer a feasible alternative to the currently accepted nitrate removal technologies of ion exchange and reverse osmosis. While ion exchange is an accepted technology for the removal of nitrate and arsenic, competing contaminants limit its cost-effective application in the City's groundwater wells. Limited disposal options for the brine residual streams generated from ion



exchange and reverse osmosis processes further restrict the applicability of these technologies for the City and other inland communities.

1.1 Site Background

The City of Ripon currently maintains nine (9) groundwater wells that have, at one time or another, been used to supply potable water to the surrounding community. Nitrate, with a maximum contaminant level (MCL) of 45 mg/L as NO₃⁻, has been detected in the City’s wells at concentrations as high as 67 mg/L. Arsenic, with a new MCL of 10 µg/L, has been detected in the City’s wells at concentrations as high as 14 µg/L. Other inorganic contaminants of concern have also been detected in Ripon’s groundwater at levels below current regulatory limits; most notably hexavalent chromium, uranium, and vanadium.

In recent years, diminished groundwater quality has forced the City to remove three wells from its potable supply and decrease the production rates of another two wells. Well 5 and Well 11 have been converted from potable to non-potable use due to elevated levels of nitrate and arsenic. Well 12 is currently offline and the City has reduced the total production rates of Wells 3 and 14 by more than 50% of their rated capacities due to high nitrate concentrations. Well 12 was selected as the pilot testing site for this project. A summary of the City’s well system as of 2006 is presented in Table 1-1.

Table 1-1 Summary of wells for the City of Ripon as of 2006

Well No.	System	Production Rate (gpm)	Max Nitrate Conc. (mg/L as NO ₃)	Max Arsenic Conc. (µg/L)
Well 3 ¹	Potable	800	67	7
Well 7	Potable	1,200	26	10
Well 9	Potable	800	13	13
Well 10	Potable	2,300	25	10
Well 12 ²	Potable	2,000	64	8
Well 13	Potable	3,000	9	10
Well 14 ¹	Potable	750	16	5
Well 5	Non-Potable	1,000	59.5	No data
Well 11	Non-Potable	800	48	14

¹ Well 3 and Well 14 are closely monitored and operated with controlled pumping based on nitrate concentrations.

Well 3 and Well 14 operate at less than 50% capacity, annually.

² Well 12 is currently off-line due to recent nitrate samples above the MCL.

Values entered in **bold** font represent samples at or above 80% of the MCL.



1.2 Arsenic Treatment

The City has installed full-scale wellhead arsenic coagulation/filtration treatment for Wells 9 and 10. This treatment option was selected over numerous other arsenic removal alternatives because it is cost effective, relatively easy to implement, does not require centralized treatment, and can meet all arsenic treatment goals. In this type of a coagulation/filtration system, arsenic is adsorbed onto freshly precipitated ferric hydroxide [Fe(OH)₃] solids formed by dosing ferric chloride (FeCl₃) into the raw water. Precipitates are subsequently filtered and the product water is chlorinated and pH adjusted prior to entry into the distribution system.

In 2005, bench- and pilot-scale studies performed with Well 9 groundwater demonstrated that the coagulation/filtration process can effectively reduce arsenic concentrations to the treatment goal of less than 8 µg/L (80% of the current MCL of 10 µg/L). The noteworthy conclusions drawn from the five-week study were 1) granular media and membrane filters each remove arsenic to similarly acceptable levels; 2) coagulant type – ferric chloride and ferric sulfate – did not significantly impact arsenic removal; and 3) pH depression improved arsenic removal, but was not required to achieve the target effluent arsenic concentrations. Based on these findings, the City opted to utilize coagulation followed by filtration to treat arsenic-contaminated groundwater. The City contracted with Kinetico, Inc. to provide the coagulation/filtration equipment.

1.3 Nitrate Treatment

For nitrate treatment, the City has relatively few treatment options. Currently available drinking water nitrate treatment processes include ion exchange and reverse osmosis (RO).

Unfortunately, each of these technologies has significant disadvantages that limit their widespread applicability (most notably a lack of brine disposal alternatives). SMI-III[®], which removes nitrate via chemical reduction, is a potentially viable treatment technology for the City because it can remove nitrate but will not produce a high volume of hazardous residuals.

SMI-III[®] is a patented, iron-based granular media that has been developed for the removal of nitrate, metals, and other compounds from water. Although the actual nitrate removal

mechanisms occurring within or on the surface of the SMI-III[®] media are not fully understood, research performed with other zero-valent metals has led to the development of three plausible theories: 1) direct reduction/electron transfer at the surface of the metal, 2) indirect reduction of nitrate with corrosion byproducts, and 3) reduction by surface bound iron corrosion byproducts (Siantar et al., 1996; Cheng et al., 1997; Huang, et al. 1998; Westerhoff, 2003).

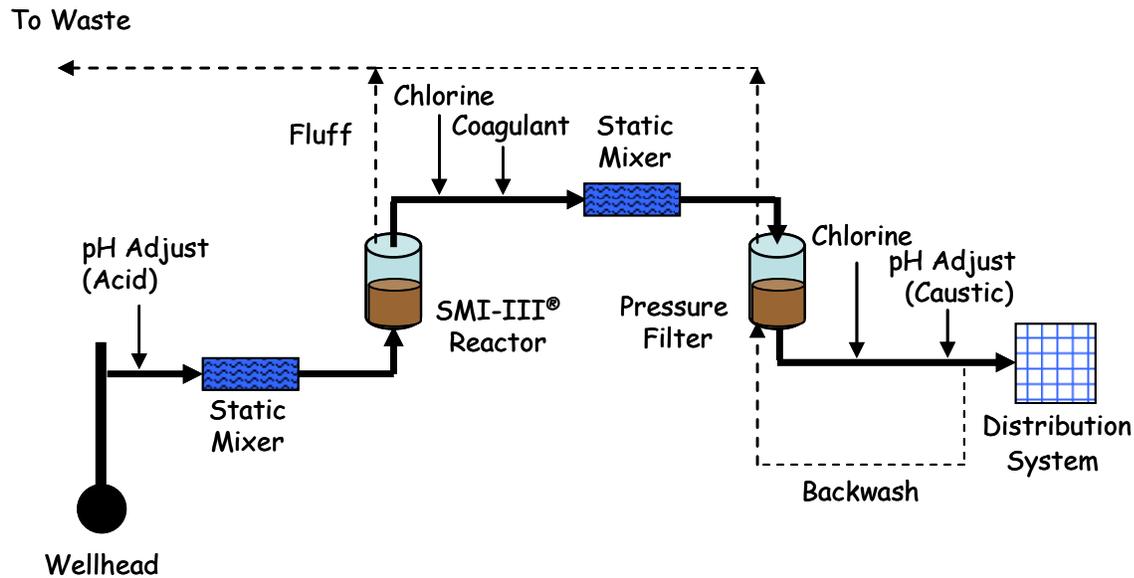
Regardless of the actual removal mechanism, experimental data strongly suggest that the reduction of nitrate is accomplished – or catalyzed by – a series of oxidation/reduction reactions. The half-reactions of SMI-III[®] most likely involve oxidation of zero-valent iron (ZVI, [Fe⁰]) to ferrous iron (Fe²⁺) (Eqn 1 and Eqn 2). The reducing half reactions responsible for the chemical destruction of nitrate, likely produce ammonium (NH₄⁺) and nitrogen gas (N₂) as end products (Eqn 1a and Eqn 2a). In both sets of oxidation/reduction reactions, hydrogen ions are consumed (i.e., pH increases) and ferrous iron is released.



The generation of ferrous iron through the reactor (Eqn 1 and Eqn 2) may ultimately impact the overall viability of the SMI-III[®] process. In previous tests, soluble iron concentrations in water treated with SMI-III[®] media were tested at levels above the drinking water secondary MCL regulation of 0.3 mg/L (Schreier, 2001; 2003; and 2006).

However, the iron released from the SMI-III[®] reactor can provide a synergistic benefit when used in conjunction with a traditional arsenic coagulation/filtration process. The ferrous iron released from the SMI-III[®] will reduce or altogether eliminate the need for coagulant addition in a downstream arsenic coagulation/filtration processes. This type of integrated system, as shown in Figure 1-1, may provide significant cost savings for treating waters with both elevated nitrate and arsenic concentrations.

Figure 1-1 Conceptual schematic of an integrated SMI-III[®]/coagulation/filtration treatment system



The first step of the treatment process is to suppress pH of the raw well water. This serves to improve nitrate removal and reduce the formation of calcium precipitates. The acidified water then passes through an up-flow pressure vessel packed with SMI-III[®] media. As nitrate is reduced via a series of oxidation-reduction reactions through the packed bed, soluble iron is released. Sodium hypochlorite is added to the iron-laden process stream to oxidize ferrous iron to an insoluble ferric hydroxide particle and to oxidize arsenic from the non-adsorbable As(III) state to the adsorbable As(V) state. As the ferric hydroxide particles form, arsenic in the As(V) state adsorbs onto the particle. After oxidation, the flow passes through a pressure filter to remove filterable solids. In full scale operation this would be followed by disinfection and the addition of caustic solution before entering the distribution system for consumption. However in the pilot study, no additional treatment will occur after filtration as the water will be sent to waste after the water quality has been analyzed.

1.4 Summary of Previous SMI-III[®] Research

Studies performed at both bench- and pilot-scale have demonstrated that SMI-III[®] can remove nitrate from groundwater. These studies also identified important issues that need to be addressed by additional testing. The following sections describe the relevant issues as they pertain to the SMI-III[®] media and summarize any pertinent previous research efforts. An



explanation of how these issues were addressed within the context of this pilot study is also provided.

1.4.1 Nitrate Removal

Several previous tests with SMI-III[®] media have shown evidence of nitrate removal but the extent of nitrate removal has not been sufficiently quantified under typical long-term operating conditions. Although there are a few directly relevant SMI-III[®] studies, the majority of the peer-reviewed research of chemical reduction to date has focused on nitrate removal by ZVI. There have been no direct studies comparing the similarities and differences between SMI-III[®] and ZVI media, but initial indications suggest that the removal mechanisms are similar. While the SMI-III[®] manufacturer believes sulfur modification regulates the environment of reactions to achieve greater and a consistent nitrate reduction, it is worthwhile to discuss relevant ZVI research along with the SMI-III[®] studies. The current state of knowledge of both ZVI and SMI-III[®] will be addressed in the following sections.

In small-scale column tests with SMI-III[®] media, Schreier (2001) reported nitrate removal in a California groundwater at approximately 19% to 25% at an empty bed contact time (EBCT) of approximately 25 minutes and at initial nitrate concentrations ranging from 26 mg NO₃⁻/L to 35 mg NO₃⁻/L. Nitrate removal increased substantially at longer EBCTs (86% to 91% at 120-minute EBCT). In a follow-up pilot-scale test, Schreier (2003) found nitrate removal to be highly variable (18% to 96%) at an influent nitrate concentration of approximately 35 mg NO₃⁻/L and an EBCT of 20 minutes. The author notes numerous problems that may have impacted the validity of the results. These issues include inappropriate sampling, inadequate preparation of the media, and variability in the designed EBCT. In a small-scale column study performed with native Ripon groundwater, Schreier (2006) reports an average nitrate removal of approximately 14% to 30%. These tests were performed at an EBCT of 15-minutes, an influent nitrate concentration of approximately 50 mg/L mg NO₃⁻/L, and variable pH conditions (6.0 to 7.0).

In batch tests performed with ZVI, complete nitrate removal has been observed by numerous researchers (Siantar et al., 1996; Cheng et al., 1997; Huang et al., 1998, Westerhoff, 2003) though the reaction rate is highly dependent upon other experimental parameters such as the iron:nitrate ratio, temperature, pH, etc. Column tests showed that the percentage of nitrate



removal ranged from approximately 10% at an EBCT of 20 minutes (Westerhoff, 2003) to less than 10% to 90% at EBCTs between 1 to 3 hours (Westerhoff and James, 2003).

ZVI research suggests that the reduction of nitrate and other oxo-anion contaminants is mainly diffusion controlled where mixing may be an important parameter necessary to achieve efficient nitrate reduction. Since it is impossible to apply mixing mechanism in a packed bed, nitrate reduction in these processes is limited by the transport of nitrate from bulk solution to the surface of the ZVI. To improve mixing, Chen et al (2005) investigated nitrate removal within fluidized ZVI beds. In a fluidized bed, the iron media is suspended within the reactor by pumping untreated water through the column at a high velocity. The improved mixing caused by fluidizing the bed increases the rate of external mass transfer on the media surface and hence, speeds up the chemical reduction reaction. At a hydraulic residence time of 15 minutes, the authors report nitrate removal between 13% and 92% depending on the influent pH conditions.

In this pilot-scale study, nitrate removal was monitored with grab samples analyzed in the laboratory and in real-time with the aid of raw and treated water online nitrate analyzers. This nitrate data allows for the nitrate removal efficiency to be compared at differing EBCTs, pH conditions, and variable water quality conditions.

1.4.2 Empty Bed Contact Time

As is characteristic of chemical reactions, the extent of nitrate reduction via SMI-III[®] media is highly dependent upon the EBCT (i.e., the reaction time). Studies have shown that increasing the EBCT increases nitrate removal, but the increase is not linearly proportional for ZVI. (Huang and Zhang, 2005). Due to size and capital cost considerations, packed media columns are typically limited to a maximum EBCT of between 20 to 30 minutes. This pilot test program evaluated the efficacy of an SMI-III[®] reactor operated at EBCTs of up to 30 minutes.

Numerous studies have made attempts to model nitrate reaction kinetics for SMI-III[®] and ZVI. There is significant variability in reported data with reaction orders varying from zero-order (Schreier [2001]) to nearly second-order (Huang et al. [1998]). The majority of the research suggests that the nitrate reduction reaction kinetics are pseudo-first order with respect to nitrate (Cheng et al., 1997; Choe et al., 2000; Choe et al., 2004; Su and Puls, 2004, Chen et al., 2004).



Considering the variability in the range of reported reaction orders, it is not surprising that the times reported for complete nitrate reduction vary substantially in the literature and are highly dependent upon experimental conditions such as initial nitrate concentration, temperature, pH, particle size, etc. In the typical EBCT range of 20-30 minutes, reported nitrate removal in packed column tests varied between 10% for laboratory-scale ZVI tests (Westerhoff 2003) to up to 96% for SMI-III[®] tests (Schreier 2003).

In fluidized beds, the hydraulic residence time (analogous to the EBCT in a fixed-bed reactor) can be substantially decreased relative to packed columns because of improved mass transfer. Cheng et al., (2005) found that nitrate removal up to 87% could be achieved with hydraulic residence times as short as 3 minutes.

The primary focus of this pilot study was to evaluate whether acceptable nitrate reduction can be achieved at practical EBCT conditions (≤ 30 -min) in a fixed-bed SMI-III[®] reactor. Over the course of the study, EBCT was varied by adjusting the hydraulic loading rate (e.g., the flow rate). The minimum EBCT that can be evaluated with the pilot system based on the reactor design was approximately 10 minutes and cannot be decreased since the reactor dimensions, media depth, and maximum flow rate will be fixed. The EBCT is calculated by dividing the volume of the reactive media by the flow rate. The maximum EBCT was limited by the ability to control water flow rates and chemical feed rates. The maximum EBCT evaluated was 30 minutes, the practical limit for full-scale reactor design.

1.4.3 pH Effects

Decreasing the pH within the packed bed improves nitrate reduction and may prevent some operational problems. However, a drop in pH will increase the amount of soluble iron released causing faster degradation of the reactive media, reducing bed life, and increasing effluent iron concentrations. Optimal long-term operation of an SMI-III[®] reactor requires a better understanding of the advantages and disadvantages associated with operating at reduced pH conditions.

Numerous studies have demonstrated that nitrate removal is improved by lowering the pH (Cheng et al., 1997; Choe et al., 2004; Huang and Zhang, 2004; Chen et al., 2005). In batch tests with ZVI, Cheng et al. (1997) reports that the nitrate reaction rate increases by a factor of 4 when



the pH is reduced from 7.0 to 5.0. Huang et al. (1998) reports rapid nitrate removal at $\text{pH} \leq 4.0$ but did not observe nitrate removal at $\text{pH} \geq 5.0$. Westerhoff (2003) found that a drop in pH from 5.0 to 2.0 improved the nitrate removal efficiency between 25% to 35% at pH 5.0 to between 40% to 99% at pH 2.0. Buffering the initial water with an organic buffer (HEPES) helped maintain the pH in the reactor and improved nitrate removal (Zawaideh and Zang, 1998, Westerhoff 2003). In column tests, pH has been shown to increase through the column in the range of 0.5 to 1.0 depending on the designed EBCT (Westerhoff and James, 2003; Schreier 2001).

This pilot study thoroughly evaluated the impact that pH has on nitrate removal and iron release through the SMI-III[®] reactor. An acid feed system was integrated into the pilot system that will allow pH to be adjusted to any desired value lower than ambient conditions.

1.4.4 Solids Precipitation

Perhaps the most critical operational concern of continuous-flow fixed-bed iron reactors is the potential for clogging or cementation of the media. When operated over long periods (>6 months) at natural conditions, iron and calcium solids have been shown to precipitate within the media matrix (Westerhoff and James, 2003). The accumulation of precipitates is most prevalent in the inlet to the reactor, but is present throughout most of the packed-bed (Westerhoff and James, 2003; Huang and Zhang, 2005). The precipitation process decreases the overall porosity of the reactor, increases the head loss through the column, and will eventually force the media to be replaced.

Several process modifications have been proposed to alleviate column cementation but these corrective actions have not been evaluated under normal operating conditions. One proposed solution to the cementation process is to lower the influent pH before it is introduced to the iron reactor. This adjustment will theoretically limit clogging since many potential precipitates are soluble at low pH. Schreier (2006) tested three pH conditions ranging from 6.0 to approximately 8.3 and found that pH adjustment prohibited calcium deposition within the media. Although promising, these tests were only performed for 30 days, and the long term efficacy of pH adjustment on cementation are still unknown. Another mechanism that has been proposed to prevent cementation of the media is frequent hydraulic backwashing or “fluffing”. During the



fluffing process, water is pumped through the media bed at a velocity high enough to fluidize the media and break up any clogged areas. The effect of this process on long-term operation and nitrate removal has not yet been evaluated. Another proposed mechanism that may help control cementation is the addition of certain cationic species (Huang and Zhang, 2005).

This pilot study evaluated two mechanisms for controlling cementation within the reactor. The pH was adjusted prior to the SMI-III[®] reactor in an attempt to prevent deposits of calcium and iron precipitates. Routine hydraulic fluffing was also used to maintain the column porosity and minimize head loss across the media bed.

1.4.5 Influent Nitrate Concentration

The literature consistently shows that nitrate removal is inversely related to the initial nitrate concentration, but the nature of the relationship is not well understood. Siantar (1996) reports complete nitrate removal after 14 minutes in tests with an initial nitrate concentration of 57 mg/L, but only 5% was transformed in the same amount of time with an initial concentration of 2.73 g/L. Huang et al. (1998) reports a similar relationship with lower initial nitrate concentrations (88 to 286 mg NO₃⁻/L). Westerhoff and James (2003) also report an inverse relationship between nitrate reduction and initial nitrate concentration.

The effect that influent nitrate concentration has on nitrate removal will be addressed in this pilot-scale study in a limited capacity. Historical nitrate levels in the water that will be used for the pilot study have ranged from 27 mg NO₃⁻/L to 64 mg NO₃⁻/L; however, all sample results since July 2004 have been at least 59 mg/L NO₃⁻.

1.4.6 Nitrogen Balance

Identifying the fate of the nitrogenous species through the SMI-III[®] media bed is important to better understand the nitrate reaction mechanism and to ensure that no harmful byproducts are released. Substantial research shows that the primary by-products of the nitrate reduction reaction are ammonia and nitrogen gas. Other nitrogenous intermediate or end products have been proposed, but there is no direct evidence to prove their formation.

The available literature consistently demonstrates that the predominant byproduct of the reaction is ammonia. In tests with ZVI, Cheng et al. (1997), Huang et al. (1998), and Westerhoff (2003)



report 100% of the reacted nitrate was converted to ammonia. Westerhoff and James (2003) reported that between 50% and 70% of the reduced nitrate was accounted for by ammonia in laboratory-scale tests. In batch and column experiments with SMI-III[®], the primary byproduct of the reduction reaction was ammonia, but the nitrogen balance could not be closed with ammonia alone (Schreier 2001; 2003; 2006). In more recent work, Chen et al (2005) reports that ammonia recovery decreases at lower pH conditions. Complete ammonia recovery was observed at pH 8.5, but less than 45% was recovered at pH ≤5.

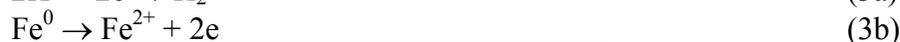
Nitrite, a potential intermediate of the denitrification process and a regulated contaminant, has been detected but does not account for substantial portions of the total nitrate removed and, if present, is thought to be quickly reduced to ammonium (Siantar et al., 1996; Huang et al., 1998; Westerhoff and James, 2003).

This pilot study attempted to close the nitrogen mass balance across the SMI-III[®] reactor. Nitrate concentrations were measured using grab samples and online nitrate analyzers, and ammonia, nitrite, total and dissolved inorganic nitrogen samples were collected. Nitrogen and ammonia gases were not monitored due to a lack of effective sampling techniques.

As discussed above, ammonia can be a predominant byproduct from the nitrate reduction process. Effluent ammonia concentrations were closely monitored during the pilot study to determine if downstream mitigation measures, such as breakpoint chlorination, are needed to avoid potential challenges such as unintentional chloramination with the potential for distribution system nitrification.

1.4.7 Soluble Iron

In addition to reacting with nitrate, ZVI (or SMI-III[®]) reacts directly with water to generate hydrogen gas and ferrous iron (Eqn 3a to Eqn 3c).



The generation of ferrous iron through the reactor (Eqns 1 through 3) may ultimately impact the overall viability of the SMI-III[®] process. Understanding the relationships between the iron



release rate, pH, and nitrate removal is critical to optimizing a demonstration-scale design. In previous tests, soluble iron concentrations in water treated with SMI-III[®] media were tested at levels above the drinking water secondary MCL regulation of 0.3 mg/L (Schreier, 2001; 2003; and 2006). The release of soluble iron increases at lower pH conditions. Thus, if SMI-III[®] is used as a stand-alone process, an additional treatment step would be necessary to remove iron prior to releasing the water into the distribution system.

Iron concentrations were monitored throughout the pilot system to understand iron release through the SMI-III[®] media bed and effectiveness of the downstream coagulation/filtration system to remove the released iron.

1.4.8 Particle Size

The impact of SMI-III[®] (or ZVI) particle size on the extent or rate of nitrate removal is uncertain. A focused study with SMI-III[®] media and nitrate-spiked deionized water demonstrated that decreasing the particle size from 10x60- to 60x80 mesh increased nitrate removal by a factor of 2 (Schreier 2001). The implied reason for the increased nitrate removal is an increase in the iron's surface area, i.e., smaller particles have a greater surface area to mass ratio. However, this result contradicts previous work that shows no correlation between the rate or extent of nitrate disappearance or other oxo-anions and iron surface area (Westerhoff 2003; Su and Puls 2001).

The effect that SMI-III[®] particle size has on nitrate removal efficiency was investigated during the intermediate media size small-column investigation.

1.4.9 Iron to Nitrate Ratio

There is some evidence that an optimal nitrate reaction rate can be achieved by designing the reactor based on a minimum ratio of the initial nitrate concentration and the mass of reductive media (ZVI or SMI-III[®]). Chen et al. (2005) report improved nitrate removal efficiencies with increased iron to nitrate ratios. The increased efficiency, however, tends to diminish at relatively high iron to nitrate ratios. Huang et al. (1998) report an optimal iron to nitrate ratio of 390g Fe⁰/g NO₃⁻. Iron to nitrate ratios greater than the optimal point provided no additional nitrate removal. Westerhoff (2003) reported that the relative rate of nitrate removal was faster in column tests than in batch tests due to larger solid iron to liquid concentration ratios.



The impact of iron to nitrate ratio on nitrate removal was not directly addressed in this study.

1.4.10 Metals Treatment

Brandhuber et al. (2004) investigated the use of SMI-III[®] media to remove hexavalent chromium [Cr(VI)] from groundwater using laboratory-scale testing methods, including batch isotherm tests and flow-through mini-columns. SMI-III[®] media was demonstrated to have excellent Cr(VI) treatment performance, referring to >90% chromium removal, and was recommended for further pilot testing. The mechanisms of Cr(VI) control by SMI-III[®] media – Cr(VI) sorption or Cr(VI) reduction to Cr(III) with removal by the iron precipitates – and post-treatment requirements for iron control were identified for future research.

2.0 Pilot System Description

The water used for the study is pumped from the City's Well 12. The pilot skid consists of two primary pieces of treatment equipment: an SMI-III[®] reactor and granular media filters. The pilot-scale test equipment is discussed in the following sections.

2.1 SMI-III[®] Equipment

The pilot-scale SMI-III[®] reactor was designed to replicate what is envisioned as necessary for full-scale operation. The pilot-scale test equipment was designed so that, if proven successful, it can be directly used as part of a full-scale treatment process. Thus, the pilot-scale equipment, media size, and flow rates will not need to be scaled up for full-scale operation (i.e., the scaling factor is 1:1). The design was based on typical design criteria (e.g., EBCT, hydraulic loading rate, bed depth) used for granular-based reactors and adsorbers which are typically limited by hydraulic constraints. The diameter of the pilot unit was constrained by the lateral system used. To create representative hydraulic conditions, it was desirable to use a hub and lateral system, which required a minimum reactor diameter of three feet. This larger reactor diameter reduces the likelihood of wall effects that can occur with smaller diameter columns. The height of the media was established to provide a maximum EBCT of 30 minutes. Total height of the reactor was large enough to allow for 100% expansion of the media during fluff cycles.



2.2 Coagulation/Filtration Equipment

The granular media filtration system, provided by Kinetico Inc., will be comprised of two (2) 24” x 72” fiberglass filter tanks loaded with Macrolite[®] ceramic media. Macrolite media was used in this study because it was rigorously tested by the City at pilot-scale for arsenic treatment at other City well sites. In these tests, the City evaluated three different filtration technologies and after a competitive procurement process selected Kinetico’s Macrolite[®] media for full scale coagulation/filtration installation based on cost and performance.

This system operates with one filter operational while the other is in standby mode. The backwash frequency for the pressure filters is user programmable. The filter backwashes are triggered via elapsed time. A summary of the design parameters for the SMI-III[®] reactor and coagulation/filtration system is shown in Table 2-1.

Table 2-1 Design parameters for the SMI-III[®] reactor and coagulation/filtration equipment

Parameter	Units	SMI-III [®]	Coagulation/ Filtration
Vessels	#	1	2
Diameter	in.	36	24
Height	in.	192	72
Media Height	in.	84	24
Flow Rate	gpm	15-20	15-20
Flow Direction		Upflow	Downflow
HLR	gpm/ft ²	2.1-2.8	4.8-6.4

2.3 Chemical Feed Systems

The pilot system supports two independent chemical feed systems. The first feed system was positioned upstream of the SMI-III[®] reactor to pump diluted sulfuric acid into the system for pH control. The second chemical feed systems was positioned downstream of the SMI-III[®] reactor and upstream of the granular media filters to feed sodium hypochlorite which serves as the oxidant in the coagulation/filtration process. The chemical feed pumps for the sulfuric acid and sodium hypochlorite were Pulsafeeder Electronic Metering Pumps.



2.4 Online Instrumentation

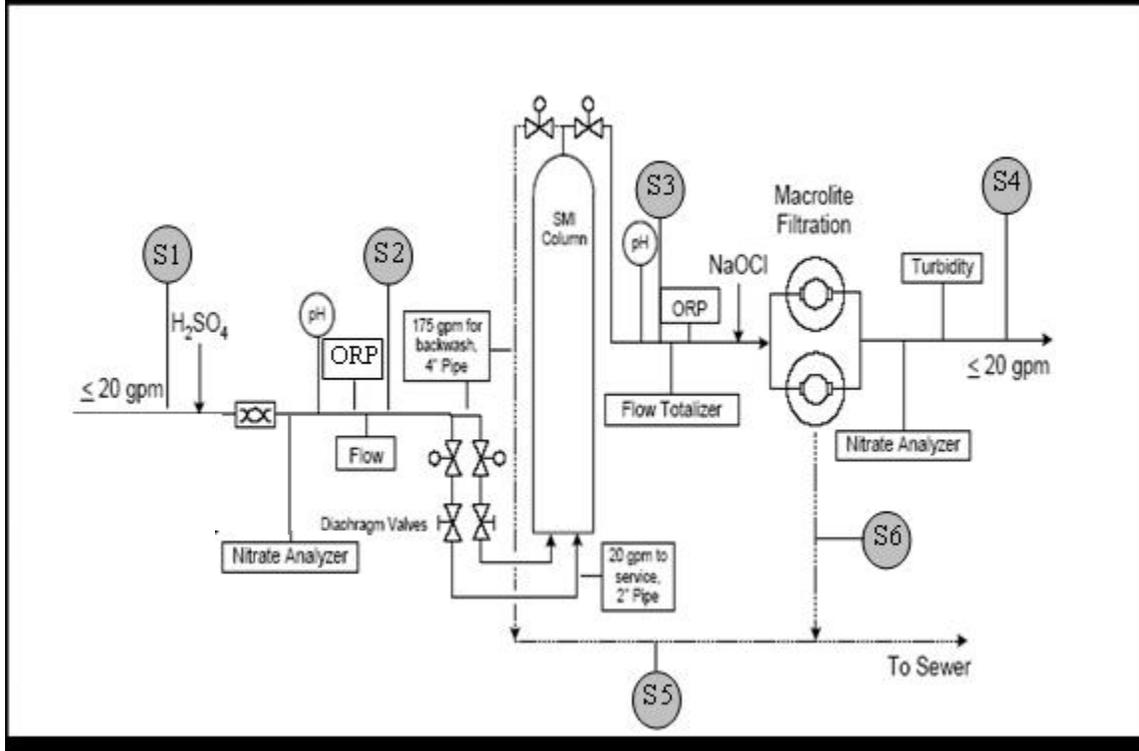
The pilot skid included two online nitrate analyzers that monitor the influent and effluent nitrate concentrations in real time. Additional online monitors were integrated throughout the process to measure the system flow rate, pH, oxidation-reduction potential (ORP), differential pressure and turbidity. A listing of the manufacturers and models of the online analyzers used in the pilot study is provided in Table 2-2.

