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Hybrid anion exchange nanotechnology (HAIX-Nano) for concurrent trace contaminant removal with partial desalination: laboratory and field-scale investigations

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HYBRID ANION EXCHANGE NANOTECHNOLOGY (HAIX-NANO) FOR CONCURRENT TRACE CONTAMINANT REMOVAL WITH PARTIAL DESALINATION: LABORATORY AND FIELD-SCALE INVESTIGATIONS

by

Michael S. German

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FINAL DISSERTATION SIGNATURE SHEET

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AA= activated alumina

BC= bone char

BVs= bed volumes

CapEx= capital expenses

CCF= cumulative cash flow

CDN= Catholic Diocese of Nakuru (Nakuru, Kenya)

DPR= detailed project report

DTW= deep tubewell

EBCT= empty bed contact time (volumetric flow rate/volume of packed-bed material)

EDF= electrolytic defluoridation

FinEx= financial expenses

FMI= Fluid Metering, Inc.

FRU= fluoride removal units

HAIX= hybrid anion exchange resin

HAIX-NanoFe= hybrid anion exchange resin impregnated with nanoparticles of ferric (hydr)oxide

HAIX-NanoZr= hybrid anion exchange resin impregnated with nanoparticles of zirconium (hydr)oxide

HAP= hydroxyapatite

HCIX= hybrid cation exchange resin

HCIX-NanoFe= hybrid cation exchange resin impregnated with nanoparticles of ferric (hydr)oxide

HIX= hybrid ion exchange resin

HIX-NanoFe= hybrid ion exchange resin impregnated with nanoparticles of ferric (hydr)oxide

HIX-NanoZr= hybrid ion exchange resin impregnated with nanoparticles of zirconium (hydr)oxide

HR-TEM= high-resolution transmission electron microscopy

ICP= inductively coupled plasma

INR= Indian Rupees

LPH= liters per hour

NDC= Nakuru Defluoridation Company (Nakuru, Kenya)

NEERI= National Environmental Engineering Research Institute (Nagpur, India)

NGO= non-governmental organization

OpEx= operating expenses

PDCD= partial desalination with concurrent defluoridation

PHED= Public Health Engineering Department

pI= isoelectric point

ppb= parts per billion

ppm= parts per million

PZC= point of zero charge

RWSS= Rural Water Supply & Sanitation Project

SAC= strong acid cation exchange resin

SAC-Al= strong acid cation exchange resin in aluminum ion-form

SAC-Fe= strong acid cation exchange resin in ferric-form

SBA= strong base anion exchange resin

SBA-NanoFe= strong base anion exchange resin impregnated with nanoparticles of ferric oxide

SEM= scanning electron microscopy

SEM-EDX= scanning electron microscopy with energy-dispersive X-ray spectroscopy

SHRI= Sanitation and Health Rights in India

SLV= superficial linear velocity (volumetric flow rate/cross-sectional area of the packed-bed)

STHF= Society for Technology with a Human Face (STHF, an NGO based in Kolkata, India, formed by Prasun Sengupta (President) under advisement by Dr. Arup K. SenGupta)

TCLP= toxicity characteristic leaching protocol

TDS= total dissolved solids

TEM= transmission electron microscopy

THAK= Thakurpukur

TSF= Tagore-SenGupta Foundation (501(c)3 non-profit created by Dr. SenGupta in Bethlehem, PA)

UNICEF= United Nations International Children's Emergency Fund

UP= Uttar Pradesh

WAC= weak acid cation exchange resin

WBA= weak base anion exchange resin

WB= the state of West Bengal, India

WHO= World Health Organization

WIST= Water Innovation with Science and Technology, Inc. (a start-up company co-founded by: Minhaj Chowdhury (CEO), Michael German (General Supervisor of Development), and Dr. Arup K. SenGupta (Research Director))

WISE= Water Innovation with Science and Engineering, LLC (an LLC co-founded by: Michael German (Vice President) and Dr. Arup K. SenGupta (President))

XRD= X-ray diffraction

μS/cm= micro Siemens per centimeter

ABSTRACT

Millions of people across the Indian subcontinent are at risk of chronic exposure to arsenic and fluoride in aquifers with excess TDS (>500 mg/L). Hybrid anion exchange resins with nanoparticles of zirconium oxide (HAIX-NanoZr) were created for effective fluoride removal; zirconium oxide selectively bound fluoride, silica, and phosphate. The zeta potential of HAIX-NanoZr was directly correlated to the fluoride removal capacity. Thus, to increase fluoride capacity and achieve partial desalination concurrently, a weak acid cation (WAC) exchange pretreatment was used to lower alkalinity, hardness, pH, and TDS. Consistent partial desalination (~50%) occurred in proportion to influent alkalinity and hardness. With regular acid conditioning of WAC, the fluoride capacity of HAIX-NanoZr increased 10x, 300 bed volumes (BVs) to 3500 BVs. Upon regeneration with 2% NaOH, >95% of capacity was restored; fluoride treatment was identical over three consecutive cycles with water from a fluoride-contaminated well (Nakuru, Kenya). Passive pH adjustment (pH 6.5-8.5) of HAIX-NanoZr effluent was achieved with WAC-Na form and/or dolomite.

Pilot-scale production of HAIX-NanoZr was researched and developed in Kolkata; analysis of zirconium content and fluoride capacity were performed at Lehigh. Modifications to washing/drying steps were critical for high fluoride capacity. Concurrently, Drinkwell (WIST, Inc., USA; WIST Systems Pvt. Ltd., India) was founded to scale-up HAIX-NanoZr across the Indian subcontinent. An exclusive licensing agreement for HAIX-NanoZr to an Indian partner company was created to pursue Indian government grants and tenders for arsenic and fluoride treatment. Under government supervision, HAIX-NanoZr was piloted for fluoride/TDS removal in Andhra Pradesh, Assam, Madhya Pradesh, Odisha, and West Bengal; HAIX-NanoFe/Zr was piloted for arsenic removal in Chhattisgarh, Jharkhand, and West Bengal. After initial lessons, treatment systems have met Indian drinking water standards.

A cash flow model of HAIX-Nano as an entrepreneur-owned small business was developed and Monte Carlo analysis was performed. After being capitalized, self-sustaining operations with market-rate wages were achievable under a range of scenarios. But, capitalization will be difficult for most operations. Price of water and number of customers (TR = P x Q) were the most sensitive input variables, i.e., the most critical factor to financially sustainable water treatment was good business practices.

1. Introduction

Quality, quantity and accessibility of water varies greatly across regions, but is a necessity for all people. Proper physical and human infrastructure for treatment and distribution of surface water to individual homes is an ideal long-term development goal for dense urban populations, but it is less appropriate for rural communities with lower population densities and higher per capita operating costs. In locations without adequate infrastructure, groundwater is a preferred source because it tastes good and is biologically-safe, except for human contamination, and is locally owned and controlled. Compared to microbiologically unsafe surface water (e.g., ponds, rivers), groundwater improves public health metrics through reduced waterborne illnesses. Increased groundwater use in the Indian subcontinent began in the 1960s as part of intensive irrigation programs with the Green Revolution. In the 1970s, large social engineering efforts pushed mass installations of tube wells as “safe” potable water sources, especially for rural communities. Since then, tube well installation increased dramatically due to their convenience, symbol of status, and perceived safety. In Bangladesh alone, there are over 10 million tube wells (1,2). In the short-term, the quality of life improved greatly from the decrease in acute water-borne illnesses. Unfortunately, many groundwater locations in the Indian subcontinent have geogenic arsenic, fluoride, hardness and/or iron, making the water either undesirable or unsafe for long-term use.

To address these problems, a novel, multi-contaminant treatment process was developed and tested at the lab-scale (10 mL sorbent) and field-scale (100L sorbent) at Lehigh University and in India. A start-up company was created to commercialize the new process, who has earned funding ($1M) through multiple avenues, and has worked with public and private organizations to increase installations of the process. Cash flow models of long-term operations by a micro-entrepreneur were analyzed with Monte Carlo to determine potentials for profitability and sustainability of the systems. Work will be on-going to improve system performance and decrease expenses. The long-term goal is to expand access to safe water and generate employment in communities impacted by arsenic- and fluoride-contaminated water through financially sustainable operations.

1.1 Water Quality Concerns

1.1.1 Arsenic

There is no safe level for consumption of arsenic. Natural arsenic contamination was first recognized in 1982 in India and 1984 in Bangladesh as arsenicosis (3), and in 1999 in Cambodia (4–8). Arsenicosis initially causes gruesome physical effects on hands and feet, and then various cancers and early death, **Figure 1.1**. Over the past 20 years of increased scientific and humanitarian effort, thousands of papers have been published detailing the scope and magnitude of arsenic contamination across the Indian subcontinent (9,10). Yet today millions of people remain at-risk of drinking water well above the WHO recommended limit (0.010 mg/L or ppm As) (11). In long-term health studies in Bangladesh during the previous decade there were significant associations between arsenic exposure through drinking water and mortality rates, with 43,000 annual deaths in Bangladesh being related to arsenic (12,13). Thousands of broken "arsenic filters" exist across India, Bangladesh, Nepal, Burma, Vietnam, Cambodia, Laos, China, etc. (14–18).

Yet, finding economically sustainable approaches to remediation has proven a major challenge.

Figure 1.1. Millions of people across the Indian subcontinent are at-risk of arsenicosis, which yields a wide range of physical symptoms and effects.

1.1.2 Fluoride

Although not as lethal as arsenic, the chronic consumption of fluoride can cause debilitating aesthetic issues and functional deformities to teeth and bones, **Figure 1.2**. Dental fluorosis was first attributed to geogenic fluoride in 1931 in the US and France (19–21). Over 100 million people are at risk of high fluoride consumption (1.5 ppm, WHO limit) throughout East Africa and the Indian subcontinent, where fluoride-contaminated groundwater is the most viable water resource, **Figure 1.3** (22–24). In 1975 the “Nalgonda technique” was created to address fluoride in India and was considered the status quo until recently, but it is a labor-intensive, sludge-producing process (25).

Figure 1.2. Early stage dental fluorosis symptoms (Left); and later-stage skeletal fluorosis effects (R) in Jabhua, Madhya Pradesh, India. Note: an effective treatment system for fluoride and total dissolved solids (TDS) removal was installed in this community using hybrid ion exchange resins.

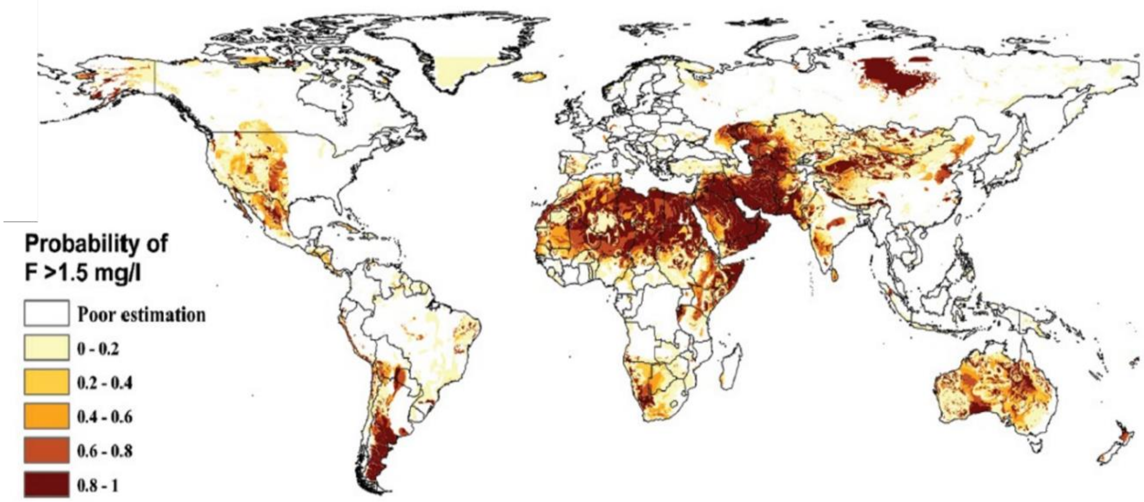


Figure 1.3. Probability map of global fluoride contamination (24).

1.1.3 Total Dissolved Solids (TDS)

The total dissolved solids (TDS) concentration in water is both a taste and health concern; some may consider the tongue to be a sensitive conductivity/TDS meter. Across India, many fluoride-contaminated aquifers are also slightly brackish (500-1,500 mg/L), **Figure 1.4**. In these locations, efforts to remove fluoride must also address the need for partial desalination.

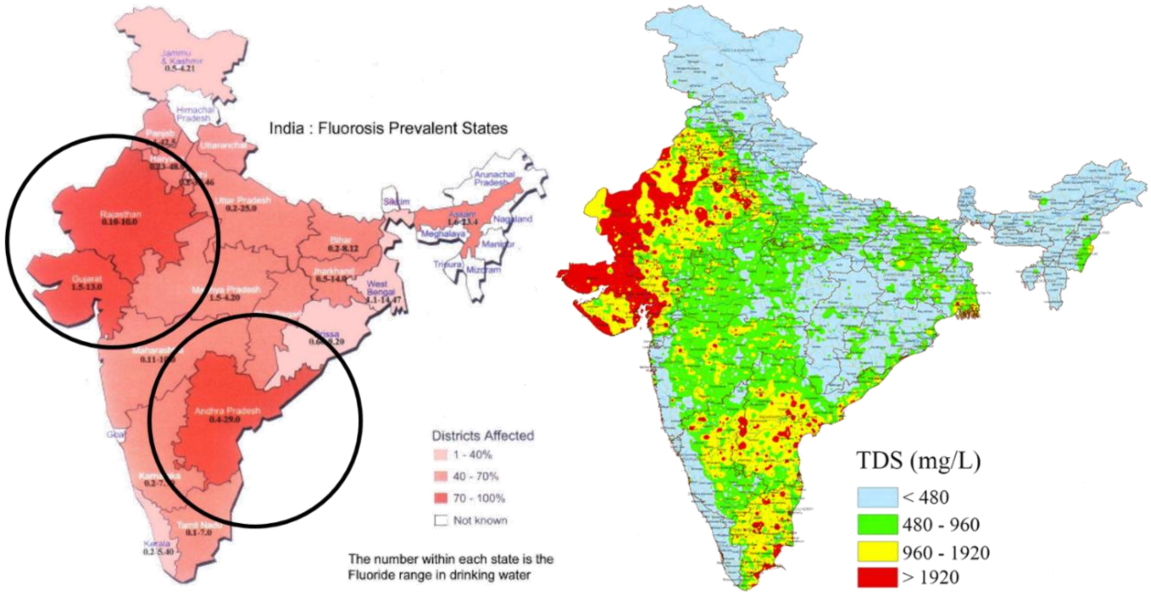


Figure 1.4. Map of fluoride (Left) and TDS (Right) concentrations across India. Note: two zones are highlighted on the left map that have high fluoride and high TDS contamination.

1.1.4 Iron, Hardness, and Alkalinity

Iron, hardness, and alkalinity are common constituents of groundwater that are a scaling risk and aesthetic concern more than a health problem. Iron gives water a metallic taste and forms brown suspended solids, i.e., ferric oxides. Hardness and alkalinity precipitate as scale inside plumbing and along heating surfaces. As such, these water constituents have not received much attention during groundwater treatment in remote communities by NGOs or government agencies. However, for social acceptance and economic sustainability of long-term water consumption, water aesthetics are equally, if not more, important than trace contaminant removal (26). **Figure 1.5** pictures untreated and treated water from two locations in rural West Bengal, India where iron and hardness (i.e., calcium) removal are key to sustainable business operations. Like anyone drinking water, people impacted by arsenic or fluoride want clean, clear water.

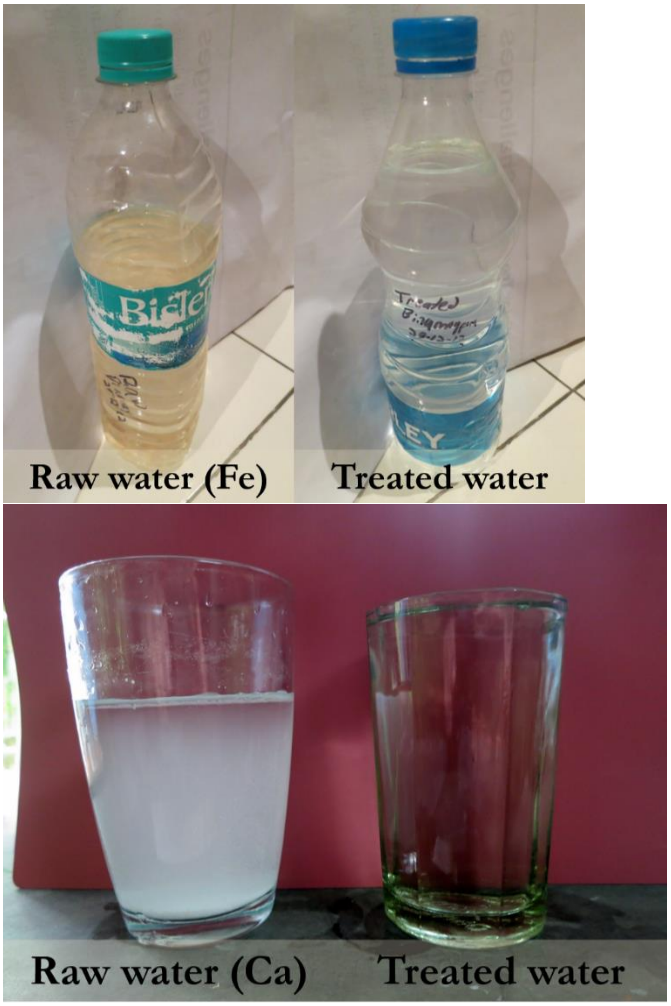


Figure 1.5. Visual improvement after iron removal (Left, Binimaypara, N. 24 Parganas, West Bengal); hardness removal reduces white precipitates (Right, Simurali, Nadia, West Bengal).

1.1.5 Indian Water Quality Standards

Per Indian standards (IS-10500), there are two limits for water quality: (1) Requirement (Acceptable limit); and, (2) Permissible Limit. The water requirement closely parallels WHO standards. The permissible limit relaxes several parameters because of lack of capital, operating, and technical resources for ensuring short-term or long-term adherence to the "requirement". In

Table 1.1, water quality parameters treated by hybrid ion exchange treatment systems are listed.

Table 1.1. IS-10500 water quality standards for parameters of concern.

Parameter	**Requirement (Acceptable Limit)**	**Permissible Limit (in the absence of Alternate Sources)**
pH value	6.5-8.5	No relaxation
Aluminum (as Al), mg/L	0.03	0.2
Arsenic (as As), mg/L	0.01	0.05
Calcium (as Ca), mg/L	75	200
Fluoride (as F), mg/L	1.0	1.5
Iron (as Fe), mg/L	0.3	No relaxation
Total alkalinity (as $CaCO_3$), mg/L	200	600
Total dissolved solids (TDS), mg/L	500	2000
Total hardness (as $CaCO_3$), mg/L	200	600

1.2 Broad Aims

Previously developed arsenic removal materials have high arsenic capacity, but cannot remove fluoride. New materials need to be created with both high arsenic and fluoride removal capacity, e.g., hybrid anion exchange resins loaded with nanoparticles of zirconium oxide (HAIX-NanoZr). Besides arsenic and fluoride capacity, it is important that any new process addresses all aspects of water chemistry out of compliance with water standards, e.g., using a weak acid cation exchange resin in proton form (WAC-H) to perform concurrent partial desalination and increase fluoride capacity. Broad aims to achieve these goals through HAIX-NanoZr and WAC-H were as follows:

1) Create and test small quantities of HAIX-NanoZr for high capacity fluoride removal with concurrent partial desalination (via WAC-H);
2) Scale-up HAIX-NanoZr production in India;
3) Commercialize HAIX-NanoZr with multiple field partners;
4) Demonstrate effective operation at the field-scale level (~100L packed-bed columns);
5) Analyze long-term water treatment processes using a cash flow model of community-scale operations; identify process sensitivities with Monte Carlo simulations.

1.3 Trace Contaminants

It is common for groundwater to be potable and palatable with minimal treatment. Trace contaminants occur at concentrations below 50 mg/L, without any taste, color, or odor indicating their presence. At such low concentrations, it is most energy efficient to have highly selective removal of the contaminant, e.g., ion exchange, ligand exchange, and/or sorption, versus physical separation of the contaminant from the bulk liquid.

1.3.1 Coagulation-Flocculation and Membrane Treatment

As a general water treatment strategy, coagulation-flocculation is effective at removing suspended and dissolved solids: ferric chloride has significant arsenic capacity and aluminum electrocoagulation has significant fluoride capacity (27–32). However, the large capital and operating requirements exclude coagulation-flocculation from small-scale use. Membrane treatment, e.g., reverse osmosis (RO), is a broad-scale treatment strategy to remove nearly all TDS from water (27). People also recognize RO-treated, packaged water as a more desirable luxury item than a handpump tubewell (33–37). But, membrane processes use electricity continuously, have high water rejection (up to 60%), and are operationally complex.

1.3.2 Adsorption

A significant proportion of arsenic adsorption technologies, if not all, use innocuous hydrated metal oxides (HMOs) with high ligand affinity, including iron, aluminum, titanium and zirconium (38–43). Polymeric ligand exchange was also demonstrated to be a viable arsenic-selective sorbent (44–48). In developed countries, many different adsorbents based on HMOs have been successfully commercialized for specific uses, including Siemens Granular Ferric Hydroxide (GFH), Severn Trent GFO/AdEdge Sorb33 and DOW Adsorbsia (49). But, these materials lack mechanical stability and regenerability, making them inappropriate options for rural communities in developing countries, unless supply chains were localized via in-country production facilities.

In considering potential fluoride sorbents, there are several materials that form strong complexes with fluoride. Calcium is present in teeth and bones as minerals of $\mathrm{Ca_5(PO_4)_3(OH)}$ or hydroxyapatite (HAP). Hydroxide-fluoride ion exchange on HAP is responsible for the physical benefits, and ill effects, of fluoride consumption. Insoluble calcium species include $\mathrm{CaF_2}\left(\mathrm{K_{sp}} = 5.3\mathrm{x}10^{-9}\right)$ and $\mathrm{Ca_5(PO_4)_3(OH)}\left(\mathrm{K_{sp}} = 3.7\mathrm{x}10^{-58}\right)$ (50). Aluminum hydroxide and activated alumina both form insoluble fluoride complexes. Zirconium oxychloride and SPADNS form the indicator for fluoride, **Figure 1.6**. (Zirconium hydroxide complexes with SPADNS and develops a strong red color that absorbs light at 570nm, but when fluoride is in solution, zirconium preferentially binds to fluoride, dissociates from SPADNS and becomes colorless.)

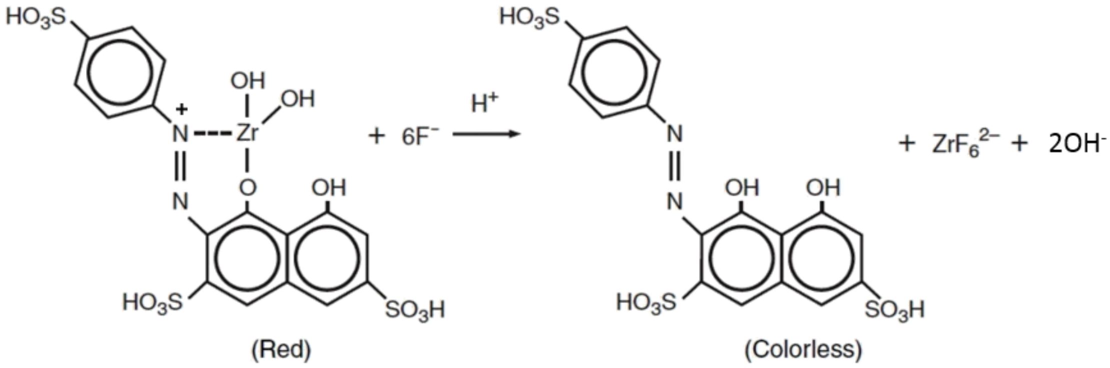


Figure 1.6. SPADNS transition from red-colorless with zirconium fluoride binding.

1.3.3 User-Centered Design

Besides focusing on end-user consumption, it is also critical to consider desirability-of-use for the system. It is often assumed that end-user labor in developing countries is essentially free, and thus the value of human resources is not considered when evaluating capital expenses (CapEx) or operating expenses (OpEx). By disregarding wages, affordable processes will be designed to be labor intensive. To produce safe water for a community of 100 households, for example, a decentralized model using household-based filters appears more economical if end-user labor is free, e.g., a "Brita filter" model. If 100 households diligently pay for materials and fees, and do maintenance properly, then a "Brita filter" company could be quite profitable. However, consistent preventative maintenance is a challenge on systems that show no evidence of failure.

In rural regions of the Indian subcontinent without water delivery infrastructure, water must be transported to the house. A centralized water treatment system could be created with dedicated, paid employees, e.g., one trained operator and two delivery personnel. The operator would be intimately familiar with the system and would ensure water treatment efficacy. The delivery personnel would eliminate the burden of water transportation for customers. Thus, a centralized system would reduce labor hours per day for the community and generate greater employment opportunities versus a decentralized system, **Figure 1.7**.

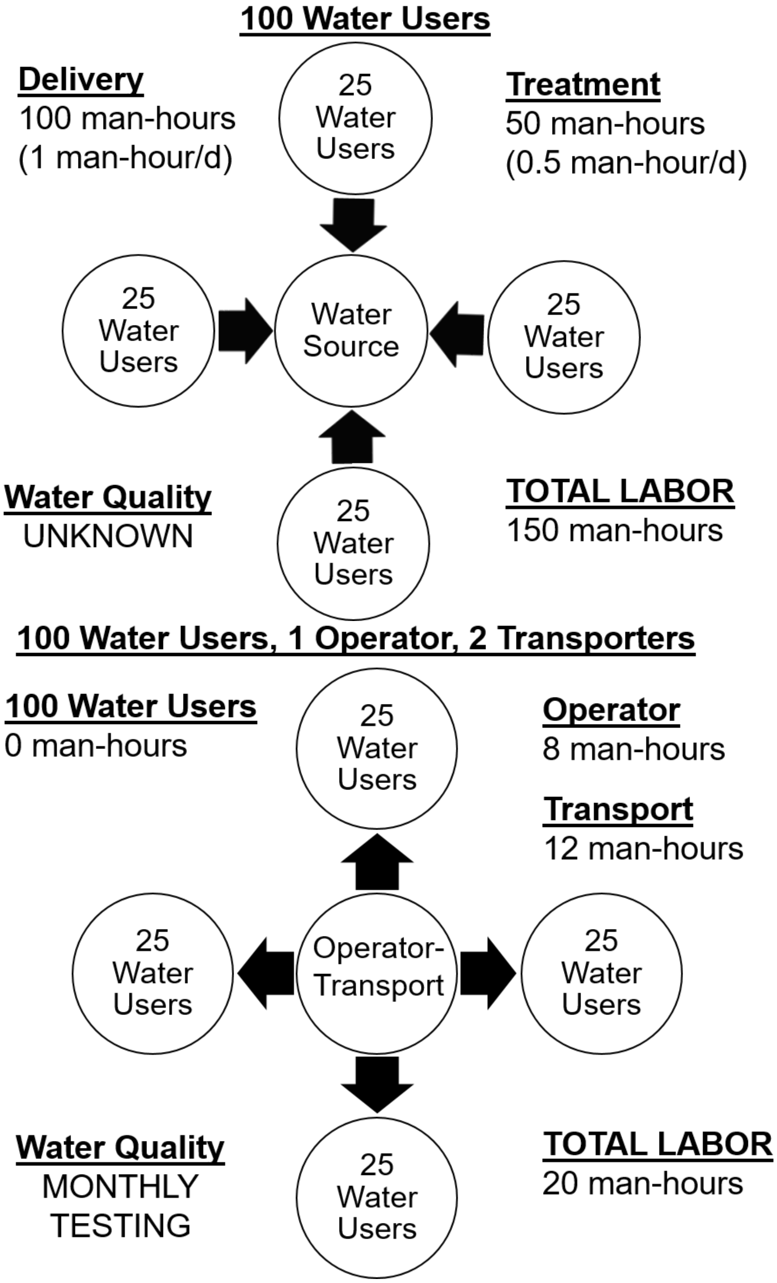


Figure 1.7. Decentralized, home-based water treatment for 100 households in rural India/Bangladesh that required 150 man-hours/day and produced water of unknown quality (Top). Centralized water treatment for 100 water users operated by one operator (8 man-

hours/day) and two delivery personnel (6 man-hours/person) can save a community 130 man-hours/day, generate three jobs, and ensure high quality water (Bottom).

In addition to jobs created during daily operations, annual regeneration and maintenance must be performed on the adsorbent to maintain treatment capacity. The combination of daily and annual operations can be thought of as a self-sustaining cash flow cycle, **Figure 1.8**.

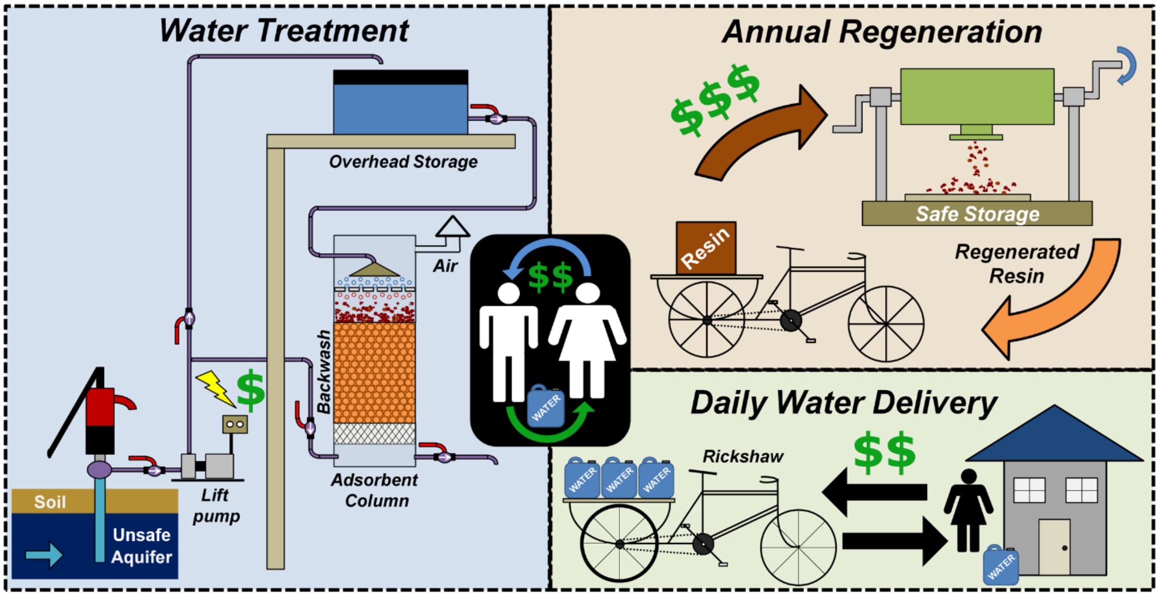


Figure 1.8. A general overview of a sustainable, interconnected water ecosystem to produce safe water and sustain good-paying local jobs. (51)

1.4 Water Treatment Ecosystem

1.4.1 History of Hybrid Ion Exchange (HIX)

Technology-based development initiatives must be grounded in robust and effective science and engineering. Over the last 20 years, Dr. Arup K. SenGupta has been one of the leading-experts on selective trace contaminant removal, especially for arsenic and fluoride. He pioneered the subfield of hybrid ion exchange (HIX) materials, where polymeric ion exchange resin supports and metal oxide nanoparticles have high capacity for trace contaminants because of the synergy of functionalities (52–54). In 2004, an anion exchange resin was impregnated with nanoparticles of ferric oxide to create HAIX-NanoFe that had high efficiency arsenic and phosphate removal (55–57). In 2013, Dr. SenGupta and Dr. Surapol Padungthon patented HAIX impregnated with zirconium oxide nanoparticles (HAIX-NanoZr) to achieve high capacity arsenic and fluoride removal (58–61).

1.4.2 Field Results

Over the past 15 years, over 200,000 people have been served across the Indian subcontinent by arsenic treatment systems designed by Dr. SenGupta. HAIX-Nano arsenic treatment systems have been successfully installed and operated in rural communities of developing countries for up to ten years. Such longevity is possible because of a focus on a holistic water treatment ecosystem. The first use of HAIX-NanoFe to produce potable water from naturally arsenic-contaminated water occurred near Nabarun Sangha Community Club, Ashok Nagar, N. 24 Parganas, West Bengal, India in 2004. Today, people drink arsenic-safe and iron-free water at Nabarun Sangha from multiple treatment columns, profits are returned back to the community, and the caretakers/water distributors have permanent employment. A passive and robust waste management process for community and environmental protection is followed to protect against arsenic sludge (62,63). The local caretakers often discuss aspirations of expansion and greater sales.

1.4.3 Knowledge Transfer: US-India and Vice-Versa

US-originated research at Lehigh was replicated in India and brought to the field through in-country collaborations with the Indian Institute of Engineering Science and Technology, Shibpur (IIEST-Shibpur, formerly Bengal Engineering & Science University), Society for Technology with a Human Face (STHF, an NGO), Tagore-SenGupta Foundation (TSF, US 501(c)3), Ramkrishna Water Enterprise (Durgapur, West Bengal), and Drinkwell (WIST, Inc.). Drinkwell, STHF, and TSF have been critical for expansion of HAIX-Nano-based systems from India to Nepal and Bangladesh. Drinkwell, a private venture-capital-raising startup co-founded by Minhaj Chowdhury, Mike German, and Dr. Arup K. SenGupta, works to scale-up safe water solutions using HAIX for people across the subcontinent.

1.5 Financing Options

Community-based water treatment systems have significant upfront CapEx and logistical challenges for rural communities. The main options for funding CapEx are individual investment, private or NGO donation/purchase, public contracts, or financial services. Each option presents challenges. Wealthy individuals or community organizations with philanthropic or entrepreneurial mindsets are uncommon in impacted areas. Many NGOs actively support water and sanitation, and many have supported groundwater treatment initially. However, long-term sustainability of those well-meaning efforts was problematic: NGOs require an entrepreneurial mindset and long-term vision. A challenge with public contracts is that in India they must go to the lowest bidder who meets specifications. Collusion between bidders is common, as is graft in government decisions. Implementation often minimizes material costs and decreases system performance. Contract payment can take a year or more after completion, complicating cash flow planning. As for financial services, private investment of $5,000-$10,000 could be supported by a competitive marketplace of microfinance institutions throughout the Indian subcontinent at higher interest rates (20-40%), but access to bank funding at lower commercial business interest rates (~12%) requires proof of decreased risk via successful business track record and demonstrated ability to pay back loans.

1.6 Objectives

Despite past efforts, there was a lack of a process for concurrent high capacity fluoride and TDS removal with potential to scale in use across the developing world. Novel HAIX-Nano resins have potential for high fluoride removal capacity when impregnated with HMOs that have high fluoride affinity. Lab-scale characterization and testing of a novel HAIX-Nano fluoride sorbent is a prerequisite before pilot-scale or larger production. The eventual goal would be to have a novel HAIX-Nano fluoride sorbent usable in community-scale systems across the Indian subcontinent through a local partner company. More complete testing would be possible at full-scale systems because of the added human impact of a caretaker and real consumers. For predictions on likely economic outcomes, cash flow data from a variety of operational systems, i.e., arsenic and/or fluoride, will be used to model community-scale water treatment operations to understand the potential feasibility of such systems given a variety of financial situations.

2. Background- Hybrid Ion Exchange

Hybrid, synergy, and nexus are words that have become ubiquitous in titles and descriptions of new technological discovery words, or, one may say, “buzz words” in academia (64). But, the original aim of such descriptions was noble: that by virtue of combining multiple (disparate) resources or processes, something new is created that is greater than either part on its own. This definition of hybrid and synergy fit well with the on-going development of hybrid ion exchange (HIX) processes. The water treatment industry often works on infrastructure-type projects where the process is designed to be used over a wide range of conditions for upwards of >50 years (e.g., utility schemes). Such long-term infrastructure requires a robustness and reliability that is opposite the original creations of typical academic research, where fragile materials are synthesized and operationally-sensitive processes are tested. Design of water treatment processes must have future use cases in mind if the work is to not only exist in a bubble, but to have potential for use at-scale. For instance, bone char (BC) was widely researched and developed to be a potential sustainable solution to arsenic and/or fluoride contamination, especially in developing countries and communities (65–68). But, the raw materials supply chain for bone char could not support the widespread adoption of BC, regardless of its actual performance, which will later be seen as sorely lacking (69–73). Such research in a vacuum from a systems-scale approach can lead to significant wasted time, resources, and effort.

2.1 Lewis Acids/Bases and Hard-Soft Acid-Base (HSAB) Theory

2.1.1 Background

When thinking about effective removal of trace ionic contaminants, it is necessary to consider their aqueous nature: ionic character, oxidation state, solvation, acidity-basicity, octanol-water partition coefficient, etc. At groundwater conditions (pH 6.5-8.5), As(V) and fluoride both have pK_a or pK_{a1} values below neutral and exist as conjugate bases; As(III) (pK_a= 9.2) exists as an uncharged species at groundwater conditions. But, the Arrhenius or Bronsted-Lowry definitions of acids and bases only reflect when a molecule becomes (de)protonated and do not indicate how these species may be selectively removed from water via precipitation or sorption onto another surface. The electron donating or withdrawing capacity of a species, or the likelihood of bond formation, is indicated by the Lewis acidity-basicity; this also applies to bond formation with a proton.

To determine which bonding, and removal option, is more favorable, it is important to be able to compare the strength of the Lewis acidity/basicity. In 1963, RG Pearson first described the hardness and softness of Lewis acids-bases in his seminal JACS paper; harder ions have higher electron density, while softer ions have more labile valence electrons (74–76). More specifically, harder ions have higher charge densities (i.e., smaller size and higher charge), are less polarizable, and are harder to oxidize, while softer ions have lower charge densities (i.e., larger size and lower charge), are more polarizable, and easier to oxidize, **Table 2.1-Table 2.2**. Trends in sizes, electronegativity, and polarizability have been developed in theoretical and experimental work to describe the hardness and softness of an ion; some methods to do so are discussed in **Chapter** 2 Appendix. However, real cations and anions in groundwater exist as hydrated aqueous complexes with many ligands and attached molecules, not as bare, individual ions, as listed. Yet, there is still qualitative value of the non-hydrated species with the aqueous complexes, even though their structure, form, and specific stability constants are different.

Table 2.1. Classification of acids according to the HSAB principle of Pearson. (77)

Acids		
Hard	*Borderline*	*Soft*
$H^+, Li^+, Na^+, K^+, Rb^+, Cs^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Al^{3+}, Sc^{3+}, Ga^{3+}, In^{3+}, La^{3+}, Gd^{3+}, Lu^{3+}, Cr^{3+}, Co^{3+}, Fe^{3+}, \boldsymbol{As^{3+}}, Si^{4+}, Ti^{4+}, \boldsymbol{Zr^{4+}}, Hf^{4+}, Th^{4+}, U^{4+}, Pu^{4+}, Ce^{4+}, WO^{4+}, Sn^{4+}, UO_2^{2+}, VO^{2+}, MoO_2^{2+}$	$Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Sn^{2+}, Sb^{3+}, Bi^{3+}, Rh^{3+}, Ir^{3+}, B(CH_3)_3$	$Cu^+, Ag^+, Au^+, Tl^+, Hg^+, Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}, CH_3Hg^+, Co(CN)_5^{2-}, Pt^{4+}, Te^{4+}, I^+, Br^+, Tl^{3+}$

Table 2.2. Classification of bases according to the HSAB principle of Pearson. (77)

Bases		
Hard	*Borderline*	*Soft*
$H_2O, OH^-, \boldsymbol{F^-}, CH_3COO^-, PO_4^{3-}, SO_4^{2-}, Cl^-, CO_3^{2-}, ClO^{4-}, NO_3^-, ROH, RO^-, R_2O, NH_3, RNH_2, NH_2NH_2$	$C_6H_5NH_2, C_5H_5N, N_3^-, Br^-, NO_2^-, SO_3^{2-}$	$H_2S, R_2S, RS^-, I^-, SCN^-, S_2O_3^{2-}, R_3P, R_3As, (RO)_3P, CN^-, RNC, CO, C_2H_4, H^-, R^-$

2.1.2 Application to Environmental Processes

The hardness and softness of ions were experimentally determined via their relative stability constants with a reference hard acid or hard base (74,75). The hard-soft rule states: hard acids prefer to bind to hard bases and soft acids prefer to bind to soft bases (78). Concepts of “hardness” and “softness” are very valuable for environmental engineers aiming to develop high capacity aqueous or gas-phase adsorbents for contaminants of concern, e.g., mercury (soft acid), lead (borderline hard-soft acid), phosphate (hard base), perchlorate (hard base), and chromate (soft base). Fluoride is a very small anion and the most electronegative element: fluoride is one of the hardest bases, besides hydroxide. Arsenate or As(V) and phosphate are, also, hard bases; phosphate is smaller than arsenate and is harder. However, As(III) is a softer Lewis base (79). As hard bases, hard acids are required for the removal of arsenic and fluoride. Most hard acids are non-noble metal ions that occur as metal oxides of various oxidation states in aqueous systems, depending on the local pH and redox conditions. As a precipitated solid, metal oxide surfaces are often hydrated, and referred to as hydrated metal oxides or HMOs.

2.2 Metal Oxide Surfaces

Metal oxides, e.g., activated alumina (AA), granular ferric (hydr)oxide (GFH, GFO), zirconium oxide (Isolux® by MEL), have been researched and used to remove a wide range of chemical contaminants (31,80–85). Metal oxides can be thought of as a polymeric network of metals and oxide ligands (e.g., oxygen, hydroxyl, water). In this structure, the metals are less electronegative than oxygen and contain higher filled orbitals than oxygen. With these more labile electrons and the differences in electronegativity, the metal is the electron donating group (i.e., Lewis acid), while oxygen is the electron withdrawing group (i.e., Lewis base). Thus, the surfaces of metal oxides contain a diversity of Lewis acid-base groups, depending on the local pH and pE conditions, **Figure 2.1**.

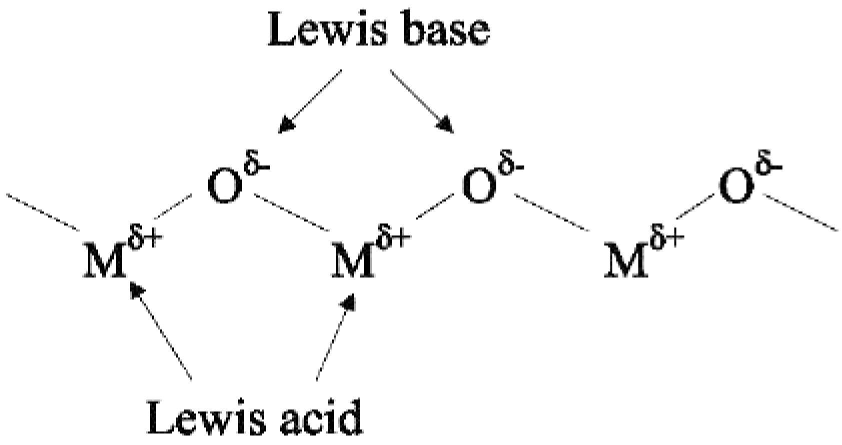


Figure 2.1. Diagram of the metal oxides and the different partial charges on the metal atoms $(M^{\delta+})$ and the oxygen atoms$(O^{\delta-})$. (86)

Hard-hard interactions on metal oxide surfaces are described as the formation of inner-sphere complexes (87), versus looser outer-sphere interactions related to nonspecific electrostatic or hydrophobic interactions, **Figure 2.2** (88). Notably, metal oxides of Al(III), Fe(III), Ti(IV), and Zr(IV) are capable of Lewis acid-base ligand sorption through formation of inner-sphere complexes (41,89–94).

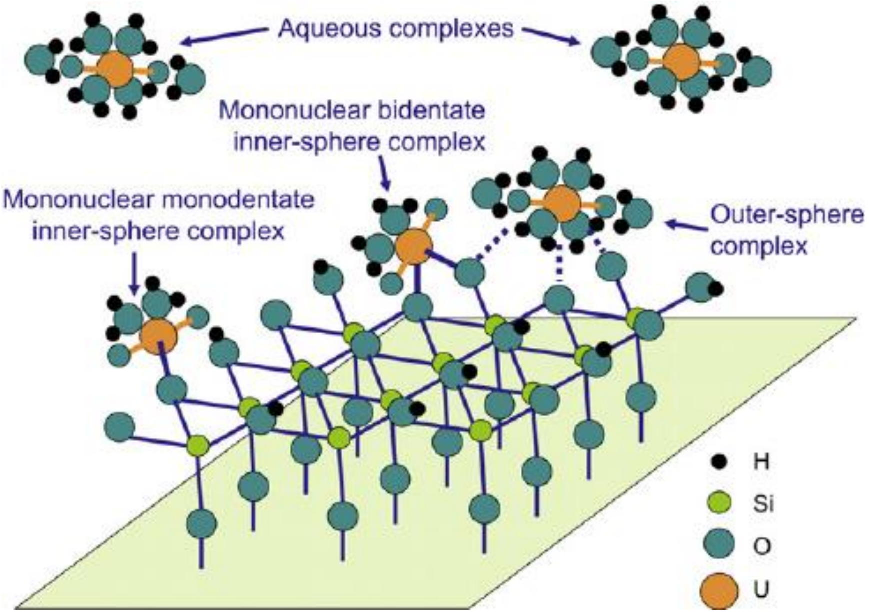


Figure 2.2. Diagram of the different types of surface interactions between aqueous complexes and metal oxide surfaces: mononuclear monodentate inner-sphere complex, mononuclear bidentate inner-sphere complex, outer-sphere complex. (88)

With highly specific and tunable selectivity for trace Lewis acids-bases through hard-hard interactions, HMOs are important materials for removal of compounds of environmental concern. To maximize the potential of HMOs for real-world applications, the surface area should be maximized, or the particle size minimized. However, many HMOs of interest are physically weak by nature, e.g., GFH/GFO crumble under thumb pressure, **Figure 2.3**. As crystalline or amorphous nanoparticles less than 100nm in diameter, GFH/GFO particles are unable to be used in a continuous process without significant downstream separations. Many efforts have gone into making HMOs into robust, high porosity treatment media, but capacity is often lost through aggregation, and calcining creates very brittle materials.

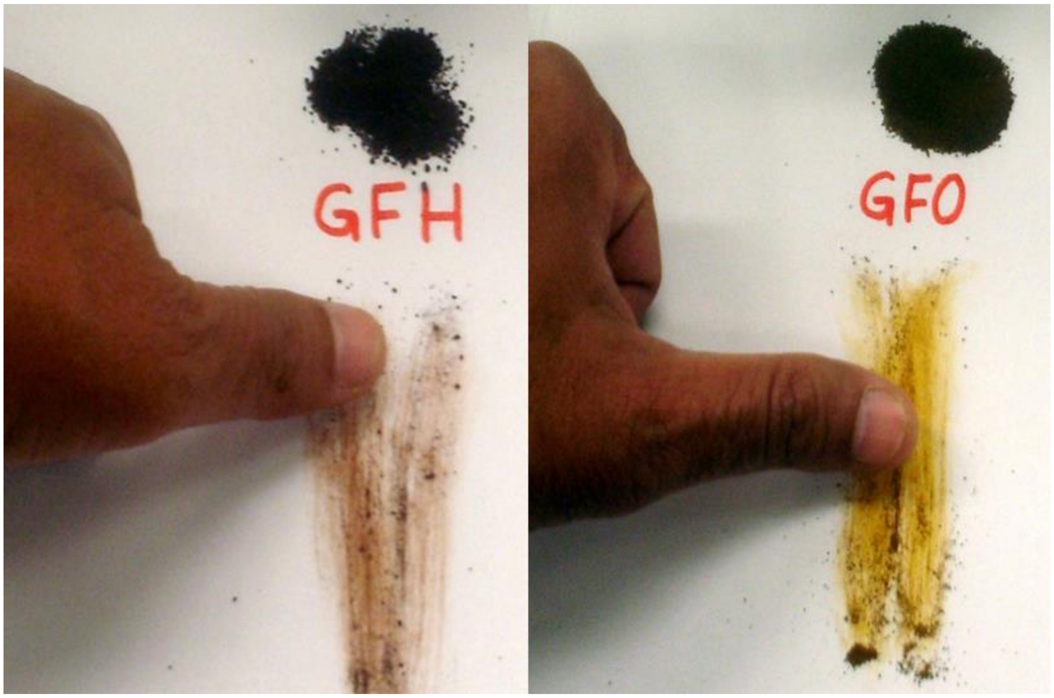


Figure 2.3. GFH and GFO are physically weak and crumble under thumb pressure. Such physically weak materials are designed for single-use without the possibility of reuse. (95)

2.3 Point of Zero Charge (PZC)

Metal oxide surfaces have a heterogeneity of pKa values. A typical zirconium oxide may have two acid dissociation constants near groundwater conditions ($\mathrm{pK_a} = 6.5, 7.8$). From these two dissociation constants, there are three pH ranges and related surface functional groups of ZrO_2. A predominance diagram in **Figure 2.4** has zirconium oxide speciation in comparison to As(V) and fluoride. The net surface charge properties are defined by the pH point of zero charge (PZC); when the number of positively and negatively charged surface groups are equal. A list of PZC values for various metal oxides is provided in

Table 2.3. Systems can be engineered to take advantage of the switchable (or tunable) properties of the metal oxides at pH values below (δ^+), at (δ^0), or above (δ^-) the PZC, e.g., switching between low and high affinity towards target species.

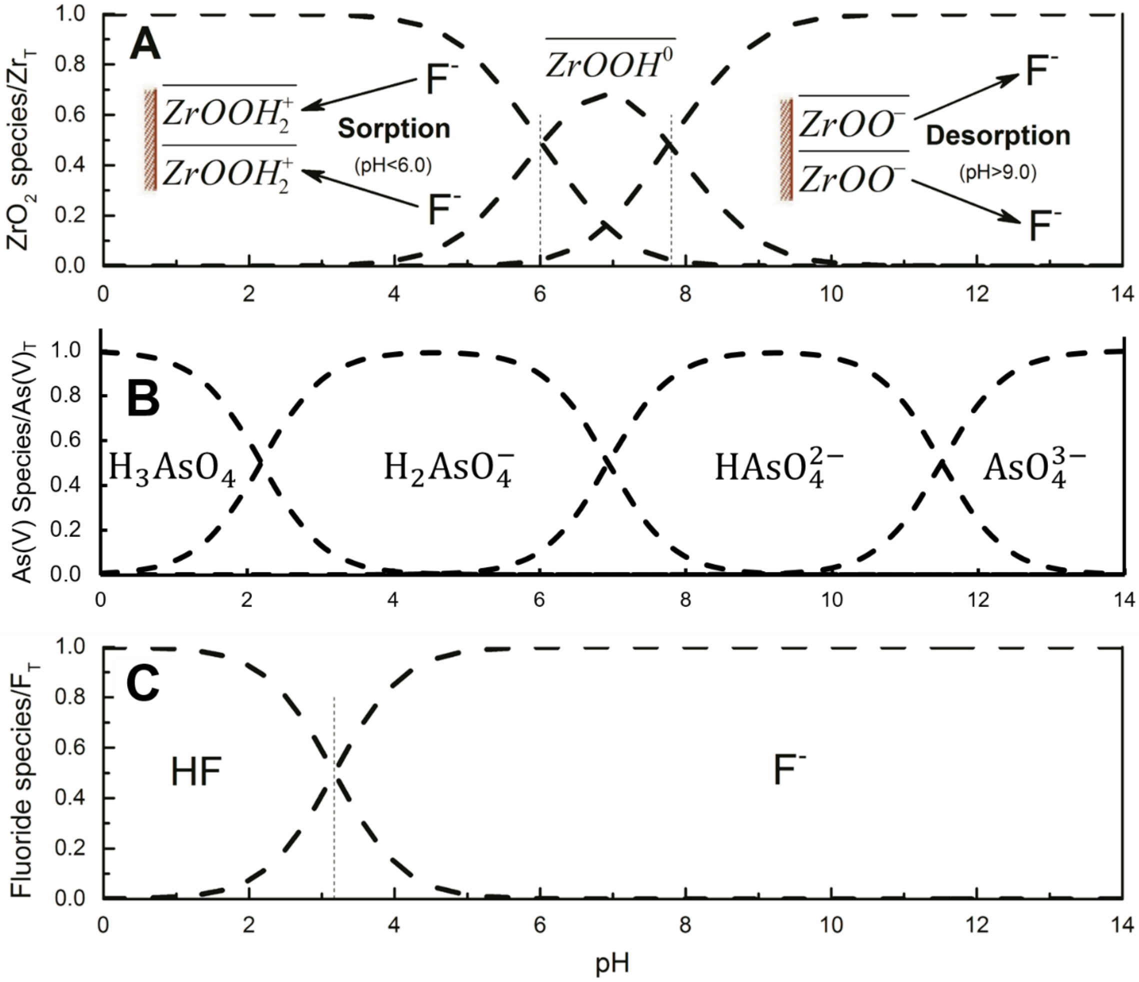


Figure 2.4. (A) Distribution of surface functional groups of hydrated zirconium oxide particles (symbols with overbars) with pH; (B) pC-pH diagram of As(V) (pK_{a1}= 2.19, pK_{a2}= 6.94, pK_{a3}= 11.5); and, (C) fluoride (pK_a= 3.17). (58)

Table 2.3. PZC values of various metal oxides.

