FINAL REPORT

Nitrate Treatability Study

DECEMBER 12, 2013

NORTHERN ARIZONA UNIVERSITY
Bero Engineering LLC

Final Report: Nitrate Treatability Study

Table of Contents

1.0 Introduction

This document is the final report for the Nitrate Treatability Study (NTS) for domestic single family style well drinking water delivery systems. The NTS is funded by Bero Engineering LLC and is administered by the Environmental Engineering department at Northern Arizona University. This report details the NTS project background, technology selection, synthetic water for experiments, scale up calculations, and recommended system configuration. The project shows the process of selecting a technology, applying the technology in a laboratory setting on a small scale, and providing recommended system configurations to meet the project constraints and criteria developed in the project proposal.

1.2 Purpose

Dr. Bridget Bero, The Chair of the Civil and Environmental Engineering program at Northern Arizona University has made a request for the study of nitrate removal technologies. The goal of the study is to select a nitrate treatment technology to treat groundwater for nitrate contamination in single family households in the United States of America who get drinking water from a contaminated aquifer via a well. Nitrate contaminated aquifers are common in areas where there is agricultural activity. Currently there are very limited options on the market for nitrate treatment systems for small scale applications.

The project will be considered a success if the following constraints and criteria are met.

Project Criteria:

- Concentration of modeled groundwater is 20 mg/L NO_3-N and 40 mg/L SO_4
- Flow rate of modeled groundwater is 0.2 gallons per minute

Project Constraints:

- The recommended system must have a short implementation time
- The recommended system must be cost effective due to limited economic support for small private water treatment systems
- The recommended system will remove at least 80% of the initial concentration of nitrate
- The recommended system must have a service period of at least 1 month
- The recommended system must be low maintenance

1.3 Project Background

Agricultural activities have been shown to cause nitrate contamination in shallow groundwater aquifers as shown in a recent nationwide study. The study shows that concentrations of nitrate over 1 mg/L or 1 ppm indicate human activity (Dubrovsky, 2010). Citizens who employ a private well drinking water delivery system who live in areas with nearby agricultural activity are in danger of the negative health effects associated with nitrate contaminated groundwater. The EPA is Responsible for determining safe levels of nitrate at which no negative health effects are likely, as informed by the Safe Drinking Water Act (SDWA) which calls for Maximum Contaminant Level (MCL) of 10 mg/L NO_3-N (US EPA – Drinking Water MCL, 2013).

1.3.2 Nitrate in Drinking Water

Nitrogen is the most abundant element in the atmosphere as it comprises 80% of air (Haller, 1999). Gaseous nitrogen is found in many forms, the major ones being N_2, N_2O, NO, NO_2, NO_3 and NH_3. Some of these gases readily react with rain water, or surface water, to produce nitrate and ammonium ions. These ions become part of the soil layer, eventually permeating through into groundwater aquifers creating a natural background concentration of nitrate and ammonium ions in shallow groundwater aquifers. Described in Figure 1 blow are some sources of groundwater nitrate contamination in agricultural areas.

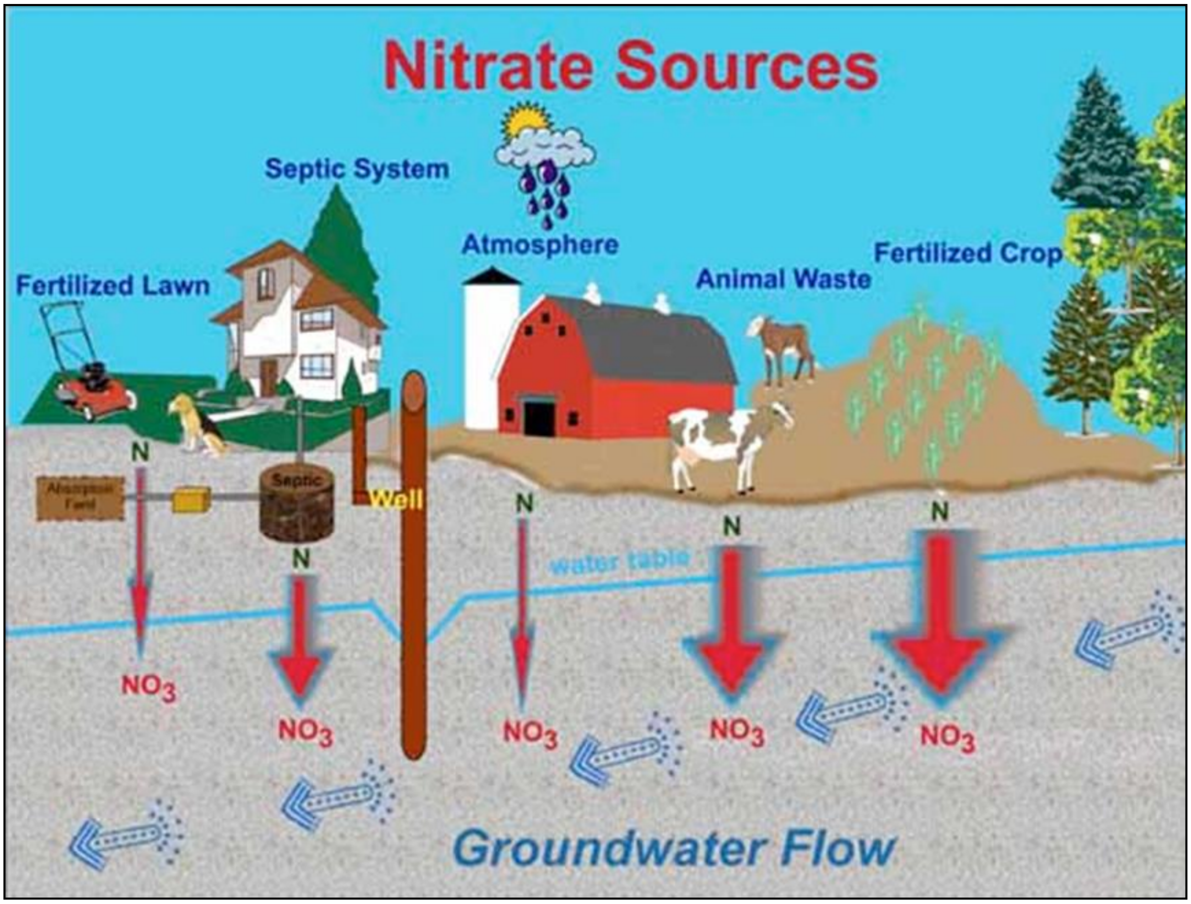


Figure 1: Sources of Nitrate in groundwater in areas of agricultural activity (Portage, 2013)

The sizes of the red arrows in Figure 1 are proportional to the severity of the sources contribution to nitrate contamination in groundwater. As seen in Figure 1, sources for nitrate contamination include leaking septic tanks, ineffective septic leach fields, surface water runoff containing chemical fertilizers and pesticides, animal manure, and erosion of natural deposits (Portage, 2013). Some nitrate also enters water from the atmosphere, which carries nitrogen-containing compounds derived from automobiles, coal-fired generating units and other sources (US EPA - Basic Information about Nitrates, 2011).

Groundwater harvested in the United States of America from domestic single family style well drinking water delivery systems may be contaminated by nitrate. A large portion of the United States of America uses groundwater as its main source of drinking water. Groundwater availability varies geographically, but many properties have aquifers that can supply drinking water to single family households.

