Arsenic Team Final Report

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Part I
Introduction

As part of AguaClara's goal to provide access to safe, sustainable drinking water to meet global water needs, our team is researching water treatment technologies that can remove arsenic from groundwater. AguaClara's current plant design utilizes hydraulic flocculation and sedimentation to remove clay particles from surface water, and there has been strong evidence that flocculation could be an effective removal technique for arsenic as well. However, we also are researching alternative removal methods, such as fixed-bed reactors and media filtration, in order to determine the most effective technology for a future AguaClara design. In addition to researching removal methods, our team has researched and written a lab procedure that will allow us to safely work with arsenic in the lab. Finally, we created a Mathcad document that will allow future AguaClara teams to input certain parameters that will output a given experimental design. To create this Mathcad document, we based our equations on the current experimental design used by the Flocculation and Sedimentation Optimization team, adjusting constants as necessary to apply the design to arsenic removal instead of clay removal.

Part II
Background

In many parts of the world, groundwater is the main source of drinking water. Some regions, due to the geography of the area or because of anthropogenic inputs, experience high concentrations of arsenic in local groundwater sources. Arsenic can cause numerous health problems when consumed in large doses, and studies have shown that exposure to low to moderate concentrations of arsenic over a length of time can result in various types of cancers [1]. The World Heath Organization (WHO) adopted a new acceptable arsenic concentration standard of 10 ppb in 1993, but it has yet to be consistently met in many parts

of Southeast Asia. In Bangladesh especially, arsenic concentrations are well above even the Bangladeshi standard of 50 ppb [2].

Two speciations of arsenic commonly found in water are arsenite, or As(III), and arsenate, or As(V). Of the two, As(V) is more easily removed from water[2, 3]. As(III) is water soluble and often undergoes oxidation to transform it to the particulate As(V) before being treated [4]. It is now relatively inexpensive to detect the two arsenic speciations. Arsenic kits can be purchased online for a little over 100 USD.

The process of removing arsenic from water is based on both traditional treatment methods and on novel approaches. Many promising coagulants are being researched with the potential to be used in a flocculation, sedimentation, or filtration system, or in some combination of these three. Research is also being done on the use of different media filtration techniques, including iron-coated sand, gravel beds with iron sludge, and manganese greensand. Additionally, a number of fixed-bed removal methods are being developed that use fixed adsorbents (such as activated alumina or granular ferric hydroxide) or are fixed-bed upflow bioreactors that utilize the oxidation of iron and manganese ions to remove arsenic [94].

Part III
Research

1 Lab Use of Arsenic

1.1 Obtaining Arsenic

We can buy arsenic in both solid and liquid forms from sources such as Cole Parmer [5], and we may also be able to go to the Cornell Chemistry Stockroom in Baker Lab. In order to purchase the arsenic from the stockroom we would need an account. If there isn't one established already through the CEE department, we may have to talk to the CEE department to help coordinate with the Chemistry Stockroom [6].

1.2 Maintaining Arsenic

1.2.1 Labeling

Labels can be generated from Cornell University's EH&S website [7]. Figure 1 shows an example of such a label. These labels give information on the following:

1. Statement of Hazards: information on the health hazards associated with working with the compound of concern

Arsenic Trioxide
Danger! Toxic! Cancer Hazard! Irritant!
CAS#: 1327-53-3
NFPA RATINGS (SCALE 0-4): Health=3 Fire=0 Reactivity=0

Statement of Hazards:

Potentially fatal if swallowed. Respiratory tract irritation, skin irritation, eye irritation, allergic reactions, cancer hazard (in humans).

Precautionary Statements:

Avoid all exposure to this material. Avoid heat, flames, sparks and other sources of ignition. Avoid generating dust.

First Aid:

Inhalation: Remove from exposure immediately. Perform artificial respiration if needed. Skin contact: Remove contaminated clothing, jewelry, and shoes immediately. Wash with soap or mild detergent and large amounts of water until no evidence of chemical remains (at least 15-20 minutes). Eye Contact: Wash eyes immediately with large amounts of water or normal saline, occasionally lifting upper and lower lids, until no evidence of chemical remains. Ingestion: If vomiting occurs, keep head lower than hips to help prevent aspiration. If person is unconscious, turn head to side. Get medical attention immediately.

Figure 1: Example of an EH&S generated arsenic label

2. Precautionary Statements: methods to reduce risk of exposure
3. First Aid: steps to take if exposed

1.3 Storage

Arsenic should be kept in a tightly closed non-metallic container [8]. It should be stored in a cool, dry, and well-ventilated location [8].

1.3.1 Lab Equipment

Examples of lab equipment used in arsenic research were found on the Hach Company website [9], and their information is listed below.

1. Arsenic Low Range Test Kit: has a range of 0-500 ppb; costs $152
2. EX Arsenic High Range Test Kit: has a range of 0-4000 ppb; costs $62

3. Distillation Apparatus Set: can purchase one that works for arsenic specifically at $300, or one that also works for ammonia, cyanide, fluoride, phenols and selenium for $600

4. Standard bottles, glass, graduated cylinders

1.4 Handling Arsenic

1.4.1 Dangers of Arsenic

Reaction

Arsenic dust should be kept away from fire to avoid explosion [10]. Arsenic is incompatible with strong oxidizers, acids, alkalines, active metals, bromine azide, and hydrogen gas [8].

Toxicity

Arsenic affects skin, the liver, kidneys, eyes, the nervous system, the circulatory system, the digestive system, and the respiratory system [8, 10]. Arsenic (III) compounds are corrosive, and swallowing arsenic can even lead to death [8]. Thus, one should avoid swallowing arsenic, breathing in arsenic, and/or touching arsenic with his/her skin or eyes [10].

Cancer

Arsenic is known to cause lung and lymphatic cancer [10]. Arsenic exposure has also been linked to bladder, lung, kidney, nasal, liver, and prostate cancer [95].

1.4.2 Lab Space

Selection and Registration

Since working with arsenic is much more hazardous than most current AguaClara research activities, either setting aside a separate room for arsenic research or sharing space in a lab with similar toxicity and carcinogenic risks is suggested. Otherwise, other AguaClara researchers working on non-arsenic research will need to wear personal protective equipment, take much more serious safety precautions, and follow much stricter hygiene practices than what is normally necessary for them. The selected lab space for arsenic research will need to be registered with Cornell University Environmental Health and Safety's Hazard Assessment Signage Program (HASP) and display appropriate signage to indicate the carcinogen and corrosive risk level [11].

Equipment

The selected lab space should have an emergency shower and an eyewash station [8]. A fume hood or a glove box for work with solid arsenic will reduce the likelihood of breathing in arsenic dust [12]. Dedicating a special area for experiments involving arsenic-contaminated water is suggested [8].

Rules

Nothing that touches the mouth (eg. food, drinks, chewing gum) should ever be found in the selected lab space [13]. Preferably, all personal belongings (eg. backpacks, coats) would be left in a different room and not be brought into the selected lab space. The floor should be routinely vacuumed instead of cleaned by brushing or blowing with compressed air [14].

1.4.3 Personal Safety

Education

All persons who will enter the selected lab space, not just the AguaClara arsenic researchers, should be informed about the dangers of arsenic and how they should protect themselves. As for EH&S training classes, all AguaClara arsenic researchers must take Hazard Communication, Laboratory Safety, Carcinogen Awareness, and Chemical Waste Disposal, and they are recommended to take Laboratory Inspections as well as Chemical Storage and Segregation [15].

Good Practices

At all times, researchers should wear a lab coat, chemical safety goggles, full face shield, and latex/nitrile/other gloves impermeable to water and arsenic dust [8]. After working with solid arsenic or after a spill, the lab coat should be removed, put in a sealed container, and not worn again until all the arsenic has been removed [13]. All personal protective equipment should be disposed of as arsenic-contaminated waste or left inside before the researchers exit the lab space [16]. Face, hands, and forearms must be cleaned comprehensively by scrubbing with soap and rinsing with water immediately afterward [13].

