

Comparative Analysis of Adsorptive Media Treatment
for Arsenic at SRP Groundwater Wells

by

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ABSTRACT

Arsenic (As) is a naturally occurring element that poses a health risk when continually consumed at levels exceeding the Environmental Protection Agencies (EPA) maximum contaminant level (MCL) of 10 ppb. With the Arizona Department of Water Resources considering reliance on other sources of water other than just solely surface water, groundwater proves a reliable, supplemental source. The Salt River Project (SRP) wants to effectively treat their noncompliance groundwater sources to meet EPA compliance. Rapid small-scale column tests (RSSCTs) of two SRP controlled groundwater wells along the Eastern Canal and Consolidated Canal were designed to assist SRP in selection and future design of full-scale packed bed adsorbent media. Main concerns for column choice is effectiveness, design space at groundwater wells, and simplicity. Two adsorbent media types were tested for effective treatment of As to below the MCL: a synthetic iron oxide, Bayoxide E33, and a strong base anion exchange resin, SBG-1. Both media have high affinity toward As and prove effective at treating As from these groundwater sources. Bayoxide E33 RSSCT performance indicated that As treatment lasted to near 60,000 bed volumes (BV) in both water sources and still showed As adsorption extending past this operation ranging from several months to a year. SBG-1 RSSCT performance indicated As, treatment lasted to 500 BV, with the added benefit of being regenerated. At 5%, 13%, and 25% brine regeneration concentrations, regeneration showed that 5% brine is effective, yet would complicate overall design and footprint. Bayoxide E33 was selected as the best adsorbent media for SRP use in full-scale columns at groundwater wells due to its simplistic design and high efficiency.

DEDICATION

I dedicate this thesis to all of those who have supported and encouraged me throughout the highs and lows in this brief—yet exhilarating—segment of my life. I thank my father for inspiring me to not only become an engineer, but the man I am today. To my mother, who wrote the book on compassion (and stress—just kidding!) and was always available to talk with me through my worries and fears. Thanks also to my brother and sister for being amazing siblings able to cope with my craziness. To the rest of my family, whom have established and reinforced the belief that family is always there, no matter what. And my final dedication extends to my grandmother who was a loving, caring woman, teaching me to reciprocate selfless love no matter the circumstances—until we meet again, may you rest in peace.

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CHAPTER 1

INTRODUCTION

With increasing concern about the drought in the Colorado River Basin, the Arizona Department of Water Resources is looking towards reliance on other water sources than just surface water from the Colorado River and other rivers within Arizona. The Salt River Project (SRP) being responsible for canal systems in Phoenix and Tempe, may require increased use in groundwater that contains arsenic concentrations exceeding the Environmental Protection Agency's (EPA) maximum contaminant level (MCL) of 10 µg/L As.

Background on Arsenic in Arizona Groundwater

Arsenic is the twentieth most abundant element in the earth's crust with an average concentration of 2 mg/kg (Mohan & Pittman, 2007; U.S.EPA, 2000). These concentrations, however, vary based on the regions geologic formation with arsenic being a major component of mineral species within igneous and sedimentary rocks. Higher arsenic concentrations within groundwater in the Western and Southwestern United States is derived from a combination of sedimentary deposits typically associated with sulfide ores of copper, lead, silver and gold from mines and shale, and iron oxide media with incorporated arsenic (Spencer, 2000; U.S.EPA, 2000; Welch, Westjohn, Helsel, & Wanty, 2000). Weathering and dissolution of the sulfide minerals and microbial redox of iron oxide rocks has contributed to the elevated concentrations of arsenic within Arizona ground waters (McArthur, Ravenscroft, Safiulla, & Thirlwall, 2001). Over 800 groundwater wells from a U.S. Geological Survey were found in Arizona, with nearly 247 of these used for public drinking water; half of these drinking water wells contain

greater than 5 $\mu\text{g As/L}$ (Spencer, 2000). Figure 1.1 describes the various wells within Arizona alongside their respective concentrations.

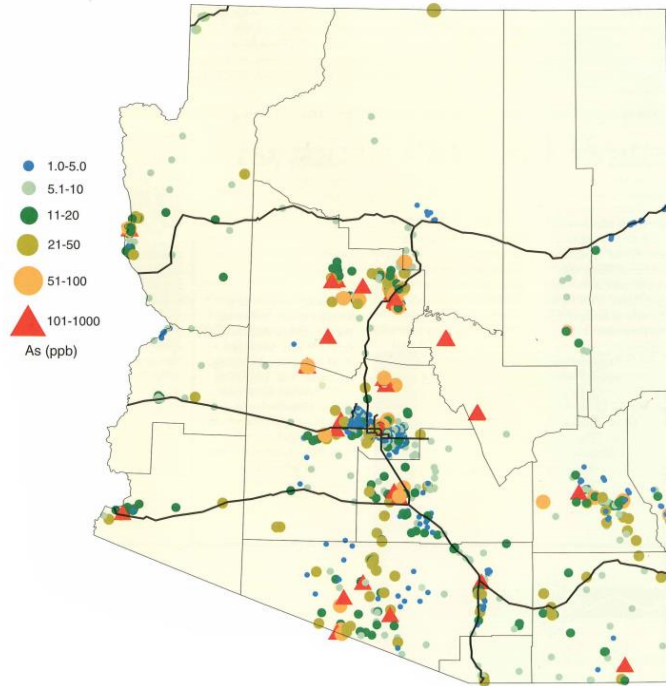
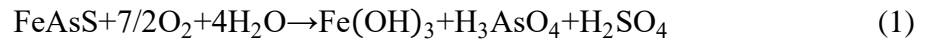


Figure 1.1: Arsenic Concentrations from Select Groundwater Wells (Spencer, 2000)

Arsenic occurs naturally in two forms: organic (carbon-based compound) and inorganic. Organic arsenic exists in the forms of monomethylarsionic acid (MMAA), dimethylarinic acid (DMAA), trimethylarsine (TMA), and trimethylarsine oxide (TMAO), and are commonly used within industrial processes or agricultural applications (Mohan & Pittman, 2007; U.S.EPA, 2000). While organic forms of arsenic are usually associated to terrestrial applications, organic arsenic compounds may be found within water sources. Organic arsenic introduction to surface water occurs in the forms of agricultural and industrial waste discharge/runoff or microbial reduction within soils and sediments (U.S.EPA, 2000; Welch et al., 2000). Inorganic arsenic is more prevalent in

water than organic arsenic and is present in four oxidation states: -3, 0, +3, and +5 with the +3 and +5 being most common within water sources (Gupta & Chen, 1978; Mohan & Pittman, 2007; U.S.EPA, 2000). Introduction of inorganic arsenic into groundwater is a result of geochemical, biological, and electrochemical reactions within the weathering and dissolution processes. Equation 1 highlights an example of microbial oxidation of arsenopyrite through *T. ferrooxidans* and the subsequent release of arsenic acid into water (Panagiotaras, Panagopoulos, Papoulis, & Avramidis, 2012; Welch et al., 2000).



Arsenic redox chemistry.

Arsenic exists in oxidation states of -3 (arsine), 0 (arsenic), +3 (arsenite), and +5 (arsenate). Arsenite (As(III)) and arsenate (As(V)) are the two most common oxidation states of arsenic in aqueous systems, and both demonstrate anionic behavior at higher pH values. Figure 1.2 highlights the speciation of As(III) and As(V) species of water across pH and redox potentials.

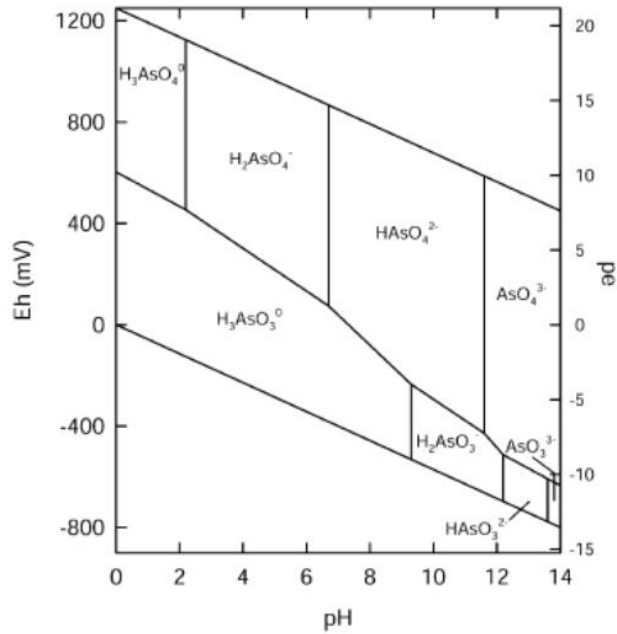
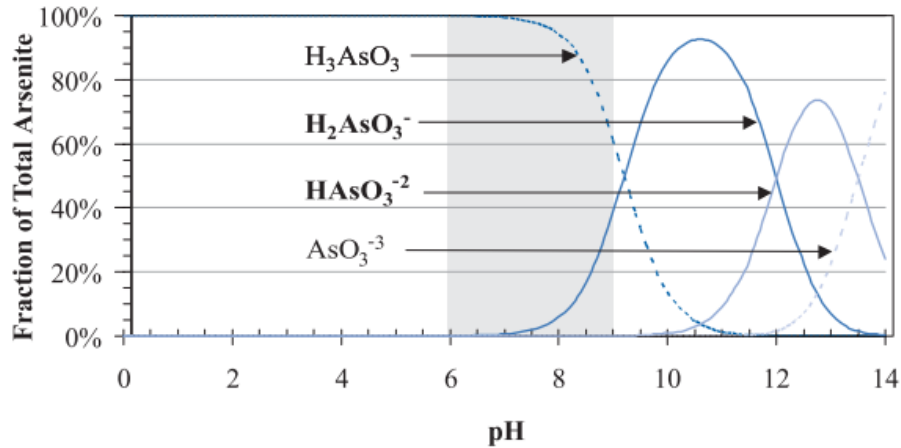
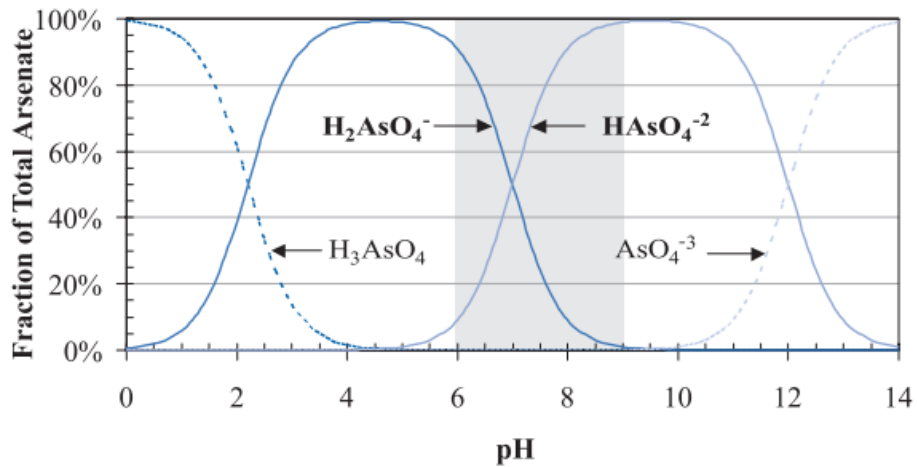


Figure 1.2: Eh-pH Diagram for Arsenic (Panagiotaras et al., 2012)

The dominance of one state over another is a function of pH and redox conditions (Mohan & Pittman, 2007; Panagiotaras et al., 2012; U.S.EPA, 2000). Arsenite predominates in reduced conditions like groundwater whereas arsenate species predominate in oxidized conditions like surface water (Mohan & Pittman, 2007). Figure 1.3 highlights the dissociation of As(III) and As(V) forms across pH. Ultimately, As(III) within a pH range of 6.5-8.5 predominates in the undissociated arsenious acid form (H_3AsO_3) whereas As(V) dominates as dissociated arsenic acid ($H_2AsO_4^-$ and $H_2AsO_4^{2-}$).



a)



b)

Figure 1.3: Speciation Diagram of (a) Arsenite and (b) Arsenate (U.S.EPA, 2003)

The chemical speciation is critical in determining treatment of arsenic in various water sources. Considering that both oxidation states of arsenic (As(III) and As(V)) maintain anionic charges, adjustment of water characteristics may facilitate adsorption, anion exchange, and co-precipitation processes. Since As(III) is neutrally charged within the 6.5-8.5 pH range as arsenious acid, As(V) is most commonly treated due to the negative charge at neutral pH.

Adverse health effects of arsenic exposure.

Inorganic arsenic is a well-known and documented poison that causes a plethora of symptoms. It has been documented that oral doses greater than 60 ppm result in death, whereas lower doses (0.3 – 30 ppm) causing stomach and intestinal irritation (U.S.DHHS, 2013). Symptoms include dryness of the mouth, dysphasia (difficulty speaking), colicky abdominal pain, nausea, vomiting, and diarrhea (Gorchev & Ozolins, 2011; U.S.DHHS, 2013). These are all results of acute arsenic poisoning; the majority of drinking water sources within the United States rarely ever reach concentrations causing acute symptoms (Choong, Chuah, Robiah, Gregory Koay, & Azni, 2007; Gorchev & Ozolins, 2011; U.S.DHHS, 2013). The more prevalent As exposure is chronic. Chronic oral exposure results in arsenicosis (chronic arsenic poisoning) and typically results in four stages of poisoning ranging from clinical effects affecting the skin through dermal lesions, hyperpigmentation and hypopigmentation to complications affecting internal organ function and finally carcinogenic effects (Gorchev & Ozolins, 2011). The World Health Organization states that dermatological symptoms only appear after 5 to 10 years of chronic exposure, and has revised the guideline for arsenic from 50 ppb to 10 ppb back in 1993 to prevent the adverse effects of arsenicosis (Choong et al., 2007; Gorchev & Ozolins, 2011). Following suit, the U.S. EPA reduced its permissible arsenic concentration from 50 ppb to 10 ppb on January 23, 2006, labeled arsenic as a known carcinogen, and has since established an maximum contaminant level goal (MCLG) of 0 for arsenic (U.S.EPA, n.d.-b).

The Arizona Department of Environmental Quality (ADEQ) adopted the United States Environmental Protection Agency's (U.S.EPA) maximum contaminant levels

(MCL) for chronic arsenic exposure, which is set at 10 ppb arsenic under the Safe Drinking Water Act to prevent arsenicosis (ADEQ, n.d.; U.S.EPA, n.d.-b). As a result, water systems must comply with the MCL in order to provide adequate protection to the residents that drink the water.

Salt River Project's concerns with arsenic.