Material	**pH**	**Material**	**pH**
α-Al_2O_3 (Corundum)	9.1	δ-MnO_2 (Birnessite)	2.8
α-$Al(OH)_3$	5.0	β-MnO_2	7.2
γ-AlOOH	8.2	SiO_2	2.0
CuO	9.5	$ZrSiO_4$	5.0
Magnetite	6.5	Feldspars	2-2.4
α-FeOOH (Goethite)	7.8	Kaolinite	4.6
α-Fe_2O_3 (Hematite)	8.5	Montmorillonite	2.5
$Fe(OH)_3$am	8.5	Hydroxyapatite	7.6
MgO	12.4	Albite	2.0
Calcite	9.5	Chrysolite	>10
ZrO_2	**4.0-8.6**	Rutile TiO_2	5.8

2.4 Donnan Membrane Principle

In order to take advantage of high surface area HMOs, it is necessary to impregnate the nanoparticles in a physically durable scaffold with high intraparticle diffusivity. Alginate, zeolites, activated carbon, and chitosan have been attempted as physical supports for HMO nanoparticles (83,96–98). Each of these materials has different degrees of fixed, negatively charged groups within their structure and cation exchange capacity. The Donnan membrane principle (99,100) is an application of the Law of Electroneutrality to completely ionized electrolytes in a heterogeneous system with both a liquid-phase (e.g., aqueous cations and anions) and a solid-phase (e.g., fixed functional groups). The presence of non-diffusible, fixed charges within a bead decreases the local co-ion and increases the counterions in order to maintain electroneutrality between the local and bulk solution. In **Figure 2.5**, three cases are depicted: (I) without fixed charges; (II) with fixed negative charges; and, (III) with fixed positive charges.

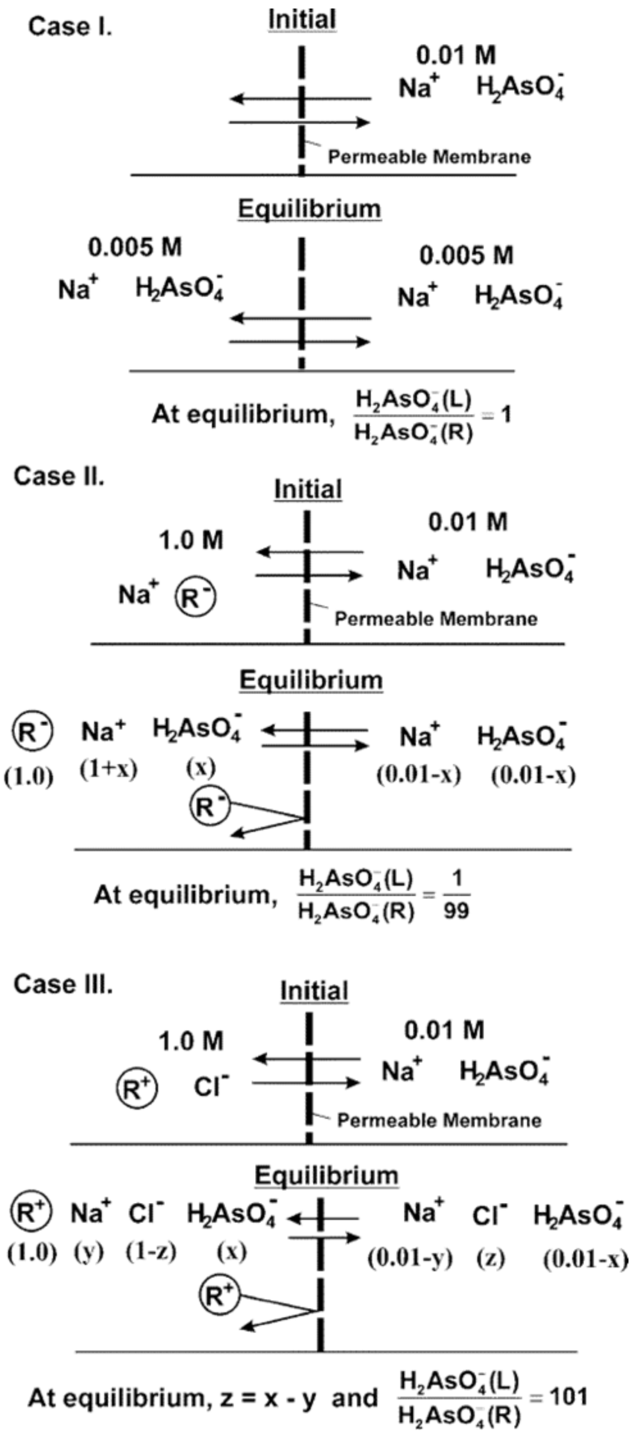


Figure 2.5. Depiction of three specific cases presenting the Donnan distribution of arsenate ($H_2AsO_4^-$), when the membrane is permeable to all ions and there is no fixed group (Case I); there are fixed R^- groups (Case II); and there are fixed R^+ groups (Case III). (56)

2.5 Ion Exchange

Ion exchange materials are polymers with high concentrations of fixed charges (functional groups) paired with mobile counterions, in compliance with the Law of Electroneutrality, **Figure 2.6-Figure 2.7**. The surface of an ion exchange material can be thought of as the permeable membrane in **Figure 2.5**, where there is high flux of ions from the bulk solution to the pore space. Ion exchange can be used at a variety of packed-bed scales for the separation and removal of any ion. The most common application is for hardness removal by sodium-calcium/magnesium exchange with polymeric strong acid cation exchange resins (101–106):

$$\overline{2(R - SO_3^-)Na^+} + M^{2+} \leftrightarrow \overline{(R - SO_3^-)_2M^{2+}} + Na^+ \tag{2.1}$$

The cation exchange is reversed with brine solutions (5-15% NaCl) to regenerate the calcium removal capacity.

Regeneration requirements versus contaminant capacity of ion exchange resins is not ideal for many treatment requirements. Competition between similar ions can lead to poor removal: sulfate is often at much higher concentrations and out competes arsenate; fluoride is the least preferred anion. Or ions can be removed with very high affinity and require intensive regeneration that generates contaminated brine with disposal problems, e.g., nitrate, perchlorate, uranium.

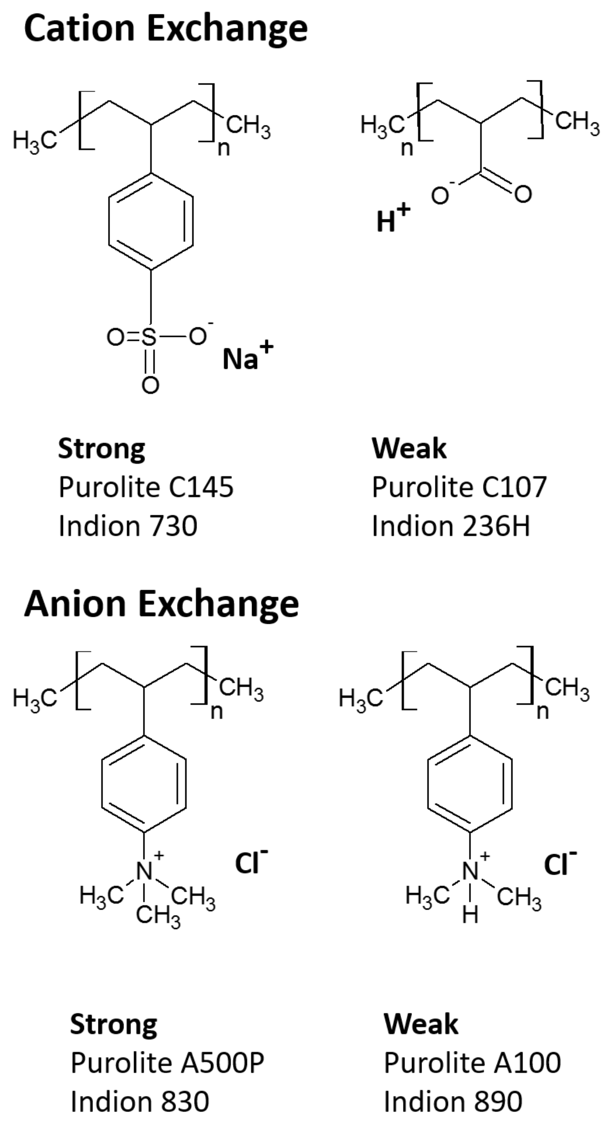
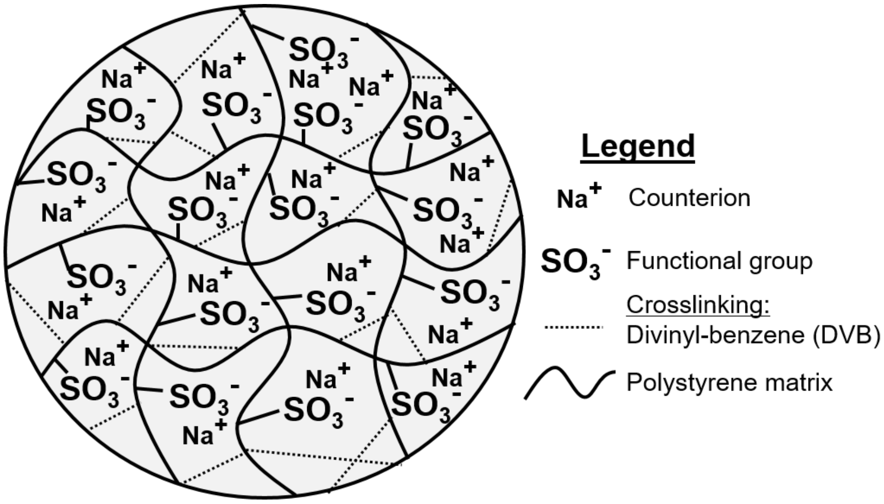


Figure 2.6. Typical monomers (parent resin and functional group) that comprise polymeric cation exchange resins and anion exchange resins. Note: strong and weak are in reference to the ability of the resin to be (de)protonated, e.g., weak acid resins are protonated at pH < 3 and do not participate in ion exchange.



Commonly represented as: **$R\text{-}SO_3^- Na^+$**

Figure 2.7. Diagram of a strong acid cation exchange resin with the polystyrene matrix, divinylbenzene crosslinking, sulfonic acid functional groups, and sodium counterions.

2.6 HIX-Nano Materials

2.6.1 HIX-Nano: Iron-Impregnated (HIX-NanoFe)

The Donnan co-ion exclusion effect from a material with fixed negative charges, such as Case II in **Figure 2.5**, decreases the intraparticle diffusion and the removal capacity for anionic Lewis bases, e.g., As(V) and/or fluoride. In 2003, DeMarco et al. successfully impregnated nanoparticles of hydrated ferric oxides (HFOs) within a polymeric strong acid cation exchange (SAC) resin, or a polymeric-inorganic hybrid sorbent (40). The capacity of HCIX with nanoparticles of HFOs (HCIX-NanoFe) for As(V) was significantly greater than an untreated parent anion exchange resin (IRA-900) because of the high surface area of HFOs and strong inner-sphere complexes of As(V) to HFOs. Indicating the presence of HFOs was more significant than the Donnan effect.

In 2005, Cumbal et al. further demonstrated the Donnan membrane effect by loading HFOs within SAC resins, non-functionalized ion exchange (NIX) resins, and strong base anion exchange (SBA) resins (56). The volume treated for As(V) increased 1000x as the Donnan membrane effect towards As(V) changed from co-ion exclusion (SAC), no influence (NIX), and counterion attraction (SBA), **Figure 2.8**. Hybrid anion exchange resins loaded with nanoparticles of HFOs (HAIX-NanoFe) were a synergy of the polymer and inorganic properties to yield high arsenic capacity. Both the polymeric and inorganic properties of HAIX-NanoFe act concurrently, both high removal efficiency by ion exchange (e.g., perchlorate, chromate, uranium, nitrate) and by Lewis acid-base interactions (e.g., As(V), phosphate, silica, fluoride, technetate), **Figure 2.9**.

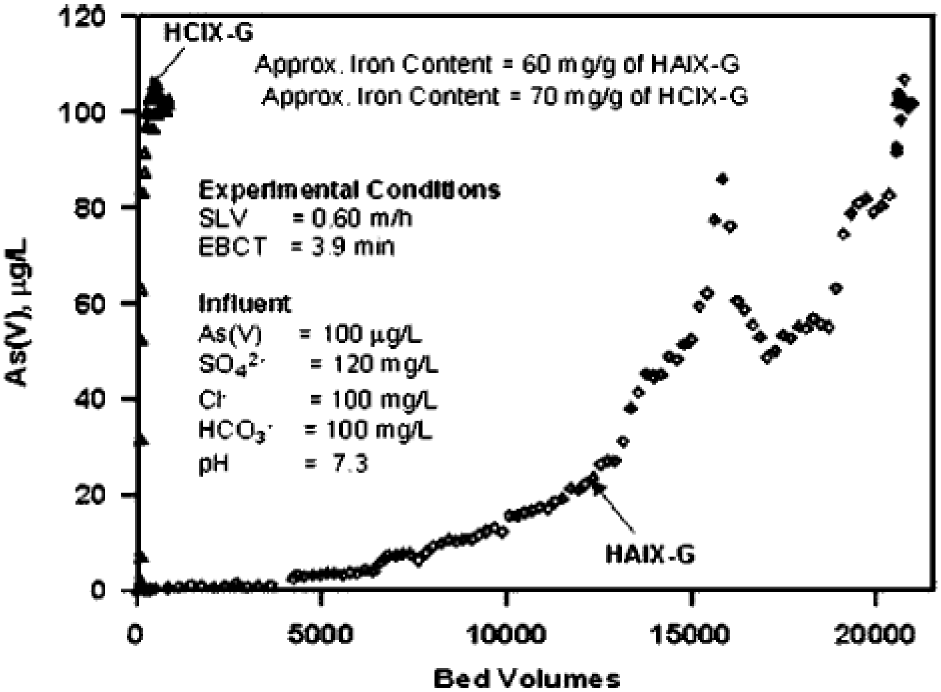


Figure 2.8. Comparison of As(V) effluent histories between HCIX and HAIX for two separate column runs under otherwise identical conditions. (56) **Note:** Bed volumes (BVs), volume treated over volume of packed-bed material, are a dimensionless unit used to compare performance of packed-bed systems of different sizes. By using dimensionless parameters, performance of materials in a 10 mL lab system can be effectively compared with a 1000 L form-factor when ideal plug-flow behavior is maintained and hydraulic

operation remains consistent, e.g., empty bed contact time (EBCT, flow rate/volume of material) and superficial liquid velocity (SLV, volumetric flow rate/material surface area).

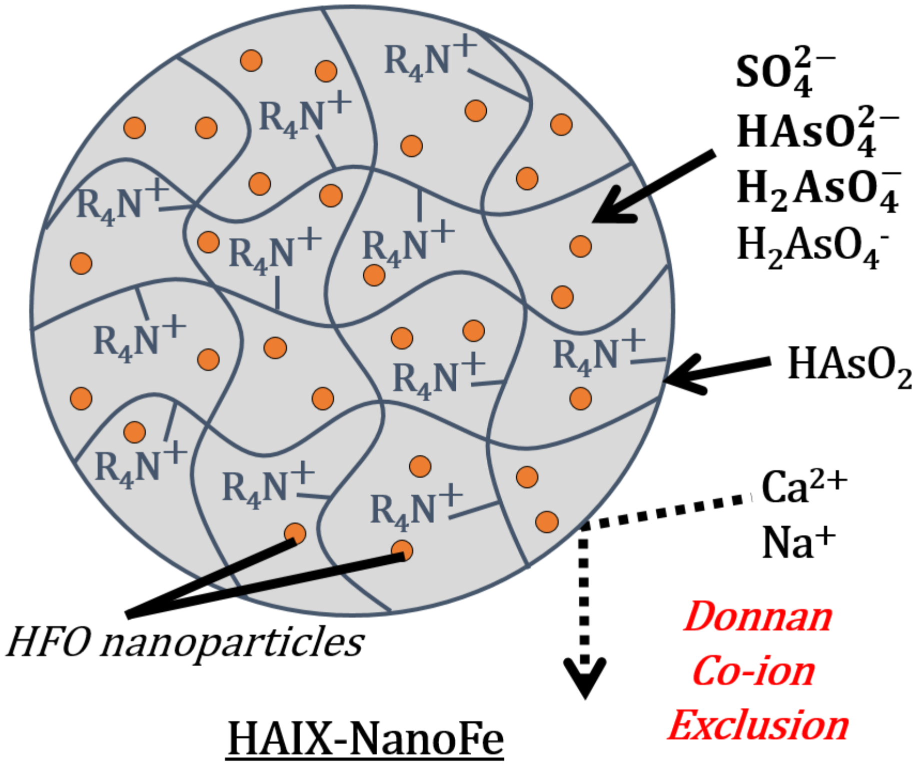


Figure 2.9. Diagram of an HAIX-NanoFe resin bead with the anion exchange resin support impregnated with nanoparticles of HFOs. Note the transport of counterions (i.e., anions) through the resin per the Donnan Membrane equilibrium and rejection of co-ions (i.e., cations) per Donnan co-ion exclusion.

The HMO nanoparticles did not leach out of HAIX-NanoFe during treatment of arsenic-laden synthetic groundwater: maximum iron effluent concentration was 5 µg/L. The physical durability of the polymeric ion exchangers prevented shearing or physical degradation of the HMOs and no fines were generated during use. During packed-bed operation, regular backwashing is necessary to remove fines and prevent system clogging for AA, GFH, and GFO because of their physical instability.

By retaining the HMOs securely within HAIX-Nano, it is possible to perform multiple cycles of regeneration-exhaustion via pH swings (acid-alkali dosing) to switch the metal oxide surfaces between positive-negative charges. As the surface groups change from Lewis acids (low pH) to Lewis bases (high pH), retained Lewis bases are quickly and efficiently rejected. The positive surface charge and Lewis acid character of the HMOs, can later be restored by dosing an acid solution, **Figure 2.10**. HAIX-NanoFe regeneration with 3% NaCl-3% NaOH yielded 95% capacity recovery within 10 BVs. Throughout cycles of exhaustion-regeneration, HMOs retain their amorphous structure (52).

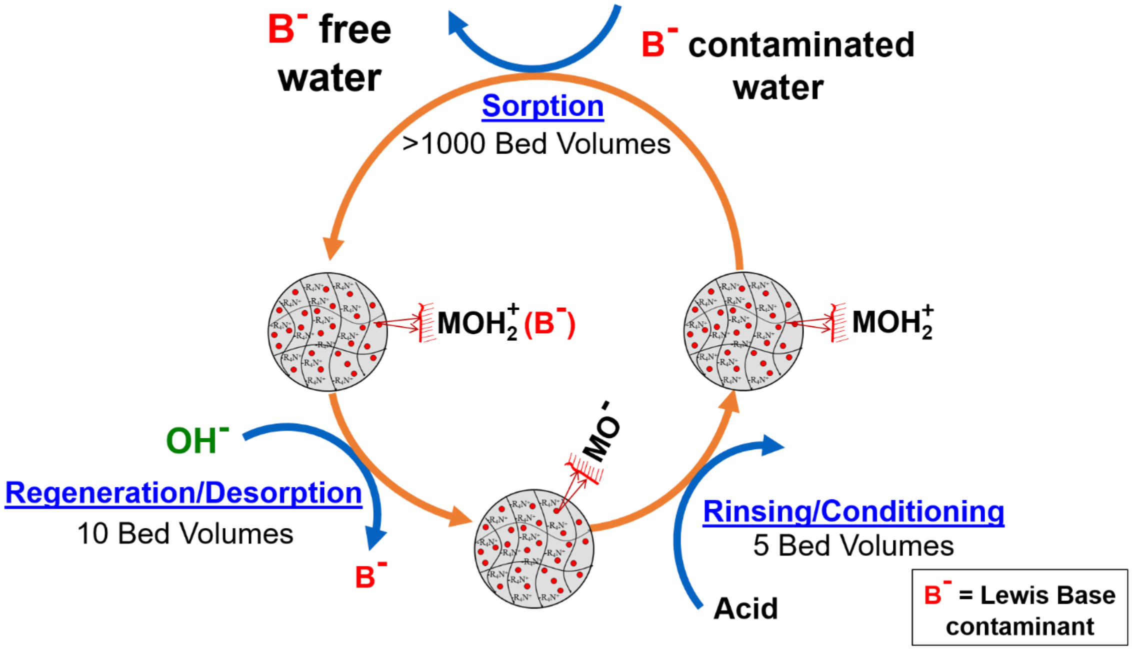


Figure 2.10. A general HAIX-Nano material used for cyclic removal of a Lewis base (B^-) via cyclic sorption-regeneration: (1) sorption of B^-; (2) regeneration/desorption by alkali solution (10 BVs); (3) re-acidification of the metal oxide surface groups (5 BVs).

In summary, the advantages of HAIX-Nano include:

1) Nanoparticles of HMOs are able to be precipitated inside a robust material with high intraparticle diffusivity, where they retain their morphology and functionality over multiple cycles of exhaustion-regeneration;
2) Properties of both polymeric and inorganic materials are retained for multi-contaminant removal during use through multiple mechanisms; and,
3) Donnan membrane effect can be tuned to enhance removal of contaminants of concern and reject other aqueous species.

2.6.2 HAIX-Nano: Zirconium-Impregnated (HAIX-NanoZr)

2.6.2.1 Zirconium Benefits

Nanoparticles of HFOs have high capacity for As(V), As(III), and phosphate, but they lack sorption capacity for fluoride, one of the hardest Lewis bases. Calcium, aluminum, and zirconium are harder Lewis acids than Fe(III) and form strong complexes with fluoride. Although calcium and aluminum oxides are insoluble at groundwater conditions, they are significantly soluble at the acid-alkali conditions required for regeneration; neither material is usable as a regenerable sorbent for multiple cycles of use.

Zirconium has much lower solubility at high pH versus Al, **Figure 2.11**, and across a wide range of pH and redox conditions versus Fe, **Figure 2.12**. By being stable throughout reducing conditions, zirconium oxides would continue to have strong sorption for arsenic and fluoride if their exhausted form was disposed of in landfill conditions. The EPA Toxicity Characteristic Leaching Protocol (TCLP) testing is currently performed using an acetic acid solution to reach an equilibrium at slightly acidic pH conditions (pH ~5), but the solution pE is not adjusted to match the reducing conditions of landfills and their active anaerobic activity. This leads to false negatives when reporting that sorbents made of iron will not leach arsenic (62). At equilibrium with landfill conditions, solid Fe(III) will reduce to Fe(II), and As(V)/As(III) will become aqueous and mobile.

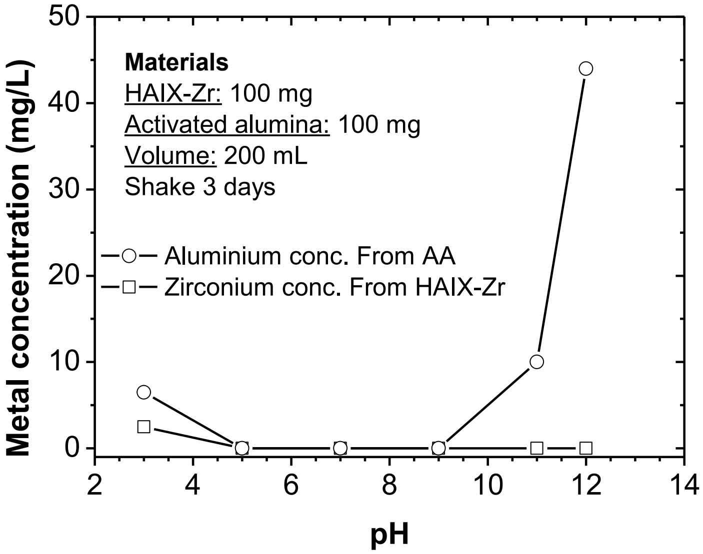


Figure 2.11. Plot of equilibrium solution zirconium from HAIX-Zr and dissolved aluminum from activated alumina (AA) from pH 3-12.

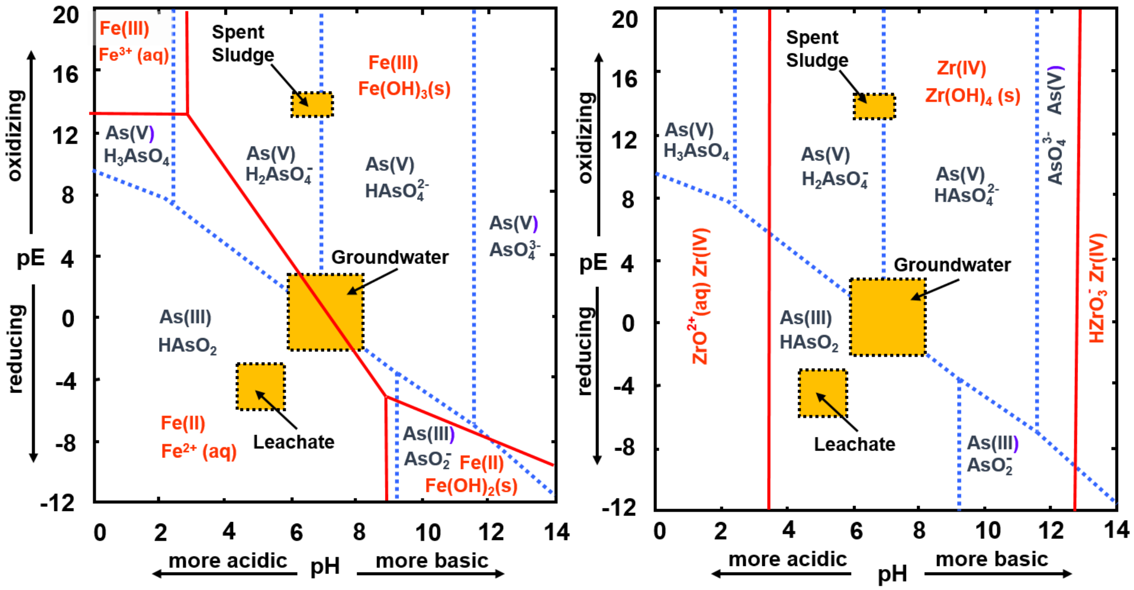


Figure 2.12. Composite predominance diagrams of Fe-As (left) and Zr-As (right). (59)

2.6.2.2 Previous HIX-NanoZr Efforts

2.6.2.2.1 TM Suzuki Method

In the past, hybrid ion exchange resins with nanoparticles of zirconium(IV) oxide (HIX-NanoZr) have been synthesized by loading polymeric resins with zirconium oxide following the method of Suzuki (90,107,108):

1) Prepare 20% zirconium oxychloride solution (methanol)
2) Mix unfunctionalized ion exchange resin with zirconium-methanol solution at 15% (w/v)
3) Dry resins under vacuum until methanol is removed
4) Mix dried resin with 28% ammonia for 5hr (precipitate amorphous zirconium oxide)
5) Wash resin until supernatant is free of precipitates
6) Autoclaving at pH 2, $150^{\mathrm{O}}\mathrm{C}$ for 15 hr (Crystallize monoclinic zirconia crystals inside the resin)
7) Ethanol wash
8) Dry at $50^{\mathrm{O}}\mathrm{C}$

The material had significant As(V) removal capacity (Q= 35 mg/g) for acidified DI water spiked with very high arsenic concentrations (pH 5.0, [As(V)]= 10.0 mg/L); data at relevant groundwater conditions was not available. The material had repeated regenerability (98% recovery) by 1M NaOH-0.2M Acetate (pH 4.2). However, arsenic capacity would have been significantly improved with a resin that contained fixed positive charges and the related Donnan membrane effect.

The prior studies of Suzuki on fluoride sorption used a similar method, but with tetra (n-butoxy) zirconium as the zirconium. At synthetic influent conditions $(\mathrm{pH}\ 3.0, [\mathrm{F}^-] = 100\ \mathrm{mg/L})$, the material had significant fluoride removal capacity (Q=15 mg/g); no data were present at relevant fluoride conditions. The fluoride sorbent was readily regenerated with 1) 1M NaOH; 2) 1M HCl, without significant zirconium losses (<2%). However, Suzuki et al. noted a quick decrease in fluoride capacity and performance at more realistic groundwater pH values near the PZC of zirconium (pH 7-8).

2.6.2.2.2 Puttamraju (SenGupta)

Puttamraju et al. (2006) followed a method similar to that of Suzuki, but without heating (107). Their HCIX-NanoZr variant focused on the concurrent rejection of arsenic anions and removal of Cu(II) cations as part of the tunable nature of hybrid ion exchangers. The Donnan co-ion exclusion effect from the parent sulfonic acid functional groups of the cation exchange resin inhibited intraparticle diffusion of arsenic anions. Another study on HAIX-F-NanoZr, or hybrid anion exchange fibers loaded with zirconium nanoparticles (108), detailed the affinity for organic Lewis bases, especially phthalate and oxalate. There was clear evidence of the selective removal of Lewis base ligands by forming inner-sphere complexes with the zirconium oxides, but no testing was done with arsenic or fluoride.

2.6.2.2.3 Padungthon (SenGupta)

Padungthon et al. synthesized hybrid anion exchange resins loaded with nanoparticles of zirconium oxide (HAIX-NanoZr) via dissolution of zirconium oxide solids (60):

1) Create a 15% (w/v) ZrO_2 solution (using waste zirconium oxide) with either 10% sulfuric acid or 20% H_2SO_4 with methanol at a 50:50 ratio (note: methanol decreases the dielectric constant)
2) Mix anion exchange resin beads in Zr solution for 15 hr
3) Decant and dry the resin
4) Mix dry resin with equal volume 5% NaOH

The HAIX-NanoZr produced by Padungthon et al. had significant arsenic capacity (Q= 20 mg As(V)/g at pH 7, As(V) = 1000 ppb, batch test) and fluoride capacity (Q= 3.5 mg F/g at pH 5.5, column study) (58,59). Although successful in synthesis and in Lewis Base removal, production by Padungthon et al. required high concentration sulfuric acid and methanol for transporting zirconium inside the resin. Both solvents should be avoided for safe and effective production in developing communities.

2.7 HAIX-NanoZr: Increased Capacity and Concurrent Partial Desalination

Many fluoride-impacted regions have aquifers that are more saline than desirable (500-2000 mg/L TDS). In natural aquifers, a significant portion of the TDS is hardness (i.e., divalent cations) and alkalinity (i.e., bicarbonate system). Lime softening is common for hardness removal and partial TDS reduction, however, the process is sensitive to influent conditions and requires careful operation. Thus, lime softening is not ideal for small-scale community operations, especially in regions lacking trained water operators.

Ion exchange processes are typically not used for desalination at TDS = 500-2000 mg/L because their operation requires the use of significant volumes of strong acid and alkali regenerants, and disposal of the waste regenerant. The cost of operating ion exchange is a function of regeneration frequency, which is proportional to the equivalents of ions in solution; higher concentrations require more frequent regeneration. However, for partial desalination, a fraction of TDS could be removed through a neutralization reaction, i.e., precipitation (**Chapter 2 Appendix**) or evaporation. Through the carbonate system, alkalinity can be removed through the creation of carbonic acid, which is in equilibrium with carbon dioxide gas. . If influent was passed through a weak acid cation exchange resin in proton-form (WAC-H), divalent cations would exchange with protons, alkalinity would be protonated, and CO_2 could be degassed from the effluent:

$$2\overline{\mathrm{R-COOH}} + \mathrm{Ca}^{2+} \rightarrow \overline{(\mathrm{R-COO}^-)_2\mathrm{Ca}^{2+}} + 2H^+ \tag{2.2}$$

$$2\mathrm{H}^+ + 2\mathrm{HCO}_3^- \rightarrow 2\mathrm{H_2O} + \mathrm{CO_2(g)}\uparrow \tag{2.3}$$

$$\text{Overall: } 2\overline{\mathrm{R-COOH}} + \mathrm{Ca}^{2+} + 2\mathrm{HCO}_3^- \rightarrow \overline{(\mathrm{R-COO}^-)_2\mathrm{Ca}^{2+}} + 2\mathrm{H_2O} + \mathrm{CO_2(g)}\uparrow \tag{2.4}$$

By using WAC-H, hardness, alkalinity, and pH would decrease. Concurrently, the pH decrease would increase the positive surface charge of the zirconium oxides inside HAIX-NanoZr. A more protonated metal oxide surface would create a stronger Lewis Acid and higher fluoride sorption capacity, **Figure 2.13**.

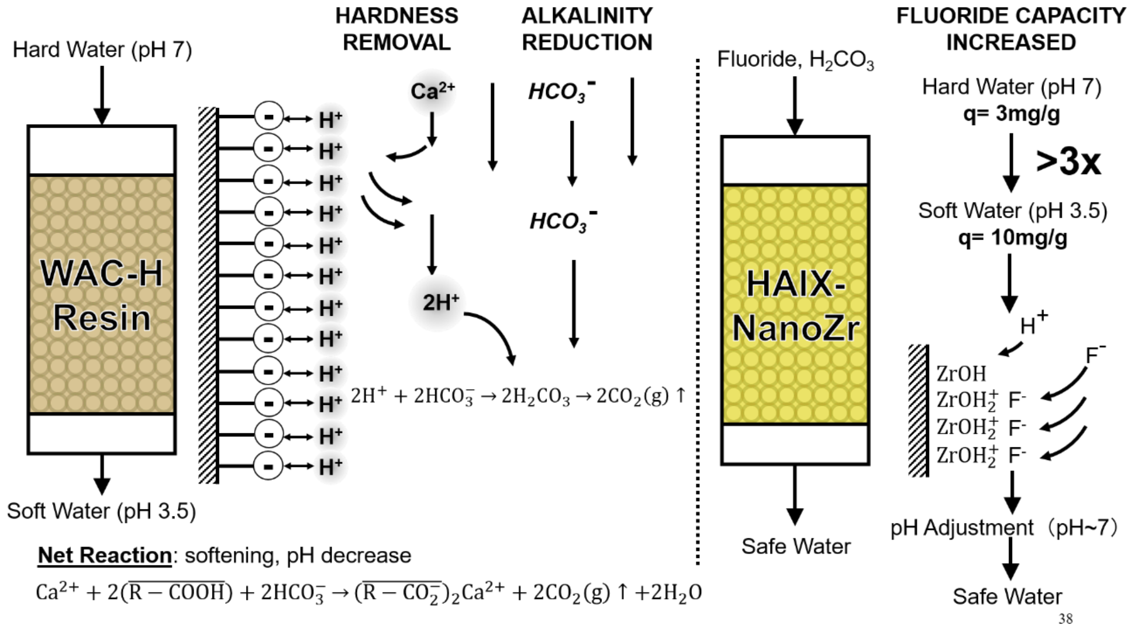


Figure 2.13. Mechanism of WAC-H proton exchange and hardness/alkalinity removal (Left). Increased fluoride capacity of HAIX-NanoZr at lower pH (Right).

2.8 Hardness and Alkalinity Removal: Weak Acid Cation Exchange (WAC) Resin at a Field Sites

A community-scale arsenic treatment facility using HAIX-NanoFe (from the US) was designed in an identical manner to other past systems described in literature (51,54), and was installed for testing new business models through ownership by a single female entrepreneur. The system was installed at a home owned by a female entrepreneur (Ruplekha Banerjee) and founder of Aqua Bengal Enterprises (Enayetpur, Simurali, Nadia District, West Bengal), **Figure 2.14**. The goal of the system was to demonstrate the effectiveness of women entrepreneurs and managers for water sales. Ruplekha Banerjee was a seasoned arsenic treatment worker after many years of work in other local NGOs that also aimed to address arsenic. She was even part of an NGO (SATHEE, Nadia District, West Bengal) that installed similar systems through the same contractor, except with activated alumina instead of HAIX resins; the work performed by this NGO was described in previous publications co-authored by Dr. Arup K. SenGupta (52–54,109).

The arsenic treatment system for Ruplekha Banerjee was installed on April 15, 2013; April 15th is Bengali New Year, an auspicious day. However, the treated water showed undesirable amounts of white precipitate soon after beginning operation, e.g., calcium carbonate, **Figure 2.15**. Using an earlier version of partial desalination with concurrent trace ion removal, a small (5L) WAC resin column in proton-form (e.g., Purolite C107, Ion Exchange INDION 236, Thermax CXO-9) was installed at this system on July 14th, 2013, **Figure 2.16**. Later, after proof of success in eliminating the white precipitate via use of the small WAC column, a larger (50 L) WAC column was installed in order to minimize regeneration frequency and improve ease of operation. However, long-term health issues soon after afflicted Ruplekha Banerjee that required outside financial assistance to afford a lifesaving surgery. Soon after healing, she faced a bed-ridden pregnancy where the child died a few weeks after delivery. The sum of financial, medical, and emotional stressors made it impossible for meaningful long-term data collection regarding the efficacy of Ruplekha Banerjee as a single, female water entrepreneur versus typical community operations. There are many uncertainties and unknowns when planning field research.

Figure 2.14. (L) Image of the original arsenic treatment system in Simurali on opening day; (R) Ruplekha Banerjee, entrepreneur and owner of Aqua, selling water to a local customer on opening day.

Figure 2.15. Calcium carbonate precipitation present in the A) treated effluent from the arsenic treatment system on May 14, 2013 (L) and B) calcium carbonate from the side of the treated water tank.

Figure 2.16. Image of the installation (L) and finished (R) small WAC column (V= 5L) with contractor Pranab Pramanik (Ramkrishna (Water Solution) Enterprise, Durgapur, West Bengal, India).

2.9 Example Community Site: Haldi, Ballia District, Uttar Pradesh

This detailed background is provided for Ballia District as a representation of similar work related to arsenic that happened in many other districts across India. Many other publications have detailed the work of testing and predicting arsenic levels in groundwater, soil, and human samples (e.g., blood, hair, and nail) across the Indian subcontinent and other regions (110–119). Arsenic testing across Ballia District was performed by Jadavpur University in 2005 with support from UNICEF (120–122). Further testing occurred across other districts in UP by the UP Jal Nigam (Water Corporation), leading to tests of 110,000 sources across >50 districts. It was found that 2,610 habitations across twenty districts had arsenic concentrations in excess of 50 µg/L. An additional 10,434 habitations across eleven more districts had arsenic concentration in excess of 10 µg/L.

The initial strategy (2006-2007) by the UP government to address the arsenic crisis involved deep tube wells (DTWs): 475 DTWs were installed across Ballia District and Lakhimpur Kheri District. The UP Water Corporation then made the following installations: 103 habitations have 498 extra deep India Mark-II hand pumps; 81 habitations have “safe water” through twenty protected water supply schemes; 117 habitations have 37 piped water supply schemes; and, nine habitations have future planned extra deep hand pumps.

The Secretary of the Ministry of Drinking Water and Sanitation then declared it ill advised to drill DTWs through arsenic-contaminated aquifers in 2008. Sanitary shallow wells were then encouraged and installed, but were soon found to also be at risk of arsenic contamination and halted. Separately, M/s Water Aid India (WAI) approached the UP Water Corporation about replicating the work by Water for People in West Bengal, which was designed by Dr. Arup K. SenGupta (Lehigh University).

Figure 2.17. Members of the water committee in Ballia discussing plans for a future arsenic treatment system. Note: On the far left is Mr. Ashok Singh.

2.10 Detailed Aims

Previously developed HAIX-NanoFe resins have high arsenic capacity, but cannot remove fluoride. Recent HAIX-NanoZr resins had both high arsenic and fluoride capacity. However, HAIX-NanoZr fluoride capacity was limited and effluent water was not treated to drinking water standards in all cases. WAC resins could both enhance fluoride capacity and achieve partial desalination because of the pH-sensitive nature of fluoride removal by zirconium oxide and the significant fraction of TDS comprised by hardness and alkalinity.

Aims to achieve holistic application of this work were as follows:

6) Synthesize and characterize lab-scale quantities of HAIX-NanoZr for high capacity defluoridation with concurrent desalination at Lehigh University and in India;
7) Scale-up HAIX-NanoZr from lab-scale samples at Lehigh to pilot-scale production in India;
8) Commercialize HAIX-NanoZr through a US start-up (Drinkwell, WIST, Inc.) with Indian and Kenyan partners;
9) Field-scale demonstrations of concurrent trace contaminant removal w/ partial desalination;
10) Analyze cash flow of long-term HAIX-Nano-based water treatment, develop a model for community-scale operation, and perform Monte Carlo simulations.

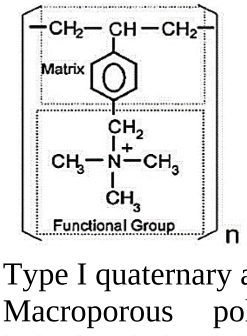
3. Materials and methods

3.1 Materials (Lehigh University)

3.1.1 From the US

Zirconium oxide and anion exchange resins are available worldwide and the synthesis process, as developed during this study, can be replicated in countries impacted by fluoride. Non-hazardous, easy-to-transport and widely available ZrO_2 was the starting material for the synthesis process. For tests at Lehigh, the zirconium materials were obtained from MEL Chemicals (Flemington, New Jersey). The macroporous anion exchange resin with quaternary ammonium functional groups (Purolite A-500P) was provided by Purolite Co. (Philadelphia, PA). The structure, composition of the matrix and other pertinent details are provided in **Table 3.1**, but no endorsement is implied; other strong base macroporous anion exchange resins could have been used. The preparation of HAIX-NanoZr was refined through several iterations and carried out at ambient temperature to promote formation of amorphous ZrO_2 nanoparticles within the anion exchange resin beads. The final synthesis protocol is included in detail in other places (60).

Table 3.1. Salient properties of polymeric anion exchange resins.

Ion Exchangers	**Purolite A-500P Anion Exchanger**
Structure	
Functional Groups	Type I quaternary ammonium
Polymer Matrix	Macroporous polystyrene cross-linked with divinylbenzene
Capacity (meq/mL)	1.0
Manufacturer	Purolite Co., Philadelphia

All chemicals used in the lab study at Lehigh University were reagent grade from the major lab chemical companies, e.g., Fisher Scientific and Sigma Aldrich. Some unique chemicals, beyond typical salts, acids, and bases, included: SPADNS solution (HACH), Zirconium ICP standard (Sigma). The mechanism of SPADNS interaction with fluoride is depicted in **Figure 1.6**. Water used throughout the study was deionized (DI) water, unless specified otherwise, which was purified by reverse osmosis and activated carbon.

The common arsenic/phosphate sorbents used in comparison to HAIX-NanoZr included activated alumina and LayneRT (HAIX-NanoFe). The common fluoride sorbents used in comparison to HAIX-NanoZr included activated alumina (AA), bone char (BC), hydroxyapatite (HAP), and strong acid cation exchange resins in aluminum form (SAC-Al). Oxide India Co. (Durgapur, India) manufactured AA that was used as a control sorbent during batch and packed-bed studies; their AA is commercially available, widely used across India, and is well-characterized (53). Nakuru Defluoridation Company (NDC) in Kenya manufactured the BC and HAP used during testing.

3.1.2 From Kenya

It is well described in literature that fluoride has lower selectivity than chloride for strong base anion exchange resin. Thus, using SBA resins as a control fluoride sorbent versus HAIX-NanoZr is not necessary, as there will be no/minimal fluoride removal. The current standard of fluoride removal is AA, but BC is heavily used in Eastern Africa because of price and availability, e.g., Ethiopia, Kenya, and Tanzania. But, BC has lower capacity, aesthetic challenges, and cultural/religious barriers to acceptance versus AA. Up to several tons of BC per year have been produced by NDC to fill the treatment columns they install at local companies; the production process is pictured in **Chapter 3- Appendix**.

Dr. Ecker delivered a shipping container-mounted system for production of HAP to the NDC facility. In recent years, NDC has produced several hundred kilograms of HAP that they have used in a variety of filters; the production process is depicted in **Chapter 3- Appendix**. The NDC HAP filter materials are the basis for the technical issues described in the previous section. Nevertheless, HAP was marketed to and purchased by several local organizations; a HAP filter quotation for a local, prominent water drilling and treatment company has been included in **Chapter 3- Appendix**. HAP samples were tested in Kenya and, also, returned to the US for future testing.

3.2 HAIX-NanoZr: Lab Testing (Lehigh University)

3.2.1 Water Aesthetics

A major concern about the different selective sorbents was the physical durability of the materials. A preliminary, quasi-scientific test about the resiliency of the different sorbents was a shake test, where 5 g of material was placed in a 50 mL Falcon tube with synthetic feed water and shaken for 12 hr on a table-top orbital shaker on low. Afterwards, only the color of the water and consistency of the sorbents were qualitatively compared because the differences between the materials were stark.

3.2.2 Feed Water

Water from the NDC lab (20 L) was imported on return from Kenya, to the mild confusion/concern of security agents at Nairobi Airport, to compare initial HAIX-NanoZr testing in Nakuru with more controlled conditions at Lehigh University. Undergraduate students also brought home several liters of water from a highly fluoride-contaminated well several kilometers from NDC that was dangerously hot upon leaving the tubewell. Water chemistry from this other well was tested to see other regional fluoride conditions, but was not used for evaluation of any fluoride sorbents.

By collecting groundwater once at the NDC laboratory in Nakuru, Kenya for future use at Lehigh University, the influent compositions for future tests were virtually constant because the well-sealed storage containers have low sorption capacity for fluoride, **Table 3.2**. Synthetic Kenyan Water, based on NDC specifications, was made for other fluoride tests, as described in **Table 3.2**.

Table 3.2. Water chemistry of four water samples (5 L each) returned from Nakuru Defluoridation Company (NDC, Nakuru, Kenya). **Note:** high silica, high alkalinity, and lack of divalent/trivalent cations. Tested by Jinze Li.

Element	**Bottle #**			
	1	*2*	*3*	*4*
Ca^{2+}	0	0	0	0
Mn^{2+}	0	0	0	0
Mg^{2+} (mg/L)	0.03	0.03	0.03	0.03
Fe^{3+} (mg/L)	0.23	0.2	0.24	0.25
Na^{+} (mg/L)	124.8	121.6	123.4	123.2
pH	8.10	8.15	8.16	8.16
PO_4^{3-} (mg/L)	0.48	0.39	0.62	0.49
SiO_2 (mg/L)	76	77	75	77
F^- (mg/L)	5.4	5.9	5.65	5.9
Alkalinity (mg/L as $CaCO_3$)	245	252	284	299
Conductivity (µS/cm)	365	327	321	413
NO_3^- (mg/L)	0.49	0.40	0.37	0.37

Table 3.3. Water quality parameters for synthetic Nakuru water made to similar conditions as NDC.

Parameter	**NDC Synthetic**
pH	8.3
Conductivity (µS/cm)	1040
Sodium	To balance
Calcium	N/A
Alkalinity as $CaCO_3$ (meq/L)	5
Fluoride (mg/L)	5.8
Chloride	To balance
Sulfate (mg/L)	20
Silica as SiO_2 (mg/L)	72
Phosphorus as P (mg/L)	0.25

3.2.3 Zirconium Content

Total zirconium content of synthesized HAIX-NanoZr resins was determined by a 72 hr acid digestion with 50% sulfuric acid. The zirconium content of the supernatant from the batch digestion was then determined using an Inductively Coupled Plasma-Optical Emission Spectrophotometer (ICP-OES).

3.2.4 HAIX-NanoZr: Mini-Column Batch Test

The fluoride removal process is very sensitive to solution pH and it is very difficult to maintain a constant pH during batch tests. Therefore, all of the equilibrium data for HAIX-NanoZr was generated by Jinze Li using the mini-column technique. About 0.5 g of HAIX-Zr was filled into eight mini-columns (i.e., 5 mL micropipette tips), as shown in **Figure 3.1**. The HAIX-NanoZr in the mini column was sealed with glass wool to prevent the resin from leaking out. About 6000 BVs of synthetic fluoride-contaminated feed across a range of different pH values (pH 2-9) were passed through each mini-column by gravity. Effluent concentration of fluoride was measured throughout to confirm equilibrium- influent and effluent fluoride being equal. After saturation, the mini-columns were briefly rinsed with DI water to eliminate calculation error from the dead space. Then the mini-columns were regenerated simultaneously with 100 mL 2% NaOH/2% NaCl solution. Fluoride concentration of the regenerant was tested and the capacity was calculated.

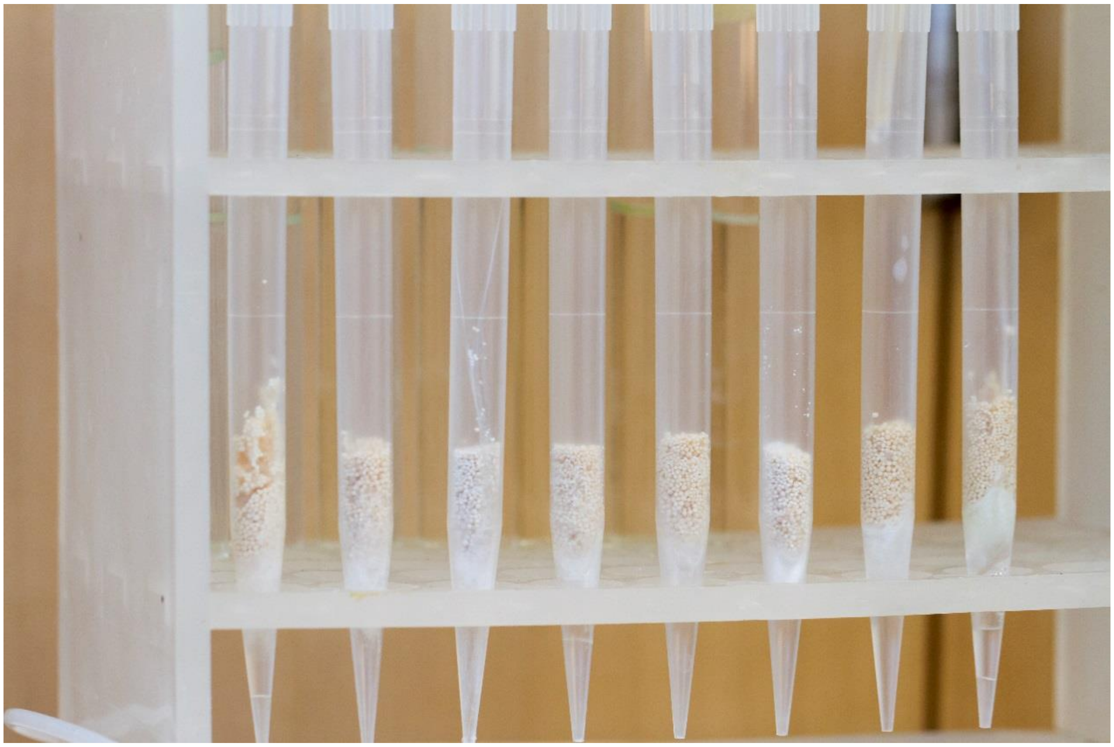


Figure 3.1. Mini-column setup for HAIX-NanoZr used for capacity testing under different pH values. Created by Jinze Li.