1.4.4 Regulation Compliance

Some of the protocol proposed above are adopted from recommendations and regulations for workplaces governed by 29 CFR 1910 subpart Z, which we are not actually subjected to as laboratory researchers [17]. However, we need to follow 29 CFR 1910.1450, which partly means we either adapt the Cornell University Laboratory Safety Manual and Chemical Hygiene Plan or have something similar of our own [18].

1.5 Disposing of Arsenic

Arsenic waste at a concentration greater than 5.0 mg/L is considered toxic and hazardous by the Resource Conservation and Recovery Act (RCRA) [19], and will therefore need to be disposed of by Environmental Health & Safety. The two primary types of arsenic waste we will be dealing with are liquid waste and solid waste. Liquid waste includes any water used for testing, rinsing, backwash, or acid neutralization, while our solid waste is the sludge generated from the sedimentation process. Solid waste can also include spent resins, filter media, or membranes, though this would only be a concern if the arsenic-contaminated water were to be run through the stacked rapid sand filter [20].

When disposing of arsenic waste, one must wear nitrile rubber gloves, eye protection, and a lab coat. The containers used to hold the waste must be clearly labeled as hazardous waste and have a description of the contents [22]. The containers must be in good condition and kept closed at all times. The waste must then be boxed for pickup by EH&S.

Any surface that may become contaminated (including fume hood surfaces) should be covered with absorbent paper and also wiped with a damp paper towel on a regular basis. Any paper that becomes contaminated should be folded and placed in a plastic bag, and then labeled as hazardous waste to be picked up by EH&S [12].

In the event of a small spill, one must still wear nitrile rubber gloves, eye protection, and a lab coat. Avoid breathing any dust, and brush the spill into a container to take to the fume hood. If it is a small liquid spill, you can use an absorbent material from the lab's spill closet to clean it up. If a larger spill takes place, leave the area immediately and contact EH&S [12].

In the lab where AguaClara arsenic research is conducted, there needs to be a Department of Transportation (DOT) approved box, which is a storage area within the lab where EH&S personnel can remove the hazardous waste [23]. We can ask for a DOT box when making the first pick-up request at http://www.old-site.ehs.cornell.edu/rad/ChemWasteForm.cfm [23].

In speaking with Bill Leonard from Cornell University Environmental Health & Safety, and after conducting research online, it was discovered that under no circumstance can arsenic waste be dumped down the sink [21]. It is technically possible to pour a solution of up to 5 ppm arsenic down the drain according to EH&S, but it is not believed that this is an ethical way to dispose of the waste. The tests that we would be running would more than likely produce waste under 5 ppm, but we would still be increasing the chances of contaminating wastewater treatment plant effluent. Depending on our set-up, we can expect to produce three to five liters of arsenic containing solution with each test. This should

not be a problem to store in a large container within the lab which is clearly marked. There are hazardous waste pickups from the EH&S locations every Wednesday and Friday, but we can also call them to do a pickup if we have an unusually large amount of solution. Good containers for waste storage are often the same ones in which our reagents may come shipped to us in, or any other plastic container which we can securely close. We then need to put these filled containers in a marked box in the pickup location. The DOT boxes are strongly suggested to store the solution until pickup, but almost any box will do. Since EH&S will pick up any amount of the solution, we really don't need a way to reduce the volume of the solution, but this could be useful for storage. If we ever have problems or questions, we can always contact Bill at 607-255-5616.

2 Water Type and Interactions

2.1 Arsenic's Interaction with Dissolved Organic Matter

2.1.1 Arsenic Matter Complexes

Arsenic can be found in groundwater as either arsenite or arsenate. Arsenite is soluble in water while arsenate exists in particulate form. Arsenite is the more abundant of the two species, and it is also more toxic [25]. There are several different compounds which are also found in groundwater which arsenic may interact with; these include aluminum, iron, and clay minerals. In a study performed by Goldberg [24], it was found that the different species of arsenic interact with these other compounds at different pH values. This is important to us because we would need to know the effect of pH on arsenic removal in order to have an efficient treatment system.

Arsenate had higher adsorption rates onto metal oxides and clays when the pH of the solution was lower and had diminishing capacity as pH increased. Arsenite had its highest adsorption rate at around a pH of 8.5 and its capacity exhibited parabolic behavior. Knowing how arsenic is binding to other common components in groundwater is important because it may be easier to remove through flocculation. Arsenic is small in comparison to something such as a clay particle, so if it were possible to use a coagulant to flocculate not only free arsenic, but bound arsenic, then our removal efficacy may be higher.

One study found that the incubation of natural organic matter (NOM) with either arsenate or arsenite can produce aqueous complexes of the two substances, but the extent to which this complexation occurred varied noticeably between NOM samples from different sources (but all diluted to 10 mg/L) [26]. Buschmann et al. also observed such complexation in their experiments, where dissolved organic matter (DOM) held onto approximately a tenth of the arsenate when the mixtures had 5 mg/L of dissolved organic carbon (DOC), a pH of 7, an ionic strength of 0.05, and 67 nM of arsenate [27]. Furthermore, they saw

that increasing the concentration of DOC increased the proportion of arsenate ions that were bound. Redman, Macalady, and Ahmann suggested that this phenomenon relied on “a ternary complexation mechanism, in which cationic metals mediated the strong association between NOM functional groups and arsenic oxyacids”–a mechanism that is also known as metal bridging [26]. Lin, Wang, and Li proposed that Ca, Mg, Fe, Al, and Mn might be involved in metal bridging between arsenate and the organic matter in water extracts of compost [28], but Buschmann et al. reported that introducing Al(III) had no noticeable effect on arsenite's binding to DOM and actually decreased arsenate's binding to DOM [27]. The latter group also found that, for their sets of experimental conditions, phosphate reduced arsenate's binding to DOM [27].

2.1.2 Organic Matter's Influence on Arsenic's Binding to Metal Compounds

Redman, Macalady, and Ahmann reported that NOM competes with arsenate and arsenite for binding to hematite, "a model metal oxide" [26]. Specifically, NOM interfered with arsenite's binding to hematite more than with arsenate's binding to hematite [26].

From an examination of how dissolved organic matter affects the size of the Fe-(oxy)hydroxide aggregates to which arsenic is bound, Bauer and Blodau found that for molar ratios of ferric ions versus DOC between 0.02 and 0.1, there exists a tight positive linear relationship between the Fe/C ratio and the proportion of arsenate bound to aggregates that are over 0.2 m in diameter [29]. Increasing Fe/C ratios resulted in smaller Fe-(oxy)hydroxide aggregates as well [29]. pH and redox speciation also appear to be influential [29]. Comparing pHs of 4, 6, and 8, it seems that lowering pH raised the proportion of arsenate in aggregates that are over 0.2 m in diameter [29]. Bauer and Blodau additionally showed that at a pH of 6, more arsenite ions than arsenate ions were bound to the smallest aggregates [29].

2.1.3 Redox Reactions

After observing that the addition of arsenite to all of their NOM samples resulted in some oxidation to free arsenate, Redman et al. concluded that these redox changes were probably due to the activity of functional groups on the NOM, rather than due to metals or oxygen [26].

2.1.4 Relevance

DOC is said to be abundant in groundwater [30]. Ahmed et al. presents groundwater DOC measurements that range between 1.15 and 14.2 mg/L [30]. This paper also cited that, for the most part, Bengal Delta Plain groundwater has pH values of 6.5-7.6, little dissolved oxygen, and Eh (conductivity) values from +0.594 to -0.444 V [28]. These interactions are something AguaClara may want

to research in the future, depending on the potential sites for an AguaClara arsenic removal plant and the organic matter present in sourcewater at these sites.