Currently, the Salt River Project (SRP) owns 30 groundwater wells along canals within Phoenix and Tempe that exceed 10 µg/L total arsenic, and 7 wells that exceed 20 µg/L total arsenic. SRP works with the City of Phoenix and other communities in the Phoenix metropolitan area to establish programs that help monitor the quality of the 325 billion gallons of water that is distributed to customers. For groundwater wells, SRP blends the groundwater with canal water that contains a lower concentration of arsenic and nitrate as a form of nitrate and arsenic control (SRP, n.d.). Considered a viable strategy for arsenic mitigation before reaching the distribution system, blending is a process involving the mixing of water sources to effectively reduce contaminant concentration. Alternatively viewed as dilution, the U.S. EPA considers blending as an effective method to avoid the need for treatment (U.S.EPA, 2003). However, with reduced availability of surface waters to use for blending due to increased experiences with droughts in the Colorado River Basin, the Arizona Department of Water Resources (ADWR) has looked towards developing regional analysis of the optimal yield from Arizona's groundwater to meet long-term water security as local reliance on the groundwater supplies increases (ADWR, 2014).

Potential reliance on groundwater to meet current and projected demands may result in SRP requiring increased groundwater well operation. Longer well operation

indicates blending would become an issue to meet compliance with the 10 µg/L arsenic MCL as the blending ratio of the water sources change. As a result, SRP is looking towards effective arsenic treatment strategies to implement at current groundwater wells that fail to meet compliance. The U.S. EPA has detailed various arsenic mitigation strategies for water providers to utilize: sorption, membrane, or precipitation/filtration treatment processes (U.S.EPA, 2003). While these treatment technologies are all proven to work for arsenic, intercity groundwater well sites are limited in space. Since SRP operates groundwater wells within the cities of Phoenix and Tempe, groundwater well site footprints are relatively small and would require a treatment technology with a small footprint. Figure 1.4 shows both an Eastern Canal Groundwater Well and a Consolidated Canal Groundwater Well and their overall space and locations.



a)



b)

Figure 1.4: (a)32.4E -2N Eastern Canal Groundwater Well and (b)Consolidated Canal Well taken from Google Maps.

From the images of the two groundwater wells that were tested, their respective location and space may limit options possible treatment technologies for arsenic. The two technologies most affected are membrane and precipitation/filtration. Membrane processes typically involve reverse osmosis, a pressure-driven membrane separation process that effectively removes 97% As(V) and 92% As(III) (U.S.EPA, 2003). However, this process is susceptible to membrane fouling from various inorganic ions (majority being common within groundwater systems) and biological growth, thereby reducing treatment efficiency. In consideration of precipitation/filtration treatment processes, majority of the traditional processes are considered uneconomical for groundwater treatment, requires appropriate disposal for sludge waste, and requires space for the processes and chemical storage, a luxury not provided at the groundwater well sites (U.S.EPA, 2003). Thus the remaining treatment technology for SRP's arsenic containing groundwater is adsorptive media.

Adsorptive media treatment for arsenic.

Adsorption is often defined as a mass transfer operation in which particles within a liquid phase accumulate on a solids surface, effectively removing them from the liquid. Adsorptive processes often undergo physical or chemical interactions, often referred to as physical adsorption and chemisorption respectively (J. C. Crittenden, Trussel, Hand, Howe, & Tchobanoglous, 2012). Physical adsorption processes operate under relatively weak forces and energies of bonding that are reversible when the adsorbate concentration decreases (J. C. Crittenden et al., 2012). Chemisorption occurs when the adsorbate reacts with the surface, forming a covalent or ionic bond. Adsorbates bound by chemisorption often have shorter bond lengths and higher bond energy preventing layered accumulation as the surface-adsorbate bond is specific to particular sites or functional groups across the surface of the adsorbent (J. C. Crittenden et al., 2012).

Adsorptive media arsenic treatment methods rely upon the principles of physical-chemical interactions between the contaminant and the surface of the media and remains an evolving defense against arsenic that continues to show great promise (Mohan & Pittman, 2007). Three main technologies appear under adsorption treatment for arsenic: activated alumina, metal (hydr)oxide, and ion exchange. Among these treatment types, activated alumina is a common treatment technology for fluorine, and is tricky to work with under certain conditions. Several constituents compete and interfere with the adsorption process (chloride, fluoride, silica, sulfate, etc.) and may require water to undergo pre-filtration and treatment before arsenic adsorption (U.S.EPA, 2003). Also, activated alumina performance longevity is increased upwards of 5 to 20 times when

operated under acidic conditions. As a result, activated alumina was not considered for SRP's treatment needs due to the technical limitations of the media.

Metal (hydr)oxides.

The most common release of arsenic into groundwater systems is from the weathering and dissolution of iron oxides containing adsorbed arsenic. Consequently, arsenic's high affinity towards iron minerals has established iron based sorbents (IBS) as an emerging arsenic treatment technology (Badruzzaman, Westerhoff, & Knappe, 2004; Choong et al., 2007; U.S.EPA, 2003; Westerhoff, Highfield, Badruzzaman, & Yoon, 2005; Wilkie & Hering, 1996). Currently, there are various iron based sorbents for the specific treatment of arsenic. Ranging from granular ferric hydroxide (GFH) to the Severn Trent Services developed Bayoxide E33. This treatment technology has been characterized with high capacity arsenic treatment under neutral pH. However, the mechanisms that drive the sorption process on these iron (hydr)oxides are still being researched and developed.

Current mechanisms that drive the iron (hydr)oxide adsorption processes of arsenic have been described through a four stage pore-surface diffusion model with the last stage inducing the actual adsorption to the iron media. The four stages of this adsorption process are diffusion through bulk liquid and film diffusion, intraparticle diffusion and then finally concluding with adsorption to the surface of the media (Badruzzaman et al., 2004). It has been noted that the bulk liquid diffusion and adsorption processes occur rapidly while the film and intraparticle diffusion processes are limited. Film diffusion is limited by the concentration gradient across the hydrodynamic boundary layer to the adsorbent surface and intraparticle diffusion is limited by being

dominated by pore diffusion or surface diffusion within the pores of the media (Aragon & Thomson, 2002; Badruzzaman et al., 2004). Surface diffusion is assumed as the dominant process for arsenic adsorption as the polarity of As(III) and As(V) species requires an electrostatic attraction (chemisorption), yet not all functional sites have the requisite binding energy required for the electrostatic bond. Upon reaching the adsorption site, adsorption is rapid, typically undergoing chemisorption, indicating that diffusion controls the mass transfer rate. As a result, utilization of packed bed columns is required to maximize arsenic adsorption onto the iron oxide media.

Selection of iron oxide media to use in arsenic treatment relies on operating conditions and required performance of the media. All forms of iron oxide media have shown treatment of arsenic into the thousands of bed volumes at a neutral pH (Aragon & Thomson, 2002; Westerhoff et al., 2005). Under more acidic conditions, iron oxide treatment increases, most notably removing As(V) species than As(III) species. However, competition from other anionic species (phosphate, vanadium, and silica) reduce adsorption sites and impact total arsenic removal (Choong et al., 2007; Westerhoff et al., 2005). Another drawback to the technology is that the adsorption process is irreversible as the arsenic forms permanent bonds with the media (Aragon & Thomson, 2002; U.S.EPA, 2003; Westerhoff et al., 2005). Despite this issue, the media passes most toxicity and leaching protocols, indicating that the media, once spent, is not classified as a hazardous waste and can be disposed at landfills.

This thesis utilizes the Bayoxide E33 media as the metal oxide adsorbent for the arsenic treatment comparison. The Bayoxide E33 media, while utilizing a smaller surface area than granular ferric hydroxide (GFH) (120-200 m²/g compared to 250-300 m²/g),

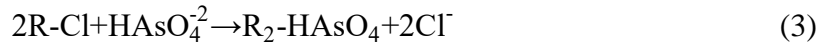
performs comparatively better than GFH under neutral pH conditions, with GFH increasing total bed volumes treated by 40,000 when pH was adjusted from 8.3 to 7.0 and E33 only increasing by 12,000 (Nguyen, Chen, Young, & Darby, 2011; Severn Trent Services, n.d.). Considering that SRP would require treatment at groundwater well heads, an iron oxide media that operates better under higher pH's provides a benefit not easily ignored. Another issue considered is the susceptibility of the iron oxide media to competing ions, most notably silica and vanadium. Granular ferric hydroxide was found to be more sensitive to silica concentration than E33 by decreasing total bed volumes treated to 18,700 and 6,800 respectively when silica concentration increased from 33 to 73 mg/L. Vanadium showed insignificant effects on arsenic adsorption in E33 media while indicating a linear effect on GFH (Nguyen et al., 2011). Based on these results, E33 was chosen as the most efficient iron oxide media to undergo a comparative analysis against ion exchange media for groundwater treatment.

Ion exchange resins.

Ion exchange resins are a physical-chemical process wherein ions on a functional group attached to a polymer backbone are swapped between the bulk fluid and the solid resin. While the application of ion exchange resins is widespread for water softening of cationic minerals (calcium, magnesium, sodium, etc.), ion exchange applications extend into separation, combined, and simultaneous treatment of various heavy metals and toxic contaminants (Clifford, 1999; Dąbrowski, Hubicki, Podkościelny, & Robens, 2004; Ficklin, 1983; Hristovski et al., 2008; Kim & Benjamin, 2004; U.S.EPA, 2003; Vaaramaa & Lehto, 2003). Various forms of ion exchange resins exist; ranging from strong and weak acid cationic resins to strong and weak base anion resins, each form of ion

exchange resin treats specific contaminants based on selectivity (Clifford, 1999; Dąbrowski et al., 2004). However, based on arsenite and arsenate speciation at various pH values, arsenic treatment is preferred on strong base anion exchange resins due to their anionic charge and relatively neutral to high pH (weak base anion exchange resins operate under acidic conditions) (Ficklin, 1983; Horng & Clifford, 1997; U.S.EPA, 2003). This is due to the mechanisms that drive the adsorption process.

Strong base ion exchange resins (SBA-IX) operate under the mechanistic properties of swapping anions from the bulk solution with the anions from the respective functional group. All forms of ion exchange resins operate under a polymer chain structure (matrix) with a respective functional group. A strong base anion exchange resins functional group is a quarternary amine structure ($\text{—N}^+(\text{CH}_3)_3$), and the capacity of a SBA-IX resin is measured by the number of fixed charge sites per unit weight of resin (Clifford, 1999). In order to maximize capacity, resins are engineered with a porosity to increase functional surface area per unit weight. Each functional site is pre-loaded with either hydroxide or chloride as the interchangeable anionic species since the quaternary amine functional group is so strongly basic that it remains ionized over a pH range of 0-13 (Clifford, 1999). Under neutral pH, As(III) resides as the undissociated arsenous acid (H_3AsO_3) which retains a neutral ionic charge; As(V) resides in two dissociated arsenic acid forms, monovalent (H_2AsO_4^-) and divalent (HAsO_4^{2-}). Treatment of As(III) requires oxidation to As(V) to allow ion exchange adsorption (Horng & Clifford, 1997; Korngold, Belayev, & Aronov, 2001; U.S.EPA, 2003). Equations 2 and 3 highlight the ion exchange process between monovalent and divalent As(V) and SBA-IX resins respectively (Korngold et al., 2001).



However, arsenic is not the only anionic species removed by SBA-IX resins. Commonly used for nitrate treatment, SBA-IX resins follow a selectivity pattern wherein other present anionic species in the water contribute to reduced arsenate adsorption. Selectivity is a factor based on the valence state and atomic number as well as the physical properties of the ions. Higher valence states and atomic numbers increase the overall selectivity of the ion with minor exceptions to the rule (J. C. Crittenden et al., 2012). The selectivity sequence follows sulfate (SO_4^{2-}) > divalent arsenate (HAsO_4^{2-}) > nitrate and carbonate (NO_3^- , CO_3^{2-}) > nitrite (NO_2^-) > and chloride (Cl^-) (Clifford, 1999). If SBA-IX resins are operated past arsenate exhaustion (complete breakthrough of arsenate), they become susceptible to chromatographic displacement when sulfate concentrations are orders of magnitude higher than arsenate concentrations, a common occurrence in groundwater sources. Should operation persist under such conditions, arsenate sites will be displaced and sent into the effluent as a singular concentration of arsenate that could exceed the MCL (Korngold et al., 2001; U.S.EPA, 2003). Simply ceasing SBA-IX column operation prior to arsenate exhaustion or sulfate breakthrough prevents chromatographic peaking issues. Otherwise, pretreatment for sulfates would be required to improve arsenate removal capacity (Kim & Benjamin, 2004).

One of the main draws towards SBA-IX resins as a treatment technology is the ability for the functional sites to be regenerated with the base functional anion. Regeneration occurs by initializing a backwash, regenerate the column with a brine (chloride regen) or caustic soda (hydroxide regen), a slow rinse with water, followed by a

quick rinse (U.S.EPA, 2003). For SBA-IX resins, sodium chloride (NaCl) or hydrochloric acid (HCl) are viable to regenerate with chloride ions while sodium hydroxide (NaOH) regenerates with hydroxide anions. Hydrochloric acid actually provides greater regeneration as monovalent and divalent arsenate are weak acids and will form arsenic acid in the eluate, a neutrally charged compound (Korngold et al., 2001; U.S.EPA, 2003). However, hydrochloric acid and sodium hydroxide generate waste solutions, and would typically present chemical handling and waste disposal issues with regeneration. Other concerns regarding the waste is the total concentration of arsenic contained, with any concentration >5 mg/L (> 5 ppm) being considered hazardous waste (U.S.EPA, 2003).

Selection of an SBA-IX resin for comparison to Bayoxide E33 within the thesis was determined based on previous performance at other groundwater wells. SBG-1, a ResinTech Inc. SBA-IX resin with a trimethylamine functional group shipped in the chloride ionic form, is in use at the Coachella Valley Water District for arsenic treatment (Bowen, 2014; ResinTechInc, n.d.). SBG-1 has a high affinity for divalent anions, such as sulfate and arsenate, resulting in effective treatment for arsenate if column regeneration occurs prior to chromatographic displacement. SBG-1 chloride affinity occurs at a total dissolved salt (TDS) greater than 5,000 ppm, with regeneration recommended between 2-10% sodium chloride by weight. Considering the size and location of SRP groundwater wells, regeneration with brine solutions is a simpler method compared to hydrochloric acid and sodium hydroxide.

Competing species chemistry background

Many groundwater sources also contain various anionic species that compete with arsenic for adsorption sites. Most geologic formations are not comprised of solely

arsenic; typical weathering of arsenic containing minerals allow other (metal) oxyanions to dissociate, typically being vanadium, uranium, silica, sulfates, and carbonates (Bernhard, 2005; U.S.DHHS, 2008; U.S.EPA, 2000). Knowledge about the background chemistry of these competing species provides foundation in understanding potential concerns with operational performance of the adsorbent media.

Vanadium background

Vanadium (V) is the twenty-third element on the periodic table of elements, and is associated with the transition metals. As common with transition metals, vanadium exists in many oxidation valence states; the most common compounds existing in +3, +4, and +5 oxidation states (U.S.DHHS, 2008; World Health Organisation, 2000). The earth's crust contains on average concentration of 150 μg of vanadium, and that concentration within water sources varies based on location from 0.2 – 100 $\mu\text{g/L}$, with typical groundwater concentrations ranging from 1 – 6 $\mu\text{g/L}$ (World Health Organisation, 2000). Like arsenic, vanadium is commonly weathered from sulfide minerals, and is commonly mined from uranium ore carnotite (U.S.DHHS, 2008). Figure 1.5 highlights vanadium speciation valence states at varying pH and redox conditions.