Table 2-2 Manufacturer and model information for online analyzers

Analyzer	Quantity	Manufacturer	Model	Make
Nitrate	2	Hach	Nitratax	SC
pH	3	Burkert	pH Transmitter	8205
Pressure	2	Unknown	Unknown	Unknown
O.R.P.	2	Burkert	Digital O.R.P.	8206
Turbidity	2	GLI International	Steady Stream 4	T53 (Analyzer) 8324 (Sensor)

A drawing of the pilot unit including callouts of the sampling ports is provided in Figure 2-1. The sample ports are identified as S1, S2, S3, S4, S5, and S6, and the rationale behind their placement will be discussed in following section.

Figure 2-1 Conceptual diagram of the integrated nitrate and arsenic treatment system with sample locations





2.5 Sampling/Monitoring Locations

The second critical component of the sampling strategy is proper placement of sampling and monitoring equipment. Monitoring and sampling collection equipment has been positioned so that individual unit processes and the overall system can be effectively evaluated. Most operational parameters (e.g., flow rate, pressure, etc.) will be monitored in real time using the pilot system PLC and data acquisition. Several of the critical water quality parameters (e.g., pH, nitrate concentrations) will be monitored in real time, but the majority will be measured in grab samples. There are a total of six locations throughout the pilot-system at which manual grab samples are collected. These sample locations, identified as S1, S2, S3, S4, S4 and S6, were previously shown in Figure 2-1. A summary of the sampling ports including a short description of the specific process point being monitored is provided in Table 2-3.

Table 2-3 Sample port descriptions

Sample Port ID	Description
S1	Raw Water
S2	Pre-SMI-III [®] Reactor (after pH depression)
S3	Post-SMI-III [®] Reactor
S4	Finished Water
S5	SMI-III [®] Fluff
S6	Filter Backwash

3.0 Pilot Study Objectives

As stated in Proposition 50 application, the specific objectives of the pilot study are to:

- Demonstrate the ability of the integrated SMI-III[®]/coagulation/filtration treatment system to achieve treated nitrate and arsenic goals under dynamic operational conditions and economically realistic EBCTs;
 - The treated effluent goal for nitrate has been established as 36 mg/L as nitrate (NO₃⁻) (representing a 20% margin of safety for the 45 mg/L as nitrate MCL). This treated nitrate goal represents the level of removal that must be achieved for the City to consider implementing this system for full-scale use. The test conditions were altered throughout the pilot program to determine the maximum extent of nitrate removal that can be accomplished with this treatment system.



- The treated effluent arsenic goal for this pilot test plan has been established at 4 µg/L, consistently below the anticipated raw water arsenic concentration.
- The C/F system is intended to remove all of the iron from the flow stream and there is a goal to not introduce any additional iron to the system. The treated effluent iron goal has been established at 240 µg/L which represents 80% of the federal Secondary Standard of 300 µg/L.
- Determine the optimal pH condition for nitrate removal through the SMI-III[®] reactor while minimizing iron release;
- Determine the impact of fluffing on nitrate removal and operation;
- Characterize the process effluent water quality to identify and quantify treatment byproducts (e.g., ferrous iron, nitrite, ammonia, etc.);
- Estimate the longevity of the SMI-III[®] media under optimal operating conditions; and
- Evaluate the treatment system residuals.

In addition to the aforementioned treatment objectives, chromium, uranium, and vanadium were sampled in the Well 12 water and the treated water to determine their co-removal along with the target contaminants of nitrate and arsenic.

4.0 Phase A Investigation

4.1 Test Plan

The proposed pilot study was to be performed over a 26-week period. The first 13 weeks of the study, referred to as Phase A, included startup and process optimization activities. Start-up activities of the pilot-system began on April 27, 2007. Following initial start-up and calibration activities, the Phase A test plan called for the evaluation of nitrate reduction under a variety of pH and empty bed contact time (EBCT) conditions. The initial phase of testing began on May 10, 2007. The initial test conditions consisted of an EBCT of 30 minutes through the SMI-III[®] reactor and a pH of 6.0. The 30-minute EBCT corresponds with a hydraulic loading rate of 1.5 gpm/ft² and a flow rate of approximately 10 gpm. The Phase A test conditions are summarized in Table 4-1.



Table 4-1 Summary of Phase A test conditions

Approximate EBCT (min)	pH	Start Date	End Date	No. of Days
30	6.0	May 10, 2007	May 30, 2007	20
	6.5	May 30, 2007	June 13, 2007	14
	6.8	June 13, 2007	June 28, 2007	15
20	6.0	August 9, 2007	August 23, 2007	14
	6.5	August 23, 2007	September 6, 2007	14
15	6.0	July 25, 2007	August 9 2007	15
	6.5	June 29, 2007	July 25, 2007	27

The pH setpoint of 6.8 was dictated in the original Phase A test plan as 7.0. This adjustment came as a result of discussions that the pH rise across the SMI bed from a setpoint of 7.0 could create the potential for calcium carbonate deposition and media fouling. Therefore the setpoint was lowered to 6.8 to avoid those issues. The pilot system operated continuously during Phase A testing with the exception of routine maintenance and water availability from Well 12.

The Phase A sampling and monitoring frequency is summarized in Table 4-2 below. Deviations to this sampling program that occurred through the course of the Phase A investigation as a result of changing field conditions and schedule are noted in the corresponding results sections of this report. The pilot system was programmed to record a series of operational parameters from online instruments including flow, pH, ORP, differential pressure, nitrate, turbidity at five minute intervals through the programmable logic controller (PLC). The data from the PLC was supplemented with daily field testing with a Hach spectrophotometer and weekly off site laboratory analysis.

Table 4-2 Phase A sampling and monitoring schedule

Parameter	Location						Frequency	Method
	S1	S2	S3	S4	S5	S6		
Alkalinity	X	X		X			Weekly	Laboratory
Ammonia	X		X	X			Twice Weekly	Laboratory
Arsenic	X		X	X			Weekly	Laboratory
Calcium	X		X	X			Weekly	Laboratory
Electroconductivity	X			X			Weekly	Laboratory
Dissolved Iron	X		X	X			Weekly	Laboratory
Total Iron	X		X	X			Weekly	Laboratory
Nitrate		X		X			Twice Weekly	Laboratory
Nitrite	X			X			Twice Weekly	Laboratory
Total Nitrogen	X			X			Weekly	Laboratory
Total Dissolved	X			X			Weekly	Laboratory
Chromium	X			X			As Needed	Laboratory
Vanadium	X			X			As Needed	Laboratory
Uranium	X			X			As Needed	Laboratory
Silica	X			X			As Needed	Laboratory
Flow	X				X	X	Every 5 minutes	On-Line
pH		X	X	X			Every 5 minutes	On-Line
ORP		X	X				Every 5 minutes	On-Line
Differential Pressure			X	X			Every 5 minutes	On-Line
Nitrate	X			X			Every 5 minutes	On-Line
Turbidity				X			Every 5 minutes	On-Line

4.2 Water Quality Results

4.2.1 Comparison of Online and Grab Sample Nitrate Results

Paramount to this pilot study is identifying the conditions that maximize the system’s ability to reduce nitrate. The test plan was developed to identify the pH and EBCT conditions that maximize nitrate reduction. Nitrate was continuously monitored by two online Hach nitrate analyzers located at the S2 (pH adjusted water) and S4 (finished water) locations. The output from the analyzers was logged by the PLC every five minutes. Laboratory samples were collected twice weekly to verify the on-line meters. A comparison of the Hach analyzer outputs

and laboratory samples collected throughout Phase A of the pilot-study is presented in Figure 4-1 and Figure 4-2 for the untreated and finished waters, respectively. In Figure 4-1 and Figure 4-2, the solid symbols represent the results of samples submitted to the laboratory and the open symbols are the corresponding data from the Hach nitrate analyzers.

Figure 4-1 Comparison of the S2 untreated water lab and Hach online nitrate results

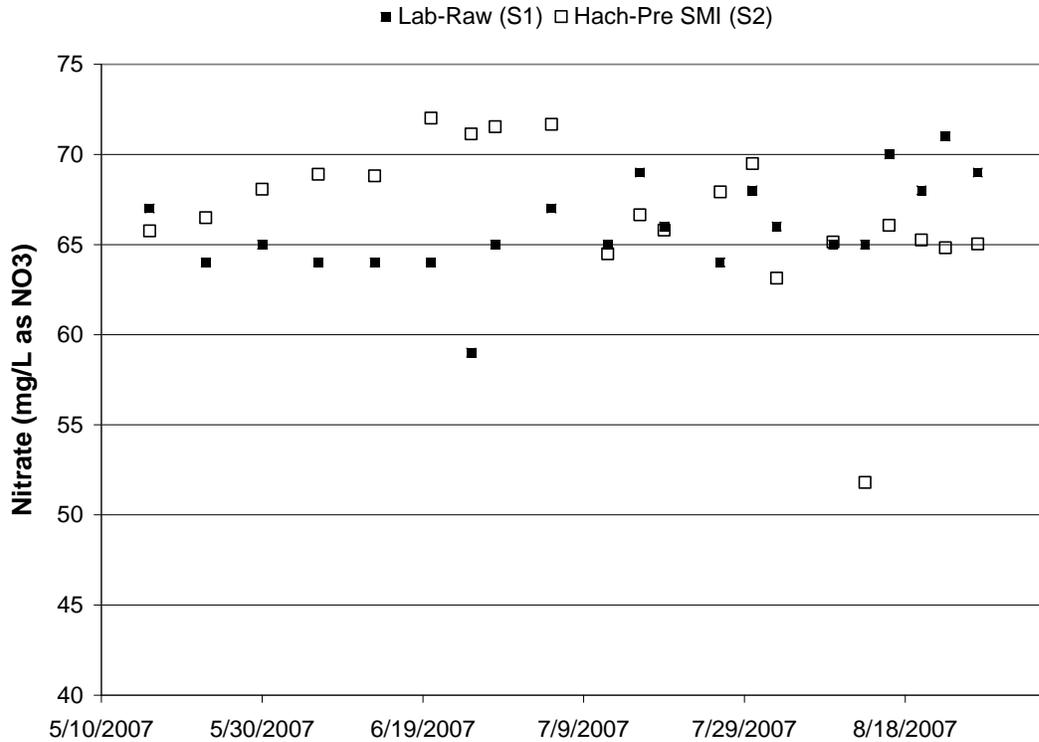


Figure 4-2 Comparison of the S4 finished water lab and Hach online nitrate results

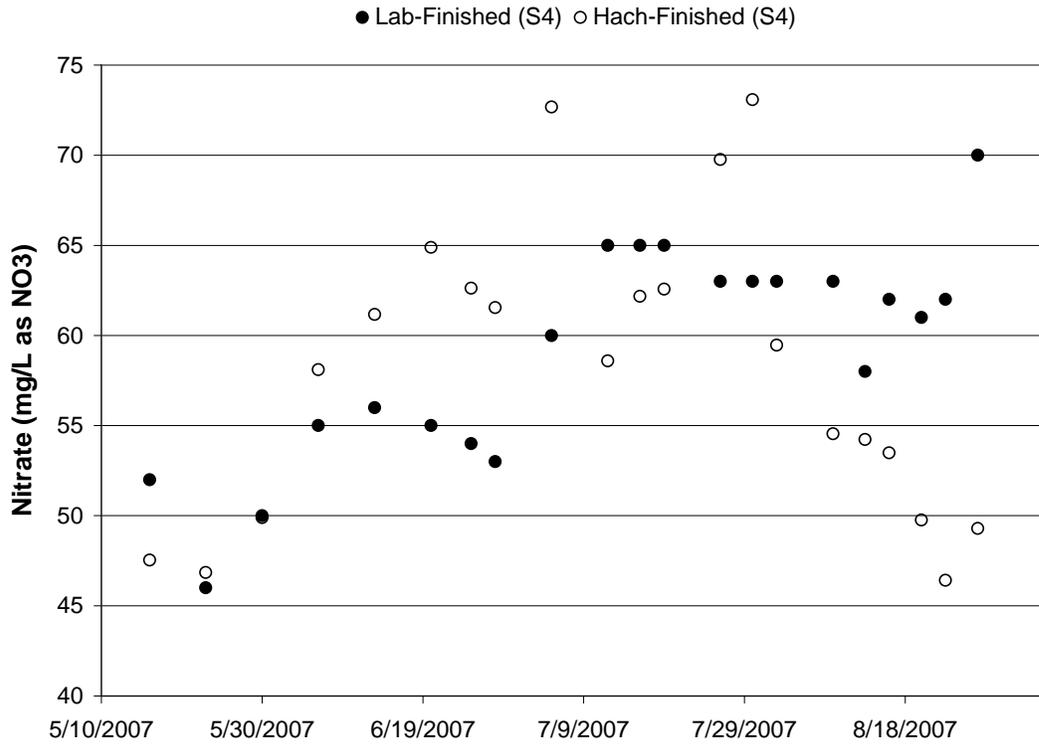
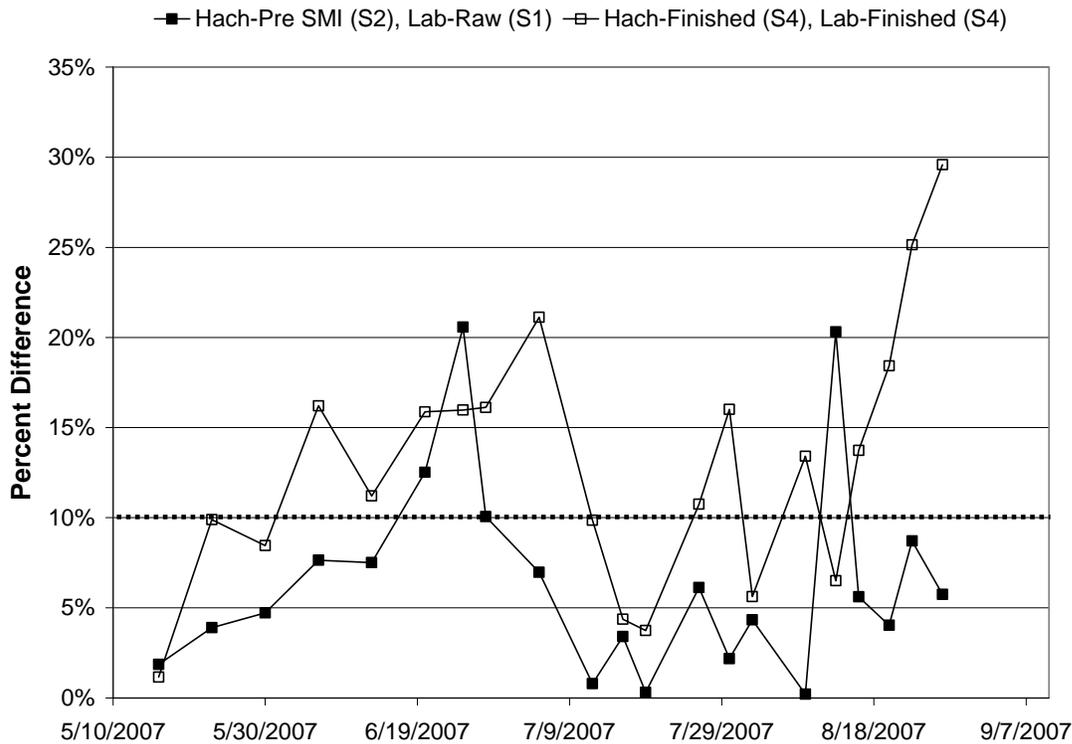


Figure 4-3 Percent difference results between paired lab and Hach online nitrate results



For purposes of this study, the criteria for acceptance and use of the online nitrate data was established as less than $\pm 10\%$ difference. As seen in Figure 4-3, a large portion of the data set has greater than 10% difference. This difference can be attributed to drift of the Hach analyzers results. The difference is likely greater with the S4 analyzer because of iron fouling the instrument’s optics. Due to these differences, the following discussion on nitrate removal focuses on the laboratory results.

4.2.2 Nitrate Removal

One of the primary objectives of this pilot-study was to identify the operational conditions that enhance nitrate reduction by SMI-III[®]. The treated effluent goal for nitrate has been established as 36 mg/L as nitrate (representing a 20% margin of safety for the 45 mg/L as nitrate MCL).

The raw and treated water nitrate results have been evaluated to determine the extent of nitrate reduction achieved under different pH conditions and EBCTs. The laboratory results for each independent test condition have been averaged and are shown in Figure 4-4. In Figure 4-4, the number of samples (count), location, pH, and EBCT are displayed on the x-axis. For each

condition, error bars have been included to indicate the high and low nitrate values observed. To clearly display the differences in nitrate reduction between the operating conditions, the low range of the y-axis has been set at 45 mg/L as nitrate (NO₃). It is important to note that this value is equal to the California nitrate MCL and is greater than project goal of 36 mg/L as NO₃. The minimum and maximum nitrate removal results for each of the paired samples have also been summarized in Table 4-3.

Figure 4-4 Phase A raw (S1) and finished (S4) water nitrate concentrations

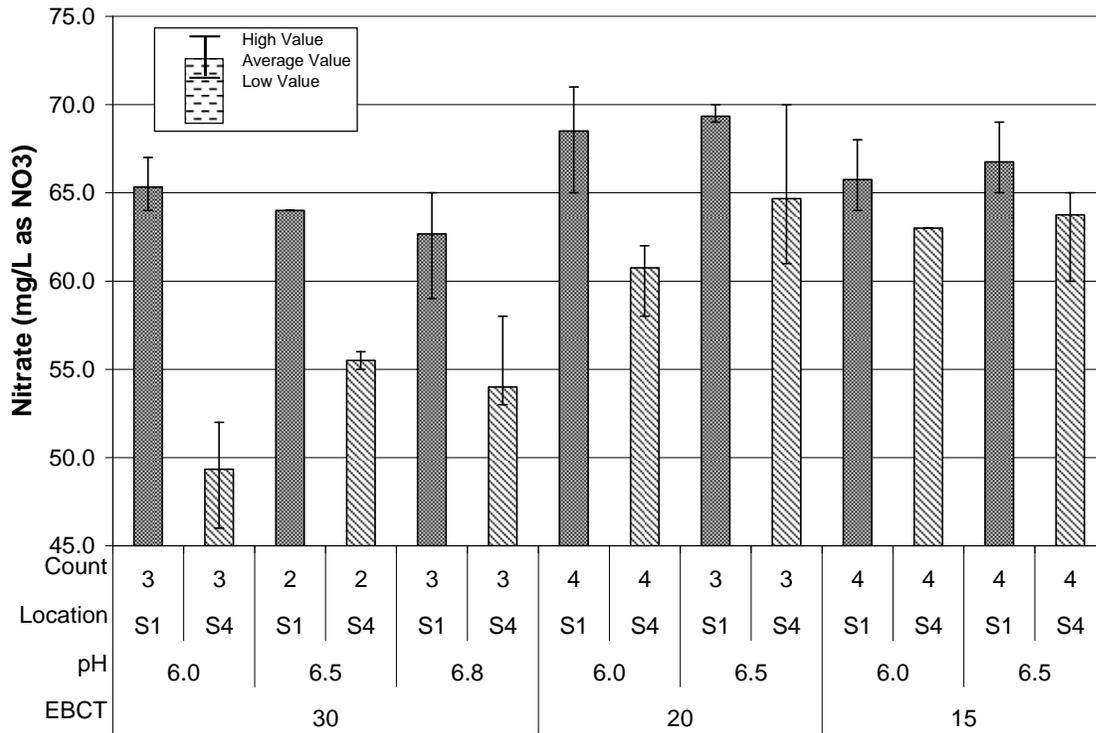


Table 4-3 Minimum and maximum nitrate reduction for each Phase A test condition

Approximate EBCT (minutes)	pH (S.U.)	Minimum Nitrate Reduction (mg/L as NO ₃)	Maximum Nitrate Reduction (mg/L as NO ₃)
30	6.0	15	18
	6.5	8	9
	6.8	5	12
20	6.0	7	9
	6.5	0	8
15	6.0	1	5
	6.5	0	7



The maximum nitrate reduction of 18 mg/L as NO₃ was experienced at the highest EBCT (30 minutes) and at the lowest pH (6.0). In general, the degree of nitrate reduction increases with increasing contact time through the reactor and decreasing pH. Phase A testing did not achieve treated nitrate results below the 45 mg/L MCL.

4.2.3 Nitrogen Balance

Identifying the fate of the nitrogenous species through the SMI-III[®] media bed is important to better understand the nitrate reduction mechanism and to ensure that no harmful byproducts are released. Substantial research shows that the primary byproducts of the nitrate reduction reaction are likely ammonia, nitrite and or nitrogen gas. Other nitrogenous intermediate or end products have been proposed, but there is limited direct evidence to prove their formation.

In efforts to monitor the nitrogen balance, the test plan originally called for weekly samples at S1 (raw water) and S4 (finished water) for nitrate, nitrite and ammonia as well as daily field samples for ammonia and nitrate. The test plan also called for weekly sampling of Total Nitrogen (TN) and Total Dissolved Nitrogen (TDN). This sampling program was modified to include additional ammonia sampling prior to sodium hypochlorite addition, and after the SMI-III[®] reactor (S3) to determine if the system is accomplishing nitrogen loss via break-point chlorination or if there is potential for chloramine formation with any remaining ammonia residual.

The sampling program did not include nitrite monitoring at the S3 location. Sodium hypochlorite rapidly oxidizes nitrite to nitrate, any nitrite that might be present at S3 would likely be observed as nitrate when the S4 location is sampled if there was sufficient chlorine supplied. To better understand if nitrite is present, nitrite will be monitored at the S3 location during the Phase B portion of the pilot study.

In order to quantify the nitrogen removal from the system, the raw (S1) and finished (S4) water ammonia, nitrite and nitrate samples have been converted to their corresponding concentrations as nitrogen. Figure 4-5, Figure 4-6 and Figure 4-7 show the results of the sampling from each of the paired samples for the S1 and S4 locations for EBCTs of 30 minute, 20 minutes and 15 minutes, respectively. In each case, the stacked column represents the “total nitrogen” comprised of the sum of the nitrate, nitrite and ammonia concentrations each reported as

nitrogen. The difference between the S1 and the S4 columns can be attributed to nitrogen removal from the system. It should be noted that the ammonia value shown in the S4 location of the first set of paired samples in Figure 4-5 is believed to be due to sampling error as total nitrogen leaving the system is greater than what was present in the raw water.

Figure 4-5 Phase A nitrogen species from S1 and S4 for an EBCT of 30 minutes

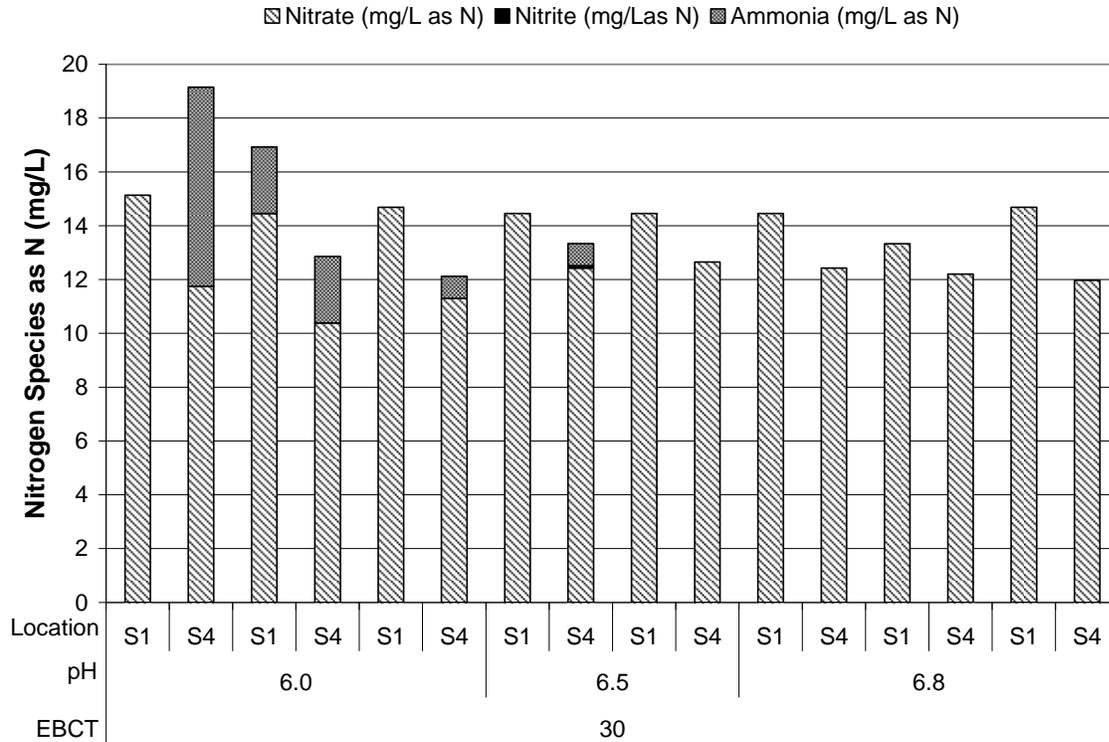


Figure 4-6 Phase A nitrogen species from S1 and S4 for an EBCT of 20 minutes

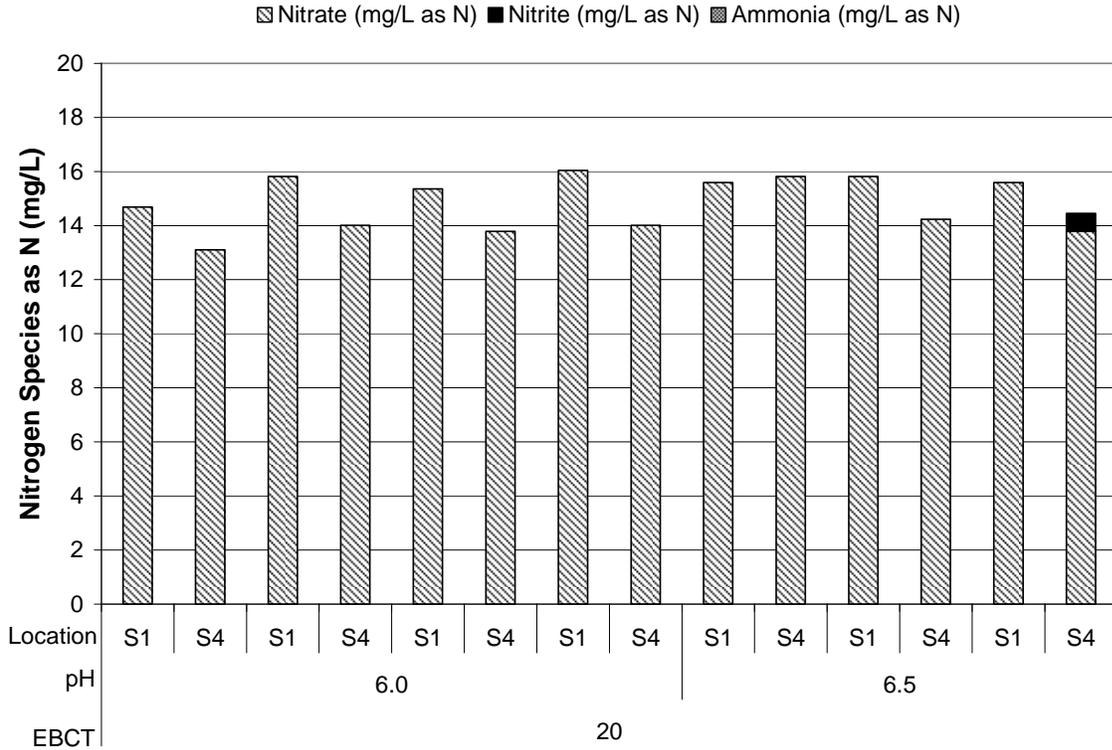


Figure 4-7 Phase A nitrogen species from S1 and S4 for an EBCT of 15 minutes

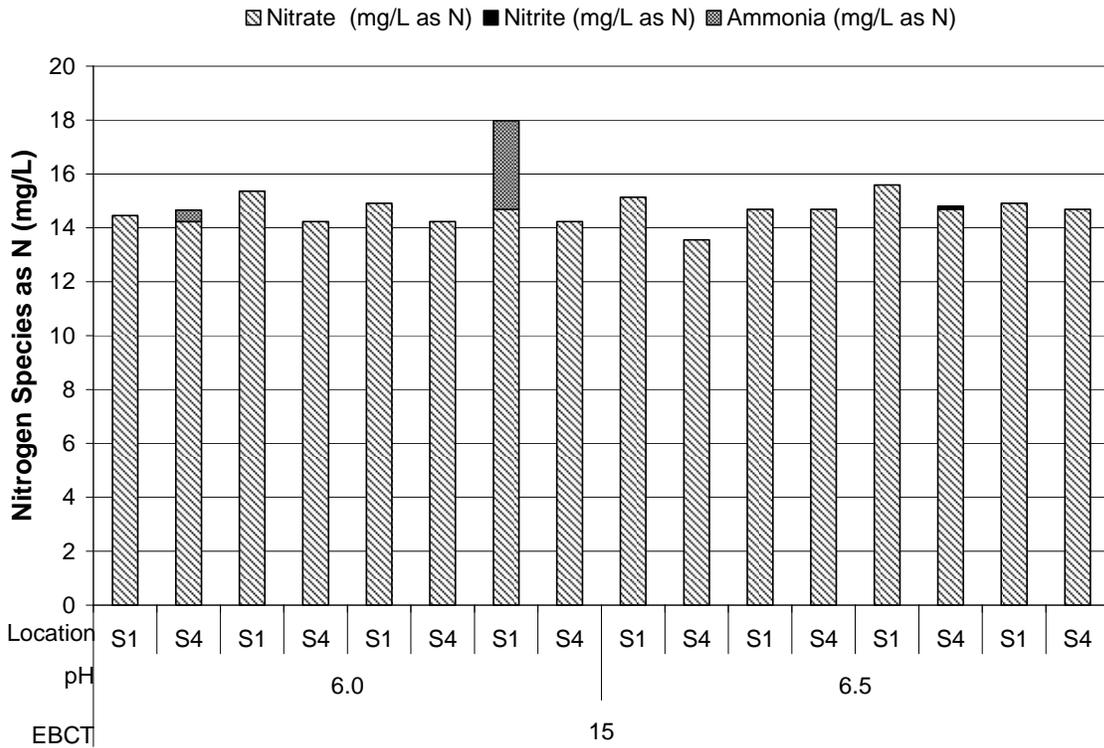


Table 4-4 Phase A nitrogen removal based on the summation of nitrogen species at S1 and S4

Approximate EBCT (minutes)	pH (S.U.)	Minimum Nitrogen Removal		Maximum Nitrogen Removal	
		mg/L as N	%	mg/L as N	%
30	6.0	0	0	4	24
	6.5	1.1	8	1.8	13
	6.8	1.3	8	2.7	18
20	6.0	1.6	10	2.0	13
	6.5	0	0	1.6	7
15	6.0	0	0	3.7	21
	6.5	0	2	0.8	10

In general, the results from Phase A testing indicate that some nitrate has been completely reduced to nitrogen gas or nitrogen species have been sequestered somewhere in the reactor as most the samples show a net reduction of nitrogen. The appearance of ammonia is most common at an EBCT of 30 minutes. Some of the S1 sample results include ammonia in the raw water samples which may be attributed to contamination of the samples or laboratory handling as ammonia is not historically found in the City’s groundwater. Nitrite was detected in 3 of the laboratory samples. A maximum nitrite concentration was observed on September 4, 2007 of 0.7 mg/L as Nitrogen (2.2 mg/L as NO₂). Although less than the MCL of 1.0 mg/L nitrite as nitrogen, it is important to recognize that if the reduction of nitrate is incomplete, there is potential for a regulated contaminant to be inadvertently released into the distribution system. However, if nitrite is present it would likely be converted back to nitrate by chlorination. A possible explanation for this nitrite spike could be that the chlorination system was not delivering the targeted chlorine dose and therefore the nitrite was not converted to nitrate. At full-scale, it is envisioned there will be a residual chlorine analyzer on the system to assure there is sufficient chlorination preventing the introduction of nitrite to the distribution system.