2.2 Water Composition

2.2.1 Bangladesh

In Bangladesh, the maximum concentrations of 18 elements exceeded both Bangladeshi and World Health Organization (WHO) standards. Arsenic concentrations experienced a maximum value of 910 g/L and average concentrations of 18 g/L (see Table 1). The WHO has set a standard of 10 g/L, but these two values exceed it [31].

2.2.2 Cornell University

Several of the elements present in Bangladeshi waters are also detectable in Ithaca waters. These include barium, copper, lead, nickel, nitrate, and sodium (see Table 2). There also are many elements in Bangladesh groundwater that are not in Cornell's water. Thus, because of the complicated composition of Bangladesh's water, it is unlikely that we would be able to replicate Bangladeshi water by using Cornell's water supply [32].

2.2.3 Raw Water Used in Previous Studies

When testing arsenic removal methods in the lab, it is important that the raw water sample used is similar in composition to that of actual contaminated groundwater. This is because many of the compounds, metals, and organic materials present in groundwater can interact with arsenic and therefore hinder the removal process. Though it is preferred that actual groundwater samples be used, this will most likely not be feasible in the AguaClara lab.

In other studies conducted on arsenic removal by coagulation, the standard NSFI-53 challenge water was used (see Table 3). This challenge water standard was created by NSF International (formerly known as the National Sanitation Foundation), which is a global independent public health organization that "provides standards development, product certification, auditing, education, and risk management for public health and the environment" [96]. This is the standard challenge water for testing arsenic adsorbents since it has a composition similar to groundwater, containing appropriate amounts of silica, sulfate, phosphate, fluoride, and hardness. All of these elements are known to affect arsenic adsorption capacity. This water is prepared using sodium nitrate, sodium bicarbonate, sodium phosphate monohydrate, sodium fluoride, disodium metasilicate nona-hydrate, magnesium sulfate heptahydrate, and calcium chloride dehydrate [33].

Analyte	25th %ile	Median	75th %ile	90th %ile	Maximum	Average	Below MDL	Below LOD	Below WHO GV	Below BD Standard
Major elements (median > 1 mg/L)										
Calcium (Ca)	14	30	70	110	520	47	0.000	0.174	n.a.	0.773
Chloride (Cl)	4	12	42	180	1900	74	0.013	0.165	n.a.	0.877
Magnesium (Mg)	6	13	24	36	210	18	0.000	0.040	n.a.	0.894
Hardness (as CaCO3)	65	138	289	434	1409	196	0.000	0.088	n.a.	0.936
Potassium (K)	2	3	5	9	520	5	0.001	0.029	n.a.	0.927
Silicon (Si)	13	17	22	27	40	18	0.000	0.740	n.a.	n.a.
Sodium (Na)	14	27	77	250	1700	87	0.000	0.036	n.a.	0.867
Minor elements (median 0.01 - 1.0 mg/L)										
Aluminium (Al)	0.035	0.051	0.087	0.160	16.0	0.098	0.021	0.875	n.a.	0.938
Barium (Ba)	0.05	0.09	0.15	0.26	1.50	0.13	0.001	0.731	0.992	n.a.
Boron (B)	0.012	0.027	0.094	0.330	3.0	0.110	0.217	0.737	0.939	0.993
Fluoride (F)	0.05	0.15	0.20	0.40	1.5	0.20	0.328	0.869	1.000	0.989
Iron (Fe)	0.24	0.71	2.30	6.10	43.0	2.22	0.109	0.324	n.a.	0.598
Manganese (Mn)	0.04	0.20	0.63	1.30	9.2	0.49	0.022	0.243	0.647	0.389
Phosphorus (P)	0.15	0.24	0.44	1.40	13.0	0.54	0.134	0.621	n.a.	0.935
Strontium (Sr)	0.09	0.16	0.31	0.47	2.50	0.23	0.000	0.033	n.a.	n.a.
Zinc (Zn)	0.009	0.015	0.034	0.077	5.5	0.046	0.078	0.825	n.a.	1.000
Trace elements (median < 0.01 mg/L)										
Arsenic (As)	0.001	0.001	0.004	0.041	0.910	0.018	0.559	0.605	0.821	0.915
Arsenic (As, Arsenator)	0.001	0.001	0.018	0.077	0.900	0.027	0.590	0.658	0.680	0.866
Cobalt (Co)	0.0003	0.0003	0.0005	0.0010	0.130	0.0006	0.741	0.740	n.a.	n.a.
Copper (Cu)	0.0003	0.0003	0.0005	0.0010	0.130	0.0006	0.741	0.740	1.000	1.000
Lithium (Li)	0.003	0.003	0.006	0.010	0.088	0.005	0.708	0.707	n.a.	n.a.
Nickel (Ni)	0.001	0.001	0.002	0.003	0.190	0.002	0.520	0.959	0.997	0.999
Molybdenum (Mo)	0.001	0.001	0.001	0.002	0.023	0.001	0.814	0.813	1.000	n.a.
Selenium (Se)	0.001	0.001	0.001	0.001	0.015	0.001	0.978	0.974	0.999	0.999
Titanium (Ti)	0.003	0.003	0.003	0.003	0.096	0.003	0.910	0.925	n.a.	n.a.
Tungsten (W)	0.001	0.001	0.001	0.001	0.022	0.001	0.917	0.946	n.a.	n.a.
Uranium (U)	0.0001	0.0001	0.0006	0.0041	0.063	0.0013	0.582	0.630	0.989	n.a.
Vanadium (V)	0.001	0.001	0.002	0.003	0.019	0.001	0.660	0.730	n.a.	n.a.

Yellow shading in the above table indicates that the value is below the Limit of Detection (LOD). Blue shading indicates that either a Bangladesh standard or a WHO guideline value is exceeded. Darker blue shading indicates both are exceeded, or that one is exceeded by a factor of ten. Several trace elements[7] were measured, but are not included in Table 1 because most or all results were below the Limit of Detection.

Table 1: Major, minor, and trace elements of contamination in the water of an average household in Bangladesh [31]

Contaminant	Units	Violation Y/N	Date of Sample	Maximum Level Detected (Range)	Regulatory Limit	MCLG	Likely Source of Contamination
Microbiological contaminants							
Turbidity	NTU	No	5/13/11	0.132	TT=<1 NTU	N/A	Soil runoff.
Turbidity samples	%	No	daily	100%	TT=95% of samples <0.3NTU	N/A	Soil runoff.
Giardia	cysts	No		0 cysts	TT=99.9% removal	0	Human and animal fecal waste
Disinfection By-Products							
Total THMs	ug/l	No	8/19/11	50 (18-99)	MCL = 80	N/A	By-product of drinking water chlorination.
Total HAA5	ug/l	No	8/19/11	25 (13-43)	MCL = 60	N/A	By-product of drinking water chlorination.
Chlorine Residual	mg/l	No	daily	1.29 (0.95-1.77)	MRDL=4	N/A	By-product of drinking water chlorination
Inorganics							
Barium	mg/l	No	12/07/11	0.022	MCL=2	2	Drilling wastes; discharge from metal refineries; erosion of natural deposits
Chromium	mg/l	No	12/07/11	0.005	MCL=0.01	0.01	Discharge from steel and pulp mills; erosion of natural deposits.
Copper	mg/l	Yes*	11/07/11	0.15 (0.01-0.26)	AL=1.3	1.3	Household plumbing corrosion; erosion of natural deposits; wood preservatives.
Lead	ug/l	Yes*	11/07/11	2.8 (ND-14)	AL=15	0	Household plumbing corrosion; erosion of natural deposits.
Nickel	mg/l	No	12/07/11	0.0013	N/A	N/A	Discharge from steel and pulp mills, erosion of natural deposits.
Nitrate	mg/l	No	12/07/11	.97	MCL=10	10	Fertilizer runoff; septic tank leaching; sewage; erosion of natural deposits.
Sodium	mg/l	No	12/07/11	21	See Water Quality, Section C	N/A	Naturally occurring; road salt; animal waste; water softeners; water treatment chemicals.
Sulfate	mg/l	No	5/19/08	14	MCL=250	N/A	Naturally occurring
Radioactive							
Gross Alpha	pCi/l	No	3/19/08	0.21	MCL=5	0	Erosion of natural deposits.