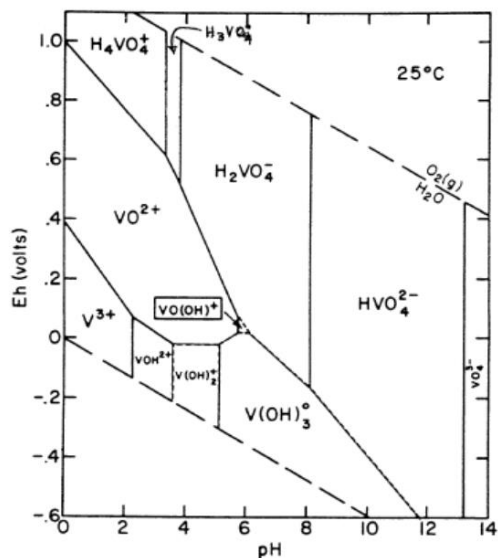


Figure 1.5: Vanadium Eh-pH Diagram (U.S.DHHS, 2008)

Within most oxidizing conditions, vanadate (V(V)) predominates over the other valence states. Reducing conditions often reduce vanadate to the more stable tetravalent vanadium state (V(IV)) which is most commonly found to dominate within groundwater systems (U.S.DHHS, 2008). However, the total vanadium concentration within the system often times dictates the species at the specific valence state. When molal concentrations of total vanadium begin to exceed 0.0001 m , decavanadate (ten vanadium nuclei) species begin to form (U.S.DHHS, 2008). As pH increases with these decavanadate species, metavanadates form more readily, and within pH 9-12 $\text{V}_2\text{O}_7^{4-}$ dominates as the prevalent species. Above pH 13, VO_4^{3-} dominates as the sole species. Yet, most aqueous systems contain very dilute concentrations ($<2 \times 10^{-5}\text{ m}$), and VO_2^+ species dominate (U.S.DHHS, 2008). Figure 1.6 highlights the speciation across pH of vanadium at different molality concentrations.

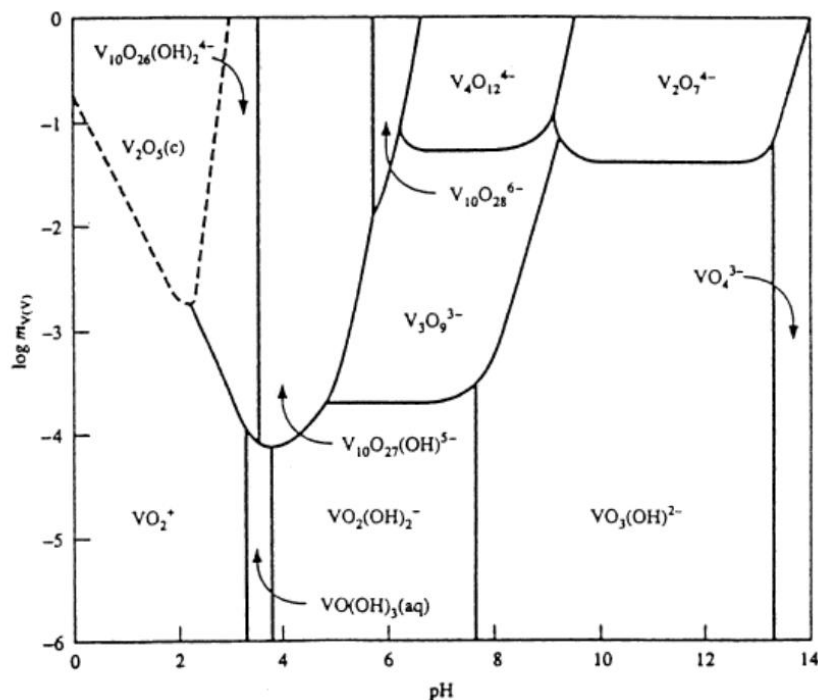


Figure 1.6: Speciation Diagram of Vanadium (U.S.DHHS, 2008)

Adverse health effects for vanadium exposure have been mostly attributed towards air exposure, and have often been relegated towards extremely high concentrations (World Health Organisation, 2000). Toxicological studies performed on animals showed that vanadium toxicity varies based on route of exposure. Typically, vanadium toxicity was determined to be high through paternal exposure, low through oral exposure, and intermediate with respiratory exposure (World Health Organisation, 2000). In humans, vanadium poisoning has been most reported through workers engaged in industrial use of vanadium, and most commonly through inhalation rather than oral exposure routes (U.S.DHHS, 2008; World Health Organisation, 2000). The U.S. EPA continually adds vanadium to its Drinking Water Contaminant Candidate List (CCL) since 1998 to establish a maximum contaminant level based on the toxicological effects; however, the EPA continues to find insufficient information to support regulation of

vanadium (U.S.DHHS, 2008; U.S.EPA, 2014). The EPA delists vanadium due to limited research on the neurotoxicity and toxicokinetics, health gaps in research since 2011, and no to low detection across nationally representative finished water data (U.S.DHHS, 2008; U.S.EPA, 2014).

Uranium background

Uranium is the ninety-second element on the periodic table of elements and is the heaviest naturally occurring element within the earth's crust (Krestou & Panias, 2004; Zavodska, Kosorinova, Scerbakova, & Lesny, 2008). Uranium belongs to the actinides chemical series in the periodic table, indicating that is a radioactive element. Three common isotopic forms of uranium exist: ^{238}U , ^{235}U , and ^{234}U (Krestou & Panias, 2004). Naturally occurring uranium typically consists of 99.27% ^{238}U , 0.72% ^{235}U , and trace amounts of ^{234}U , and uranium vanadate compounds are commonly mined for the highly sought ^{235}U isotope for nuclear fuel (Bernhard, 2005; Krestou & Panias, 2004; Zavodska et al., 2008). Despite these isotopes, uranium can exist in five oxidation states from +2 to +6 with the +4 and +6 oxidation states being the most stable oxidation states (Zavodska et al., 2008). Uranium is a relatively mobile element due to the stability of its hexavalent oxidation state (U(VI)) in aqueous systems, with reduction to U(IV) often leading to precipitation onto uranium minerals (Zavodska et al., 2008). For most aqueous systems, U(VI) is the typical oxidation state, and hexavalent uranium species form uranate anion (UO_4^{2-}) species under higher pH values and uranyl cation (UO_2^{2+}) species under low pH values. Uranate anion species typically concatenate (bond with other uranium) leading to larger uranate anion species (Bernhard, 2005). Figure 1.7 highlights the various speciation of uranium under redox conditions and pH.

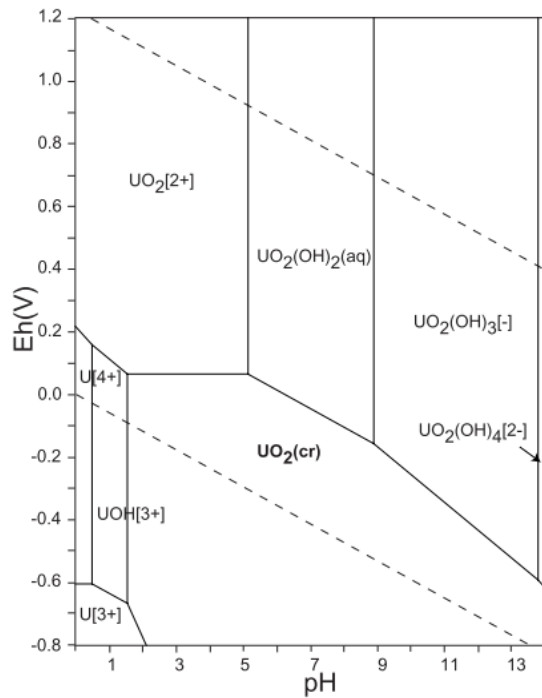
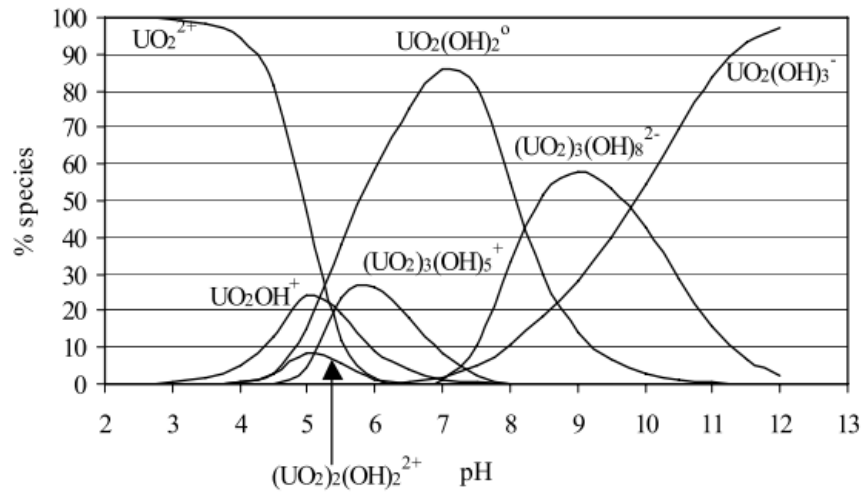
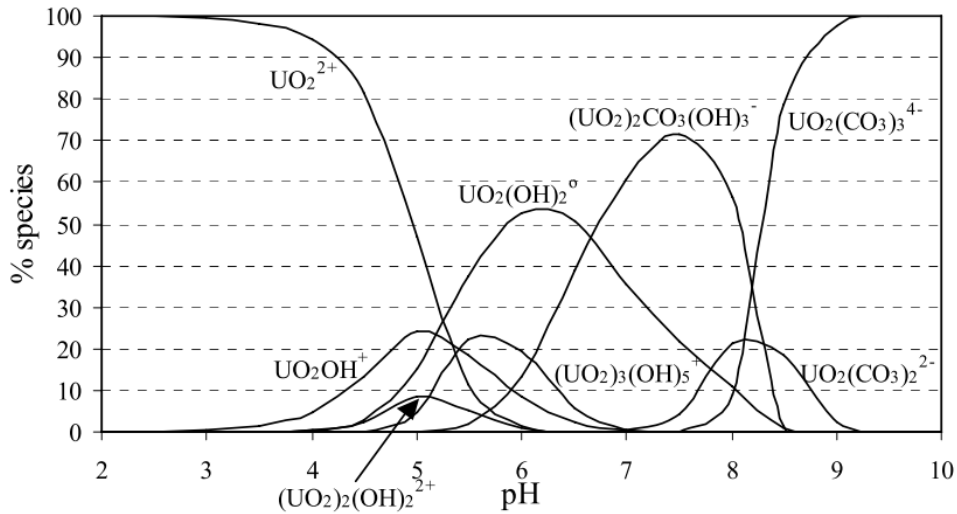


Figure 1.7: Uranium Eh-pH Diagram (Takeno, 2005)

Uranium speciation is complex with a great lack of data to accurately represent U(VI) speciation in a binary water system composed of itself and water (Bernhard, 2005; Krestou & Panias, 2004). The reason for a lack in data is associated with the complexity of U(VI) in organic rich-environments as carbonate-ligand structures are commonly formed due to a strong affinity towards uranium (Bernhard, 2005; Krestou & Panias, 2004; Zavodska et al., 2008). These carbonate-ligand structures add to the complexity of U(VI) speciation as they produce monovalent and divalent anions within a more neutral pH range as highlighted between the speciation diagrams in Figure 1.8.



a)



b)

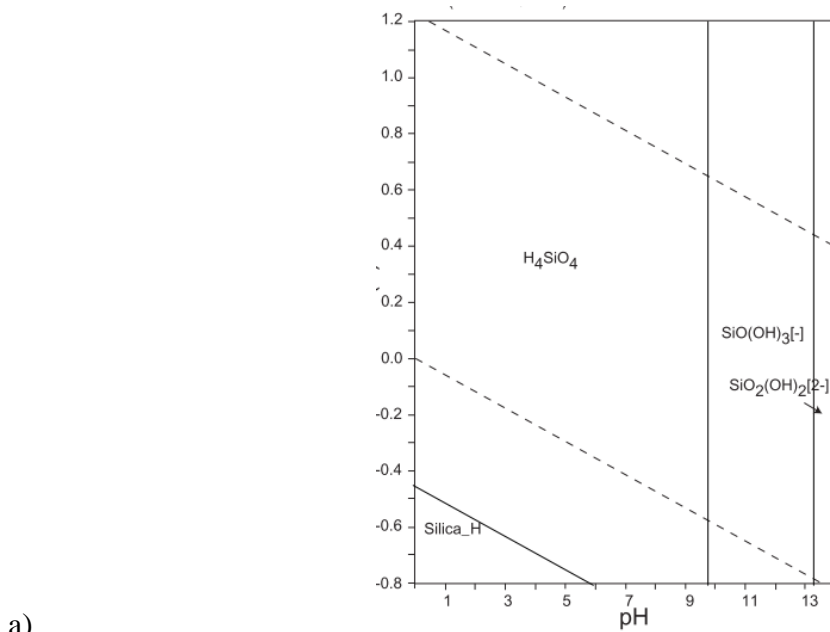
Figure 1.8: Speciation Diagram of (a) Uranium and (b) Uranium Carbonate-ligands (Krestou & Panias, 2004)

Uranium presents chemical and radiological hazards that are dangerous to human health. Studies performed have shown that chronic ingestion of uranium interferes with kidney function as soluble uranium is absorbed by the blood and eliminated through the kidney in urine (Krestou & Panias, 2004). Soluble uranium has also shown preferential absorption to bones and the liver alongside the kidney (Zavodska et al., 2008). Alongside

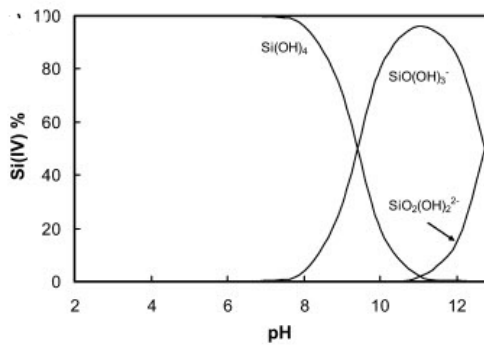
the chemical components, the radiological effects of ingesting uranium is an increased risk of cancer from chronic exposure (U.S.EPA, n.d.). As a result, the EPA has set the MCL for uranium in drinking water to 30 µg/L.

Silica background

Silica and silicates (SiO_4^{4-}) are generic names of silicon dioxide based compounds that form from the dehydration and polymerization of silicic acid ($\text{Si}(\text{OH})_4$) (Ning, 2003). Silica is extremely common within groundwater sources from the weathering of silicate rocks from carbonic acid (Ning, 2003). Silicic acid is relatively stable within water sources, and silica is particularly inert with respect to major cations and anions, preferring reactions with divalent cations under high pH (Haines & Lloyd, 1985; Ning, 2003). Silica's behavior in groundwater is mostly associated with metal species like aluminum and iron. The reactions to these metals, however, are limited by the behavior; aluminum reactions with silica occur at low pH, and ferric ions react in the formation of ferric silicate complexes. Figure 1.9 highlights the Eh-pH and speciation diagram of silica within water.



a)



b)

Figure 1.9: Silica (a) Eh-pH Diagram and (b) Speciation Diagram (Takeno, 2005; Tan, Skinner, & Addai-Mensah, 2015)

Sulfate background

Sulfate (SO_4^{2-}) is an inorganic species that is introduced into water sources through the oxidation of elemental, mineral, or organic sulfur. Being the fourteenth most abundant element in the earth's crust, sulfide mineral weathering contributes sulfate to drinking water, with most public supplies containing sulfate concentrations less than 500 mg/L (Institute of Medicine Food and Nutrition Board, 2004). At concentrations around

250 mg/L, sulfate becomes readily detectable based on odor and taste, and the EPA has set a secondary MCL for aesthetic purposes on sulfate at this concentration (Institute of Medicine Food and Nutrition Board, 2004; US EPA, n.d.). Sulfates under extremely low pH conditions (<2) form monovalent sulfuric acid, with fully protonated sulfuric acid dominated at a negative pH value—both not typically found in natural water systems.