In addition to sampling for the individual nitrogenous species, total nitrogen and total dissolved nitrogen samples were collected on a weekly basis from the S1 and S4 sampling locations. Figure 4-8 and Figure 4-9 show the averaged total nitrogen and total dissolved nitrogen for each pilot test condition. Included on the x-axis are the pilot test conditions (EBCT and pH) sample location, and the count of the samples collected for each condition. The results for the individual paired samples are summarized in Table 4-5 Phase A.

Figure 4-8 Averaged total nitrogen results for each Phase A test condition

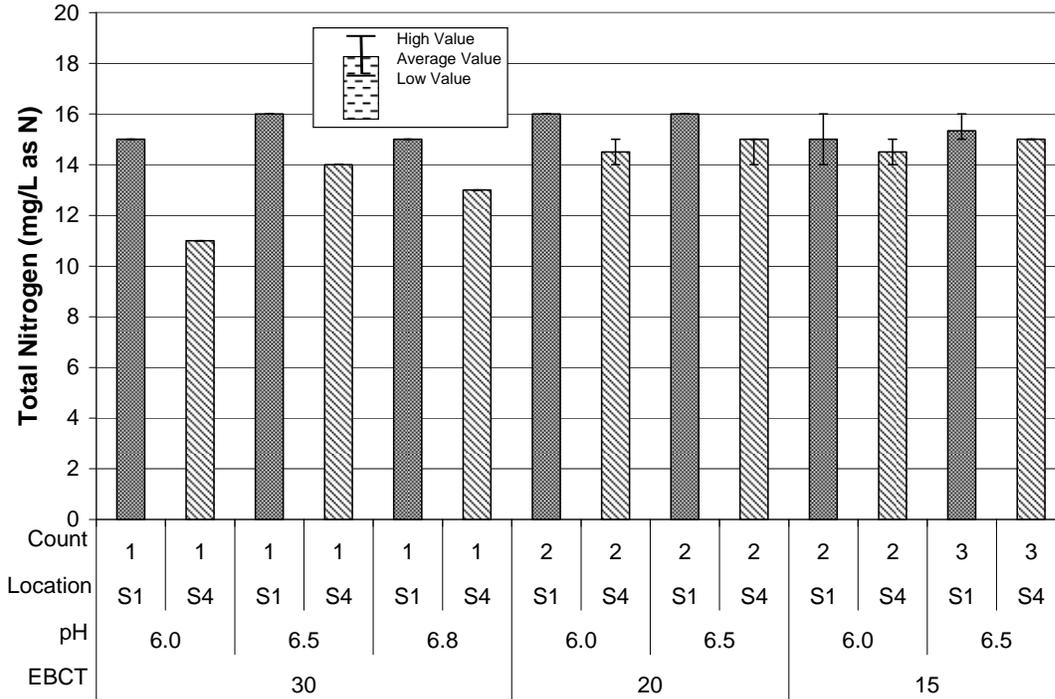


Figure 4-9 Averaged total dissolved nitrogen results for each Phase A test condition

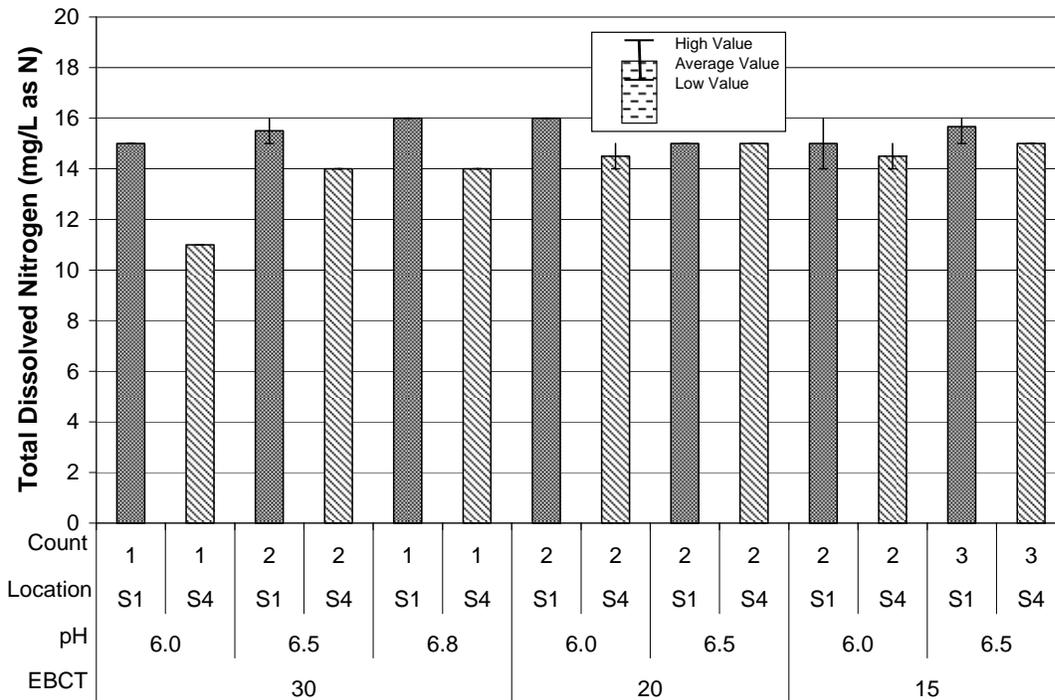


Table 4-5 Phase A total nitrogen and total dissolved nitrogen removal results

Approximate EBCT (minutes)	pH (S.U.)	Total Nitrogen Removal (mg/L as N)		Dissolved Nitrogen Removal (mg/L as N)	
		Min.	Max	Min.	Max
30	6.0	4	4	4	4
	6.5	2	2	2	2
	6.8	2	2	2	2
20	6.0	1	2	1	2
	6.5	1	1	1	1
15	6.0	1	1	0	1
	6.5	0	1	0	1

The maximum nitrogen removal from the system is 4.0 mg/L which correspond with the most aggressive operating conditions of pH 6.0 and an EBCT of 30 minutes. In general, the degree of nitrogen removal from the system increases with a decreasing pH and increasing EBCT. No operational condition produced finished water which meets the regulatory requirements or the project goal for nitrate.

4.2.4 Iron Release

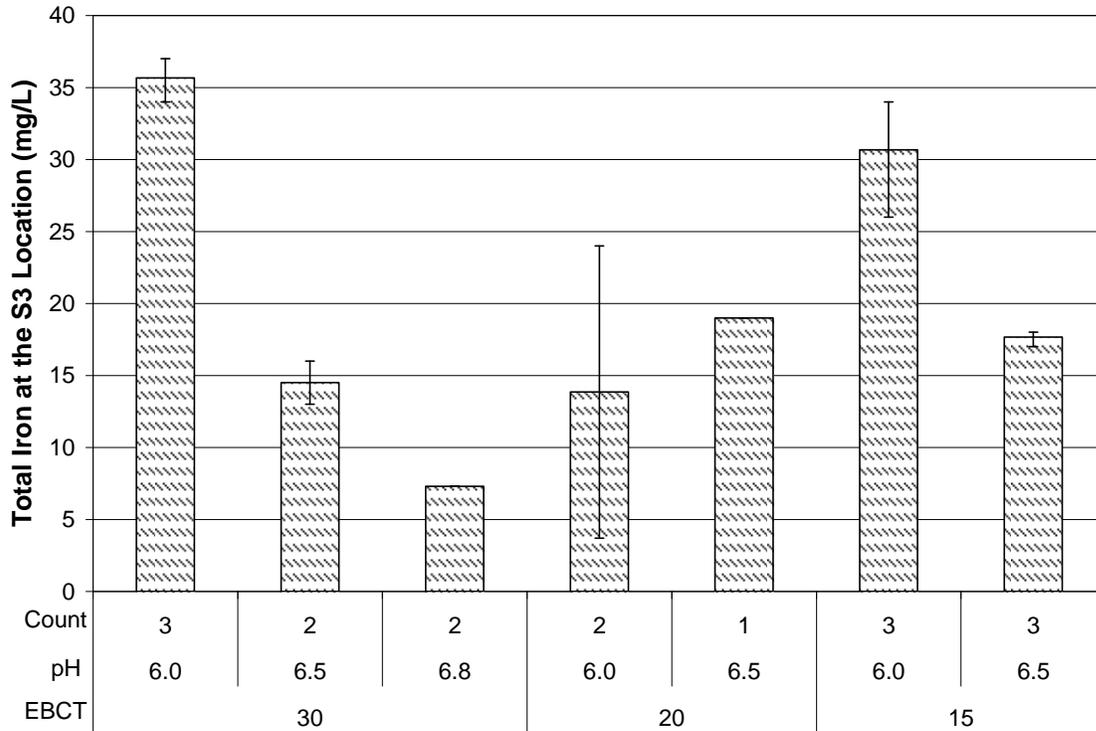
Another parameter critical to the operational success of the integrated arsenic and nitrate removal system is the SMI-III[®] media’s propensity to release dissolved iron. Iron causes aesthetic challenges when present at elevated concentration in drinking water. Iron is regulated with a Secondary MCL of 0.3 mg/L.

Although pH depression has been shown to increase the degree of nitrate reduction, it also increases the rate of iron dissolution from the SMI-III[®] media. Iron release is beneficial for the downstream coagulation filtration system because it can eliminate the need for an additional coagulant; however, excessive iron release is not desirable as it can be problematic for the downstream coagulation filtration process. Iron was monitored at three locations S1 (raw water), S3 (post-SMI), and S4 (filtered water). The sample locations were selected in order to determine the amount of iron released by the SMI-III[®] media and the ability of the Macrolite pressure filters to remove the flocculated iron.

Figure 4-10 shows the average total iron release at the different pilot test conditions. The total iron samples shown in Figure 4-10 were obtained from sample port S3 (post-SMI). The raw Integrated Nitrate and Arsenic Treatment Demonstration
 FINAL REPORT

water for the pilot-study does not contain detectable levels of iron. Therefore all the iron measured at the S3 location can be attributed to release from the SMI reactor. On Figure 4-10 the sample count and test conditions (EBCT and pH) are indicated on the x-axis. The whiskers represent the minimum and maximum sample results.

Figure 4-10 Average total iron release for each Phase A test condition



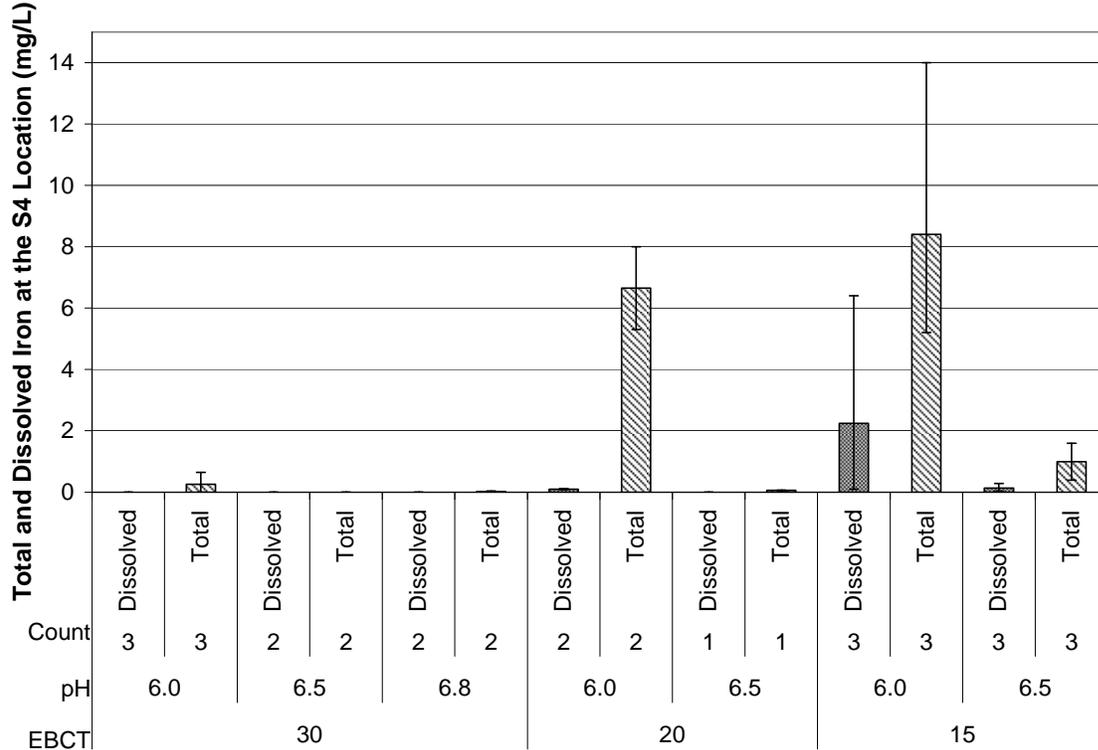
During Phase A, the maximum iron release from the SMI-III[®] column was 37 mg/L at a pH of 6.0 and EBCT of 30 minutes. The lowest total iron release of 4 mg/L also occurred at pH 6; however, with the longest EBCT of 20 minutes at that pH condition. The whiskers in Figure 4-10 represent the high and low values for each test condition. When the whiskers are taken into account, it appears the iron release has some dependency on EBCT, but pH appears to be the main controlling factor.

4.2.5 Iron Removal

The iron released from the SMI-III[®] media must be reduced to less than 0.3 mg/L to meet federal standards. In the pilot system, this is achieved by oxidation of the ferrous iron with sodium hypochlorite followed with filtration by two pressure filters loaded with Macrolite[®] media.

Macrolite was selected for the pilot system because the City has moved ahead with the installation of full-scale C/F systems in which Macrolite is the filtration media. The effluent iron goal has been established at 0.24 mg/L which represents 80% of the federal secondary standard. Figure 4-11 shows the finished water (S4) total and dissolved iron concentrations are show for each pilot test condition. The pH and EBCT are indicated on the x-axis. Cases where the total iron is greater than the dissolved iron indicate particulate iron breaking through the Macrolite filters. The Macrolite filters were set to backwash on an hourly basis in order to protect the downstream instrumentation from iron fouling and were therefore not optimized with respect to filter run length during Phase A.

Figure 4-11 Phase A total and dissolved iron at the S4 location



Generally, the iron removal was adequate; however, there were two instances where the dissolved iron leaving the filters exceeded the Secondary MCL of 0.3 mg/L and three instances that exceeded the project goal of 0.24 mg/L. Additionally, there were 10 instances where the total iron was above the secondary MCL of 0.3 mg/L and the project goal. These results suggest that the contact time following chlorine addition is inadequate which can result in a portion of the iron not being oxidized (accounting for the dissolved fraction) or the development of small

“pin-sized” iron flocs (accounting for the total iron minus the dissolved fraction). This is substantiated by the fact that there is minimal iron breakthrough at the EBCT condition of 30 minutes which corresponds to the longest contact time through the pressure filters.

4.2.6 Arsenic Removal

Iron release from the SMI-III[®] media is beneficial if there is also arsenic in the source water. The leached iron from the nitrate removal portion of the process train can eliminate or reduce the need for an additional iron-based coagulant, such as ferric chloride, that is used in conventional CF processes for arsenic removal. While the Well 12 water that is used for the pilot-study does not contain arsenic levels in excess of the 10 µg/L MCL, it does contain an average of 6 µg/L and serves as a means to evaluate the synergistic nature of the integrated nitrate and arsenic removal pilot system.

Arsenic was sampled weekly at the S1 (raw water), S3 (post-SMI) and S4 (post-filter) locations. Raw water arsenic concentrations have ranged from 4 µg/L to 6 µg/L with an average concentration of 5.1 µg/L. Arsenic was not detected at the S4 sample location which is located after the point of chlorination and subsequent filtration. The treatment goal for arsenic has been achieved for all finished water samples. The sample results are presented in Table 4-6.

Table 4-6 Arsenic results at the Raw Water (S1) and Finished Water (S4) locations

Location	Raw Water (S1)	Finished Water (S4)
Average Concentration (µg/L)	5.1	ND (< 2 µg/L)
Minimum Concentration (µg/L)	4	ND (< 2 µg/L)
Maximum Concentration (µg/L)	6	ND (< 2 µg/L)

4.2.7 Co-Contaminant Removal

One set of paired samples (S1 and S4) for chromium, vanadium and uranium were collected during Phase A testing. Although these co-contaminants are not directly associated with the project goals, the sample results indicate the ability of the treatment technology to remove these constituents. The samples were collected on June 13, 2007 while the system was operating with a pH of 6.5 and an EBCT of 30 minutes. The results from the sampling event are summarized in Table 4-7 below.

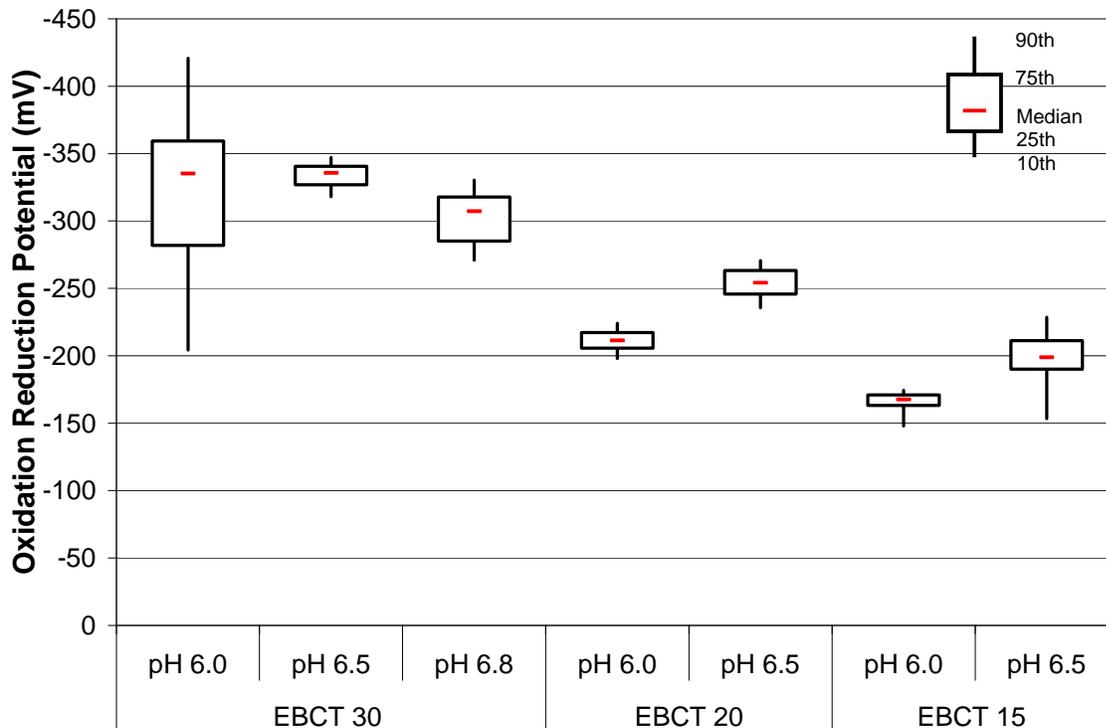
Table 4-7 Summary of Phase A paired sample results for chromium, uranium, and vanadium

Location	Chromium (µg/L)	Uranium (µg/L)	Vanadium (µg/L)
Raw Water (S1)	4	<5	40
Finished Water (S4)	<1	<5	11

4.2.8 Oxidation Reduction Potential

The oxidation reduction potential (ORP) is a parameter that indicates reductive capacity for water. In general terms, the lower the ORP (more negative) the greater the nitrate reducing conditions are. ORP was monitored at the effluent of the SMI reactor and recorded by the PLC. The ORP data is presented in a box and whisker plot in Figure 4-12. The box and whisker plot is a statistical means to show the spread of the data set. The top and bottom “whiskers” represent the 90th percentile and the 10th percentile; respectively. The box represents the spread of the data between the 25th percentile and 75th percentile. The dash in the center of the box represents the median of the data. Note that the data on the y-axis is presented in reverse order (e.g. increasing negative values).

Figure 4-12 Phase A oxidation reduction potential monitored at the S3 location



The reduction potential increases (becomes more negative) as the EBCT becomes longer. The ORP does not appear to be effected by the pH conditions.

4.2.9 Calcium Carbonate Deposition

Previous research with SMI-III[®] has shown hydraulic problems due to the precipitation of aragonite, a calcium carbonate mineral. Calcium carbonate minerals begin to precipitate near a pH of 8.2. There is approximately a 0.5 to 1.5 unit pH rise across the SMI reactor and the raw water pH is approximately 7.8. The integrated arsenic and nitrate treatment system includes an acid feed system to counteract the calcium precipitation and increase nitrate reduction. To monitor the effectiveness of the acid feed system, calcium samples were collected at three locations: S1, S3, and S4. Figure 4-13 shows the results from these sample locations. In Figure 4-13, the solid diamonds represent the raw water (S1) calcium concentration, the open circle is the calcium concentration following the SMI reactor (S3), and the open squares are the post filter sample results (S4). The EBCT and pH conditions have been overlaid for clarity. The scale on the y-axis begins at 50 mg/L in order to emphasize the relative differences between the three sample locations.

Figure 4-13 Calcium concentrations during Phase A testing

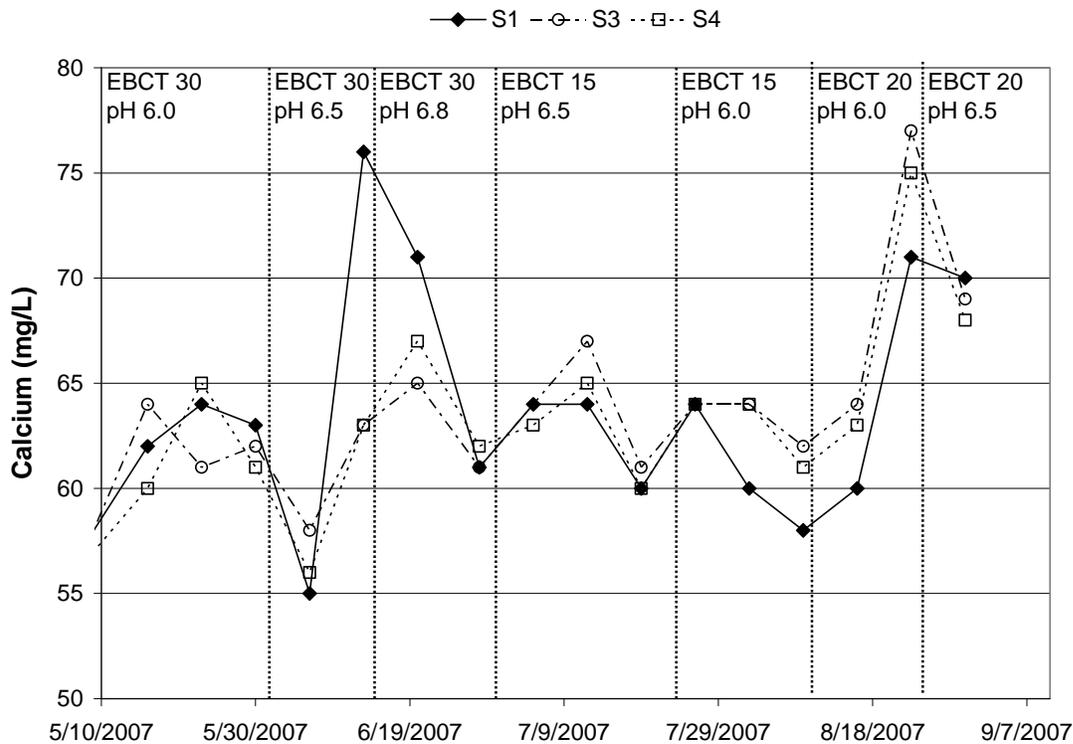


Figure 4-13 indicates little differences in the calcium sample results at the S1, S3, and S4 locations suggesting no calcium carbonate precipitation. This demonstrates that the acid feed

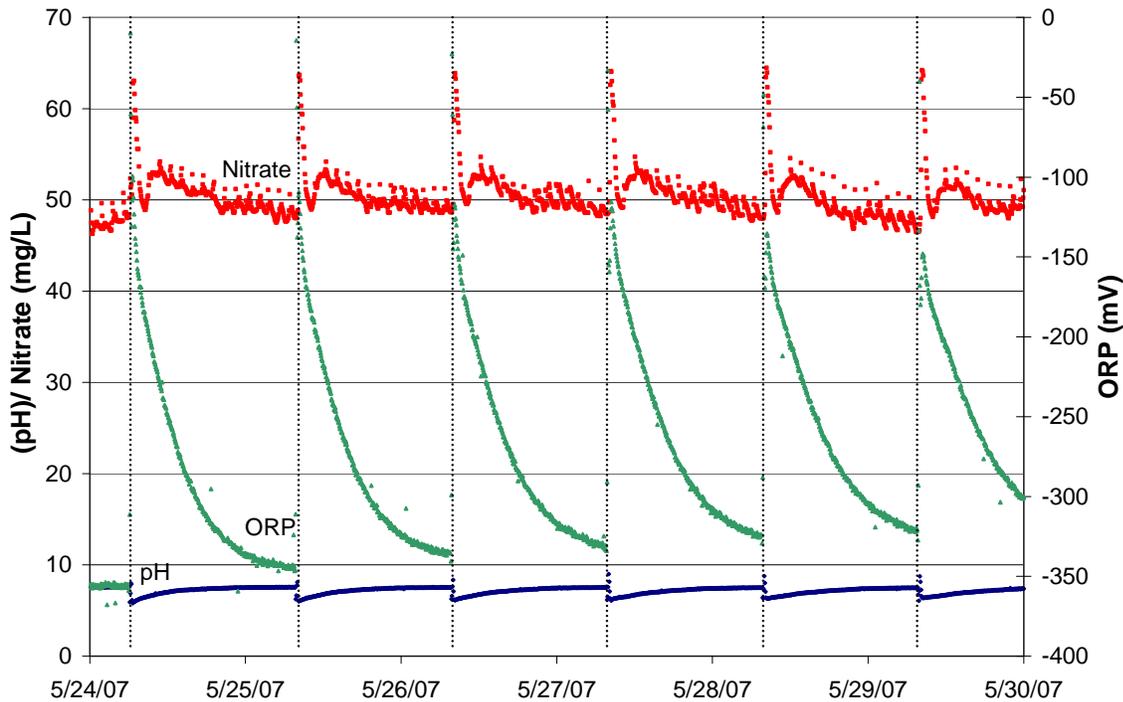
carbonate precipitation. This fact is supported by the differential pressure results presented in a subsequent section.