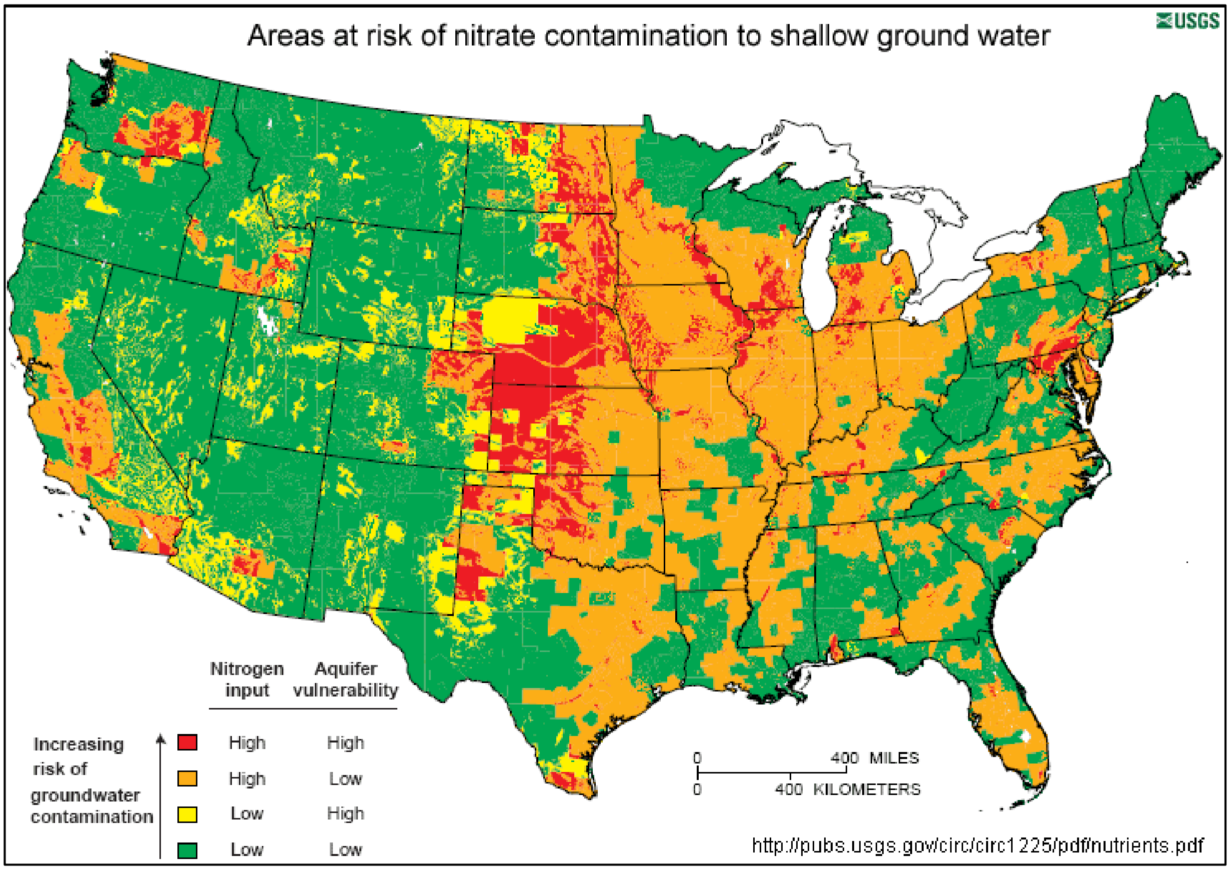


Figure 2: Areas of the United States with the highest risk for contamination of shallow groundwater by nitrate (Dubrovsky, 2010)

Nitrogen contamination is more of a problem in shallow aquifers therefor it is necessary to be aware of aquifers in the United States that would be more at risk for nitrogen contamination (Perlman, 2012). The United States Geological Survey (Dubrovsky, 2010) study developed the map seen in Figure 2. The map shows areas of the United States with risk for nitrate contamination of shallow groundwater aquifers.

Single family households that ingest nitrate at a concentration above 10 mg/L NO_3-N are considered to be at risk by the (US EPA – Drinking Water MCL, 2013). Undetectable to our senses, nitrate has no color, taste or smell at concentrations observed in drinking water supplies. Nitrate does not cause discoloration of plumbing fixtures and does not affect laundering or other non-potable domestic water uses. Nitrates present in a water supply can be indication of other contaminants in that source of water (DeSilva, 2003).

1.3.3 Impacts Due to Nitrate in Drinking Water

Approximately 15% of Americans who live in the United States rely on a personal water supply to provide drinking water for their household. The majority of domestic single family-style wells draw from groundwater as their primary source of drinking water. The USGS estimated 98% of self-supplied drinking water is from groundwater wells (Kenny, 2009). Furthermore, the USGS documented nitrate levels above MCL under SDWA in over 20% of shallow drinking water wells in agriculture areas of the United States (Stewart, 2012).

In humans, too much nitrate can cause a restriction of oxygen transport in the blood stream. Infants younger than 6 months of age lack the enzyme necessary to remedy the condition thereby acquiring Methaemoglobinemia commonly known as "blue baby syndrome" (US EPA - Basic Information About Nitrates, 2011). Pregnant woman and children less than 1 year of age should never drink water contaminated with nitrate. Nitrate has also been shown to cause shortness of breath in some adults with weakened immune systems and elderly.

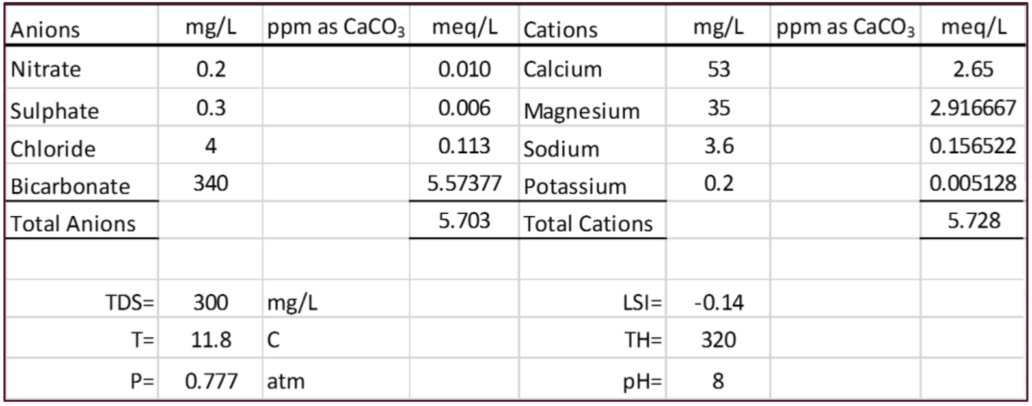
2.0 Synthetic Water for Experiments

The purpose of the Synthetic Water for Experiments is to mimic contaminated groundwater. The synthetic water will be used to confirm the selected technologies ability to meet the goal of the NTS project in the laboratory. Raw water from Flagstaff Arizona's Lake Mary groundwater treatment facility was chosen as the base of the Synthetic Water for Experiments with the selected technology. Lake Mary groundwater was selected for the following reasons:

- The Lake Mary water treatment plant provided a water analysis of the Lake Mary groundwater so there was no need to conduct an analysis of the raw water
- Lake Mary groundwater contains contaminants common to many groundwater aquifers used for drinking water

See Table 1 on the next page for the raw groundwater analysis from the Lake Mary treatment facility. Although the raw Lake Mary groundwater is similar to many groundwater aquifers, the concentration of nitrate was well below the project constrained modeled water concentration of 20 mg/L NO_3-N and 40 mg/L SO_4. To add a bit of a factor of safety over the modeled water concentration levels the concentrations in the synthetic water where increased to 26 mg/L NO_3-N and 40 mg/L SO_4 by adding sodium nitrate (Na-NO_3) and sodium sulfate (Na_2-SO_4) to the Lake Mary groundwater. The modified Lake Mary groundwater is considered to be the Synthetic Water for Experiments. See Table 2 on the next page for the theoretical analysis of the Synthetic Water for Experiments.