Figure 1.10 highlights the Eh-pH and speciation diagram of sulfate at varying pH.

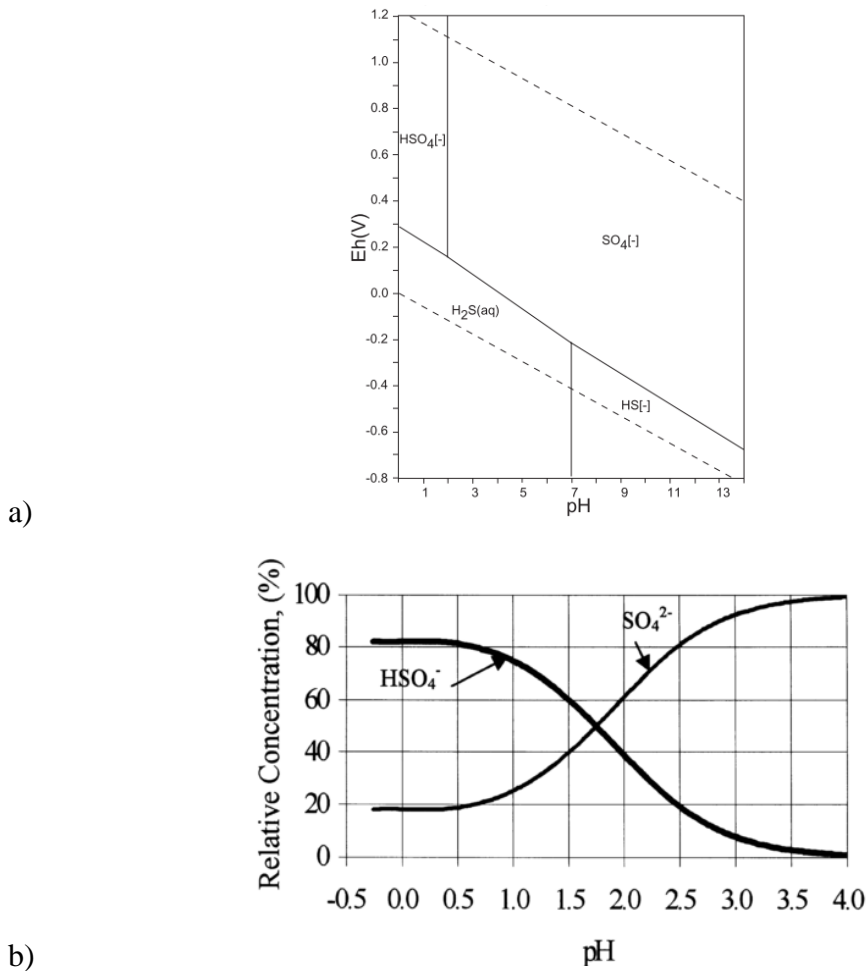
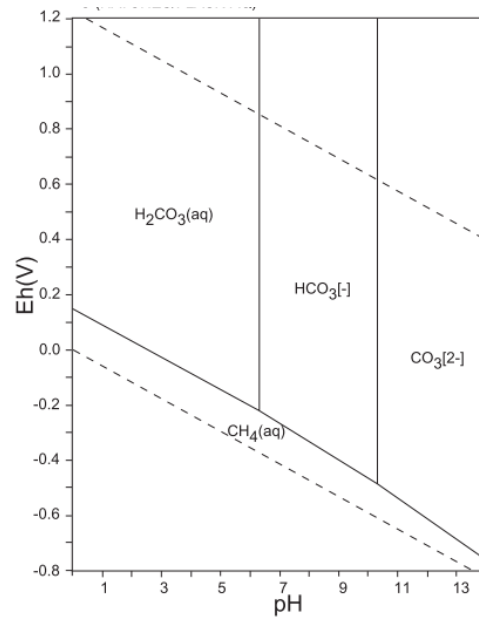


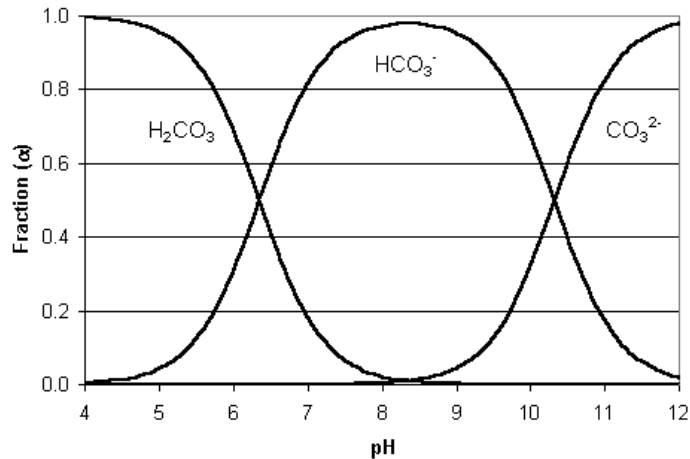
Figure 1.10: Sulfate (a) Eh-pH Diagram and (b) Speciation Diagram (Casas, Alvarez, & Cifuentes, 2000; Takeno, 2005)

Carbonate background

The carbonate cycle within water is well known and taught as a basic introduction into water chemistry and the carbon cycle. In essence, carbon dioxide gas is in equilibrium with water, forming carbonic acid (H_2CO_3) which readily weathers mineral formations to yield bicarbonate (HCO_3^-) and other ions within the water. Then, bicarbonate reacts with calcium to form calcium carbonate precipitate (CaCO_3) which balances out the pH. Within groundwater, however carbon dioxide is under a partial pressure that one to two orders of magnitude greater than air, thereby increasing carbonic acid and the weathering of minerals yielding greater bicarbonate concentrations (Macpherson, 2009). Figure 1.11 highlights the Eh-pH and speciation diagram of carbonate.



a)



b)

Figure 1.11: Carbonate (a) Eh-pH Diagram and (b) Speciation Diagram (Macpherson, 2009)

Scope of the Thesis

This thesis describes the comparative analysis of adsorbent media for the treatment of arsenic (As) at these Salt River Project (SRP) groundwater wells within Arizona. The analysis consists of rapid small-scale column tests (RSSCTs) of an iron oxide, Bayoxide E33 (Severn Trent Services), and strong base anion exchange resin, SBG-1 (ResinTech, Inc.), of two groundwater sources located along SRP controlled canals upstream of municipal water treatment plants.

Upon performing the comparative analysis between both Bayoxide E33 (Severn Trent iron oxide) and SBG-1 (ResinTech SBA-IX resin), a recommendation for the most optimal media treatment will be provided for the Salt River Product company decision.

Main objectives of the thesis are as follows:

- Determination of optimal performing media between Bayoxide E33 and SBG-1 for arsenic treatment of AZ groundwater sources.

- Address common issues and concerns regarding each treatment technology at SRP controlled groundwater wells.
- Determine an effective brine concentration for regeneration of SBG-1 functional sites.
- Recommend future research and applications regarding adsorptive media treatment of elevated arsenic groundwater throughout Arizona.

CHAPTER 2

MATERIALS AND METHODS

Rapid Small Scale Column Tests (RSSCT)

The rapid small-scale column test (RSSCT) was developed as an approach to design large-scale packed bed adsorbers from bench scale column studies (J. Crittenden, Berrigan, Hand, & Lykins, 1987). Within this work, a dimensional analysis was performed on the dispersed-flow, pore-surface-diffusion model (DFPSDM), a mass transfer model, as the DFPSDM accounts for multiple transport and kinetic phenomena that occur within diffusion into the adsorbent. These include film transfer, axial mixing caused by dispersion, and internal mass transfer resistances of both pore and surface diffusion (J. Crittenden et al., 1987). Development of the scaling equations focused on the intraparticle mass transfer resistances, specifically effective surface diffusivities and the relation to particle size (J. Crittenden et al., 1987; J. C. Crittenden et al., 1991; Westerhoff et al., 2005). Assuming that surface diffusivity is linearly proportional to the particle radius and is the dominant mechanism avoids potential dissimilarities when surface diffusivity (D) assumed independent of particle size (d) (Equation 1). This assumption results in the dimensionless scaling equation (Equation 2) where the adsorbent particle diameters ($d_{p,LC}$ and $d_{p,SC}$) and the empty bed contact times ($EBCT_{LC}$ and $EBCT_{SC}$) scale the full-scale column down to RSSCT columns (J. C. Crittenden et al., 1991; Westerhoff et al., 2005).

$$\frac{D_{SC}}{D_{LC}} = \frac{d_{p,SC}}{d_{p,LC}} \quad (1)$$

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \frac{d_{p,SC}}{d_{p,LC}} \quad (2)$$

This assumption is considered the proportional diffusivity (PD) scaling approach, and results in differing spreading from dispersion and external mass transfer that would have been equal under constant diffusivity (CD). Proportional diffusivity was chosen over constant diffusivity as previous studies showed that decreasing the particle size decreased the surface diffusivity proportionately and adversely affected CD column performance (J. Crittenden et al., 1987; Westerhoff et al., 2005). It has also been shown that within these RSSCT columns during an on-off pumping cycle that internal mass transfer is limiting (Westerhoff et al., 2005). Proportional diffusivity scaling is most appropriate when internal mass transfer rates are limiting.

As a result of using proportional diffusivity scaling, the hydraulic loading rate (V) requires consideration of minimizing the effects of dispersion and external mass transfer to maintain similarity. Minimizing the Reynolds number (Re), a dimensionless ratio of inertial forces over viscous forces that describes fluid flow, produces a flow in which the effects of dispersion are insignificant (Westerhoff et al., 2005). The product of the Reynolds number and the Schmidt number (Sc), a dimensionless ratio of the diffusion of momentum over diffusion of mass, can be used to determine the minimum required Reynolds number. If the product of the Reynolds number and Schmidt number is within the mechanical dispersion region of 200-200,000, then dispersion effects are negligible. Equations 3 through 6 highlight the calculation of hydraulic loading rates, Reynolds number, Schmidt number, and Reynolds-Schmidt number respectively (J. C. Crittenden et al., 1991; Westerhoff et al., 2005).

$$\frac{V_{SC}}{V_{LC}} = \frac{d_{p,LC}}{d_{p,SC}} \times \frac{Re_{SC} \times Sc}{Re_{LC} \times Sc} \quad (3)$$

$$Re = \frac{V \times \rho_L \times d_p}{\mu} \quad (4)$$

$$Sc = \frac{\mu}{D_L \times \rho_L} \quad (5)$$

$$Re \cdot Sc = \frac{V \times \rho_L}{D_L} \quad (6)$$

Values of the liquid diffusivity of arsenate (D_L) found from literature is 1.1×10^{-9} m²/s, and the dynamic viscosity (μ) is equal to 8.34×10^{-4} Pa·s (Aragon & Thomson, 2002). Using these values, a bed porosity of 0.25, a simulated full-scale column loading rate of 4.9 gpm/ft², and a 2.5 min EBCT, the design of the RSSCT columns was calculated (Westerhoff et al., 2005). Results from Equations 2.2-2.6 are tabulated in Table 2.1 as design parameters for the columns. The simulated full-scale column parameters are included within Table 2.1.

Table 2.1:

Summary of RSSCT Design Parameters and Full-Scale Column

Design Parameter	Simulated Full-Scale Column	RSSCT (PD)
Particle Diameter (mm)	1.16	0.128
Column Diameter (cm)	244	1.10
Empty Bed Contact Time (min)	2.50	0.280
Reynolds-Schmidt Number	15500	2000
Hydraulic Loading Rate (gpm/ft ²)	4.90	5.76
Bed Length (cm)	85.3	6.50
Bed Volume (mL)	----	6.10
Flow Rate (mL/min)	----	22.3
Mass of Media (g)	----	9.10

Adsorbent media preparation.

Both Bayoxide E33 (Severn Trent Services) and SBG-1 (ResinTech Inc.) media were prepared in advance to RSSCT column packing. Bayoxide E33 media is shipped as

dry, compacted, synthetic iron oxide pellets with particle sizes ranging from 2mm down to 0.5mm (mesh No. 10x35), with 20% of max media passing through U.S. mesh 35 and 5% max retained on U.S. mesh 10 (Severn Trent Services, n.d.). SBG-1 resin is shipped as spherical gel beads composed of a styrene/DVB polymer structure with trimethylamine as the functional group. Size distribution of shipped SBG-1 beads are U.S. mesh 16x50 (1.19mm down to 0.297mm) with 1% passing mesh 50. SBG-1 may ship in either the chloride or hydroxide ionic forms; this thesis utilizes the chloride ionic form of the SBG-1 resin (ResinTechInc, n.d.). Both media were crushed to U.S. mesh 100x140 (0.149mm down to 0.105mm) for a nominal size of 0.128mm for use in RSSCT column operations. Media was crushed using a mortar and pestle and wet-sieved with deionized water through mesh 100x140 to maintain appropriate particle diameter accounting for hydrated radius. All media retained on U.S. mesh 140 were collected and stored in 125ml HDPE Fisherbrand™ wide-mouth bottles for use in RSSCT packing.

RSSCT column packing, operation, and sampling.

All RSSCTs columns were constructed of glass, Teflon and stainless steel to minimize organic adsorption and introduction to the columns. Glass columns (ACE Glass, Inc.) of 1.1cm diameter and 30.5cm length were packed in a stratified bed of glass wool, borosilicate glass beads (VWR; 5mm diameter), and the packed media. Glass wool supports the media and disperses flow throughout the column. Borosilicate glass beads maintain even dispersion of flow and prevent short-circuiting of effluent water. Ends of the column were capped off with Teflon caps. Figure 2.1 highlights RSSCT column design for visual reference.