4.3 Operational Results

4.3.1 Effects of Fluff Cycle

In combination with pH adjustment, the SMI-III[®] reactor undergoes a daily, 20-minute fluff cycle to prevent media cementation. During the fluff cycle, the SMI-III[®] reactor is taken out of service and the hydraulic loading rate is increased to approximately 20 gpm/ft² to provide 100% expansion of the media bed. A review of the data shows that the end of the fluff cycle is marked with a decrease in pH and an increase in the oxidation reduction potential both of which contribute to decreased nitrate removal. To highlight this point, the pH, ORP, and nitrate concentration of the SMI treated water (S3) are shown in Figure 4-14 where the start of the daily fluff cycle is indicated by the vertical dashed lines. Figure 4-14 is developed from data during a time period when the nitrate analyzer had less than 10% difference from the laboratory data and is therefore appropriate for this purpose.

Figure 4-14 pH, ORP, and nitrate concentration of the SMI treated water (S3)





In each of the three data trends above a cyclic pattern that corresponds to the fluff cycle can be observed. The data suggest there is a “recovery time” after the fluff cycle where the effluent ORP and pH are in a range similar to the raw water. As time progresses the ORP decreases and the pH increases. pH and ORP are the main water quality parameters that dictate the amount of nitrate reduction. In full scale operation, the recovery time may be an important design parameter as water may need to be sent to waste, recycled or blended with a parallel SMI-III[®] reactor until a suitable amount of time has passed to achieve the necessary reduction.

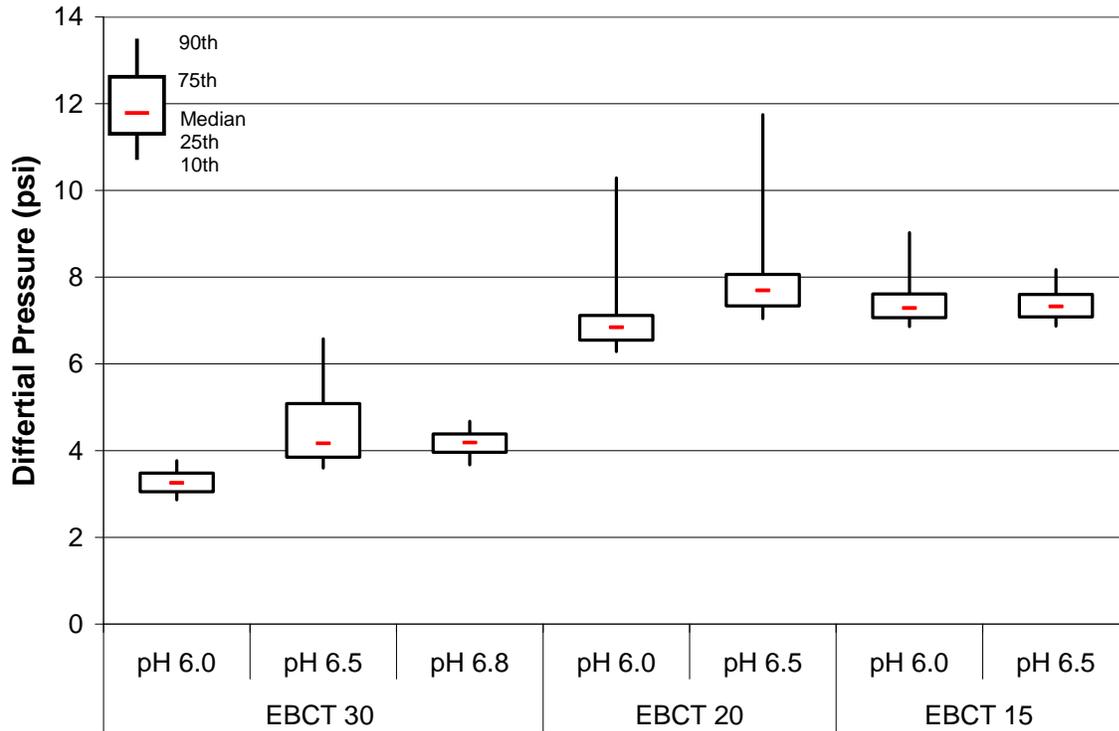
The data also show that the nitrate concentration is continuing to decrease until the fluff cycle initiates. In this initial phase of investigation, a conservative daily, 24 hour fluff cycle was implemented to provide assurance against media cementation. The time between fluff cycles will be extended during the Phase B investigation to determine whether nitrate reduction continues to increase over time or if a steady-state condition, when nitrate reduction is constant, can be achieved.

4.3.2 SMI-III[®] Reactor Differential Pressure

Although not specifically stated in the Project Objectives, maintaining the hydraulic character of the SMI-III[®] reactor is paramount to the success of the integrated nitrate and arsenic treatment system. Operational provisions such as pH reduction to control calcium carbonate cementation and daily fluffing were introduced to maintain the hydraulics of the SMI-III[®] media bed. A means of evaluating the hydraulics of the media bed is to monitor the pressure differential across the SMI-III[®] reactor.

The SMI-III[®] reactor is outfitted with a pressure transducer at the influent and effluent service ports. Data from the transponders is recorded to the PLC on five minute intervals. The pressure differential data are presented in a box and whisker plot in Figure 4-15 for all experimental conditions. The box and whisker plot is a statistical means to show the spread of the data set. The top and bottom “whiskers” represent the 90th percentile and the 10th percentile; respectively. The box represents the spread of the data between the 25th percentile and 75th percentile. The dash in the center of the box represents the median of the data.

Figure 4-15 Box and whisker plot of the differential pressure across the SMI-III[®] reactor



The differential pressure across the SMI-III[®] reactor remains relatively constant at the EBCT condition of 30 minutes. As would be expected, there is an increase in head loss across the reactor as the EBCT decreases or the flow rate through the reactor increases; however, there is not a discernable difference between the EBCT of 15 minutes and an EBCT of 20 minutes. Based on the differential pressure, it appears there has not been a noticeable change in the hydraulic character of the SMI-III[®] reactor. This operational parameter will continue to be monitored during the next phase of investigation.

4.3.3 Media Consumption

A weighted average of the iron release was determined in order to develop an estimate of the media consumption throughout the Phase A experimentation. Based on an average total iron concentration of 20 mg/L measured at the S3 (Post SMI) location, approximately 165 pounds of iron are released per million gallons of production which is equivalent to 1.1 cubic feet per million gallons.



4.4 Phase A Investigation Summary

The primary purpose of the Phase A investigation was to identify the operational conditions (EBCT and pH) where nitrate reduction was maximized. These conditions were found to be an EBCT of 30 minutes and a pH of 6.0. The maximum nitrate reduction observed for these conditions was 18 mg/L as nitrate. These results demonstrate the viability of the SMI-III[®] media to reduce nitrate. Given that the average raw water nitrate concentration during the Phase A study was greater than 60 mg/L as nitrate, these conditions did not result in finished water nitrate concentrations that meet the project goal of 36 mg/L as nitrate. Additional study during Phase B testing will evaluate if extended EBCT and further depressed pH conditions can achieve the project goal.

The treatment system was successful in removing arsenic. All finished water arsenic sample results during Phase A testing were below the laboratory detection limit of 2 µg/L.

Last, the Phase A results demonstrate the operational viability of the integrated SMI-III[®] and coagulation/filtration process. The pilot system operated reliably without any hydraulic challenges that have been previously encountered with SMI-III[®] media testing.

5.0 SMI-III[®] Media Size Small-Scale Column Investigation

Previous research has indicated that smaller particle size (e.g. greater surface area) SMI-III[®] media can achieve greater nitrate reduction than larger particle size media. SMI-III[®] media has typically been produced in a size range from 40 to 60 mesh. This size range was the most cost effective for manufacturing given the capabilities of SMI-Inc.'s original contract manufacturer. Cost effective production of smaller particle size SMI-III[®] media was considered infeasible because that would require sieving the media post-production, resulting in a loss of the larger sieve size material and corresponding higher costs. During the course of the Phase A investigation, SMI-Inc. changed contract manufacturers and the new manufacturer can produce the smaller sieve size SMI-III[®] media at a cost that is competitive with the original 40 to 60 mesh material. The City elected to conduct side by side small-scale column testing of the existing SMI-III[®] media used during the Phase A investigation and the newly available smaller particle size material to determine the difference in nitrate reduction performance.



5.1 Experimental Set-up

The small-scale column study consisted of two- 2” columns: one containing the same SMI-III[®] media used during the Phase A investigation and one column containing 60 x 80 mesh SMI-III[®] media. The columns were designed and constructed to mimic the operational conditions of the pilot-scale SMI-III[®] reactor. The columns were supplied pH adjusted water from the pilot system. The feed line was then split to provide service flow to each of the columns. Each of the feed lines was instrumented with a flow meter (rotameter), flow control (needle valve), back flow prevention (ball check valve), a pressure gauge, and a sample port. The ½” feed line entered the bottom of the 2” diameter clear PVC column that contains approximately 6 feet of SMI-III[®]. The SMI-III[®] media was supported by glass wool packed in the bottom of the columns. The columns had at least 6’ of freeboard above the media to allow for 100% bed expansion during fluff cycles. The flow exited the column through a ½” HDPE line equipped with a sample tap and a pressure gauge to allow for differential pressure readings.

Each column had a fluff flow line tapped from the pilot system. The fluff line was equipped with flow control and flow metering. The fluff cycle was used as a tool for maintaining the hydraulic character of the SMI-III[®] media bed. The fluff flow was manually set to allow for an upflow velocity sufficient to cause 100% bed expansion. Overall, the columns were operated in a similar fashion to the pilot system with regards to empty bed contact time, pH conditions, and fluff cycles. Table 5-1 summarizes the design parameters for the media size small-scale column study. A schematic of the small-scale columns system, as they were situated on the pilot skid, is shown in Figure 5-1. Photographs of the constructed column are presented in Figure 5-2.

Table 5-1 SMI-III[®] media size small-scale column investigation design parameters

Design Parameter	Value
Column Dia. (in.)	2
Media Height (ft)	6
Media Volume (ft ³)	0.13
Media Weight (lbs)	~20
Flow Rate (gpm)	0.03-0.07
EBCT (min)	15-30
HLR (gpm/ft ²)	2-4
pH Range (SU)	6.0-6.5
Fluff (min)	20
Fluff Flow (gpm)	0.43
Fluff HLR	19.8
Fluff pH (SU)	6.0-6.5

Figure 5-1 SMI-III[®] media size small-scale column investigation schematic

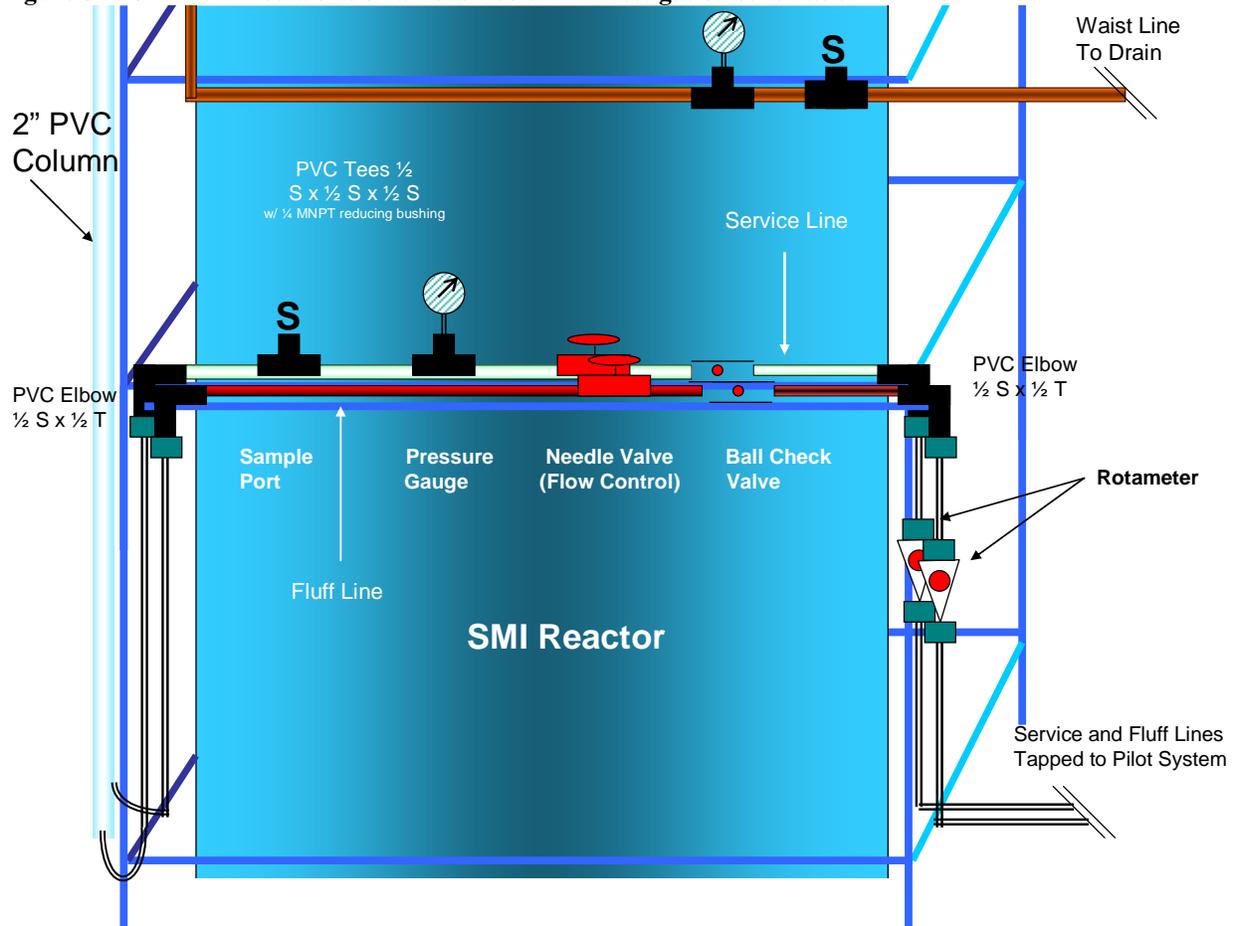


Figure 5-2 SMI-III[®] media size small-scale column investigation photographs

Top left: Completed columns attached to the pilot skid. Top right: Front view of the columns as situated on the SMI pilot skid. Bottom: Close-up of the influent instrumentation for one of the columns



5.2 Experimental Schedule

The media size small-scale column investigation was scheduled to last for five weeks in September and October 2007. The first week incorporated column fabrication, quality assurance



and system start-up. Prior to start up, flow rates provided by the rotameters were verified with a volumetric technique using 200 mL graduated cylinders. Once the flow rates were verified, the media was loaded into each of the columns. The required height of the media was pre-measured and marked on the clear columns. The SMI-III[®] media was loaded from above while service flow was provided in the column to remove the “ultrafine” particles which are suspected to attribute to hydraulic fouling of media. Once the media was loaded, an extended fluff cycle occurred to further rinse the media. After the media was washed, the columns were placed into service and flow rates were adjusted to account for the additional head loss caused by the media.

Once in service a combination of daily monitoring and sampling was conducted. Table 5-2 describes the sample locations and Table 5-3 is a summary of the parameters that were monitored throughout the course of the study. The S2 sample point represents the depressed raw water for the small-scale columns and SMI-III[®] reactor.

Table 5-2 SMI-III[®] media size small-scale column investigation sample location descriptions

Sample Port ID	Description
C1	Effluent of small scale column containing “old” SMI-III [®] media
C2	Effluent of small scale column containing “new” small sieve size SMI-III [®] media
S2	Pre-SMI-III [®] reactor (following pH depression)
S3	Post-SMI-III [®] reactor

Table 5-3 SMI-III® media size small-scale column investigation sampling and monitoring schedule

Parameter	Location				Frequency	Method
	C1	C2	S2	S3		
pH	✓	✓	✓	✓	Daily	Hand-held meter
Service and Fluff Flow Rates	✓	✓	Set by PLC		Daily	Rotameter/ Graduated Cylinder
Pressure Differential	✓	✓			Daily	Pressure Gauges
Iron	✓	✓		✓	3x Weekly Mon, Wed, Fri	Laboratory Analysis
Nitrate	✓	✓	✓	✓	3x Weekly Mon, Wed, Fri	Laboratory Analysis
Nitrite	✓	✓		✓	3x Weekly Mon, Wed, Fri	Laboratory Analysis
Ammonia	✓	✓		✓	3x Weekly Mon, Wed, Fri	Laboratory Analysis

The columns were operated with a 30-minute EBCT and a pH of 6.0 for 4 weeks. This mimics the best nitrate reduction conditions experienced during Phase A of the pilot study. Following the 4 week period, operation of the small scale columns was terminated. The pH was controlled by the pilot skid, therefore the influent pH of each column and the pilot system was identical. The columns were targeted to have a 30-minute EBCT which corresponds to flow rates of approximately 120 mL/minute.

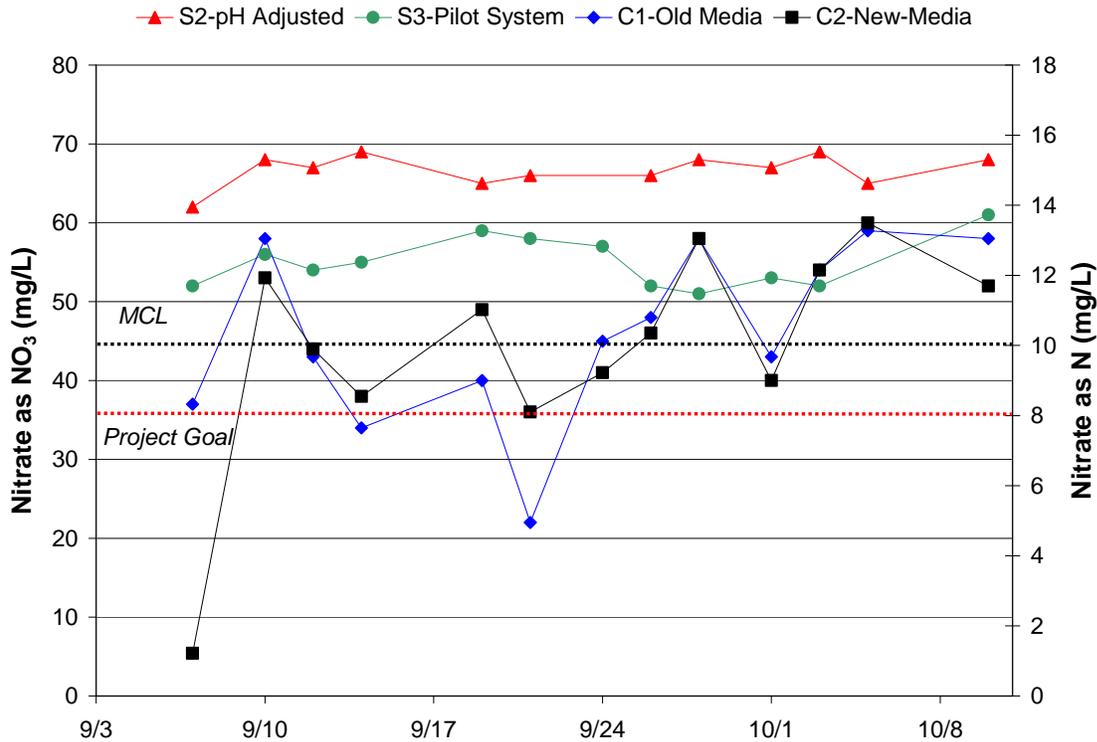
5.3 Experimental Results

The performance of each column with regards to nitrate reduction, nitrite production, ammonia production, total nitrogen removal and iron release was evaluated and compared with the results of the pilot-scale system. These results are presented in the following sections.

5.3.1 Nitrate Removal

Nitrate was monitored at four locations throughout the course of the investigation. The laboratory results for the nitrate analysis are show in Figure 5-3. The nitrate results are reported both as the concentration as nitrate and the equivalent concentration as nitrogen.

Figure 5-3 SMI-III[®] media size small-scale column investigation nitrate results



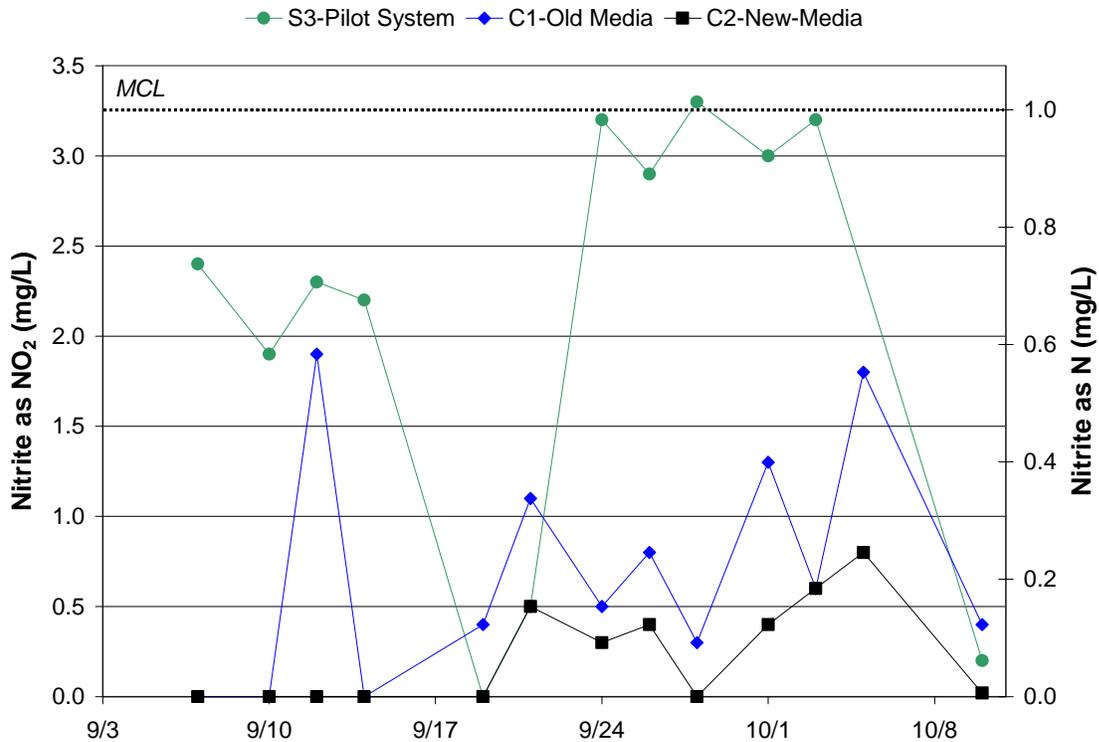
The S2 samples represent the untreated or influent nitrate concentrations. In general the nitrate reduction was better for the columns (C1 and C2) than the media in the pilot-scale SMI-III[®] reactor (S3) which achieved an average nitrate reduction of 12 mg/L as NO₃ and a maximum nitrate reduction of 17 mg/L as NO₃. The S3 samples were never below the MCL of 45 mg/L as NO₃.

Column 1 (C1) which contained the “old” SMI-III[®] had an average nitrate effluent concentration of 46 mg/L as NO₃ which corresponds to an average reduction 20.5 mg/L as NO₃, and a maximum nitrate reduction of 44 mg/L as NO₃. Column 2 (C2) which contained the “new” SMI-III[®] had an average nitrate effluent of 44 mg/L as NO₃ which corresponds to an average reduction 22 mg/L as NO₃ and a maximum nitrate reduction of 57 mg/L as NO₃.

5.3.2 Nitrite Production

Nitrite is a regulated contaminant with an MCL of 1 mg/L as nitrogen. Figure 5-4 shows the effluent nitrite concentration for the columns and the SMI-III[®] reactor.

Figure 5-4 SMI-III[®] media size small-scale column investigation nitrite results

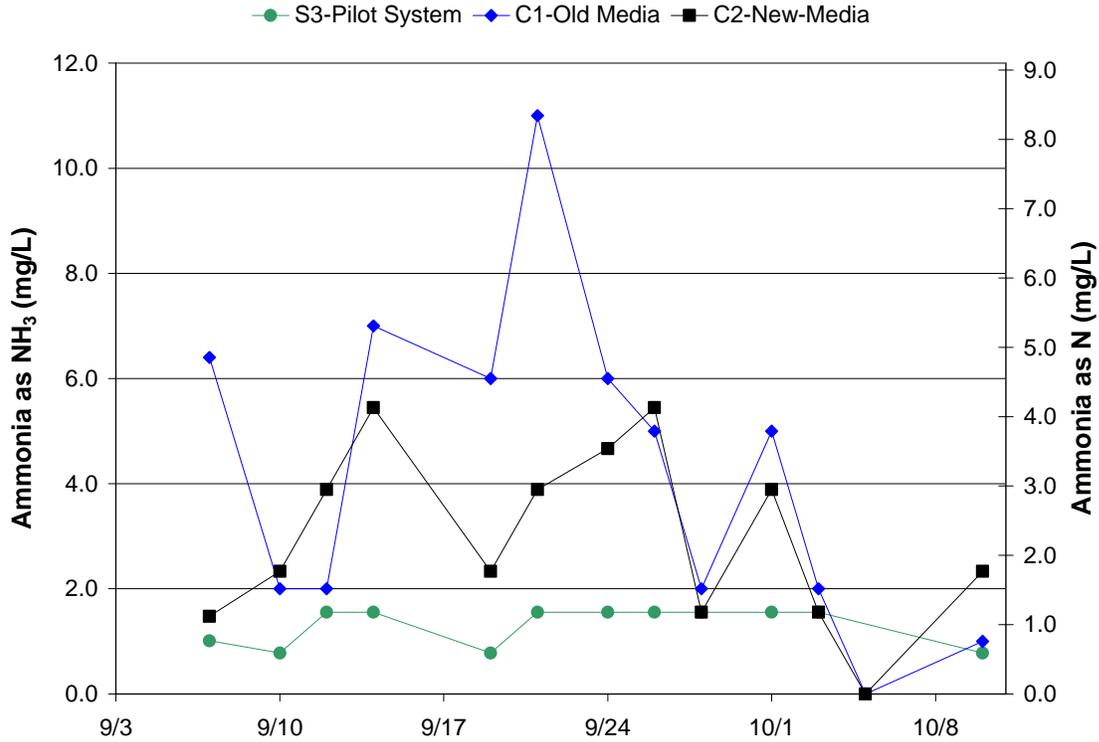


The results at each sample location indicate that nitrite is being formed as an intermediate byproduct of nitrate reduction. The new media (C2) generally shows the lowest propensity for nitrite formation. Although the results indicate there is incomplete reduction of nitrate, the nitrite can be oxidized to nitrate with the addition of chlorine, as demonstrated by the Phase A pilot testing results.

5.3.3 Ammonia Production

Ammonia was monitored at the effluent of the small-scale columns and pilot-scale reactor throughout the course of the investigation. Figure 5-5 shows the effluent ammonia concentration data for the columns and the SMI-III[®] reactor. It should be noted that the ammonia from the pilot reactor never exceeded 2.0 mg/L.

Figure 5-5 SMI-III[®] media size small-scale column investigation ammonia results

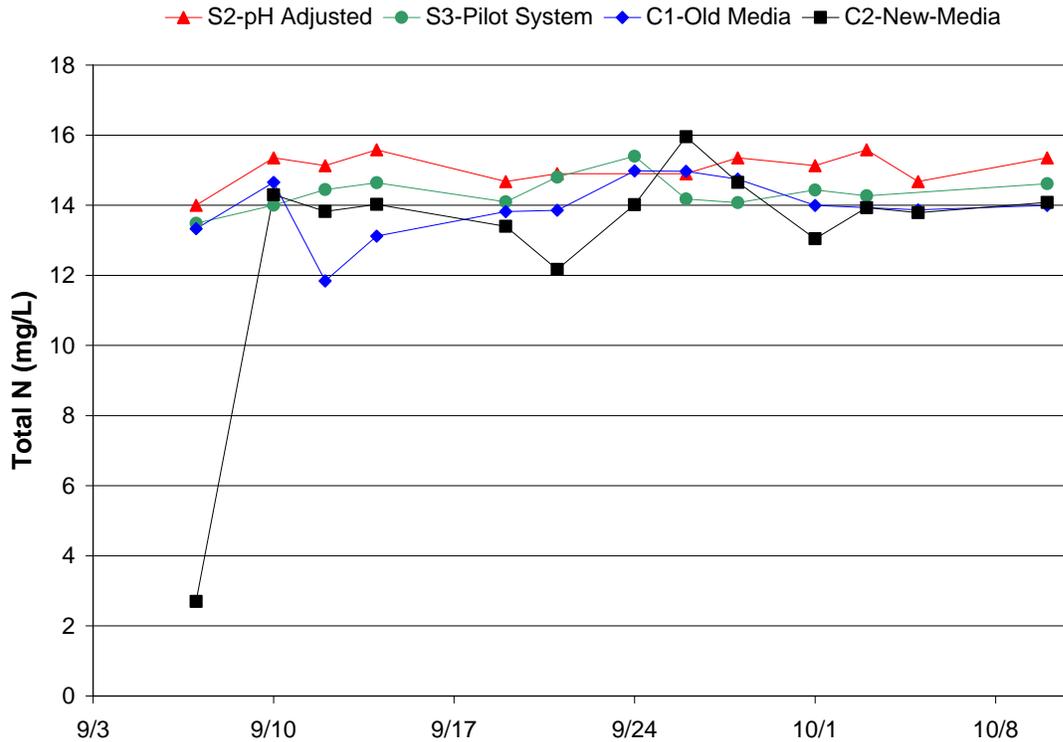


As seen in Figure 5-5, the small columns showed greater ammonia production than the SMI-III[®] reactor in most cases which remained below 2 mg/L as NH₃ throughout the course of the investigation. A maximum ammonia concentration of 11 mg/L was observed for Column 1 which contained the old SMI-III[®] media.

5.3.4 Nitrogen Removal

The nitrate, nitrite, and ammonia samples for each location have been summed and are presented in Figure 5-6 as total nitrogen to describe the nitrogen balance. The nitrogen removal from the system is assumed to be the difference from the untreated water (S2) concentration on any sample date.