3.2.5 HAIX-NanoZr: Fluoride Capacity- Batch (Shake test)

Synthetic groundwater made identical to groundwater from Nakuru, Kenya, except spiked with 20 mg F/L, was used for batch capacity testing different versions of HAIX-NanoZr and other fluoride adsorbents. 0.10 g of HAIX-NanoZr was added to 200 mL feed water and shaken for 48 hr on a benchtop rotary shaker. After 24 hr, the pH of the batch would be adjusted with HCl to attain a consistent final pH value across the different adsorbents being tested. After shaking, fluoride would be compared between a control of feed water alone and feed water plus HAIX-NanoZr or other adsorbents.

3.2.6 Packed-Bed HAIX-NanoZr Fluoride Treatment

In order to test fluoride removal, a constant flow rate pump fed fluoride-contaminated groundwater through a packed-bed of (1) WAC-H/SAC-H; (2) HAIX-NanoZr; (3) Dolomite/WAC-Na, which was connected to a fractional collector, **Figure 3.2**.

#1: 75% C107, 25% C145 (top-bottom). Operation: Down-flow; Acid conditioning: Up-flow.

Operation (groundwater):

$$2\overline{\mathrm{R-COOH}} + \mathrm{Ca^{2+}} + 2\mathrm{HCO_3^-} \rightarrow \overline{\mathrm{R-(COO^-)_2Ca^{2+}}} + \mathrm{H_2CO_3}$$

$$2\overline{\mathrm{R-SO_3H}} + \mathrm{Ca^{2+}} + 2\mathrm{HCO_3^-} \rightarrow \overline{\mathrm{R-(SO_3^-)_2Ca^{2+}}} + \mathrm{H_2CO_3}$$

Conditioning (HCl):

$$\overline{\mathrm{R-(SO_3^-)_2Ca^{2+}}} + 2\mathrm{H^+} \rightarrow 2\overline{\mathrm{R-SO_3H}} + \mathrm{Ca^{2+}}$$

$$\overline{\mathrm{R-(COO^-)_2Ca^{2+}}} + 2\mathrm{H^+} \rightarrow 2\overline{\mathrm{R-COOH}} + \mathrm{Ca^{2+}}$$

#2: 100% HAIX-NanoZr. Operation: Down-flow; Regeneration: Down-flow

Operation (groundwater):

$$\overline{\mathrm{R^+ :: (ZrOH_2)^+}} + \mathrm{F^-} \rightarrow \overline{\mathrm{R^+ :: (ZrOH_2)^+F^-}}$$

Regeneration (NaOH + dilute acid):

$$\overline{\mathrm{R^+ :: (ZrOH_2)^+F^-}} + \mathrm{OH^-} \rightarrow \overline{\mathrm{R :: (ZrO)^-}} + \mathrm{F^-}$$

$$\overline{\mathrm{R :: (ZrO)^-}} + \mathrm{F^-} \rightarrow \overline{\mathrm{R^+ :: (ZrOH_2)^+}}$$

#3: Dolomite $\left(Ca_xMg_y(CO_3)_{x+y}\right)$: Operation: Down-Flow

Operation (groundwater):

$$\mathrm{Ca_xMg_y(CO_3)_{x+y}} + (\mathrm{x+y})\mathrm{H^+} \rightarrow \mathrm{xCa^{2+}} + \mathrm{yMg^{2+}} + (\mathrm{x+y})\mathrm{HCO_3^-}$$

Specifically, an FMI QG20 constant flow-rate pump (Fluid Metering, Inc., Syosset, NY) fed groundwater collected from the Nakuru Defluoridation Company (NDC) testing facility in Nakuru, Kenya through (1) 5 g of Purolite C107; (2) 5 g of HAIX-NanoZr; and, (3) 5 g WAC-Na, each in a 7 mm diameter glass column (ACE Glass, Vineland, NJ). The effluent from the third ion exchange column was collected by a fractional collector (Teledyne ISCO Cygnet, Lincoln, NE or Eldex Laboratories, Inc., Napa, CA). The ratio of column diameter to the adsorbent diameter was approximately 20:1; previous work with similar geometry columns for chromate and phosphate removal had ideal plug-flow without leakage from wall effects (47,123). The hydrodynamic conditions such as empty bed contact time (EBCT) and superficial liquid velocity (SLV) were recorded for each experimental column run.

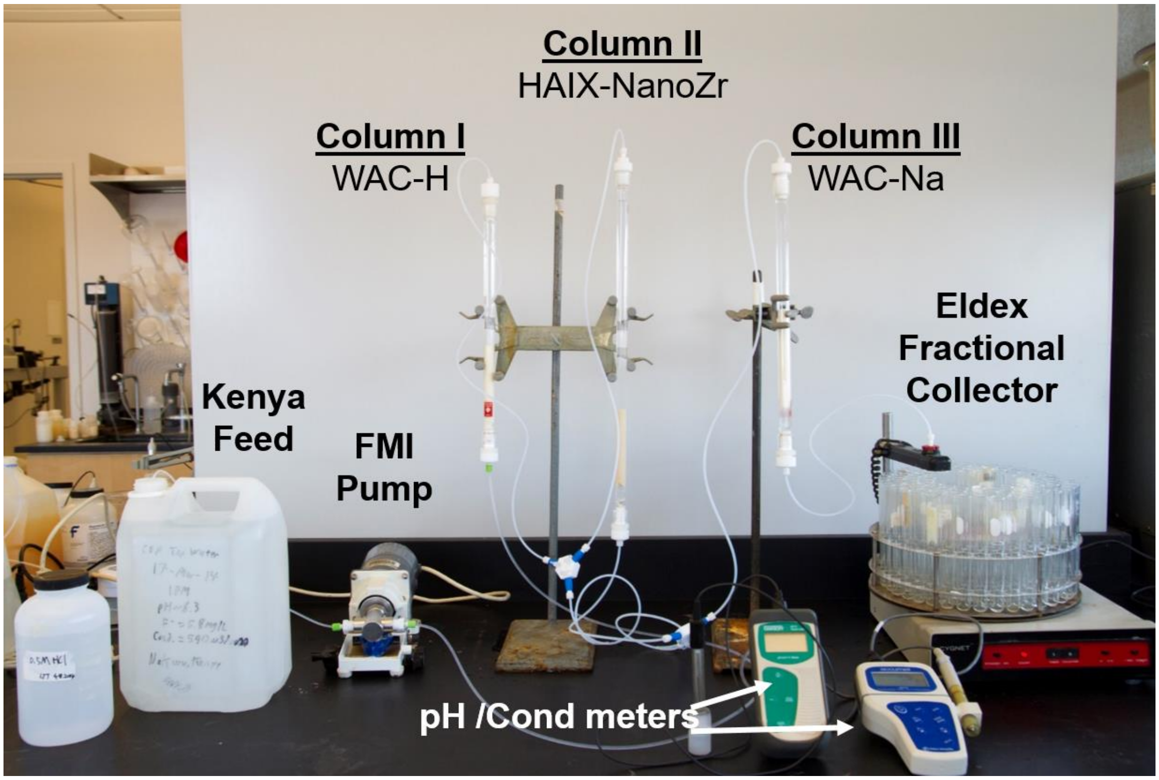


Figure 3.2. Ion exchange three column test-bed used at Lehigh University for testing fluoride removal performance. In sequential order, water flows from a storage container → FMI pump → Column I→ Column II → Column III → fractional collector

3.2.7 Regeneration

It was determined that HAIX-NanoZr was exhausted when the effluent fluoride had surpassed 50% of the influent concentration or reached 2 mg F/L, whichever came last. Exhausted hybrid nanosorbents were regenerated using a mixed solution of 3% NaOH/3% NaCl. Prior to starting the next run, the bed was rinsed with CO_2-sparged water (pH 3.2) for about 10 bed volumes (BVs) to bring the hybrid sorbent to working conditions.

3.2.8 Zirconium Leachate: Apparatus & Operation

Zirconium does not have a maximum contaminant level (MCL) for drinking water because it is not expected to be present in drinking water from natural occurrence or industrial releases. Additionally, based on equilibrium, at groundwater conditions, zirconium is very insoluble and virtually absent from the aqueous phase. Nevertheless, one potential concern is whether or not zirconium or zirconium oxide is present in the effluent. With the expected near-zero concentration, zirconium was attempted to be measured 1) directly and 2) indirectly by ICP-OES.

Direct measurement occurred by testing the zirconium content from individual fractions collected during typical groundwater testing. Indirect measurement of effluent zirconium was performed by measuring the fluoride removed by any suspended zirconium oxide in the collected effluent. This was accomplished by the following general procedure:

1) Treating 5 L (675 BVs) of synthetic Nakuru groundwater with a packed bed of HAIX-NanoZr (bulk volume = 7.5 mL);
2) Collecting the total effluent in one container;
3) Filtering the effluent through a 0.20 μm nylon membrane (Millipore);

4) Testing the effluent fluoride concentration;
5) Leaching and collecting fluoride from any filtered and retained zirconium oxides by recycling 50 mL-5%NaOH (3x);
6) Measuring the concentration of fluoride in the leachate and relating it to the amount of zirconium on the membrane by knowing the concentration of fluoride in the NaOH effluent, the sorption capacity of the resin for fluoride, zirconium content of the resin, and volume of water treated.

3.3 HAIX-NanoZr: Lab-Scale Testing in Nakuru Kenya, Spring 2014

3.3.1 Background

After returning back to Lehigh from Kolkata in Spring 2014, guidance was given to undergraduate students in a social business/sustainable development course aiming to improve businesses in regions surrounding Nairobi, Kenya during a fifteen-day research trip (March 3-18, 2014). There was a group with specific focus on fluoride filters in Nakuru, Kenya with a religious organization (Catholic Diocese of Nakuru or CDN) that created a fluoride treatment company (Nakuru Defluoridation Company Ltd. or NDC) testing HAIX-NanoZr. They actively produced, sold, and installed BC and HAP water filters in a fluoride-impacted region. On-site NDC had analytical water testing equipment and a good relationship with Dr. SenGupta from previous conferences/meetings. Images of their objectives, logo, and laboratory are featured in **Figure 3.3**.

Figure 3.3. NDC advertisement, logo, and laboratory (clockwise from top left).

3.3.2 Materials and Methods

Bone Char or BC (three different sizes) and hydroxyapatite were produced and available on-site at NDC, **Figure 3.4**. The bone char process was developed by Peter Jacobsen and different variants have been in use at NDC for over a decade. In the newest versions of BC, chemical precipitation or CP is used on the outside of BC to enhance capacity; past results are available from NDC. The HAP process and equipment were developed and provided by Dr. Michael Ecker (GmbH, Riedlingen, Germany); HAP is also known as Fluorolith in Germany (124). Before using BC or HAP for testing for fluoride removal ability, the materials were washed with DI till no dust was visible and the effluent water had an acceptable aesthetic. Four hand washings in a beaker was required for BC. However, washing HAP had to be performed in a very careful manner to avoid physical degradation of the materials.

Figure 3.4. HAP production system (Left); HAP (top right); BC (bottom right).

In order to test HAIX-NanoZr in Nakuru, materials transported from Lehigh University included: 3-ACE Glass columns (10 mm) and related fittings, 1-constant flowrate FMI pump (Model: QG20), Purolite C107, HAIX-NanoZr (Lehigh), electrical transformers (220V-120V), plug adapters. The NDC lab had been performing regular research with international organizations, e.g., EAWAG, and had analytical and lab equipment available on-site, including analytical balance, conductivity meter, fluoride ISE, furnace, micropipette, packed-bed columns, peristaltic pumps, pH meter, ring stand, stir plate, titration supplies, and Wi-Fi. Both distilled water and fluoride-contaminated groundwater were available on site and a local chemical store was available to pick-up reagents that were not already in stock. Walter Olekulet and Charity Cheppu-Chep, **Figure 3.5**, were the two lab technicians from NDC required to do all of the analytical testing: conductivity, fluoride, and pH.

Figure 3.5. Charity, Walter, and Mike in the CDN Lab (Left-Right).

Within two hours of starting the FMI pump, the pump overheated and shut off. The 0.5A fuses of the transformer were burnt out and replaced, but a new 500W transformer was installed as a replacement. After another two hours, the pump, again, overheated and shut off, but the fuses in the new transformer were fine. It was soon realized that the electrical frequency in Kenya is 50Hz, instead of 60Hz in the US, which caused the pump to run at a lower power factor and to overheat. The differences in electrical frequency between the US and Kenya were not considered before this pump failure. The only long-term solution in Kenya using the original pump would have required a variable frequency drive (VFD), which was not accessible financially or logistically. Thus, the FMI metering pump and its related connections to the ACE glassware were unable to be used in Kenya. The peristaltic pump available on-site, thankfully left by previous researchers, was then "connected" to the ACE columns through various adhesives and ingenuity; the columns remained open to the atmosphere and were restructured for gravity-driven flow, **Figure 3.6**.

Figure 3.6. Original FMI pump attached to a single column with sealed fittings (L). The gravity-driven system and peristaltic pump- open to the atmosphere, with columns at different elevations (R).

The presence of HAP materials at NDC was not known before arriving on site. The narrow diameter of the ACE columns versus the HAP pieces (11 mm vs. 3 mm) meant that the columns brought from Lehigh should not be used for testing HAP as there could be significant channeling and poor hydraulics through the column. Thankfully, there was an available column (diameter ~ 50 mm) that provided a column: sorbent ratio of approximately 20:1, a column size ratio that has shown good column hydraulics, **Figure 3.7** (125,126). The unexpected challenges of doing testing overseas are numerous, especially in new locations for short durations.

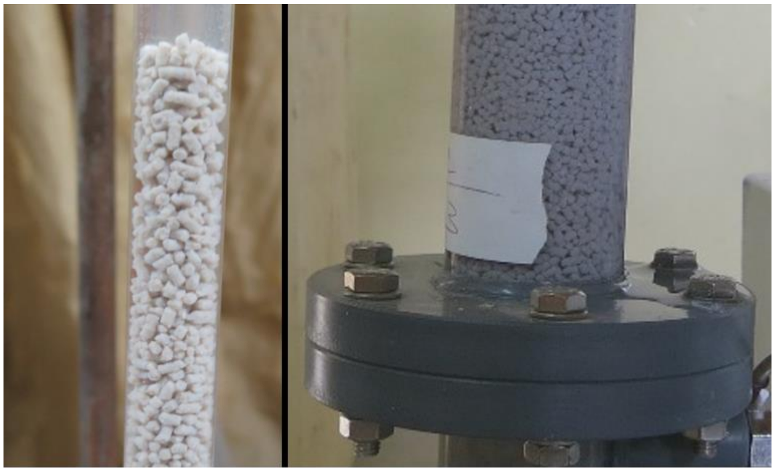


Figure 3.7. Poor hydraulics with testing HAP in ACE Glass columns from Lehigh (L). Plug flow with HAP in wider diameter column (R).

3.4 HAIX-NanoZr: Production in Thakurpukur

3.4.1 Materials

3.4.1.1 Zirconium

Zirconium raw materials were eventually sourced from Bhalla Chemical Works Pvt. Ltd. (Gurgaon, India). Like other suppliers in India, minimum purchase orders were 50 kg or 2-25 kg bags. However, initial supplies from Bhalla were of a low-quality grade, distinguishable by their yellow hue that were not amenable to effective dissolution and HAIX-NanoZr synthesis. The zirconium turned more yellow with exposure to the air. A brief survey of literature led to no information about why the zirconium material should turn yellow or why the more yellow material would have performed worse. Although, as seen in the results section, after zirconium impregnation, HAIX-NanoZr had a beige/yellow hue versus the white parent resin. Thus, it is possible that the yellow zirconium was a less soluble form of zirconium oxide. After several conversations about our disappointment, assurances were made and future zirconium materials have been pure white with good performance.

3.4.1.2 Ion Exchangers

Anion exchange resins were initially sourced from multiple sources across India, including: Doshion (Ahmedabad, India), Ion Exchange (Mumbai, India), Purolite (Pune, India), and Thermax (Pune, India). Distributors and companies in India were unwilling to provide research sample quantities (~1 L), and the minimum purchase order from small-scale, local distributors was 50 L (2-25 L bags). Local distributor prices were up to 2-3x higher than prices for large-scale orders (>1000 L) from central headquarters, and had significant delays in delivery. Initial procurement and sourcing was frustrating and expensive. Quality, pricing, scalability, availability, and professionalism were all considerations in decisions about which company to purchase anion exchange resins from, even though the product sheets for the different companies indicated the products were very similar in nature. Many of these problems are location specific and it can be expected that, even though, zirconium and anion exchange resins are available in urban centers across the world, economies of scale and efficient global trade dictates that supply chains can be optimized in certain locations or settings, and local production is not always required or recommended.

3.4.1.3 SPADNS Solution

HACH SPADNS solution was very costly to import from outside of India, from a financial and time standpoint. The following recipe was provided by Dr. Sudipta Sarkar (IIT-Roorkee) and used for synthesis of SPADNS:

1. Dissolve 958 mg SPADNS (MW= 570.4) in DI and dilute to 500 mL
2. Dissolve 133 mg zirconyl chloride octahydrate in 100 mL DI. Add 350 mL concentrated HCl and dilute to 500 mL with DI
3. Mix equal volumes of SPANDS solution and zirconyl-acid reagent

The SPADNS solution was found to be effective and give accurate measurements for reference fluoride solutions.

3.4.1.4 Other Chemicals

Other more common laboratory reagents, e.g., acids, bases, and salts, were sourced for both laboratory-scale and pilot-scale quantities. For early lab testing and confirmation of synthesis performance, lab-scale quantities were originally purchased from Merck Specialties Pvt. Ltd. (Kolkata, India) and follow-up/refill orders were purchased from Bharati Chemical & Scientific Works (Kolkata, India). Dey’s Chemical Works (Kolkata, India) were more economical per unit quantity as a technical-grade, medium-scale distributor. However, having product data sheets or accurate specifications/labelling of products was more problematic with Dey’s and information was generally conveyed by word of mouth, e.g., 50 L hydrochloric acid (concentrated) arrived in containers labelled for sodium hypochlorite.

3.4.2 Testing: Packed-Bed Columns, Fluoride, and Arsenic Analysis

In order to do capacity testing, lab-scale packed-bed columns were assembled using narrow PVC pipe and PEX tubing available at local plumbing stores. High quality dosing pumps were not available for controlled flowrate, but instead the column was gravity fed through a reservoir with semi-constant head. For parameter testing in lab, HACH Pocket Colorimeter II, Fluoride test kits were purchased from eBay in the US and imported on personal flights for lab and field use testing. Palintest Arsenator Digital Arsenic Test Kits were purchased online and imported; refill reagents were imported during subsequent personal travel. Reported field results from community-scale systems were tested by local accredited labs, e.g., Scientific Research Laboratory (ISO 9001, OHSAS 18001, Kolkata), RV Briggs (NABL-accredited, Kolkata).

3.4.3 Pilot-Scale Synthesis

Attempts of pilot-scale production of HAIX-NanoZr began in earnest during summer 2014 (May-August) with Anil Shaw and Mike German using the different raw materials that had been sourced since December 2013. Through the philanthropic activities of Society for Technology with a Human Face (STHF), the lab at Thakurpukur was supplied with an analytical balance, buret, conductivity meter, distillation system, glassware, heater/stirrer plate, spectrophotometer (Spectroquant Pharo 100 by Millipore) and related reagents, and pH meter. This lab-scale equipment allowed for research of HAIX-NanoZr synthesis on the 10-50 g scale and testing raw material quality before pilot-scale tests.

However, for pilot-scale synthesis, larger process equipment was required for the different steps outlined in the patent. At that time, Fulbright-Nehru Research funding had ended and Drinkwell was yet to exist in any real capacity: there was a minimal budget available for work. However, the process was designed to be simple, safe, and straightforward, so only rudimentary process equipment was required. As concentrated acid with alcohol was used to dissolve the calcined zirconium oxide, acid-resistant materials were required, e.g., non-metals or organics. A 20 L plastic bucket was used as the reactor and local, washed bamboo sticks were used as manual agitators. Plastic sheets and oscillating fans were used for drying. A two-sided, manual balance with plastic guards was used for measuring large quantities (<100 g).

There were several safety concerns from materials on-site: concentrated acids, caustic alkali, open reactors, lack of closed-toed shoes, and noxious fumes. Lack of process safety equipment on first attempt of pilot-scale synthesis indoors at Thakurpukur was quite dangerous due to fumes; initial attempts of working indoors while not breathing and then going outside to breathe were quickly found to be unsustainable. Respirators with activated carbon treatment were quickly ordered from the US for safety. Additionally, work was shifted outdoors to avoid confined fumes and additional airflow was provided with an oscillating fan. Although not OSHA approved, typical open-toed sandals were continually worn by workers because they were the predominant shoe and they are easily washed. Sodium carbonate and a bucket of water were always kept on hand in case of spills.

Over the summer of 2014, several hundred liters of HAIX-NanoZr was synthesized in India over multiple small batches (~10 L) where the goal was to optimize the mechanics of production with rudimentary tools. Decanting, drying, heating, mixing, settling, and washing during HAIX-NanoZr production with a bamboo stick, funnel, lungi strainer, and plastic bucket (20 L) while handling caustic, corrosive, and noxious materials in a safe manner, was a logistical and physical challenge, as much as it was a scientific puzzle, **Figure 3.8A**. The distraction of physical exertion and safety in action led to different steps being forgotten or poorly performed, which were then found to be important to ensure zirconium precipitation within the resin, **Figure 3.8B**. The initial months of pilot-scale production testing were qualitative in nature and, generally, data was not recorded. The main qualitative goals were to increase the density of the resin (i.e., higher dry weight ~ higher zirconium content), observe resin color change (i.e., due to internal ZrO_2 precipitation), and produce final product without zirconium residue on the surface (e.g., white powder). There was also a qualitative focus because zirconium content could not be accurately quantified in Kolkata; ICP zirconium measurements were only available in one laboratory, but at an unaffordable price. At this time there was, also, a lack of a motorized rotating drum, table-top shaker, or lab-scale column test system for doing batch or continuous fluoride capacity measurements.

Figure 3.8. A.) Anil Shaw weighing out zirconium on the balance; Anil mixing materials outdoors; close-up of materials mixing; Mike next to drying materials (Clockwise from top left). B.) Mangoes and coconuts to provide electrolytes in the summer heat; drinking a coconut; notes during testing; high energy (Clockwise from top left).

3.4.4 Nuapada, Odisha

3.4.4.1 Installation of Single Community-Scale HAIX-NanoZr System

On November 14, 2014, the executive engineer of RWSS from the Jal o Parimal Bhawan, Unit-V in Bhubaneswar, Odisha requested the three manufacturers who had responded to the EoI to get certification by the Council of Scientific and Industrial Research-National Environmental Engineering Research Institute (CSIR-NEERI; Nagpur) of their fluoride removal technology, including M/s. HES Water Engineers Pvt. Ltd. (OxiMax/Bio-F; Nagpur), M/s. Ion-Exchange (INDION-RS-F; Mumbai), and Rite Water (HAIX-NanoZr). The technical details of OxiMax/Bio-F have been unclear, but the material can be regenerated by alum, which indicates that it is an aluminum oxide-based inorganic adsorbent. INDION RS-F is likely an SAC-Al-type process. The locations of their installations are provided in **Table 3.4**.

Table 3.4. Details of the four sampling locations used by the three manufacturers.

S.N.	Location (Village)	Manufacturers	Latitude (N)	Longitude (E)	Altitude (m)
1	Dhumabhata	M/s. HES Water Engineers Pvt. Ltd., Nagpur	20^{O}35'35.8"	83^{O}9'32.1"	278
2	Kandetara	M/s Ion Exchange, Mumbai	30^{O}37'39.9"	82^{O}41'08.7"	287
3	**Musapali**	M/s RITE Water Solution (L), Nagpur	20^{O}36'07.8"	82^{O}39'49.8"	288
4	Haripur	M/s Ion Exchange, Mumbai	20^{O}49'22.2"	82^{O}34'44.2"	352

Conversations began two weeks later (around November 28, 2014) as to how to install and implement the first community-scale HAIX-NanoZr system. The original request from Rite Water was to install the system within 10 days, without knowing the specific site location or site water chemistry at the time of request. The limited timeframe, lack of field testing/process familiarity, lack of human/material resources, and importance of successful execution led to a combination of non-ideal conditions, with the feeling from Lehigh/Drinkwell/STHF that there was a high risk for failure. Note: the 1 L-scale HAIX-NanoZr system in Piraya was only installed three weeks prior to conversations about the community-scale system.

3.4.4.2 Installation of Twenty Community-Scale HAIX-NanoZr System

As during the first system installation, locations of HAIX-NanoZr systems were provided by the RWSS via work order on a pilot-basis without input from Drinkwell or Rite Water; the sites are detailed in **Table 3.5**. It would have been ideal if water chemistry, socioeconomics, and water committee/caretakers would have been considered before a location decision was made, so that the longevity of systems could be optimized. But, by virtue of the government providing documentation, land ownership and usage discussions and problems were avoided.

Table 3.5. Locations of HAIX-NanoZr sites provided to Rite Water by RWSS-Odisha.

Gram Panchayat	**Village**	**Habitation**	**Latitude (N)**	**Longitude (E)**	**Altitude (m)**
Nagalbod	Nuamalpada	Jagannath-pada	20°29'38.5	82°39'01.9	323
Nagalbod	Nuamalpada	Khandal-pada	20°29'38.5	82°39'01.9	319
Nagalbod	Nuamalpada	Talpda	20°29'38.5	82°39'01.9	319
Nagalbod	Nuamalpada	Jamunaba-halkitkitapada			
Nagalbod	Nuamalpada	Nuamalpada School			
Nagalbod	Nuamalpada	Shivman-dirpada, Bairagipada			
Nagalbod	Nuamalpada	Butimajhi			
Nagalbod	Nuamalpada	Pontipada, Panam singh majhi	20°29'38.5	82°39'01.9	326
Nagalbod	Nuamalpada	Khandapada School	20°29'38.5	82°39'01.9	321
Nagalbod	Nuamalpada	Bandhpada (Right)			
Nagalbod	Nuamalpada	Bandhtal-pada	20°29'38.5	82°39'01.9	320
Nagalbod	Nuamalpada	Near podh house			
Nagalbod	Nuamalpada	Podhpada, near bhuban			
Kendumunda	Dagnikhol	Bendura Hans	20°03'33.1	82°34'21.9	276
Kendumunda	Dongrikhol	AWC, Near school	20°03'33.1	82°34'22.0	272
Jharbandh	Kendumunda	Malipada			
Jharbandh	Kendumunda	Rafpuria Pada	20°00'22.1	82°36'31.6	296
Jharbandh	Kendumunda	Khutakkhun-apada			
Jharbandh	Kendumunda	Dhanua pada			
Jharbandh	Kandamunda	Kanda-munda School	20°00'25.9	82°36'58.9	287

All twenty hand-pump connected single-column fluoride removal units were installed in Odisha by April 15, 2015, but were empty without any media. By this point, the other two manufacturers had completed installation of their twenty systems, respectively. Delays in bringing the systems online were caused by:

1) HAIX-NanoZr material supply chain to Kolkata;
2) Lack of human resources and production capacity in Kolkata;
3) Poor logistics in coordinating materials and people between Nagpur and Kolkata.

In mid-March, notice was given to everyone that single-column fluoride removal systems needed to be delivered in 30 days. Each column would be filled from top-bottom with 10 L-Indion 236 (WAC, H-form), 30 L-HAIX-NanoZr, and 10 L-Indion 236 (Na-form), **Figure 3.9**. With 300 L of Indion 860S (WBA) in Kolkata, 1000 L of Purolite INA-100 (WBA) due in two weeks, and 600 kg zirconium arriving soon, plus existing zirconium supplies, it was believed that 300 L of HAIX-NanoZr could be produced and delivered within two weeks. However, it was not until April 20, 2015, five weeks later, that 300 L HAIX-NanoZr and pre/post-treatment WAC were prepared by and picked up from Kolkata for delivery to Odisha. The lack of material for the other ten systems forced Rite Water to use another available fluoride selective material for the interim during initial NEERI testing, e.g., SAC-Al with alum as the regenerant. For the second set of ten systems, HAIX-NanoZr was prepared in and picked up from Kolkata on May 8, 2015, but the ordered WAC (Thermax CXO-9) for these systems was yet to arrive. Thus, during initial testing by NEERI on May 12, 2015, Systems #9-18 were filled with SAC-Al; additionally, Systems #1, 2, 5, 13, 15, and 19 had broken handpumps.

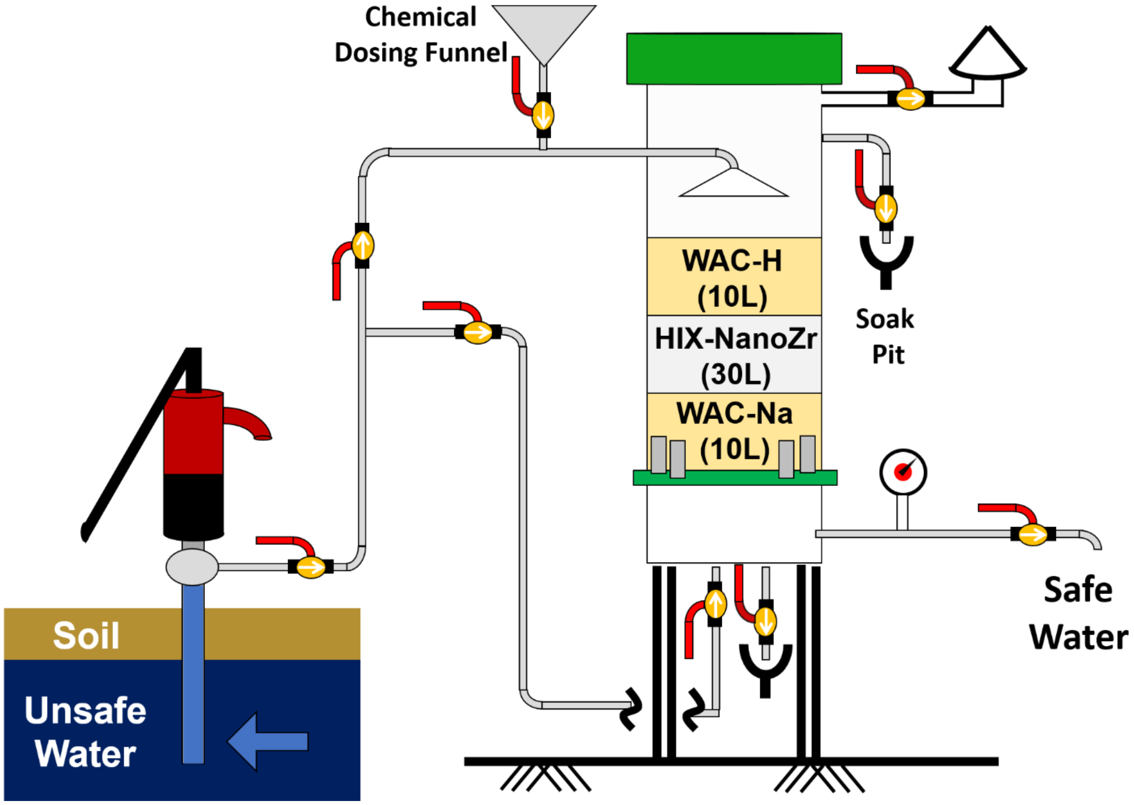
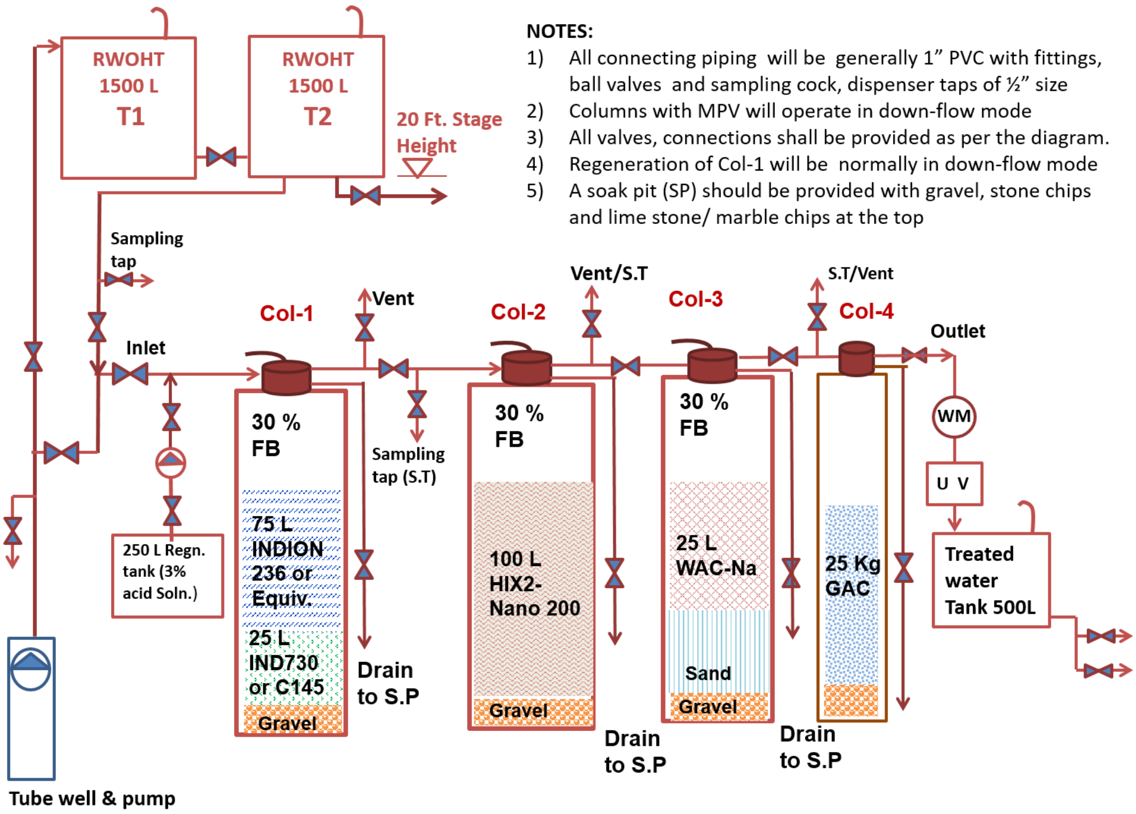


Figure 3.9. Diagram of a single-column HAIX-NanoZr fluoride removal unit that was installed in Odisha for review by RWSS and NEERI.

3.4.5 Nalhati, Birbhum District, West Bengal, India

As part of Milestone 2 for US-ISTEF, Drinkwell and Rite Water needed to install three community-scale HAIX-NanoZr systems. Several districts near the border of the states of West Bengal and Bihar have high levels of arsenic and/or fluoride, depending on the side of the tributary. After extensive work with the West Bengal PHED Arsenic Task Force over the last decade, and their approval of HAIX-NanoFe for arsenic removal, the West Bengal PHED Fluoride Task Force decided HAIX-NanoZr should be tested for fluoride removal with challenging groundwater to see the extent of performance at Laxmi-Narayanpur A. J. Adibasi High School, Nalhati, Birbhum, West Bengal. Raw water samples prior to Nalhati installation had the highest pH values and fluoride concentrations ever tested by Drinkwell, up to pH 9.4 and F^- = 45 mg/L. Unlike other locations, the TDS at Nalhati was often below 500 mg/L and was not a regulatory concern. US-ISTEF funding was used to make Nalhati the keystone fluoride installation of Milestone 2.

The HAIX-NanoZr-based treatment system for the effective long-term removal of fluoride from groundwater in community-scale, as applied in Nalhati, had four columns and UV in series for: (1) partial desalination; (2) fluoride removal; (3) pH control; (4) polishing (activated carbon); (5) UV, **Figure 3.10**.



NOTES:
1) All connecting piping will be generally 1" PVC with fittings, ball valves and sampling cock, dispenser taps of ½" size
2) Columns with MPV will operate in down-flow mode
3) All valves, connections shall be provided as per the diagram.
4) Regeneration of Col-1 will be normally in down-flow mode
5) A soak pit (SP) should be provided with gravel, stone chips and lime stone/ marble chips at the top

Figure 3.10. Process flow diagram for the HAIX-NanoZr fluoride treatment installation in Nalhati.

3.4.6 Baduria, N. 24 Parganas, West Bengal

During construction of a large-scale system on behalf of PHED in Baduria, Drinkwell was asked to install a community-scale system for a local community with high arsenic levels, **Figure 3.11**. Thus, this was the second HAIX-NanoZr site during Milestone 2, and the only arsenic-contaminated site. A four-column arsenic treatment system was installed in late May 2016, **Figure 3.12**. Water chemistry of the untreated groundwater was significantly higher than WHO standards, **Table 3.6**. The system included a pre-treatment SAC-Fe column (Column I) with a ferric chloride dosing tank and pump, **Figure 3.13**. HAIX-NanoZr (Column II) was installed next in series, followed by a pH adjustment column (Column III), and an activated carbon column to ensure high quality taste (Column IV). People accessed water through use of a water ATM, **Figure 3.14**.

Figure 3.11. Early arsenicosis symptoms (keratosis) on the hands of a community member from Baduria.

Table 3.6. Raw water chemistry at Baduria on May 13, 2016. Note: Shaded cells have values in excess of the acceptable limit.

Parameter	Unit	Value
Coliform Organism	CFU/100 mL	15
E. coli	CFU/100 mL	Absent
Turbidity	NTU	23.3
pH value	-	7.4
Conductivity	µS/cm	1010
Alkalinity	mg/L as $CaCO_3$	472
Iron	mg/L as Fe	4.31
Calcium	mg/L as $CaCO_3$	294
Arsenic	mg/L as As	0.32

Figure 3.12. Baduria arsenic treatment system with three treatment columns (SAC-Fe, HAIX-NanoZr, and WAC-Na) and one activated carbon post-treatment column. (R-L: Influent→I→ II→III→IV). Black chemical dosing tanks (200 L) for Column I (ferric chloride) and Column III (sodium carbonate) can be seen behind the respective tanks. The stainless steel treated water storage tank can be seen on the right.

Figure 3.13. Close-up of 200 L chemical dosing tank behind Column I with chemical-resistant pump at the Baduria treatment system.

Figure 3.14. Water ATM installed in Baduria for automatic, metered water dispensing without requiring the presence of a caretaker.

3.4.7 Moparlapalli, Roddam Mandal, Anantapur District, Andhra Pradesh

After Rite Water submitted bids to use HAIX-NanoZr technology for fluoride treatment tenders in Anantapur District, Andhra Pradesh, the local RWSS selected the village of Moparlapalli for the first pilot-scale treatment system (500 LPH), **Figure 3.15**. Moparlapalli was then chosen as the third installation site out of three for HAIX-NanoZr during Milestone 2 of US-ISTEF; four more HAIX-NanoZr systems are in different phases of construction for Milestone 3 of US-ISTEF as of March 2017.

At this location a three-column system was installed with UV post-treatment before treated water storage for assurance of microbiological safety. Successful installation, operationalization, and treatment at Moparlapalli were prerequisites before Rite Water would be eligible for more tender contracts with RWSS. Site evaluation and water testing of the HAIX-NanoZr system at Moparlapalli by the RWSS occurred on March 13, 2016 and the RWSS report on the performance at Moparlapalli was delivered on April 22, 2016.

Figure 3.15. 500 LPH HAIX-NanoZr system installed at Moparlapalli by Rite Water.

3.4.8 Ghetugachi (SAR-HAIX-NanoZr), Nadia District, West Bengal

As part of Global Innovation Initiative (GII) funding by the International Institute of Education (IIE) in collaboration with Dr. Bhaskar Sen Gupta, inventor of the subterranean arsenic removal (SAR) process, an HAIX-NanoZr column was installed in series after a SAR treatment system in Ghetugachi, WB, **Figure 3.16**. The SAR process works by pumping water from underground, aerating it above ground, and pumping the oxygenated water below ground to precipitate iron in-situ as ferric (hydr)oxides with high arsenic sorption capacity. As demand for the treated water tripled above the original design capacity, problems arose with poor hydraulics around the tubewell from the high amount of iron precipitates and the inadequate arsenic removal at higher flowrates.

Figure 3.16. A) Building containing the original SAR system (L) and B) the post-treatment HAIX-NanoZr column placed in series after SAR treatment (R).

3.5 HAIX-NanoFe Systems

3.5.1 Haldi, Ballia District, Uttar Pradesh

In mid-2013, Mr. Ashok Singh approached Dr. SenGupta and STHF to install an arsenic treatment system in his rural village in Ballia, UP, **Figure 3.17A**. Mr. Singh showed great passion towards his vision of a permanent safe water treatment system being operated in his community. After conversations, STHF felt confident that Mr. Singh would oversee activities in a sustainable fashion based on several qualitative factors: his persistence in approaching STHF, their detailed correspondences, and his commitment of financial support for preparations (e.g., site preparation, water analysis). Different qualitative descriptors and decision matrices can be used to evaluate new partnerships, but the value of intuition about a person or organization based on field experiences and cultural understanding cannot be understated when operations are beyond structured governance. Mr. Singh took a twelve hour overnight train to meet Mike, Dr. SenGupta, and STHF in-person in Kolkata, where their relationship was formalized. System capital expenses was borne by Rite Water Solutions (I) Pvt. Ltd. (Nagpur, Maharashtra, India), construction was completed by Ramkrishna Water Enterprise (Durgapur, West Bengal), and the system was operational by November 2013, **Figure 3.17B**. This system served as the first arsenic treatment system Rite Water installed, an important pre-qualification for government arsenic treatment tenders.

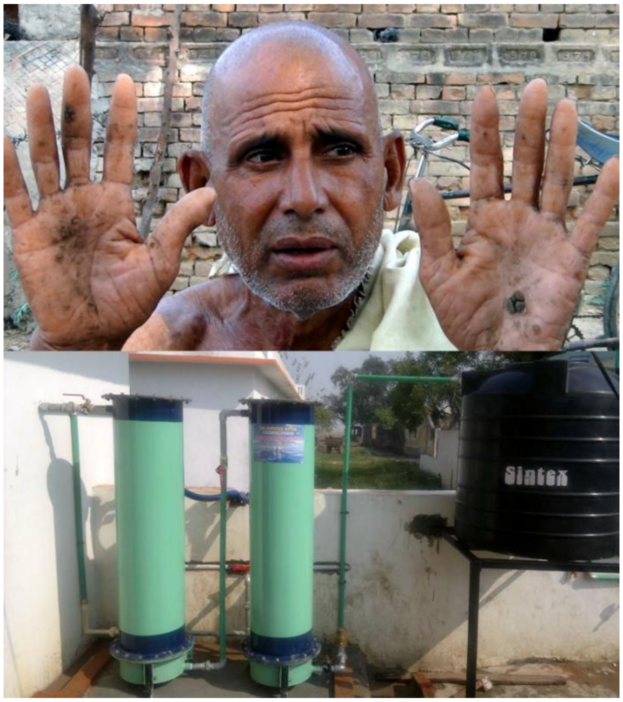


Figure 3.17. (A) A resident of Ballia, UP suffering from arsenicosis lesions on his hands before the installation of the arsenic treatment system (top); (B) the installed, simple HAIX-NanoFe system, which produced over 1 million liters of arsenic-safe water since opening.

3.6 Analytical Techniques

3.6.1 Material Properties

The HAIX-NanoZr resins were characterized by scanning electron micrograph (SEM), SEM accessorized with energy dispersive X-ray (SEM-EDX), X-Ray Diffraction (XRD) and high resolution transmission electron microscopy (HR-TEM).

3.6.1.1 Zeta Potential

The point of zero charge (PZC) for zirconium oxide precipitates was measured using the Malvern Zetasizer Nano ZS with MPT-2 Titrator with 0.1M $NaNO_3$ buffer, **Figure 3.18**.

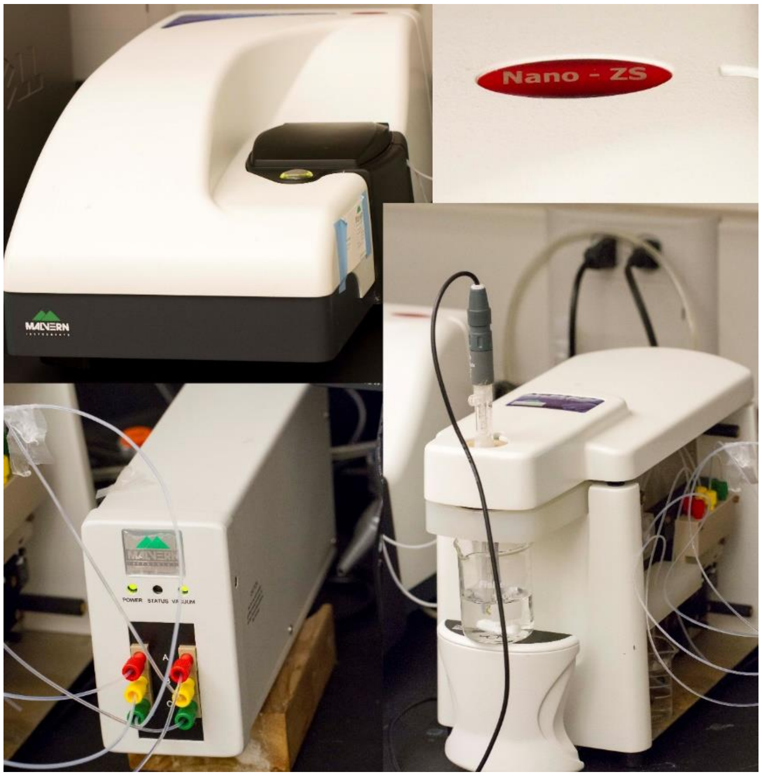


Figure 3.18. Malvern Zetasizer Nano ZS, and MPT-2 Titrator used for zeta potential measurements. Credit: Jinze Li.

3.6.1.2 SEM

High resolution SEM images of parent anion exchange resin and zirconium-impregnated resin were taken with a Hitachi 4300LV Schottky-emission scanning electron microscope in SE mode at 15 keV. Prior to scanning, the resins were cross-sectioned by microtomy and coated with Ir.

3.6.1.3 TEM

Additional microscopy work was performed at the University College Dublin, Institute of Biomolecular and Biomedical Research Imaging Facility, as part of a Global Innovation Initiative program funded by the US State Department; the UK Department of Business, Innovation and Skills; and the British Council. Ms. Tiina O'Neill performed TEM analysis of HAIX-NanoFe and HAIX-NanoZr resins in Dublin.

In preparation, HAIX-NanoZr and HAIX-NanoFe needed to first be embedded in a resin. The embedding process was as follows, with the resin beads in a beaker on a slow rotating shaker:

1) Dehydration
    a. 30% ethanol (10 min)
    b. 50% ethanol (10 min)
    c. 70% ethanol (10 min)
    d. 90% ethanol (10 min)
    e. 3x 100% ethanol (10 min)
2) 2x acetone (15 min)
3) 30% acetone:Epon (60 min)
4) 50% acetone:Epon (60 min)
5) 70% acetone:Epon (overnight)
6) 100% Epon (60 min)
7) 100% Epon (120 min, $37^{O}C$, no lid)
8) Polymerization (24hr, $60^{O}C$)

Note: Epon was comprised of: 24 g Agar 100 resin, 9.5g DDSA (dodecenyl succinic anhydride), 16.5 g MNA (methyl nadic anhydride), and 1 g DMP-30 (2,4,6-tri(dimethylaminoethyl)phenol).

For TEM analysis, survey section areas of HAIX-NanoZr were identified and ultrathin sections of 80 nm were obtained using a Leica EM UC6 ultramicrotome (Leica, Germany). These sections were mounted on EM grids (200-mesh carbon-formvar copper grids) and stained with 2% uranyl acetate for 20 min and 0.4% lead citrate for 10 min before being examined by a Tecnai G2 20 (FEI Company, USA).

3.6.1.4 SEM-EDX

A JEOL JSM-6360A (SEM) equipped with a JED-2300 (EDX) was operated at voltages in the range of 0.5-30 kV. The beads were embedded in a mixture of epoxy resin and hardener with a ratio of 10:1 to enhance the solidification process. The specimen disc was held parallel to the polishing surface to produce uniformly thin specimens. A conductive layer of platinum was deposited on the sample by a sputter coater to reduce surface charging during SEM analysis. A cross-section of polymeric beads was prepared by embedding the beads into epoxy resin, which was then solidified by heating on a laboratory hot plate and subsequently ground carefully using a Gatan disc grinder in order to obtain the cross-sectional view.

3.6.2 Chemical Analysis

At Lehigh University, fluoride testing was carried out by using a Hach UV-VIS spectrophotometer model DR 5000 by following SPADNS method (127). In India, fluoride was measured using homemade SPADNS with a handheld fluoride colorimeter (HACH Pocket Colorimeter II, Loveland, CO). Chloride and sulfate were analyzed using a Dionex Ion Chromatography system (model DX-120). In the US, the aqueous silica and zirconium concentration was determined by using an ICP-OES (PerkinElmer Optima 2000 DV, Waltham, MA).

4. Develop synergistic trace contaminant removal with partial desalination (Aim 1)

4.1 Testing at NDC (March 4-18, 2014)

After establishing consistent hydraulic conditions, fluoride-contaminated tap water was treated with BC (fine and medium), HAP (small column, large column), HAIX-NanoZr, and C107H-HAIX-NanoZr. With only one set of testing columns functional, materials were tested at different times throughout the week. During each test, a 1L beaker would be filled with raw water that would last for approximately 350 min before being refilled; the flowrate was recorded throughout and was generally around 2.5 mL/min. Raw water pH and conductivity were virtually constant throughout the two weeks of testing and were not always tested for each test. Fluoride varied from 5-6 mg/L throughout the duration of testing, but fluoride was mostly between 5.7-6.0 mg/L. The greater variations may have been more of a result of changes in ISE calibration than in actual water concentration changes.

4.1.1 BC at NDC

Fluoride effluent from treatment by BC (fine, medium) is in **Figure 4.1**. In the 11mm glass column, the larger sized BC materials may also have led to significant channeling, non-ideal hydraulics, and decreased capacity. In field operations, BC columns have very low loading rates and high empty bed contact time or EBCT (up to 1 day) because of their low capacity and the operational need to have the columns last several months before regeneration. Such slow flowrates are atypical for packed bed media and not amenable to lab testing: lab EBCT was 7.5 min (BC-fine) and 4.5 min (BC-medium).