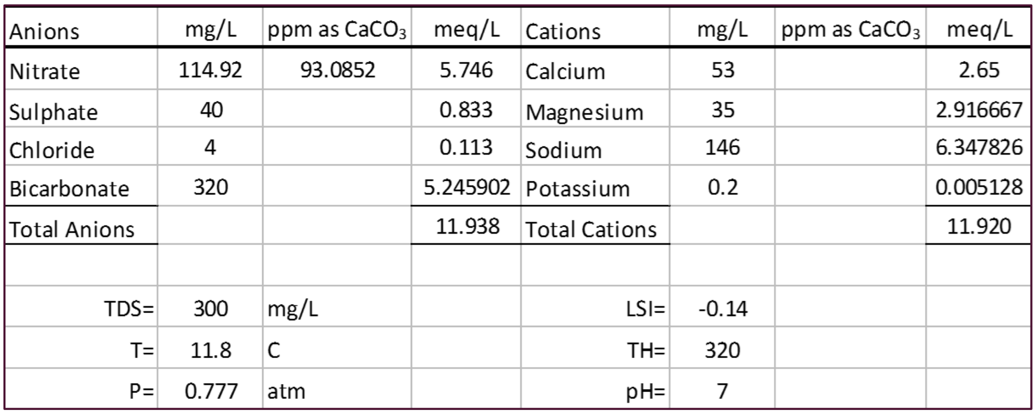
Table 1: Lake Mary Raw Groundwater



Anions	mg/L	ppm as CaCO$_3$	meq/L	Cations	mg/L	ppm as CaCO$_3$	meq/L
Nitrate	0.2		0.010	Calcium	53		2.65
Sulphate	0.3		0.006	Magnesium	35		2.916667
Chloride	4		0.113	Sodium	3.6		0.156522
Bicarbonate	340		5.57377	Potassium	0.2		0.005128
Total Anions			5.703	Total Cations			5.728
TDS=	300	mg/L		LSI=	-0.14		
T=	11.8	C		TH=	320		
P=	0.777	atm		pH=	8		

Table 1 above shows the raw water analysis from the Lake Mary treatment facilities' groundwater well. Notice that the nitrate concentration is 0.2 mg/L NO_3 and 0.3 mg/L SO_4. To convert from mg/L NO_3 to mg/L NO_3-N multiple by a factor of (1/4.42). Table 2 below shows the water theoretical water analysis for the Synthetic Water for Experiments.

Table 2: Synthetic Water for Experiments



Anions	mg/L	ppm as CaCO$_3$	meq/L	Cations	mg/L	ppm as CaCO$_3$	meq/L
Nitrate	114.92	93.0852	5.746	Calcium	53		2.65
Sulphate	40		0.833	Magnesium	35		2.916667
Chloride	4		0.113	Sodium	146		6.347826
Bicarbonate	320		5.245902	Potassium	0.2		0.005128
Total Anions			11.938	Total Cations			11.920
TDS=	300	mg/L		LSI=	-0.14		
T=	11.8	C		TH=	320		
P=	0.777	atm		pH=	7		

Table 2 above shows the Synthetic Water for Experiments. Notice that the nitrate concentration has increased to 114.5 mg/L as NO_3 or 26 mg/L as NO_3-N and the sulfate concentration has increased to 40 mg/L SO_4. The concentration of sodium has increased significantly due to the addition of sodium nitrate and sodium sulfate with the increase of the concentration of nitrate and sulfate. Also notice that the total anions and cations increase with the addition of sodium nitrate and sodium sulfate. The laboratory protocol for making the Synthetic Water for Experiments from Lake Mary groundwater can be found in Appendix 4.

3.0 Technology Selection

The purpose of this technology selection was to choose a technology for treatment of nitrate in domestic single family style well drinking water delivery systems. The technology was selected based on advantages and disadvantages of 5 major treatment options. The 5 major treatment options are ion exchange, reverse osmosis, electrodialysis, biological denitrification, and chemical deniftrication (Jensen, 2012). For the purposes of this report reverse osmosis and electrodialysis will be grouped together under the technology membrane filtration because both of these technologies use a membrane as their primary treatment mechanism. The primary source of information for the selection of the nitrate removal technology was the *Technical Report 6: Drinking Water Treatment for Nitrate* prepared for the California Nitrate Project by the Center for Watershed Science at the University of California, Davis.

3.1 Contaminated Water Description

A single family household is 1 of the many that obtains drinking water from a well. The well is tapping into 1 of the many aquifers contaminated with nitrate. The selected technology for the NTS project will need to be able to treat contaminated water with the concentration equal to the concentrations seen in Table 2: Synthetic Water for Experiments.

3.2 Technology Introduction

In the subsections below ion exchange, membrane filtration, biological denirification and chemical dentrification are introduced.

3.2.1 Ion Exchange

Ion exchange is a reversible reaction in which a charged ion (for the NTS project nitrate) in solution is exchanged for a similarly charged ion. The charged ion in solution will then be stuck to an immobile solid particle called a resin. Ion exchange is generally used for water softening but can be used to remove salts like nitrate. Ion exchange technology is used in individual homes and wastewater treatment plants (Davis, P. 333, 2011).

3.2.2 Membrane Filtration

Reverse Osmosis and electrodialisis are membrane processes that use the difference of the permeability of water constituents as a separation technique. In reverse osmosis the water migrates across the membrane due to a concentration gradient generated by osmotic pressure leaving a concentrated form of the contamination on one side and clean water the other side. In electodialylis an electrical current is used in conjunction with a membrane to desalinated water by separating the ions in the water. Both membrane process produces a desalinated water stream and a concentrated salt waste stream (Davis, P. 369, 2011). In our case the concentrated salt stream would be nitrate.

3.2.3 Biological Denitrification

Denitrification consists of a sequence of enzymatic reactions leading to the evolution of nitrogen gas. Biological denitrification occurs naturally when certain bacteria uses nitrate as there terminal electron acceptor in the repertory system in the absence of oxygen (SOARES, P. 2, 2000). The process involves the formation of a few nitrogen intermediates presented below.

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

Treatment of the water can take place in the aquifer or above ground in large reactors. The denitrifying bacteria require suitable carbon and energy source to thrive. The bacteria may be difficult to stabilize.

3.2.4 Chemical Denitrification

Chemical denitrification uses metals to transform nitrate into other nitrogen species like nitrogen gas. Chemical denitrification is a relatively new technology so there are no full scale systems for the treatment of drinking water for nitrate contamination in the United States of America (Jensen, P.9, 2012). So far the application of chemical denitrification for removal of nitrate in drinking water is limited to pilot or bench scale. Chemical denitrification has the potential to become a feasible option for the NTS project but will require a lot of time and money to implement.

3.3 Technology Advantages and Disadvantages

The general advantages and disadvantages, with respect to nitrate treatment, of the 5 major nitrate removal technologies: ion exchange, reverse osmosis, electrodialysis, biological denitrification, and chemical deniftrication will be presented in this section of the NTS report. Electrodialysis and reverse osmosis will be clumped together under the technology membrane filtration for the rest of this report because they both use membranes as there nitrate treatment mechanism. The table in Appendix 1 was obtained from *The Technical Report 6: Drinking Water Treatment for Nitrate* and presents the advantages and disadvantages of the 5 major treatment options with respect to nitrate treatment in drinking water. *The Technical Report 6: Drinking Water Treatment for Nitrate* was select for the primary source of information for the technology selection component of the NTS project because the purpose of the report was "…to provide a detail guide to the current state of nitrate treatment alternatives that can be used as a reference tool for the drinking water community." (Jensen, P.1, 2012).

3.4 Engineering Analysis of Nitrate Removal Technologies

The Technology Evaluation Criteria have been generated to be used in the evaluation of the 4 major nitrate removal technology alternatives. Each of the alternatives will be rated with respect to the evaluation criteria from 1 to 5 (1 being low and 5 being high).

The technology will be considered good if the technology scores well in a decision matrix with the following Technology Evaluation Criteria: Size, Cost, Waste Stream, Complexity, Resource Demand and Efficiency. Below is a list that describes the Technology Evaluation Criteria used to evaluate the 4 major types nitrate treatment technologies.

Technology Evaluation Criteria:

Size, the nitrate removal system will have to fit into a shed, garage or small outbuilding. A score of 1 in this field means that the technology requires a lot of space. A score of 5 in this field means the design will easily fit in a small space.