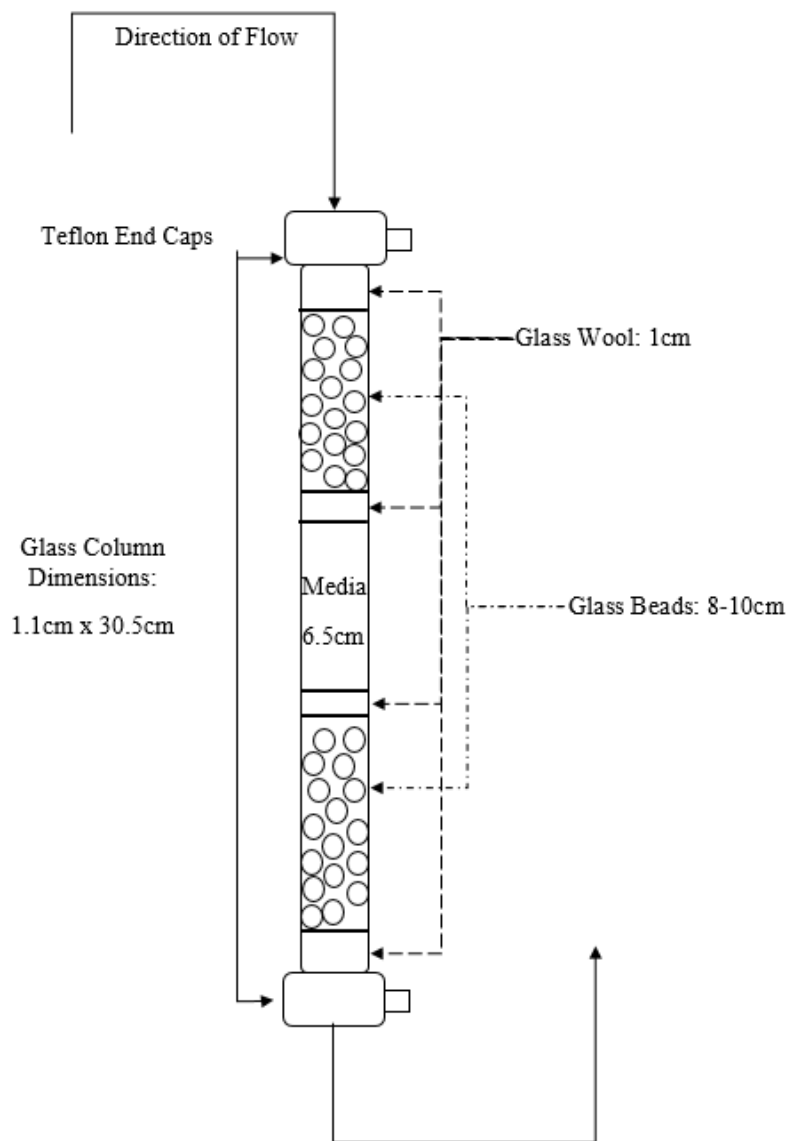


Figure 1.1: RSSCT Column Design

Column packing follows a sequence to ensure even distribution of materials throughout the column. All materials packed within glass columns are first soaked in ultra-pure water to reduce introduction of air bubbles. Glass columns are first pumped full with ultra-pure water using Teflon tubing (3.2mm) and piston pumps (FMI QG150). Glass wool is shredded and added in pieces through a modified stainless steel wire to

avoid introduction of air bubbles to the column. Borosilicate glass beads are introduced through a funnel while gently tapping the column to reduce large gap formation from bead settling. On top of the glass beads, glass wool is reintroduced for media support. The sieved adsorbent is added through the funnel in portions to prevent column overflow and meet column length requirements. Any adsorbent remaining on the funnel or along column walls is flushed using ultra-pure water. Columns are backwashed to remove fines by operating in upflow mode with distilled water to a bed expansion of approximately 40% until the effluent water ran visually clear. After the adsorbent media settles, glass wool is reintroduced to pack the media bed and prevent movement. Glass beads then fill the remaining column space until 1cm from the top, which is capped with glass wool and a Teflon end cap.

Finished columns are fitted with Teflon tubing attached to piston pumps (QG150) for full operation. Teflon tubing lines weighted with stainless steel weights were introduced into source water samples (55 gallon drums) and attached to piston pumps to allow for column operation. Effluent tubing lines were positioned into a constructed waste drain to allow for effective discharge and sample collection. All RSSCT columns were packed with adsorbent media to a length of 6.5cm and operated at 22.3 mL/min flowrate for an EBCT of 0.28 minutes at a hydraulic loading rate of 5.76 gpm/ft². Operation length varied between adsorbent media.

Bayoxide E33 column operation

Operating length for iron oxide based media in previous studies and manufacturer specifications has shown treatment into the thousands of bed volumes of media (Severn Trent Services, n.d.; Westerhoff et al., 2005). As a result, Bayoxide E33 RSSCTs are

expected to treat similar quantities of water, and planned for 100,000 BVs of treatment. RSSCT operation length is expected at approximately 19 days and to treat 610 L (161 gal) of water. Water samples were collected to test for total arsenic and for competing species of vanadium, silica, and uranium. Sampling of effluent water is planned initially at every 120 BVs for the initial four hours for silica breakthrough and switched to 5,000 BVs for the remaining operating run time. Figure 2.2 displays final Bayoxide E33 columns.



*Figure 2.2: Bayoxide E33 Packed Column for Treatment of SRP Groundwater Wells
SBG-1 column operation*

Operating length for ion exchange resins is not as lengthy as iron oxide based media for groundwater treatment based on salts and competing ions (Bowen, 2014; ResinTechInc, n.d.). SBG-1 resin RSSCTs were expected to treat 2,000 BVs of water before arsenic exhausts the sites. As a result, SBG-1 RSSCTs operated for 9 hours before regeneration. Effluent water samples were collected for total arsenic and for competing

species such as vanadium, silica, and uranium. Sampling occurred every 100 BVs throughout the RSSCT operation. Three columns were prepared with SBG-1 resin media for regeneration at varied brine concentrations and labeled as A, B, and C. Figure 2.3 displays final SBG-1 resin columns.



Figure 2.3: SBG-1 Packed Columns for Treatment of SRP Groundwaters.

Regeneration of SBG-1 RSSCTs was performed at three brine concentrations for their effect on regeneration: 5% (Column A), 13% (Column B), and 25% (Column C) NaCl by weight. Regeneration of RSSCTs required lower flow rate for an increased regenerant contact time, allowing arsenate mobilization and chloride replacement at functional sites. Flow rate for the columns was reduced to 8 mL/min (0.26 gpm/ft²) for 1 hour as per ResinTech recommendations (ResinTechInc, n.d.). The 75 BVs regenerant (450 mL) was prepared for each brine solution. Brine preparation required measuring out 5g/100mL (5%), 13g/100mL (13%), and 25g/100mL (25%) NaCl for dissociation in

500mL of ultra-pure water. The resulting masses (25g, 65g, and 125g) were placed into three 500mL Erlenmeyer Flasks and filled with ultra-pure water to 500mL. Sonication of each flask for approximately 2 minutes allowed thorough dissociation and mixing of each brine solution. A displacement rinse of remaining brine and eluate in each column after each regeneration cycle was performed with 10 BVs of ultra-pure water for 10 minutes at the regenerant flow rate. After displacement rinse, a fast rinse at 22.3 mL/min was performed for 10BVV for 3 minutes before being reconnected to groundwater sources for operation.

Groundwater collection.

Groundwater samples collected for RSSCT adsorbent media testing were provided by two SRP groundwater wells: 32.4E -2.0N Eastern Canal Well and 30.4E - 2.0N Consolidated Canal Well (shown in Figures 1.4(a) and (b)). Two 55 gallon drums, lined with a double layer of plastic drum lining, were driven and filled at the well head site. A garden hose was attached to the well head to allow for pressure driven filling of each 55-gallon drum. Once filled, each plastic lining was zip-tied individually to prevent water leaking and contamination. At ASU, drums were unloaded and left at ambient temperature as columns operated. No adjustments were made to the water.

Initial water samples of both sites were taken to measure total arsenic, vanadium, silica, uranium and pH levels. Multiple influent samples were taken directly from the 55-gallon drums to ensure no major changes occurred in pH and constituent concentrations during RSSCT operation. Water quality data provided by SRP was also provided to compare values. Table 2.2 highlights SRP groundwater quality data.

Table 2.2:

SRP Groundwater Quality

SRP Groundwater Quality		
Parameter	Consolidated Canal Groundwater Well 30.8E - 2.0N	Eastern Canal Groundwater Well 32.4E - 2.0N
Alkalinity [mg/L CaCO ₃]	123	113
Arsenic [µg/L]	10	23
Bicarbonate [mg/L]	150	138
Chloride [mg/L]	276	305
Conductivity [UMHOS/CM]	1270	1340
Hardness [mg/L CaCO ₃]	160	164
Nitrate as Nitrogen [mg/L]	1.07	0.79
Silica [mg/L]	31.9	36
Sulfate [mg/L]	42.9	43.6
Total Dissolved Solids [mg/L]	630	691
Uranium [µg/L]	2	4
Vanadium [µg/L]	11	8
pH	8.4	8.3

Sample analysis.

All water samples were collected in 15mL plastic test tubes, preserved using 3% ultra-pure nitric acid (ULTREX, Sigma-Aldrich) and stored in a dark cold-room until analysis. Filtering was not performed on the column samples as all RSSCT Teflon end caps were fitted with a fritted filter disc (ACE Glass, Inc.) of 25-50 microns. Total arsenic, vanadium, silica and uranium concentrations were measured using inductively coupled plasma with mass spectrometry (ICP-MS) following EPA's approved Multi-Analyte Method 200.8 modified for silica.

CHAPTER 3

RESULTS AND DISCUSSION

Breakthrough Curves

Breakthrough curves are a visual representation of effluent concentration during a column test. As water runs through the RSSCT, arsenic is adsorbed onto the packed media leaving a quantifiable residual in the effluent stream. The independent variable within breakthrough curves is the total volume of water treated as the adsorbent media requires water to pass through for adsorption to occur. This volume of water is usually presented in bed volumes (BV), a normalization of the water treated to the volume of the packed media bed. Bed volumes benefit analysis in two primary ways. First, the quantity of water treated at any time interval can be readily calculated by just multiplying bed volumes treated by the volume of the packed bed, which scales with the packed bed volume. Second, bed volumes can be multiplied by the empty bed contact time (EBCT), the time it takes a unit of water to flow through the entire volume of an empty packed bed, to yield total operation time independent of column volume. Considering that RSSCTs are developed as scalable treatment columns based on particle size, scaling up RSSCT design to full scale columns retains treatment performance despite the change in packed bed volumes.

Bayoxide E33 results.

Operation of both Bayoxide E33 RSSCT columns was cut short to approximately 60,000 BVs due to biological growth. The top portion of the media in both columns began to darken with the glass wool turning a light green, indicating biological growth. To avoid any negative impact to column adsorption, operation ceased and final effluent

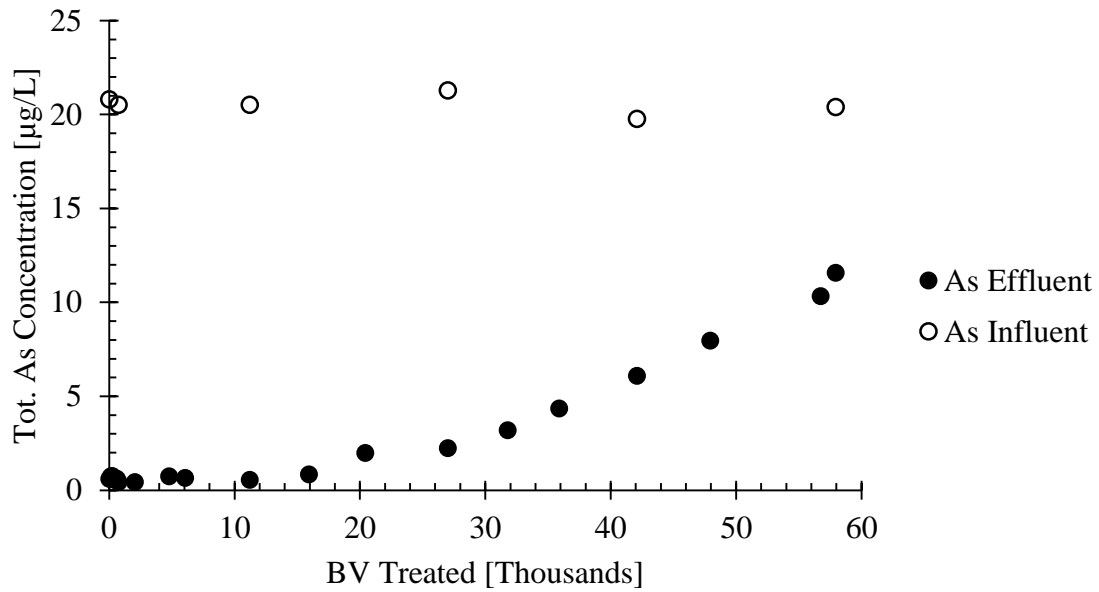
and influent samples collected (Panagiotaras et al., 2012). No replicate columns were operated as Bayoxide E33 removal performance was expected to treat upwards of 100,000 BVs of water before complete As breakthrough.

Arsenic breakthrough curves.

RSSCT results in Figure 3.1(a) for the Eastern Canal groundwater shows Bayoxide E33 performance in treating total arsenic. When breakthrough starts at 15,000 BVs treated, E33 adsorption continued to treat arsenic to levels below 2 µg/L (ppb), well under the 10 µg/L MCL. This progressed linearly until column operation ceased (60,000 BVs) at a rate of 0.26 µg/L per 1,000 BV treated. Exhaustion of the column was not observed since biological growth ceased column operation; however, the 10 µg/L MCL was not reached in the effluent stream until 55,000 BVs of water were treated.