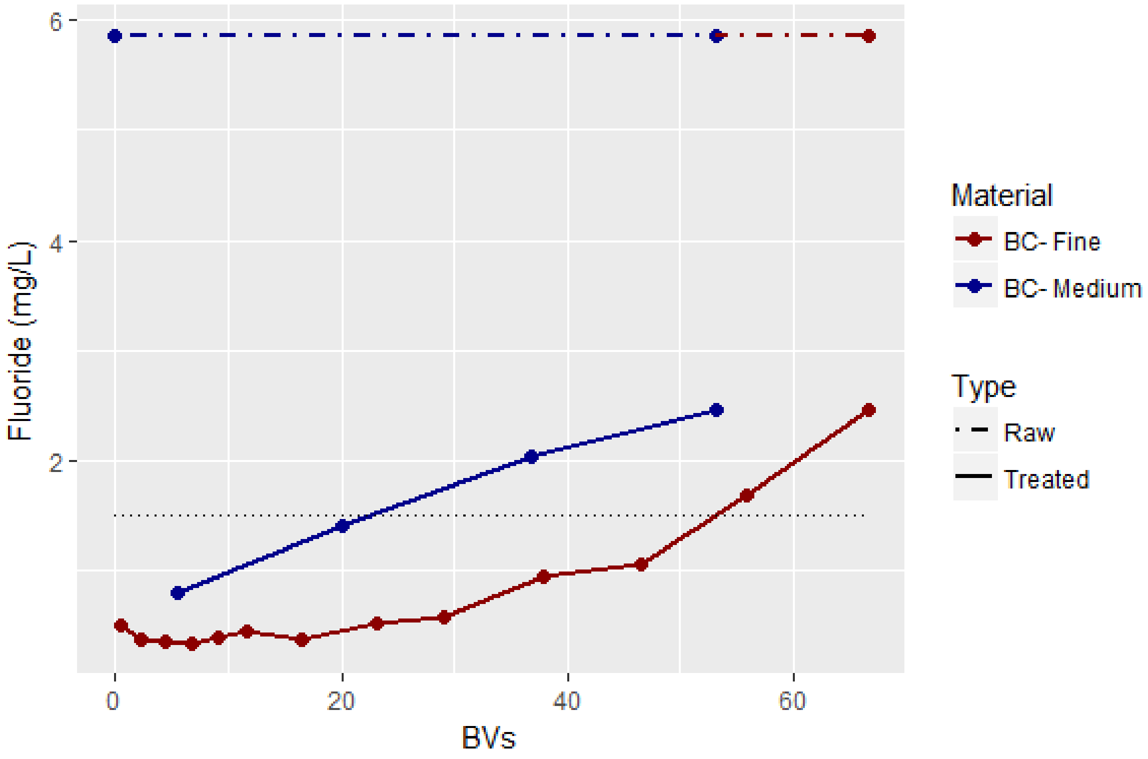


Figure 4.1. Fluoride effluent from BC (fine, medium) treatment in a 11mm ACE Glass column at NDC. Note: breakthrough of medium-sized BC occurred at 22BVs, breakthrough of fine-sized BC was at 53BVs.

There is no chemical difference in the makeup of fine and medium size BC, but there is a significant difference in fluoride removal before breakthrough: 22 BVs vs. 53 BVs (medium vs. fine). The porosity and internal structure of BC is a function of the material and the charring process. It is difficult to have consistent creation of sorbents with high porosity because of the raw materials and limited process controls. Thus, the intraparticle diffusivity of BC is low, and the fluoride removal is mostly a surface phenomenon, where the fluoride capacity of BC is proportional to surface area; the majority of the internal fluoride sorption capacity is unused. Low intraparticle diffusivity was further confirmed by a 12 hr interruption test, where the effluent fluoride dropped from 2.5 mg/L to 1.5 mg/L for BC-medium. As BC-fine had a much smaller diameter than BC-medium, the surface area and removal capacity of BC-fine was twice as great than BC-medium. The higher EBCT for BC-fine may also have contributed to longer removal before breakthrough, but EBCT = 4.5 min is common for packed-bed systems and necessary for having a reasonably sized bed with lower capital expenses.

4.1.2 Hydroxyapatite (HAP) at NDC

Hydroxyapatite (HAP) is a difficult material to work with because of its low physical durability. Under finger pressure, HAP easily crumbles, **Figure 4.2**. When wet, HAP is extremely soft and can be smeared onto surfaces, **Figure 4.3**. The lack of minimal physical integrity means that transport of HAP from the production line to the installation site (dry) and from the shipping vehicle to inside of the column (possibly wet) are both potentially damaging steps; it is not possible to fill a column with HAP by pumping a HAP slurry. The small particle diameters seen in the figures have caused column clogging and prevented water flow in previous installed systems. Bags of HAP always accumulate a layer of HAP dust at the bottom from HAP degradation, but today installations use pre-filled drums, **Figure 4.4**.

Figure 4.2. Fresh HAP in a beaker (L). HAP crumbles after finger pressure (R).

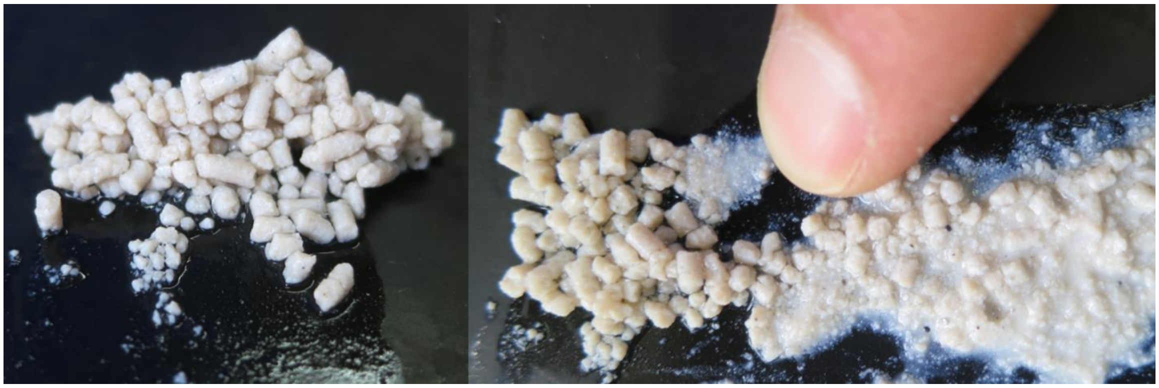


Figure 4.3. Wet HAP on a table (L); the same wet HAP moments later after light pressure (R).

Figure 4.4. Drums of HAP sold by NDC for community defluoridation.

As mentioned, the existence, production, and use of HAP was not known prior to being on-site at CDN. Hence, testing equipment to accommodate larger diameter sorbents were not brought over from Lehigh. Fluoride removal performance of HAP in a small (11 mm) and large (50 mm) column is shown in **Figure 4.5**. By carefully placing HAP inside the small column, and not subjecting the media to excessive flow shear, HAP remained in good condition during operation, **Figure 4.6**.

With inconsistent hydraulic conditions, raw data for fluoride removal during HAP treatment in **Figure 4.5** has several apparent outliers: the dip in HAP-Small near 200 BVs, the constant values from 100-200 BVs for HAP-large is due to a 9 hr overnight pause, the dip at 400 BVs for HAP-large occurred after another 10 hr overnight pause. When paused, intraparticle diffusion of fluoride throughout the adsorbent averages out the fluoride concentration throughout the adsorbent, decreasing the surface fluoride concentration. The diffusion increases the concentration gradient between the adsorbent and the solution and the removal performance increases temporarily. After the pause, effluent fluoride concentration may temporarily decreases or stay constant longer than expected. Based on the fitted lines, the larger diameter column had removal performance 25% greater than the smaller column because of channeling and wall effects present at the lower column: resin diameter ratio.

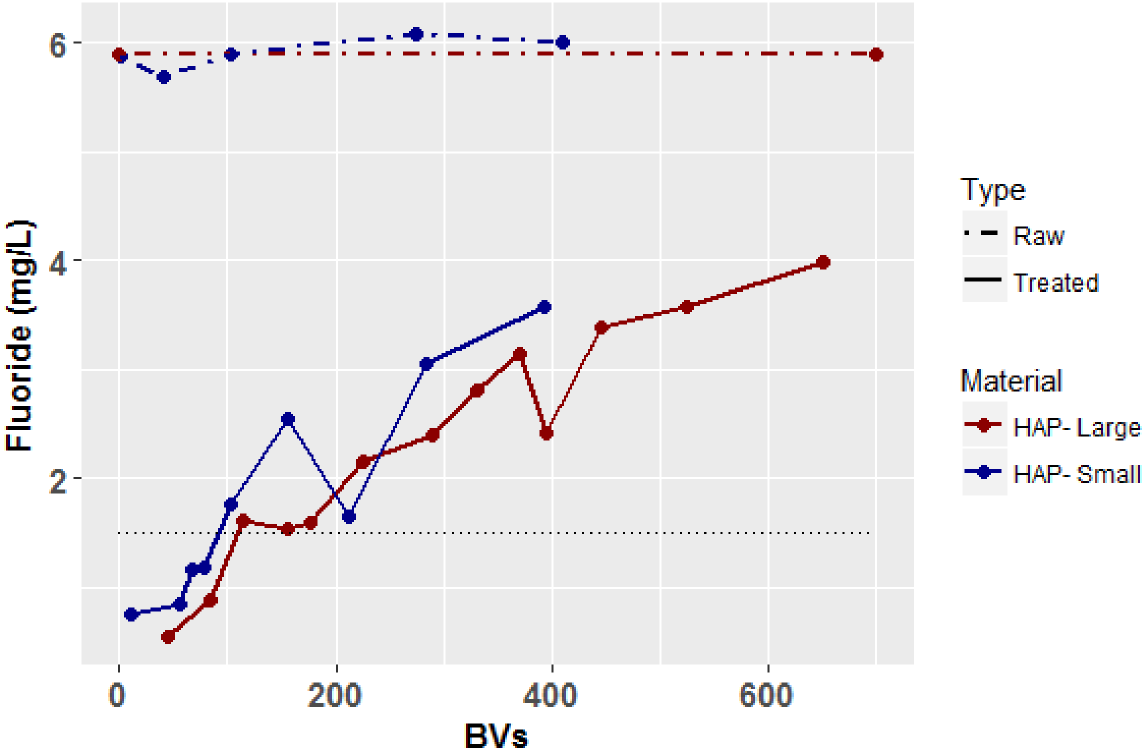


Figure 4.5. Fluoride treatment by HAP in the small (11 mm) and large (50 mm) diameter columns. Note: "HAP-Small" is effluent from the 11 mm column, and HAP-Large is effluent from the 50 mm column.

Figure 4.6. HAP before (L) and after (R) testing in the small diameter glass column.

4.1.3 HAIX-NanoZr at NDC

Lehigh-synthesized HAIX-NanoZr was tested both in a single column without pre-treatment and with C107H pre-treatment. Testing of HAIX-NanoZr without pre-treatment was done for a baseline comparison with other materials. In the last step of synthesis, immediately prior to testing, HAIX-NanoZr was equilibrated at pH 5.5. Fluoride removal performance without WAC pre-treatment, for comparison to BC and HAP-Large at groundwater conditions, is in **Figure 4.7**. In this test, HAP and HAIX-NanoZr had similar fluoride capacity. The fluoride capacity of HAIX-NanoZr was a strong function of solution pH.

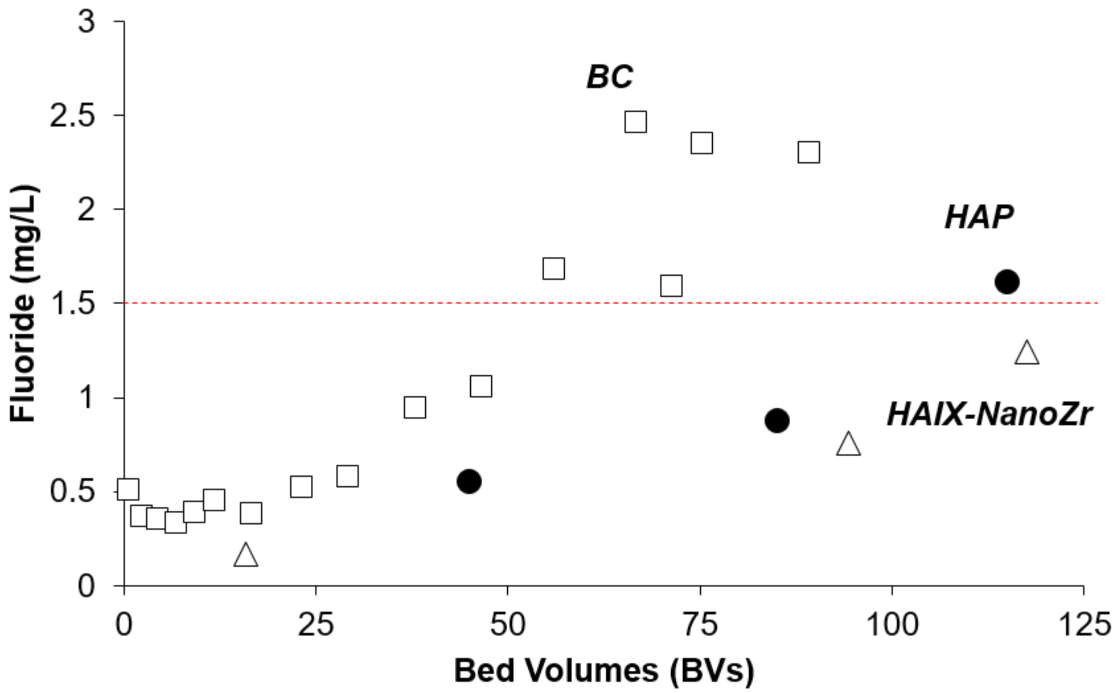


Figure 4.7. Fluoride removal of BC, HAP, and HAIX-NanoZr at NDC without pre-treatment.

If HAIX-NanoZr was only operated at groundwater pH and had comparable capacity to HAP, it would still be a more desirable fluoride sorbent for real use because of its physical integrity and capacity for reuse over multiple regeneration cycles. However, the intention was to perform partial desalination with concurrent defluoridation (PDCD) through the use of WAC pretreatment. In PDCD, divalent cations and alkalinity are removed by WAC and off-gassed after the WAC column; the influent pH to HAIX-NanoZr is reduced to boost capacity. Effluent fluoride and pH during WAC-HAIX-NanoZr testing are in **Figure 4.8**. With WAC pre-treatment, fluoride is removed from raw water concentrations of 6 mg/L to below WHO standards (1.5 mg/L) for nearly 400 BVs- a 3.5x improvement over without WAC.

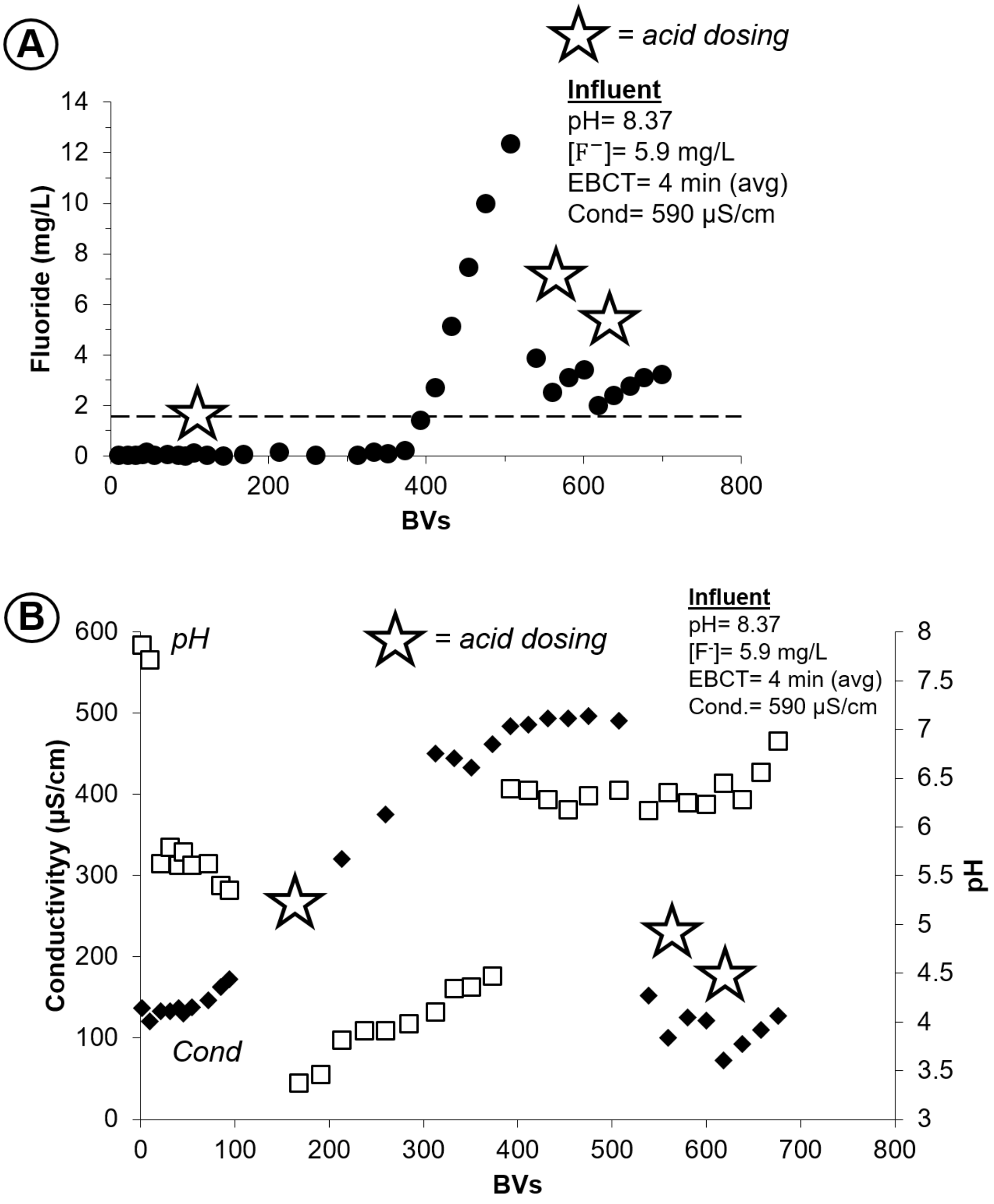


Figure 4.8. A) Effluent fluoride and pH; B) Effluent conductivity from WAC-HAIX-NanoZr testing at NDC. Note: star symbols indicate times at which HCl was dosed to condition the WAC resin.

During the first 100 BVs of operation, the system was operated with one column because of the difficulties in maintaining plug flow hydraulics with two columns, given unexpected operating difficulties. The large production of carbon dioxide from the WAC in the small diameter columns, and inability to degas the column without mixing the resins (degassing is performed by inverting the column multiple times), caused concern about proper plug flow.

At effluent pH > 4.0, over 100 BVs fluoride desorption from zirconium oxide occurred and fluoride effluent increased from 0.2 mg/L to >10 mg/L. After effluent pH 6.5 (500 BVs), 18 mL-1M HCl was dosed through the WAC in Column #1 and then drained; no acid was passed through Column #2. The effluent pH after acid conditioning was unchanged, but the effluent fluoride was reduced (12.3 mg/L -> 3.9 mg/L) and effluent conductivity decreased (500 µS/cm -> 100-150 µS/cm). This indicates that zirconium oxide was reprotonated, alkalinity was being reduced by the WAC column, and low pH effluent was exiting the column; alkalinity reduction was also evident from the carbon dioxide production and off-gassing. However, as the effluent pH did not change and effluent fluoride was not <1.5 mg/L, the zirconium oxide was not fully reprotonated and the fluoride sorption capacity not fully restored. Based on best practices now, the low pH effluent from Column #1 during acid conditioning would have been passed through Column #2 to help reprotonate the zirconium oxide and improve fluoride removal capacity.

After 700 BVs, with the high effluent pH- high being a relative term of pH > 4.5- and fluoride not being reduced below 2 mg/L, HAIX-NanoZr was removed from Column #2 and equilibrated with acidified tap water (pH 3.5) for 45 min. However, without the time and resources to control the pH, HAIX-NanoZr was, again, not fully reprotonated. Effluent pH was decreased to pH 4.5 briefly, but immediately began increasing again, concurrently with effluent fluoride concentrations. After 50 BVs above effluent pH 5.5, fluoride desorption from the zirconium oxide occurred again from influent fluoride concentration ($C = C_0$) to double the influent concentration ($C = 2C_0$). Time restrictions on developing an appropriate acid conditioning procedure for the new system design led to suboptimal performance in terms of alkalinity, fluoride, and hardness removal. But, in this, the importance of proper WAC operation and conditioning was understood as critical for overall system performance.

For comparison purposes, a summary figure of effluent fluoride for BC-Fine, HAP, HAIX-NanoZr, and WAC-HAIX-NanoZr is presented in **Figure 4.9**.

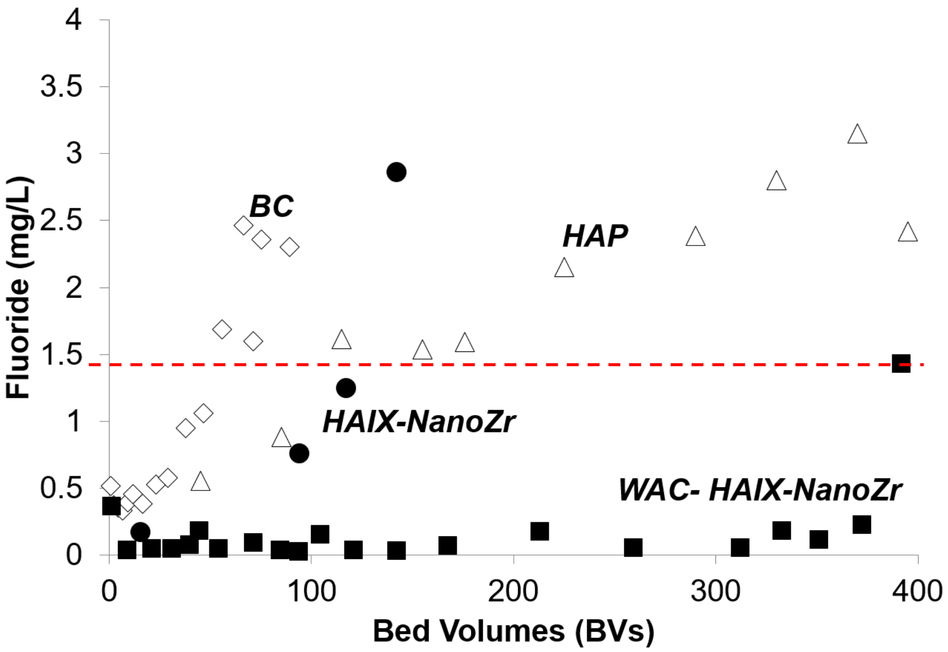


Figure 4.9. Effluent fluoride from BC-Fine, HAP, HAIX-NanoZr, and WAC-HAIX-NanoZr.

4.1.4 Unique Water Chemistry in Fluoride-Impacted Aquifers at NDC

After being in Nakuru for two weeks, the uniqueness of fluoride-contaminated groundwater was more fully understood. High alkalinity, low hardness, high silica, and high TDS were noticed as characteristic to water from Nakuru and other Rift Valley regions with high fluoride. Similar water was also found at different locations of India. Previous work around arsenic treatment work was often in aquifers with moderate alkalinity, moderate hardness, and moderate TDS. Thus, the fluoride removal benefit of WAC pre-treatment was realized to be only one of the benefits: the concurrent partial desalination and hardness/alkalinity reduction by WAC were requirements for treated water to meet aesthetic and WHO standards. Other fluoride sorbents only focused on fluoride removal, which is inadequate for water with multiple constituents that exceed WHO standards.

But, concentrations of divalent vs. monovalent cations is important when considering weak acid cation exchange. Carboxylate groups on WAC resins have much higher selectivity of divalent cations versus monovalent cations than SAC resins, because of the sterics of ion exchange and the pH changes. The pH effects as protons exchange with different cations:

$$\overline{RCOOH} + Na^{+} \leftrightarrow \overline{RCOO^{-}Na^{+}} + H^{+}$$

$$2\overline{RCOOH} + Ca^{2+} \leftrightarrow \overline{(RCOO^{-})_2Ca^{2+}} + 2H^{+}$$

4.2 HAIX-NanoZr: Lab Testing of US Materials (Lehigh University)

4.2.1 HAIX-NanoZr Physical Characterization

4.2.1.1 HAIX-NanoZr: Visual Characterization

When the four different fluoride adsorbents are handled, with or without gloves, the difference in the physical integrity is immediately apparent because of the residues that remain. Even after chemical washing, (in)organic remnants are still attached to the BC. As precipitated and calcined inorganics, AA and HAP are somewhat brittle and their surface layers come off to different extents upon contact. Having a robust polymer for the metal oxide support, HAIX-NanoZr holds the distinction of being designed for physical integrity and does not degrade. The differences in durability are evident in **Figure 4.10**.

Figure 4.10. Fluoride adsorbents after a 12 hr shake test: bone char (BC), activated alumina (AA), hydroxyapatite (HAP), and HAIX-nanoZr (from left-right). Images by Jinze Li.

4.2.1.2 SEM Scans

After synthesis, zirconium oxide precipitation inside of HAX-NanoZr is apparent by the change in color of HAIX-NanoZr from white to beige, **Figure 4.11**. However, after taking a cross-section of a resin bead and looking inside, the presence of zirconium does not seem to impact the internal morphology or pore structure, **Figure 4.12**.

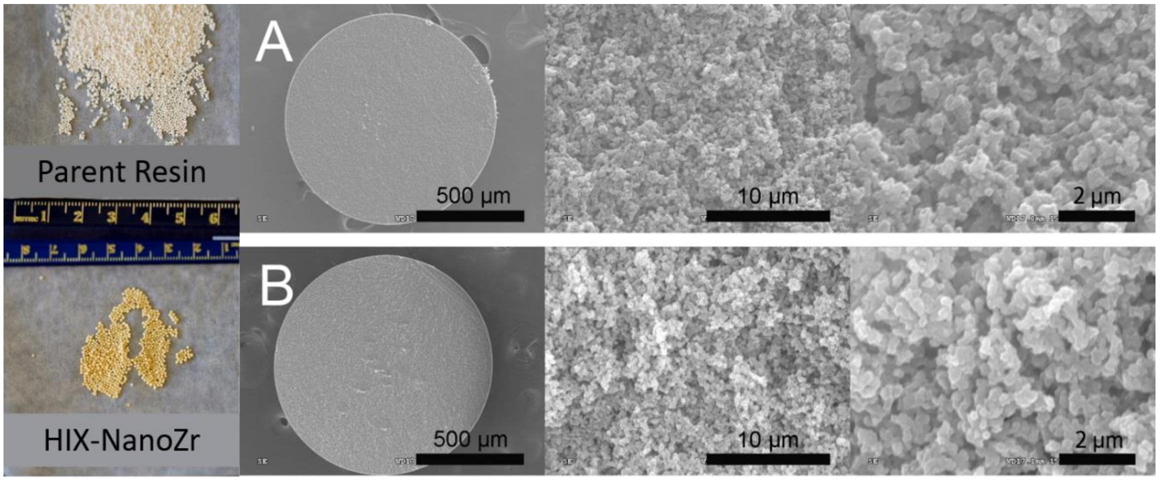


Figure 4.11. Comparison of parent resin (top) and HAIX-NanoZr (bottom) at 1x, 100x, 5,000x, and 10,000x (Left-Right). Images by Jinze Li.

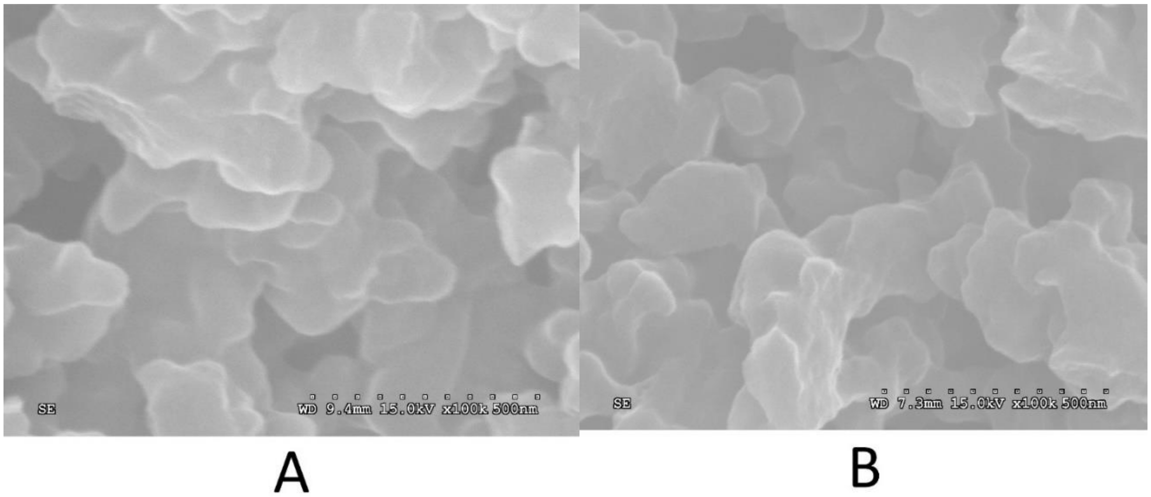


Figure 4.12. High resolution SEM image taken at 15 keV of a cross-sectioned HAIX-NanoZr bead that was coated with Ir. (A) Parent Purolite resin (100,000X); (B) Purolite HAIX-NanoZr (100,000X). Good morphology contrast indicated that there was no apparent change of pore sizes after loading ZrO nanoparticles. Images by Jinze Li.

4.2.1.3 TEM Scans

Samples of HAIX-NanoZr made at Lehigh using Purolite parent resin were provided to Dr. Debra Phillips as part of a GII grant, **Figure 4.13**. Notably, HAIX-NanoZr appears very different than under SEM scan performed at Lehigh (**Figure 4.11**-**Figure 4.12**). At higher zoom, the irregular, amorphous zirconium oxide structure is visible.

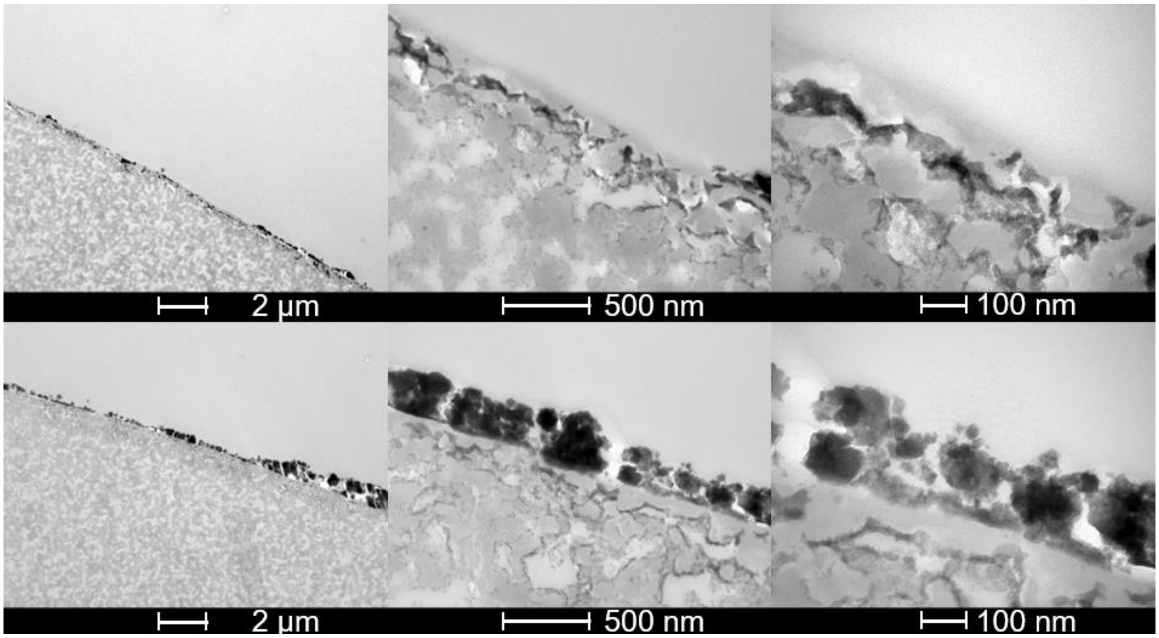


Figure 4.13. TEM scans of HAIX-NanoZr at (1) 6000x; (2) 43,000x; and, (3) 105,000x (Left-Right). Scans were performed at the University College Dublin.

4.2.1.4 SEM-EDX Analysis: Elemental Distribution

Cross-sections of HAIX-NanoZr were analyzed by SEM-EDX after treating groundwater containing fluoride, phosphorus, and silica, **Figure 4.14**. Zirconium (Zr) is precipitated in a bright magenta donut pattern. Fluoride (F), phosphate (P), and silica (Si) are Lewis bases with high affinity for strong Lewis acids, e.g., Zr, and can be found in a matching donut pattern as to Zr inside of the resin. As F, P, and Si will not participate in anion exchange, they are not found in the middle of the resin, where Zr is missing. Chloride (Cl) and sulfate

(S) do not form inner sphere complexes with Zr, but participate in anion exchange with the quaternary ammonium groups, which are present homogenously across the anion exchanger. As such, Cl and S are seen in a homogenous pattern across HAIX-NanoZr without a concentration gradient that favors Zr.

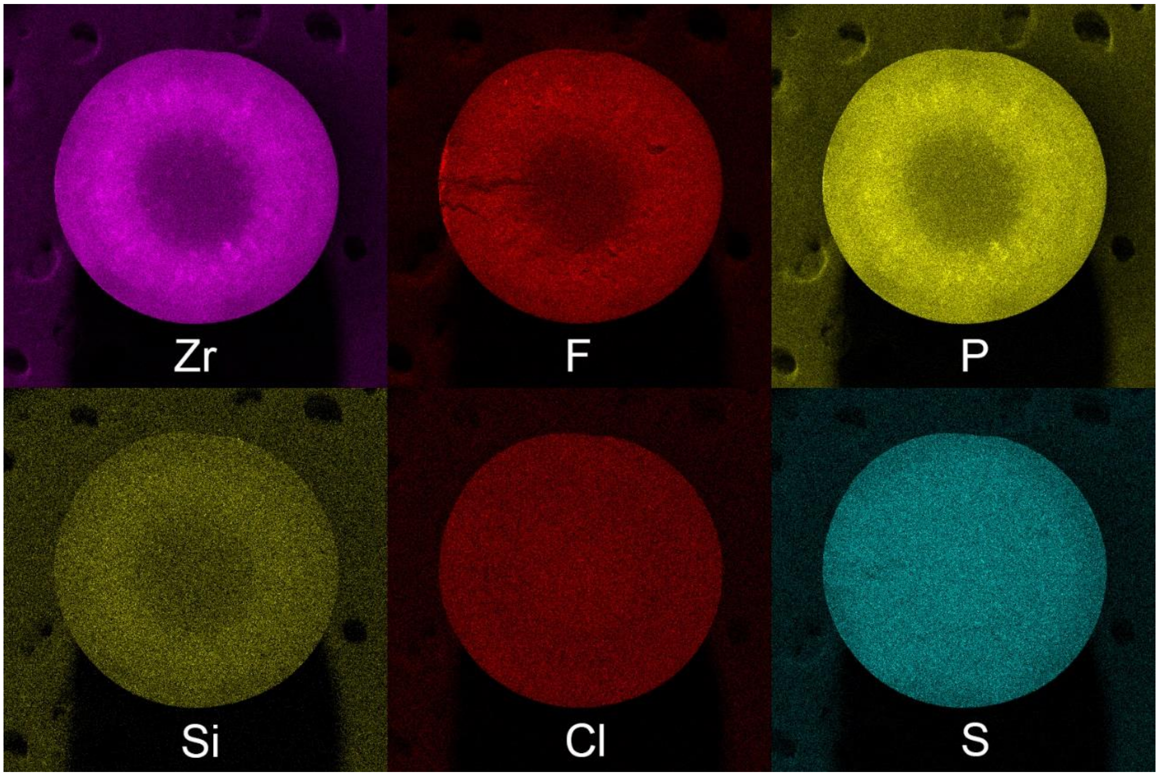


Figure 4.14. SEM-EDX scan of HAIX-NanoZr for six different elements: zirconium (Zr), fluoride (F), phosphorus (P), silicon (Si), chloride (Cl), and sulfur (S). Note the donut pattern in Zr, F, P, and Si and homogenous contrast in Cl and S. Scans by Jinze Li

4.2.1.5 XRD: Zirconium Morphology

Freshly precipitated zirconium oxide nanoparticles inside HAIX-NanoZr have an amorphous structure. For consistent performance over time, it is important that the zirconium geometry is unchanging across significant pH and TDS due to regeneration. Morphology of zirconium was tested for HAIX-NanoZr (virgin and after five cycles) by obtaining x-ray diffraction (XRD) patterns using the Rikagu Model MiniFlex II, **Figure 4.15**. Neither of the ground HAIX-NanoZr samples had any distinguishable peaks: the zirconium oxide is almost completely amorphous. No enhanced crystallinity peaks corresponding to monoclinic or tetragonal forms, were observed after five cycles of operation. Amorphous zirconium is preferable to crystalline forms because of its higher surface area and capacity.

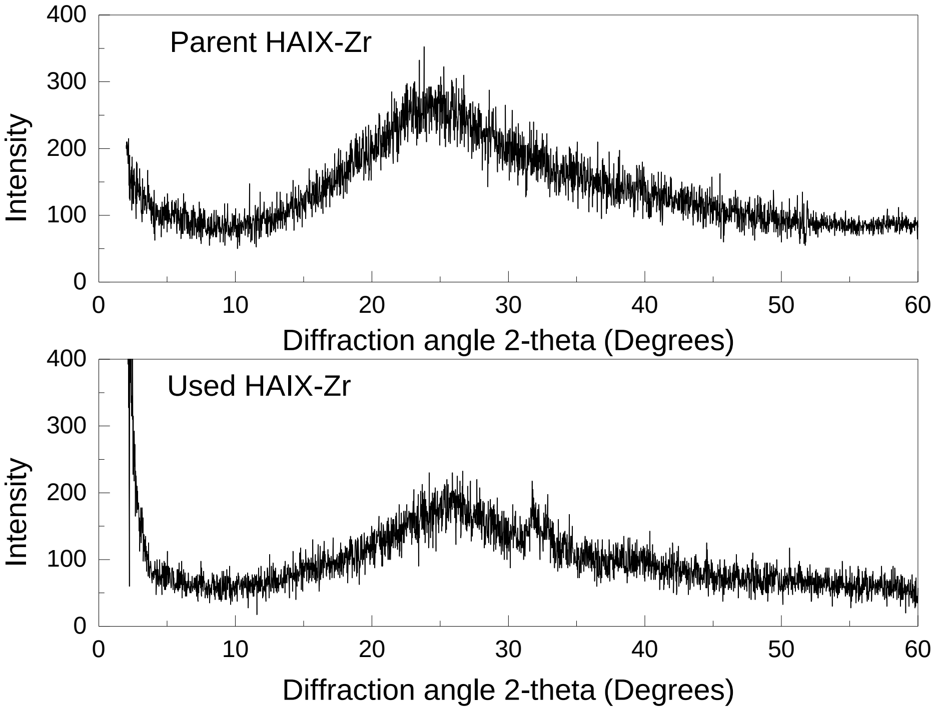


Figure 4.15. X-Ray diffraction (XRD) patterns of virgin and used (five cycles) HAIX-NanoZr. Tested by Jinze Li.

4.2.2 Comparison with Other Adsorbents: Batch Capacity and Packed-Bed Test

4.2.2.1 Batch Capacity Comparisons

As an initial comparison of HAIX-NanoZr performance, fluoride batch capacity tests versus BC and AA were performed at pH 3.0, 5.0, **Figure 4.16**. At pH 3.0, HAIX-NanoZr has 870% and 60% higher fluoride capacity than BC and AA, respectively. Notably, HAIX-NanoZr was more sensitive to the pH difference and had a greater difference in capacity between pH values (40%) than BC (5%) or AA (20%).

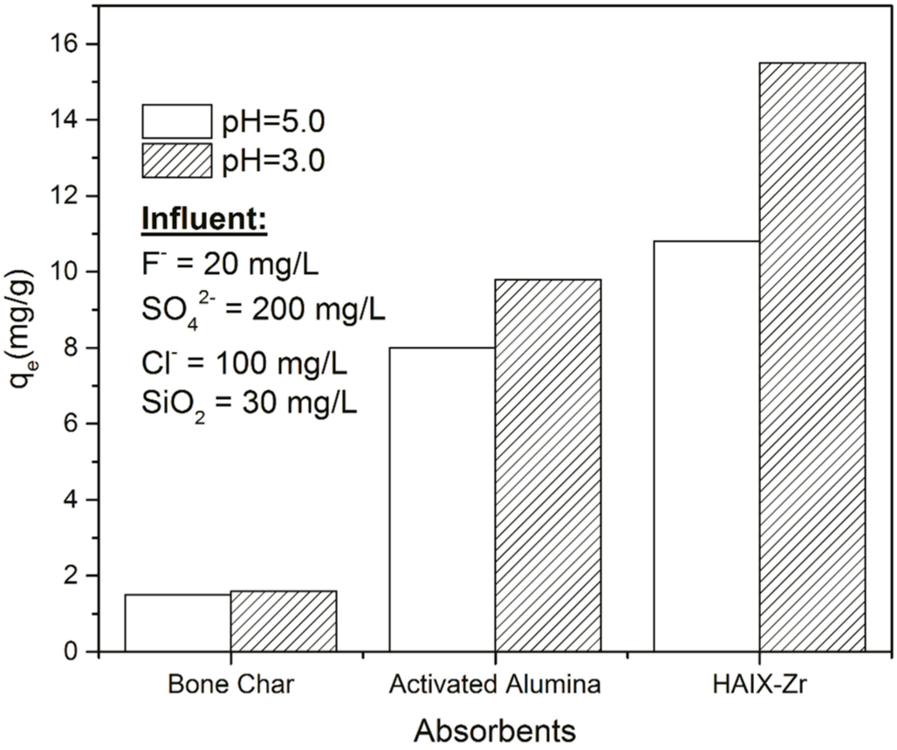


Figure 4.16. Batch capacity (q_e) of bone char, activated alumina, and HAIX-NanoZr at pH 3.0, 5.0. Tested by Jinze Li.

4.2.2.2 Packed-Bed Comparisons

During packed-bed column treatment of synthetic groundwater (pH 8.3), **Figure 4.17**, the difference in fluoride removal capacity between the adsorbents was much greater: BC (5

BVs), AA (15 BVs), HAIX-NanoZr (275 BVs). HAIX-NanoZr was able to reduce the influent fluoride concentration (5.8 mg/L) below WHO limits (1.5 mg/L) for 50x and 18x more than BC and AA, respectively.

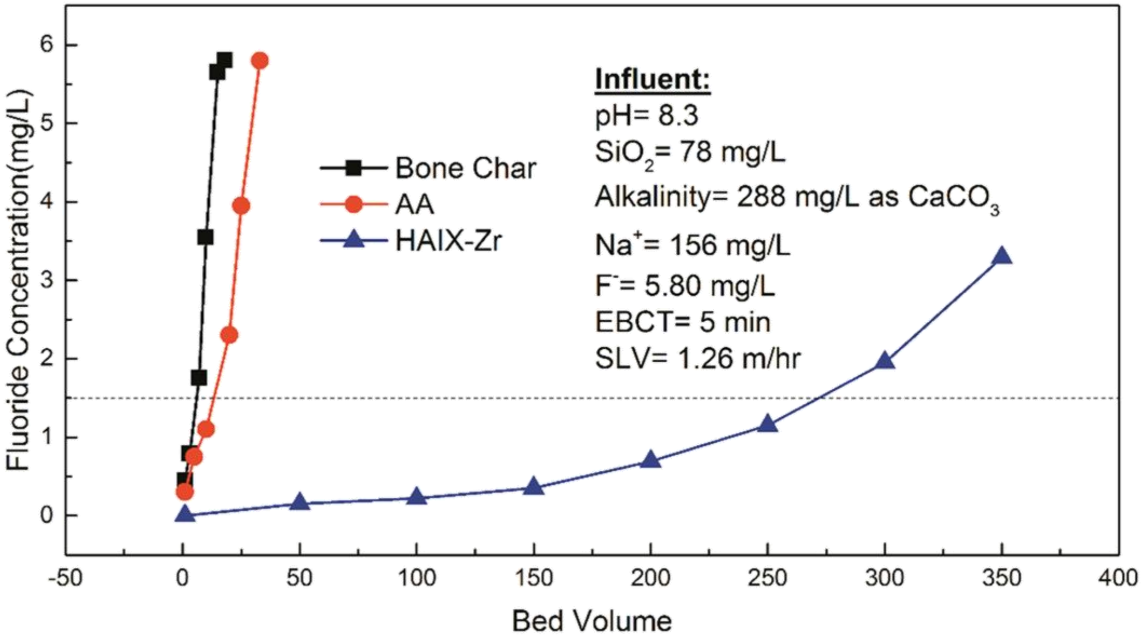


Figure 4.17. Fluoride effluent of synthetic groundwater after packed-bed treatment by BC (5 BVs), AA (15 BVs), HAIX-NanoZr (275 BVs). Tested by Jinze Li.

4.2.2.3 AA Packed-Bed Treatment (pH 4.2)

A packed-bed column of AA from Oxide India treated about 750 BVs of synthetic, acidified (pH 4.2) Kenya groundwater to an effluent fluoride concentration under 1.5 mg/L, **Figure 4.18**. The total capacity was calculated to be about 4.85 mg F/mL AA. Concurrently, there was significant SiO_2 removal for 100 BVs, **Figure 4.19**. While passing acidified synthetic Kenyan groundwater, the effluent pH slowly decreased over time from pH 6 → 5, **Figure 4.20**.

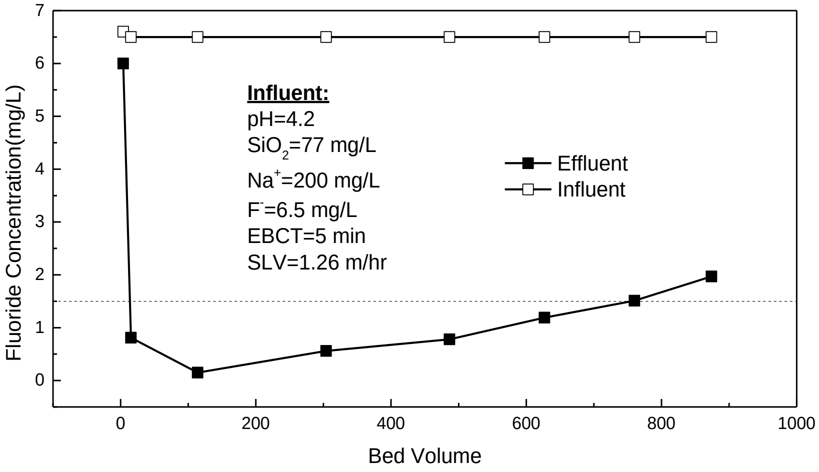


Figure 4.18. Effluent fluoride history from packed-bed treatment of synthetic Kenya (pH 4.2) with Indian AA. Tested by Jinze Li.

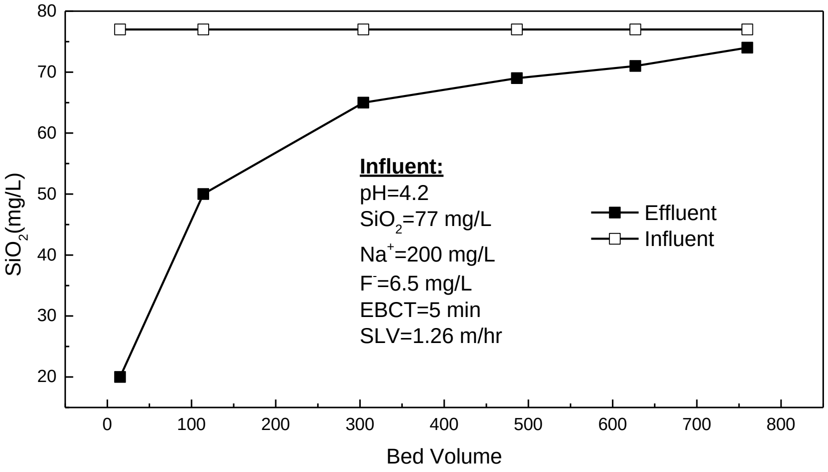


Figure 4.19. Effluent SiO_2 history from packed-bed treatment of synthetic NDC groundwater (pH 4.2) with Indian AA. Tested by Jinze Li.

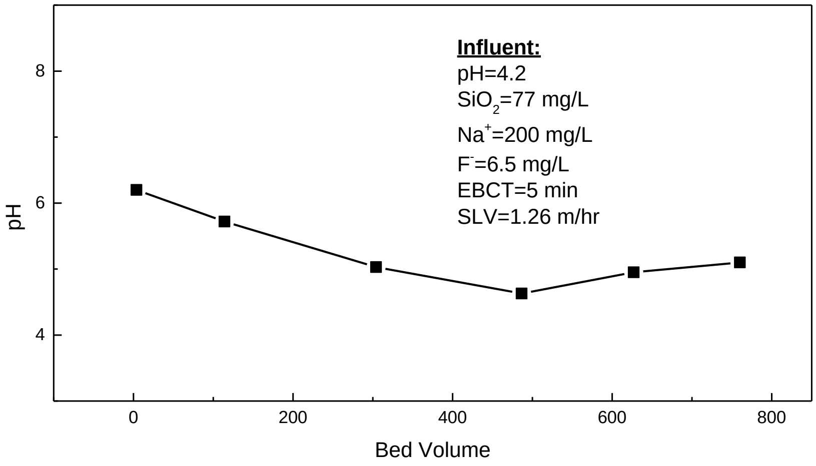


Figure 4.20. Effluent pH history packed-bed treatment of synthetic NDC groundwater (pH 4.2) with Indian AA. Tested by Jinze Li.

4.2.3 HAIX-NanoZr Fluoride Capacity- Mini-Column

At pH 2.0, HAIX-NanoZr showed the highest adsorption capacity for fluoride at 13 mg F/g resin, **Figure 4.21**. Notably, this is lower than the pK_a value of HF and closer to the solubility regime of zirconium oxide. According to the Donnan membrane effect, the proton concentration will be lower inside an anion exchange resin than in the aqueous phase. Thus, zirconium nanoparticles impregnated inside HAIX-NanoZr are less susceptible to dissolution at pH 2.0.

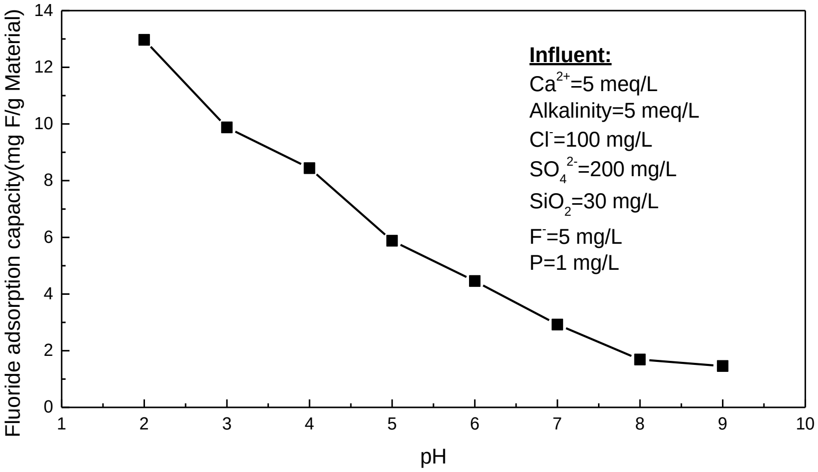


Figure 4.21. Mini column result of fluoride adsorption capacity at equilibrium under different pH values, Tested by Jinze Li.