*Lead and Copper samples were collected November 7 but should have been collected before September 30.

Table 2: Cornell University's Water Composition [32]

Cation	mg/L	meq/L	Anion	mg/L	meq/L
Ca^{2+}	40.1	2.00	HCO_3^-	183.0	3.0
Mg^{2+}	12.6	1.04	SO_4^{2-}	50	1.04
Na^+	88.87	3.864	Cl^-	71.0	2.0
			NO_3-N	2.0	0.143
			F^-	1.0	0.053
			PO_4-P	0.040	0.0013
			SiO_3-SiO_2	20.0	0.666
			As(III)/(V)	0.05	
Σ=	141.57	6.904	Σ=	327.09	6.904

Table 3: Composition of NSFI-53 challenge water [33]

Many studies also prepared raw water samples by diluting prepared stock samples with tap water, and then adjusting the pH using sodium hydroxide or sulfuric acid [34]. These stock solutions contained arsenic along with other inorganic solutes, including NaCl, $NaHCO_3$, Na_2SO_4, $NaNO_3$, K_2HPO_4 and NaF [34]. High purity water, at least 18 M, is used to prepare stock solutions [35].

Though some studies have been conducted simply using spiked tap water or spiked deionized water [36], this is not appropriate for the purposes of our lab. Because we aim to discover the most effective coagulant for arsenic removal from groundwater, our water samples need to be as close as possible to the composition of actual groundwater so that we can account for reactions taking place between arsenic and other compounds.

2.3 Laboratory Arsenic Forms

2.3.1 Arsenite As(III)

One form of arsenite that is available for use is sodium (meta)arsenite ($NaAsO_2$); it is soluble in water at a variety of temperatures and is sold as a solid or as a solution [37].

2.3.2 Arsenate As(V)

One form of arsenate that is available is sodium arsenate dibasic heptahydrate ($Na_2HAsO_4 \cdot 7H2O$); it has a solubility of 610g/L water at 15°C and is sold as a solid [37]. Another form of arsenate that is available is potassium arsenate monobasic (KH_2AsO_4); sold as a solid, it has a solubility of 19g/100g water at 20°C [38]. Yet another form of arsenate that is available is magnesium arsenate ($Mg_3(AsO_4)_2$); it has a solubility of 5Œ10^{-5} M and is sold as a solid [40].

3 Arsenic Removal Methods

In order to best utilize AguaClara's current water treatment design with flocculation and sedimentation, we focused our research on coagulants used for arsenic removal. If the process of arsenic removal via flocculation and sedimentation was better understood, AguaClara plants could be designed to more effectively remove arsenic from solution as well as turbidity.

In choosing a coagulant, some research must be done on the type of water used and on the target contaminant. It is important to consider how different coagulants will affect the pH and alkalinity of the water. Different coagulants will also have an effect on the quantity and quality of sludge produced and on the total dissolved solids concentration of the treated water [41]. These factors were taken into consideration when describing the relative pros and cons of using a certain coagulant regimen.

3.1 Coagulants

3.1.1 Polyaluminum Chloride (PACl)

PACl, or polyaluminum chloride, is a commonly used coagulant for water treatment. Because the net charge of As (V) is negative at neutral pH, it is more easily removed by PACl then As (III), so oxidation is necessary [47]. Although PACl is capable of arsenic removal, success rates have not been high, with studies showing removal rates ranging from 19-66% [48]. However, when used with $FeCl_3$, the removal efficiencies ranged from 79-84% [48]. Although slightly higher removal efficiencies (up to 90%) could be achieved with a very high dose of $FeCl_3$ (300 mg/L) without the use of a second coagulant, this high dosing could cause other water quality issues so the combination of PACl and $FeCl_3$ would be preferred. The combination is also preferred because ferric chloride is difficult to handle, especially at the high doses required if it is the only coagulant. By using a combination of the two coagulants, high removal rates can still be achieved with a much smaller ferric chloride dose [47]. One study found the most effective dosing was 30 mg/L of PACl followed by 10 mg/L of $FeCl_3$[48]. PACl can achieve higher removal rates at higher dosages. In one jar test study, the arsenic concentration in water was reduced from 13 g/L to 6 g/L by 15 mg/L of PACl, and was reduced from 13 g/L to 4 g/L by 25 mg/L of PACl [47].

3.1.2 Alum

Alum has been shown to remove solids and dissolved metals in water treatment, and therefore may be an effective coagulant for use in an AguaClara arsenic removal system. The use of alum as a coagulant is more effective if arsenic is first oxidized to As (V) and if the pH of the water is reduced to 7 or less. Studies have shown that with the use of an oxidant and with pH reduction to 7, alum can remove arsenic at a rate of 90% [41]. Alum has a smaller effective pH range of 7.2-7.5 compared with effective pH ranges for iron coagulation, which are from 6-8.5 [48]. Alum coagulation can achieve up to 90% removal, but at relatively high doses (more than 30 mg/L) when compared to ferric compounds [50]. It is thought that this higher dose is needed because a significant portion of the aluminum added remains as a soluble complex, and therefore cannot be used to remove arsenic [50]. However, it has been shown that at the appropriate concentrations and at pH of 7.6 or lower, alum and iron coagulants achieve the same removal efficiency [50].

3.1.3 Ferric Coagulants

Ferric Chloride and Ferric Sulfate

Adding ferric chloride to water leads to the precipitation of ferric hydroxide and the acidification of the solution [51]. Ferric chloride is very corrosive and is usually purchased "as a 40 to 43% by mass $FeCl_3$ dark brown syrupy solution" [52].

Ferric chloride is better at removing As(V) than at removing As(III), but significant As(III) removal may still be possible [53-55]. If high removal of As(III) is required, perhaps as much as 30 mg/L of ferric chloride is recommended; however, if an oxidation step is included and if the pH is low, around 6 mg/L of ferric chloride may be sufficient for high As(V) removal [55]. When 50 g/L of As(III) or As(V) was added to NSFI-53 challenge water, ferric chloride was the cheapest coagulant–compared with alum, $ZrCl_4$, $ZrOCl_2$, $TiCl_4$, $TiCl_3$, and $TiOCl_2$–for lowering the As(V) and As(III) concentration to 10 g/L [55]. It has been observed that 20 mg/L of silica interfered with ferric chloride's removal of arsenic (namely As(III) as pH went up), whereas silica plus phosphate at 40 g/L phosphorus interfered only with As(V) removal, particularly at a pH of 6.5 and 7.5[55]. Vanadate at 50 g/L vanadium in addition to silica and phosphate, however, did not change arsenic removal efficiency [55].

Ferric sulfate is an iron salt used frequently in waste water for phosphorous removal. It is also known to be effective at removing heavy metals such as arsenic, chromium, and selenium. Ferric sulfate is lower in cost than other coagulant salts and works well over a wider range of pH, particularly in comparison to alum. It is, however, slightly corrosive and can wear away metal pipes and fittings [56]. Some studies have shown that ferric sulfate may produce lower density flocs and may be difficult settle out [57]. One study showed 74% removal of arsenate at a coagulant concentration of 40 mg/L. When using ferric salts, operators have to be concerned with the concentration of residual iron in the effluent. The same study found a residual iron concentration of 446 g/L; the allowed Turkish standard (where the study was located) is 200 g/L [57].