Figure 5-6 SMI-III® media size small-scale column investigation total nitrogen results

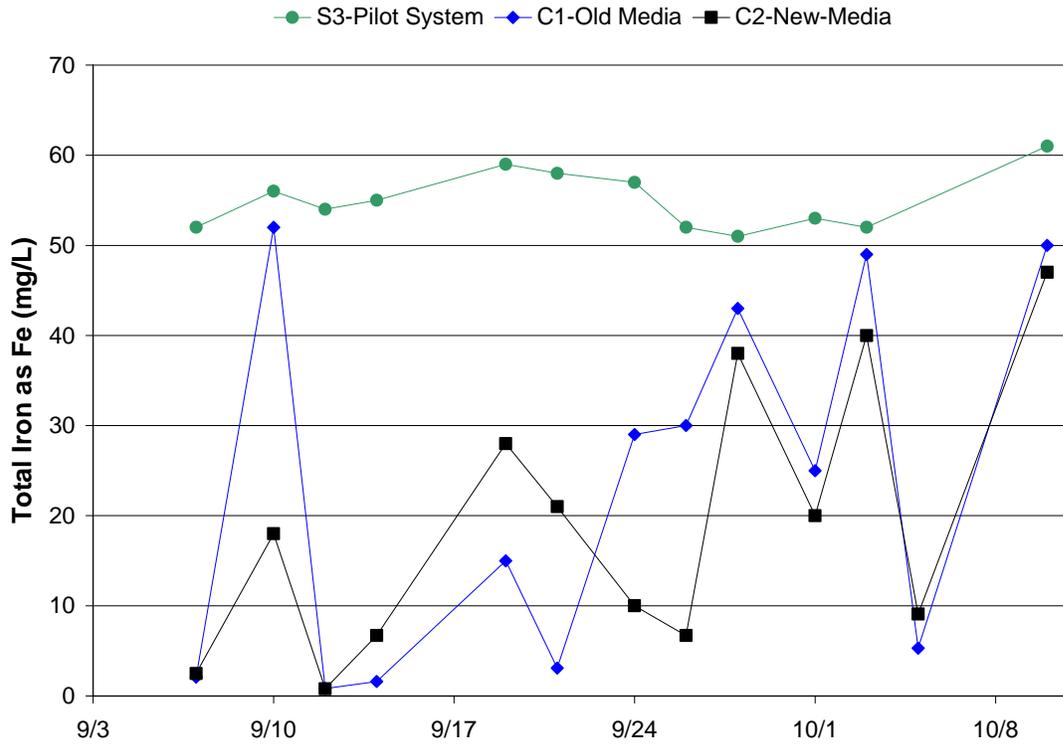


Although the columns showed increased nitrate removal when compared to the SMI-III® pilot-scale reactor, Figure 5-6 suggests that in most cases the majority of the nitrate is not removed from the system, but reduced to nitrite and ammonia.

5.3.5 Iron Release

Total iron was monitored at the C1, C2, and S3 locations. Figure 5-7 shows the results for total iron at these locations. The iron in the raw water was consistently below the laboratory detection limit.

Figure 5-7 SMI-III[®] media size small-scale column investigation total iron results



The pilot-scale SMI-III[®] reactor consistently released between 50 mg/L and 60 mg/L of iron throughout the course of the small column investigation. Generally, the small columns released less iron; however, the iron release does trend upwards with the final C1 and C2 results showing 47 mg/L and 50 mg/L, respectively.

5.4 SMI-III[®] Media Size Small-Scale Column Investigation Summary

The results of the small-scale column investigation suggest that although the SMI-III[®] media is reducing some nitrate, the reduction is largely incomplete, resulting in the formation of nitrite and ammonia. The new smaller SMI-III[®] media did not significantly differentiate itself from the old media in terms of nitrate reduction.

6.0 Phase B Investigation

The Phase B Test Plan was originally intended to “...evaluate the long-term effectiveness of the process at removing nitrate and arsenic, to identify any operational issues that may arise with the relatively long operation, and to better define bed-life.” Since an operational condition was



not identified during the Phase A testing where the water quality objectives were met, Phase B continued to evaluate operational conditions to meet the objective. The following section discusses additional data analysis conducted following the conclusion of Phase A that provided direction for the Phase B activities. Additionally, SMI-Inc. developed a newly formulated media following Phase A, but prior to Phase B, and initial test results for the new media are presented. The section concludes with the recommended Phase B test plan.

6.1 Additional Data Analysis

During the Phase A project update meeting held January 11, 2008, TAC member Paul Westerhoff recommended the nitrate and nitrogen data be further analyzed to understand the effects of pH and EBCT on nitrate reduction. The Phase A results, as originally presented, suggested that there is a direct correlation between nitrate reduction and decreased pH and/or increased EBCT. To further investigate this point, the nitrate and total nitrogen data are presented here based on EBCT and pH.

Figure 6-1 and Figure 6-2 show the nitrogen removal based on raw (S1) and finished water (S4) sample locations as function of pH and EBCT, respectively. Nitrogen removal was calculated base on the total nitrogen results collected from McCampbell Analytical. The percent nitrogen removal is calculated based on the following equation.

$$\%Nitrogen\ Removal = 1 - \left(\frac{Total\ Nitrogen\ @\ S4}{Total\ Nitrogen\ @\ S1} \right)$$

Figure 6-1 Phase A nitrogen removal as a function of pH

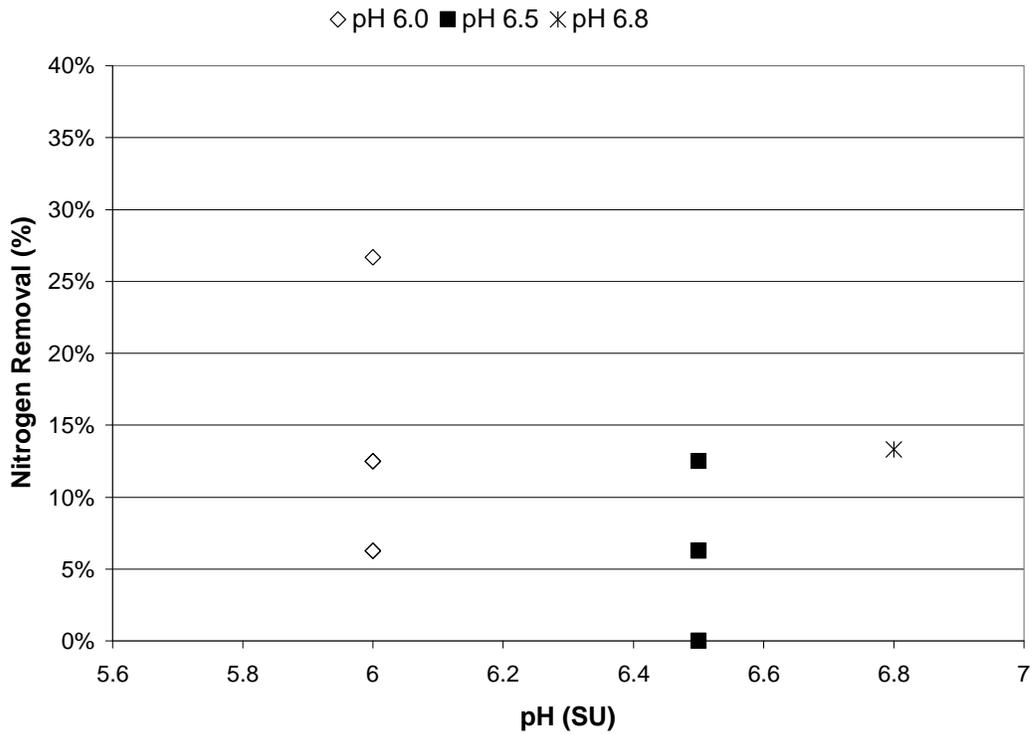


Figure 6-2 Phase A nitrogen removal as a function of EBCT

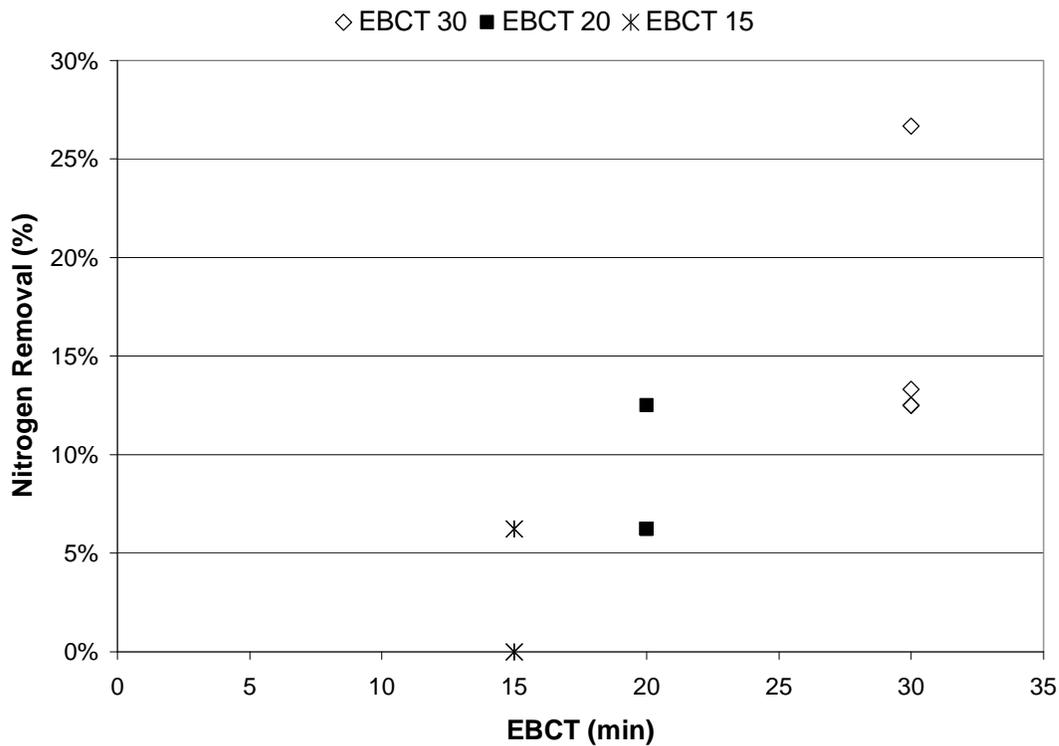




Figure 6-1 shows the effects of pH on nitrogen removal from the pilot system. In general, as pH increases, there is not a strong corresponding decrease in nitrate removal as was originally suspected. However, Figure 6-2 suggests a strong relationship between nitrogen removal and EBCT, where higher EBCT results in greater nitrogen removal.

These findings are supported by Figure 6-3 and Figure 6-4 where the change in nitrate concentration is plotted against the change in nitrogen from the system. Change in nitrate is calculated as difference of the summed nitrogenous species (nitrate, nitrite, and ammonia) reported as nitrogen for the S4 and S1 sample locations. In these instances, the slope of the best fit line represents the ratio of nitrate to nitrogen removed from the system. A slope less than one indicates the conversion of nitrate to a nitrogenous byproduct, namely ammonia or nitrite rather than removal as total nitrogen. In Figure 6-3 and Figure 6-4, the X and Y axis have been plotted on a 1:1 scale and the equation of the each trendline is shown on the right margin for clarity.

Figure 6-3 Change in nitrate versus change in nitrogen as a function of pH

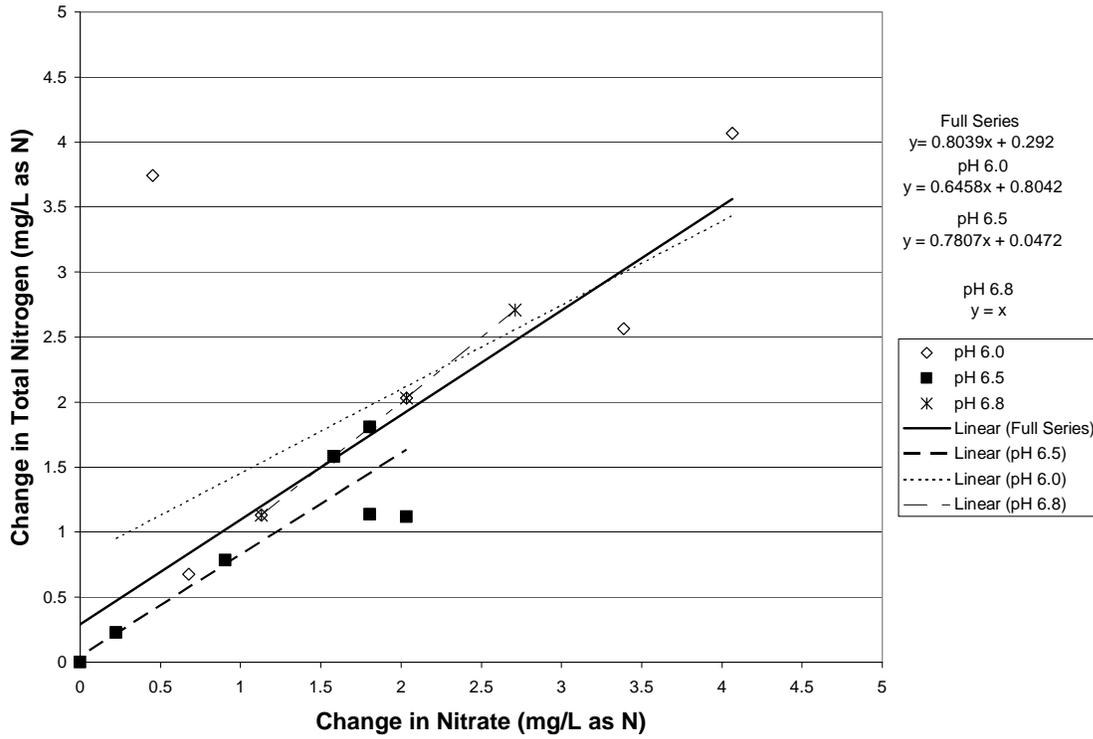


Figure 6-4 Change in nitrate versus change in nitrogen as a function of EBCT

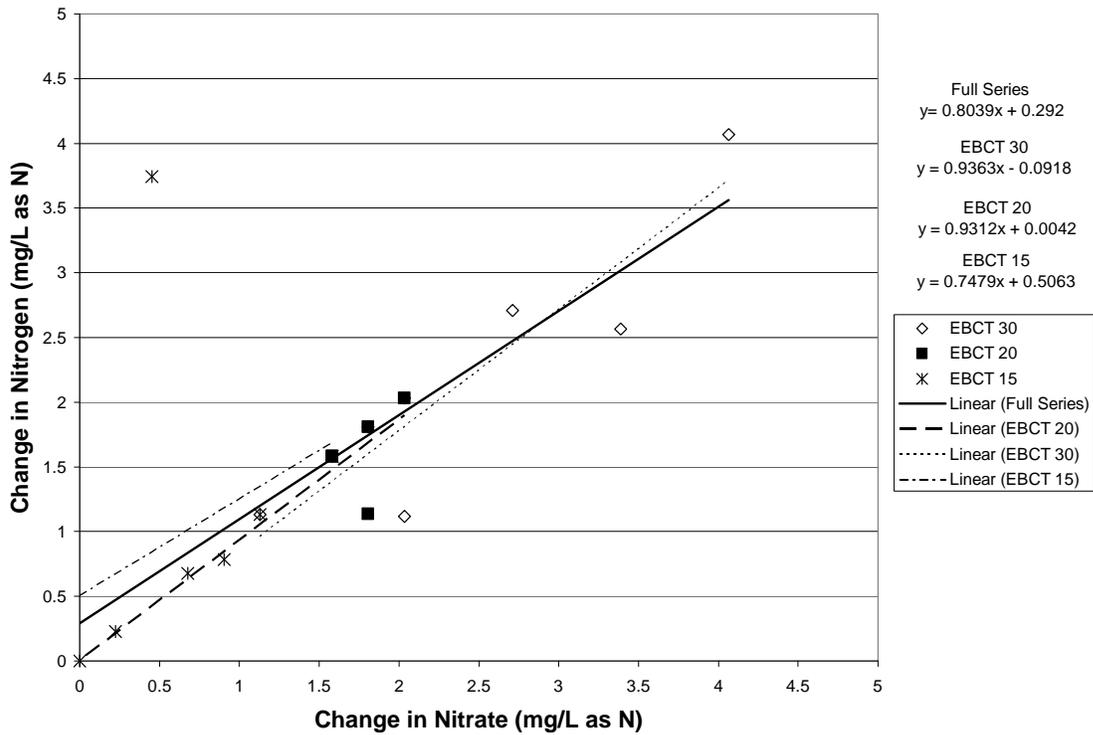


Figure 6-3 suggests that more nitrogenous byproducts are produced at a lower pH and the slope of the best fit line increases as pH increases. Figure 6-4 shows fewer byproducts are produced as the EBCT is increased. The figures presented in this section suggest that pH may be important for hydraulic control of the columns; however, it may not be a critical control for nitrate reduction.

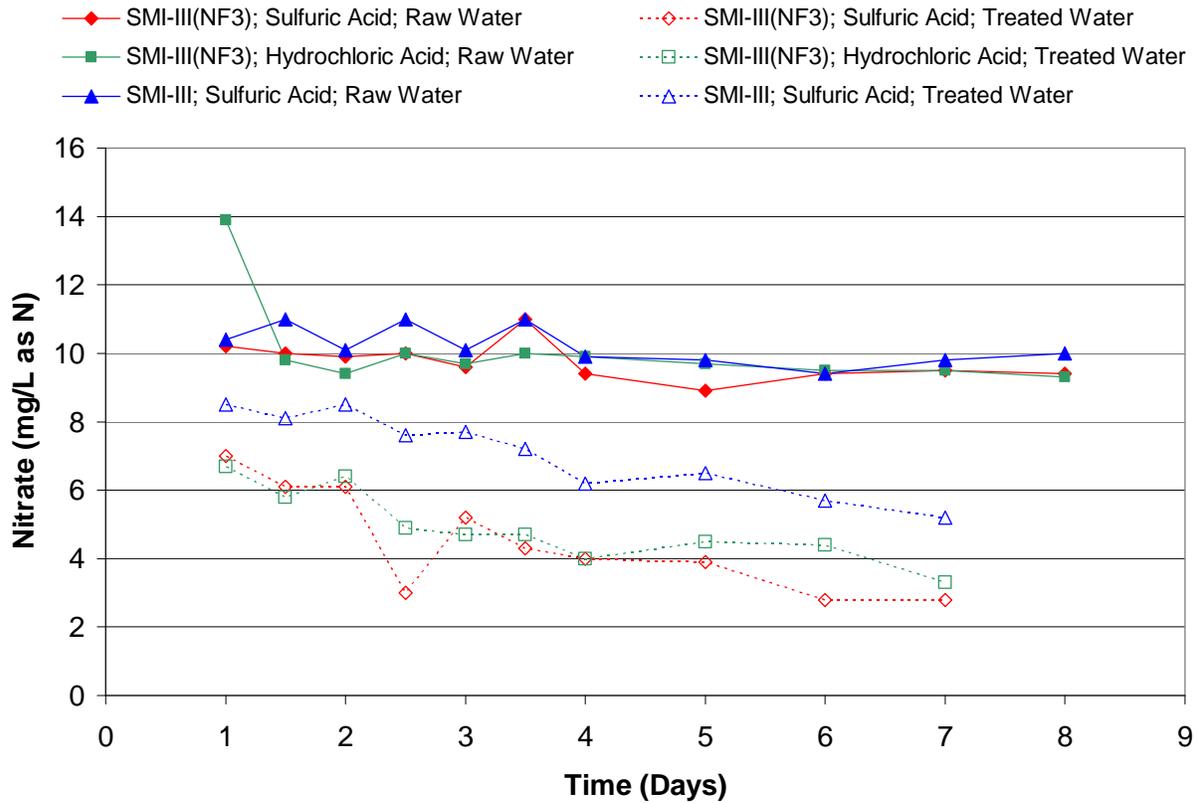
Based on these findings, Phase B began with an operational pH of 6.8. Operating the system at a higher pH will decrease the amount of acid required and iron release from the media. This will also reduce the chlorine demand to oxidize the released iron, increase filter run length and long-term media life. Each of these factors decreases the operational cost of the system.

6.2 New SMI-III[®] (NF-3) Media Development

Following the conclusion of the Phase A study, SMI-Inc. refined the media production process with a new manufacturer, North American Höganäs, Inc (NAH). The SMI-III[®] media used in Phase A is no longer commercially available. The new manufacturer is using a new iron base. For clarity, the refined material will be referred to as SMI-III(NF3) in this report, but is still commercially referred to as SMI-III[®].

In order to determine if the newly formulated SMI-III(NF3) has increased nitrate reduction capabilities as compared with the previous media, side-by-side small columns were evaluated by an independent laboratory. The study was conducted with three 2-inch diameter columns operated at an approximate EBCT of 20 minutes and an influent pH of 6.0. A control column was established using the original SMI-III[®] and sulfuric acid to depress the pH, while the other two columns utilized SMI-III(NF3). One of the SMI-III(NF3) columns used sulfuric acid while the other used hydrochloric to determine if there was an effect of the different acid feeds on nitrate reduction. Figure 6-5 shows the preliminary results from the three columns. In Figure 6-5, the solid symbols and lines represent the raw water nitrate concentrations as nitrogen and the open symbols and dashed lines represent the treated water nitrate concentrations and nitrogen.

Figure 6-5 Results of side-by-side column testing of SMI-III and SMI-III(NF3) with alternative acid feeds



These preliminary results suggest that SMI-III(NF3) has greater nitrate reduction capacity as compared with SMI-III[®]. The results do not show a substantial nitrate reduction difference between sulfuric and hydrochloric acid used for pH depression. Based on the increased performance of the new SMI-III(NF3) media, coupled with the fact that the original SMI-III[®] used in Phase A is no longer commercially available, it was recommended to utilize SMI-III(NF3) media for Phase B testing.

6.3 Phase B Test Plan

The Phase B testing will be conducted for 13 weeks. The first week of testing will commence with a 24-hour rinse of the media. This rinse period will use a sustained fluff cycle of the media to remove any fines that may be present. The flow rate for the rinse period will start at 100 gpm. The rinse water will be visually monitored and sampled periodically as the flow rate is gradually increased up to 200 gpm (the Phase A fluff flow setpoint) or to a point where there is evidence that media is escaping from the reactor. It is important to note that since the bulk density of the



new SMI-III(NF3) media is up to 30% less than the original SMI-III[®], the rinse rate may be significantly less than what was required during Phase A.

Following the rinse cycle, the pilot system will operate with a 30 minute EBCT at a pH of 6.8 for three weeks with daily fluff cycles. These conditions offer the greatest chance of meeting the water quality goal for nitrate minimizing nitrogenous byproducts such as ammonia. The daily fluff cycle will also assist in preventing hydraulic issues with the media; however, like the rinse cycle, the fluff flow may need to be reduced so media is not inadvertently lost from the reactor. In the early stages of the Phase B testing, the optimal fluff flow will be determined in the field with a combination of grab samples and visual inspection of the fluff water.

The initial three week testing time period will allow for laboratory analytical results to be received prior to changing the operating conditions. If these results suggest that the treated water quality goals have been achieved, then the EBCT will be decreased. If the treated water quality goals have not been met, then the pH will be decreased to 6.0 for another three weeks.

Figure 6-1 and Figure 6-3 suggest that pH is not a substantial controlling factor; however, some examples in the literature contradict this finding and it is also uncertain if the SMI-III(NF3) media will behave in the same fashion as the SMI-III[®] media. At the conclusion of these first two test conditions, a brief interim period will allow for laboratory samples to be processed and to conduct a cursory review of the data.

If these either of the initial conditions meet the treated water quality goals, it is proposed that the remainder of Phase B testing be conducted under that EBCT and pH. Other operational conditions such as the fluff cycle duration and frequency and other factors that help address the original Phase B goals of long-term system evaluation and media life will then be addressed. The fluff cycle appears to disrupt the reductive conditions inside the SMI reactor (Figure 4-14). By increasing the duration between fluff cycles, the reactor may achieve a steady state condition with maximum nitrate reduction. Additionally, the frequency of the fluff cycle effects the overall water efficiency of the pilot system. A daily fluff cycle (120 gpm for 20 minutes), accounts for approximately 13% water loss from the system. If the fluff frequency can be extended to occur once per week, without negative impacts on the hydraulic character of the bed,

then as little as 2% water loss could be achieved. In addition, these values could be further reduced if the fluff water were to be recycled to the head of a full-scale treatment system.

If either of the initial conditions meets the treated water quality goals, then the EBCT will be extended in 15 minute increments and assessed over two week periods at the pH that demonstrated the most nitrate reduction until the project nitrate goal is met or the pilot system service flow is out of the low-range of the chemical feed pumps. The purpose of this exercise is to determine the necessary EBCT to achieve the treated water quality goals for the project. Once this is achieved, then operational costs for the integrated arsenic and nitrate treatment system can be calculated to determine if it would be a cost feasible technology. The proposed Phase B activities are summarized in Table 6-1 below.

Table 6-1 Summary of proposed Phase B test conditions

Week	pH	EBCT	Comments
	(SU)	(min)	
1	6.8	30	30 minute EBCT; pH 6.8
2			
3			
4	6.0 or 6.8	30 or 20	If the initial results suggest that the treated water quality goals have been achieved, then the EBCT will be decreased. If the treated water quality goals have not been met, then the pH will be decreased to 6.0
5			
6			
7	<ul style="list-style-type: none"> If neither of the initial conditions meets the treated water quality goals, then the EBCT will be extended in 15 minute increments at the pH that demonstrated the greatest nitrate reduction If these either of the initial conditions meet the treated water quality goals, it is proposed that the remainder of Phase B be conducted under that EBCT and pH. Other operational conditions such as the fluff cycle duration and frequency and other factors that help address the original Phase B goals of long-term system evaluation and media life will then be addressed. 		
8			
9			
10			
11			
12			
13			

In the interim period between Phase A and Phase B, all of the online instruments referenced in Table 6-1 were cleaned and calibrated. All check valves downstream of the SMI reactor were also cleaned. The online Hach nitrate analyzers were removed and sent to the factory for recalibration.

The laboratory sampling schedule was modified for Phase B testing. Most notably, the laboratory sampling frequency was increased from two to three times weekly (Monday, Wednesday, and Friday) with additional sampling of nitrite and nitrate at the S3 location. Table 6-2 summarizes the laboratory samples that were collected and analyzed by JL Analytical. Online operational parameters remained the same as the Phase A testing.

Table 6-2 Summary of Phase B laboratory samples

Sample Location	S1	S2	S3	S4
Alkalinity	X	X		X
Ammonia	X		X	X
Arsenic	X			X
Calcium	X			X
Conductivity	X			X
Iron (dissolved)	X			X
Iron (total)	X			X
Nitrate	X		X	X
Nitrite	X		X	X

In addition to the items listed in Table 6-2, a series of other water quality and residuals character parameters were periodically evaluated during the course of Phase B. Table 6-3 summarizes the type of sample, frequency and location of these samples.

Table 6-3 Additional parameters to be analyzed during Phase B

Parameter	Sample Location and Frequency					
	S1	S2	S3	S4	S5	S6
Chromium	1 total			1 total		
Uranium	1 total			1 total		
Vanadium	1 total			1 total		
Total Nitrogen	Weekly			Weekly		
Total Dissolved Nitrogen	Weekly			Weekly		
TTHMs				Monthly		
CAL-WET (STLC): SMI-III [®]					1 total	
CAL-WET (TTLC): SMI-III [®]					1 total	
TCLP: SMI-III [®] Media					1 total	

6.4 Phase B Test Conditions

The Phase B testing was executed intermittently between June 5 and December 2, 2008. As per the test plan, the system operated for 13 weeks; however, equipment failures and water supply issues did not allow for the system to operate continuously throughout the Phase B investigation. During the course of the Phase B testing, the pilot system was shut down and restarted three times for tank repairs and well pump replacement. The primary focus of Phase B was to evaluate operational conditions as identified through the results of Phase A that had the highest probability of producing finished water that is compliant with all regulatory requirements and meeting the water quality goals for the project as identified in Section 3.0. The schedule of the conditions that were investigated in Phase B is shown in Table 6-4 below.

Table 6-4 Phase B testing schedule

Week	Date Range	EBCT (min)	HLR (gpm/sf)	pH	Fluff Frequency
1	June 9 – June 13	30	1.4	6.8	Daily
System shutdown for FRP tank repair June 14 – August 15					
2	August 18 – August 21	30	1.0	6.8	Daily
3	August 25 – August 29	30	1.0	6.0	Daily
System shutdown for well pump replacement September 1 – September 15					
4-6	September 15 – October 9	30	1.0	6.0	Daily
System shutdown for well pump replacement October 10-October 14					
7-11	October 15- November 12	30	1.0	6.0	Daily
12-13	November 13 – December 3	30	1.0	6.0	Every 3 days

The following sections summarize the operational and water quality findings for the Phase B testing.

6.5 SMI-III[®] Media Change Out and Startup

In the period of time between Phase A and Phase B, the SMI-III[®] media was reformulated by North American Höganäs (NAH), a company that specializes in powdered metal products. NAH made changes to the media that they believe enhances the nitrate reductive capabilities.

Table 6-5 compares some of the basic physical characteristic of the original and modified SMI-III[®] media.

Table 6-5 Physical parameters of the original and modified SMI-III[®]

Parameter	Original SMI-III[®]	Modified SMI-III[®]
Bulk Density (g/cm³)	2.35	1.90
BET Surface Area (Base Iron – m²/kg)	73	170
Sieve Analysis (% retained)		
Mesh Size (µm)	Original SMI-III[®]	Modified SMI-III[®]
+20 (+850)	0.4	0.01
+40 (+425)	40.1	13.9
+60 (+250)	36.6	28.1
+80 (+180)	21.3	21.0
+100 (+150)	1.2	9.3
-100 (-150)	0.4	27.7

As seen in Table 6-5, the modified SMI-III[®] is more porous and therefore has a decreased bulk density and increased surface area when compared to the original media.