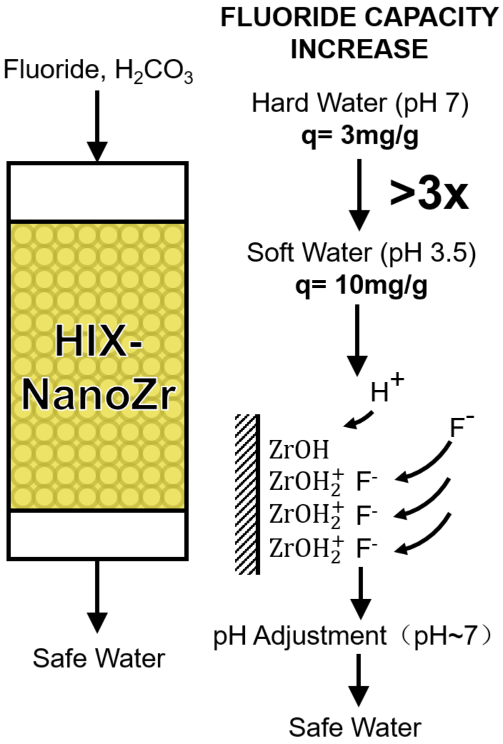


Figure 4.22. Diagram of fluoride capacity as affected by WAC pre-treatment. WAC-treated groundwater had 3x higher capacity for HAIX-NanoZr than untreated groundwater because zirconium oxide becomes protonated. After HAIX-NanoZr treatment, the pH is passively adjusted to drinking water standards.

4.2.4 Fluoride Capacity versus Equilibrium Sulfate

As a hybrid ion exchange resin, HAIX-NanoZr contains both functional groups from anion exchange resins and metal oxides for Lewis Acid-Base interactions. Sulfate is a divalent anion with strong affinity for anion exchange sites based on Coulombic interactions, but, as sulfate is a highly hydrated, weak base, it does not act as a ligand or form Lewis acid-base interactions with metal oxides. Thus, it is expected that solution sulfate concentrations will not impact fluoride removal. In batch tests with synthetic groundwater (10 mg/L fluoride), neither fluoride capacity nor equilibrium fluoride concentration were significantly impacted by changes in sulfate concentration from 150 mg/L to 500 mg/L, **Figure 4.23**.

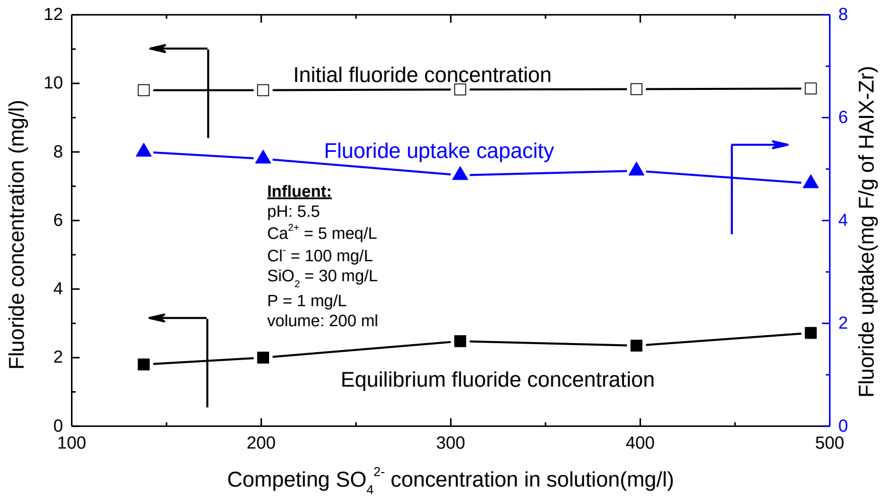


Figure 4.23. HAIX-NanoZr fluoride uptake capacity and equilibrium fluoride concentration as a function of competing sulfate ion concentration. Tested by Jinze Li.

4.2.5 Zeta Potential

Strong base anion exchange resins, e.g., Purolite A500P, have fixed positively charged functional groups, i.e., quaternary amine, that are not susceptible to (de)protonation. Thus, their zeta potential is positive across a wide range of pH values, followed by a sharp eventual accumulation of negative charges and an alkaline isoelectric point (pI) or points of zero charge (PZC), **Figure 4.24**.

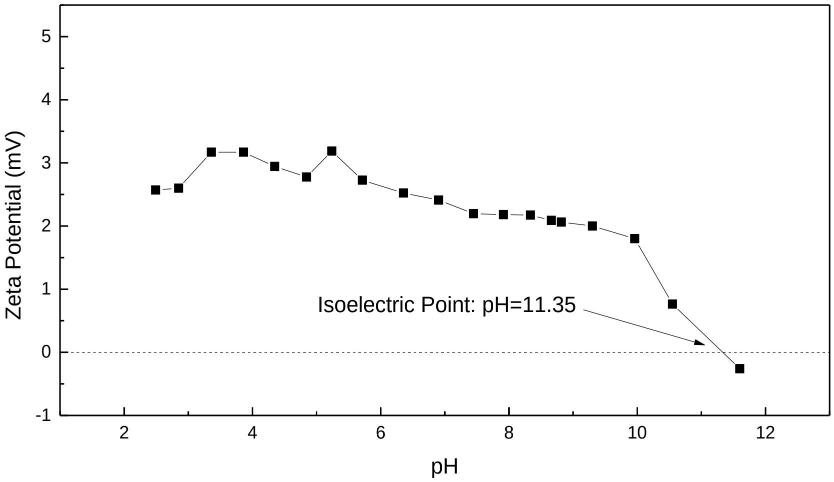


Figure 4.24. Zeta potential as a function pH for Purolite A500P resin; pI = 11.35. Tested by Jinze Li.

The zeta potential of zirconium oxide synthesized at Lehigh was tested at 0.1M $NaNO_3$ and PZC occurred at pH 7.59, **Figure 4.25**. From literature, zirconium oxides produced by different groups had PZC 4.0-8.6 (128). Different morphologies of zirconium oxide can yield significantly different PZC values: monoclinic zirconium has a much higher PZC than amorphous zirconium or other crystalline forms. Additionally, silica has high affinity for zirconium oxide, especially at alkaline pH conditions, and surface impurities can greatly impact zeta potential and PZC determination. These factors should be considered with regard to zirconium oxide PZC measurements.

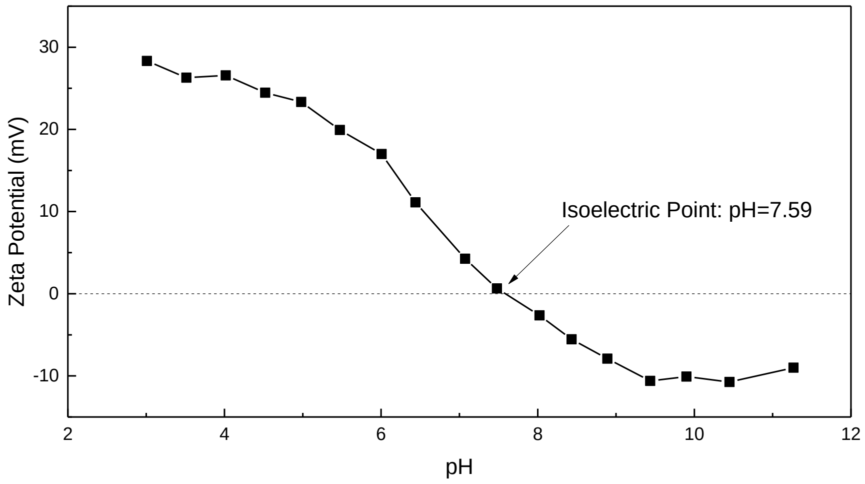


Figure 4.25. Isoelectric titration graph for precipitation of zirconium oxide particles with a 0.1M $NaNO_3$ solvent. As tested, pI = 7.59. Points in the figure are weighted mean zeta potential and mean pH values. Tested by Jinze Li.

Fluoride capacity (**Figure 4.21**) and zeta potential (**Figure 4.25**) of HAIX-NanoZr are both strong functions of pH that decrease with increasing pH. When overlaid, fluoride capacity and zeta potential parallel each other and indicate clear correlations between the surface charge of zirconium oxide and fluoride removal capacity, **Figure 4.26**.

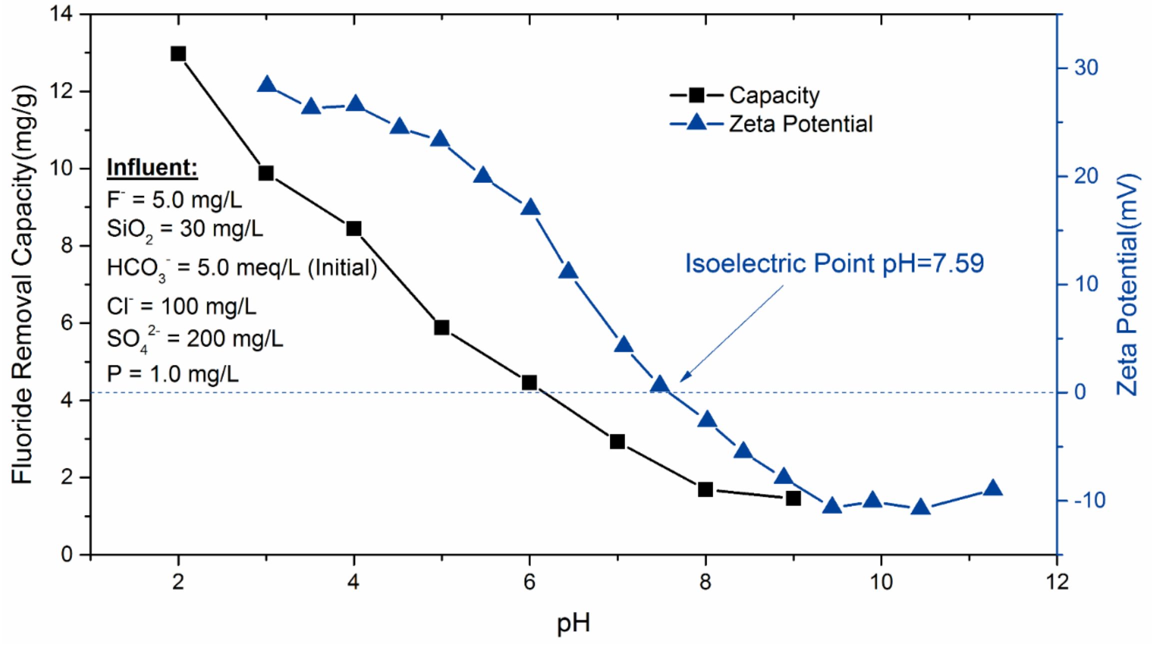


Figure 4.26. Fluoride capacity and zeta potential of HAIX-NanoZr as a function of pH.

4.2.6 *Packed-Bed HAIX-NanoZr Fluoride Treatment (Synthetic groundwater)*

A single packed-bed column of HAIX-NanoZr was used for treatment of acidified synthetic groundwater (pH 4.5) at Lehigh. Effluent histories for pH, fluoride, and SiO_2 over 3500 BVs are in **Figure 4.27-Figure 4.29**. The initial pH increased to pH 6.0 possibly due to insufficient pH conditioning of the newly made material. After 1500 BVs, the effluent pH value was lower than the influent pH value, and remained constant at pH 4.0. As pH decreased, fluoride concentration decreased to <1.0 mg/L in the effluent until 3200 BVs. Simultaneously, there was significant silica removal for 500 BVs. Synthetic feed solution was prepared and tested every 600 BVs; influent chemistry is described and graphed on **Figure 4.27-Figure 4.29**.

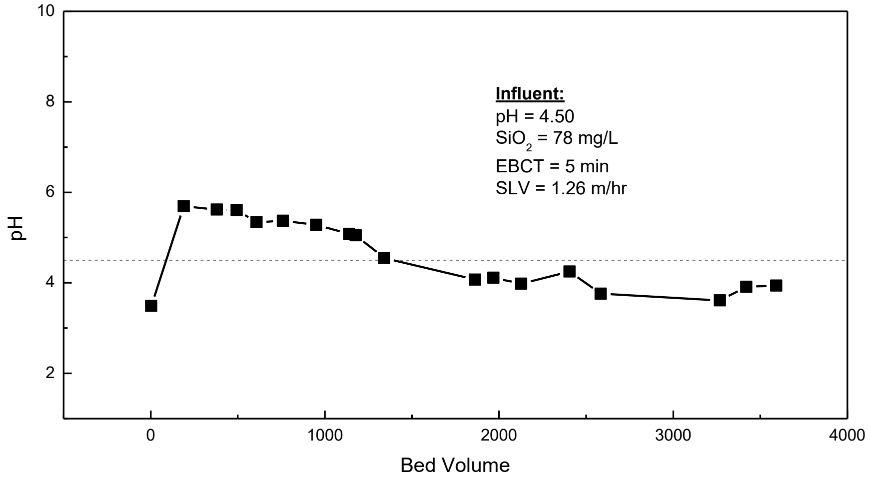


Figure 4.27. Effluent pH history from packed-bed treatment of synthetic NDC groundwater (pH 4.2) with HAIX-NanoZr. Tested by Jinze Li.

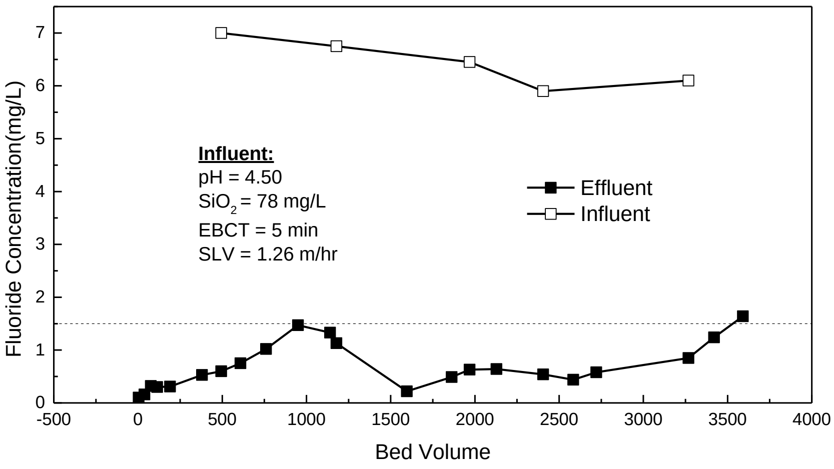


Figure 4.28. Effluent fluoride history from packed-bed treatment of synthetic NDC groundwater (pH 4.2) with HAIX-NanoZr. Tested by Jinze Li.

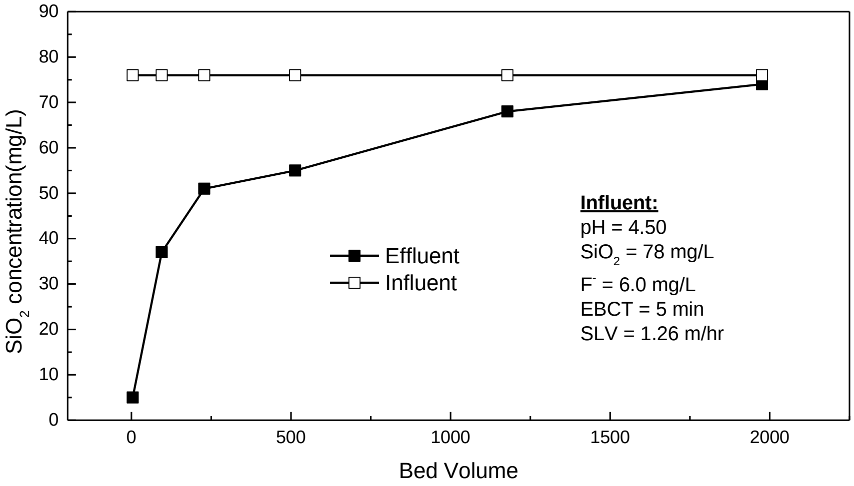


Figure 4.29. Effluent SiO_2 history from packed-bed treatment of synthetic NDC groundwater (pH 4.2) with HAIX-NanoZr. Tested by Jinze Li.

4.2.7 Packed-Bed HAIX-NanoZr Fluoride Treatment (NDC Groundwater)

Groundwater returned from NDC was treated by HAIX-NanoZr in a three-column system (1) WAC/SAC; (2) HAIX-NanoZr; and, (3) Dolomite/WAC-Na) over three cycles of exhaustion-regeneration; after three cycles, there was not enough groundwater for another cycle of treatment. Effluent fluoride, pH/conductivity, and zirconium are in **Figure 4.30-Figure 4.32**, respectively. Each cycle has similar fluoride effluent histories and breakthrough at 1.5 mg/L happens consistently at 3500 BVs. Significant fluoride removal (>50%) continues until 5000 BVs. Effluent conductivity is consistently 40% less than influent conductivity, indicating partial desalination is happening concurrently with defluoridation; WAC in the 1st column caused significant reduction in alkalinity and TDS. Effluent pH is within drinking water standards (pH 6.5-8.5) even though WAC in Column #1 decreases influent pH into HAIX-NanoZr (Column #2). Only one cycle of effluent conductivity and pH are graphed on **Figure 4.31** because of the difficulty in deciphering the three cycles when overlaid. Effluent zirconium concentration was tested during Cycle 1 to ensure no leakage of fresh zirconium oxide, but all measured effluent concentrations were below detection limits.

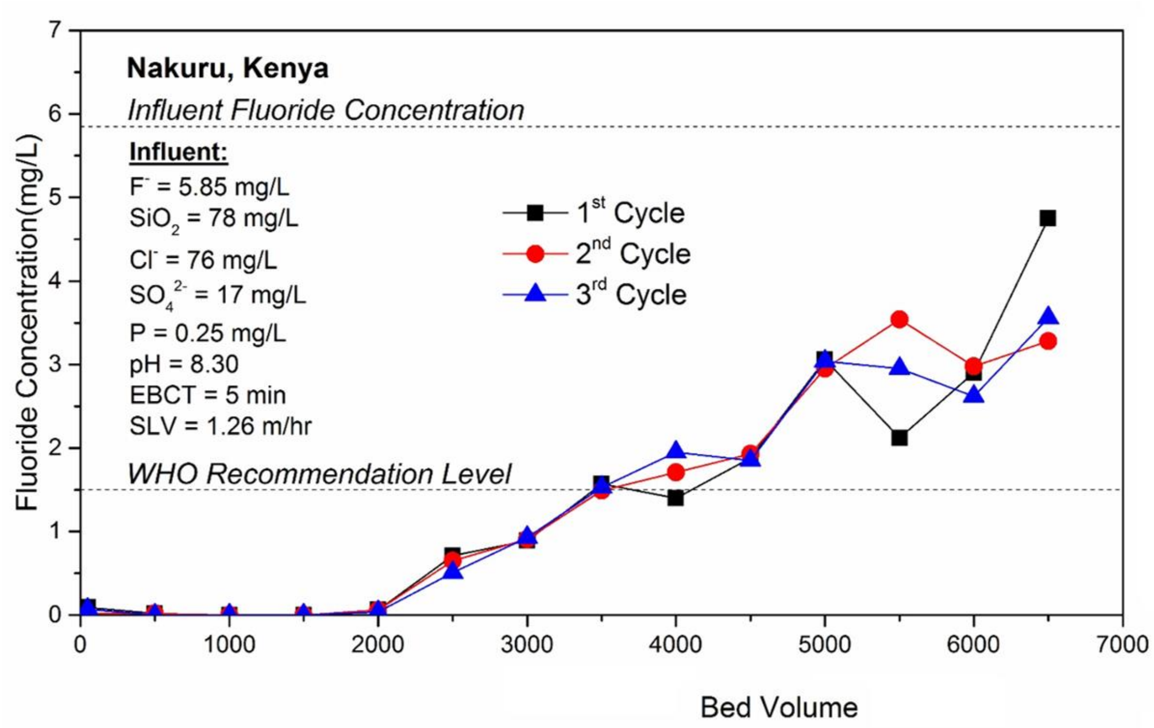


Figure 4.30. Fluoride effluent history from HAIX-NanoZr treatment of groundwater from NDC over three cycles of sorption-regeneration. Tested by Jinze Li.

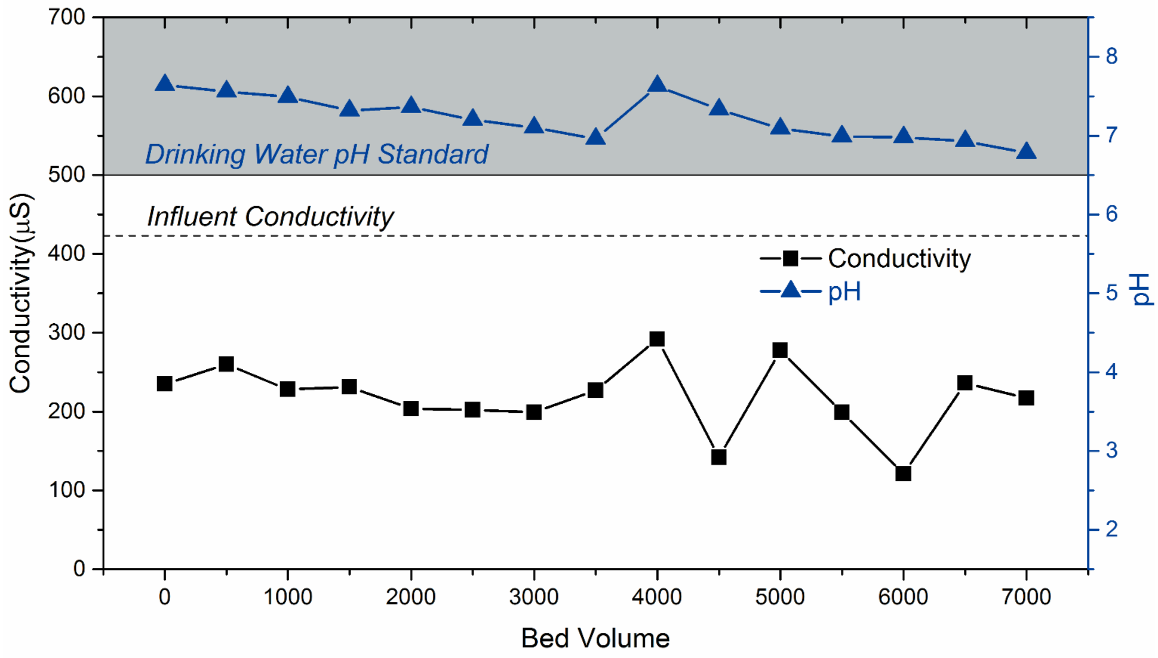


Figure 4.31. Effluent pH and conductivity history from HAIX-NanoZr treatment of groundwater from NDC (Cycle 1). Note: similar results were seen during Cycle 2-3. Tested by Jinze Li.

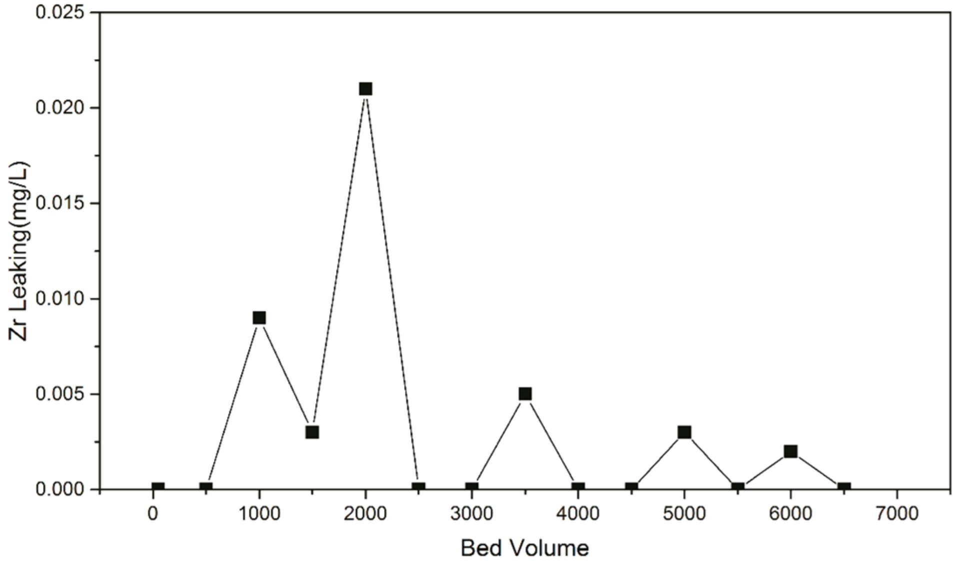


Figure 4.32. Zirconium concentration in the effluent of HAIX-NanoZr treatment of NDC groundwater (Cycle 1). Note: concentrations presented are below detection limits. Tested by Jinze Li.

4.2.8 *Regeneration*

HAIX-NanoZr resin was able to be used for multiple rounds of fluoride treatment because the fluoride capacity was regenerated through alkali desorption of fluoride ligands and re-protonation of metal oxide surfaces. Effluent fluoride history during regeneration by 1.5% NaOH is in **Figure 4.33**. Efficient regeneration with a sharp peak concentration happened in 10 BVs. A low volume of regenerant solution is important for minimizing waste production and decreasing operational costs. Similar regeneration effluents occurred during Cycle 2 & 3.

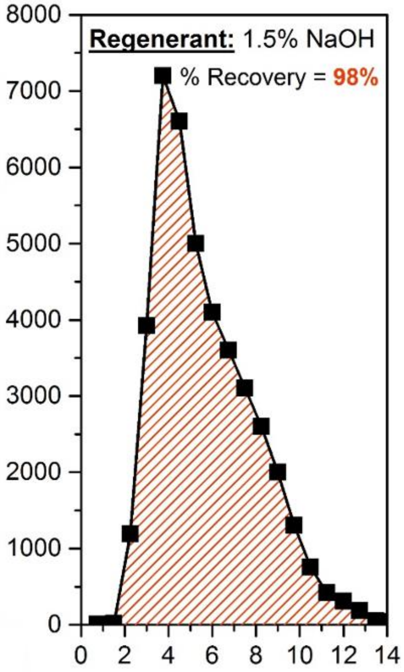


Figure 4.33. Fluoride effluent history during HAIX-NanoZr regeneration with 1.5% NaOH. Note: 98% recovery was achieved over multiple cycles. Tested by Jinze Li.

4.2.9 Spent Regenerant Treatment

Treatment of spent regenerant was considered a trivial matter of adding surplus aluminum or calcium salts until complete precipitation had occurred. However, in conversations with

West Bengal Public Health Engineering Department (WB PHED) authorities, regenerant treatment was found to be a significant concern, where explaining the basic theory was inadequate for them. This was the case even though the majority of their installed fluoride treatment systems fail within <6 months and the regenerant treatment process was detailed in previous reports and references. As such, additional lab testing was performed to demonstrate that high pH, high fluoride waste can easily be neutralized to groundwater conditions for pH and fluoride via addition of aluminum or calcium chloride.

The spent alkaline regenerant had an average fluoride concentration of 200-500 mg/L. Aluminum dosing and pH adjustment of the spent regenerant led to fluoride precipitation as a low volume sludge of aluminum hydroxide. At pH 6.5-7.0, residual dissolved fluoride concentration decreased to <5 mg/L, achieving 90-95% fluoride removal.

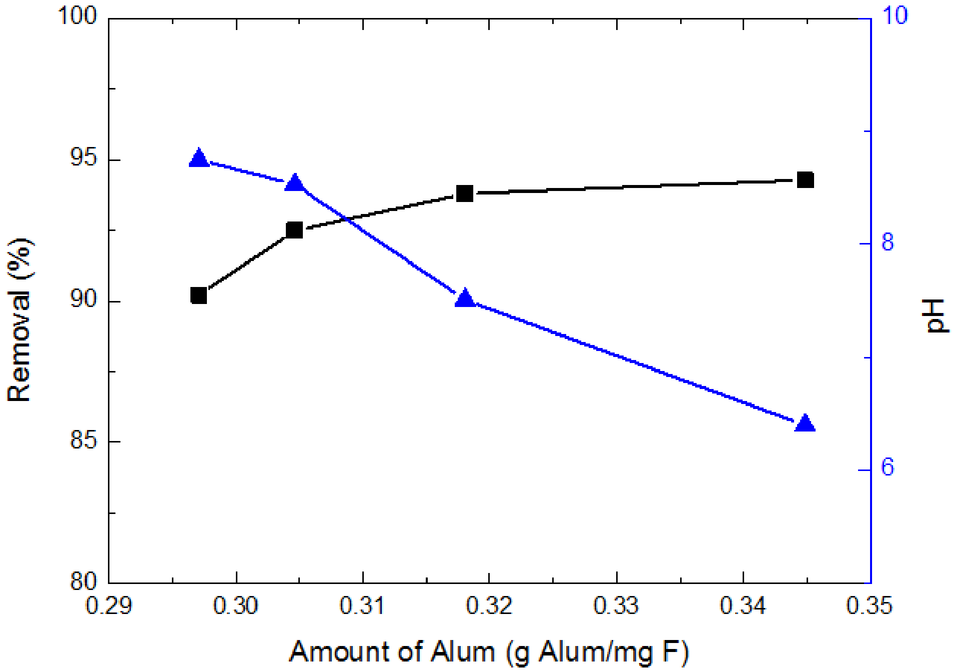


Figure 4.34. Fluoride removal and equilibrium pH after dosing alum to spent regenerant from HAIX-NanoZr. Tested by Jinze Li.

Besides low fluoride concentration in the regenerant solution, the precipitated solids must also prevent the leaching of fluoride across potential landfill conditions. To validate low fluoride leachability, an extended toxicity characteristic leaching procedure (TCLP) was performed on fluoride-rich aluminum precipitate from alum-treated spent regenerant, 38.75 mg F/g dry solids. The fluoride concentration in the leachate was consistently less than 1 mg/L for pH 3.01 – 9.04, **Figure 4.35**.

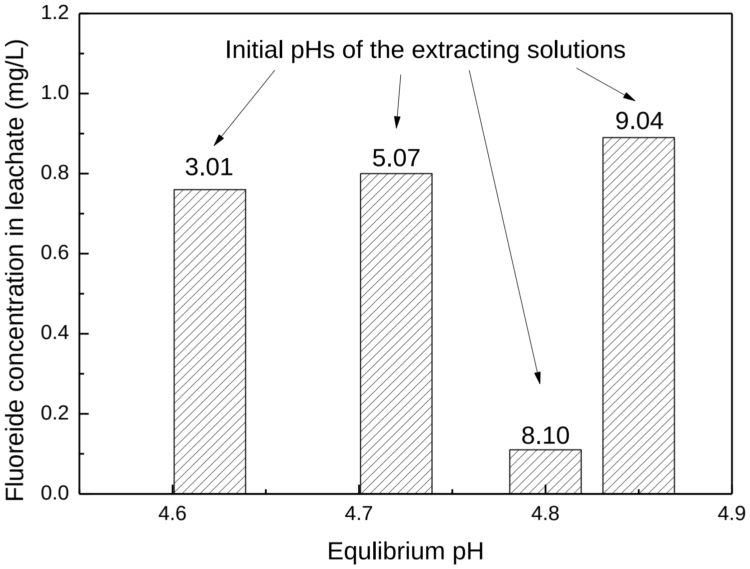


Figure 4.35. Fluoride concentration of the leachate after extended-TCLP testing of spent regenerant sludge. Tested by Jinze Li.

Batch testing was performed with synthetic fluoride regenerant waste with pH 13, [F$^-$] = 500 mg/L and different dosing amounts of aluminum and calcium chloride for a stoichiometric ratio of 2:1. After mixing on a shake table for 24 hr, the solution was filtered through a 0.45 µm filter to remove solid precipitates. After filtration, the fluoride concentration was tested. In real applications, fluoride concentration testing of waste regenerant may or may not be possible and it is likely that additional precipitant will be used as a safety factor. Solids from precipitation would be allowed to settle >24hr before draining off the supernatant.

5. Commercialization and Scale-Up: Creation and Growth of Drinkwell

5.1 Fulbright Beginnings

During the Spring 2012 semester, Dr. Arup K. SenGupta was based at IISc-Bangalore on a Fulbright Award and Minhaj Chowdhury was working with BRAC in Dhaka, Bangladesh. Both people were trying to address chronic arsenic tubewell contamination issues across the region by continuing their past work: Dr. SenGupta using activated alumina and HAIX-NanoFe in community-based systems with capital expenses supported through donations, Minhaj Chowdhury working with BRAC to implement household SONO filters purchased by households. Dr. SenGupta and Minhaj met in Kochi, Kerala, India at the South Asia Fulbright Conference when Dr. SenGupta was giving a talk on his work. Both people had something the other needed: as a professor Dr. SenGupta did not have the time or freedom to create and scale-up a water treatment company in India, Minhaj did not have a robust technology or operational model that was capable of being scaled-up. After conversations, Minhaj understood how the technology of Dr. SenGupta was superior and Dr. SenGupta had confidence in the commitment and passion of Minhaj to address the arsenic crisis through a scalable model.

Upon return to the US, both Minhaj and Dr. SenGupta restarted their "normal" professional activities, but Dr. SenGupta, Minhaj, and Mike German were able to meet at Lehigh and begin conversations about how to move forward a water treatment company that could create a scalable solution in the Indian subcontinent, **Figure 5.1**. Mike soon after went to India for his Fulbright-Nehru Fellowship (November 2012-Febuary 2014), where he would try and create the base in India for eventual Drinkwell activities in collaboration with the on-going work of Dr. SenGupta.

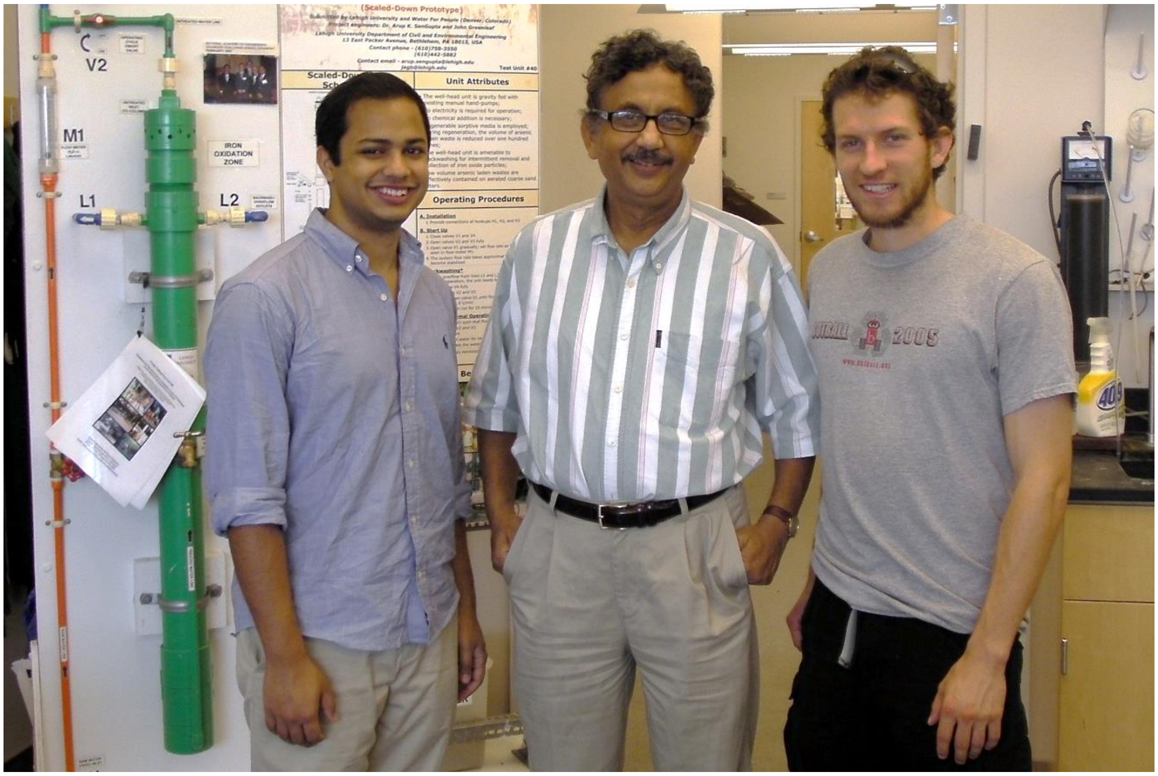


Figure 5.1. Image of the three co-founders of Drinkwell on September 3, 2012 (Minhaj Chowdhury, Dr. Arup K. SenGupta, and Mike German, Left-Right).

5.2 Early Fundraising

With the different locations and schedules of the three co-founders, the September 2012 meeting would be the only meeting until a board meeting on April 16, 2016, **Figure 5.2**. Drinkwell (WIST, Inc.) was incorporated as a C corporation in Delaware on June 11, 2013. Minhaj began getting connected with the start-up community in Boston and began participating in business plan competitions. Through The Indus Entrepreneurs (TiE) Network, Minhaj met Sanjay Verma who became our first investor and Board Member.

Much success was had on the business pitch circuit, **Figure 5.3**, which led to connections with other high net worth individuals (HNWIs) and funds who invested in Drinkwell.

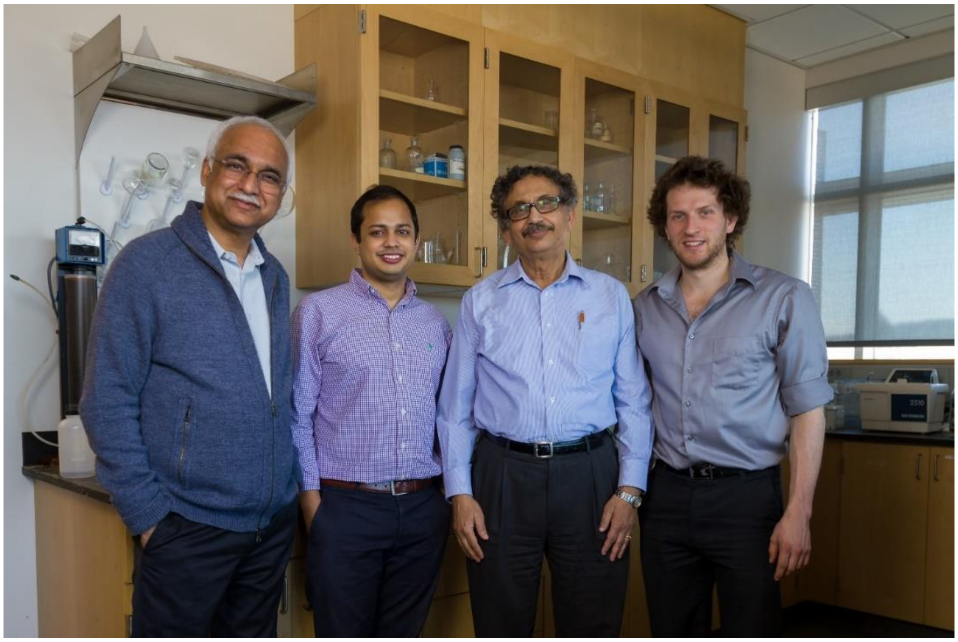
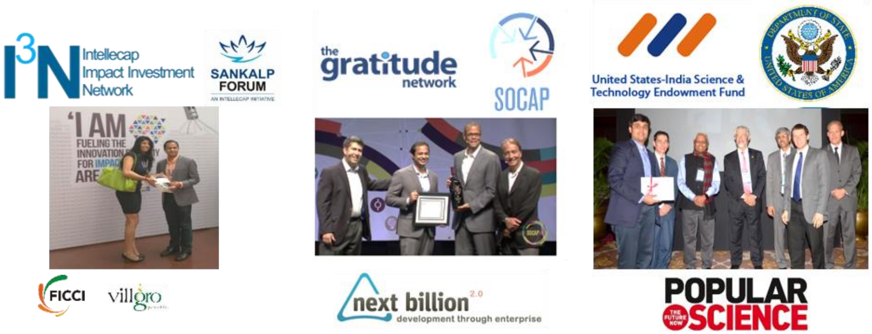


Figure 5.2. Board meeting on April 16, 2016 at Lehigh University with Sanjay Verma (first investor), Minhaj Chowdhury (CEO), Dr. Arup K. SenGupta (Research Director), and Mike German (General Supervisor or Development).



2015 Sankalp Competition 2nd Place

2014 Gratitude Health & Wellness Award at SOCAP

2014 US-India Sci Tech Endowment Fund Awardee

2015 Global Social Venture Competition 1st Place

2014 MassChallenge $100K Diamond Award

2015 Forbes 30 Under 30 Social Entrepreneur

Figure 5.3. Through the efforts of the board members and many mentors, Drinkwell earned top awards and prize money at several business pitch competitions from 2013-2016 (Total: ~$1M).

5.3 Steps to Indian Government Approval

In order to use HAIX-NanoZr in field systems that impact others, Dr. SenGupta licensed HAIX-NanoZr to Drinkwell for use in developing regions of the Indian subcontinent and East Africa. Then Drinkwell needed to license HAIX-NanoZr to a company capable of doing government contracts. But, efforts to commercialize any water treatment technology throughout India via public government tenders (or contracts), has the requirement that the technology first be approved by the governmental agency. In a bit of a "which came first, the chicken or the egg?" dilemma, the government, also, requires the water treatment company to have had a number of years of experience or a number of successfully completed installations, of sufficient scale, before being eligible for their tenders.

In order to receive governmental approval, there is a lengthy process between an eligible water treatment company and the governmental organization that involves the following major steps:

1) The company proposes the technology to the government through meetings and documentation, e.g., a detailed project report (DPR)
2) The government expresses interest in piloting a small community system by the company
3) The government selects an appropriate location for testing the new treatment technology
4) The company and government work with the local government and community for site preparation
5) The company installs, commissions, and operationalizes the system
6) The government chooses a time to inspect the installation and test the influent and treated water to confirm performance
7) The government tests the water and compiles a report based on their findings for whether or not the technology should be approved

Although straightforward in theory, actually working through the local governmental bureaucracy who lack the financial incentives of the water treatment company can be very time- and energy-intensive. Nevertheless, this process was followed through with the involvement of many individuals and, today, there are multiple sites across India that are using HAIX-NanoZr produced in Kolkata for pilot-scale testing and community-scale operations. Some of these locations are detailed in different sections and the performance results are featured in the Results section.

5.4 Development of Rite Water Partnership

While Dr. SenGupta and Minhaj were on Fulbright (Spring 2012), Mike participated in GBEN 498: Bench to Market where he reached out to Abhijeet Gan, President of Rite Water Solutions (I) Pvt. Ltd. (Nagpur, India), in very early efforts to commercialize HAIX-

NanoZr. Rite Water had earned government tenders across multiple states of India since they were established in 2004 and was ISO 9001:2008 certified. While in India on Fulbright, Mike met with Abhijeet on several occasions in Kolkata, Nagpur, and New Delhi to discuss potential options with HAIX-NanoZr and to test early material versions in their factory. During this time, Dr. SenGupta also met with Abhijeet in Kolkata and began communicating with him. But, without dedicated funding for workers and equipment, the partnership with Rite Water led to half-hearted testing and disappointing results that did not match previous efforts.

After attending and presenting at the “Indo-US Workshop on Water Quality and Sustainability” in IIT-Madras (Chennai, India) from Jan 6-10, 2013, Dr. SenGupta and Mike continued conversations with Nilesh Shah and Noopur Singh (US State Department) on how to see real progress and results. Mike was then invited to the "Rural Drinking Water Roundtable: Thirst for a business model" organized by the U.S. Embassy in partnership with the Department of Science & Technology (DST) and the Federation of Indian Chambers of Commerce & Industry (FICCI) in New Delhi on April 8, 2013. Mike invited Abhijeet to attend the workshop and conversations were continued on future HAIX-NanoZr expansion.

Through the continued connection, Mike was encouraged to apply to the United States-India Science & Technology Endowment Fund (US-ISTEF) for up to $400,000 in Fall 2013 on behalf of Drinkwell and a partner organization. Mike (Drinkwell) and Rite Water then submitted a joint application to US-ISTEF. Drinkwell licensed HAIX-NanoZr to Rite Water to improve the application potential. The partnership between Drinkwell and Rite Water was further formalized through a two-year exclusivity agreements as part of the application and awarding of the US-ISTEF grant, **Figure 5.4**.

Figure 5.4. Mike German (left) and Abhijeet Gan (right) holding the US-ISTEF certificate in Delhi NCR in November 2014.

After confirmation of support by US-ISTEF, Rite Water began to market HAIX-NanoZr as a novel arsenic and fluoride solution to various Public Health Engineering Departments (PHEDs) and Rural Water Supply and Sanitation (RWSS) offices in response to Expression of Interest (EOIs). There was significant interest in partial desalination with concurrent defluoridation (PDCD) by local governments and concerted efforts were made to pilot the technology and gain a firm grasp on the operational nuances.

5.5 Upskilling Local labor

For short-term or long-term production of HAIX-NanoZr and servicing of HAIX-NanoZr field systems, it is critical to have well-trained production staff and service engineers. While in India, Mike worked closely with Anil Shaw from May-August 2014. Anil had a disciplined, hardworking personality, but he had barely graduated high school and lacked significant prior work experience. Anil was trained in basic water chemistry, HAIX-NanoZr synthesis, use of laboratory glassware and instruments, and water system operations. Anil learned fast and asked many good questions. He quickly became a skilled service technician knowledgeable enough to train others confidently in the lab (**Figure 5.5**), to lead HAIX-NanoZr synthesis (**Figure 5.6**), and to repair community-scale installations (**Figure 5.6**). Anil was invaluable from March 2014-March 2017 for daily technical synthesis of HAIX-NanoZr in Kolkata and operation and maintenance of HAIX-NanoZr systems across India.

Figure 5.5. Anil Shaw instructing Dipu Sinha on basic lab principles (L). Anil Shaw measuring solutions with a pipette (R).

Figure 5.6. Mike German and Anil Shaw wearing respirators outdoors while testing synthesis procedures for HAIX-NanoZr (L). Anil Shaw and three production staff members he trained with a 20 L bucket of HAIX-NanoZr they produced (R).

Figure 5.7. Anil Shaw and Mike German installing an SAC-Fe system in Binimaypara (N. 24 Parganas, West Bengal); a technician from Ramkrishna Water Mission is partially off-screen.

5.6 Increasing HAIX-NanoZr Production at Picnic Gardens

With interest from multiple government PHEDs and financial support by US-ISTEF, a combination production, testing, and office facility was sought after by Drinkwell. The deposit was provided by and the rental agreement signed by Rite Water in early February 2015. But, the location required general repair, e.g., the waste drain was clogged, and construction to meet the needs for HAIX-NanoZr production, **Figure 5.8**.

Figure 5.8. Alleyway beside Picnic Gardens; lab counterspace in Picnic Gardens; 25L bags of Purolite C145; manufacturing space with multiple washing stations and FRP water treatment columns in the back (Clockwise from top left).

5.7 HAIX-NanoZr Production in Suqing (Wuxi, China)

In Fall 2015, an opportunity to go to China on a two-week business trip arose for Drinkwell because they had won the MassChallenge Diamond award ($100K) in Spring 2015. The trip was sponsored by MIT-CHIEF (Massachusetts Institute of Technology- China Innovation and Entrepreneurship Forum) as a means of connecting many MIT-based start-ups to markets and opportunities in China. With reoccurring manufacturing issues in India, Jinze Li and Mike German reached out to one of the best regarded ion exchange manufacturing companies in China, Suqing Resins (Jiangsu Suqing Water Treatment Engineering Group Co. Ltd.; Hetang, Jiangyin, Jiangsu, China), to discuss scale-up opportunities. Mike visited Suqing in August 2015 and Jinze Li was on the teleconference line for translation purposes. The facilities were found to be of high quality (clean, professional, well-labelled) and the annual production volume was enormous, **Figure 5.9**. The investment by Suqing on wastewater treatment and their caution with a new process and potential waste production, i.e., HAIX-NanoZr, provided confidence in their integrity. After a good impression from this initial meeting and many follow-ups, a Chinese-English Confidential Disclosure Agreement (CDA) was signed between Suqing and Lehigh for IP protection. Suqing then was instructed on the synthesis of HAIX-NanoZr, and produced pilot-scale samples of HAIX-NanoZr using different anion exchange resins; the virgin parent resins were also sent to Lehigh with the complete HAIX-NanoZr.

Figure 5.9. Mike with two hosts from Suqing after a day of conversations and tours; supersacks (1000 L) of finished resins; safety signage outside of buildings; clean buildings on-site (Clockwise from top left).

6. Up-scale Lehigh lab HAIX-NanoZr synthesis to India-based pilot-scale production (Aim 2)

6.1 Testing of HAIX-NanoZr from Thakurpukur in the US

In mid-August 2014, approximately 20 L of resins and 100 g Zr were brought back to Lehigh from Kolkata for analysis, characterization, and synthesis; multiple samples have been couriered by other travelers since that time. Specifically, HAIX-NanoZr resins made with three SBAs from three different manufacturers: Thermax A-27MP, Indion 810, and Doshion ASB 8040D. After acid digestion and ICP analysis, resins from the three manufacturers showed significantly different Zr content that were all significantly lower than HAIX-NanoZr made at Lehigh by Jinze Li, **Figure 6.1**. Between the resins produced in India, there was a 2.5x difference in Zr content between Thermax (2.5%) and Doshion (6.9%) resins. But, Doshion resin produced in India had 2x less Zr than the Purolite resin synthesized by Jinze Li.

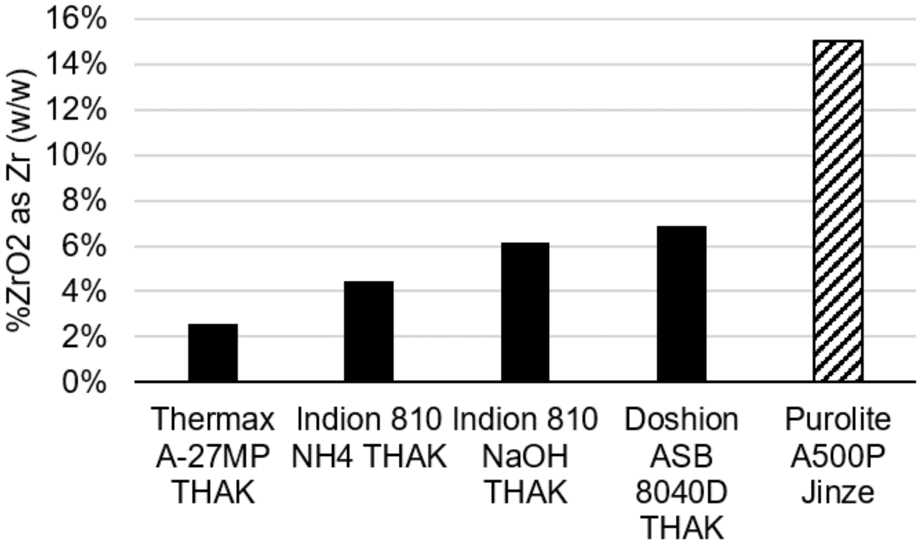


Figure 6.1. ZrO_2 content of four different types of HAIX-NanoZr manufactured in Thakurpukur (THAK)- Thermax A-27MP, Indion 810 with NH4OH, Indion 810 with NaOH, and Doshion ASB 8040D- and one manufactured by Jinze Li at Lehigh (Purolite A500P). ZrO_2 content of four different types of HAIX-NanoZr manufactured in

Thakurpukur (THAK)- Thermax A-27MP, Indion 810 with NH4OH, Indion 810 with NaOH, and Doshion ASB 8040D- and one manufactured by Jinze Li at Lehigh (Purolite A500P).

With the additional HAIX-NanoZr brought back to the US from India, samples were retreated with Zr from MEL and acid-alcohol solution for two different synthesis methods. In the first synthesis procedure (I), the resin was washed more before drying than in the second method (II). A comparison of the Zr content of the different types of HAIX-NanoZr made in Thakurpukur (THAK), Lehigh batch I (I), Lehigh batch II (II), and by Jinze Li (Jinze), are shown in **Figure 6.2**. The method of production in THAK and Lehigh I were less effective than Lehigh method II. Indion, Doshion, and Purolite all had similar Zr content with method II at Lehigh, but Thermax was not able to contain as much Zr. However, the small differences in the method of synthesis by Jinze had 25% greater Zr content, even though method II at Lehigh was “identical”. These discrepancies in final product emphasize the importance of consistent practices in production, even during non-quantitative steps such as decanting, drying, washing, etc.