Adding more ferric coagulant tends to increase arsenic removal [53-55, 58, 59], but the marginal gains may diminish [54]. Most studies observed that the removal of arsenic by ferric coagulants is dependent on pH [53-55, 58 ,59]. Optimal pH range of arsenic removal by ferric coagulants, which varies between pH 5 and 8 for both As(III) and As(V) [53-55, 58, 59], has been claimed to be larger than that of alum [54], but a slight departure from the optimal range can result in a sharp decrease in arsenic removal. It has also been found that warmer water temperatures may enhance the removal of As(V) [59] and turbidity [60] by ferric coagulants.

Polyferric Chloride and Ferric Sulfate

Polyferric chloride can be prepared by heating ferric chloride or by adding in sodium hydroxide or calcium hydroxide [60]. The first method keeps the pH of the polyferric chloride solution similar to that of the original ferric chloride solution, whereas the second method results in a higher pH due to the use of bases [60]. In contrast, polyferric sulfate can be produced by oxidizing ferrous sulfate [61].

As(V) removal by polyferric chloride and polyferric sulfate was reported to exhibit similar dependence on dosage, pH, and temperature as As(V) removal by monomeric ferric coagulants, but the performance of the polyferric coagulants might be better [59]. However, purchase decisions will have to depend on the local availability of coagulants.

Word of Caution About Ferric Coagulants

The relatively low cost and relatively high effectiveness of ferric coagulants make them an attractive choice for AguaClara as it explores the possibility of altering current designs for arsenic removal. However, at least one study has raised the concern of high iron concentrations in the effluent of the water treatment plant [57]. If such a problem occurs, possible solutions may include incorporating iron removal step(s), switching to aluminum coagulants, reducing ferric coagulant dosage by using a combination of aluminum and ferric coagulants [48], optimizing the conditions, and/or oxidizing dissolved Fe(II) if it is naturally abundant in the influent.

3.2 Non-coagulation Methods

In order to stay objective in our research, we also explored alternative methods of arsenic removal other than coagulation. Although we would like to utilize AguaClara's current design, many alternative methods show promising results and may be more effective than a coagulant-based system.

3.2.1 Ion exchange resin

Ion exchange resins remove arsenic by taking advantage of the arsenic ion's negative charge. The resins contain another negatively charged ion, typically chloride ions, located at exchange sites on the resin [42]. The feed water is then passed through these exchange sites and the arsenic ions take the place of the chloride ions. This results in a lower arsenic concentration in the water exiting the resin, but unfortunately means the water also has an increased chloride concentration [43]. As all of the exchange sites are eventually changed from chloride ions to arsenic ions (or other negatively charged ions), the resin becomes exhausted [43]. The resin will need to be regenerated using a brine solution with high chloride ion concentration to refill the exchange sites with chloride ions [42]. This removes the arsenic from the ion exchange resin and puts it in a waste water stream to be disposed of [42]. Regeneration must take place frequently, making the cost of salt significant. Because this method relies on the charge of arsenic ions, it is more effective for As (V) removal than for As (III) removal and therefore an oxidant should be used to pretreat the water. However, oxidants such as chlorine can often harm ion exchange resins [42]. It is also important to note that some anions will be preferred over arsenic, such as sulfate. In waters with high concentrations of sulfate ions, arsenic removal rates will be reduced [43]. High concentrations of dissolved solids can also interfere with the resin's

efficiency [43]. In feed waters with high sulfate concentrations or total dissolved solids (TDS), this process is generally not economically feasible [43]. Optimal removal rates can be achieved with oxidation of arsenic to As (V) and a pH of at least 7.5 [42]. Studies have found that exchange resins can achieve removals rates greater than 95% [42].

3.2.2 Granular Ferric Hydroxide

Another removal technique is the adsorption of arsenic to granular ferric hydroxide, which can then be filtered out by microfiltration. This adsorption process again is dependent on the arsenic ion's charge, so it is more effective for As (V) than for As (III). Additionally, it has been shown that with higher initial arsenic concentrations, the granular ferric hydroxide is more effective at a lower pH [44]. Increased temperature has also shown to increase removal efficiency [45]. Granular ferric hydroxide is extremely porous, making it ideal for adsorption because this maximizes surface area [45]. Typically, the granular ferric hydroxide is used on a fixed-bed, similar to activated alumina [45]. It has shown to achieve high removal rates, up to 95%, and the process results in a solid waste that must be disposed of [46]. Because the granular ferric hydroxide must continually be replaced as it becomes exhausted, this method is often used for small plants or point of use systems [46].

3.2.3 Activated Alumina

The use of activated alumina for arsenic removal is a physical and chemical process during which arsenic ions in the influent water are sorbed to an oxidized activated alumina surface. Because of this, it is considered an adsorption process. However, the reaction that allows the sorption to take place is actually an ion exchange [50]. Activated alumina is created through the dehydration of $Al(OH)_3$ at high temperatures [50]. It is used in packed bed reactors where influent water is continuously passed through and surface hydroxides on the alumina are exchanged with arsenic ions. Since this is an ion exchange process, the bed must be regenerated using a strong base solution once all the adsorption sites are filled [50]. The pH must be kept below 8.2, with an optimum range of 5.5-6, so that the activated alumina has a positive charge, allowing negative arsenic anions to be adsorbed[50]. Like other adsorption methods, As (V) is more easily removed than As (III), so oxidation is necessary. One benefit of activated alumina over other ion exchange resins is that it tends to be more specific for arsenic removal and is not as greatly affected by the presence of other ions. Studies have shown that activated alumina systems can reduce arsenic concentrations by up to 92% [50].

3.2.4 Iron Oxide Coated Sand

Iron oxide coated sand consists of sand particles coated with ferric hydroxide. It is used in a fixed bed reactor and as influent water is passed through, arsenic

ions are exchanged with surface hydroxides on the sand [50]. Like other ion exchange processes, the bed eventually becomes exhausted and must be regenerated, usually with sodium hydroxide. Studies have shown this method to be more effective at lower pH values (approximately 5.5) rather than higher ones (around 8.5) [50]. This method is also more effective at As (V) removal than As (III) removal. This method has shown to be greatly affected by the presence of organic matter, with one study finding that the addition of 4 mg/L of DOC reduced As (V) sorption by 50% [50].

4 Pretreatment

As mentioned in the previous section, the vast majority of arsenic removal methods are more effective at removing As(V) than removing As(III). Therefore, in order to design the most effective treatment system, we will need to oxidize the As (III) ions in our influent water to As (V). Many oxidation methods are being researched, including the use of ozone, hydrogen peroxide, atmospheric oxygen, and chlorine [94]. Below we focus on the two most promising oxidation agents: permanganate and hypochlorite.

4.1 Oxidation

4.1.1 Permanganate

The exact mechanism by which permanganate oxidizes As (III) is still unknown, but a proposed mechanism is as follows [62]:

5 As(3+) + 2MnO_4- + 16 H+ –> 5 As(5+) + 2 Mn (2+) + 8H_2O in acidic conditions

5 As(3+) + 2MnO_4- + 8H_2O –> 5 As(5+) + 2 $Mn(OH)_2$ + 12OH- in basic conditions

This proposed mechanism indicates that 1 mole of Mn(VII) can oxidize 2.5 moles of As (III) [62]. However, this fails to account for the additional matter in the water that will react with permanganate. Based on the lab study in the figure below, it was found that in natural groundwater with an arsenic concentration of 14.6 g/L, potassium permanganate achieved 80% oxidation after 1 minute and 98% oxidation after 15 minutes with an oxidant concentration equal to about 60 times the arsenic concentration [63]. When tested on natural groundwater with a higher arsenic concentration (50 g/L), 98% oxidation was achieved within the first minute when the oxidant was dosed at a concentration equal to about 20 times the arsenic concentration [63]. Therefore, we would require a dosing of approximately 20 times the arsenic concentration. The addition of potassium permanganate does not require any special mixing [64], so a rapid mix orifice at the inlet of our entrance tank would suffice.