Cost, The operation cost and the initial investment cost will be important because the small farming community is expected to have limited economic support. A score of 1 means that that the operation/installation cost of the technology is relatively high with respect to the other technologies being evaluated. A score of 5 means that the operational/installation cost is relatively high with respect to the other technologies being evaluated.

Waste Stream, it is important to have a waste stream that is easily managed. A score of 1 in this evaluation criteria means the waste stream generated by the technology will be hard to dispose of. A score of 5 means the waste stream is easily disposed of.

Complexity, the complexity of the technology will be evaluated to required time necessary to evaluate technology in the lab. A technology will receive a score estimate of 1 if that technology is very complex and requires hard to use equipment to analyze. A technology will receive a score estimate of 5 if that technology is simple and requires relatively simple equipment to analyze.

Resource Demand, the amount of resources (electricity or other) required to operate the technology will be estimated. A score of 1 will reflect a system that uses a lot of resources to operate. A score of 5 will reflect a system that requires very few resources to operate.

Efficiency, the efficiency of the system will be considered to be the resource demand in kilograms per nitrate as nitrogen removed in kilograms. A score of 1 means that the efficiency as stated above is relatively high when compared to the other technologies. A score of 5 means that the efficiency is relatively low when compared to the other technologies.

3.4.1 Evaluation of Alternative Nitrate Removal Technologies

Each of the 4 major nitrate treatment technologies will evaluated using a decision matrix in this section. Each technology will be given a rated using the *Technology Evaluation Criteria* and Appendix 1. The *Technology Evaluation Criteria* all have the same weight. The ratings will be stored in the decision matrix. The ratings for all *Technology Evaluation Criteria* will be summed for each of the nitrate treatment technologies. The highest scoring technology will be the technology that best fits the technology evaluation criteria. Table 3: Decision Matrix on the next page presents the decision matrix for the NTS project.

Table 3: Decision Matrix

Treatment Technology	Size	Cost	Waste Stream	Complexity	Resource Demand	Efficiency	Total
Ion Exchange	4	5	2	5	4	3	23
Membrane Filtration	5	1	2	1	2	3	14
Biological Denitrification	1	1	4	1	5	3	15
Chemical Denitrification	3	2	5	2	4	3	19

Table 3 above shows the total score of the sum of all the Technology Evaluation Criteria for each treatment technology. The reason behind each sore is explained below.

The Ion exchange technology has been evaluated using Appendix 1 from *The Technical Report 6: Drinking Water Treatment for Nitrate*. Ion exchange received a score of 4 for the size because it is used in large and small systems. For NTS the treatment system is considered small. Ion exchange received a score of 4 for cost because ion exchange is financially feasible. Ion exchange received a score of 2 for waste stream because you have to dispose of the brine recharge solution that contains nitrate. Ion exchange received a score of 4 for complexity because there is a lot of information about how it works and good documentation on ion exchange from vendors. Ion exchange received a score of 4 for resource demand because you need a lot of sodium chloride to create the brine recharge solution. Ion exchange received a score of 3 for efficiency because the system requires addition pump power and sodium chloride for operation.

The membrane filtration (reverse osmosis and electrodialysis) technology has been evaluated using Appendix 1 from *The Technical Report 6: Drinking Water Treatment for Nitrate*. Membrane filtration received a score of 5 for size because it fits a small foot print and is good for small POU applications. Membrane filtration received a score of 1 for cost because it is typical for membrane filtration systems to have high capital and operation and maintenance costs. Membrane filtration received a score of 2 for the waste stream because the waste stream is high concentrated and may need special handling for disposal. Membrane filtration received a score of 1 for complexity because membrane filtration systems are highly complex. Membrane filtration received a score of 2 for resource demand because membrane systems have a high energy demand. Membrane filtration received a score of 3 for efficiency because the resulting treated effluent is of a high quality but the required centricity to operate the system is high.

The biological denitrification technology has been evaluated using Appendix 1 from *The Technical Report 6: Drinking Water Treatment for Nitrate*. Biological denitrifcation received a score of 1 for size because systems required a large footprint. Biological denitrification received a score of 1 for cost because it requires a high capital cost. Biological denitrification received a score of 4 for waste stream because the system will produce a low amount of sludge waste. Biological denitrification received a score of 1 for complexity because a high level of monitoring and significant post treatment requirements are needed as well as a high system complexity similar to membrane filtration. Biological denitrification received a score of 5 for resource demand because limited chemical input is required. Biological denitrification received a score of 3 for efficiency even though low chemical input is required there are a lot of man hours required to operate a biological denitrification system.

The chemical denitrification technology has been evaluated using Appendix 1 from *The Technical Report 6: Drinking Water Treatment for Nitrate*. Chemical denitrification received a score of 3 for size because a chemical denitrification system does not take a large amount of space. Chemical denitrification received a score of 2 for cost because the reliability of the system and the implementation cost is unknown. Chemical denitrification received a 5 for waste stream because there is no brine regenerations solution of concentrated waste stream associated with this technology. Chemical denitrification received a score of 2 for complexity because of a large number of unknowns like lack of reliability and operating complication information as well as possible partial denitrification. Chemical denitrification received a score of 4 in resource demand because you need some but not a lot of resources to run a chemical denitrification system. Chemical denitrification received a score of 4 for efficiency because of the possibility of partial denitrification.

3.5 Selected Technology

The resulting scores from the decision matrix evaluating the nitrate removal technologies give ion exchange the highest score. There are 2 options for types of ion exchange resin for removal of nitrate from water. The first type is a non-selective strong base anion exchange resin. The second type is a selective strong base anion exchange resin (PuroLite – Choosing an ion exchange system for nitrate removal, 2013). A selective resin was chosen for this project because it is common for there to be competing ions present in groundwater that do not need to be removed because they are not at levels harmful to human health as suggested by SDWA. If the competing ions are removed with a non-selective resin the exchange capacity for nitrate is lowered. A lower exchange capacity converts to a larger required ion exchange bed volume to remove the same amount of nitrate. Thus, a selective strong base anion exchange resin fits the NTS project

Purolite is a producer of all varieties of ion exchange resins. The Purolite application guide for choosing an ion exchange system for nitrate removal was used to further select a resin (PuroLite – Choosing an ion exchange system for nitrate removal, 2013). See the reference list at the end of this document for a link to a pdf version of the application guide for choosing an ion exchange system for nitrate removal from Purolite. A520E resin was selected out of the 13 resin options presented by Purolite in the application guide because it is a nitrate selective strong base anion exchange resin and because it has relatively low nitrate leakage amount when compared to the other Purolite selective strong base anion exchange resins. The Engineering Bulletin for the Purolite A520E resin contains technical information on the resin and can be found in Appendix 2. The Material Safety Data Sheet (MSDS) for Purolite A520E shows that the hazards for the resin are very low and can be found in Appendix 3.

4.0 Flow Through and Batch Experiments

Flow through and a Batch laboratory experiments where constructed. The purpose of the laboratory experiments is to evaluate the resin to ensure the resin behaves as stated in the Engineering Bulletin by Purolite in Appendix 2. In the Flow Through Experiment the difference in the initial and final concentration of the Synthetic Water for Experiments was analyzed with respect to the amount of water treated in the Flow Through Experiment. In the Batch Experiment the initial and final concentration of the Synthetic Water for Experiments was analyzed for each batch with respect to the amount of resin added to each batch and the volume of Synthetic Water for Experiments in each batch.

The primary goal of the Flow Through Experiment is to prove that the A520E resin behaves consistently after reaching capacity and being recharged. The secondary goal of the flow through experiment is to develop Freundlich parameters to create a solid phase capacity for the A520E resin. The primary goal of the batch experiments is to create more Freundlich parameters to compare with the parameters generated in the flow through experiment. Purolites guide to laboratory testing of ion exchange and adsorbent resins and was used to create the Flow Through experiment. Due to time constraints the recommended bed volume as stated in the Purolite laboratory testing of ion exchange and adsorbent resins document was reduced from a minimum of 50 mL to 10 mL and the flow rate in bed volumes per hour was increased from 500 ml per hour to 2600 ml per hour. The laboratory protocol for the flow through experiments can be found in Appendix 5.