On June 5, 2008 a newly reformulated SMI-III[®] media, supplied by North American Höganäs, Inc, was loaded to a depth of 66” in the SMI reactor. Prior to the media loading, the original SMI-III[®] media was extracted from the SMI vessel. Once the reactor was emptied, it was pressure washed, steam cleaned, and the service flow laterals were replaced. There were some areas where the media had aggregated to the tank surface and formed solid particles. There was also noticeable clogging of the service flow laterals. Each lateral was removed and pressure washed prior to media. A photograph of one of the laterals before cleaning is shown in Figure 6-6.

Figure 6-6 Service flow lateral before cleaning for Phase B



As can be seen in Figure 6-6, the fouling was severe enough to cause pitting. It is believed that the fouling was caused by insufficient lateral design in which the slot openings were both too numerous and large. When combined, it is hypothesized that these factors resulted in a service flow velocity that was insufficient to wash solids from the openings.

The modified media was loaded into the SMI reactor using an approach similar to used for the Phase A testing. Once loaded, the media was subjected to a prolonged rinsing period ranging from 125 gpm to 175 gpm to remove the ultrafine particles from the media matrix.

Following the initial rinsing, the system was placed in service flow. The Phase B test plan called for an initial testing condition of 30 minute EBCT and a pH of 6.8. The 30 minute EBCT corresponds with a flow rate of 9.6 gpm and a HLR of 1.4 gpm/ft².

When the system was placed in service, after the media was loaded, a leak was identified coming from the SMI reactor vessel in the vicinity of the lower manway. The leak was believed to have been caused from impact to the fiberglass SMI reactor vessel from a front end loader during the extraction of the original media. The initial flow rate of the leak was measured as approximately

2 to 3 gallons per hour. During the first week of operation, the leakage rate slowly increased. Sometime over the first weekend of operation, the leak escalated and ultimately resulted in the catastrophic failure of the fiberglass SMI reactor vessel. When the tank failed, the majority of the media was displaced from the vessel. This was discovered by the pilot systems operator after the media had likely been on the ground for more than 48 hours. The SMI media was manually shoveled into 55 gallon barrels and placed under water until the tank could be repaired. Photographs of the failed manway and the media are shown in Figure 6-7.

Figure 6-7 Photographs of SMI reactor vessel failure and media loss
 From top left (a) Failed manway (b, c) SMI-III^(R) that exited the tank due to manway failure (d) SMI-III^(R) media placed in 55 gallon drums after the failure



The tank repair occurred during the week of August 5, 2008 and media reloading occurred during the week of August 12, 2008.

6.6 Water Quality Results

6.6.1 Nitrate Removal

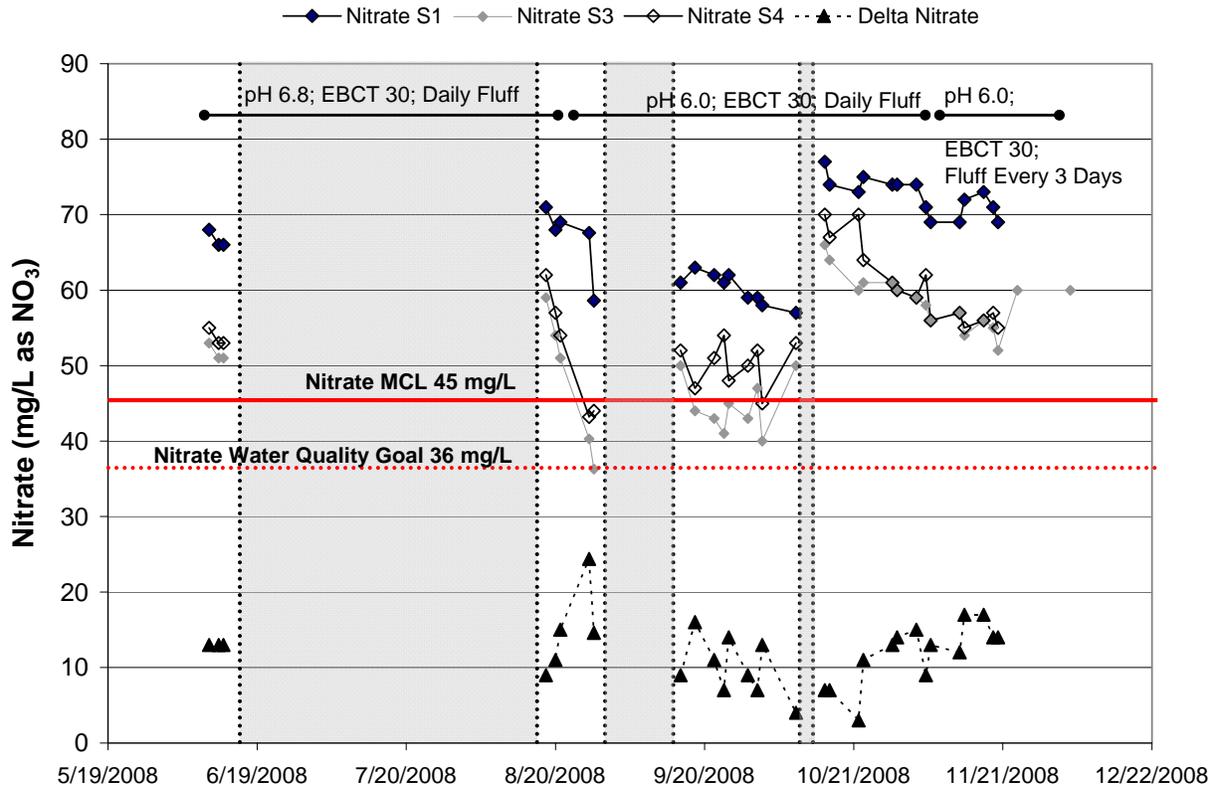
The primary goal of Phase B testing was to identify operating conditions that can consistently achieve treated water nitrate concentrations below the water quality goal of 36 mg/L as nitrate.

Nitrate was sampled at three locations (S1, S3 and S4) over the duration of Phase B testing. The results of these analyses are summarized in Table 6-6 and the time series data for S1, S4 and delta nitrate are shown in Figure 6-8. In Figure 6-8, delta nitrate is calculated as the difference between the S1 and the S4 nitrate samples.

Table 6-6 Summary of Phase B nitrate results

Test Condition	pH 6.8 EBCT 30 min Daily Fluff			pH 6.0 EBCT 30 min Daily Fluff			pH 6.0 EBCT 30 min Fluff Every 3 Days		
	S1	S3	S4	S1	S3	S4	S1	S3	S4
Location	S1	S3	S4	S1	S3	S4	S1	S3	S4
Count	6	6	6	21	21	21	5	5	5
Minimum (mg/L)	66	51	53	57	32	43	68	52	55
Maximum (mg/L)	71	59	62	77	62	70	73	60	70
Average (mg/L)	68	53	56	67	46	55	71	55	59
Median (mg/L)	68	52	55	68	47	53	71	55	56

Figure 6-8 Phase B nitrate data



The Phase B testing produced some sample results that were below the nitrate MCL at the S4 location and one sample achieved the water quality goal of 36 mg/L-NO₃ at a test condition with



a pH of 6.0 and an EBCT of 30 minutes. These conditions were achieved when the raw water nitrate concentration was below 60 mg/L. Over the course of Phase B testing for all conditions, delta nitrate ranged from 3 mg/L to 24 mg/L with a median value of 13 mg/L and an average value of 12 mg/L.

It is possible that an extended EBCT could have increased nitrate reduction; however, this could not be supported with the instrumentation and controls available on the pilot skid (design flow rate of 20 gpm; operational flow rate for EBCT 30, 7 gpm).

6.6.2 Nitrite Production

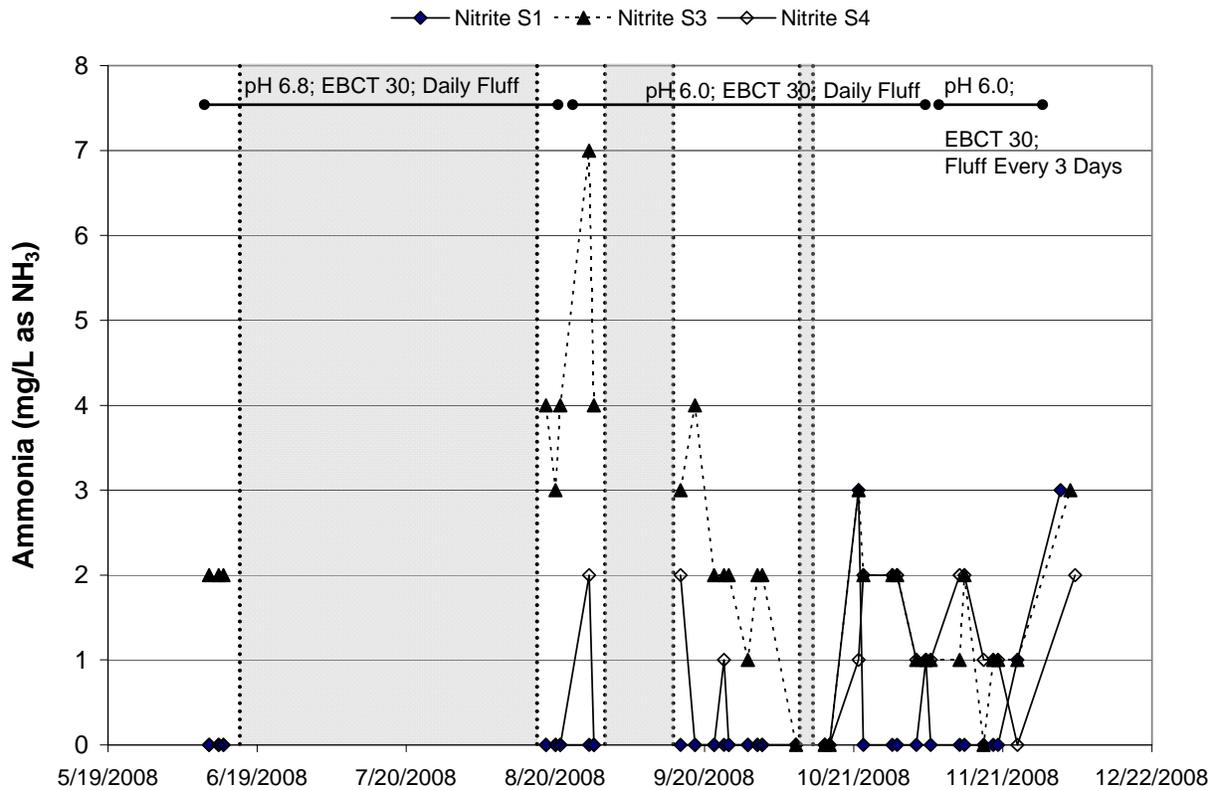
Nitrite is believed to be an intermediate of the nitrate reduction reaction via SMI-III. Nitrite was monitored at three locations the: raw water (S1), post-SMI-III (S3), and finished (S4). The nitrite results are summarized in Table 6-7 and shown as a time series plot in Figure 6-9.

Table 6-7 Summary of Phase B nitrite results

Test Condition	pH 6.8 EBCT 30 min Daily Fluff			pH 6.0 EBCT 30 min Daily Fluff			pH 6.0 EBCT 30 min Fluff Every 3 Days		
	S1	S3	S4	S1	S3	S4	S1	S3	S4
Count	6	6	6	21	21	21	5	5	5
Minimum (mg/L)	ND	ND	ND	ND	ND	ND	ND	0.5	ND
Maximum (mg/L)	ND	ND	ND	0.2	1.4	1.4	ND	0.8	0.3
Average (mg/ L)	0	0	0	0.0	0.5	0.1	0	0.7	0.1
Median (mg/L)	0	0	0	0	0.3	00	0	0.6	0

Chlorine is added and the process water is filtered between the S3 and S4 locations. Nitrite is readily oxidized to nitrate by chlorine. This is likely the reason that nitrite is generally higher at the S3 location than the S4 location.

Figure 6-10 Phase B ammonia data



6.6.4 Nitrogen Removal

Although the ability of SMI-III[®] to reduce nitrate is important, it is also important to understand how much nitrogen is removed from the system as the intermediate reductive products, namely nitrite and ammonia, will be affected when the process water is disinfected with chlorine.

Chlorine will oxidize any available nitrite to nitrate and depending on dosage, ammonia will either form chloramines or be removed from the system via break point chlorination. In order to ascertain the degree of nitrate removed, the sum of the nitrogenous species (nitrate, nitrite, and ammonia) was calculated from the lab results. Figure 6-11 and Figure 6-12 show the total influent nitrogen (S1) plotted against the nitrogen concentrations post-SMI (S3) and the finished water (S4). A line with a slope of 1 has been imposed on Figure 6-11 and Figure 6-12. The further a given data point lays below the line, the greater the extent of total nitrogen removal. If a data point falls on the line, the nitrogen was conserved through the system. Figure 6-11 shows the total nitrogen at the raw water location versus the post SMI, S3 location. Figure 6-12 shows the total nitrogen at the raw water location versus the finished water, S4 location.

Figure 6-11 Raw water (S1) total nitrogen versus post SMI (S3) total nitrogen

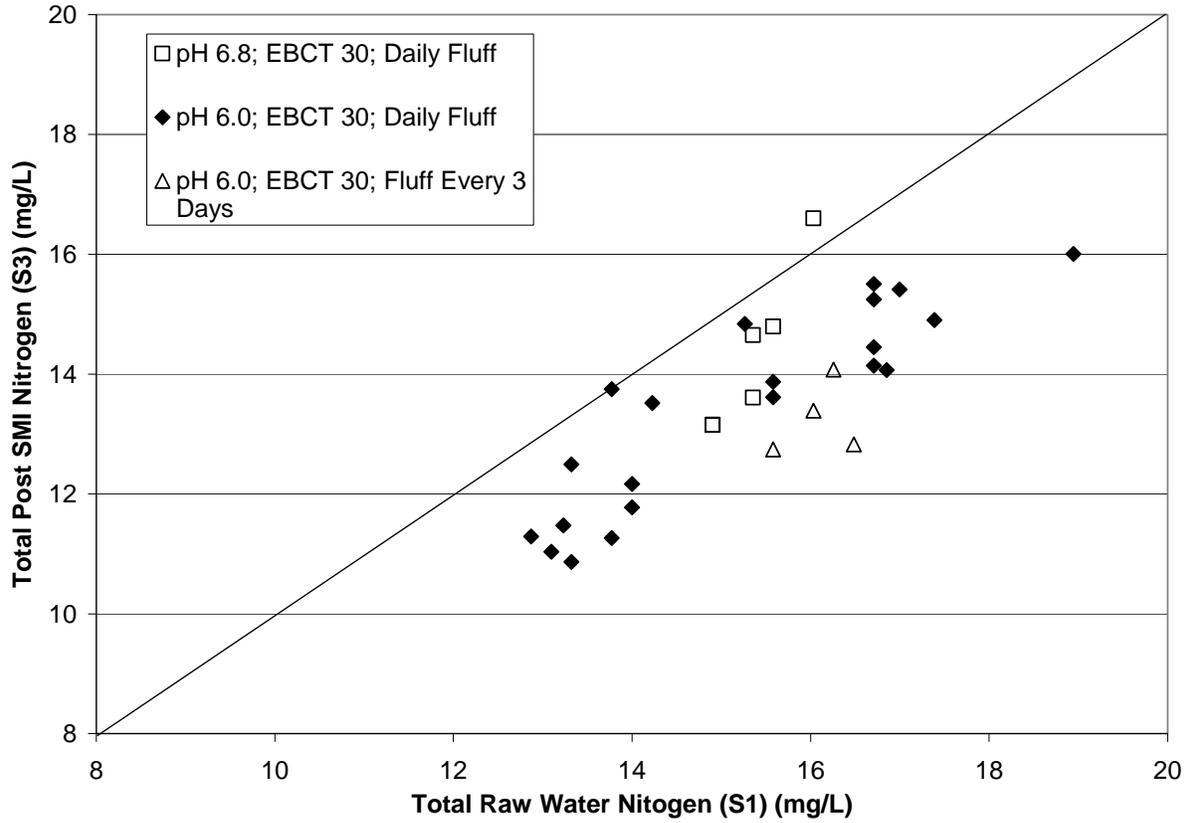
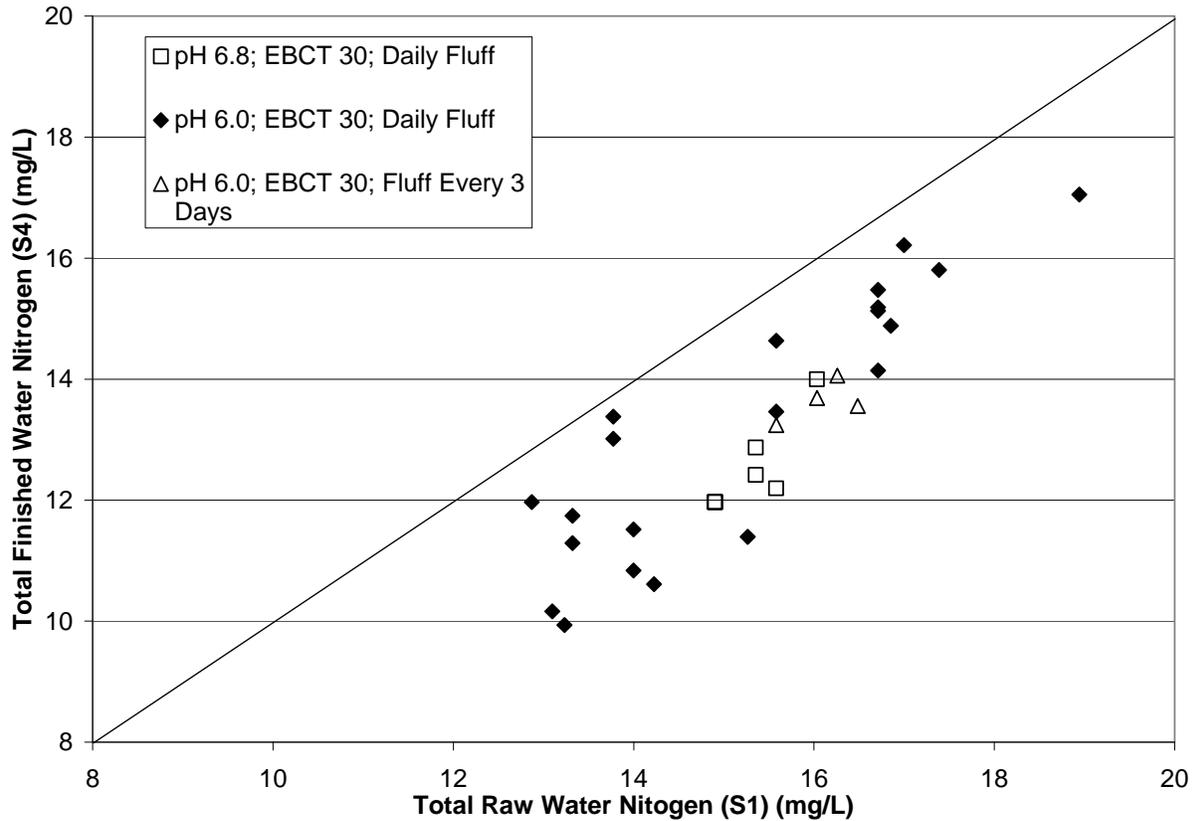


Figure 6-12 Raw water (S1) total nitrogen versus finished water (S4) total nitrogen



A comparison of Figure 6-11 and Figure 6-12 shows a similar distribution of data points for both S3 and S4. Additionally the points remain a similar distance from the line throughout the range of the S1 nitrate. This suggests that the nitrate removal is constant with respect to the raw water concentration.

A comparison of the Post-SMI (S3) and finished water (S4) nitrate results is shown in Figure 6-13.

Figure 6-13 Post SMI (S3) total nitrogen versus finished water (S4) total nitrogen

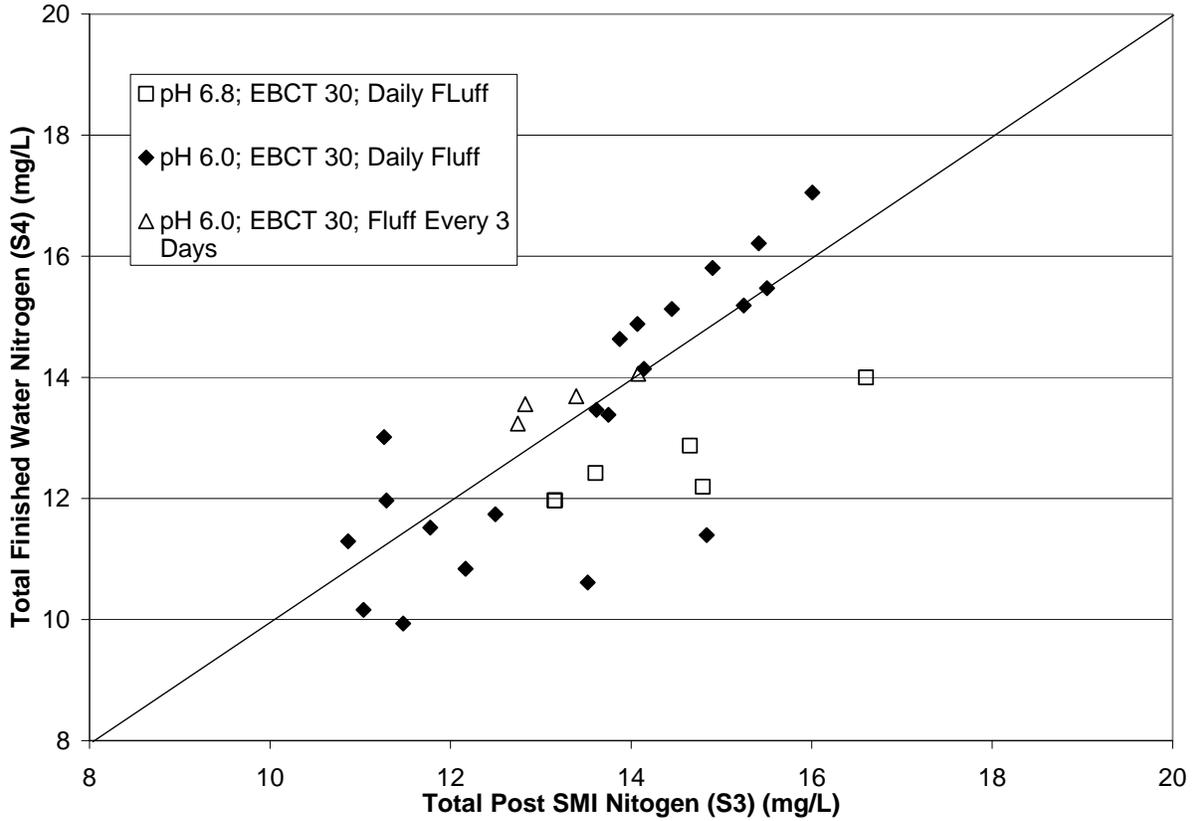


Figure 6-13 shows the data points are generally distributed about the centerline. This result suggests that although the nitrogenous species may shift as a result of chlorination, there is not additional nitrate removal from the system. The data used to create Figure 6-11 through Figure 6-13 is summarized in Table 6-9.

Table 6-9 Summary of summed nitrogenous species from the S1, S3, and S4 sample locations

Test Condition	pH 6.8 EBCT 30 min Daily Fluff			pH 6.0 EBCT 30 min Daily Fluff			pH 6.0 EBCT 30 min Fluff Every 3 Days		
	S1	S3	S4	S1	S3	S4	S1	S3	S4
Count	6	6	6	21	21	21	4	4	4
Minimum (mg/L)	14.9	13.2	12.0	12.9	10.8	9.9	16.1	12.7	13.2
Maximum (mg/L)	16.0	16.6	14.0	18.9	16.0	17.0	16.5	14.1	14.1
Average (mg/L)	15.4	14.3	12.6	15.2	13.4	13.2	16.1	13.3	13.6
Median (mg/L)	15.4	14.1	12.3	15.3	13.8	13.2	15.6	13.4	13.7

6.6.5 Total Nitrogen and Total Dissolved Nitrogen

In addition to sampling for the individual nitrogenous species of nitrate, nitrite, and ammonia, total nitrogen (TN) and total dissolved nitrogen (TDN) samples were collected on a weekly basis from the S1 and S4 sampling locations. Total dissolved nitrogen accounts for all nitrogen in the aqueous phase, while total nitrogen is a measure of the dissolved nitrogen and any nitrogen species that may be bound to particulate matter. The results of these analyses are shown in Figure 6-14 and summarized in Table 6-10.

Figure 6-14 Total nitrogen and total dissolved nitrogen at the S1 and S4 sample locations

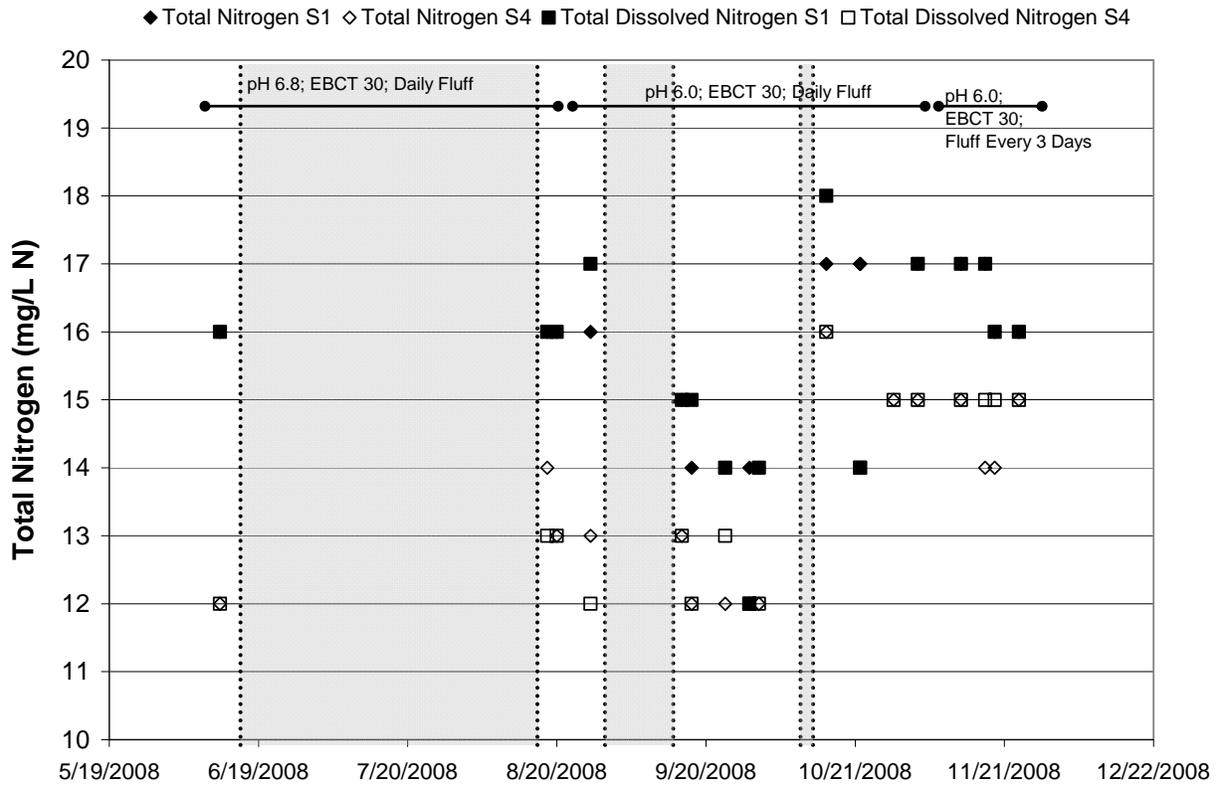


Table 6-10 Summary of total nitrogen and total dissolved nitrogen

Test Condition	pH 6.8 EBCT 30 min Daily Fluff				pH 6.0 EBCT 30 min Daily Fluff				pH 6.0 EBCT 30 min Fluff Every 3 Days			
	S1	S4	S1	S4	S1	S4	S1	S4	S1	S4	S1	S4
Analyte	TN	TN	TDN	TDN	TN	TN	TDN	TDN	TN	TN	TDN	TDN
Count	3	3	3	3	10	11	10	11	3	3	3	3
Minimum (mg/L)	16	12	16	12	14	11	12	12	16	14	16	15
Maximum (mg/L)	16	14	16	13	17	17	18	16	17	15	17	15
Average (mg/L)	16	13	16	12.5	15.5	13.6	15.3	13.5	16.3	14.7	16.3	15
Median (mg/L)	16	13	16	13	15.5	15	15	13	16	14	16	15

The results for total nitrogen and total dissolved nitrogen are consistent throughout Phase B for both total nitrogen and total dissolved nitrogen. This suggests that the nitrogen typically exists in the dissolved phase. The greatest nitrogen removal, measured as the difference between S1 and

S4 was 4 mg/L as N and the lowest removal was 0 mg/L as N. Each of the nitrogen analysis (the summed species, total nitrogen, and total dissolved nitrogen) are compared in Figure 6-15

Figure 6-15 Comparison of the summed, total, and total dissolved nitrogen analysis at the S1 and S4 sample locations during Phase B testing

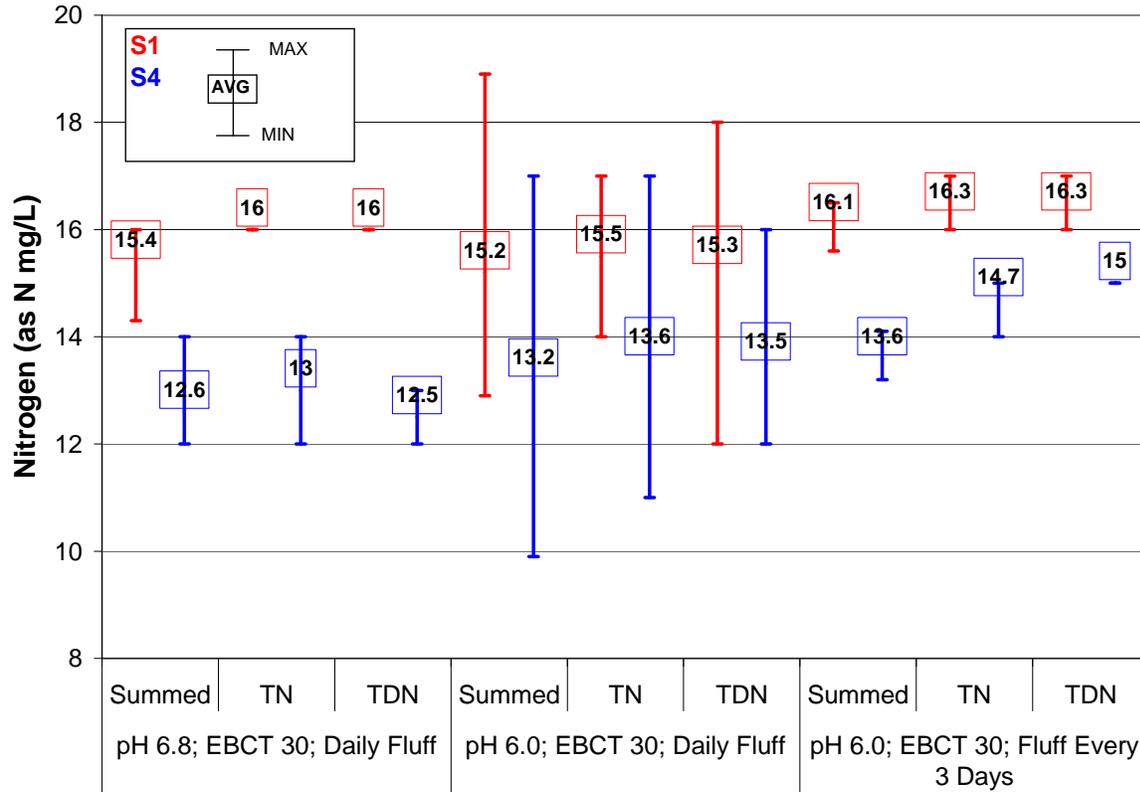


Figure 6-15 shows that each of the analysis provided similar results. The greatest spread of data can be attributed to the pH 6.0; EBCT 30; Daily Fluff test period. This is likely a result of this period corresponding to the greatest number of samples and varying raw water quality. In general each of the three methods of analyzing nitrogen in the system provided similar results.