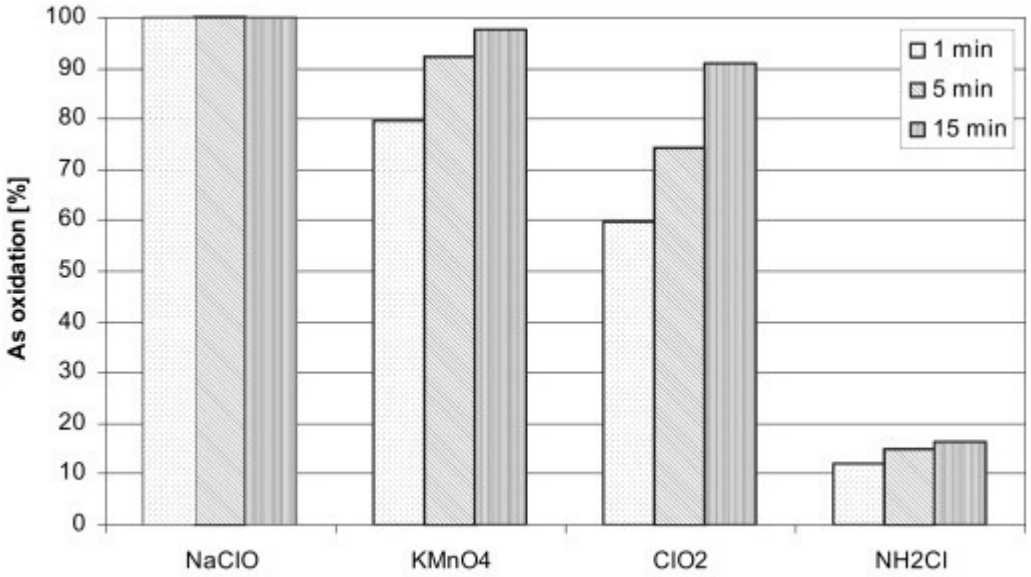

Figure 2: Results of tests run with KMnO4 concentration of 1.2 mg/L and NaClO concentration of 3 mg/L. Initial arsenic concentration was 14.6 g/L [63].

Use of permanganate often results in a slight pink discoloration of the water [65]. However, this can be removed with filtration methods. When potassium permanganate is added to water, it oxidizes arsenic and manganese dioxide forms, which is a solid that likely gives the water its pink color. This solid precipitate can be filtered out, removing the discoloration from the water [64]. The other byproducts associated with oxidation by permanganate are not of serious concern to human health [63]. Potassium permanganate is also useful for removing hydrogen sulfides from the water which tend to give water (especially well water) a rotten egg odor. $KMnO_4$ rapidly reacts with arsenic in solution which is good as it will help to reduce processing time. Another benefit to using permanganate is that the oxidation efficiency seems to be independent of the pH levels of the water being treated [63].

4.1.2 Sodium Hypochlorite

When pretreating water with sodium hypochlorite, the following reaction takes place:

$NaOCl + H_2O \rightarrow HOCl + Na+ + OH-$

The addition of 2 OH- to each arsenite (As (III)) oxidizes it into arsenate (As(V)). The amount of sodium hypochlorite needed can be found in terms

of the required chlorine dose. Oxidation requires approximately 1 mg Cl per 100 ţg of arsenite [66], or:

Chlorine Dose Required (mg/L)=(Arsenite concentration ug/L)/100 +other chlorine demand

Other chlorine demand is dependent on other elements in the water, such as iron, manganese, carbon, and sulfide [66]. In lab studies performed on groundwater samples, hypochlorite was found to be 100% effective when in a ratio of about 200 when compared with arsenite and 95% effective when in a ratio of 70 when compared with arsenite (see Figure 2) after 5 minutes of contact time. Effectiveness tends to increase with contact time [63].

These tests predicted much higher necessary hypochlorite concentrations because of the other minerals in the water (which are accounted for in the equation above in the " other chlorine demand"). Therefore, we may need to use a dosing of approximately 200 times the arsenite concentration (see Figure 2 [63]).

The reaction of water and hypochlorite produces sodium ions and hypochlorous acid. The hypochlorous acid can also dissociate into hydrogen and hypochlorite ions, though this reaction is highly dependent on temperature and pH [67]. Depending on our required hypochlorite dosage, we may need to dechlorinate. The EPA recommends there be no more than 4 mg/L of chlorine (or chloramines, which are formed from HOCl) in drinking water [68]. One option for dechlorination is hydrogen peroxide, which can destroy one pound of chlorine for every 0.48 pounds of hydrogen peroxide added [69]. Other dechlorination options include aeration, UV light, and activated carbon filters.

5 Detection Methods

5.1 Colorimetric Methods

The majority of field techniques for the measurement of arsenic are based on the century-old colorimetric Gutzeit method [70]. The key reaction involves an acid, a reductant, and arsenic and produces arsine gas (AsH_3), whose AsH_2^- displaces bromide on the mercuric bromide ($HgBr_2$) test strips. The extent of this substitution is indicated by the color of the test trips [70]. The logic behind this method is that the amount of arsenic in the water sample would be positively associated with the amount of arsine generated, and that in turn would be positively associated with the amount of AsH_2^- that replaces bromide. For such assays, hydrochloric (HCl) acid or sulfamic acid (NH_2SO_3H) is often used to reduce As(V) to As(III) initially [70] and to provide H^+ ions for reduction. The latter acid can be made from solids and is less hazardous, but it also requires more time [70]. Then, sodium borohydride ($NaBH_4$) or over 99.9% pure "zinc

granules" with less than 0.1 ppm arsenic are often used to reduce H^+ ions to hydride for the formation of arsine [70].

Kinniburgh and Kosmus highlighted hydrogen sulfide (H_2S) as a substance that disrupts the performance of field-test kits because of the dissolved gas' interaction with mercury [70]. The authors mentioned two ways to deal with H_2S before it reached the test strips, namely its removal by lead acetate (soaked onto cotton, glass wool, or filter paper) and its oxidation to sulfate [70].

Another commonly known problem with field test kits is the difficulty of accurately and precisely identifying with the human eye the exact shade of yellow on test strips, which corresponds to the arsenic concentration in the water sample. This obstacle has largely been overcome by the use of devices that provide an objective analysis of color [70-72]. For example, the Wagtech Digital Arsenator, with a detection limit around 4 g/L [70, 71] and a safety measure that prevents the escape of the hazardous gas arsine [71, 73], has been shown to compare relatively well with laboratory methods and to give readings that are positively correlated with the known concentrations of arsenic standards below 100 g/L. However, recalibration might be necessary if the internal calibration appears to be incorrect [71]. Perez and Francisca, working with Macherey-Nagel Quantofix Arsenic test kits, found relationships between the gray level of a test strip's photo and the arsenic concentration in the water sample, and they reported a relative error of approximately 6.2 g/L at the 95% confidence level when there was actually 10 g/L arsenic [72].

5.2 Electrochemical

Electrochemically testing for arsenic in water is a common technique used in arsenic studies. The process commonly used is known as anodic stripping voltammetry (ASV). ASV is used to determine specific ionic species. Testing for the species of interest begins by electroplating the analyte, thus changing the surface charge of an element and creating a uniform distribution on the electrode. Following that, the analyte is then oxidized from the electrode during the stripping step. The current is measured during stripping. When the species is oxidized, it is registered as a peak in the current signal potential and can be graphically observed [74].

There are several attractive qualities about using electrochemical processes in arsenic detection. To start with, ASV has very low detection limits on the order of 10^{-10}-10^{-9} ppb. This low detection limit is important when working with arsenic as the World Health Organization permissible limit on arsenic concentration is 10 ppb. Furthermore, this detection method is extremely sensitive, requires minimal sample preparation, and is a low cost technology [75].