The primary goal of the Batch Experiments was to develop more Freundlich parameters. The Freundlich parameters from the Flow Through Experiment will be compared to the constants developed in the Batch Experiment. The Batch Experimental Protocol can be found in Appendix 6. The laboratory protocol for the batch experiments was developed using an example problem in the Activated Carbon section Hazardous waste Management by LeGrega and the resin capacity as stated by Purolite in Appendix 2. The example problem is for activated carbon but because activated carbon and ion exchange resin are both adsorbents the example problem was adopted for ion exchange. To ensure the batches reached equilibrium the laboratory protocol was modified to have a longer equilibrium period. The Batch Experiment was done in 2 batches. Batch 1 is called Experiment 2A and batch 2 is called Experiment 2B.

The data from all laboratory experiments for the NTS project will be evaluated with a DR 2010 Spectrophotometer. The concentration of nitrate will be determined by the high resolution nitrate as nitrogen program 355. Cadmium reduction reagents are used to intensify the color of nitrate in water. Figure 3 below shows a comparison between a blank 25 mL sample and a 25 mL sample with 26 mg/L NO3-N after the Cadmium reduction reagent has been added to both samples.

Figure 3: Sample Comparison

The sample on the left is the sample with very low nitrate concentrations (below 0.2 mg/L NO_3-N) and the sample on the right is the sample with 26 mg/L NO_3-N. The HATCH DR 2010 Spectrophotometer reads the samples by evaluating what wavelengths of light get stuck in the sample and reports a concentration of mg/L NO_3-N. The HACH DR 2010 Spectrophotometer is accurate to plus or minus 0.5 mg/L NO_3-N.

4.1 Flow Through Experiment Results

The Flow Through Experiment was a huge success. The exit concentration of nitrate in the Synthetic Water for Experiments and the volume of treated Synthetic Water for Experiments from the Flow Through Experiment was used to obtain the primary and secondary goals of the Flow Through Experiment. Figure 3: A520E Resin Concentration Out is shown below and presents the exit concentration of NO_3-N in mg/L in the 10 mL bed volume column versus time in minutes.

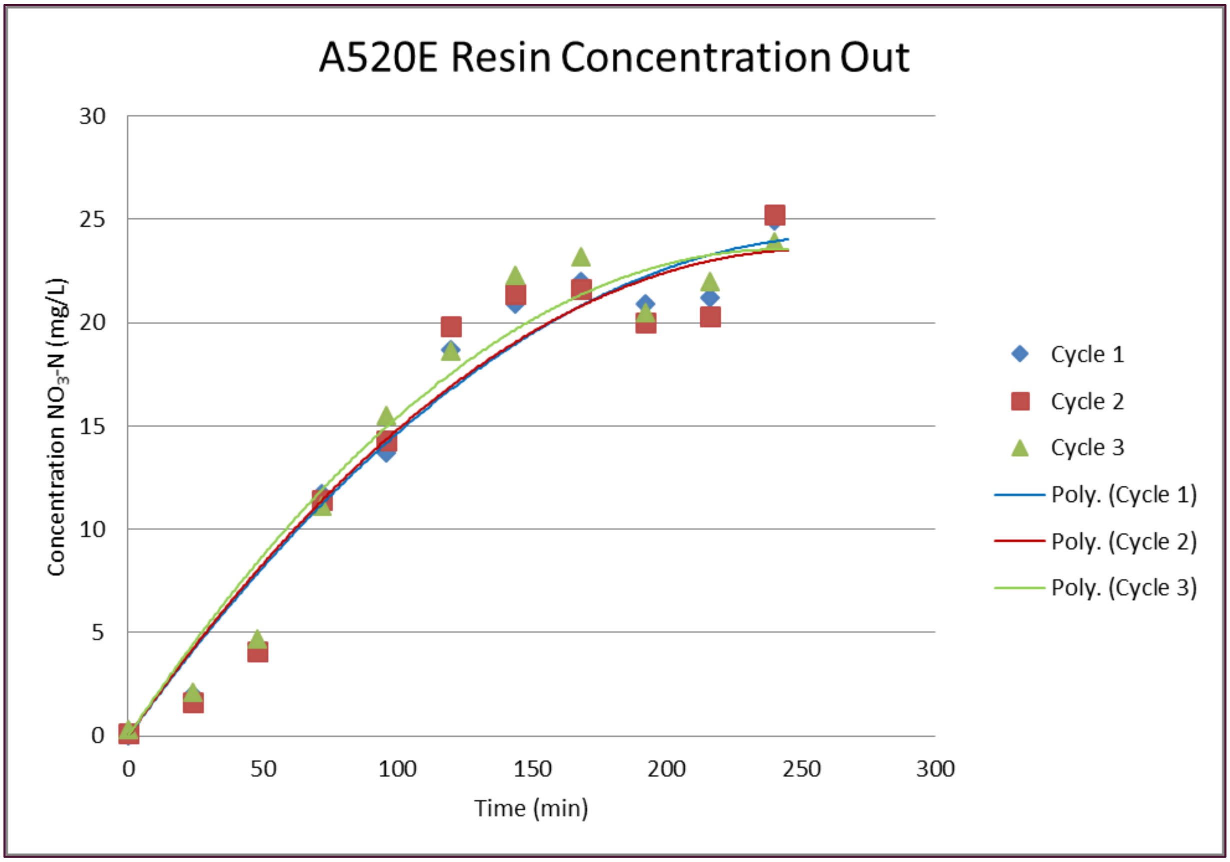


Figure 4: A520E Resin Concentration Out

The data points for each of the 3 cycles of the Flow Through Experiment are almost on top of each other for all 3 cycles. As time goes on and the 10 mL bed volume removes nitrate from the Synthetic Water for Experiments the leakage of the resin increases. The leakage of the resin bed increases as the resin bed reaches. By the time the experiment was over at around 250 minutes the resin bed is at capacity and can no longer remove any nitrate from the influent Synthetic Water for Experiments. Each trend line represents 1 cycle of the experiment. The 3 trend lines are almost on top of each other showing that the resin behaves consistently after reaching capacity and being recharged (1 cycle) and then reaching capacity again (cycle 2) and again (cycle 3).

Fruendlich parameters where generated from the data from the Flow Through Experiment in Appendix 7. The Activated Carbon section of the Hazardous waste Management book by LeGrega was used as a source of information for generating the Fruendlich Parameters. See Appendix 9 Flow Through Results and Scale Up pages 1 and 2 for the calculations to get the solid phase concentration (q in ug NO_3-N per mg resin) and concentration out (C_{out}) of the A520E resin. Figure 4: Linearization of q and C_{out} is shown below and presents the linearization of the solid phase concentration (q) and the concentration of the Synthetic Water for Experiments exiting the 10 mL bed volume column.