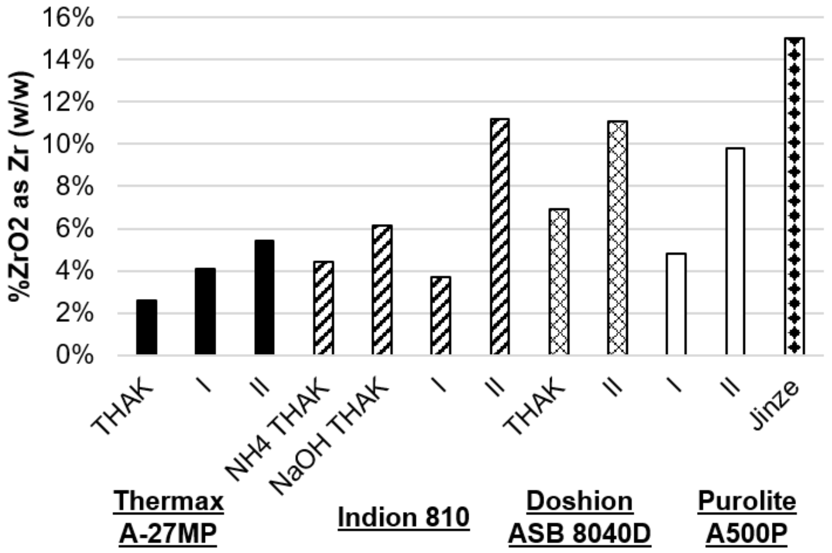


Figure 6.2. A comparison of Zr content between four parent SBAs impregnated with zirconium oxide under different conditions: in Thakurpukur (THAK), Lehigh conditions I (I), Lehigh conditions II (II), and by Jinze (Jinze).

More important than Zr content was the fluoride removal capacity. Spectroscopic characterization was not performed on resins from India because of cost limitations; it is conceivable that the ZrO_2 in some of the resins might not have the distribution, morphology, and/or size for optimal fluoride removal. Thus, rapid small scale column tests or RSSCTs were performed on several of the HAIX-NanoZr materials made in India and in the US to compare the impact of Zr content on fluoride removal capacity, **Figure 6.3**. Feed water for these tests was the synthetic version of water from Nakuru acidified to pH 4.5 to mimic WAC pre-treatment, but without having to install and regularly condition the WAC column.

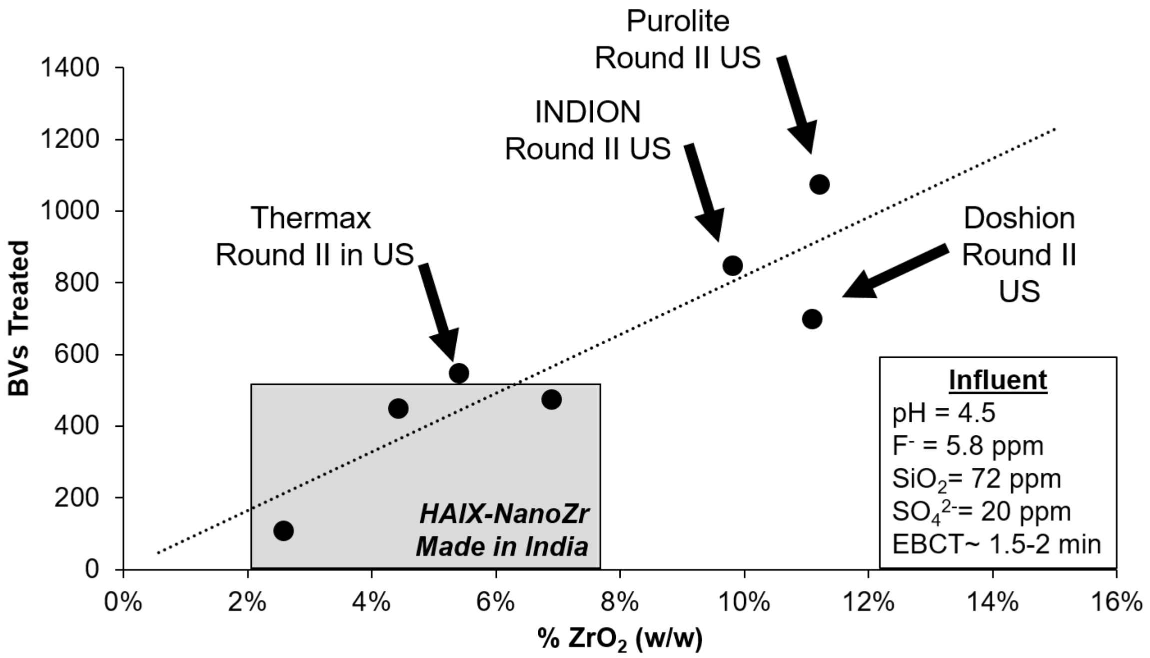


Figure 6.3. Comparison of packed-bed fluoride removal capacity of HAIX-NanoZr made from multiple manufacturers. Note the linear relationship between ZrO_2 content and volume of water treated.

In general, there is a clear linear relationship between Zr content of HAIX-NanoZr and the number of BVS of synthetic Nakuru water treated. Thus, the HAIX-NanoZr resins made in India fall to the bottom left of the curve and those made with method II in the US are at the top right. There was a stark difference between the fluoride removal capacity of HAIX-NanoZr made with Purolite and Doshion at Lehigh: 50% greater fluoride removal by Purolite with identical Zr content. Doshion is a smaller company and was a lower cost parent SBA resin. Qualitatively, Doshion ASB 8040D had a higher particle size distribution than any of the other resins; some of the resin “beads” received were like dust. Thus, from a non-scientific perspective, Doshion seemed to be a material of poorer quality and it was not surprising that this was manifested in lower fluoride removal capacity.

6.2 Production Quality in India since November 2014

Testing and production of HAIX-NanoZr continued at Thakurpukur through September 2015. During this time, variations on all aspects of synthesis were performed by Anil Shaw under the guidance of Dr. Prasun Chatterjee, Dr. Arup K. SenGupta and Mr. Mike German to improve fluoride removal capacity; variations included chemical dosing/ratios, handling (decanting, drying, washing), parent resin types. There were some periods with minimal-slow HAIX-NanoZr production tests because of a lack of raw materials due to a poor supply chain, field work at various locations, and/or repairs at the new Picnic Gardens facility.

During material performance testing from March-August 2015, there was significant variation in fluoride removal between the different batches of HAIX-NanoZr produced by Anil Shaw, **Figure 6.4**. Some batches had surprisingly long effluent histories (not graphed) near the fluoride treatment limit: Purolite A500P-3 (31,000 BVs), Indion 830-4 (10,500 BVs), Indion 810-1 (20,500 BVs). Influent test conditions- pH, fluoride, and conductivity- varied over different tests, as expected with groundwater changing over time. With respect to parent resin type or time of HAIX-NanoZr production, there were no clear changes in fluoride removal performance. It is possible that influent conditions changed during tests: there was a lack of influent conditions throughout.

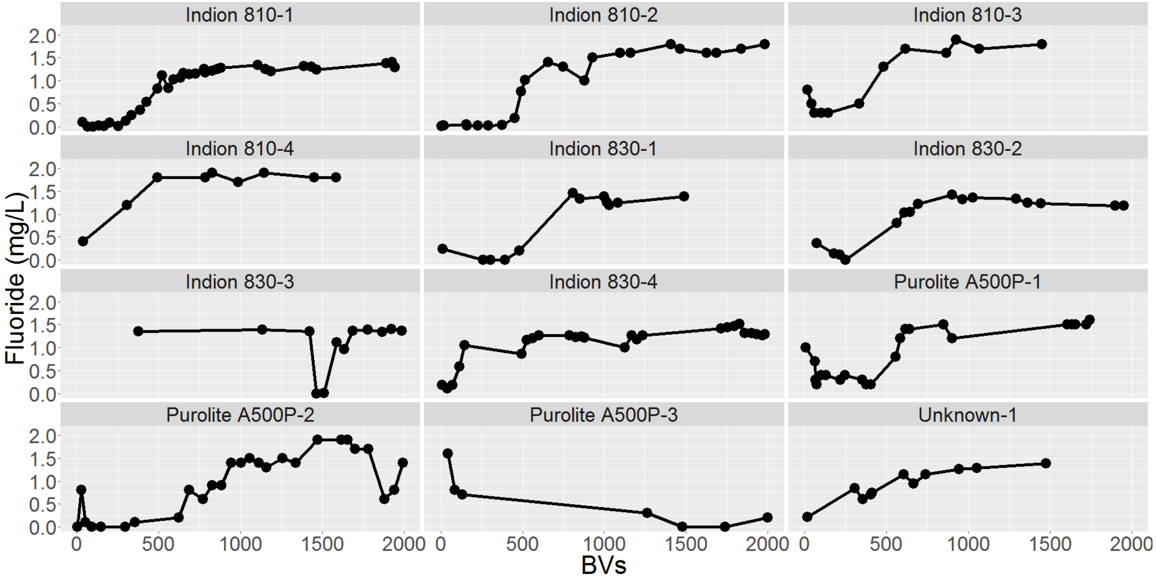


Figure 6.4. Fluoride treatment history (2000 BVs) of twelve different batches of HAIX-NanoZr produced in Picnic Gardens by Anil Shaw from March-August 2015.

Eventually, HAIX-NanoZr production began at Picnic Gardens in late September 2015,

Table 6.1, and material went to immediate use in treatment systems,

Table 6.2. Out of a total 2350 L of HAIX-NanoZr given to Rite Water, 1800 L was issued for community system FRUs (AP Tender) on 28th June 2016. Other HAIX-NanoZr systems were also installed in Haridaspur, Nalhati, West Bengal (fluoride); Machatora, Bankura, West Bengal (fluoride); Jortarai, Rajnandgaon, Chhattisgarh (arsenic).

Table 6.1. Production volume (L) records of HIX variations (HCIX-Fe, HAIX-NanoFe/Zr, HAIX-NanoZr) at Picnic Gardens from September 2015-July 2016.

	HCIX-Fe	HAIX-NanoFe/Zr	HAIX-NanoZr
9/27/2015	400	0	150
10/4/2015	300	0	100
10/11/2015	200	0	50
10/18/2015	200	0	0
10/25/2015	0	0	0
11/1/2015	300	0	150
11/8/2015	300	0	200
11/15/2015	300	0	200
11/22/2015	400	0	50
11/29/2015	600	100	0
12/6/2015	500	0	0
12/13/2015	300	0	50
12/20/2015	100	0	0
12/27/2015	400	0	0
1/3/2016	0	50	0
1/10/2016	0	0	0
1/17/2016	100	0	0
1/24/2016	500	0	50
1/31/2016	100	0	0
2/7/2016	25	0	100
2/14/2016	0	0	150
2/21/2016	0	0	100
2/28/2016	0	0	300
3/6/2016	0	100	0
3/13/2016	0	0	50
3/20/2016	0	0	250
3/27/2016	0	0	150
4/3/2016	0	0	100
5/30/2016	0	0	0
6/30/2016	0	0	0

Table 6.2. Volumes (L) of stored HIX resin at different times and points in the synthesis.

Description	**Stock (Dec 2016)**	**Synthesize (Jan– Mar 2016)**	**Synthesize (April – June 2016)**	**Project Deliveries (Sept 2015-June 2016)**	**Stock (June 2016)**
HCIX-Fe	5100	725	0	4000	1825
HAIX-NanoFe/Zr	100	150	100	175	175
HAIX-NanoZr	1050	1250	300	2350	250

Throughout production of new materials at Picnic Gardens, column tests with spiked groundwater were performed to check and validate HAIX-NanoZr arsenic and fluoride removal capacity, as seen in **Table 6.3**/**Figure 6.5** and **Table 6.4**/**Figure 6.6**, respectively.

Table 6.3. Summary of specific HAIX-NanoZr batches that underwent packed-bed testing for arsenic removal by Anil Shaw and Dr. Prasun Chatterjee. Note: Greater than symbols indicate lengthy tests that were ended prematurely before reaching breakthrough of the current permissible limit in the absence of alternative options (As = 50 µg/L).

Production Date	**Parent Resin**	**HAIX-Nano**	**Influent As (µg/L)**	**Influent pH**	**10 µg/L BVs**	**50 µg/L BVs**
Dec 2015	Indion 860S	Fe/Zr	250	6.5	3500	>8000
Jan 2016	Indion 890	Fe/Zr	220	6.9	3000	>8000
Feb-Mar 2016	INA 100	Fe/Zr	200	5.5	4000	>8000
Mar-Apr 2016	INA 100	Fe/Zr	200	4.5	8000	>11,000

Table 6.4. Summary of specific HAIX-NanoZr batches that underwent packed-bed testing for fluoride removal by Anil Shaw and Dr. Prasun Chatterjee. Note: Greater than symbols indicates lengthy tests that were ended prematurely before reaching breakthrough.

Production Date	**Parent Resin**	**HAIX-Nano**	**Influent F (mg/L)**	**Influent pH**	**1.5 mg/L BVs**
Jan 2016	Indion 890	Zr	18	3.5	>3700
Feb-Mar 2016	Indion 890	Zr	15	3.5	3200
Jul 2016	INA 100	Zr	22	4.0	3150
Aug 2016	Indion 860S	Zr	14	3.5	>2800

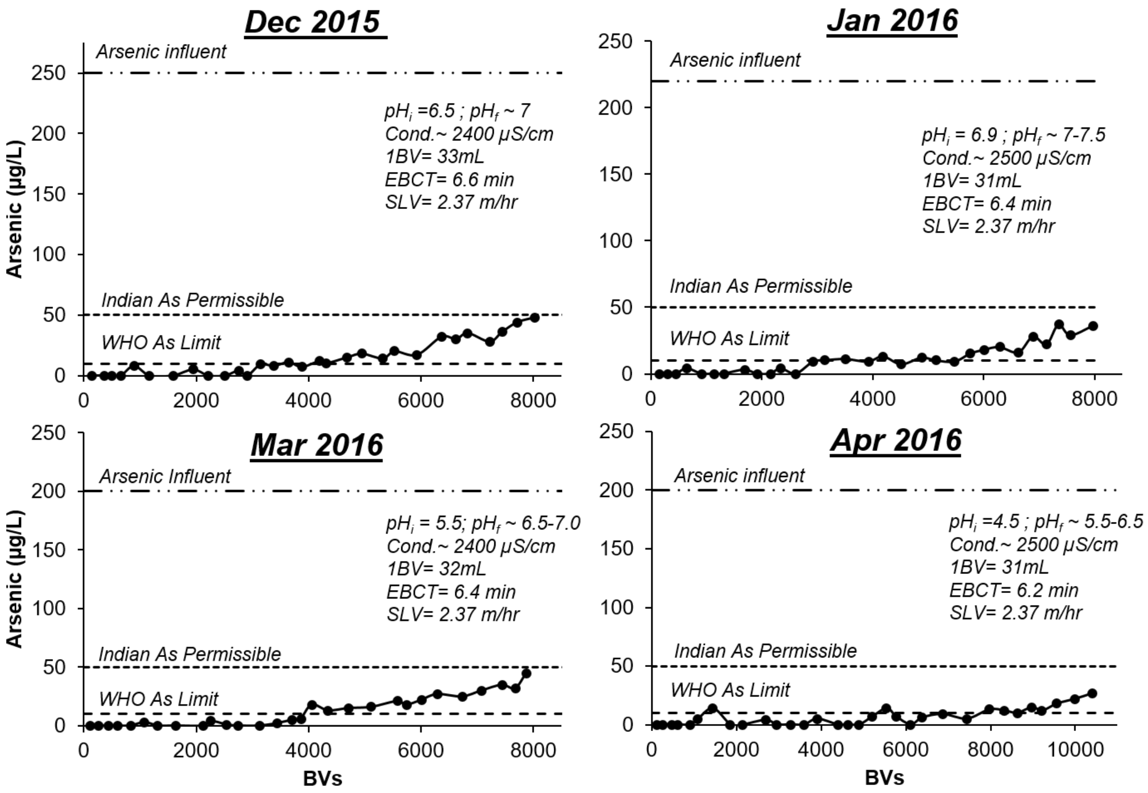


Figure 6.5. Arsenic effluent from batches of HAIX-NanoFe/Zr, summarized in Table 6.3, when treating groundwater spiked with arsenic: December 2015, January 2016, April 2016, March 2016 (clockwise from top left).

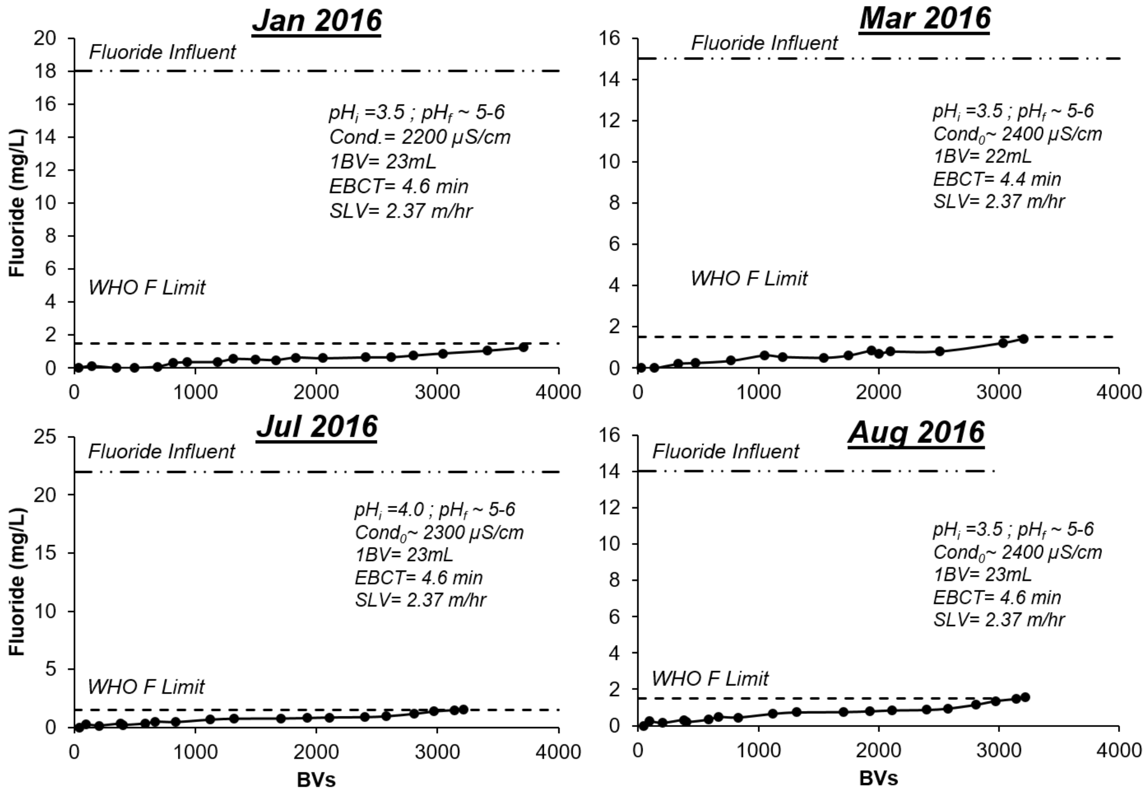


Figure 6.6. Fluoride effluent from batches of HAIX-NanoZr, summarized in Table 6.4, when treating groundwater spiked with fluoride: January 2016, March 2016, August 2016, July 2016 (clockwise from top left).

6.3 HAIX-NanoZr Sorbent: Pilot-Scale Field Testing (India)

6.3.1 Piraya, Maharashtra

6.3.1.1 Background

Piraya is a small community outside Umred, about 2-3 hr drive from Nagpur (Rite Water headquarters). Rite Water had previously installed an electrolytic defluoridation (EDF) system and a concrete superstructure for the local community. Given the ownership, operation, and maintenance of the EDF system by Rite Water, and the vicinity of Piraya to Nagpur, it was an ideal location for the installation of the first field test of HAIX-NanoZr (November 5-7, 2014).

6.3.1.2 Design and Installation

The system components were first assembled at the Nagpur factory before car transport to Piraya, based on the system sketch in **Figure 6.7**.

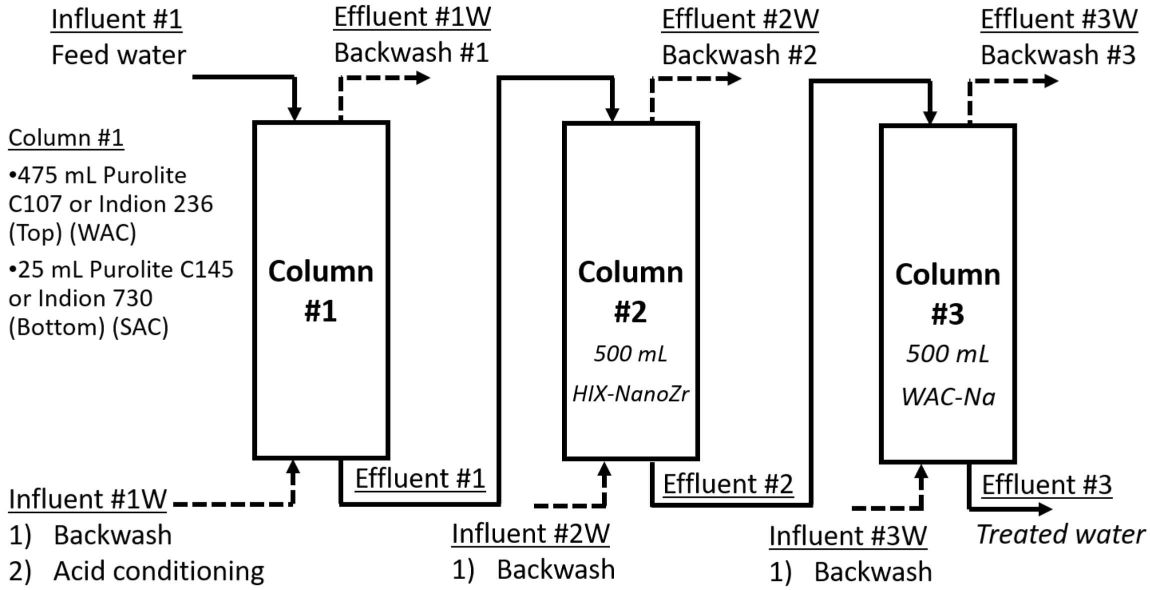


Figure 6.7. Initial three-column design for testing of HAIX-NanoZr with Rite Water.

A 250 L storage tank was placed on the roof and connected to the original raw water storage tank in order to provide raw water for the pilot-scale system on a batch basis. The system comprised of three-1 L columns in series made from 4” PVC pipes and caps with PLEX tubing and connections. A funnel was connected to the first column via flex tubing to enable chemical dosing. Originally, in **Figure 6.8**, the three columns contained: I) weak acid cation exchange resin in H^+-form; II) HAIX-NanoZr resin (made at Lehigh University); and, III) weak acid cation exchange resin in Na^+-form. The third column was soon emptied, placed in between Column I and Column II and used for carbon dioxide removal as a “decarbonator” to better demonstrate partial desalination at the small-scale,

Figure 6.9. The original goal of Column III for pH adjustment was deemed to have insignificant future operational issues, versus the more active requirements of Column I and II and the need to prove partial desalination claims.

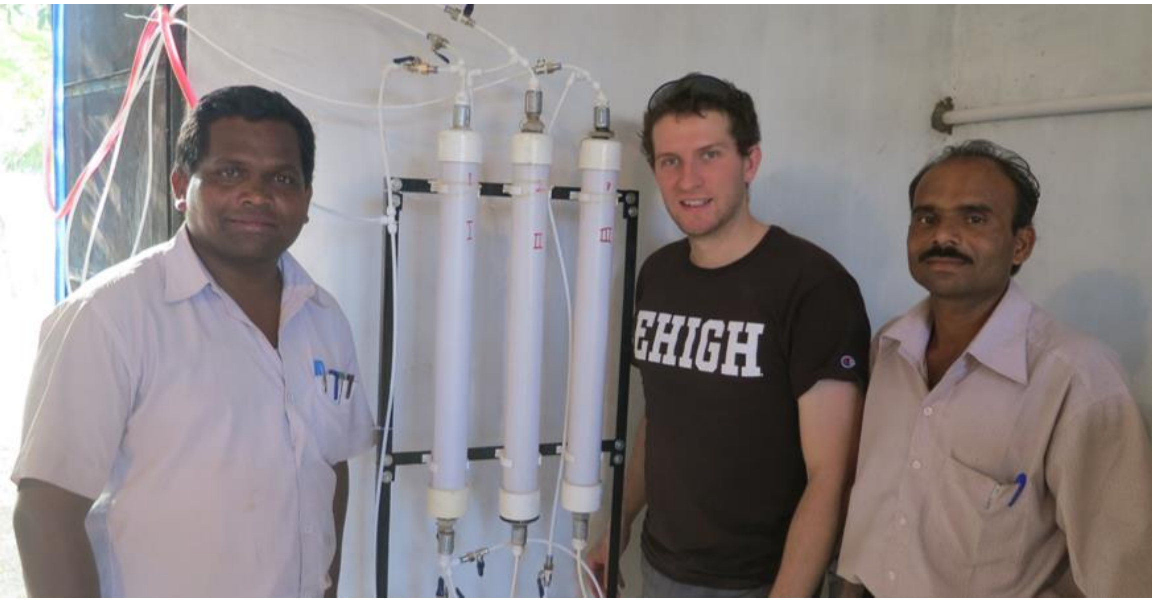


Figure 6.8. Two Rite Water installers (L-Rohit Ade, R- Hitesh Mehta) and myself after original construction of the three-column system on November 6, 2014.

Figure 6.9. (L) Original construction design of three-column system; (R) Modified three-column system to include a decarbonator.

6.3.1.3 Testing

With available funding, a dedicated B. Tech. Chemical Engineer graduate (Vaibhav Mathankar) was hired to do daily system operations and influent/effluent water quality testing. A mixture of the following test equipment was used by Vaibhav, depending on the availability of test reagents: pen-type pH meter (local), pen-type conductivity meter (local), HACH DR/850 Colorimeter, HACH Fluoride Ion Selective Electrode (ISE), fluoride field test kit, hardness field test kit (Prerna Laboratory, Mumbai), and alkalinity field test kit (Prerna Laboratory, Mumbai), **Figure 6.10**. It was only possible to hire Vaibhav, install the pilot system, and purchase the HACH ISE because of the funding from US-ISTEF secured by Mike (Drinkwell) and Rite Water. Through remote guidance via communication with Abhijeet and direct e-mail/WhatsApp with Vaibhav, regular testing was guided and monitored from November 8, 2014-April 16, 2016 over four cycles of exhaustion-regeneration. Testing did not always occur on consecutive days, but when tested there was either 150 BVs or 300 BVs passed, in 50 BV increments.

Figure 6.10. (L) HACH DR/850 used for fluoride testing along with SPADNS solution; (R) group photo of Rite Water installers, local community observers, and myself.

6.3.1.4 Results

Although Vaibhav had training as a chemical engineer, he did not have previous experience with ion exchange or researching packed-bed treatment systems. Without being present at the site and not having a past working relationship, communications between Mike and Vaibhav sometimes lagged in terms of operations: when to start/end a cycle, which instrument was being used for testing, why certain trends/values were seen, etc. This was also the first serious effort by Rite Water for testing HAIX-NanoZr, and the operational nuances were not understood at first. As such, there are noticeable operational differences between the four consecutive cycles. In terms of runtime, the number of BVs treated per cycle varied: #1) 5650; #2) 10,350; #3) 9900; and, #4) 2400. Throughout all cycles, after each 50 BVs of groundwater was treated, Column 1 was conditioned with 1 BV of 2.5% HCl to protonate the WAC functional groups (40% capacity) for continued pH reduction with concurrent hardness and alkalinity removal. Column #1 was then washed until influent and effluent conductivity were identical, to eliminate residual acid.

Summary water chemistry tables of influent (**Table 6.5**), Column #1 effluent (**Table 6.6**), and Column #2 effluent (**Table 6.7**) give initial insight into the performance of each column. The highlighted cells in **Table 6.5**-**Table 6.7** indicates which parameters are beyond the Indian water requirement or permissible limit (IS 10500). From the average values throughout the cycles. The following broad observations can be made:

- Column #1 (WAC) reduced TDS, hardness, and alkalinity to within water quality standards, and reduced pH values beyond the limits.

- Column #2 reduced fluoride to within water quality standards. Concurrently, the effluent pH value was increased closer to the water quality standards, but on average was not within water quality standards

Table 6.5. Number of BVs treated and average influent water chemistry for Cycle 1-4. Note: * = fluoride field test kits were heavily used during Cycle 3; highlighted cells greater than permissible limits.

Cycle #	**pH**	**TDS (mg/L)**	**F (mg/L)**	**Hardness (as mg/L $CaCO_3$)**	**Alkalinity (as mg/L $CaCO_3$)**
1	7.7 ± 0.3	515 ± 20	2.67 ± 0.69	140 ± 40	455 ± 85
2	7.8 ± 0.3	565 ± 75	2.20 ± 0.47	135 ± 35	400 ± 60
3	8.0 ± 0.2	605 ± 25	2 ± 0.5*	150 ± 20	400 ± 45
4	8.1 ± 0.1	615 ± 15	2.77 ± 0.28	140 ± 10	410 ± 15

Table 6.6. Average effluent (Column #1) water chemistry for Cycle 1-4. Note: * = fluoride field test kits were heavily used during Cycle 3; highlighted cells greater than permissible limits.

Cycle #	**pH**	**TDS (mg/L)**	**F (mg/L)**	**Hardness (as mg/L $CaCO_3$)**	**Alkalinity (as mg/L $CaCO_3$)**
1	5.5 ± 0.9	230 ± 50	2.58 ± 0.73	25 ± 15	90 ± 50
2	5.2 ± 0.7	210 ± 40	1.81 ± 0.73	15 ± 10	45 ± 15
3	5.4 ± 0.9	240 ± 40	2 ± 0.25*	5 ± 0	70 ± 40
4	5.0 ± 1.3	260 ± 70	1.64 ± 0.29	5 ± 0	60 ± 30

Table 6.7. Average effluent (Column #2) water chemistry for Cycle 1-4. Note: * = fluoride field test kits were heavily used during Cycle 3; highlighted cells greater than permissible limits.

Cycle #	**pH**	**TDS (mg/L)**	**F (mg/L)**	**Hardness (as mg/L $CaCO_3$)**	**Alkalinity (as mg/L $CaCO_3$)**
1	6.0 ± 0.3	205 ± 55	1.25 ± 0.49	30 ± 15	115 ± 45
2	5.6 ± 0.4	185 ± 45	0.96 ± 0.42	20 ± 15	70 ± 25
3	6.0 ± 0.3	210 ± 60	1 ± 0.5*	5 ± 0	80 ± 25
4	6.1 ± 0.2	255 ± 85	0.63 ± 0.39	10 ± 5	90 ± 15

To give a clearer overview of HAIX-NanoZr performance over time, a moving average of effluent histories for fluoride and percent reduction of TDS are presented in **Figure 6.11** & **Figure 6.12**. A moving average is necessary to visualize and distinguish multiple cycles on the same figure because of the number of data points and variations during testing.

Figure 6.13 has a history of fluoride accumulation on HAIX-NanoZr during Cycle #1-4; note the difference in Cycle 3. Figures of effluent histories from each cycle are available in the **Chapter 5 Appendix**.

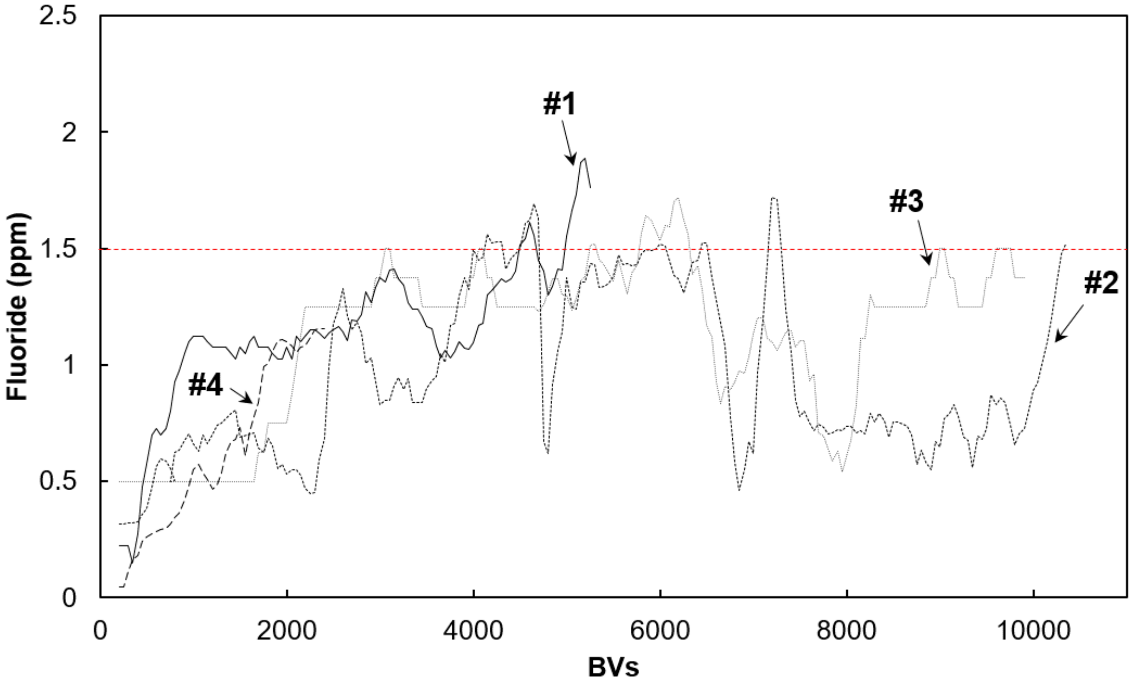


Figure 6.11. Moving average (period = 4) history of effluent fluoride from Column #2 of the HAIX-NanoZr pilot system at Piraya during Cycles #1-4.

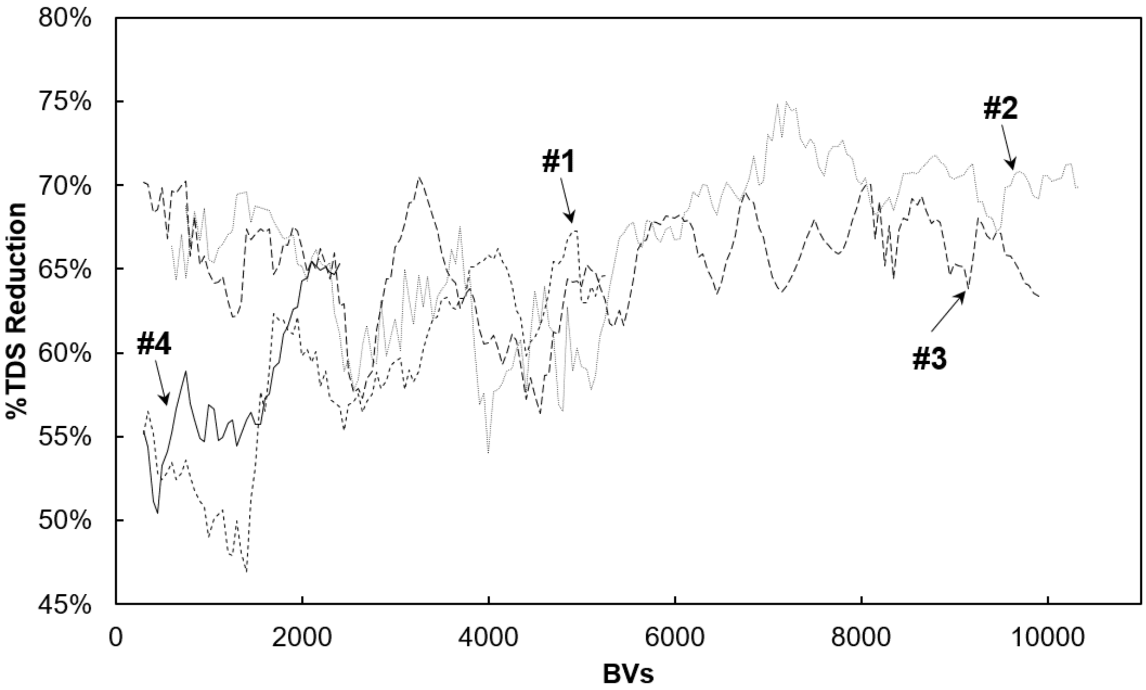


Figure 6.12. Moving average (period = 6) history of % TDS reduction of the influent by the HAIX-NanoZr pilot system at Piraya during Cycles #1-4.

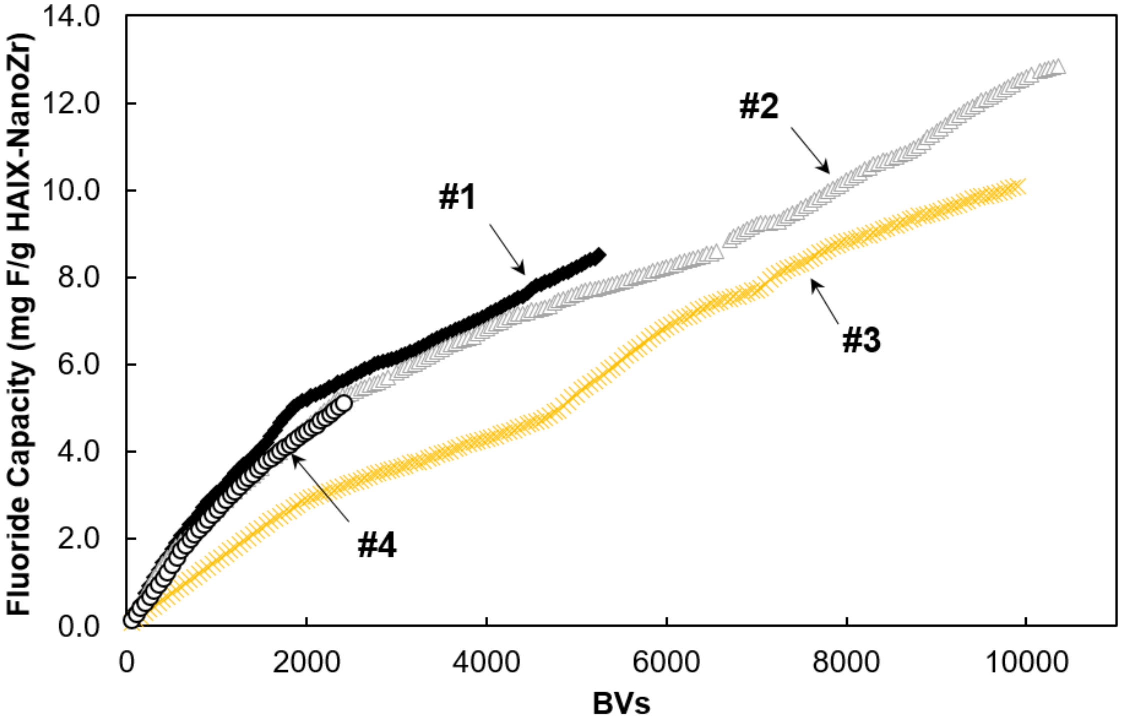


Figure 6.13. Fluoride capacity history of the HAIX-NanoZr pilot system at Piraya during Cycles #1-4.

6.3.1.4.1 Cycle 1 (February 13, 2015-April 14, 2015)

After initial installation in November 2014, testing began on February 13, 2015 and Cycle 1 continued for 5650 BVs. Fluoride measurements from Feb 13- Feb 28 were conducted with field test kits. From Feb 28-end of Cycle 1, fluoride measurements were performed with a HACH Ion Selective Electrode, **Figure 6.14**. Similar results for TDS and fluoride were seen during other cycles, **Chapter 5 Appendix**.

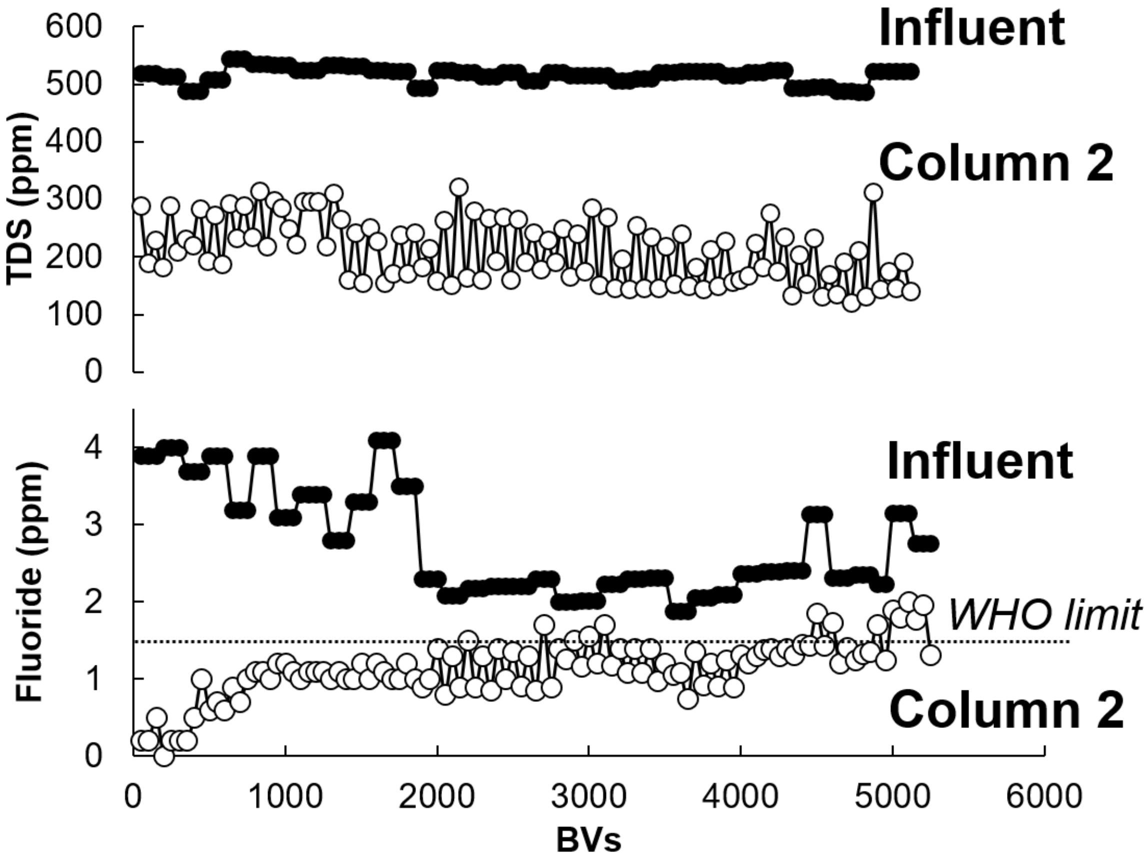


Figure 6.14. TDS and fluoride history (raw and treated) during groundwater treatment by HAIX-NanoZr in Piraya.

There are regular oscillations in pH after Column 1. The regularity suggests the cause is due to timing of testing versus timing of acid dosing of Column #1. The pH variations were not present after passing through HAIX-NanoZr. The standard deviation of effluent pH value decreased 3x between Column #1-#2. Less consistently than pH oscillations, were fluctuations in alkalinity, hardness, and TDS after Column 1 and 2 without a pattern. Even with said variations in data, the consistent trend was: 1) TDS, alkalinity, and hardness were reduced 50%; 2) effluent pH is near potable standards (without a third column pH adjustment step); and, 3) effluent fluoride is reduced from 2-4 mg/L to below WHO standards for over 4500 BVs. At the end of Cycle 1, HAIX-NanoZr had a calculated fluoride loading of 15 mg F/g resin. HAIX-NanoZr in Column #2 was regenerated with 10 BVs 2% NaOH/ 2% NaCl followed by dilute HCl until effluent pH decreased to 5 on April 27, 2015. Waste regenerant was not collected nor tested. But, regeneration efficiency can be estimated by comparing fluoride capacity of HAIX-NanoZr of Cycle 1 vs. Cycle 2.

6.3.1.4.2 Cycle 2 (May 21, 2015- November 19, 2015)

The fluoride electrode ran out of buffer solution at the end of Cycle 1 (April 29). From April 29-May 2, 400 BVs of feed water were treated, but field test kits were attempted to be used that could only report <0.5 mg/L or >2.0 mg/L. After seeing the lack of precision in the data, Mike immediately cancelled testing until proper testing instruments were available. Treatment by HAIX-NanoZr was continued on May 21, 2015. Cycle 2 was operated for 10,350 BVs. With the much longer cycle length, HAIX-NanoZr had a calculated fluoride content of 23 mg F/g resin. The fluoride content during Cycle 2 was

50% greater than during Cycle 1, indicating regeneration was performed successfully after Cycle 1.

The raw water pH and TDS were significantly higher on average in Cycle 2 than in Cycle 1, but the fluoride was significantly lower. Near 4700 BVs there was a notable change in influent and effluent water chemistry. Influent TDS increased 27%: 490±30 mg/L (0-4700 BVs) to 625±40 mg/L (4750-10,350 BVs). pH effluent from Column #1 was lower and more variable after 4700 BVs: the average pH value decreased from pH 5.4±0.3 (before) to pH 5.0±0.8 (after). Concurrently, influent raw water pH increased slightly (+0.3) without change in standard deviation. Treated alkalinity and hardness also decreased significantly after 4700 BVs: 25±10 mg/L as $CaCO_3$ to 10±5 mg/L as $CaCO_3$. But, influent alkalinity became more variable, and hardness increased: 400±40 mg/L as $CaCO_3$ to 400±75 mg/L as $CaCO_3$ (alkalinity); 115±30 mg/L as $CaCO_3$ to 155±35 mg/L as $CaCO_3$ (hardness). Raw fluoride decreased and became less variable: 2.45±0.55 mg/L to 2.00±0.20 mg/L. After closer analysis, the change is likely due to changes in system operation, but not due to testing error. No specific system or operational changes were noted in late September 2015.

6.3.1.4.3 Cycle 3 (December 17, 2015-March 10, 2016)

Cycle 3 was operated by Vaibhav for 10,000 BVs with minimal direct communication with Mike. The influent changed significantly at 1000 BVs, but was thereafter consistent until the end of the cycle. It was not realized until 2800 BVs into Cycle 3 that operations had changed and a fluoride field test kit was being used. Lack of communication and dedicated resources led to fluoride field test kits being used for the majority of Cycle 3. As such, influent values have a great possible range ≥2 mg/L and effluent fluoride values alternating between 1 mg/L and 1.5 mg/L do not give a clear indication of HAIX-NanoZr performance. At the end of the cycle, the HAIX-NanoZr fluoride content was 10 mg/g resin, but the poor fluoride measurements make resin fluoride capacity calculations unreliable in comparison to previous cycles and the capacity cannot be used as a surrogate for regeneration efficiency. Notably, when comparing the fluoride capacity history of Cycle 3 versus the other cycles, it has a lower initial slope and is lower on average.

6.3.1.4.4 Cycle 4 (March 26, 2016-April 16, 2016)

Cycle 4 was run as a confirmation that HAIX-NanoZr had not degraded in fluoride capacity because of the inconclusive Cycle 3 results from field test kits. Thus, Cycle 3 was the shortest cycle and was stopped after the fluoride effluent and fluoride capacity was seen to be similar to Cycle 1-2. Cycle 4 ended after 2400 BVs, before the effluent fluoride concentration reached breakthrough (1.5 mg/L); the final fluoride content was 5 mg/g. The pH, TDS, and alkalinity from Column #1 alternated sharply, likely because tests alternated before and after acid conditioning. However, these alterations did not affect the effluent fluoride concentration or pH value from Column #2.

6.4 Suqing Resins

Upon receipt of HAIX-NanoZr and the parent anion exchange resins, the Zr content of the two batches of HAIX-NanoZr were analyzed to be 10%-11% ZrO_2, comparable to HAIX-

NanoZr with parent resins from other manufacturers produced at Lehigh. Multiple batch fluoride capacity tests were performed of several Suqing HAIX-NanoZr samples versus using Purolite at Lehigh. However, the challenge of comparing batch test results is to make sure the final water chemistry is identical, especially given the high sensitivity of Zr fluoride capacity to pH. Over twenty separate batch tests, while trying to maintain constant final conditions, the pH value ranged from pH 3.0-5.5. But, when visualized, **Figure 6.15**, it was easy to determine that neither the parent resin nor batch of production were important factors in fluoride capacity versus final pH. The five different materials all fell along a similar inverse parabola that peaked slightly above the pK_a of fluoride (pK_a= 3.17). With improvements in production capacity in Kolkata vs. demand, HAIX-NanoZr was not purchased from Suqing, as of March 2017. But, it is valuable to know that synthesis of HAIX-NanoZr was performed well by a large manufacturer of different ion exchange resin and yielded performance as expected.

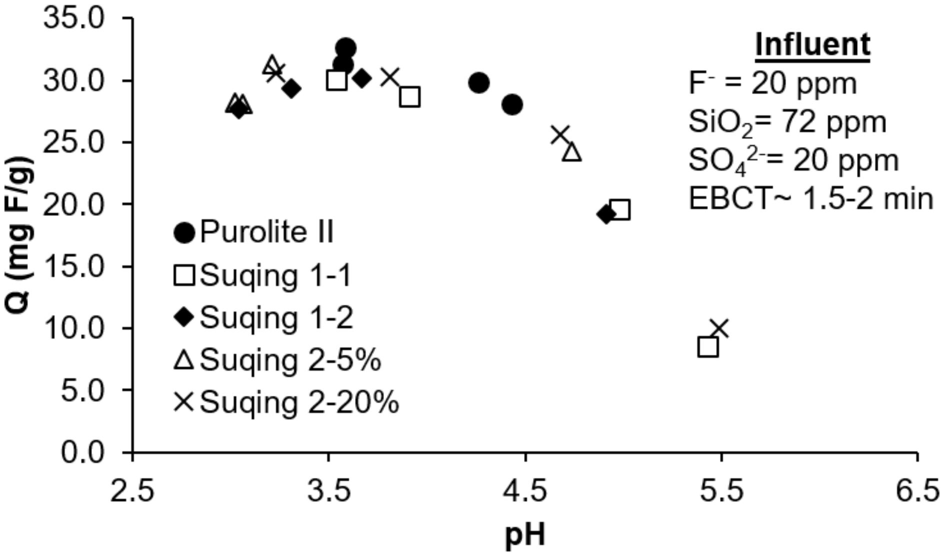


Figure 6.15. Comparison of fluoride batch capacity of HAIX-NanoZr made with SBA from Purolite and Suqing. Note the Suqing resins were made in two different batches (1 and 2) with two different washing techniques in Batch 1 (1-1 and 1-2) and two different alcohol concentrations in Batch 2 (2-5% and 2-20%).

6.5 Kenya (AvoGlobal): 2015-Present

6.5.1 Lab-Scale Test

After several meetings with the co-founders of AvoGlobal, Charles Ochola (Lehigh ’01 Ph.D.) and Christine Martey-Ochola (Lehigh ’03 Ph.D.), a decision was made to test HAIX-NanoZr in Kenya as a possible fluoride solution. During initial research studies, Ivy Otieno (AvoGlobal, Lehigh ’12 MS) constructed and operated a two-column, packed-bed system with 1L-WAC (Column #1) and 1L-HAIX-NanoZr (Column #2) in Nairobi, Kenya. The HAIX-NanoZr was made at Lehigh by Mike using Purolite parent anion exchange resin.

During operation, the majority of water quality parameters were not tested due to a lack of resources and funding. Over three months of pilot testing (April-June 2015), the fluoride effluent history was below 1.5 mg/L for >2000 BVs, **Figure 6.16**.