6.6.6 Iron Release

Iron is regulated with a Secondary MCL of 0.3 mg/L and as such a finished water quality goal of 0.24 mg/L has been established for Phase B of the study. Throughout Phase B testing, both total iron and dissolved iron were monitored at the S1, S3 and S4 locations. For the 33 samples collected, both the total iron and dissolved iron at the raw location (S1) were found to be below the laboratory detection limit of 0.02 mg/L. Total iron and total dissolved iron for the S3 and S4

sample locations are shown in Figure 6-16, where S3 represents the post SMI-III[®] reactor location and S4 is the finished water sample location.

The particulate iron is the difference between the dissolved iron and total iron data sets. Since the raw water (S1) iron concentration was found to be below the detection limit for each of the samples, the iron concentrations at the S3 location can be attributed to release from the SMI-III[®] media. Dissolved iron ranged from non-detect to 30 mg/L. Total iron at the S3 location had a maximum value of 62 mg/L and a minimum of 7.2 mg/L. The data shown in Figure 6-16 is summarized in Table 6-11 below by experimental condition.

Prior to filtration, but after the S3 sample point, sodium hypochlorite is added to the process stream to effectively oxidize the dissolved iron to solid iron particles. Dissolved iron present at the S4 location indicates that the chlorine feed was inadequate and particulate iron suggests that the filter run length was too long. The S4 sample results are shown in Figure 6-16 and the data is summarized in Table 6-11.

Figure 6-16 Total and dissolved iron results at the S3 and S4 locations

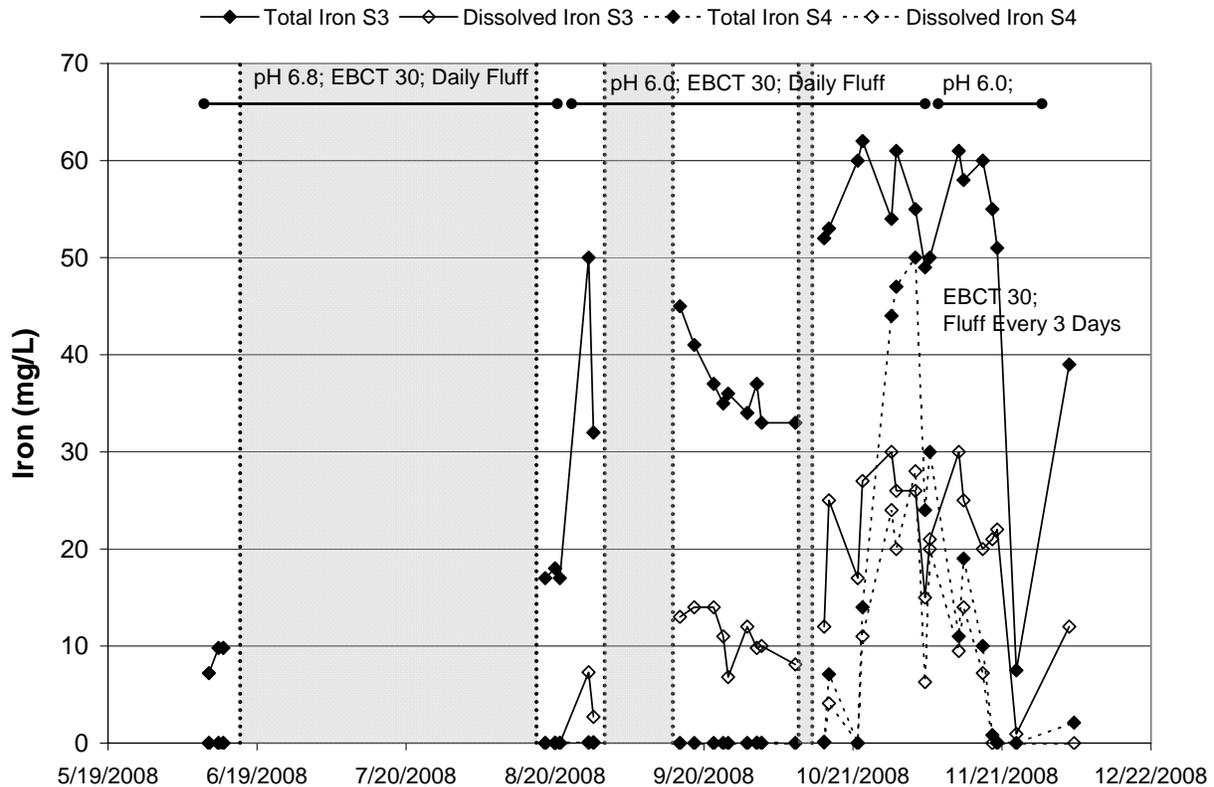


Table 6-11 Summary of iron results for the S3 and S4 sample location

Test Condition	PH 6.8 EBCT 30 min Daily Fluff				PH 6.0 EBCT 30 min Daily Fluff				pH 6.0 EBCT 30 min 1 Fluff/ 3 days			
	S3		S4		S3		S4		S3		S4	
Analyte ¹	D	T	D	T	D	T	D	T	D	T	D	T
Count	6	6	6	6	21	21	21	21	6	6	ND	ND
Minimum (mg/L)	ND ²	18	ND	ND	2.7	32	0.03	ND	1.0	7.5	14	19
Maximum (mg/L)	ND	7.2	NA ³	0.06	30	62	28	50	25	60	NA	NA
Average (mg/L)	ND	18.3	NA	NA	16.1	46.2	NA	NA	16.8	45.1	NA	NA
Median (mg/L)	ND	13.4	NA	NA	14	49	NA	NA	20.5	53	6	6

¹D = Dissolved Iron; T= Total Iron

²ND = Non-Detect

³NA Not Applicable

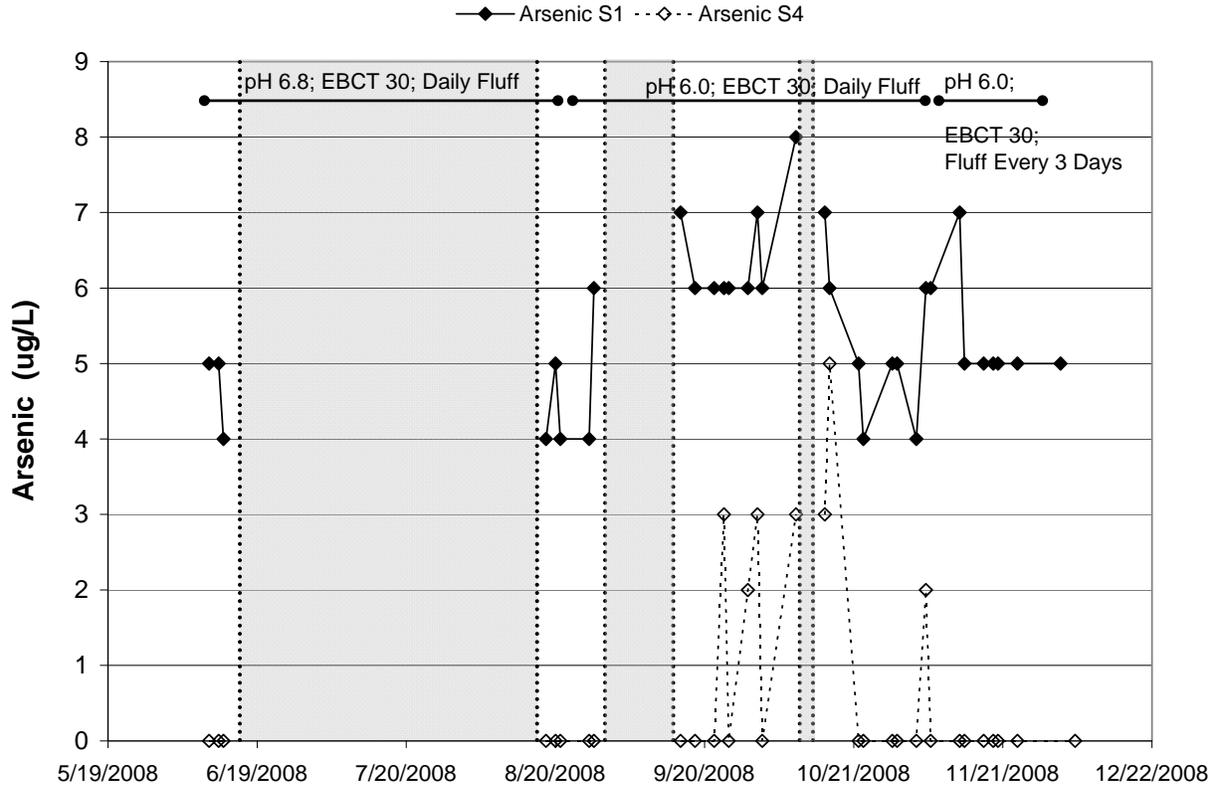
In Figure 6-16, there is a noticeable increase in the amount of both total and dissolved iron at the S4 location that begins in the latter part of October and continues through the end of the Phase B testing. The start of the iron breakthrough corresponds to a filter and chemical feed optimization exercise. The optimization effort used a dilute hypochlorite solution while iron breakthrough of the filters was monitored. However, after the optimization effort the original chemical feed system was not returned to service and sodium hypochlorite was not being fed to the system. As a result the iron was not being oxidized or filtered from the system. The issue with the sodium hypochlorite feed was noticed by an operator during a routine sampling event. The operator reinstated the sodium hypochlorite feed system, but an optimized dose was not achieved for the duration of the Phase B testing.

6.6.7 Arsenic Removal

As previously mentioned, the iron release from the SMI-III[®] media has beneficial properties if there is arsenic present in the source water. The iron release can eliminate the need for additional iron based coagulants, such as ferric chloride, that are used in conventional arsenic removal coagulation/filtration applications. During Phase B testing, the arsenic in the Well 12 source water ranged from 4 µg/L to 7µg/L. While this is below the 10 µg/L MCL, the presence of arsenic does indicate whether or not this treatment technology can reduce arsenic

concentrations. Arsenic was monitored at the S1 and S4 locations during Phase B testing. Of the 30 samples collected at S4, 23 resulted in arsenic being found below the detection limit of 2 µg/L. These results are shown in Figure 6-17.

Figure 6-17 Arsenic at the S1 and S4 sample locations



The presence of arsenic at the S4 location suggests that there were challenges with sodium hypochlorite feed system or the filtration system as there was sufficient iron available to co-precipitate the arsenic. It is recommended that future iterations of the integrated nitrate and arsenic removal systems include a chlorine residual monitor after the filters to assure that a sufficient dose is being added to oxidize the dissolved iron. Additionally, backwash of the filters should be triggered by turbidity to minimize particulate breakthrough.

6.6.8 Co-contaminant Removal

One set of paired samples from the S1 and S4 locations were collected for chromium, vanadium and uranium analyses during Phase B of the pilot study. Although these co-contaminants are not directly associated with the project goals, the sample results serve as a brief investigation

regarding the ability of the treatment technology to remove these constituents. The samples were collected on December 3, 2008 while the system was operating with a pH of 6.0 and an EBCT of 30 minutes. The results from the sampling event along with the corresponding results from the Phase A sample which were collected with an EBCT of 30 minutes and a pH of 6.8 are shown below in Table 6-12 below.

Table 6-12 Summary of paired sample results from Phase A and Phase B for chromium, uranium, and vanadium

Co-contaminant	Chromium (µg/L)		Uranium		Vanadium (µg/L)	
	A	B	A (µg/L)	B (pCi/L)	A	B
Raw Water (S1)	4	3	<5	8.3	40	38
Finished Water (S4)	<1	<1	<5	1.3	11	<3

6.6.9 Total Trihalomethane Formation

Total trihalomethanes (TTHMs) are known carcinogens that are federally regulated under the Stage 1 Disinfection Byproducts Rule at a concentration of 80 µg/L based on a running annual running average. TTHMs form when chlorine reacts with organic precursors. Following the Phase A portion of the investigation, CDPH requested TTHM sampling in Phase B. One TTHM sample was collected at the S4 location on December 3, 2008 when the system was operating at a pH of 6.0 with a 30 minute EBCT. The sample resulted in a TTHM concentration of 21.6 µg/L.

6.7 *Operational Results*

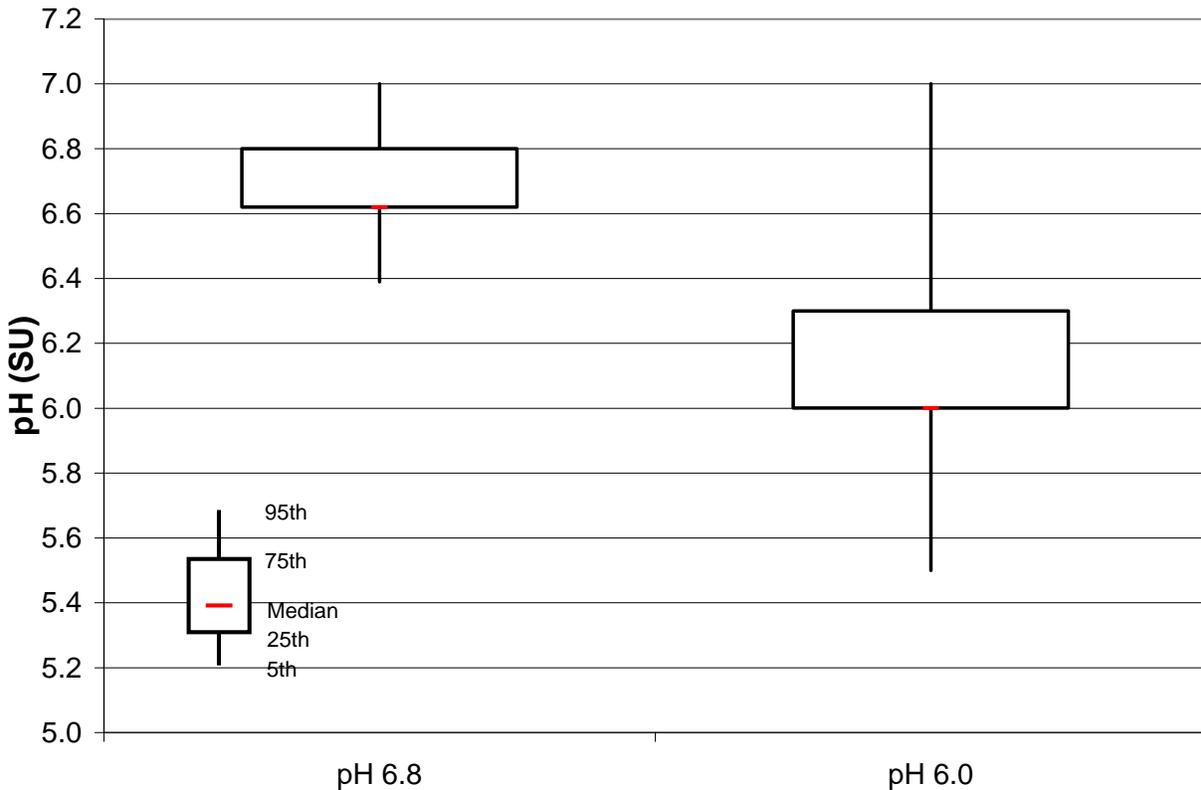
6.7.1 Flow Rate

The service flow rate is regulated by flow control valves on the effluent side of the Macrolite® filters. The flow rate is recorded at five minute intervals to the PLC. The flow rate necessary to achieve a 30 minute EBCT before and after tank failure was 9.6 gpm and 7.3 gpm, respectively, due to differences in media height. The flow rate needed to be reduced after the vessel failure as result of media loss. The median value of the flow as determined from the PLC data before and after the tank failure was 9.6 gpm and 7.3 gpm which suggests there was adequate flow control for Phase B of the pilot test.

6.7.2 pH

During Phase B testing, two pH conditions were targeted: pH 6.8 and pH 6.0. Figure 6-18 shows the statistical break down of the two pH conditions that were used during Phase B. The data used to create Figure 6-18 was collected from the PLC where the data was collected in five minute intervals.

Figure 6-18 Box and whisker plot of Phase B pH



As can be seen in Figure 6-18, the pH was fairly well controlled throughout the course of the Phase B. For the pH set point of 6.8, the median pH was 6.65, and for the set point of 6.0 the median was 6.0. The greater variability witnessed at the pH 6.0 condition can likely be attributed to the longer operational period of this pH condition and shortcomings with the feedback loop of the chemical feed system at lower pH conditions.

6.8 Media Characterization

SMI-III[®] media used in both Phase A and Phase B were collected after the completion of the Phase A and B investigations and the media characteristics were determined through TCLP and



CalWET analysis. In a full scale system, it is envisioned that since the media would be consumed through the nitrogen reduction reaction and the increased iron solubility under acidic conditions there would not be a need for media disposal, rather the media bed would periodically be supplemented with new media to replace media lost to dissolution. However, it will be important for municipalities to understand the residuals character of the media housed in the SMI-III[®] reactors. Table 6-13 shows the Phase A and Phase B CalWET results and Table 6-14 shows the TCLP results. The SMI-III[®] media was not found to be hazardous based on either of the extraction methods.

Table 6-13 CalWET results for the Phase A and Phase B SMI-III[®] media

Contaminant	Phase A	Phase B	Regulatory Limit (µg/L)
Antimony	ND	ND	15,000
Arsenic	ND	ND	5,000
Barium	ND	1,300	100,000
Beryllium	ND	ND	750
Cadmium	ND	ND	1,000
Chromium	730	1,400	5,000
Cobalt	ND	ND	80,000
Copper	ND	ND	25,000
Lead	ND	ND	5,000
Mercury	ND	ND	200
Molybdenum	ND	110	350,000
Nickel	ND	ND	20,000
Selenium	ND	ND	1,000
Silver	ND	ND	5,000
Thallium	ND	ND	7,000
Vanadium	7,100	11,000	24,000
Zinc	ND	ND	250,000



Table 6-14 TCLP results for the Phase A and Phase B SMI-III® media

Contaminant	Phase A	Phase B	Regulatory Limit (µg/L)
Arsenic	ND	ND	5,000
Barium	ND	ND	100,000
Cadmium	ND	ND	1,000
Chromium	ND	ND	5,000
Lead	ND	ND	5,000
Mercury	ND	ND	200
Selenium	120	ND	1,000
Silver	ND	ND	5,000

6.9 Residual Management

The SMI process releases iron which is then oxidized and trapped in the pressure filters along with any arsenic that may have co-precipitated with the iron solids. When the C/F portion of the system is backwashed, the arsenic laden iron solids are removed from the filter in the backwash water. During the pilot testing, the backwash water was sent directly to Ripon’s sewer system. However, this disposal practice may not be feasible for all municipalities.

In municipalities where direct sewer disposal is not feasible, the backwash water must undergo solid/liquid separation with the decant liquids recycled to the head of the treatment system and the dewatered solids sent to an appropriate landfill for disposal. The dewatered solids have the potential to be characterized in California by the CalWET as hazardous waste due to high levels of arsenic. The costs for disposing of this hazardous waste may be significant and could impact the overall feasibility of this alternative. The capital equipment necessary for solid/liquid separation often require more space than the primary treatment equipment and cost from 50 to 100% of the primary treatment equipment cost depending on the desired level of dewatering. Solids handling techniques can range from simple configurations that implement gravity settling to complex mechanical dewatering systems such as a filter press.



6.10 Phase B Operational Cost

Conceptual operation costs have been developed for the integrated pilot system. The conceptual costs include all consumables including sulfuric acid, caustic soda, and media replacement costs. At full scale it is envisioned the caustic soda will be required to return the treated water to ambient pH conditions in order to prevent distribution system challenges. The costs do not include the costs of labor or residual management, such as solids handling and disposal fees. Table 6-15 shows the operation costs for pH 6.0 and 6.8. Chemical dosages were developed using the RTW-2. The chemical costs are based on recent Central Valley vendor quotations and are expressed \$/lb of active chemical. Media replacement costs take into account the average iron release for each condition and assume that the SMI-III media must be replaced at the rate the iron is being mobilized. The estimated cost for the media is \$5/lb.

Table 6-15 Conceptual production costs

Operating Condition (pH)	Sulfuric Acid Dose (mg/L as H ₂ SO ₄)	Caustic Soda Dose (mg/L as NaOH)	Iron Release (mg/L)	Production Cost (\$/ac.ft.)
6.0	90	73	46	\$729
6.8	33	27	18	\$287

Table 6-15 shows that operating the system at a pH of 6.8 can drastically reduce the production cost. This operating condition not only reduces the amount of chemical required to achieve the pH conditions, but it less iron is mobilized which in turn reduces the media replacement costs.

As seen in Table 4-4 and Table 6-9 neither Phase A nor Phase B showed demonstrated significantly better nitrogen removal at pH 6.0 than pH 6.8 and often the nitrogen removal was greater at pH 6.8. As such, future investigations using this technology should target pH 6.8 to decrease operating cost and increase media life.

6.11 Phase B Investigation Summary

Phase B testing continued to build on the knowledge gained during Phase A testing. Although the nitrate water quality goal of less than 36 mg/L was not achieved, two sample events produced water that were below the nitrate MCL of 45 mg/L. The average nitrate reduction during Phase B was 12 mg/L as nitrate. The degree of nitrate reduction does not appear to change with raw water nitrate concentrations. Although the removal was not substantial enough to meet the project goals for the Ripon Well 12 water, the SMI-III[®] technology may prove to be viable for Integrated Nitrate and Arsenic Treatment Demonstration



systems with source water nitrate concentrations at or slightly above the nitrate MCL. With respect to arsenic removal, the system continued to effectively reduce arsenic concentrations. The instances where arsenic was detected at the S4 locations can likely be attributed to challenges with the chlorine feed system or filter run lengths.

Operationally, Phase B testing identified the SMI-III[®] media as being much more operationally robust than previously anticipated. The media did not lose any discernable hydraulic or reductive capacity as a result of the tank failure, atmospheric exposure, storage and reloading. This finding, although unintentional, is very important as it shows this technology can withstand service interruptions without detrimental effects to the media.

7.0 Hydraulic Loading Rate Small-Scale Column Testing

7.1 Background

Independent laboratory studies conducted using water Ripon Well 12 and similar EBCTs and pH conditions that were being used in the pilot test have demonstrated up to 50% nitrate reduction, yet nitrate reduction to this extent had not been matched in the field. In review of the data, it was found that although many of the operational parameters were similar to those in the field, the hydraulic loading rate (HLR) was much lower than the rates used in the Proposition 50 pilot study. Nitrate reduction with SMI-III[®] is believed to be a surface limited reaction; meaning that in order for the reaction to occur, the contaminant, in this case nitrate, must have sufficient contact time with the media. As such, it is logical to suggest that a lower HLR could provide greater potential for the nitrate reduction reaction to take place as each molecule of nitrate can remain in contact with a given media particle for a longer period of time.

A small column study was conducted in parallel with the pilot system to verify this theory that HLR may influence nitrate reduction. The study was set up in parallel with the integrated nitrate and arsenic pilot system at the Ripon Well 12 site, allowing for side-by-side comparisons of the pilot and small-column results using the same pH conditioned water. This was accomplished by operating four columns of different diameter (1.5", 2.0", 3.0", and 4.0") that were loaded with the same volume of SMI-III[®] media and subjected to the same treatment flow rate and EBCT, but different HLRs. A summary of the column design characteristics are shown in Table 7-1.

Table 7-1 Design Characteristics of the Columns used in the HLR Investigation

Column Identification	C1.5	C2	C3	C4	Pilot Column
Outer Diameter (inch)	1.5	2.0	3.0	4.0	NA
Nominal Inner Diameter (ID) (inch)	1.476	1.913	2.864	3.186	36
Cross Sectional Area (ft²)	0.01	0.02	0.04	0.08	7.1
Media Height (inch)	48.5	29.0	13.13	7.5	50
Media Volume (ft³)	0.042	0.042	0.042	0.042	28.3
Flow Rate (ml/min)	46	46	46	46	26,686
EBCT (min)	30	30	30	30	30
HLR (gpm/ft²)	1.04	0.62	0.28	0.16	1.0

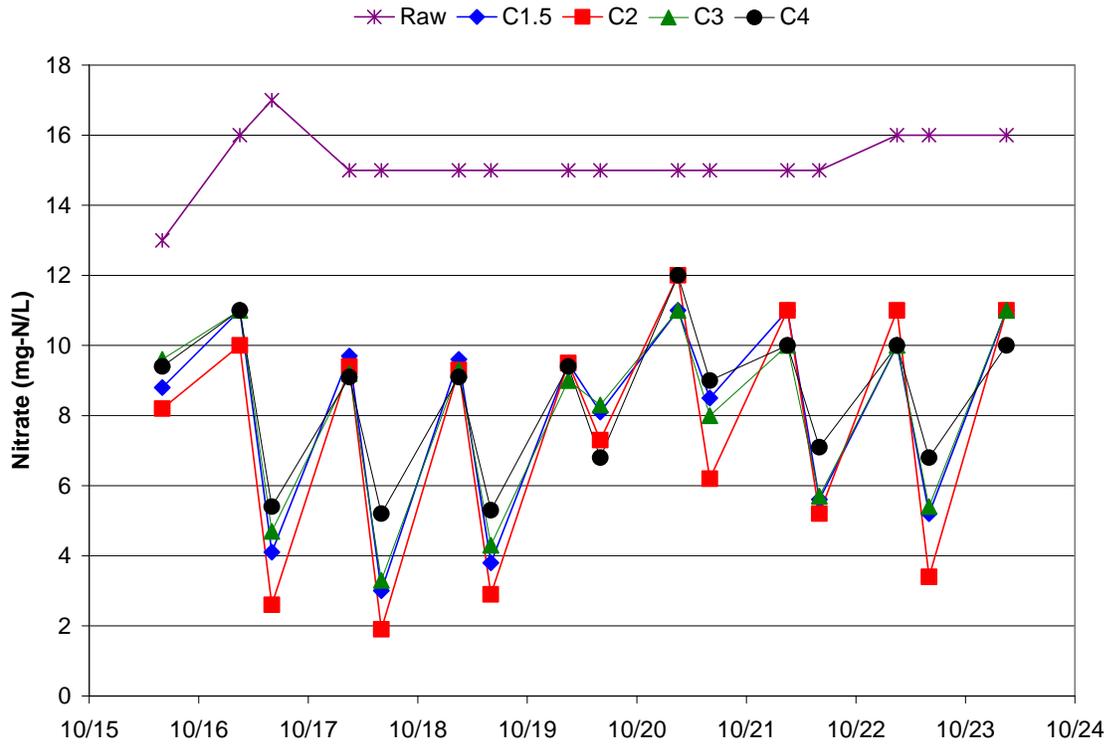
7.2 Results

The results of the HLR investigation are presented in the following sections. Samples were collected twice daily for nitrate, nitrite, ammonia, and iron. The following section presents the results for these constituents. Nitrite was not found in excess of the detection limit for any of the samples and therefore will not be discussed in any greater detail.