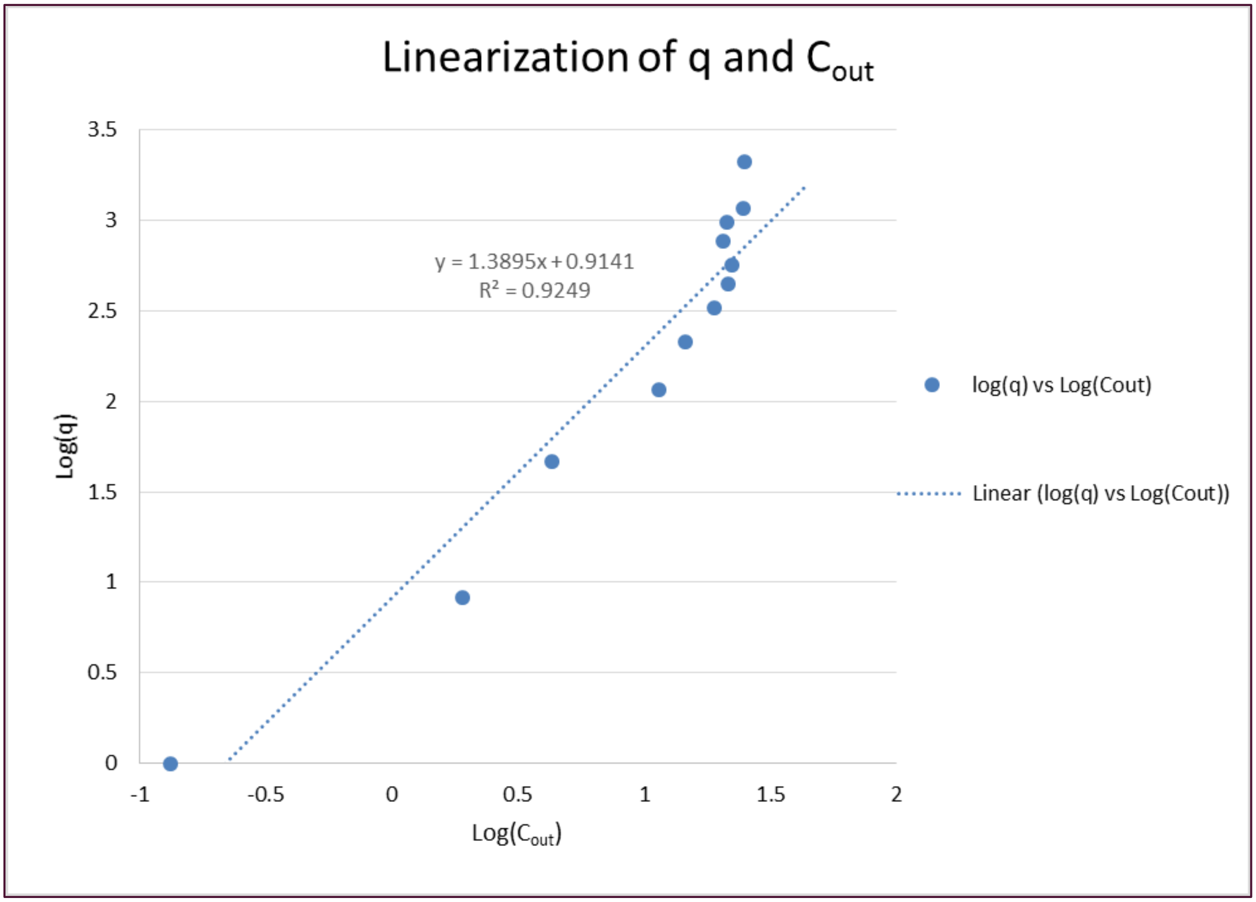


Figure 5: Linearization of q and C_{out}

The equation for the trend line that is match to the linearized solid phase capacity equation below

$$Log(q) = Log(K_f) + \left(\frac{1}{n}\right) * Log(C_{out})$$

Where K_f and (1/n) are the Freundlich parameters, Log(q) is the y-axis and Log(C_{out}) is the x-axis. Matching the resulting equation of the trend line to the equation above K_f is equal to 10^0.9141 or 8.2 and (1/n) is equal to 1.39. The Freundlich parameters are then plugged into the equation to find final solid phase concentration (q_f) for the A520E resin during the Flow Through Experiment. The Freundlich parameters are then plugged into the equation below to solve for q_f, the solid face capacity of the A520E resin.

$$q_f = K_f * C_{Out\ Design}^{1/n}$$

Where the concentration out for the design ($C_{out\ design}$) is the target concentration for the design scale up and is equal to 2 mg/L. Solving the equation for the final solid phase concentration results in q_f=21.5 ug NO_3-N per mg Resin. The final solid phase concentration will be used in the scale up calculations to determine the required column height to go from initial concentration ($C_{in\ design}$) of 20 mg/L NO_3-N and a final concentration of ($C_{out\ design}$) 2 mg/L while in the presence of 40 mg/L SO4.

4.2 Batch Experiment Results

The results for the Batch Experiment where promising but something went wrong. Experiment 2A data that is presented in Appendix 8 Batch Experiment Data results in solid phase concentration (q) that do not make sense. Furthermore the final concentration of Synthetic Water for Experiments for each volumetric flask was higher for the low mass flasks than the initial concentration of the Synthetic Water for Experiments. As you can see from the Concentration Data for Experiment 2A table in Appendix 8 Flask number 3 has a final concentration of 28.0 mg/L NO3-N and the initial concentration for the Synthetic Water for Experiments is 26 mg/L. A possible source for error is that expired HACH reagents for program 355 on the HACH DR 2010 where used because fresh HACH reagents disappeared from the laboratory. The old HACH reagents may be the reason for the strange data.

Currently a second Batch Experiment indexed 2B is underway and is awaiting fresh HACH reagents for the DR 2010 to arrive. Once the reagents arrive the data from Batch Experiment 2B will be analyzed and Freundlich Parameters will be generated and compared to the Freundlich Parameters generated in the Flow Through Experiment. It is expected that the results will generated Freundlich Parameters close in value to the Fruendlich Parameters generated in the Flow Through Experiment. As you can see in Appendix 8 the final concentration data is missing from the Concentration Data for Experiment 2A table.

5.0 Scale Up Calculations

Scale up calculations where generated using 2 methods for redundancy. The goal of the scale up calculations is to optimize a system to the constraints and criteria of the NTS Project in the purpose section of this report.

The first method is a scale up using the final solid phase capacity (q_f) generated from Fruendlich Parameters from the Flow Through Experiment. The second method is an application of Appendix 2: The A520 Engineering Bulletin from Purolite which gives guidelines on how to determine how much resin is required for a certain throughput of modeled contaminated groundwater. Both methods where calculated in Microsoft Excel and use the Table of Equivalent mass in Appendix 11. Both methods use a project constrained design period for the scale up calculation of 1 month with a flow rate of 0.2 gallons per minute.The scale up calculations for the first method can be found on page 4 of Appendix 9. The initial conditions for the scale up calculation for the first method are presented below:

- $C_{in} = 20\frac{mg}{L}NO_3 - N + 40\frac{mg}{L}SO_4$

- $C_{out} = 2.0 \frac{mg}{L} NO_3 - N + 40 \frac{mg}{L} SO_4$
- $Q = 8640\ gallons/month$
- $Design\ factor = 0.85$

The resulting required bed volume using the solid phase capacity (q_f) is 3.54 ft^3 of A520E resin. The scale up calculations for the second method can be found in Appendix 10. The initial conditions for the scale up calculation for the second method are presented below:

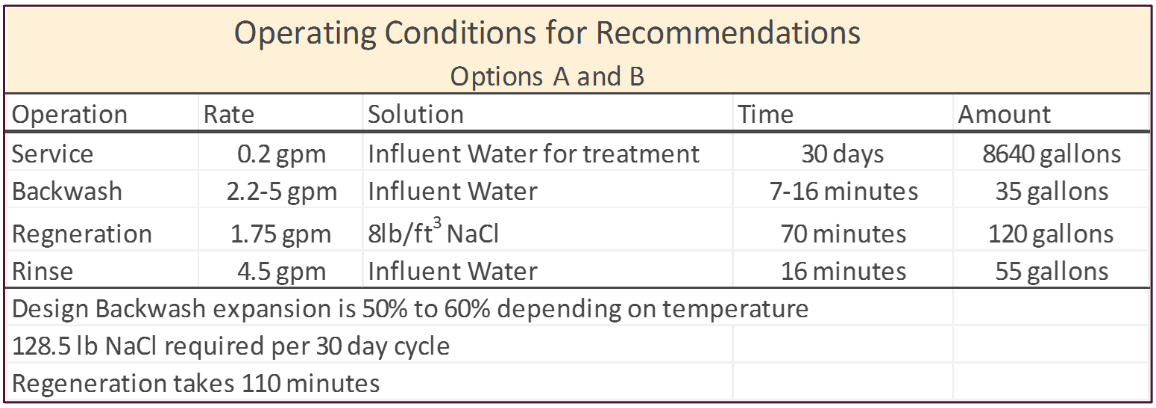
- $C_{in} = 20 \frac{mg}{L} NO_3 - N + 40 \frac{mg}{L} SO_4$
- $C_{out} = 3.6 \frac{mg}{L} NO_3 - N + 40 \frac{mg}{L} SO_4$
- $Q = 8640\ gallons/month$
- $Design\ factor = 0.85$

The resulting required bed volume using the A520E Documentation is 3.50 ft^3 of resin and the resulting concentration out (C_{out}) using the Figure 2 in Appendix is 3.6 mg/L NO_3-N. The resulting concentration out using was selected as 2 mg/L NO_3-N. Both methods result in almost the same size required bed volume. A design size of 3.50 ft^3 was selected as the design size for the recommended system configuration which is explained in the next section.