Figure 3.1(b) for the Consolidated Canal groundwater appears to display similar breakthrough as the Eastern Canal groundwater well. Like the Eastern Canal groundwater, the E33 treated total arsenic concentrations to below 2 µg/L (ppb); however, when breakthrough occurs at approximately 15,000 BVs, it occurs at a rate of 0.12 µg/L per 1,000 BVs of water treated. This lower breakthrough rate indicates that E33 performance on the Consolidated Canal groundwater is 117% more efficient than in the Eastern Canal groundwater. Also, at 60,000 BVs treated, the effluent concentration reaches 6.23 µg/L total arsenic, indicating that column operation could continue. Interpolation from the breakthrough rate estimates that nearly 23,000 BVs of water could have still been treated before the MCL was met.

a)



b)

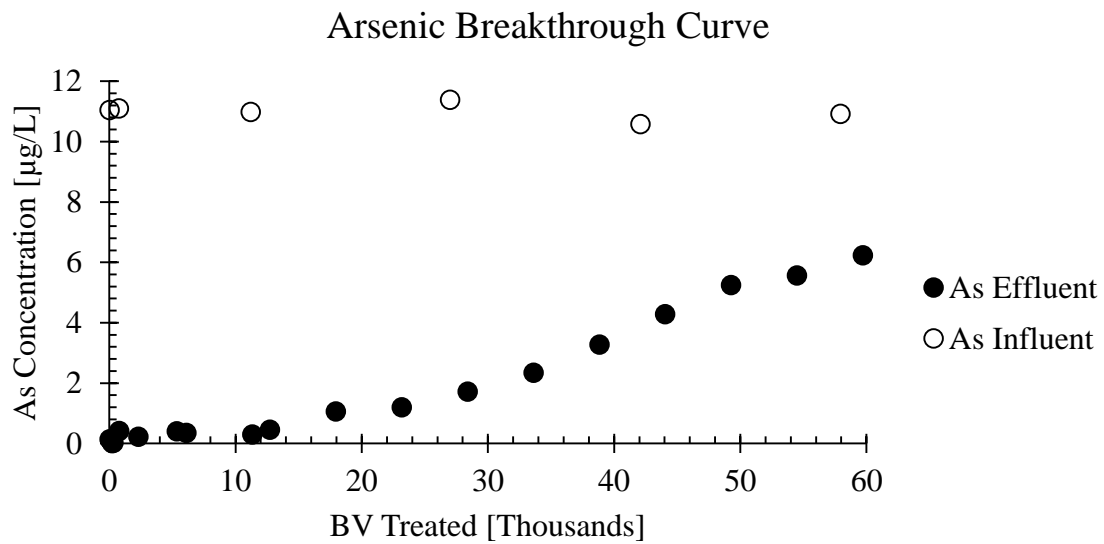


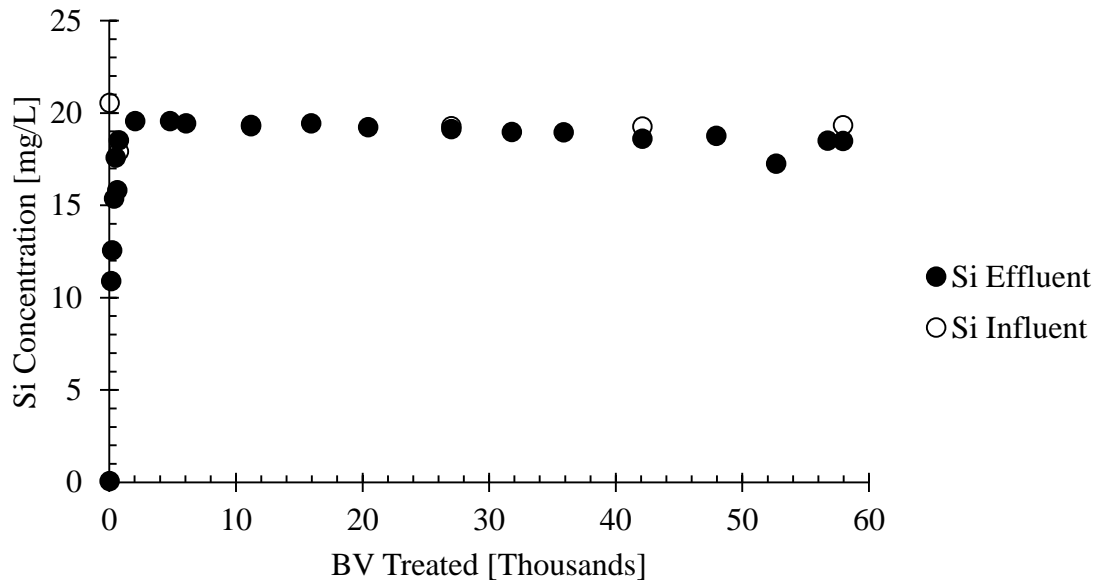
Figure 3.1: Total Arsenic Breakthrough Curve for (a) Eastern Canal Groundwater Well and (b) Consolidated Canal Groundwater E33 RSSCTs

Variation in E33 performance indicates that other factors are at work in reducing overall capacity of the adsorbent media. It has been documented that changes in bed volumes treated are more significant when arsenic concentrations are lower, even if competing anion concentrations like silica remain the same (Nguyen et al., 2011). With low concentrations of arsenic, there are more high adsorption energy sites available on the media for arsenic to adsorb.

Silica breakthrough curves.

Breakthrough curve results for silica in the Eastern Canal (Fig. 3.2(a)) and the Consolidated Canal (Fig. 3.2(b)) groundwater RSSCTs show almost immediate breakthrough. The rate of breakthrough for silica for the Eastern Canal groundwater is interpreted to be 9.59 mg/L (ppm) per 1000 BVs treated, with a rate of 14.4 mg/L per 1000 BVs treated for the Consolidated Canal groundwater. Despite being orders of magnitude higher in concentration, silica's effect on E33 adsorption performance is almost negligible. Such results indicate that silica is not a major factor in overall E33 performance, which has been observed with even higher silica concentrations (Nguyen et al., 2011).

a)



b)

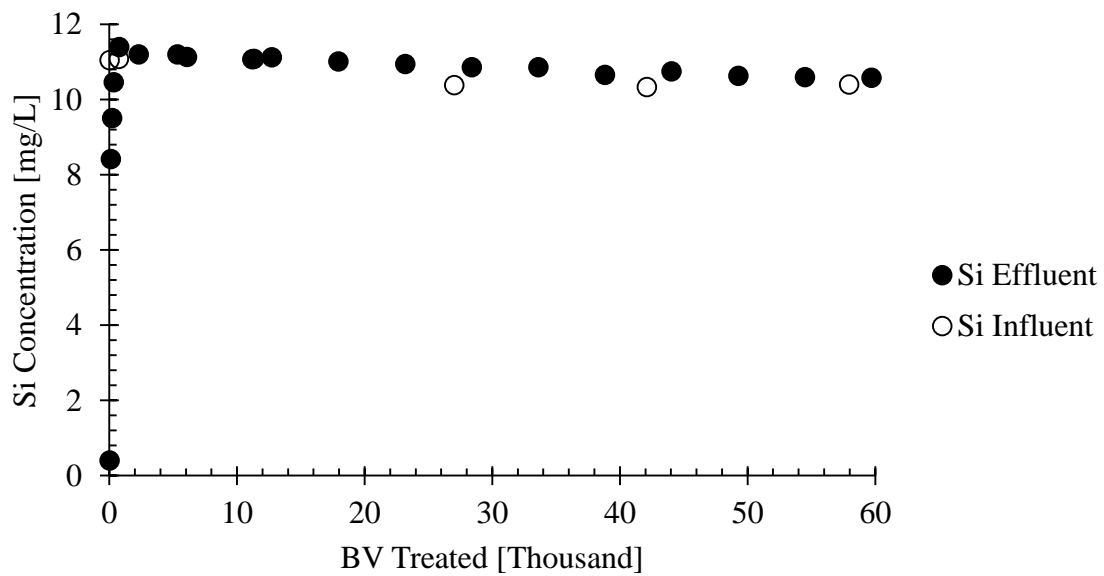


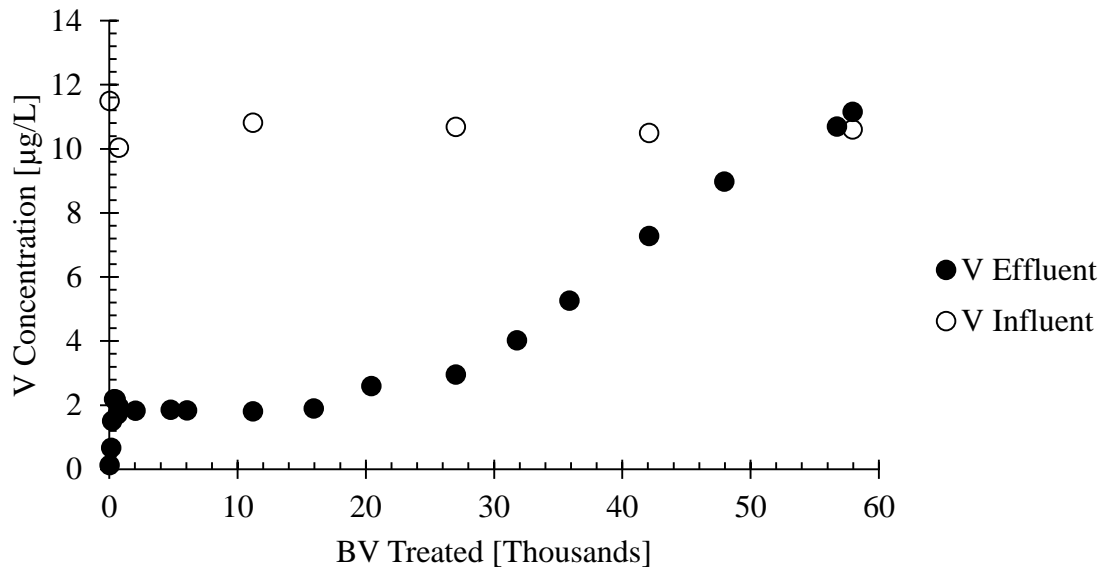
Figure 3.2: Total Silica Breakthrough Curves for (a) Eastern Canal Groundwater and (b) Consolidated Canal Groundwater E33 RSSCTs

Vanadium breakthrough curves.

The Eastern Canal groundwater RSSCT breakthrough curve for total vanadium is shown in Figure 3.3(a). Initially, vanadium appears to have instantaneous breakthrough like silica within the first 100 BVs. However, breakthrough ceases and stagnates around 2 µg/L (ppb). The cause of this rapid then halting breakthrough is attributed mostly to analytical error as replicate influent samples show steady concentration. True breakthrough begins approximately at 16,000 BVs and demonstrates linearity. The rate of breakthrough is calculated as 0.22 µg/L per 1000 BV treated, nearly identical to total arsenics rate of breakthrough. Vanadium also reaches exhaustion at 60,000 BVs treated.

Vanadium breakthrough for Consolidated Canal groundwater (Fig 3.3(b)) does not show the same rapid-then-halting breakthrough seen in the Eastern Canal groundwater, yet breakthrough begins at the beginning of column operation. Also unlike the Eastern Canal breakthrough curve, the rate of vanadium breakthrough appears to increase near 20,000 BVs treated. Both rates are estimated as 0.09 µg/L and 0.16 µg/L per 1000 BVs treated. The initially slower breakthrough rate when compared to the Eastern Canal vanadium breakthrough curve indicates that the analytical error is just a period of slow, steady adsorption onto available E33 sites until they become less available, thereby increasing the breakthrough rate. Complete vanadium breakthrough occurs again at 60,000 BVs, indicating that vanadium adsorption is consistent despite water characteristics.

a)



b)

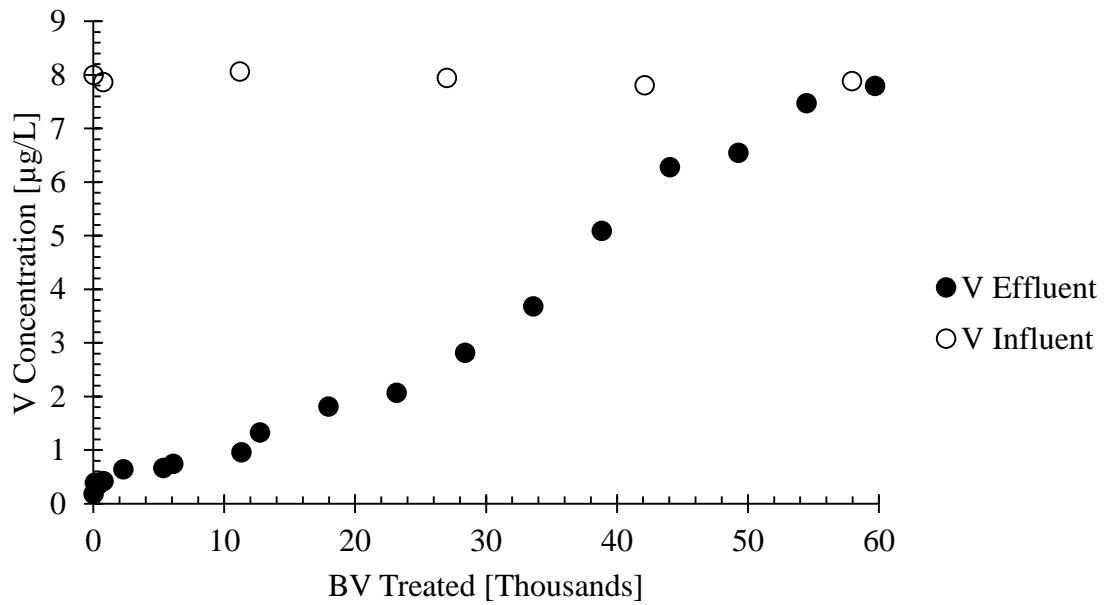


Figure 3.3: Total Vanadium Breakthrough Curves for (a) Eastern Canal Groundwater and (b) Consolidated Canal Groundwater E33 RSSCTs

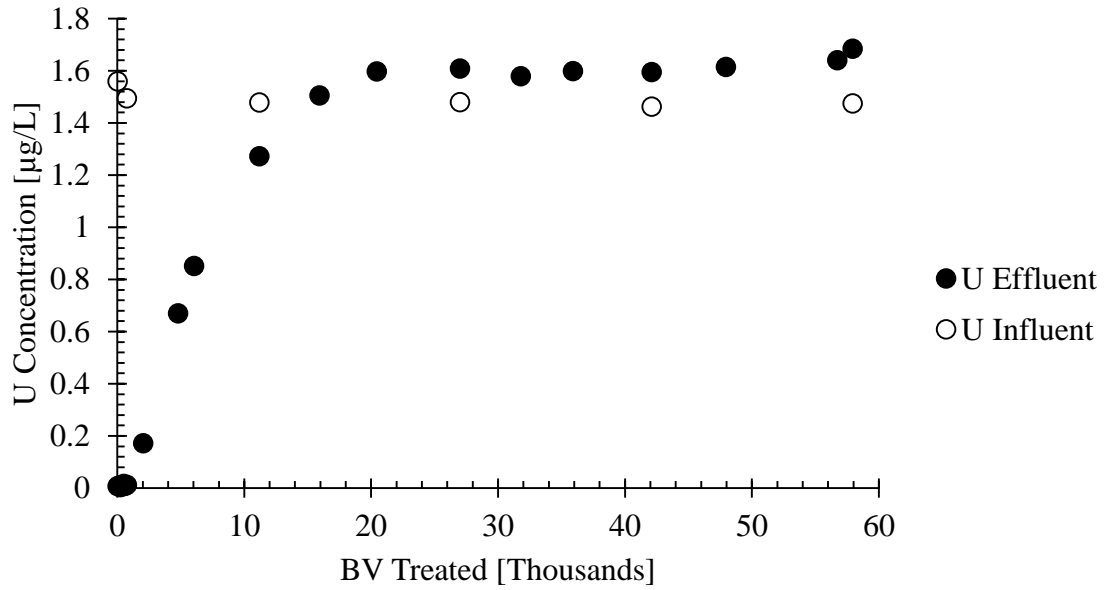
In regards to vanadium competition with arsenic for adsorption sites, vanadium appears to have very little impact on total arsenic adsorption. While vanadium breakthrough rates increase near the start of arsenic breakthrough (between 15,000 and 20,000 BVs treated), it is mostly coincidence. Considering if vanadium had a large effect on arsenic's adsorption onto E33, the visual effect would have been earlier arsenic breakthrough, not simultaneous. It has been considered that the lack of vanadium interference in arsenic adsorption is likely caused by overshadowing of silica (Nguyen et al., 2011). Therefore, E33 adsorption performance for arsenic is hardly impacted by the two main competing species for adsorption.

Uranium breakthrough curves.

Uranium is a naturally radioactive element most commonly found within the earth's crust. While uranium concentrations are not considerably high in natural groundwater, the cumulative adsorption of it could prove to classify exhausted E33 media as a different waste type. Designation of spent E33 media as a mixed waste would require disposal at a facility authorized to accept mixed waste (U.S.EPA, n.d.-a). This designation is given to any waste with residuals exceeding 0.05% by weight of uranium. As a result, uranium breakthrough curves (Figure 3.4(a) and (b)) observe total mass accumulated through a simple mass balance.