7.2.1 Nitrate Concentrations

The results of the nitrate samples for the raw water and each column are shown in Figure 7-1. In general, the morning samples provided approximately 5 mg-N/L of nitrate reduction, while the reduction rate was increased to more than 10 mg-N/L in some instances for the afternoon samples. The increased afternoon reduction is believed to be temperature dependant and is discussed in further detail in subsequent sections.

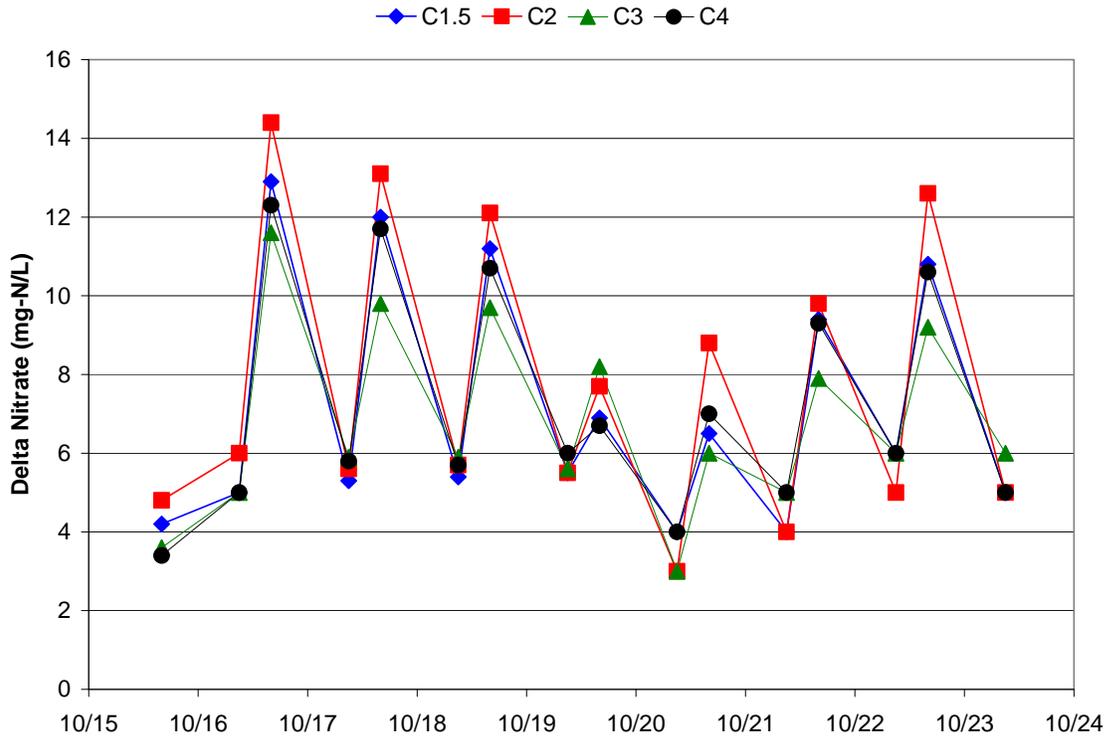
Figure 7-1 Nitrate results for the raw water and each column



In Figure 7-1, the nitrate reduction was generally greatest for C2 and the least for C4 during the afternoon samples.

The nitrate concentration results for each column were subtracted from the raw water results to determine the nitrate reduction or “delta nitrate” through each column. Delta nitrate for each of the column is shown in Figure 7-2.

Figure 7-2 Delta nitrate (Nitrate_{Raw} - Nitrate_{Column}) for each column



Nitrate reduction ranged from 3.0 mg-N/L to 14.4 mg-N/L for the samples collected.

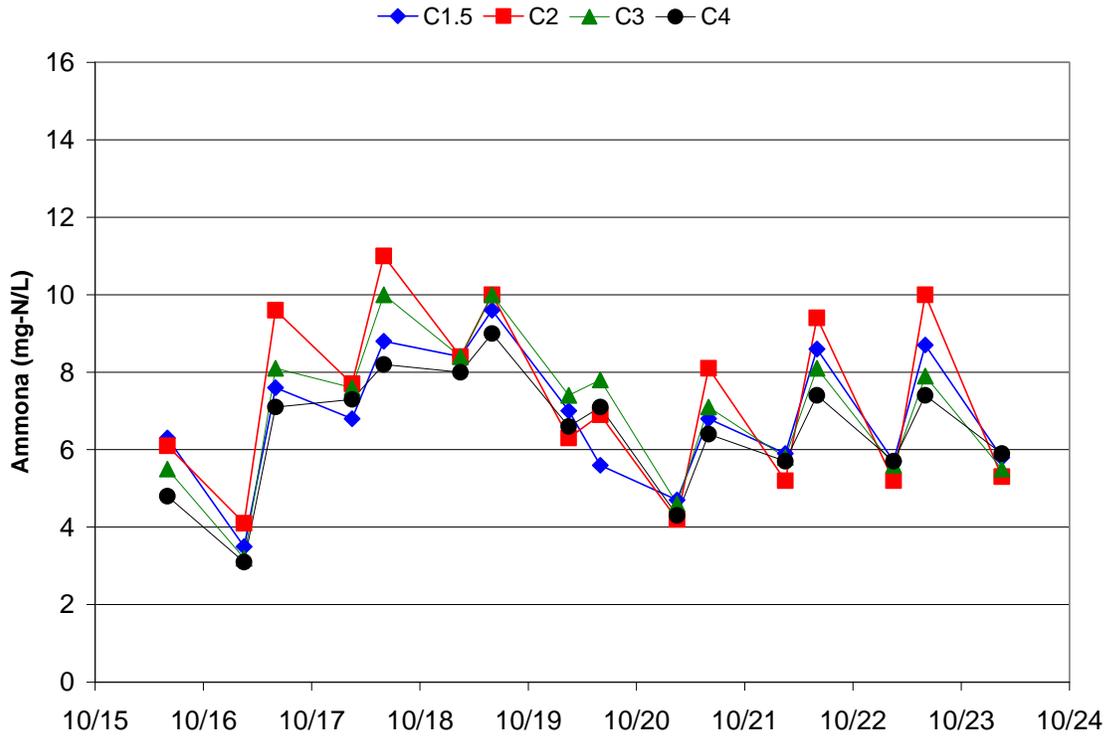
7.2.2 Nitrite Concentrations

Nitrite was not found in any of the samples at levels above the detection limit of 0.1 mg-N/L. Therefore it can be assumed that if nitrite is produced, it is as an intermediate of the nitrate reduction mechanism and is then further reduced to ammonia and/or other nitrogen reduction byproducts.

7.2.3 Ammonia Concentrations

In previous studies, the bulk of the nitrate reduction could be accounted for by reduction to ammonia. Figure 7-3 shows the ammonia concentrations for each of the columns.

Figure 7-3 Ammonia results for each column



In general, the ammonia production shown in Figure 7-3 follows a similar trend to that of the delta nitrate shown in Figure 7-2. Ammonia is not found in the raw water above the detection limit of 0.2 mg-N/L. This suggests that the end point of the nitrate reduction reaction is ammonia. To further this point, ammonia production was plotted as a function of delta nitrate in Figure 7-4. In Figure 7-4, a 1:1 nitrate to ammonia conversion would result in a data series with a slope of 1 which is represented by the solid line on the figure.

Figure 7-4 Ammonia concentration versus delta nitrate

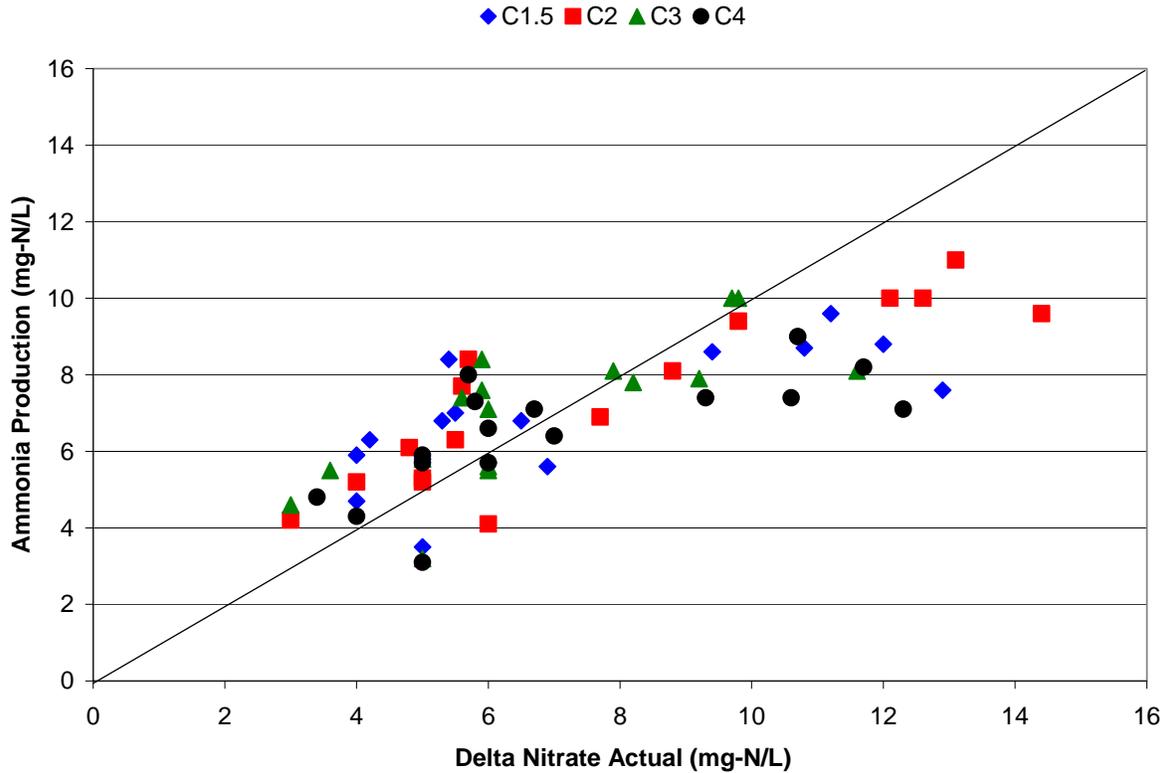
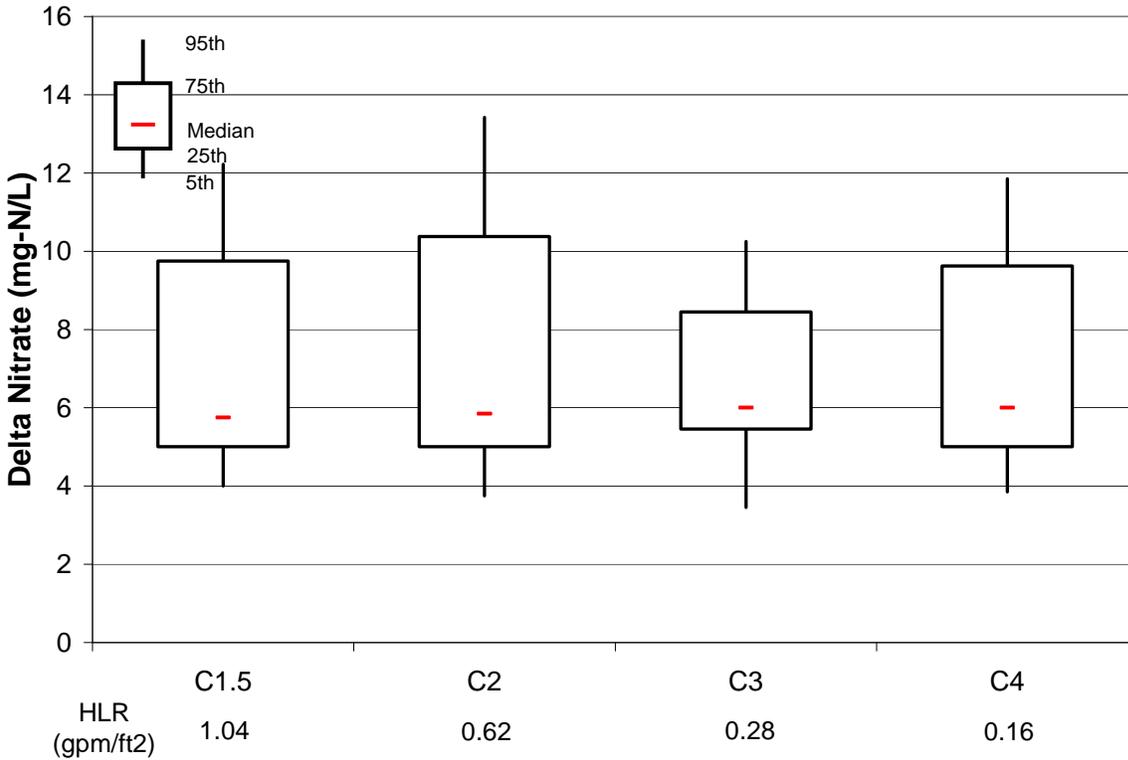


Figure 7-4, displays a clear correlation between nitrate reduction and ammonia formation. At the lower end of the scale (0 mg-N/L -6 mg-N/L), it appears that in many cases there is more ammonia produced than nitrate removed. This anomaly can likely be attributed to sampling discrepancies since these analytes are required to be collected in different bottles. The high end of the scale (> 6 mg-N/L) generally shows less ammonia production than nitrate reduction. These data points correlate to the afternoon samples where there was typically higher nitrate reduction and suggest there may be more complete reduction of nitrate at higher temperatures.

7.2.4 Hydraulic Loading Rate and Nitrate Reduction

A fundamental design parameter of many water treatment technologies is the HLR. The importance of HLR on a process can often dictate how the reactor must be designed to achieve the desired treatment performance. Nitrate reduction is shown in Figure 7-5 as a function of hydraulic loading rate for the columns.

Figure 7-5 Nitrate removal as a function of hydraulic loading rate for each the columns



The range or degree of nitrate reduction in Figure 7-5 cannot be attributed to HLR. Since the empty bed contact time, influent pH, and source water were the same for each of the columns, the difference in nitrate reduction can likely be attributed to the change in temperatures that were experienced for each sampling event.

7.2.5 Determination of Nitrate Reduction Rate Constant

Chemical reaction kinetics are often influenced by temperature. Further analysis of the data for this investigation identified that temperature plays a role in the degree of nitrate reduction by SMI-III[®]. To illustrate the impact of temperature on the reduction reaction, Figure 7-6 shows the normalized nitrate reduction ($1 - C_{\text{column}}/C_{\text{raw}}$) plotted against temperature.

Figure 7-6 Nitrate reduction plotted versus temperature

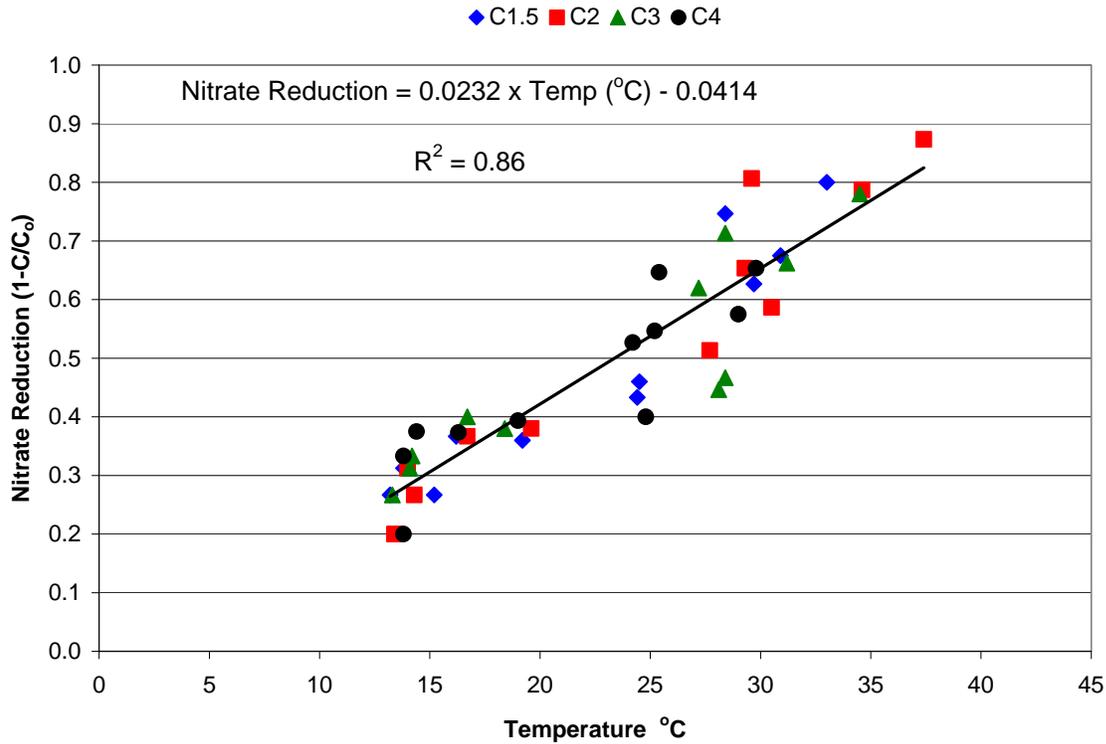


Figure 7-6 shows that nitrate reduction is correlated with temperature. Rate constants used to describe chemical reactions are only valid with respect to specific temperature criteria. In previous research, Schreier (2001) has shown that the reduction of nitrate by SMI-III[®] is a zeroth order reaction, as described by Equation 4.

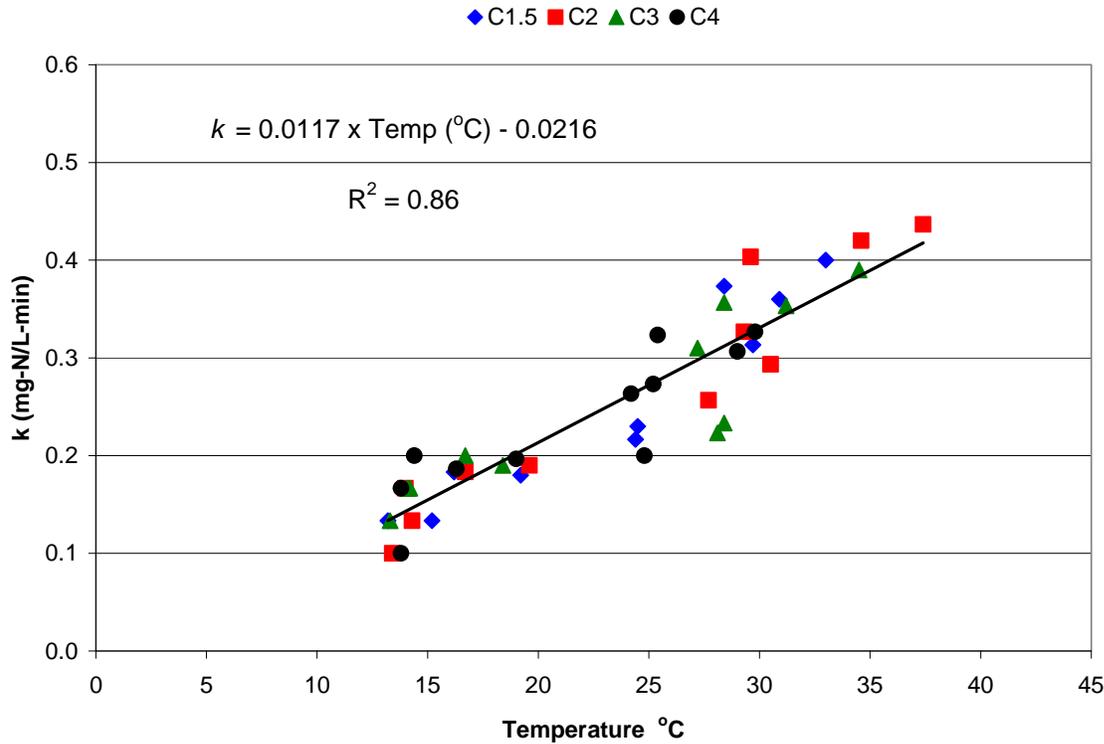
$$\text{Equation 4: } (k)EBCT = [NO_3^-]_0 - [NO_3^-]_{EBCT}$$

- Where: $[NO_3^-]_0$ is the initial nitrate concentration (mg-N/L)
 - $[NO_3^-]_{EBCT}$ is the column effluent nitrate concentration (mg-N/L)
 - k is the zeroth order rate constant (mg-N/L-min)
 - EBCT is the empty bed contact time (min)

A zeroth order reaction implies that the reduction of nitrate is dependent only on the contact time and that the reduction happens at a constant rate regardless of the concentration of the constituents. In order for this to be valid for SMI-III[®], a constant influent pH must be assumed as the Phase A results have shown that influent pH has an impact on the amount of nitrate reduced. Equation 1 was solved to find zeroth order rate constant, k , using the appropriate nitrate concentration and an EBCT of 30 minutes, corresponding to the column design parameters. The

resulting rate constants for all data from all columns were plotted versus the temperature of the sample as shown in Figure 7-7.

Figure 7-7 Rate constant k (mg-N/L-min) plotted versus temperature



The regression of the trend line was then used to develop an expression for the effect of temperature on the nitrate reduction reaction by SMI-III[®]. The mathematical expression is shown in Equation 5.

Equation 5: $k = 0.0117 \times \text{Temperature}(^{\circ}\text{C}) - 0.0216$

Equation 5 can be used as a model to predict the amount of nitrate that will be removed at a given temperature with a 30 minute EBCT and raw water pH of 6.0. To verify this, the value of k was calculated for all the temperatures measured in this study for all four columns. Each of those predicted k values were then used to calculate a model-predicted delta nitrate with Equation 5. The model-predicted nitrate reduction is then plotted versus the actual nitrate reduction as shown in Figure 7-8.

Figure 7-8 Predicted nitrate reduction plotted versus actual nitrate reduction

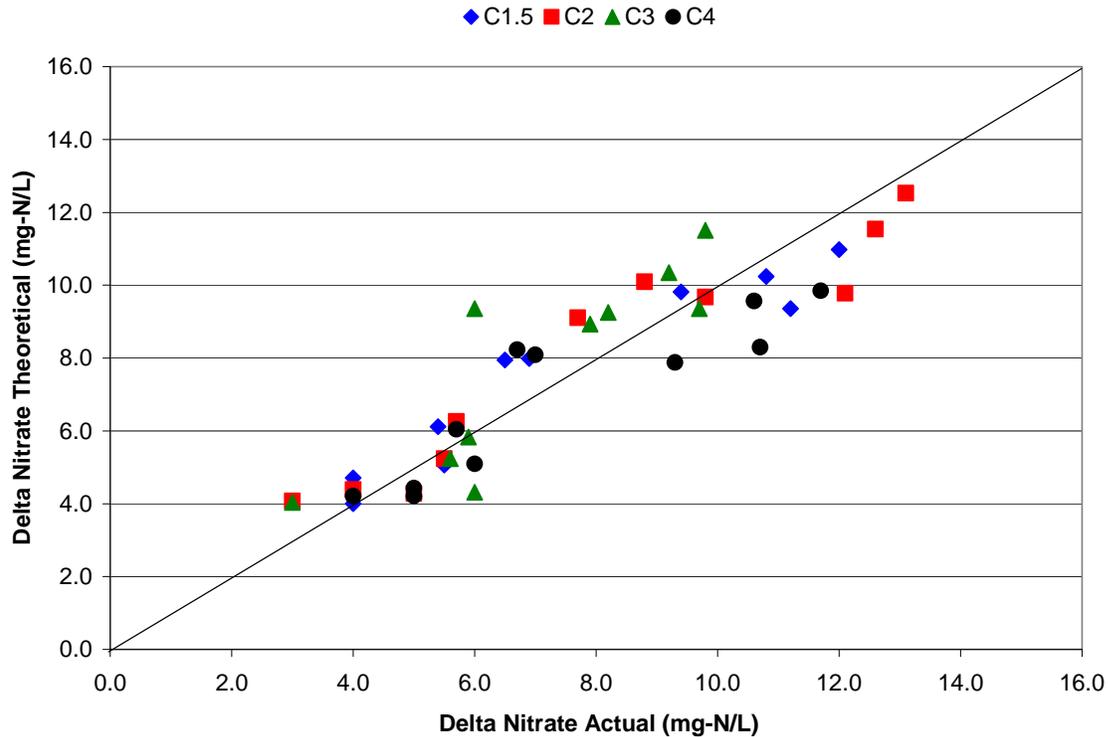


Figure 7-8 shows that Equation 5 is an effective tool for predicting the amount of nitrate removal for a given temperature with a 30 minute EBCT and raw water pH of 6.0. The model’s robustness was further verified by the data presented by Schreier (2008)¹ in Table 2 of the report entitled “*Progress Report, Evaluation of SMI (NF-3) Lot#20071219.*” The data showed the nitrate removal for a column study that had an EBCT of 20 minutes and a pH of 6. It is important to remember that EBCT is a variable in Equation 1; therefore, the relationship should be valid for columns of varying EBCTs. In that study, the average of all the nitrate reduction over then 19 day period is 4.74 mg-N/L. Using both Equation 4 and Equation 5 with an assumed indoor temperature of 22°C, the model predicted a nitrate removal of 4.72 mg-N/L.

7.3 Summary

This investigation confirmed that nitrate reduction via SMI-III[®] is independent of the HLR. Future SMI-III[®] treatment systems can be designed without restriction of the reactor vessel

¹ Schreier, Cindy. (2008). *Progress Report, Evaluation of SMI (NF-3), Lot#20071219*



dimensions. Future vessels can be adapted to existing site constraints without being limited to height:width ratios that would exist if nitrate reduction were to depend on HLR.

The results of this investigation highlight the effect of temperature on the nitrate reduction reaction and developed a cursory tool to predict the amount of nitrate reduction that can be accomplished at a given temperature, 30 minute EBCT, and a pH of 6.0. This tool can be used to assist in the design of future installations as an appropriate EBCT could be determined based on the raw water nitrate concentration and the temperature range of the source water.

8.0 References

- Alowitz, M.J. and Scherer, M.M. 2002. Kinetics of nitrate, nitrite, and Cr(VI) reduction by iron metal. *Environ. Sci & Technol.*, 36(3): 299-306.
- Brandhuber, P., M. Frey, M. J. McGuire, P. Chao, C. Seidel, G. Amy, J. Yoon, L. McNeill, and K. Banerjee. 2004. Low-Level Hexavalent Chromium Treatment Options: Bench-Scale Evaluation, Denver, CO: AwwaRF
- Choe, S., Liljestrand, H. M., Khim J. (2004) Nitrate Reduction by Zero-valent Iron Under Different pH Regimes, *Applied Geochemistry*, 19(3), 335-342.
- Chen, Y.-M., Li C.-W. and Chen, S.-S., Fluidized zero valent iron bed reactor for nitrate removal, *Chemosphere* Vol. 6, pp:753-759 (2005)
- Cheng, I.F.; Muftikian, R.; Fernando, Q.; Korte N. (1997). Reduction of Nitrate to Ammonia by Zero-Valent Iron. *Chemosphere* 35(11), 2689
- Helsel, D.R., & Hirsch, R.M. (1995). *Statistical Methods in Water Resources*, Amsterdam: Elsevier Science Publishers B.V.
- Huang Z.C. and Zhang T.C. (2005). Enhancement of Nitrate Reduction in Fe₀-Packed Columns by Selected Cations. *Journal of Environ. Eng.*, 131(4) 603-611.
- Huang, C.-P.; H.-W. Wang; P.-C. Chiu. (1998). Nitrate Reduction by Metallic Iron, *Water Research.*, 32(8), 2257.
- Huang, Y.H. and Zhang, T.C. (2004) Effects of Low pH on Nitrate Removal with Iron Powder. *Water Res.*, **38**:2621-2642.
- Schreier, Cindy G. (2001). *Report of Findings: Removal of Nitrate From Drinking Water Using Sulfur-Modified Iron (SMI)*. Unpublished report from Prima Environmental, Sacramento CA. July 3.



- Schreier, Cindy G. (2003). *Technical Review of Field Pilot Testing for the Removal of Nitrate from Drinking Water by Sulfur-Modified Iron-III (SMI-III[®])*. Unpublished report from Prima Environmental, Sacramento CA. October 15.
- Schreier, Cindy G. (2006). *Evaluation of Acid Pre-treatment to Prevent Precipitation of Calcium Carbonate in an SMI[®]III Bed*. Unpublished report from Prima Environmental, Sacramento CA. January 24.
- Schreier, Cindy. (2008). *Progress Report, Evaluation of SMI (NF-3), Lot#20071219*. Unpublished report from Prima Environmental, Sacramento CA. March 24.
- Siantar, D.P.; C.G. Schreier; M. Reinhard. (1996). Treatment of 1,2-Dibromo-3-chloropropane- and Nitrate-contaminated Water with Zero-Valent Iron or Hydrogen/Palladium Catalysts, *Water Research.*, 30(10), 2315.
- Su, C. and Puls, R. W. (2001). "Arsenate and Arsenite removal by Zero Valent Iron: Kinetics, Redox, Transformation, and Implications for In-situ Groundwater Remediation." *Environ. Sci. Technol.*, 35(7), 1487-1492.
- Standard Methods for the Examination of Water and Wastewater* (1995), 19th Edition. American Public Health Association. USA.
- Westerhoff, P. (2003). Reduction of Nitrate, Bromate, and Chlorate by Zero Valent Iron. *J. Envir. Engrg.*, 129(1), 10.
- Westerhoff, P. and James, J. (2003). Nitrate removal in zero-valent iron packed columns. *Water Research*, 37(8), 1818
- Zawaideh, L.L., and Zhang, T.C. (1998). The effects of pH and addition of an organic buffer (HEPES) on nitrate transformations in Fe⁰-water systems." *Water Sci. Technol.*, 38(7), 107-115.