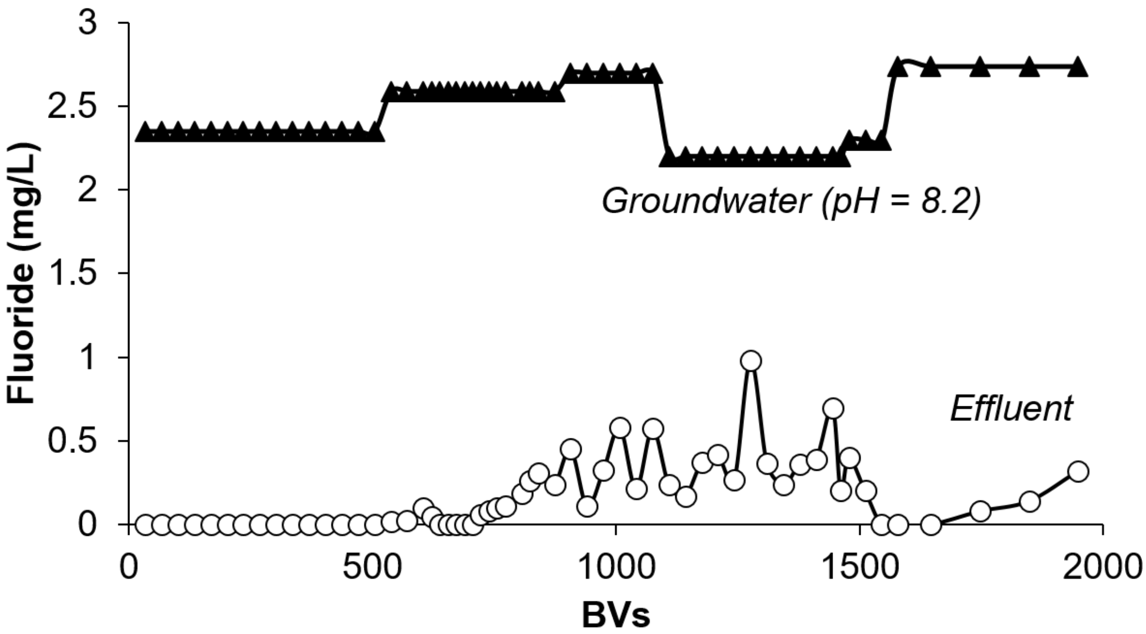


Figure 6.16. Fluoride history (raw and treated) during groundwater treatment by HAIX-NanoZr in Nairobi, Kenya by AvoGlobal.

6.5.2 Pilot Testing

AvoGlobal was impressed with HAIX-NanoZr and five pilot systems (2-10 L columns) were shipped from India to Kenya (2015); later, 100 L-WAC and 100 L-HAIX-NanoZr were also imported from Kolkata. Several attempts were made to install the systems for 12 months, but conditions were surprisingly poor at various organizations (e.g., Egerton University) and unsupportive of the work of AvoGlobal: many exorbitant bribes were requested and people were not incentivized for the work. Eventually, a water bottling plant (Sunny River) was found in Naivasha and they installed the pilot system in May 2016, **Figure 6.17**.

The system was installed by Sunny River without input from AvoGlobal. The original system plumbing did not allow for sampling or acid dosing. Repairs required several months of conversations and were not made until October. Thus, HAIX-NanoZr was used extensively without acid conditioning for six months and fluoride removal was poor, as expected without acid conditioning. Close observation of the HAIX-NanoZr installation was lacking and there were minimal water quality measurements made from April 7, 2016-May 3, 2016, **Figure 6.18**.

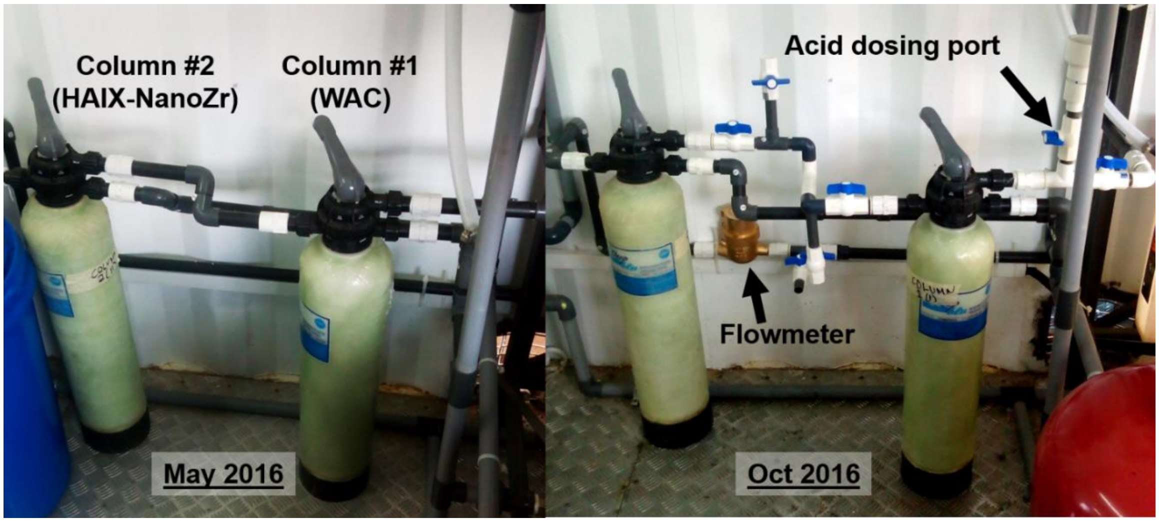


Figure 6.17. HAIX-NanoZr installation (2-10 L columns) at Sunny River bottling in Naivasha L) in May 2016 and R) October 2016.

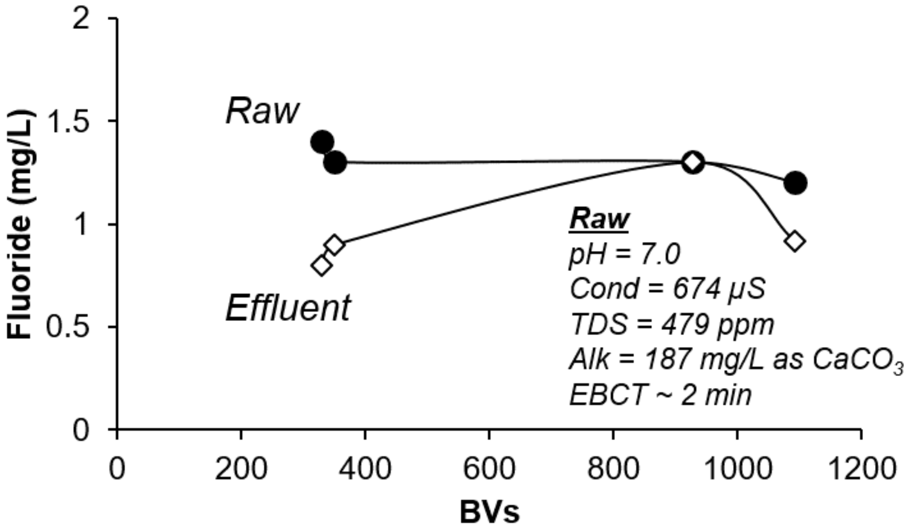


Figure 6.18. Raw and treated water quality from HAIX-NanoZr used at Sunny River in Naivasha from April 7, 2016-May 3, 2016. Note: no acid conditioning of Column #1 was performed.

In October, without Column #1 conditioning, there was no significant fluoride removal. After system repair was performed and Column #1 was conditioned with acid, fluoride decreased from 1.1 mg/L (influent) to 0.03 mg/L (effluent). The HAIX-NanoZr installation demonstrated significant resiliency in being used for thousands of bed volumes at neutral pH and having fluoride capacity return after WAC was conditioned with acid. The robust nature of polymeric anion exchange resins to undergo wide swings in influent conditions, but maintain its functionality is why they were chosen for use in HAIX-NanoZr.

On February 16, 2017 there were reports of a “residue” from Sunny River and AvoGlobal. From past experience, calcium carbonate precipitation was called a variety of terms and could be a “residue”, but it is unclear why WAC (of unknown conditioning status) and HAIX-NanoZr would increase $CaCO_3$ precipitation; when operated correctly, WAC would reduce alkalinity, hardness, and $CaCO_3$ precipitation. As of yet, no further investigation occurred to identify the "residue" or if it was caused by HAIX-NanoZr. But, as HAIX-NanoZr was the only major recent system change, Sunny River assumes the cause is related to this change. The Naivasha system was the first field installation (>1 L) of HAIX-NanoZr in Kenya and by AvoGlobal. Work is ongoing by AvoGlobal to improve understanding of HAIX-NanoZr and proper system operation before further system scale-up is possible in Kenya; many other public and private organizations in Kenya have expressed great interest in HAIX-NanoZr as a superior fluoride adsorbent.

7. Field-scale demonstrations of concurrent trace contaminant removal w/ partial desalination (Aim 3)

7.1 Nuapada, Odisha: First Community Installation

7.1.1 Background

The original Odisha system design, **Figure 7.1**, was based on a scaled-up version of what had been installed in Piraya because of successful pilot testing, which continued successfully through 2016. As previously mentioned, the original third column at Piraya was emptied and elevated to serve as a passive decarbonator tank because of the hydraulic issues that existed after first installation: low flowrates, small tubing diameters, and multiple bends/valves. The passive carbonator would be opened to the atmosphere on a regular basis to off-gas accumulated CO_2. For this scaled-up version a larger tank was envisioned with a baffle in the middle to increase residence time and avoid short-circuiting of influent water. A cut-away of the storage tank is shown in **Figure 7.2**. This design was conveyed to and approved by the local PHED. The system was installed in Nagpurat Musapali (Lat: 20°36'07.8"; Long: 82°39'49.8") by December 7, 2014, as seen in **Figure 7.3-Figure 7.4**.

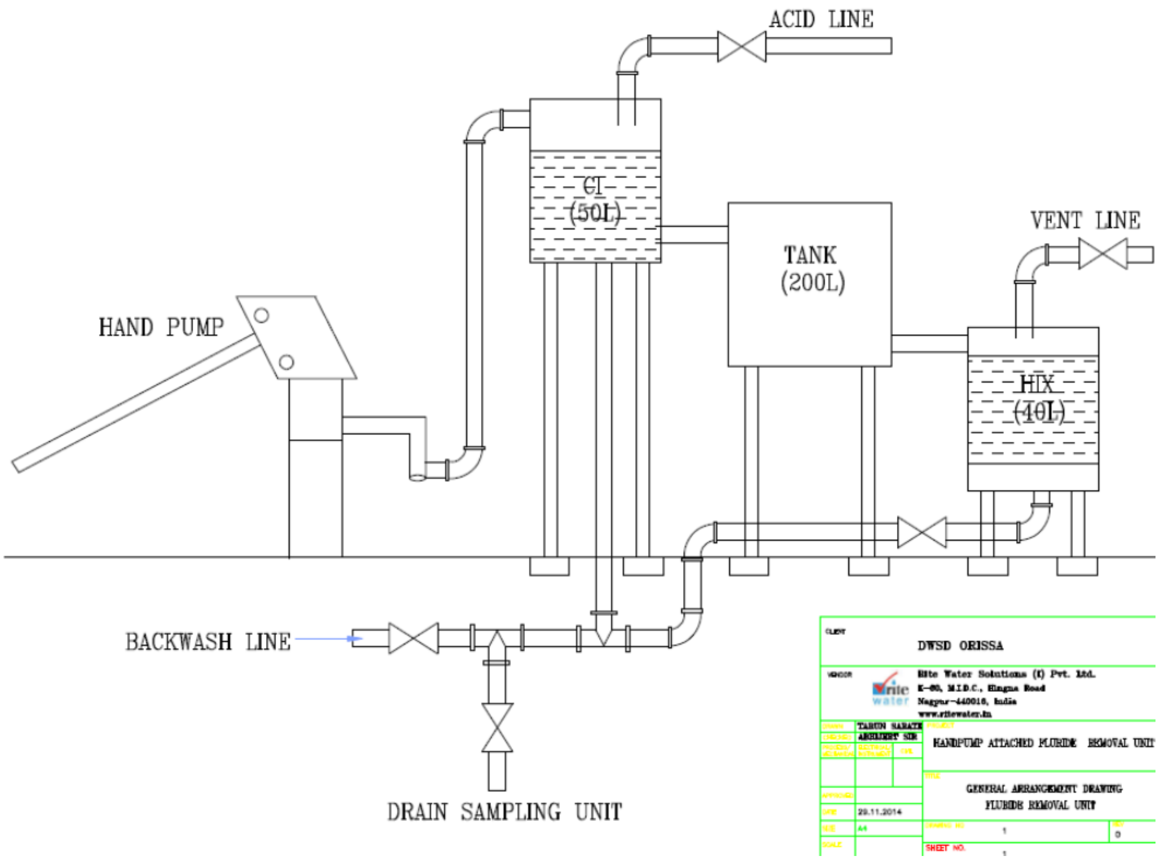
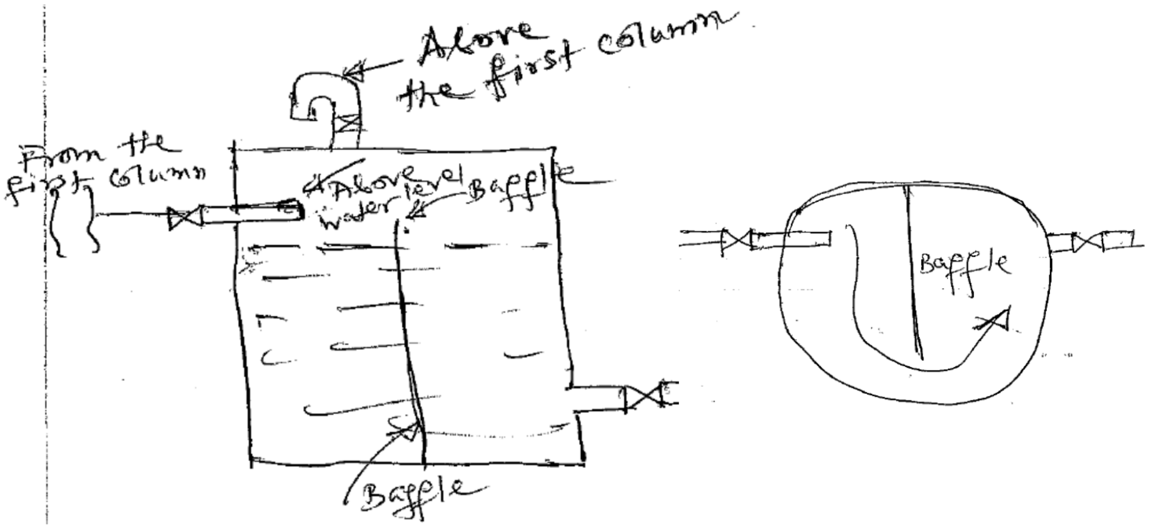


Figure 7.1. Initial sketch of the first handpump connected HAIX-NanoZr for Odisha test installation by Rite Water.



Side View **Top View**

Figure 7.2. Details of “TANK” design for the Odisha installation.

Figure 7.3. Original HAIX-NanoZr installation by Rite Water in Nuapada, Odisha. Note from Left-Right: 1) Handpump; 2) Column 1 (WAC resin); 3) storage tank/passive decarbonator; 4) HAIX-NanoZr.

Figure 7.4. Odisha installation team featuring Anil Shaw wearing a Lehigh University shirt.

Immediately after installation, it was realized that the design was flawed in several ways, especially in relation to the intended operation. Immediate issues:

1) The distance between the hand pump and the tap for treated water was approximately 8 feet. Such a long distance makes it difficult for one person to operate the system- due to the walking distance between the hand pump and faucet.
2) The elevated storage tank/passive decarbonator (3) was ~200 L in volume at an elevated height. The physical effort and time requirement to fill this tank was significant for creating adequate elevation head for filling storage bottles. If the storage tank was already filled, users did not have to pump and the burden of physical requirement was then not shared evenly between users.

The fluoride removal systems from the other manufacturers can be seen in **Figure 7.5** and the raw water and treated water results from the four locations are present in

Table 7.1.

Figure 7.5. Fluoride removal systems from HES (L, OxiMax) and Ion Exchange (R, Indion-RS-F). Note the much smaller volume of HES and Indion systems.

Table 7.1. Physico-chemical parameters of initial water samples as tested by NEERI at the four systems installed by the three companies (Dec. 10, 2014). **Note:** RW- Raw water; TW- Treated water; all concentrations are in mg/L, if not otherwise indicated.

Location (Village)		**pH**	**Turbidity (NTU)**	**TDS**	**F^-**
Dhumabhata	RW	7.3	18.5	394	3.8
	TW	7.7	0.56	395	0.1
Kandetara	RW	7.5	49.5	1494	5.4
	TW	6.4	1.8	1566	0.7
Musapali- 1st Installation	RW	7.3	9.6	367	3.2
	TW	6.4	5.4	385	1.2
Ilaripur	RW	7.1	9.4	287	3.2
	TW	6.2	1.2	443	0.2

Due to the operational issues of the first installation and later decrease in fluoride below 2 mg/L, it was decided to move the HAIX-NanoZr fluoride removal system to a new location. The local PHED asked that the design be changed to a simpler single-column design. However, HAIX-NanoZr was designed to operate in a multi-column process for several reasons:

1) Use of multiple types of ion exchange resins;
    a. Ease in installation/replacement of exhausted resins;
    b. No concerns about changes in stratification of resins during backwash
2) Separate chemical dosing of each column for conditioning and/or regeneration;
    a. Acid conditioning (pH < 2) of WAC resin would lead to dissolution of zirconium oxides from the HAIX-NanoZr and loss in arsenic/fluoride removal capacity
    b. Low pH effluent after WAC conditioning and HAIX-NanoZr protonation would eliminate pH adjustment capacity of materials in the third column, e.g., WAC-Na and dolomite

Had the initial three-column design not had physically tiring operation, from the elevated tanks and the intermediate decarbonator tank, and logistical difficulties, from a poorly placed faucet, it is likely that a multiple-column design would have still been acceptable to the local RWSS. This is comfortably known because the original hand pump-based arsenic treatment system often included two columns in series without complaint from users. The new single-column system was installed by December 22, 2014, but the fluoride concentration was only being reduced from 4 mg/L to 1.5 mg/L, although a low number of bed volumes of fluoride-contaminated water had passed through the HAIX-NanoZr resin.

On December 23, 2014, when the PHED chemist was visiting the new installation site, the treated water fluoride concentration had exceeded 2.0 mg/L (> 1.5 mg/L limit). Knowing the resin should have significant fluoride capacity, it was determined that there were not good hydraulics inside the column because of plumbing or hardware problems: significant short-circuiting of the resin, leading to very low contact time between fluoride and the resin. On December 24, 2014, a new FRP column began being shipped down to Odisha via informal transport, e.g., bus, train, from Ramkrishna (Water Solution) Enterprise, in order for the system to be repaired prior to the arrival of NEERI on December 29, 2014. The new FRP column was installed and fluoride removal performance met expectations in week-long testing by Rite Water, **Figure 7.6**, and in spot-testing of all fluoride removal systems by NEERI, **Table 7.2**.

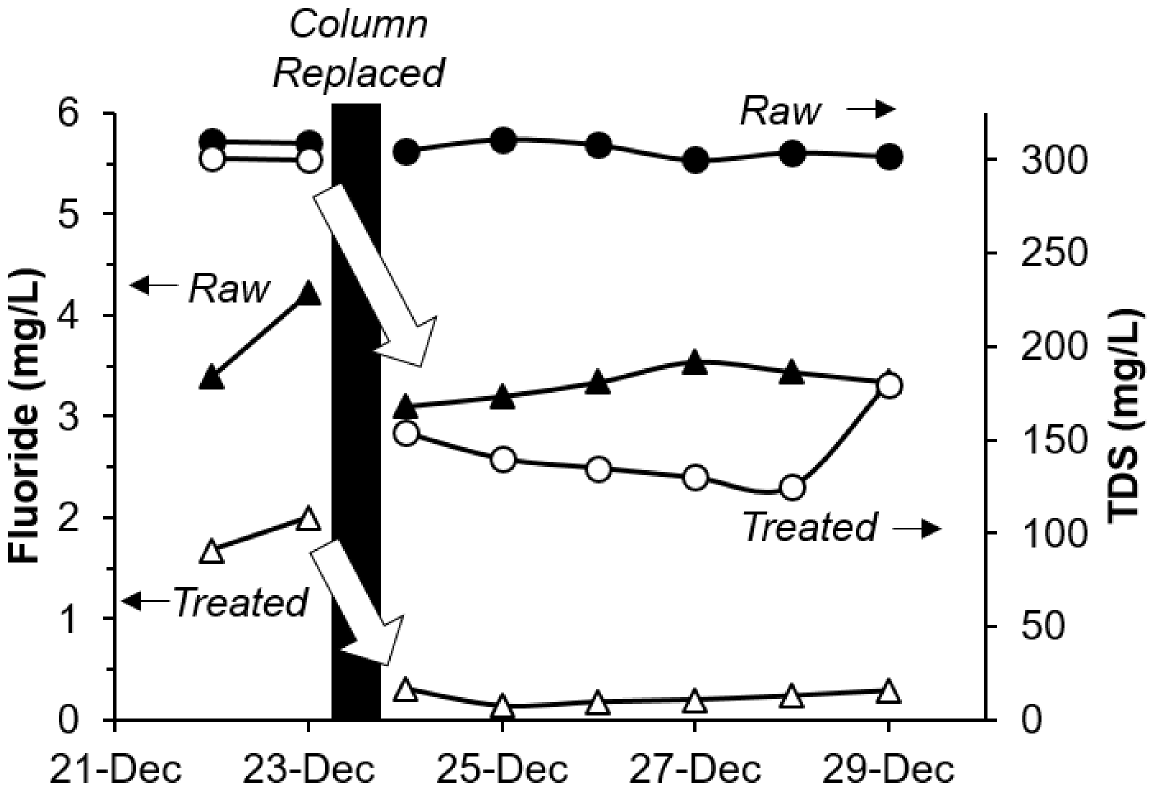


Figure 7.6. Field results by Rite Water from the first HAIX-NanoZr system being operated in Nuapada, Odisha.

Table 7.2. Physico-chemical analysis of water samples Nuapada, Odisha (Dec. 29, 2014). **Note**: all concentrations are in mg/L, if not otherwise indicated.

Village		**pH**	**Turbidity (NTU)**	**TDS**	**Total Hard. as $CaCO_3$**	**F^-**
Dhumabhata	RW	7.5	25	388	192	4.1
	TW	7.7	0.7	361	168	0.1
Kandetara	RW	7.5	5	1440	272	6.4
	TW	6.7	0.3	1662	280	0.51
Musapali	RW	7.4	4	359	188	3.4
	TW	6.4	0.7	200	32	0.43
Haripur	RW	7.3	5.3	285	200	2.7
	TW	6.5	0.4	288	188	0.1

In the report by NEERI on the three fluoride removal systems visited during two spot tests in December 2014, all systems were found to meet the fluoride removal requirement. But, several comments of concern were raised about the effluent water quality, unrelated to fluoride. As shown in **Chapter 7 Appendix Table 11.1**, the Kandetara location had raw water with TDS= 1440 mg/ L and nitrate= 189 mg/L; the treated water had slightly higher TDS and slightly reduced nitrate. All values were out of drinking water regulations and would require additional treatment to be potable. The NEERI inspection team noted that tube wells with high fluoride should be checked for co-occurring contaminants of concern because typical media-based fluoride removal processes only address fluoride. However, HAIX-NanoZr can achieve partial desalination and nitrate removal through alkalinity reduction by WAC in Column I and anion exchange in Column II, respectively. As the materials had not been tested by NEERI, or a similarly regarded laboratory, in multiple locations, they requested that RWSS- Odisha support the creation of 15-20 more installations per technology. If successful, manufacturers would be able to install 200 more systems.

7.1.2 Testing of Twenty Community-scale Systems

On May 12, 2015, NEERI collected raw and treated water samples at the twenty installed systems. With the last-minute delivery, lack of experience around HAIX-NanoZr, and lack of direct oversight from Drinkwell, proper start-up operations were not followed and NEERI reported several concerns during the site tours. Nine of the sites (1, 2, 5, 6, 8-10, 15, 17) had treated water with higher TDS than the raw water, **Figure 7.7**; up to 240 mg/L higher. Four of the systems with high TDS used SAC-Al: 9, 10, 15, 17. Two of the locations had treated water with pH > 8.5 (1, 20) and three locations had pH < 6.5 (2, 3, 14), **Figure 7.8**. Note: SAC-Al was used in system 14 Three of the locations (2, 10, 17) had treated water with fluoride above 1 mg/L, but less than 1.5 mg/L, **Figure 7.9**. The concern from NEERI and unexpectedly poor test results indicated to Drinkwell, Lehigh, and Rite Water that there were errors during setup and operation.

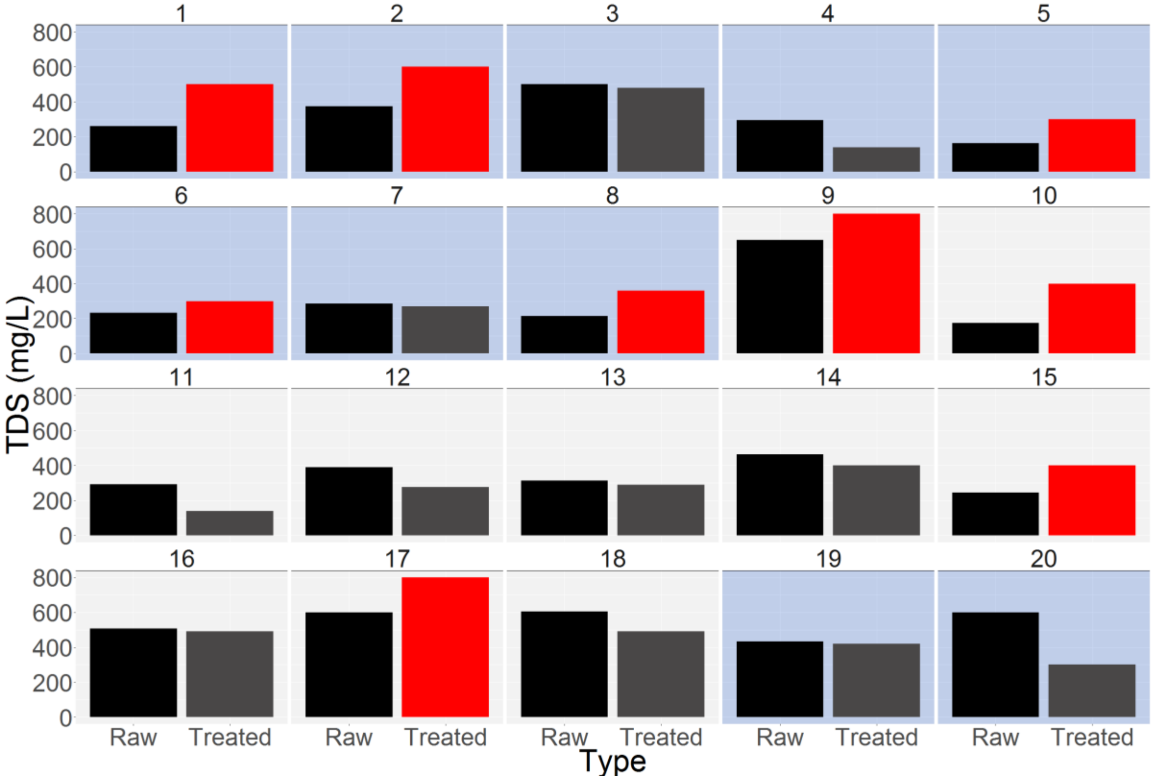


Figure 7.7. Raw and treated water TDS on May 12, 2015 at the twenty single-column, HAIX-NanoZr hand pump systems in Nuapada District. Note: bars in red indicate the treated water had higher TDS than the raw water; blue backgrounds indicate HAIX-NanoZr and white backgrounds indicate SAC-Al.

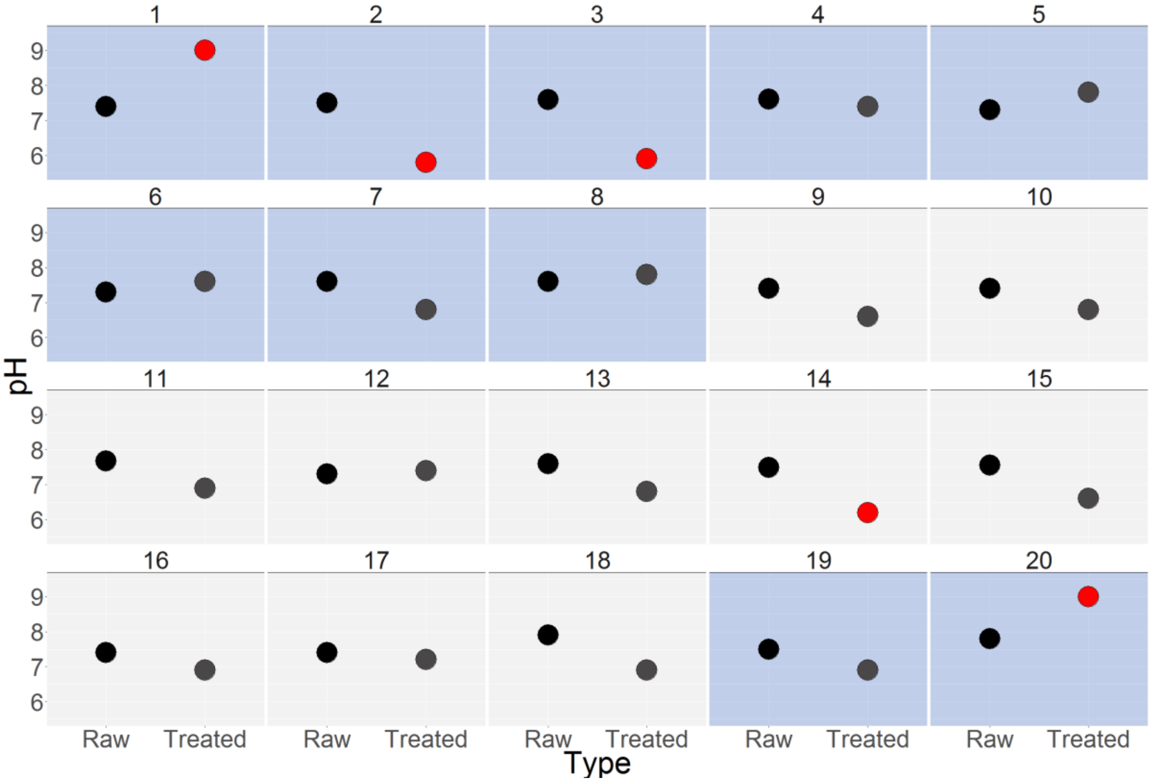


Figure 7.8. Raw and treated water pH on May 12, 2015 at the twenty single-column, HAIX-NanoZr hand pump systems in Nuapada District. Note: points in red indicate the treated water pH was outside of drinking water standards (pH 6.5-8.5); blue backgrounds indicate HAIX-NanoZr and white backgrounds indicate SAC-Al.

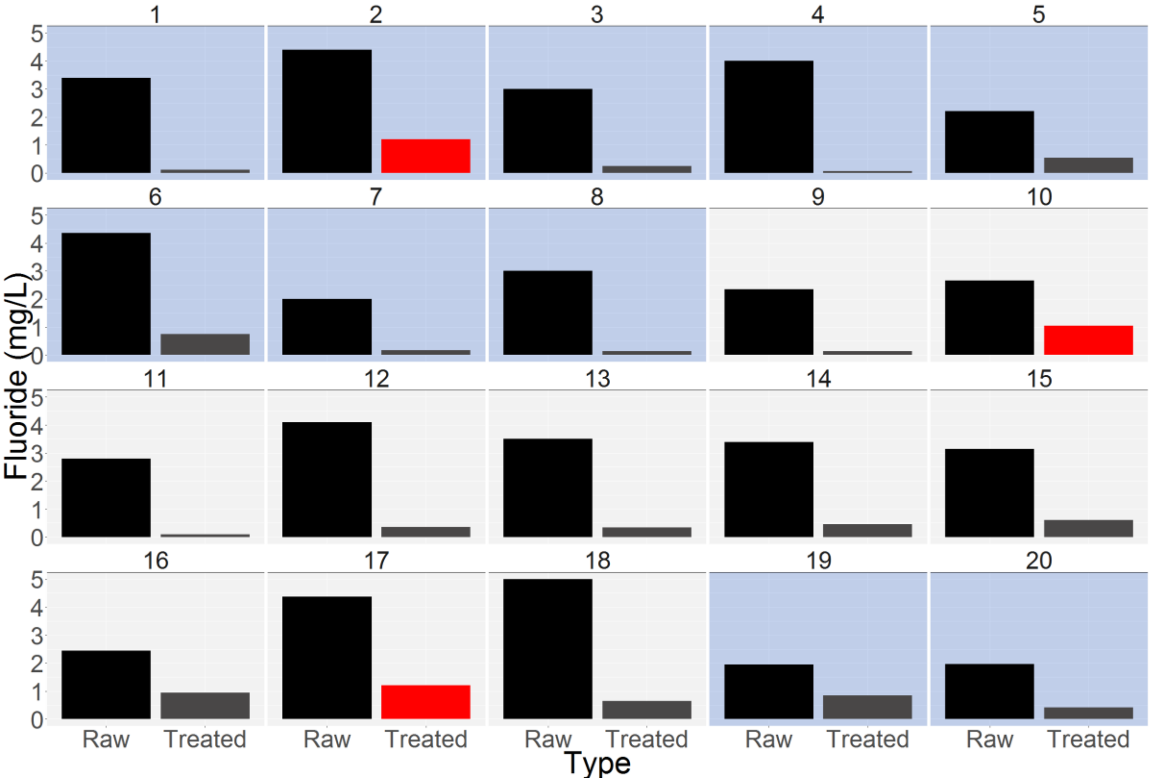


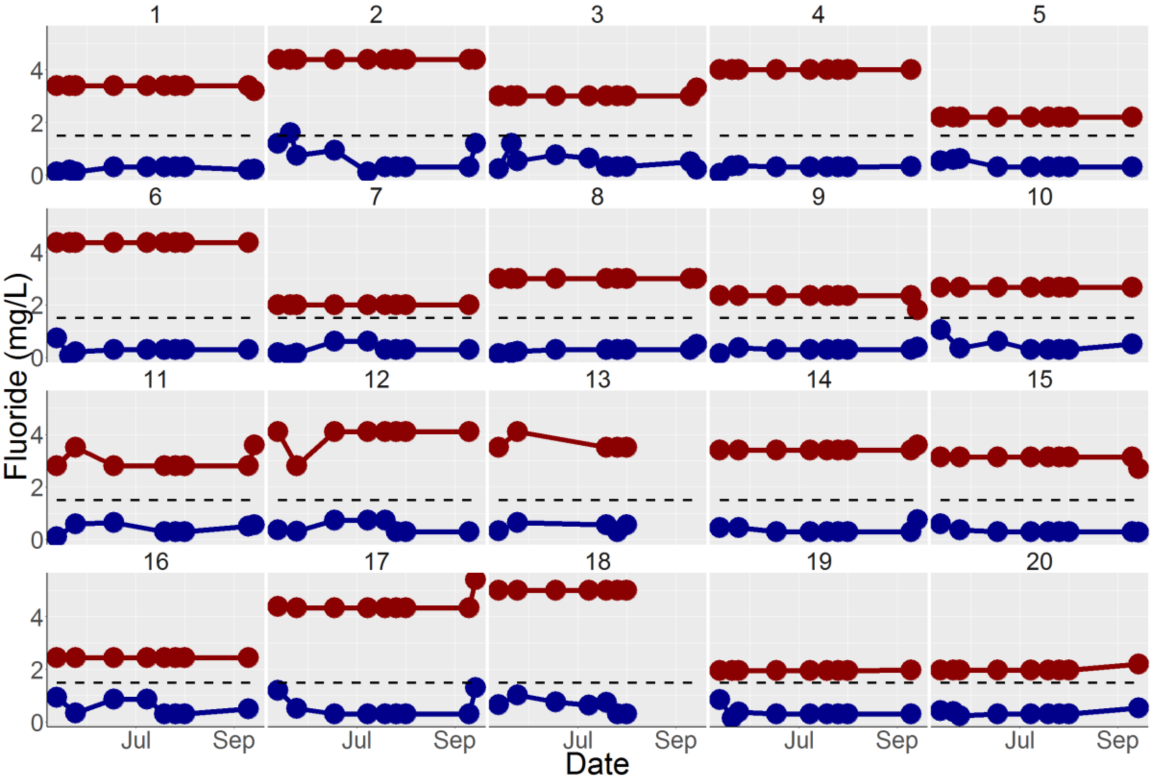
Figure 7.9. Raw and treated water fluoride concentration on May 12, 2015 at the twenty single-column, HAIX-NanoZr hand pump systems in Nuapada District. Note: bars in red indicate the treated water fluoride was greater than 1 mg/L; blue backgrounds indicate HAIX-NanoZr and white backgrounds indicate SAC-Al.

Based on high TDS, pH, and fluoride, significant bed volumes of raw water were passed and controlled acid conditioning was performed by Rite Water staff on the HAIX-NanoZr systems. Regular, controlled acid dosing is not a common field maintenance activity for hand pump-attached treatment systems of any kind in India. As such, it was expected that proper performance of this new behavior would take some time to match performance in lab-scale and pilot-scale operations. Most notably, the change in system design from three columns to one column to minimize capital cost and system “complexity”, meant that all materials would be exposed to low pH solution, instead of just WAC in Column #1. Difficulty in dosing was exacerbated by the lack of metering equipment- a funnel and graduated bucket were the only tools for operators- in order to minimize capital and operating expenses. One can imagine the difficulty in creating acid solutions of accurate concentrations and the uncontrolled dosing rate by pouring through a funnel and valves throttled to different extents.

After eight days of start-up and maintenance (May 20, 2015), HAIX-NanoZr systems were operating much closer to expected performance, **Figure 7.10**, based on lab-scale and pilot-scale testing:

- One system (#7) had TDS increase in the treated water, by a small amount (14 mg/L);
- Three systems had treated water pH < 6.5 (# 7,8,19), due to difficulties in controlled acid dosing;
- Two systems had treated water fluoride above 1 mg/L (#2 → 1.6 mg/L, #3 → 1.2 mg/L)

Four days later (May 24, 2015), all systems showed constant/reduced TDS in the treated water and fluoride at or below 1 mg/L, **Figure 7.10B**. Six systems (#2, 3, 7, 8, 11, 19) did have low pH values between pH 6.0-6.5, again, due to poor control of acid dosing, **Figure 7.10C**. After this test in late-May, subsequent testing through mid-September indicated the twenty HAIX-NanoZr systems met water quality guidelines for fluoride, pH, and TDS; there were less than four instance when a test did not meet water quality standards (low pH), **Figure 7.10**. In mid-July, HAIX-NanoZr replacement at 2-3 locations was deemed necessary by Rite Water and material was provided by Drinkwell from Kolkata.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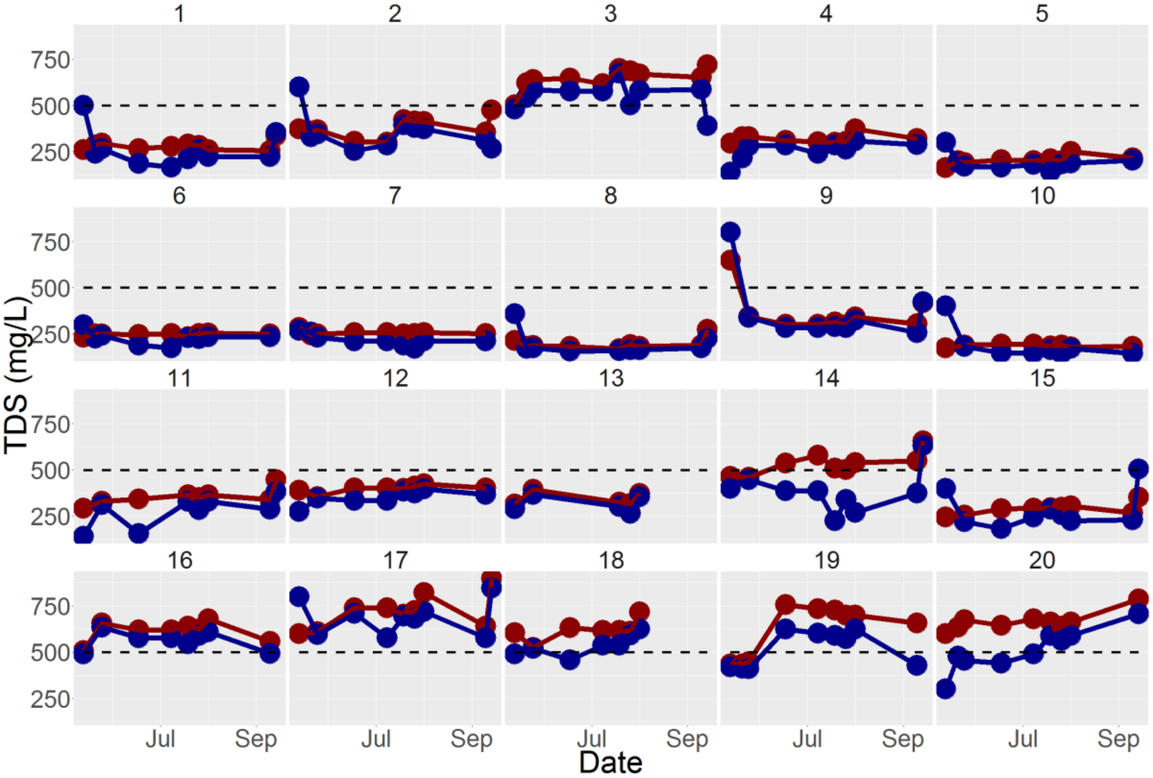
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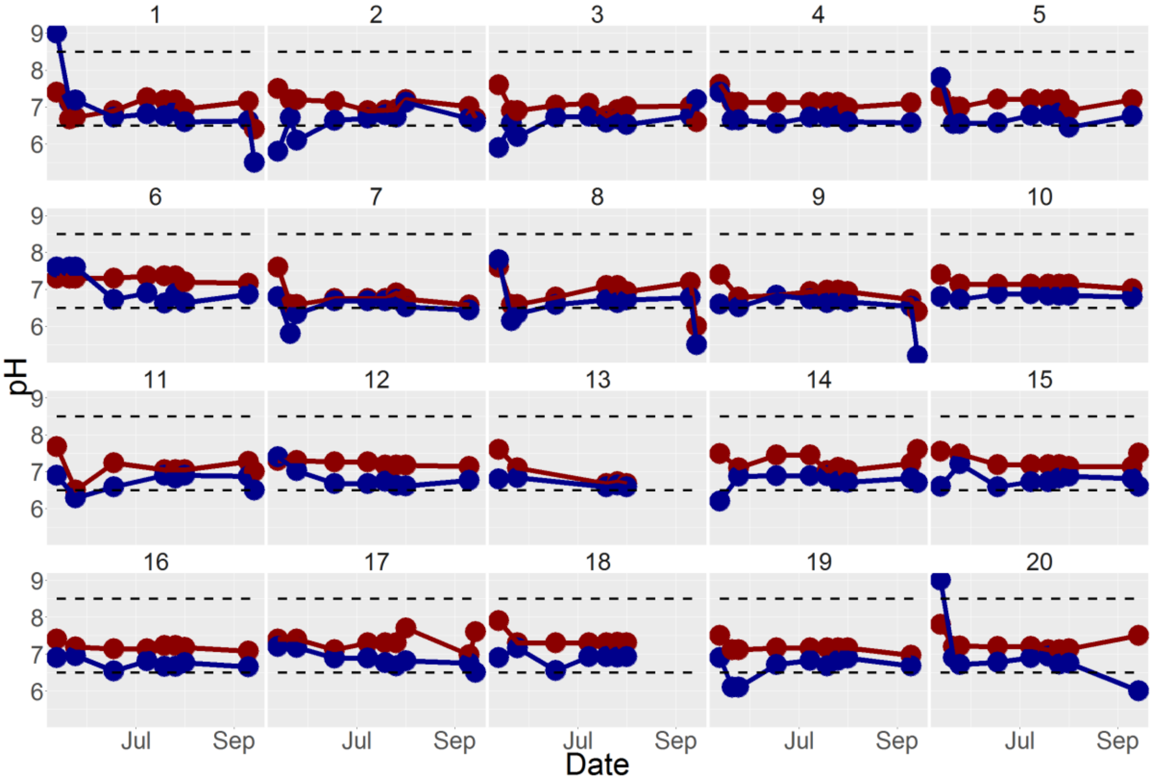


Figure 7.10. Influent and effluent water chemistry across twenty HAIX-NanoZr systems in Odisha from May-September 2015. A) Fluoride (top); B) TDS (middle); and, C) pH (bottom). <u>Note:</u> red scatter points are raw, blue points are treated.

Due to problems in system performance during the first visit and test by NEERI, Rite Water spoke with the local RWSS and NEERI at length to assure them that the results were not due to poor technology, but errors in installation because of the rushed nature of the work. In mid-July, Rite Water received a new letter from the RWSS asking NEERI to visit the Odisha installations for a second evaluation. Scientists from the Water Technology and Management Division (WT&M) of NEERI collected samples from Nuapada District on September 14, 2015 for lab testing. The NEERI inspection noted that "fluoride content [is]… below 1.5 mg/L in all the [treated water] samples" and "…performance of plants is satisfactory as far as fluoride removal is concerned." But, the final observations section was as follows:

> The defluoridation units installed by M/s. RITE Water Solution (L), Nagpur did not show consistency in water quality parameters in most of the places i.e. TDS reduced significantly in some plants whereas it did not change in rest of the plants. The pipe fittings and protection nets were found to be unsatisfactory. The people opined that the staff from the company visited villages for the past few days before NEERIs visit and they have been changing one or the other parts of the plants. The personnel of M/s. RITE Water Solution (L), Nagpur were also present at the time of people's opinion recorded at the site. Sanitary conditions at some of the plant locations were very poor. The observations were also discussed with the officials from M/s. RITE Water Solution (L), Nagpur, who also agreed with the observations.

Treated water quality as reported by NEERI had a few issues that are discussed later. But, there are several disappointing comments from the RWSS that indicate multiple errors from Rite Water to ensure proper sanitary conditions, have high quality system aesthetics, and to develop a good working relationship with the local community. The simple lack of cleanliness, accumulation of trash, and abundance of "[un]sanitary conditions" was a point of significant concern and conversation between Lehigh, Drinkwell, and Rite Water, especially as it was during their second chance with the national certification authority. It is typical for water treatment manufacturers to install equipment that is as cheap as possible in order to increase their margin. But, given the fortunate opportunity to improve their poor first impression, it would be logical to spend extra money in order to ensure a positive recommendation, if even requiring the company to lose money during the pilot. The lack of a good working relationship with the local community is evident in the people commenting negatively that Rite Water had visited recently to change parts of the system. When, in actuality, Rite Water was performing regular maintenance required of such systems for the benefit of the surrounding community, but this information was not effectively communicated, e.g., acid conditioning. Regardless of the treated water quality, the lack of professionalism from Rite Water seen by NEERI made a positive review of HAIX-NanoZr nearly impossible.

Separate from aesthetic and hygienic conditions of HAIX-NanoZr systems investigated by NEERI were questions of the treated water quality, especially with regards to inconsistencies in TDS. Diagrams of multi-column system design in previous sections showcased the use of Column I, or WAC, for partial desalination via removal of alkalinity and temporary hardness via proton exchange followed by off-gassing of carbon dioxide. Weak acid cation exchange resins have high ion exchange capacity of ~4 eq/L; equivalent to 80 g Ca^{2+}/L. Under ideal plug flow conditions with adequate contact time, all temporary hardness and related alkalinity from a solution would be removed from solution by the WAC. Later pH adjustment in Column III, or the bottom section of media in a single-column, may reintroduce alkalinity that did not off-gas. Thus, the amount of partial desalination that occurs during HAIX-NanoZr treatment is not a set percentage of the TDS or defined amount of TDS, but is dependent on the influent water chemistry and varies with time and location.

In a real system with non-ideal hydraulics, it can be assumed that dispersion and channeling through the packed-bed lead to different fractions of water having different contact times with the media. Further, the use of a single-column bed, instead of two- or three-column solution increases non-idealities and shortens the breakthrough curve. But, more influentially is the manner and regularity of acid conditioning or WAC regeneration. This was previously described as being a problematic issue in Nuapada District, especially during start-up and the earlier months.

Unlike previous testing in Nuapada by NEERI or Rite Water, during this final testing, NEERI monitored total hardness, calcium, magnesium, and alkalinity in the raw water influent and treated water effluent. The additional testing should have been performed earlier by Rite Water in order to better understand system operation. In this last test, three systems had greater conductivity/TDS in the treated water versus the raw water, but all were below or equal to 500 mg/L; system 15 was at 505 mg/L, but given the error inherent in the handheld conductivity meters, it is safe to say that this system may have met the 500 mg/L limit. In each of these systems, the treated water had total hardness concentrations that were nearly equivalent to or greater than the raw water (≥90%). Such high levels of hardness indicated that there was a problem with acid conditioning, either:

1) The WAC was not effectively exchanging protons for hardness because it was exhausted and needs acid conditioning;
2) Adequate washing had not occurred after acid conditioning and regenerant was leaking out.

General technical overviews were provided to the local RWSS and to NEERI at different points in time, but were likely not closely read. As the third-party review by NEERI is performed in their laboratories and offices separate from Drinkwell, Lehigh, and Rite Water, as it should be, NEERI did not have the opportunity to discuss their data and to understand the mechanisms of treatment taking place within the column, as it was quite different to typical systems they oversee. Their criticism and conclusions were disappointing, but understandable given the situation. The learnings, and new motivation, gained from negative review inspired increased diligence and system design improvement for future work.

The twenty single-column hand pump installations in Odisha were the first time HAIX-NanoZr was installed for community use and the first time HAIX-NanoZr was used in a single-column fashion. Although there were numerous challenges, from material production, system installation, regular operation/maintenance, and treated water quality, overall the work is considered to be a successful demonstration of the ability of HAIX-NanoZr to perform partial desalination with concurrent defluoridation (PDCD) and produce potable water. Neither partial desalination nor fluoride removal were designed to work optimally in a single-column system. But, given the change in design and non-ideal operation, the performance of HAIX-NanoZr achieved removal that was not possible versus the systems installed by the other manufacturers, i.e., PDCD. Additionally, from a combination of less robust capital equipment and less regular maintenance, the fluoride treatment systems by HES and Ion Exchange did not effectively remove fluoride when NEERI was reevaluating HAIX-NanoZr, per testing by Rite Water.

7.2 Nalhati, Birbhum District, West Bengal, India

A raw water test from April 24, 2016 is in **Table 7.3**; the original raw water test report from the Executive Engineer of the Birbhum Division of the WB PHED can be found in **Chapter 3 Appendix**. The HAIX-NanoZr system was installed as described in section 3.4.4, **Figure 7.11**, and was operational from February 2016-March 2017. Raw and effluent water chemistry history in **Figure 7.12** shows consistent fluoride removal, TDS reduction, and pH adjustment over one year with very high influent fluoride concentrations and pH values.

Table 7.3. Groundwater chemistry at the selected Nalhati tubewell on April 24, 2016 as tested by M/S R. V. Briggs & Co. (Kolkata), a National Accreditation Board for Testing and Calibration Laboratories (NABL) certified laboratory.