One drawback in using ASV is that it suffers from the interference of other metals in water, especially when they are present in high quantities [76]. Since we are planning on creating our own arsenic-spiked water for experimentation, and we want to replicate Bangladeshi water for our experiments, this may be a problem.

5.3 ICP-MS

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is used to detect metals at levels down to the order of parts per trillion (with newer machines). The sample is ionized by electromagnetic induction (by time varying magnetic fields), and this energy is used to ionize the sample. The high temperature of the plasma ensures that all forms of arsenic are ionized so that the response will not vary across species. Then, once the sample is ionized, it is sent to a mass spectrometer which separates and quantifies using the spectra of the mass of the the various molecules within the sample [77]. According to a paper by Hung et. al., where they reviewed many other papers from the past ten years, they found that the best way to use ICP-MS for analysis of arsenic is to reduce it to its trivalent form (As(III)). This is because the pentavalent form (As(V)) is electrochemically inactive. They reduced the As(V) species through a combination of potassium iodide along with ascorbic acid to ensure the iodide doesn't oxidize to triiodide (and become inactive) [77]. In terms of detectability, we would like to be able to detect arsenic levels which reach below the 10 ppb standard set by the World Health Organization, and research has been done which shows that detection levels can get down to that range using ICP-MS. In research conducted by Gomez-Ariza et al., they were able to detect down to 0.1 ppb of arsenic from marine animals using ICP-MS as well as AFS (atomic fluorescence spectrometry) [78]. In a study performed by Sheppard et. al., it was shown that arsenic speciation could be seen in concentrations as low as 0.1 parts per trillion [79]. Based off of several studies and the precision to which the arsenic is detectable using the ICP-MS method, it should certainly be a method to consider using if access to one of these machines is granted. Karim, one of the coauthors, has done work in the past with Dr. Louis Derry in the Earth and Atmospheric Science Department at Cornell University using an ICP-MS machine to measure various inclusions within carbonate minerals. One of his graduate students, Gregg McElwee, was also using the ICP-MS to measure arsenic inclusion in samples which he collected for his research.

5.4 GFAAS

Graphite Furnace Atomic Absorption Spectrometry (GFAAS) is used for measuring metals in both liquid and solid samples (though the preparation needed for solid samples is extensive). It is extremely sensitive and therefore good at measuring metal concentrations even at trace levels [80]. Typically, GFAA instruments must be used in a clean lab environment. However, as the instrument's size and weight has decreased with the advancement of electronics, it has

become more portable and theoretically could be used in the field if the proper clean and climate-controlled environment could be created [80]. GFAAS has lower detection limits than most other measurement instruments, able to detect arsenic levels down to 0.7 micrograms per liter [81]. It also allows for the direct analysis of samples, and can work with a very small sample size [80]. However, because it is a highly delicate and complicated piece of lab equipment, it is also rather expensive, costing around $37,000 [81]. GFAAS works by shooting light of a specific wavelength through the atomic vapor of the element to be tested for. The concentration is determined based on the intensity of the light (which indicates how much of the light was absorbed), which will be proportional to the concentration. In order to vaporize the sample, a graphite furnace is used, which reaches temperatures up to 3000 degrees Celsius [80].

5.5 Alternative Measurement Methods

Many arsenic measurement methods are expensive, require specialized laboratories, or are not accurate to the 10 ppb scale, so there is a need to create an affordable accurate way to measure arsenic in water samples. One such method was researched by Frisbie et. al. with the objective of finding a method that could be used locally in Bangladesh, but that's just as effective as expensive lab methods like GFAAS [81]. Using this method, arsenic is removed from the sample by reducing it to arsine gas. This gas is collected in an absorber by oxidizing it to arsenic acid. It is then colorized by reacting it into arsenomolybdate, and once it is colorized it can be measured by spectrophotometry. This method has been found to detect arsenic levels down to 7 micrograms per liter and costs about $6,700 [81].

5.6 Commercially Available Online Arsenic Measurement Systems

Three examples of online arsenic measurement systems that can be purchased are discussed below. Those who would like more information can refer to the cited sources directly or contact the manufacturers and/or the distributors of the different systems.

5.6.1 ArsenicGuard

TraceDetect's ArsenicGuard is an online arsenic measurement system [82]. It is 60 inches tall, 32 inches wide, and 13 inches deep [82]. The system has self-diagnostic and auto-calibration capabilities, and it is said to measure "total inorganic arsenic" between 1 and 100 ppb with errors at most "1 ppb or ś20%, whichever is larger" [82]. The basic system has one "dead-end type" online sample port, but it can be modified to have four online sample ports and to have "continuous flow" instead [82]. Each measurement takes under 30 minutes, and samples have to be at 0řC-40řC, 5-75 psi, and pH 2-12 [82]. The system has "field replaceable modules" and requires maintenance twice a year, while new reagents

are needed at least once every 1000 measurements [82]. The system's outputs include 4-20 mA, and it can use RS-232/485/422 as well as Ethernet/Wireless [82]. The system is sold for $34,250 on average, and the per sample reagent cost is about $0.65 [83].

ArsenicGuard performance data appear to be scarce, but Gregg et al. performed a verification test for SafeGuard, a different product from the same company [84]. SafeGuard is a trace metal measurement system that relies on anodic stripping voltammetry [84]—assumed to be the same measurement method as the one that ArsenicGuard uses. In the Gregg et al. study, the substances in the background were blamed for SafeGuard's substantial overestimation of the arsenic concentration in residential well water samples, which was only around 1.0 ppb according to ICP-MS [84]. However, the interference effect was not observed when SafeGuard was used to measure arsenic in samples from drinking water, river water, and reservoir water [84]. Neither was it observed when measuring arsenic in 10 ppb As solutions with 1 ppm Fe, 1.0 ppm Na_2S, and 3 ppm NaCl or in 10 ppb As solutions with 10 ppm Fe, 10 ppm Na_2S, and 30 ppm NaCl even though the three added chemicals were thought to possibly affect measurement accuracy [84]. Ignoring the well water results, the relative error of SafeGuard measurement averages in the study was about -28% to 11% for a "non-technical operator" as compared with ICP-MS measurement averages [84].

5.6.2 OVA5000

ASA Analytics's OVA5000 is an online arsenic-capable heavy metal measurement system that also relies on anodic stripping voltammetry [85]. It is 165 cm tall, 70 cm wide, and 35 cm deep [85]. The system includes RS-232 and LAN connections [85], and researchers can look at the data on the system's computer or through the "intra or internet" [86]. The required weekly maintenance is estimated to take around 30 minutes and involves "verifying pump calibration [and] cleaning the sample lines and analysis cells" [86]. The system is also advertised to have replacement parts that are easily installed by non-professionals and to be supported worldwide [86]. Al, Na, Ca, Mg, Cl, and other salts have not shown to interfere with its measurements [85]. A study of treated effluent from the remediation of the Vineland Superfund site reported that the correlation coefficient between OVA5000 arsenic measurements and those by ICP-MS is about 94.17%. OVA5000 seems to overestimate arsenic concentration when it is low but underestimate arsenic concentration when it is high—assuming that ICP-MS is correct [87]. Also, when arsenic concentration is under 10 ppb, OVA5000 seemed to perform better than GFAA—assuming that ICP-MS is correct again [87].

5.6.3 PSA 10.255

P S Analytical's PSA 10.255 is another online arsenic measurement system [88]. In this system, arsenic is oxidized to As(V), converted to arsine gas (hydride generation), and quantified by atomic fluorescence spectroscopy [88]. The system is designed with flexibility in mind, and it has "a 10 port stream selector" and both continuous flow and discrete injection modes [88]. It comes with the company's online software package, but it is also compatible with 4-20 mA current loops, MODBUS RTU, RS-232, OPC Server, and OPC Client [88]. Features include email transmission of data, alarms, reminders, and system control through the ethernet/internet [88].