Overall, both breakthrough curves for each groundwater source display similar curves. Initial breakthrough begins when the columns start and end at 11,000 BVs treated and 12,500 BVs treated respectively. Breakthrough rates for the Eastern Canal and Consolidated Canal E33 RSSCTs are 0.140 µg/L and 0.23 µg/L per 1000 BVs treated.

a)



b)

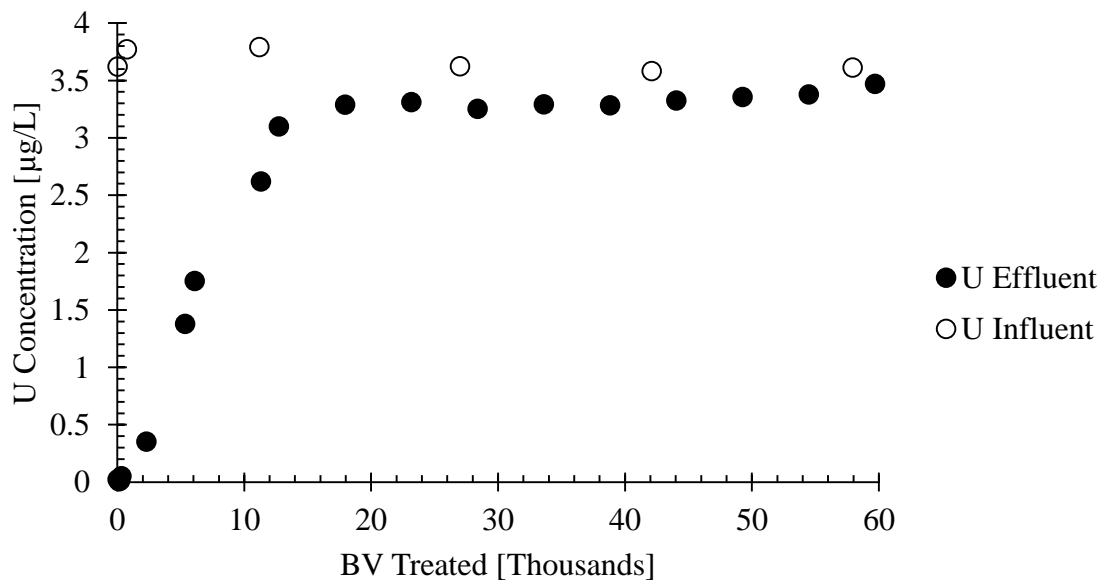


Figure 3.4: Total Uranium Breakthrough Curves for (a) Eastern Canal Groundwater and (b) Consolidated Canal Groundwater E33 RSSCTs

While not a competing anion for arsenic adsorption sites, the total mass of uranium adsorbed onto E33 is required to be known since the media, once spent, may require disposal as a mixed waste landfill which is extremely costly. Calculation of the total mass adsorbed is a simple mass balance of subtracting the effluent mass from the influent mass. This requires integration of the breakthrough curves to yield the product of the concentration and the bed volumes treated. Taking into consideration that the bed volume of the RSSCTs is 6.1 mL, the total masses of uranium adsorbed onto each E33 RSSCT were 68 μg and 227 μg . With media mass being 9.10 g, the total percent by weight of uranium adsorbed are two orders of magnitude lower than the 0.05% by weight consideration, indicating that this media is safe to dispose to landfills even when upscaling to full-sized column designs.

Bayoxide E33 performance.

Bayoxide E33 performance at treating total arsenic in both Eastern Canal and Consolidated Canal groundwater shows excellent results. Considering that silica interference overshadows any vanadium interference and still presents no discernable effects to total arsenic adsorption, Bayoxide E33 is a hearty contender to treat arsenic at groundwater wells for SRP. The only major concern to account for is arsenic concentration, as it seems to limit performance under higher concentrations as indicated by the difference in rates of breakthrough and total arsenic treated.

When considering the total treatment time for potential full-scale column operation, multiplying the BVs treated by the EBCT will yield total operation time. Considering the RSSCTs were to simulate a full-scale column with an EBCT of 2.5 min, the total treatment times for E33 columns at the Eastern Canal and Consolidated Canal

wells are 95.5 and 104 days, respectively. However, operation at the Eastern Canal could be extended by utilizing parallel or series operated columns, effectively exhausting the media and blending effluent arsenic concentrations together to meet the 10 µg/L MCL. This would push operation to upwards of 140 days. Even then the Consolidated Canal column never reached full exhaustion. If that were considered, total operation time increases to 160 days. Finally, normal EBCT values for column operation typically stay towards 5 minutes, which is double the currently designed RSSCT, and effectively doubles the operating life of the full-scale columns to 280 and 320 days. Ranging from 3-4 months to nearly a year of continuous operation brings value to E33 media as a treatment solution for arsenic.

Reproducibility of these results is mainly limited to the source water quality. Both media showed similar performance, and overall data analysis showed great accuracy as replicate influent sample concentrations in each figure demonstrate. Throughout column operation, the influent samples were taken from the same source water, and each replicate concentration never varied beyond 1 µg/L.

SBG1 results and performance.

The SBG-1 resin RSSCTs operated with only one instance of error. During the Eastern Canal groundwater SBG-1 RSSCT operation, Column A (5% brine regeneration) sheared during a retighten of the Teflon endcap after one regeneration. Also, during the fourth regeneration for both groundwater sources RSSCTs, air was introduced fully into packed bed columns, effectively short-circuiting the media and preventing adsorption. As a result, the three regeneration cycles are shown, with the Eastern Canal RSSCT column A 5% regeneration missing due to the broken column.

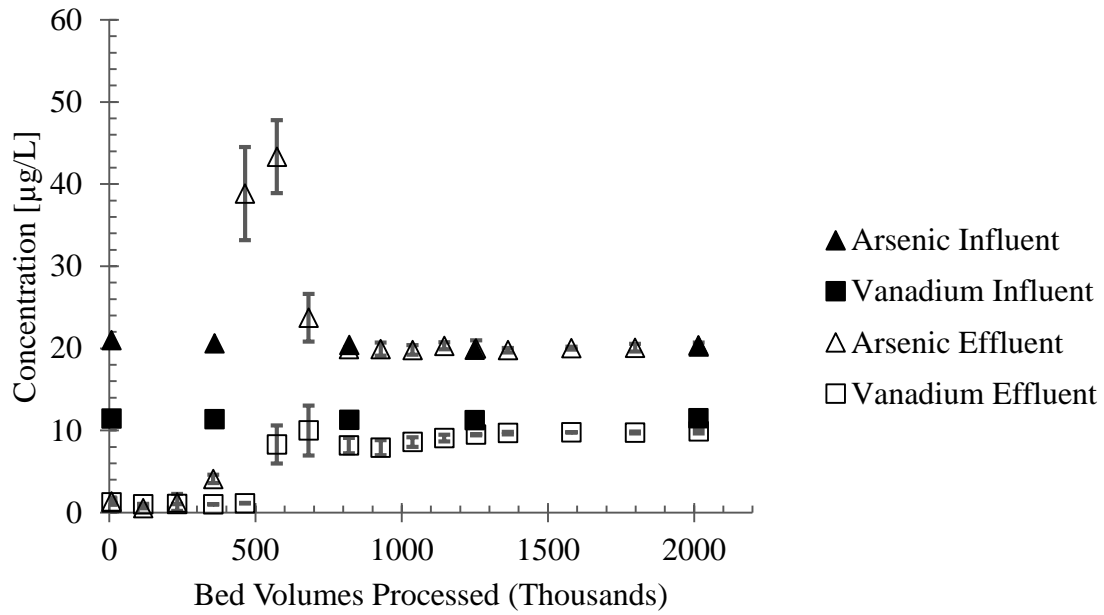
Arsenic and vanadium breakthrough curves.

Figure 3.5(a) and 3.5(b) displays the breakthrough curves for both total arsenic and vanadium on the same plot for the Eastern Canal and Consolidated Canal groundwater RSSCTs. Each column was packed with the same SBG-1 media and initially operated (virgin run) at the same time, resulting in triplicate data for treatment during the virgin operation. Error bars indicate the standard deviation of the average concentrations from all three columns (A, B, and C) operated.

Arsenic and vanadium concentration data were plotted due to both being competing species for the ion exchange sites on the crushed polymer beads. In each case, chromatographic displacement of arsenic is observed with peaks of 42 $\mu\text{g/L}$ and 15.9 $\mu\text{g/L}$ arsenic for the Eastern Canal and Consolidated Canal RSSCTs respectively. This indicates the presence of elevated TDS, most notably sulfate as previous studies have indicated chromatographic displacement being common with arsenic treatment with ion exchange (Clifford, 1999; Horng & Clifford, 1997; U.S.EPA, 2003). Further evidence of the arsenic displacement is the continued adsorption of vanadium. In each case, as the chromatographic displacement of arsenic reaches its peak, the vanadium concentration begins to plateau and follow a slower breakthrough rate than when arsenic was sorbed onto the ion exchange media. This indicates that sites once containing adsorbed arsenic, have been opened due to the displacement, and allow for further adsorption of competing anions. Prevention of chromatographic displacement requires either ceasing column operation prior to arsenic exhaustion or pre-treatment of sulfate and other competing ions before running through the SBG-1. This thesis did not observe pre-treatment, and has

lected to promote ceasing and regenerating columns prior to complete arsenic breakthrough.

a)



b)

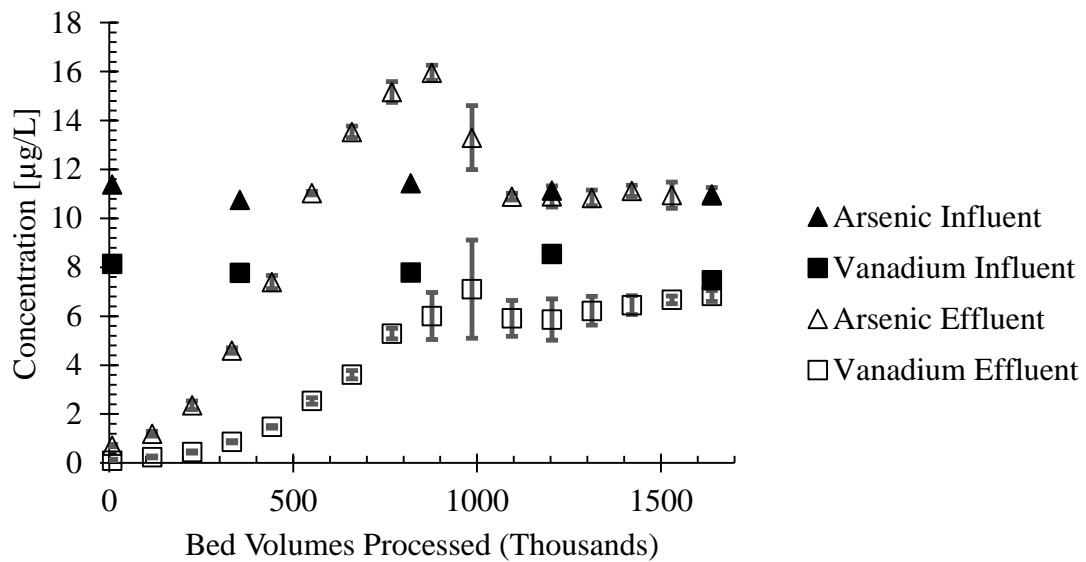


Figure 3.5: SBG-1 Virgin Resin Breakthrough Curves for (a) Eastern Canal Groundwater and (b) Consolidated Canal Groundwater

SBG-1 virgin performance for arsenic treatment in both cases shows that arsenic breakthrough occurs rapidly. The Eastern Canal SBG-1 RSSCTs arsenic breakthrough curve (Fig. 2.8(a)) displays arsenic adsorption up to 400 BVs of treatment before instantaneous chromatographic displacement occurs. In the case of the Consolidated Canal SBG-1 RSSCTs, arsenic breakthrough is gradual and reaches exhaustion at 500 BVs of treatment. Considering that the bed volume of each RSSCT was 6.1 mL, the total masses of arsenic adsorbed for the Eastern Canal and Consolidated Canal groundwaters are 41.2 μg and 15.6 μg . Also, based on an EBCT of 2.5 minutes, the total operation times before regeneration are 16.7 hours and 20.8 hours, respectively. While unconventional for ion exchange columns, if operated at an EBCT of 5 minutes, the operational times extend to 1.39 days and 1.74 days before requiring regeneration.

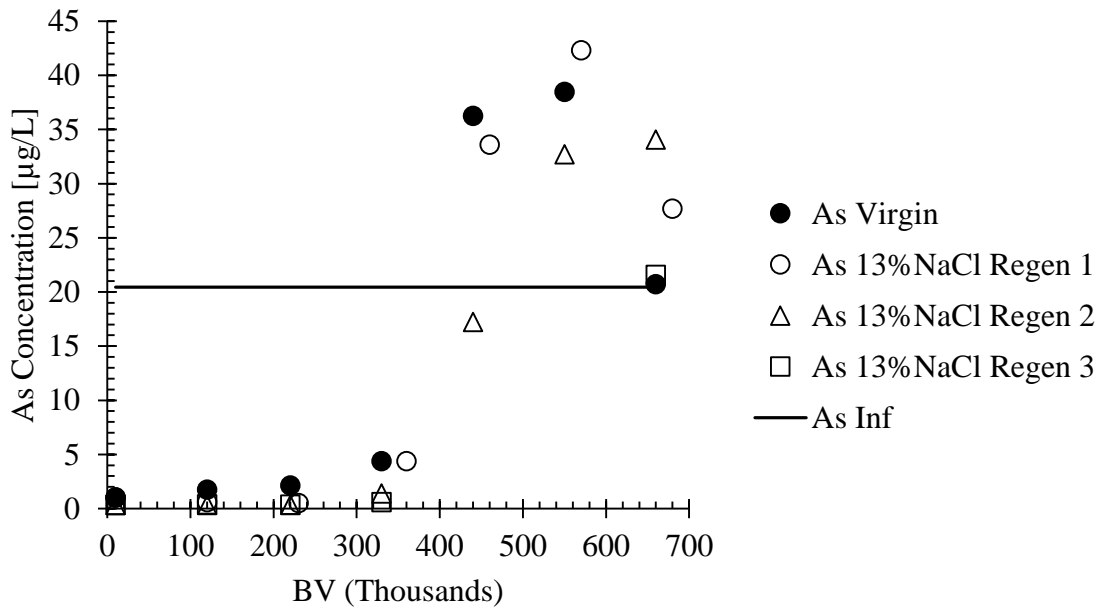
Based on the triplicate columns, the error in arsenic and vanadium analytics can provide valuable insight as to column performance. Both groundwater breakthrough curves show that relative error between each column is negligible as the error bars are smaller than data's plotted points. Only during the chromatographic displacement is greater variation observed in arsenic and vanadium concentrations. These variations are caused by the desorption of arsenic sites with lower ionic bonding energies and being replaced by other anions with greater selectivity or ionic bonding energies (sulfate, vanadium, uranium, etc.). This is represented by the continued adsorption of vanadium as vanadium effluent concentrations start varying when arsenic concentrations vary. As for

no vanadium displacement, vanadium will have a higher ionic bonding energy, preventing its replacement on the media sites.