6.0 Recommended System Configuration

The purpose of the recommended system configuration is to supply some of the primary calculations for the implementation of A520E ion exchange nitrate treatment system as well as a basic parts list and cost estimate. The recommended system configuration uses the scale up calculation inputs and the A520E Engineering Bulletin. The recommended system configuration calculations can be found on page 2 of Appendix 10. 2 recommended system configurations are provided: Option A and Option B. 2 recommended system configurations are provided to give some variance in system shape and operating pressure drop. The operating conditions for the recommendation options are presented in Table 4 below.

Table 4: Operation Conditions for Recommendations



Operating Conditions for Recommendations

Options A and B

Operation	Rate	Solution	Time	Amount
Service	0.2 gpm	Influent Water for treatment	30 days	8640 gallons
Backwash	2.2-5 gpm	Influent Water	7-16 minutes	35 gallons
Regneration	1.75 gpm	8lb/ft^3 NaCl	70 minutes	120 gallons
Rinse	4.5 gpm	Influent Water	16 minutes	55 gallons
Design Backwash expansion is 50% to 60% depending on temperature				
128.5 lb NaCl required per 30 day cycle				
Regeneration takes 110 minutes				

Table 4 shows the operating conditions for both recommendations options. The design back wash expansion flow rate and pressure drop was determined using Figures 1 and 2 in Appendix 2. The volume of backwash, regeneration, and rinse have all been chosen conservatively. The regeneration cycle should take 60 minutes to set up, 110 minutes to run, and another 60 minutes to clean up. The waste regeneration solution should be taken to the nearest wastewater treatment plant for disposal as recommended by Purolite's A520E Engineering Bulletin in Appendix 2.

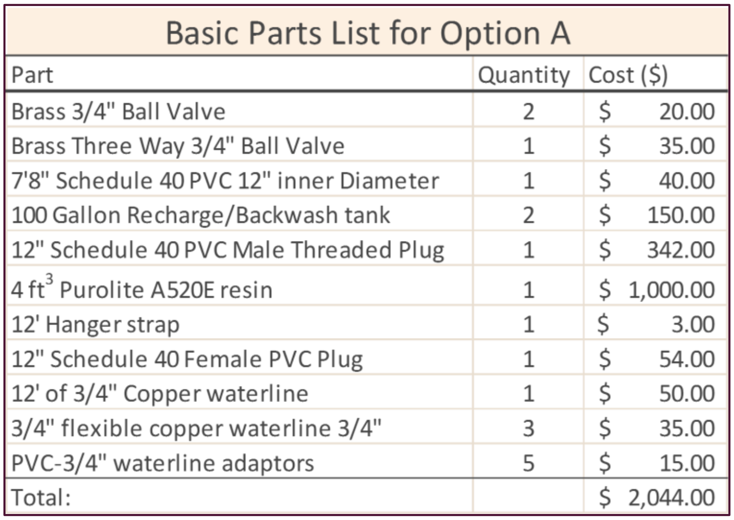
6.1 Option A

Option A is the taller option and has a filter body that is 7.5 feet tall and has a 1 foot inside diameter. The inside volume of the filter body is 60% larger than required to account for the back wash expansion. An AutoCAD representation of Option A can be found in Appendix 13. The results for the design calculations for the option A configuration are presented below:

- Service pressure drop: 5.79 to 13.4 PSI depending on temperature
- Backwash flow rate: 2.2 gpm
- Regeneration volume: 105 gallons
- Regeneration brine concentration: 8 lb/ft3
- Suggested operating temp range: 41°F to 120° F

A cost estimate for the system has been made using the parts list presented in Table 5. The parts list was developed to create the rough cost estimate. All the costs were found on trustworthy online stores and have been inflated 20%.

Table 5: Basic Parts List for Option A



Basic Parts List for Option A

Part	Quantity	Cost ($)
Brass 3/4" Ball Valve	2	$ 20.00
Brass Three Way 3/4" Ball Valve	1	$ 35.00
7'8" Schedule 40 PVC 12" inner Diameter	1	$ 40.00
100 Gallon Recharge/Backwash tank	2	$ 150.00
12" Schedule 40 PVC Male Threaded Plug	1	$ 342.00
4 ft^3 Purolite A520E resin	1	$ 1,000.00
12' Hanger strap	1	$ 3.00
12" Schedule 40 Female PVC Plug	1	$ 54.00
12' of 3/4" Copper waterline	1	$ 50.00
3/4" flexible copper waterline 3/4"	3	$ 35.00
PVC-3/4" waterline adaptors	5	$ 15.00
Total:		$ 2,044.00

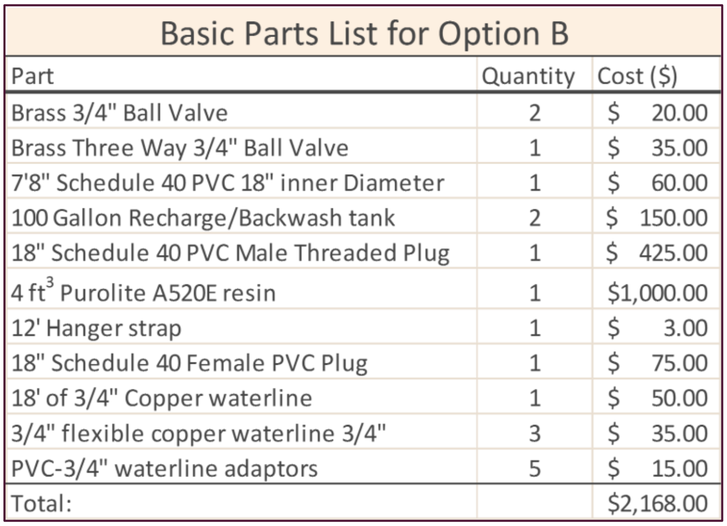
6.2 Option B

Option B is the shorter wider option and has a filter body that is 3.5 feet tall and has a 1.5 foot inside diameter. The inside volume of the filter body is 60% larger than required to account for the back wash expansion. An AutoCAD representation of Option A can be found in Appendix 14. The results for the design calculations for the Option A configuration are presented below:

- Service Pressure drop: 1.37 to 3.96 PSI
- Backwash flow rate: 5 gpm
- Regeneration volume: 105 gallons
- Brine concentration:8 lb/ft3
- Temp range: 41°F to 120° F

A cost estimate for the system has been made using the parts list presented in Table 5. The parts list was developed to create the rough cost estimate. All the costs were found on trustworthy online stores and have been inflated 20%.

Table 6: Basic Parts List for Option B



Basic Parts List for Option B

Part	Quantity	Cost ($)
Brass 3/4" Ball Valve	2	$ 20.00
Brass Three Way 3/4" Ball Valve	1	$ 35.00
7'8" Schedule 40 PVC 18" inner Diameter	1	$ 60.00
100 Gallon Recharge/Backwash tank	2	$ 150.00
18" Schedule 40 PVC Male Threaded Plug	1	$ 425.00
4 ft^3 Purolite A520E resin	1	$1,000.00
12' Hanger strap	1	$ 3.00
18" Schedule 40 Female PVC Plug	1	$ 75.00
18' of 3/4" Copper waterline	1	$ 50.00
3/4" flexible copper waterline 3/4"	3	$ 35.00
PVC-3/4" waterline adaptors	5	$ 15.00
Total:		$2,168.00

The implementation cost of either option A or B has been estimated to be $2500.00 plus or minus $200.00 assuming a technical rate of $25.00 per hour. An ongoing cost of $168.00 per year for sodium chloride to make the brine recharge solution plus $1150.00 per year in man hours required for the recharge procedure.