6 Data Collection Methods

Relevant data should be collected and stored through a program like Process Control and Data Acquisition that AguaClara already employs for lab research. This sort of program allows researchers to quickly and easily record results in delimited format, making it easier to later analyze data. The parameters that should be recorded include:

- Dissolved mineral concentrations (including As (III) and As (V), but also Ca, Fe, Cd...etc)
- Water temperature
- pH
- Coagulant dosing
- Residence time

Process Control will have to be modified to record dissolved concentrations of minerals, especially as researchers may wish to monitor the change in the chemical makeup of the water. One promising add-on is an arsenic detection software created by TraceDetect. The software is called TraceDetect ArsenicGuard Online Arsenic Analyzer and there may be a way of integrating it with Process Control. Monroe has already contacted TraceDetect regarding this idea.

7 Arsenic-Coagulant Interactions

There seems to be different and potentially conflicting theories about how arsenic sticks to coagulants and adsorbents. One theory is co-precipitation, as claimed by Lackovic et al. in an article on arsenic removal by zero-valent iron filings [90]. The researchers found arsenic in the iron precipitates on the surface of filings that were previous used to remove arsenic, and they also observed little release of arsenic from arsenic-bound filings into a solution whose high pH

should have reversed adsorption [90]. Largely based on these two findings, Lackovic et al. supported the notion that co-precipitation is the principal arsenic removal mechanism [90].

Another theory is chemical bonding, as claimed by Pierce and Moore in an article on arsenic adsorption by amorphous iron hydroxide [89]. In their 1980 study, they noticed that the isoelectric point of amorphous iron hydroxide decreased with increasing arsenite adsorption, and in their 1982 study, they observed that the adsorption of arsenic onto amorphous iron hydroxide was slow [89]. These two findings are opposites of what would be expected if the binding mechanism was based on electrostatic attraction, but they seem compatible with Pierce and Moore's idea of a combination of ionic and non-ionic bonds between surface metal atoms and arsenic species [89].

pH is said to control the availability of positively-charged binding sites on the coagulant [55]. Pierce and Moore found that at constant pH, amorphous iron hydroxide concentration of 4.45 mg/L, and As concentrations between 0.667 and 13.3 M, both arsenite and arsenate adsorption to amorphous iron hydroxide fit the Langmuir isotherm [89]. For arsenite, they observed maximum adsorption at pH 7, which is lower than the pKa1 of H_3AsO_3 at 9.2 [89]. Their explanation of this phenomenon was that when enough energy can be released from bond formation between arsenite and iron hydroxide, a proton from H_3AsO_3 can leave and then strip away a hydroxyl group from iron hydroxide to open up a binding site for H_2AsO_3- regardless of the surface charge of iron hydroxide [89]. In contrast, arsenate adsorption didn't seem to be affected by pH below a certain threshold, which becomes progressively lower as more arsenate is added [89]. This phenomenon was supposedly because both H_2AsO_4- and $HAsO_4{}^{2-}$ are relatively abundant at nonextreme pH values, and the binding of the bivalent ions would accelerate the process in which the coagulant's surface charge becomes less positive or more negative—increasing anion repulsion and discouraging further binding of arsenic ions [89]. For As concentrations between 33.4 and 667 M, both arsenite and arsenate adsorption to iron hydroxide fit a linear isotherm instead [89]. In this case, both arsenite and arsenate adsorption decreased with increasing pH [89]. Pierce and Moore attributed the change in arsenite adsorption to the increase in negative surface charges on amorphous iron oxides, which would repel arsenite anions [89]. Based on the change in the adsorption isotherms from low concentration to high concentration, they hypothesized that there are limited strong binding sites but a large or inexhaustible number of weak binding sites [89].

Goldberg and Johnston agree with Pierce and Moore on arsenate adsorption and also undermine the co-precipitation theory with their results from Raman and Fourier transform infrared spectroscopy experiments [91]. However, they disagree on arsenite adsorption and use different terminology [91]. According to Goldberg and Johnston, arsenate forms inner-sphere surface complexes

with amorphous iron and aluminum oxides, whereas arsenite forms both inner and outer surface complexes with amorphous iron oxides but only outer-sphere surface complexes with amorphous aluminum oxides [91]. These inner-sphere complexes involve more or less covalent bonds between metal atoms of the coagulant particles and oxygen atoms of arsenate or arsenite [89, 92]. The formation of inner-sphere complexes tends to, but not necessarily, alter the surface charge of the adsorbent [91, 93]. Specifically, adsorption of arsenic ions caused the adsorbent to be less positively or more negatively charged at the same pH, which would also lower the pH at which the adsorbent would have zero net surface charge [91, 93]. In agreement with the previously cited coagulant studies, adsorption increases as adsorbent concentration increases but decreases as pH increases within the range of nonextreme pH values [91]. In contrast, outer-sphere complexes involve electrostatic attraction between two ions of opposite charge that have at least one water molecule located between them [92]. The formation of outer-sphere complexes tends to fall as the ionic strength of the surrounding solution rises; specifically, arsenite adsorption on the adsorbent was reduced in more concentrated NaCl solution [91]. In both arsenite and arsenate, the bond between the arsenic atom and a hydroxyl group is weaker and longer than the bond between the arsenic atom and an individual oxygen atom, and decreasing pH makes both types of bonds stronger and shorter; these results were observed both in a model and in spectroscopy experiments [91].

8 Experimental Design

8.1 MathCad Inputs

For the Mathcad file, we have been using the design equations from the Flocculation and Sedimentation Optimization team report from spring 2012. We anticipate experiments will involve mainly flocculation and sedimentation as an important feature of the arsenic removal process. Therefore, their design works as a good starting point for an arsenic treatment experimental setup. We have left the following parameters as inputs for the file: energy dissipation rate, arsenic concentration, primary particle diameter, density of primary particle, smallest floc that can be captured, coagulant dose concentration, and collision potential. The flow rate of the system will be determined based on the energy dissipation rate. We anticipate that energy dissipation will need to be increased relative to current AguaClara designs because arsenic flocs will be much smaller than clay flocs. We also anticipate that the size of arsenic will be negligible when compared with the coagulant, so the diameter of the floc will essentially be equal to the diameter of the coagulant.

9 Testing Procedure Checklist

Here we outline the steps we recommend the next arsenic removal team should take to further this project:

1. Determine appropriate location for arsenic testing
   (a) This may be within the AguaClara lab
   (b) They may need to explore other labs on Cornell's campus that are better equipped to handle arsenic
2. Create disposal satellites
   (a) Contact Bill Leonard at Cornell EH&S (wl68@cornell.edu)
3. Design system
   (a) Start with the existing AguaClara FlocSed model to get a sense of bonding efficiencies between different coagulants and arsenic
   (b) Using the data obtained through experimentation, input parameters into Mathcad file
   (c) Through trial and error, determine the necessary type and dosage of coagulant for different arsenic concentrations
4. Obtain arsenic

10 Conclusions and Future Work

The purpose of this report was to provide a starting point for lab-based studies on arsenic removal in groundwater. It is anticipated that following lab testing, AguaClara will develop treatment facilities for areas afflicted with toxic levels of arsenic contamination in their drinking water supplies. This paper outlines steps that should be followed in getting the AguaClara lab arsenic ready. This includes information on safety precautions to take when handling arsenic and proper means of disposing of it. Furthermore, some research was done on the composition of groundwater and the potential for interaction of the groundwater components and arsenic. There are numerous different factors that affect arsenic solubility and removal. In this report, some of these factors were considered and investigated including water type, interactions with organic matter, pH, and coagulant interactions. However, there is still much to be learned about the physics of arsenic coagulation and flocculation, and the geometry of the arsenic flocs themselves. A deeper understanding of the physics of the binding process and geometry would allow AguaClara researchers to develop an efficient and cost effective way to remove arsenic from drinking water.

We recommend that the next Arsenic Team start with the checklist we compiled in the preceding section.

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