Regeneration of SBG-1.

The main focus of the regeneration cycles for the SBG-1 resin RSSCTs was to determine an efficient brine solution that would not only regenerate the resin, but also potentially improve possible adsorption performance. The three columns for each groundwater source were labeled as Column A, Column B, and Column C to indicate their respective brine concentrations of 5%, 13% and 25% NaCl by weight for regeneration. Figure 3.6 highlights the regeneration of the Eastern Canal groundwater source SBG-1 RSSCTs while Figure 3.7 highlights the Consolidated Canal groundwater source SBG-1 RSSCTs.

a)



b)

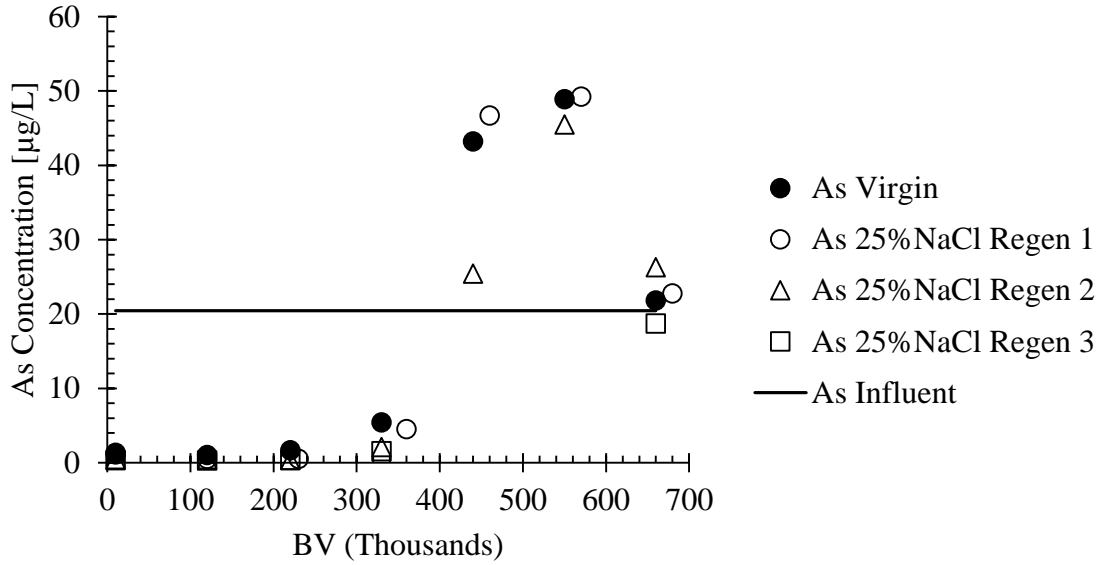
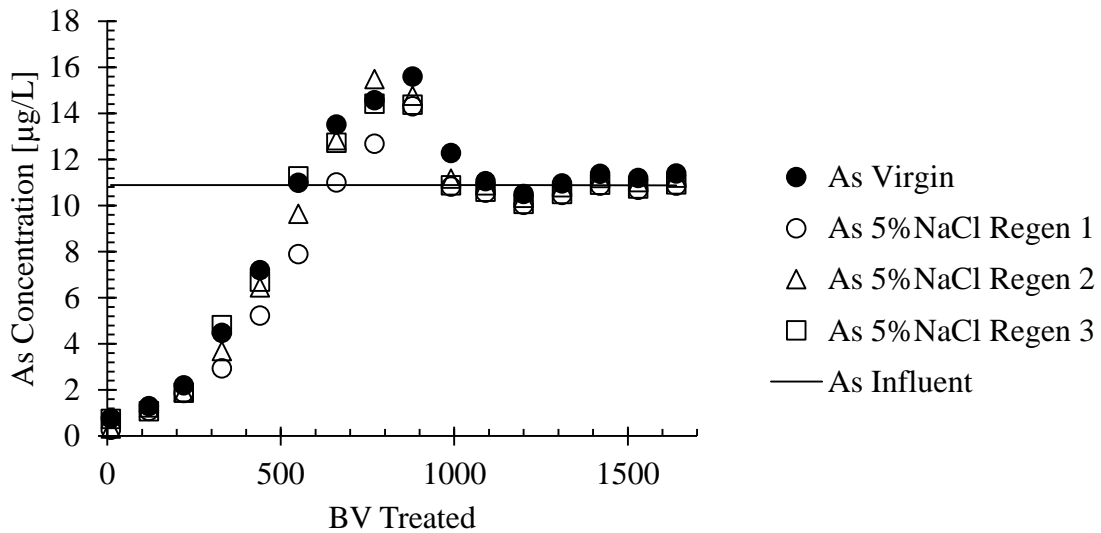


Figure 3.6: SBG-1 Regeneration Cycle Comparison for Eastern Canal Groundwater at (a) 13% and (b) 25% NaCl by Weight

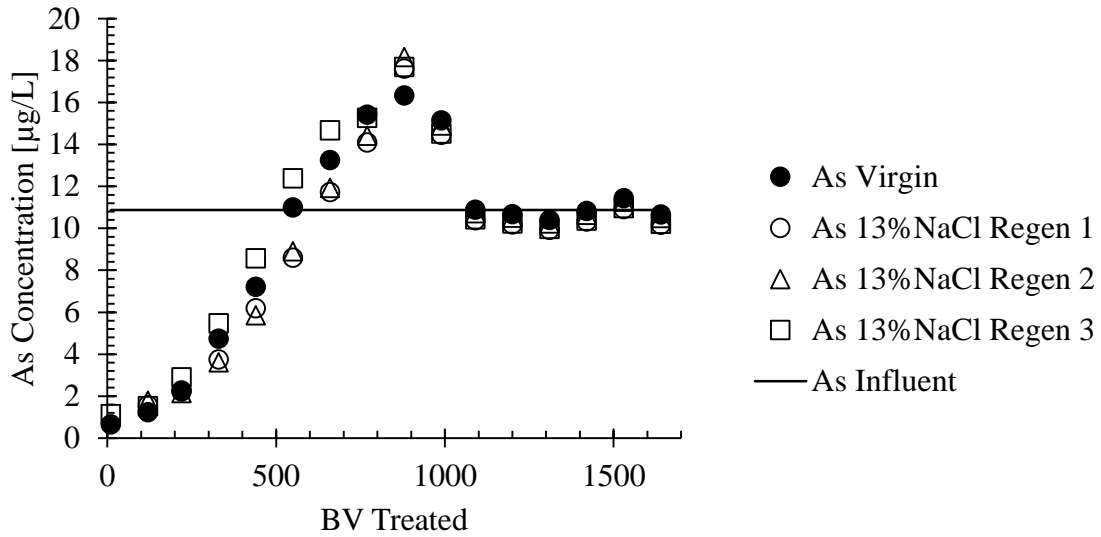
Due to Column A shearing after the first regeneration cycle, breakthrough data for 5% NaCl by weight regeneration is not available. However, observation of the breakthrough curves after regenerating with 13% NaCl show that regeneration successfully regenerates the ion exchange sites. In determining whether 13% NaCl brine improves arsenic adsorption onto the SBG-1 resin, the percent difference between the mass arsenic adsorbed from the virgin and every regeneration cycle after helps provide whether higher brine concentrations are necessary. The percent differences between regen cycles 1, 2 and 3 and the virgin run are 1.54%, 0.51%, and 0.10%. For the 25% NaCl brine, the difference between each regeneration cycle and the virgin run are 1.68%, 0.80%, and 0.57%. Unfortunately, these percentages mean that each regeneration cycle only regenerates the resin, not improve overall arsenic adsorption capacity.

When observing Figure 3.7, the same conclusions can be drawn about regeneration for the Consolidated Canal SBG-1 RSSCTs as in the Eastern Canal RSSCTs. Figure 3.7(a) highlights the regeneration of SBG-1 at 5% NaCl by weight. Regeneration at this brine concentration is successful, indicating that the 13% and 25% NaCl brine solutions are unnecessary as they only regenerate the ion exchange sites and not improve them. However, a lower brine concentration means less NaCl is required for regeneration reducing overall chemical storage required for column regeneration. The main issue to consider when operating an ion exchange full-scale column is the chemical storage and waste disposal as the brine will contain concentrations of arsenic that can exceed 5 mg/L levels, requiring additional steps in waste management (U.S.EPA, n.d.-a, 2003).

a)



b)



c)

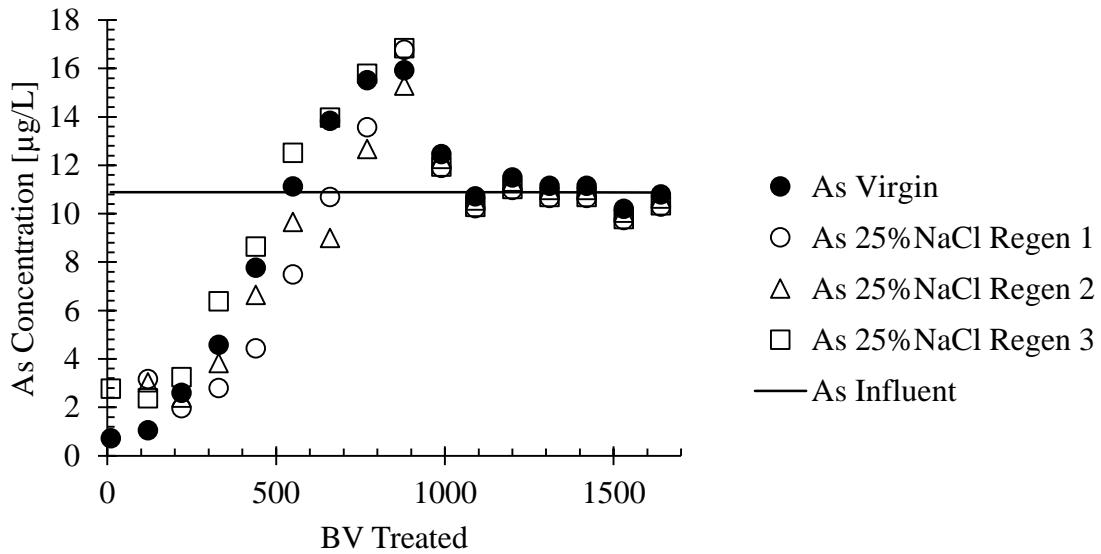


Figure 3.7: SBG-1 Regeneration Cycle Comparison for Consolidated Canal

Groundwater at (a) 5%, (b) 13%, and (c) 25% NaCl by Weight

While the performance of SBG-1 shows adequate removal of arsenic (41.2 μg and 15.6 μg), the required regeneration of the column indicates that adequate space is needed

for chemical and waste storage of brine and eluate. When taken into consideration that SRP groundwater well sites are limited in space (see Fig 1.4 for Eastern Canal and Consolidated Canal well sites), ion exchange becomes less appealing for overall treatment needs. Even taking into consideration that full-scale column design will require either columns operating in parallel or series to account for any maintenance/regeneration, the overall space requirement could exceed the footprint of the groundwater well site. Another consideration is waste management. For groundwater sources containing $> 10 \mu\text{g/L As}$, it is anticipated that spent regenerant contains at least 5.0 mg/L As (U.S.EPA, 2003). This becomes definitive if the regenerant is recycled to reduce wasting water as the arsenic concentration builds over each recycled brine regeneration. Overall, while SBG-1 ion exchange resins can effectively treat arsenic containing groundwaters, it is overshadowed by the performance of E33 in terms of operation longevity, waste management, and even simplicity in design.

CHAPTER 4

SUMMARY AND CONCLUSIONS

The major conclusions presented within this thesis include:

- Bayoxide E33, a synthetic iron oxide adsorbent from Severn Trent Services, is the most optimal adsorbent for arsenic treatment to the 10 µg/L MCL requirement for SRP controlled groundwater wells in terms of operational longevity, waste management, and overall design simplicity.
- While SBG-1, a SBA-IX resin from ResinTech, Inc., adequately treats arsenic to below 10 µg/L MCL, regeneration of the ion exchange adsorbent sites requires necessary on-site chemical and waste storage. SRP groundwater well sites are limited in size, and designing a full-scale IX column with appropriate storage systems within a small footprint complicates design.
- Regeneration of SBG-1 only requires a 5% NaCl brine to achieve full regeneration. Higher brine concentrations only regenerate adsorbent sites and do not improve overall performance. Regenerant waste is also classified as hazardous due to the arsenic concentration, warranting specialized disposal.

Recommendation to SRP

A summarization of Bayoxide E33 and SBG-1 operational conclusions is provided in Table 4.1 to highlight differences between the media

Table 4.1:

Summary of Operational Conclusions

Parameter		Adsorbent Media	
		E33	SBG-1
Expected Operation Time [Days]	2.5min EBCT	95.5 - 104	0.7 - 0.87
	5.0min EBCT	191 - 208	1.4 - 1.74
	5min EBCT (Complete Exhaustion)	280 - 320	1.4 - 1.74
Competing Anions Affect Adsorption/Operation		No	Yes
Regenerable Media		No	Yes
Brine Concentration Required for Regeneration [% by weight]		-	5%
Waste Concerns		Direct Landfill Disposal	Once through Regeneration: Discharge to sewer system Recycled Brine Regeneration: Hazardous waste disposal from concentrated As
Design Complexity		Only requires packed bed column setup to well head and disposal when exhausted. Reducing pH not necessary	Requires packed bed column setup to well head alongside brine storage tank for regeneration. Waste discharge to sewer line or to be stored in brine regenerant tank.

Considering that the Colorado River Basin is undergoing a drought and that surface water from the CAP Canal and Salt and Verde Rivers will be limited, SRP may have to rely on increased groundwater sources. With over 30 groundwater wells greater than 10 $\mu\text{g/L}$ As, and 7 of those greater than 20 $\mu\text{g/L}$, SRP's best treatment technology choice for arsenic removal is packed bed media columns of Bayoxide E33. With column operational lengths spanning from several months to a year based on design, SRP should utilize the RSSCT design presented in this thesis to design full-sized columns that meet treatment requirements at various groundwater well sites.

Concerns regarding Bayoxide E33 use as a treatment technology are limited to specific water characteristics and possible biological growth. Water characteristics can alter overall E33 performance. While silica and vanadium are not major concerns despite being competing anions, high arsenic concentrations will reduce adsorption performance. Simply designing a conservative full-scale E33 column for the highest arsenic concentration allows the column to be implemented at any groundwater well. However, these columns should be regularly inspected to observe for biological growth as this could oxidize the E33, releasing adsorbed arsenic into the effluent.

Future Research Considerations

Possible considerations for future research include the following:

- Design and implementation of RSSCTs across various Arizona groundwater wells with other iron oxide based adsorbent media to determine best possible media for local residencies/aquifers.

- Design and implement a pilot-scale E33 column for implementation at a SRP groundwater well and monitor downstream and treatment plant influent concentrations for arsenic to determine impact of source treatment.
- Design and test a mobile full-scale column for implementation at seasonal SRP groundwater wells.

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