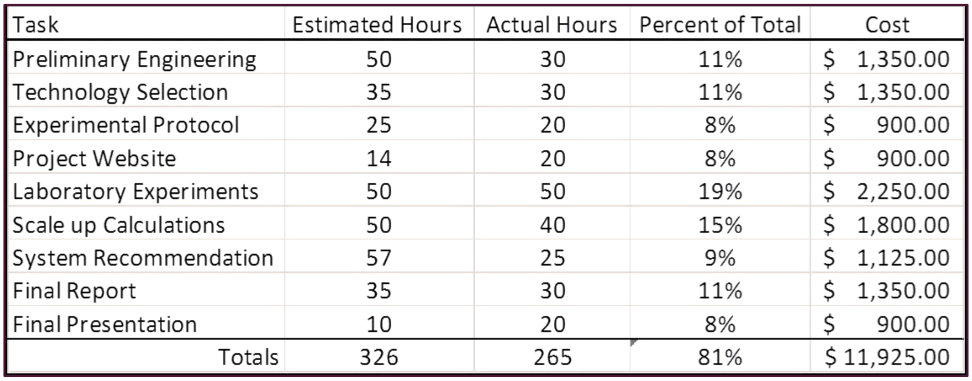
7.0 Conclusion

The NTS project was a success. Ion Exchange is a viable option to treat nitrate contaminated groundwater while being within project criteria and constraints. The NTS project met all of the project constraints and criteria.

The recommended systems were designed to treat contaminated groundwater at a rate of 0.2 gallons per minute with an influent concentration of 20 mg/L NO_3-N and 40 mg/L SO_4. The treatment system's A520E ion exchange resin is ready to go directly after preconditioning so the implementation time is short. The preconditioning is a short brine recharge cycle. The system is cost effected due to very limited alternatives for small nitrate treatment systems. Both scale up methods and recommended options result in over 80% remove of nitrate. Both design recommendations and scale up calculation techniques are designed around a 1 month (30 day) service cycle. After 30 days the bed volume needs to be backwashed to free and suspended solids that have become stuck to the resin bed, regenerated with a brine solution, and rinsed before the resin bed is ready for another 30 day service cycle. The system is low maintained with an estimated 46 man hours required each year to service the resin bed each year.

To conclude on the project I have included a Table 7 which presented a distribution of the hours spent on this project. The Table breaks the project down to hours spent on Tasks. The tasks in this table correlate to the final NTS project schedule that is included in Appendix 15. Table 7 below presents the distribution of hours spent on the NTS project.

Table 7: Distribution of Hours by Task



Task	Estimated Hours	Actual Hours	Percent of Total	Cost
Preliminary Engineering	50	30	11%	$ 1,350.00
Technology Selection	35	30	11%	$ 1,350.00
Experimental Protocol	25	20	8%	$ 900.00
Project Website	14	20	8%	$ 900.00
Laboratory Experiments	50	50	19%	$ 2,250.00
Scale up Calculations	50	40	15%	$ 1,800.00
System Recommendation	57	25	9%	$ 1,125.00
Final Report	35	30	11%	$ 1,350.00
Final Presentation	10	20	8%	$ 900.00
Totals	326	265	81%	$ 11,925.00

The NTS project was completed in 81 percent of the hours that where estimated for the project during the proposal phase. The NTS project totaled 265 engineer hours at a rate of $45.00 per hour totaling $11,925.00. An addition $100.00 was spent on printing and an addition $100.00 was spent on laboratory materials. The total cost of services for this project is $12,125.00.

Finally I would like to thank you for your interest in my project. Please direct any questions or concerns related to the references, laboratory experiments, scale up calculations, and system configuration recommendations to either my email or phone number supplied below.

Zach Raymond-Becker, EIT

Email: Ztr5@nau.edu

Phone: (206) 948-5615

Reference List

Davis, M. (2011). *Water and Wastewater Engineering*. McGraw Hill Professional. Print.

DeSilva, Francis J. "Nitrate Removal by Ion Exchange." *Water & Wastes Digest.* (2003): 9-11,30. Print.

Dubrovsky, N.M., et al. (2010). The quality of our Nation's waters—Nutrients in the Nation's streams and groundwater, 1992–2004: *U.S. Geological Survey Circular 1225.* Retrieved on 10/10/13 from: pubs.usgs.gov.cric1225/pdf/nutrients.pdf

Haller, L., McCarthy, P., OBrian, T., Riehle, J., & Stuhldreher, T. (1999). Nitrate pollution of groundwater. Retrieved 3/20/2013 from http://www.reopure.com/nitratinfo.html

Jensen, V.B., Darby, J.L., Seidel, C. & Gorman, C. (2012) *Drinking Water Treatment for Nitrate, Technical Report 6* in: Addressing Nitrate in California's Drinking Water with a Focus on Tulare Lake Basin and Salinas Valley Groundwater. Report for the State Water Resources Control Board Report to the Legislature. Center for Watershed Sciences, University of California, Davis.

Kenny, J.F., Barber, N.L., Hutson, S.S., Linsey, K.S., Lovelace, J.K., and Maupin, M.A. (2009). Estimated use of water in the United States in 2005: U.S. Geological Survey Circular 1344

LaGrega, M. D., Buckingham, P. L., Evans, J. C., & Environmental Resources Management (Firm) (2010). Hazardous waste management. Long Grove, Ill: Waveland Press, Inc. Print.

Perlman, H. (06 Mar 2012) *Nitrate and Water* Accessed: 21 Apr 2013. From: http://ga.water.usgs.gov/edu/nitrogen.html

PuroLite – Choosing an ion exchange system for nitrate removal (2013). Retrieved on Tuesday December 8th, 2013 from http://purolite.com/Customized/CustomizedControls/Products/Resources/rid_743.pd

PuroLite – Laboratory testing of ion exchange and adsorbent resins (2013). Retrieved on Tuesday December 8th, 2013 from http://www.purolite.com/Customized/Customized Controls/Products/Resources/rid_838.pdf

Portage (2013). Retrieved on 4/25/2013 from http://www.co.portage.wi.us/groundwater/undrstnd/no3.htm

Stewart, S. State of Oregon Department of Environmental Quality, Water Quality Division. (2012). *Nitrate in drinking water* (11-WQ-012)

SOARES, M. I. M. (2000). Biological denitrification of groundwater. Kluwer Academic Publishers, 123, 183-193. Retrieved from http://download.springer.com/static/pdf/940/art%3A10.1023%2FA%3A1005

US EPA - Basic Information about Nitrates. (2011). Retrieved on 4/25/2013 from http://water.epa.gov/drink/contaminants/basicinformation/nitrate.cfm

US EPA – Drinking Water MCL. (2013). Retrieved on 9/12/2013 from http://water.epa.gov/drink/contaminants/

Appendix List

1. Appendix 1: Treatment Comparison
2. Appendix 2: Purolite A520E Engineering Bulletin
3. Appendix 3: Purolite A520E MSDS
4. Appendix 4: Laboratory Protocol for Synthetic Water
5. Appendix 5: Laboratory Protocol for Flow Through Experiment
6. Appendix 6: Laboratory Protocol for Batch Experiment
7. Appendix 7: Flow Through Experiment Data
8. Appendix 8: Batch Experiment Data
9. Appendix 9: Flow Through Experiment Results
10. Appendix 10: Scale up Design using A520 Engineering Bulletin
11. Appendix 11: Table of Equivalent Mass
12. Appendix 12: Lab Rig Flow Rate Tests
13. Appendix 13: Recommended Configuration Option A
14. Appendix 14: Recommended Configuration Option B
15. Appendix 15: NTS Project Schedule by Task