Water Parameters	**Units**	**Raw**
Turbidity	NTU	2.5
pH		9.2
TDS	mg/L	416
Alkalinity	mg/L	76
Silica as SiO2	mg/L	10.1
Iron as Fe	mg/L	0.2
Calcium as Ca	mg/L	3
Magnesium as Mg	mg/L	2
Sulphate as SO_4^{2-}	mg/L	<5
Fluoride as F	mg/L	18.6
Total Hardness as $CaCO_3$	mg/L	16
Temporary Hardness	mg/L	16
Permanent Hardness	mg/L	0

Figure 7.11. (Clockwise from top-right) A school girl cleaning her Midday Meal bowl; a boy and woman getting safe water in Nalhati; the three column HAIX-NanoZr system installed by Rite Water and Drinkwell; Anil Shaw, Joydev Das, Dr. Prasun Chatterjee, and Ajit Nath standing proudly in front of the system they commissioned.

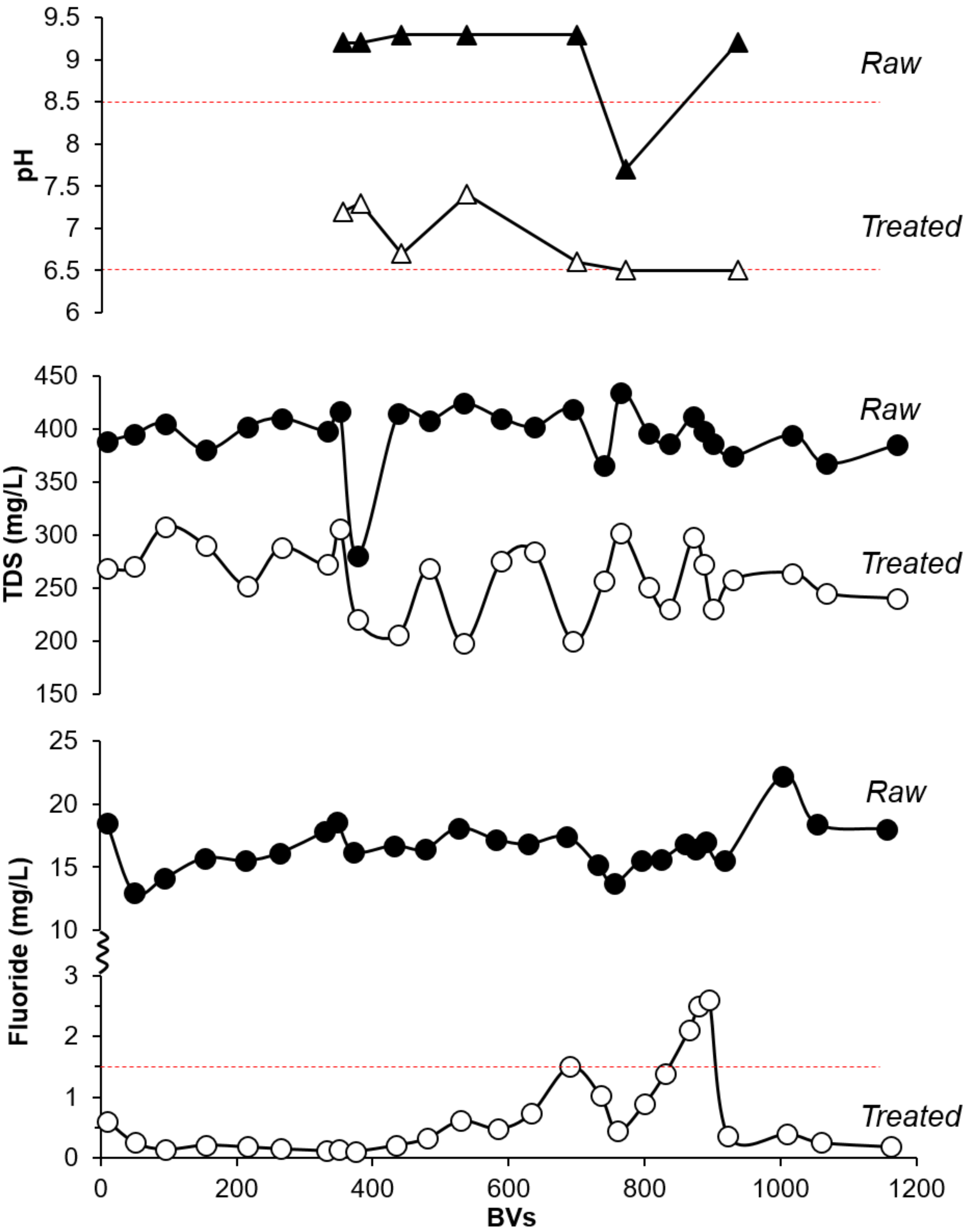


Figure 7.12. Fluoride, TDS, and pH of raw and treated water from the community-scale HAIX-NanoZr system in Nalhati from February 2016-January 2017. Note: horizontal dashed lines indicate water requirement levels (pH 6.5-8.5, F^- < 1.5 mg/L); vertical line indicates HAIX-NanoZr regeneration.

The West Bengal Fluoride Task Force visited and evaluated the Nalhati system on August 25, 2016; this was the first visit by the WB PHED to an HAIX-NanoZr fluoride treatment site. Based on provided water treatment reports from a third-party lab, they found the fluoride removal and pH adjustment to meet drinking water standards. They noted that 400 students in the school drink treated water from HAIX-NanoZr and their food is Midday Meal is prepared with the treated water. As of their visit, 57,500 L of water had been treated (575 BVs). The Task Force was concerned that acid conditioning of the media would require skilled personnel and that the operations would be complicated, although a local youth was operating the system.

7.3 Baduria, N. 24 Parganas, West Bengal

The HAIX-NanoFe/Zr system was successfully installed in Baduria mid-May 2016, to complete Milestone 2 requirements for US-ISTEF. As a site impacted by arsenic and iron, the treated water was noticeably better to consumers immediately with low turbidity and low iron, **Figure 7.13**. Knowing the risk of arsenic and seeing the much better water quality, the community was using the system after opening, **Figure 7.14**. Although a water ATM was installed, it was not used as of March 2017 because no business model for water sales through the ATM had been developed or implemented. There was a lack of water quality reports from Baduria, **Figure 7.15**, but water consumption had increased over the first 10 months indicating the water was of high quality.

Figure 7.13. A community member holding a bottle of raw groundwater and a bottle of HAIX-NanoZr treated water. Notice the aesthetic difference in water quality due to concurrent iron removal: 4.3 mg/L -> <0.1 mg/L.

Figure 7.14. A woman filling her bottle with safe water in Baduria; community members giving their water ATM card to the system caretaker (Left-right).

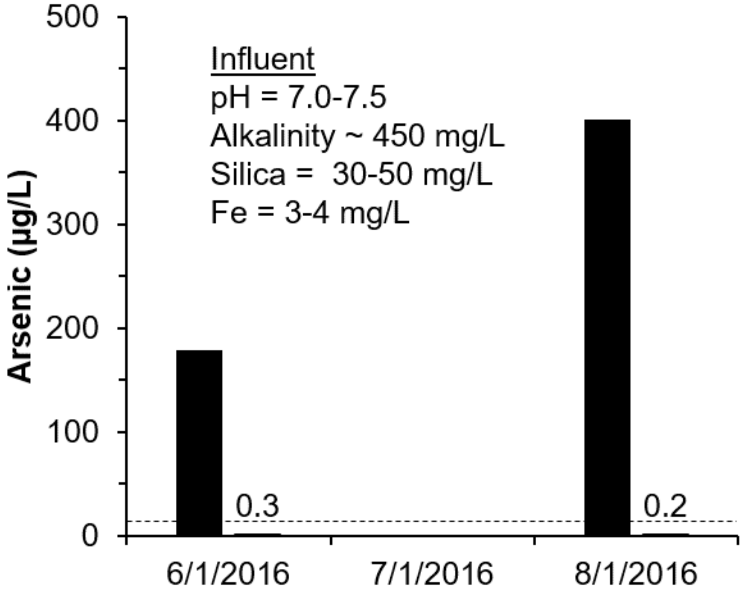


Figure 7.15. Arsenic influent and effluent during operation of HAIX-NanoFe/Zr community-scale system in Baduria from May 2016-August 2016. Note: the two labelled values (0.3, 0.2) are treated water with concentrations far below the Indian standard.

7.4 Moparlapalli, Roddam Mandal, Anantapur District, Andhra Pradesh

From November 16, 2015- December 9, 2015, acid conditioning of the WAC column was performed using citric acid. From December 14, 2015-onwards, HCl was used for WAC conditioning. Detailed monitoring of system operation occurred during the first service cycle and early after the first regeneration by Rite Water (**Figure 7.16**) and local RWSS (**Figure 7.17**). Upon review by the Office of the Executive Engineer for the RWSS of Anantapur, the fluoride and TDS removal performance of HAIX-NanoZr met drinking water standards and the technology,

Table 7.4. An official letter dated April 22, 2016 from RWSS approved HAIX-NanoZr for use in Andhra Pradesh. The WAC pre-treatment showed effective reduction in alkalinity, hardness, and conductivity/TDS across five months of operation. The significant reduction of nitrate to within drinking water standards required the hybrid removal capacity of HAIX-NanoZr for both anion exchange and Lewis acid-base interactions. A contract from RWSS was awarded to Rite Water for 12-500 LPH and 9-1000 LPH systems using "HIAX - Nano resin technology" worth Rs. 165 lakh (~$250K). However, only eleven systems were constructed, as nine systems were cancelled due to local demand for RO was awarded to other vendors.

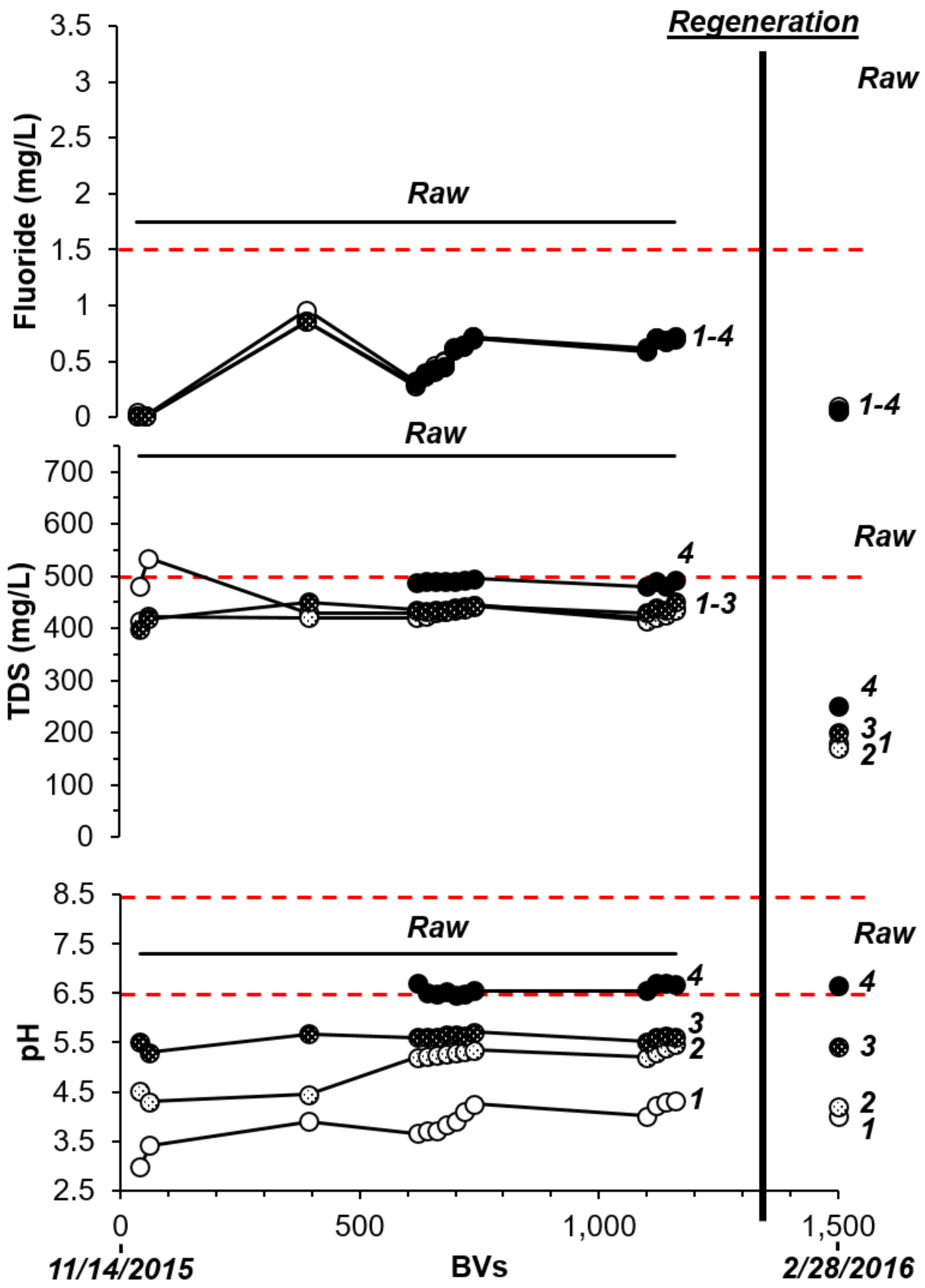


Figure 7.16. HAIX-NanoZr water chemistry (fluoride, TDS, and pH) at Moparlapalli from Column #1, 2, 3, 4 (#4= "treated effluent"). Testing was performed by Rite Water. Raw water was assumed to be consistent by Rite Water during the first service cycle. Regeneration by 3% NaOH/3% HCl was performed soon before 1500 BVs.

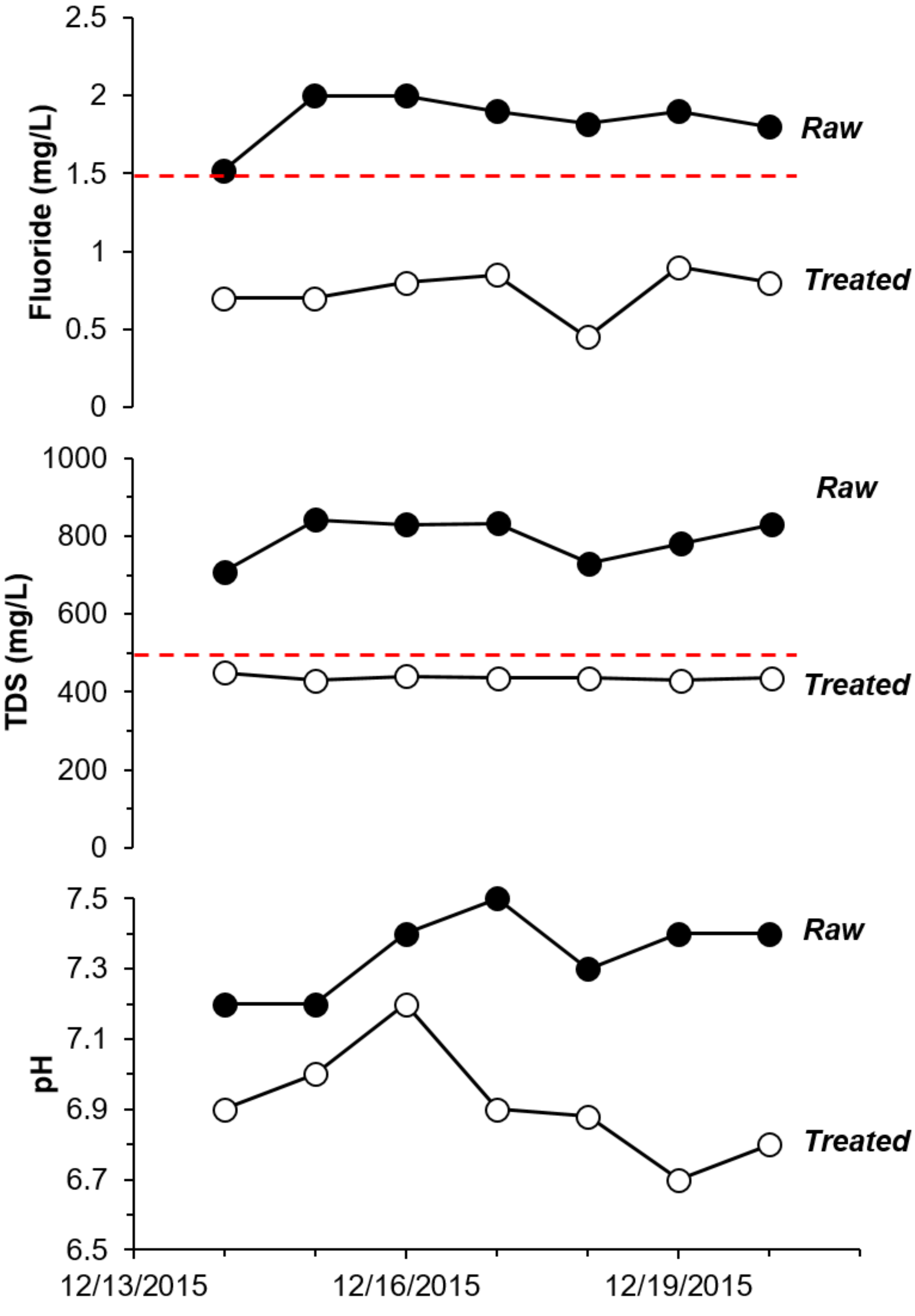


Figure 7.17. RWSS-certified testing of the HAIX-NanoZr system in Moparlapalli from December 14-20, 2015.

Table 7.4. Raw and treated water from HAIX-NanoZr in Moparlapalli as sampled and tested by the RWSS. Note: Cells shaded yellow are outside of the drinking water requirement.

		November 27, 2015		*March 13, 2016*	
Parameter	**Units**	**Raw**	**Treated**	**Raw**	**Treated**
pH	-	7.54	6.56	7.58	7.22
Conductivity	µS/cm	1377	980	826	275
TDS	mg/L	**895**	**637**	**537**	179
Total Alkalinity	mg/L as $CaCO_3$	**320**	148	168	56
Total Hardness	mg/L as $CaCO_3$	**344**	58	**228**	76
Calcium	mg/L	52.8	8	37	13
Magnesium	mg/L	51.5	8.7	33	11
Fluoride	mg/L	**2.21**	0.75	**4.18**	0.09
Chloride	mg/L	115	141	102	37
Nitrate	mg/L as NO_3^-	**115**	27	10.3	3.4
Iron	mg/L	0.13	0.07	0.03	0.03
Sulfate	mg/L	36	1	35	12
Sodium	mg/L	211	135	66	22
Potassium	mg/L	33.4	4.6	2.1	0.7

7.5 Ghetugachi (SAR-HAIX-NanoZr), Nadia District, West Bengal

There are many underperforming arsenic treatment systems with arsenic breakthrough at low concentrations (10-50 µg/L) in need of additional polishing. As a packed-bed system, HAIX-NanoZr could be a modular add-on to existing treatment systems across a wide range of scales. But, capacity curves are a function of solution concentration, and high ligand capacity at high concentrations does not imply high ligand capacity at low concentrations.

From 2009-2015, local aquifer arsenic concentration was 125-175 µg/L, which was decreased by SAR to 10-15 µg/L at a production rate of 3000 LPD. However, in 2015, demand and production increased to 10,000 LPD and the effluent arsenic increased to 30 µg/L; the electric cost was US$30/month. In order to control the arsenic level at higher flowrates, a 100 L-HAIX-NanoZr was installed after the SAR system. During SAR-HAIX-NanoZr testing, a tubewell 75 m from the SAR-treated tubewell had the following water chemistry: As = 130-165 µg/L, Fe = 3.5-4.0 mg/L, and ORP = -55 mV -> -60 mV (reducing). Arsenic, ORP, and iron history of SAR and HAIX-NanoZr effluent, from December 2015-November 2016, is in **Figure 7.18**. The groundwater “influent” had lower arsenic and iron concentrations, and higher ORP than other local aquifers because of the long-term SAR activity. During this time, ~600 people and two schools depended upon the safe water supplied by the SAR-HAIX-NanoZr system.

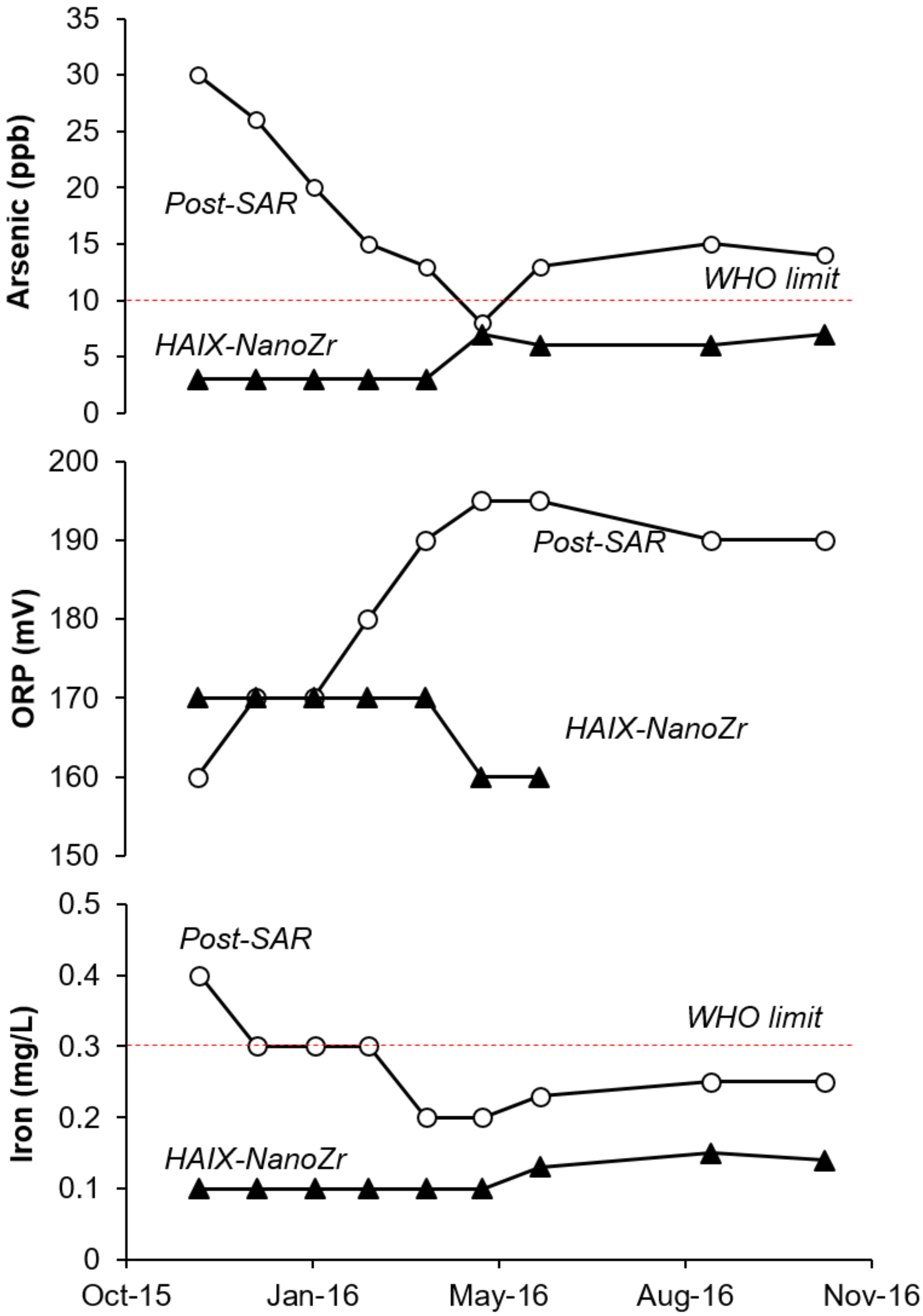


Figure 7.18. Arsenic, ORP, and iron history of SAR and HAIX-NanoZr effluent from December 2015-November 2016.

8. Analyze cash flow of long-term HAIX-based water treatment, develop a model for community-scale operation, and perform Monte Carlo simulations (Aim 4)

8.1 Community Water Treatment Systems

8.1.1 N. 24 Parganas District, West Bengal

8.1.1.1 Nabarun Sangha and Sakthi Sadhana

Nabarun Sangha is one of the oldest, continuously operating arsenic treatment installations using HAIX-Nano (2004-present). The system was originally installed with one HAIX treatment column, but high water demand on Column #1 necessitated a parallel column to boost output. Column #1 produced 6.5 million liters of safe water (2004–2013) and Column #2 produced 5.5 million liters of safe water (2010–2013). Throughout operation, the number of consumers and the amount of revenue grew until the water committee decided to cap production volume, **Figure 8.1**.

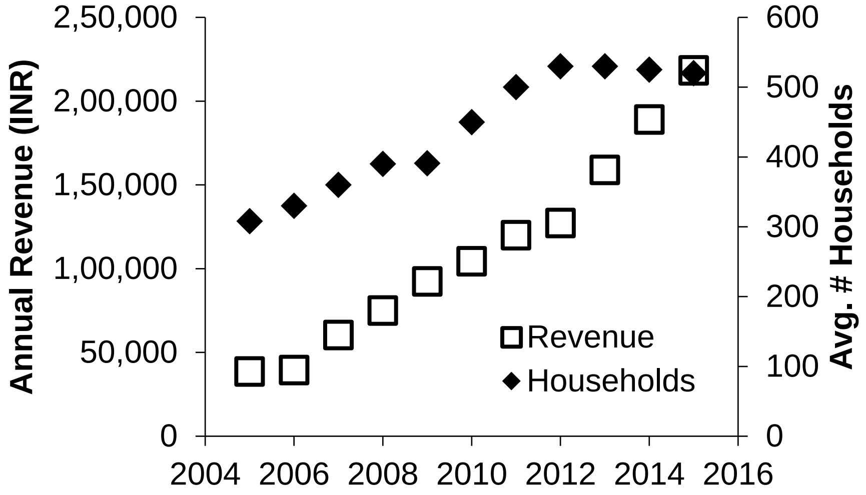


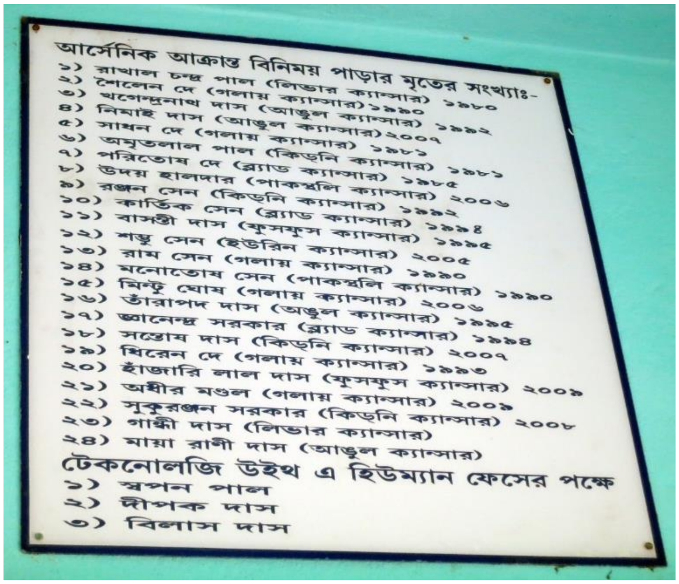
Figure 8.1. Water revenue records over 10 years at Nabarun Sangha, N. 24 Parganas, WB.

In 2012, another local community organization, Sakthi Sadhana, asked STHF to install a treatment system. By 2014, 700 families collected safe water on a daily basis at this site and the community club afforded treatment expansion with revenue from the operation, **Figure 8.2**. At both Nabarun Sangha and Sakthi Sadhana, profits from water sales have been reinvested into expansion of water delivery and community events. Economic performance at these two site and several others in the region was corroborated independently by Mr. Duncan McNicholl (University of Cambridge) during dissertation research in the region from Jan-Mar 2016.

Figure 8.2. HAIX-NanoFe customers at Sakthi Sadhana Community Club.

8.1.1.2 Binimaypara

Binimaypara is a small, poorer village of 1000 people that had many casualties due to arsenic. Their arsenic treatment system had been in different states of operation since 2006, but was turned into the “flagship” HAIX-Nano arsenic treatment system in late 2012 after it was repainted, a memorial for arsenicosis victims was hung by STHF (**Figure 8.3**), and the old columns and media were replaced. Soon after (December 2012), the local government sent a cease and desist order to the community for illegal water sales, in order to earn baksheesh, but did not give the community another safe water option. Water treatment continued through the order from the government. In 2014, an HAIX-NanoFe column was installed for arsenic pre-treatment. From 2013-2016, the site was visited by many prestigious organizations, investors, and researchers, e.g., MIT, Stanford, Oxford, US State Department, Arun LLC, Village Capital, Chemists without Borders, DelAgua Health India, etc.



আর্সেনিক আক্রান্ত বিনিময় পাড়ার মৃতের সংখ্যাঃ-
১) রাখাল চন্দ্র পাল (লিভার ক্যান্সার) ১৯৮০
২) শৈলেন দে (গলায় ক্যান্সার)১৯৯০
৩) খগেন্দ্রনাথ দাস (আঙুল ক্যান্সার) ১৯৯২
৪) নিমাই দাস (আঙুল ক্যান্সার)২০০৭
৫) সাধন দে (গলায় ক্যান্সার) ১৯৮১
৬) অমৃতলাল পাল (কিড়নি ক্যান্সার) ১৯৮১
৭) পরিতোষ দে (ব্ল্যাড ক্যান্সার) ১৯৮৫
৮) উদয় হালদার (পাকস্থলি ক্যান্সার) ২০০৬
৯) রঞ্জন সেন (কিড়নি ক্যান্সার) ১৯৯২
১০) কার্তিক সেন (ব্ল্যাড ক্যান্সার) ১৯৯৪
১১) বাসন্তী দাস (ফুসফুস ক্যান্সার) ১৯৯৫
১২) শম্ভু সেন (ইউরিন ক্যান্সার) ২০০৫
১৩) রাম সেন (গলায় ক্যান্সার) ১৯৯০
১৪) মনোতোষ সেন (পাকস্থলি ক্যান্সার) ১৯৯০
১৫) মিন্টু ঘোষ (গলায় ক্যান্সার) ২০০৬
১৬) তাঁরাপদ দাস (অঙুল ক্যান্সার) ১৯৯৫
১৭) জ্ঞানেন্দ্র সরকার (ব্ল্যাড ক্যান্সার) ১৯৯৪
১৮) সন্তোষ দাস (কিড়নি ক্যান্সার) ২০০৭
১৯) খিরেন দে (গলায় ক্যান্সার) ১৯৯৩
২০) হাঁজারি লাল দাস (ফুসফুস ক্যান্সার) ২০০৯
২১) অধীর মণ্ডল (গলায় ক্যান্সার) ২০০৯
২২) সুকুরঞ্জন সরকার (কিড়নি ক্যান্সার) ২০০৮
২৩) গান্ধী দাস (লিভার ক্যান্সার)
২৪) মায়া রাণী দাস (আঙুল ক্যান্সার)
টেকনোলজি উইথ এ হিউম্যান ফেসের পক্ষে
১) স্বপন পাল
২) দীপক দাস
৩) বিলাস দাস

Figure 8.3. A memorial to twenty-four members of the Binimaypara community who died due to the effects of arsenicosis.

As part of the system revitalization, in 2013, a new caretaker (Partho Das, **Figure 8.4**), was appointed by the local water committee and hired by STHF to operate the system under the direct instruction of STHF and Dr. SenGupta. In this manner, there was a new contractual arrangement, as Partho operated the local system in obligation to an outside organization who was paying him. The hygiene and performance of the system improved under the management of Partho. The number of families increased from 150->170 in two months, a significant increase in a community of 200-250 families. Over time Partho was trained by STHF and Drinkwell to do more maintenance work and he travelled to different systems in other locations.

Figure 8.4. Partho Das in an STHF uniform with Prasun Sengupta (Purchasing Director, Drinkwell), Anil Shaw (Engineering Manager, Drinkwell), and a local community member (L-R) in Binimaypara.

But, in any financial operation, vigilant oversight of operations is important because humans are imperfect agents. During 2016, as Partho was collecting monthly tariffs he did not deposit them to the local water committee and, upon further review, determined that he embezzled over Rs. 1,00,000 ($1500). After pressing Partho for the money, he disappeared from Binimaypara and there is a First Information Report (FIR) for his arrest from the local police as of March 2017. There are many people at fault in this case: Partho for embezzling the money; the local water committee for not being diligent in collecting funds and managing the account; STHF/Drinkwell for being unaware of the actions of Partho while working with him and paying him.

Transactions in India are dominated by cash, especially at more rural levels; this was true even during the demonetization by Prime Minister Modi. Cash-based businesses face significant management risks from fraud and theft, as seen by the example at Binimaypara. Without appropriate controls in place, the use of cash can disrupt a sustainable business model. The shift towards water ATMs and eliminating caretakers by Drinkwell and other organizations is, in part, to eliminate the cash risk; assuming loading cash value onto the ATM card is performed securely.

8.1.2 Haldi, Ballia District, Uttar Pradesh

8.1.2.1 Operations and Performance

The HAIX-NanoFe facility under management by Mr. Ashok Singh was well-operated by paid caretakers (Rs. 5500/month) since day one. The long-term tenacity of management to have high quality drinking water for their community was an unquantifiable factor that led to long-term system success. Over three years of operation, the simple HAIX-NanoFe system in Ballia consistently produced WHO quality safe water from raw water that regularly exceeded the arsenic and iron standards, **Figure 8.5**. From system start, members of the community have paid for safe water (Rs. 100/month/family), which was used for operator salary, consumable materials, Temple Mandir donation, and monthly water quality testing, **Table 8.1**. The revenues, profit, and savings during this time are detailed in **Table 8.2**.

Table 8.1. Total expenses from the HAIX-NanoFe system in Ballia from Dec 2013-Mar 2017.

Item	*Operator Salary*	*Operating Expenses*	*Temple Mandir*
Debit (Rs.)	1,90,050	34,145	22,990

Table 8.2. Total credits from the HAIX-NanoFe system in Ballia from Dec 2013-Mar 2017.

Item	*Revenue*	*Profit*	*Savings*	*Bank*
Credit (Rs.)	3,41,950	1,43,905	1,17,155	57,600

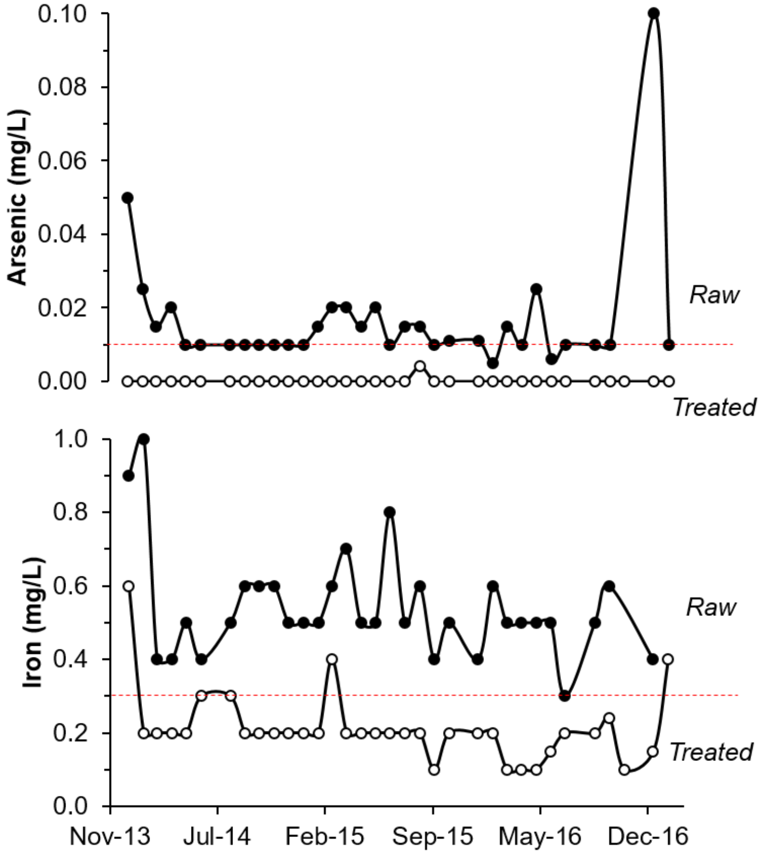


Figure 8.5. Raw and treated water history for arsenic and iron from the HAIX-NanoFe system in Ballia.

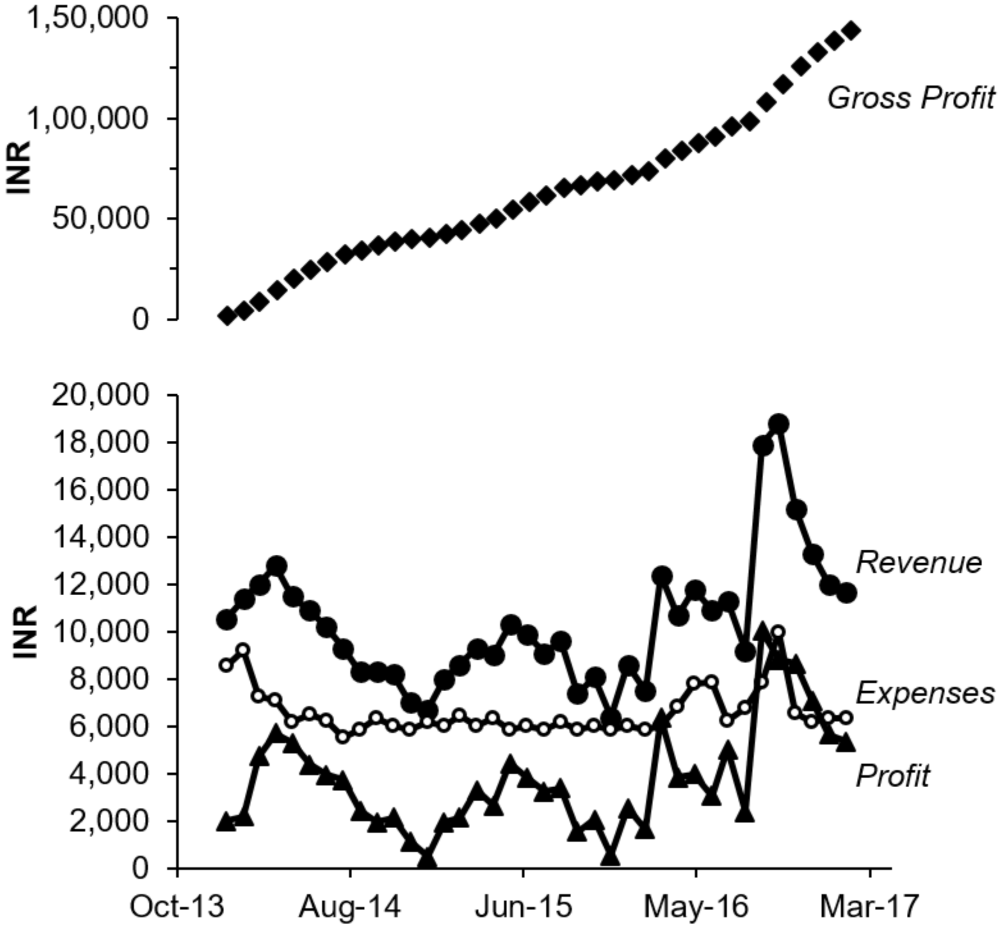


Figure 8.6. Economic data during operation of HAIX-NanoFe in Ballia: gross profit (top); revenue, expenses, and profit (bottom).

Several months after installation, Mr. Singh faced some local water sales competition from other NGO/government offerings, which negatively impacted his peak sales and revenue. He also expressed concern about light hardness precipitation issues, but his community waited for repairs; a post-treatment WAC system in July 2015 eliminated scaling. In August 2016, significant flooding from the Ganga river inundated the region. There was minimal drinking water available in the region as many hand pumps were submerged with the flood waters. The HAIX-NanoFe system in Ballia was one of the few options for safe drinking water. With the humanitarian crisis, HAIX-NanoFe treated water was made free for everyone. At higher usage rates and lower revenue, Aug 2016 was one of the least profitable since opening. But, revenue and profit in Sep-Oct 2016 was over 50% greater than in Jul 2016. Through the winter months (Dec 2016-Feb 2017), a time of typically low revenue in 2015-2016, revenue did not dip below water sales in Jul 2016.

Water quality during the time of increased sales was not noticeably different than before, but more important than water quality was local business acumen. Free water for many new customers in other terms might be "a month long promotional and humanitarian marketing campaign". A humanitarian act with significant costs in lost revenue led to higher sales and immediate returns on investment. Similar to other new technologies, sustainable financial operations of HAIX comes from applying good small business practices.

8.1.2.2 Financing

As a small community operation, Mr. Singh opted for a basic system and utilized existing resources, minimizing his total system CapEx to approximately INR 2,50,000 (~$4,000). Without automated RFID water purchases and data collection/transmission, CapEx was lower, but monthly accounting and water chemistry information was submitted in a timely fashion through the diligence of Mr. Singh and his caretakers. The initial CapEx at Ballia was fully subsidized and operations would not have been able to pay for CapEx within typical loan terms (≤5 years) of microcredit because of the low population density and customer base (N= 100 families per month). But, operations pay caretaker employee wages and are self-sustaining and profit-generating after the CapEx subsidy. The system was cash-flow positive, operating marginally profitably each month for three years. Earnings beyond expenses and wages amount to a few dollars daily, on average, with clear seasonal swings. Based on Monte Carlo simulations with field data later in the chapter, cash flows like these systems appear likely to be typical; operating costs that can be covered, but capital investments that might take long periods to pay back.

8.1.3 SHRI: Bihar (Nemua, Supaul)

Sanitation and Health Rights in India (SHRI, NGO) has a community toilet block of 16 stalls (8-male, 8-female) that serves 800 daily users in the rural village of Nemua outside of Supaul, Bihar, India, at no cost to users. In order to subsidize toilet expenses and to create an inclusive water and sanitation hub, in March 2015 SHRI purchased a community water treatment system using HAIX-NanoFe from Drinkwell to treat the water for arsenic, iron, and bacteria. Paid caretakers and water delivery drivers have operated the system and earned at least INR 5000/month ($75) from the sale of water.

From March 2015-March 2017, water quality remained consistently within WHO limits, but sales fluctuated. Initial sales increased through word-of-mouth excitement over the new installation, water quality, affordable price, and ease of delivery. **Figure 8.7** shows monthly revenue, expenses, and operating profit during this time. Sales stagnated and decreased beginning in May 2015 when the water temperature in black storage tanks reached >55^{O}C in the sun. Instead, people opted for lower temperature, untreated water from underground aquifers, despite lower quality taste/color and the potential for arsenic or bacterial contamination. To meet consumers' aesthetic demands, SHRI purchased a water chiller (INR 60,000, US$925). Sales, also, decreased during Ramadan (June 2015) with the changes in daily behavior, but increased steadily after October 2015. The influent water had moderate iron levels, which were well removed. Between sales variabilities and consistent effluent water quality, no correlations were found between water chemistry (e.g., arsenic, bacteria, or iron) and cash flows of the water system.

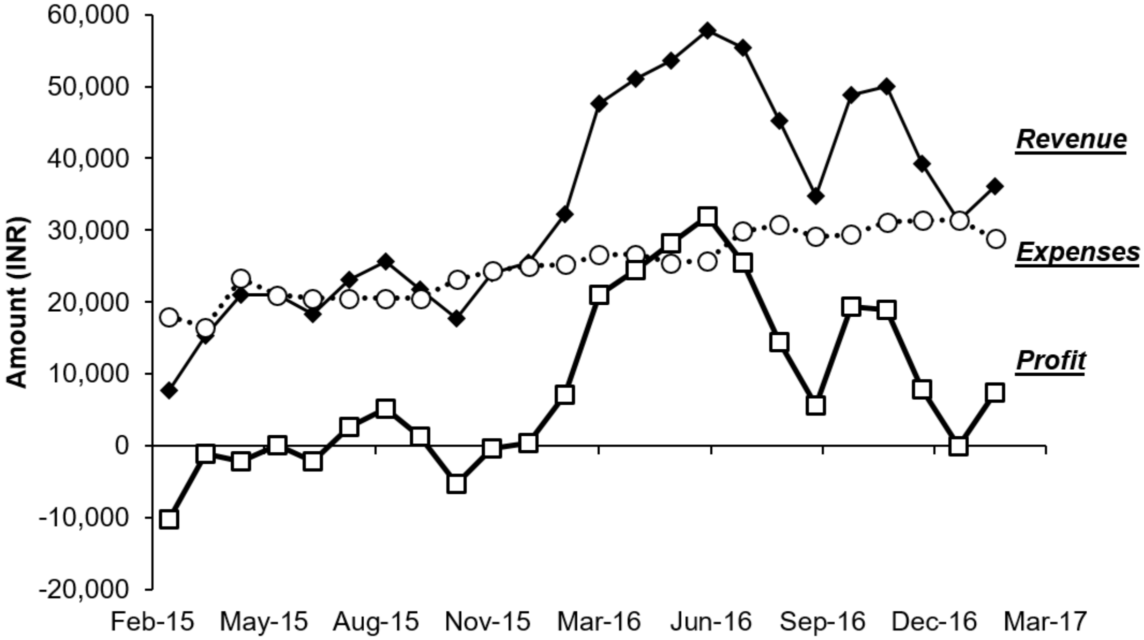


Figure 8.7. Monthly revenue, expenses, and operating profit at SHRI's HAIX-NanoFe system in Nemua (March 2015- Feb 2017).

Box and whisker plots of daily production by month from Jan 2016-March 2017 are in **Figure 8.8**. In Nemua, the preference for delivery increased over time and there were possible increases in variability of daily consumption during festival seasons (August, October). The seasonal trend is verified with a significant correlation between average three-day temperature and average three-day consumption, **Figure 8.9**.

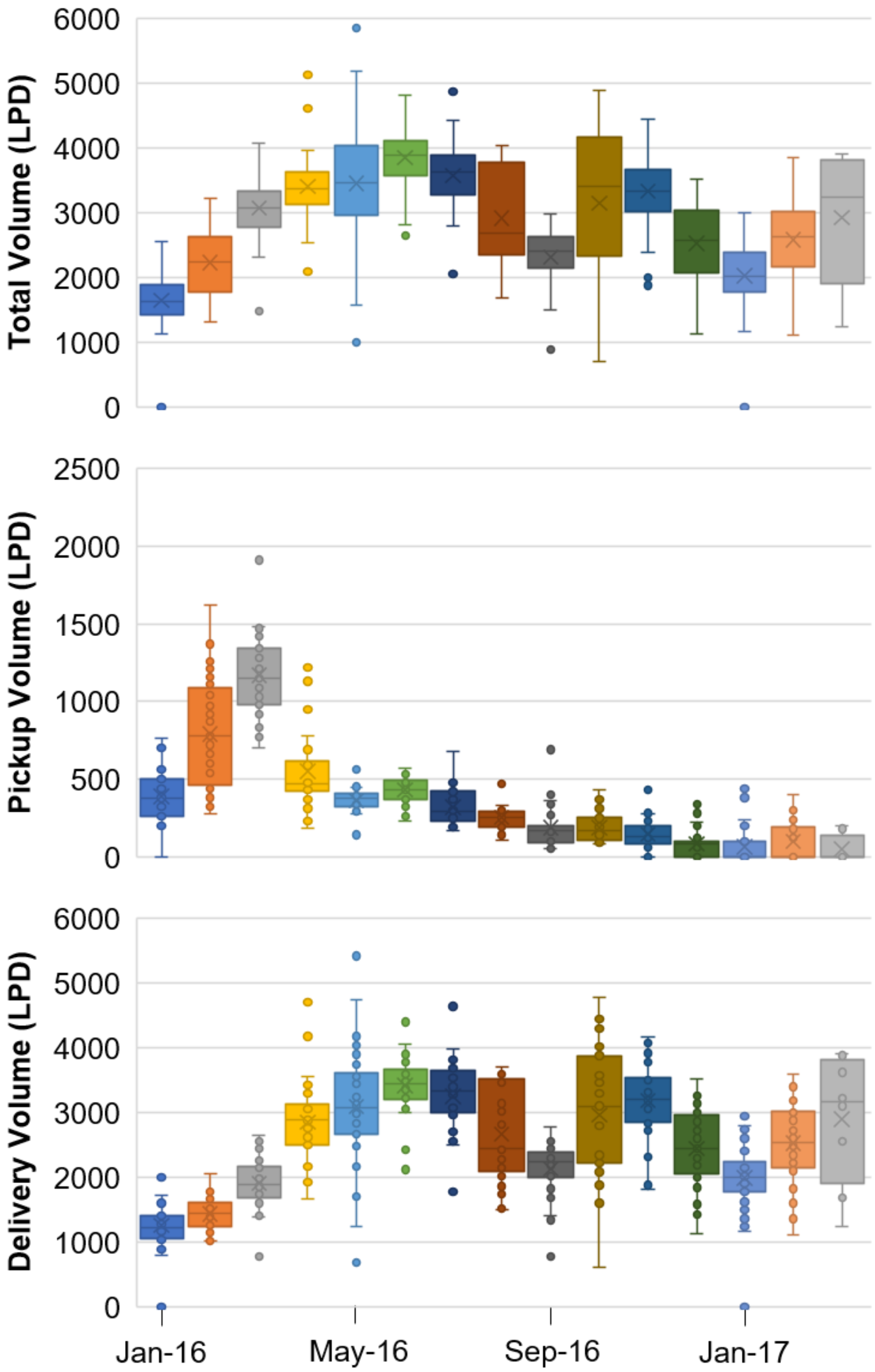


Figure 8.8. Box and whisker plot of daily water consumption at the Nemua HAIX installation by month and category (total, pickup, delivery), (top-bottom).

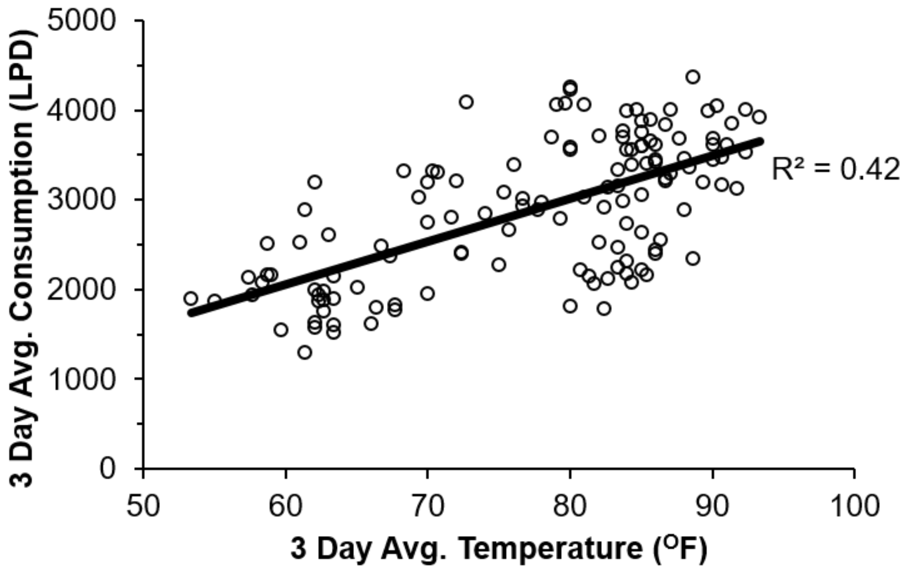


Figure 8.9. Three-day average consumption as a function of three day average temperature at the Nemua HAIX installation. Note: the daily temperatuire is from Patna, Bihar (145 km aerial distance); average temperature gave a better fit than low/high temperature or heat index.

8.1.4 Betila, Manikganj, Bangladesh

Another Drinkwell HAIX-NanoFe system, was installed in Manikganj, Bangladesh in February 2015, after being imported from Kolkata. This was the first community-based arsenic treatment system in Bangladesh to use HAIX-NanoFe materials. The installation was a collaboration between Grameen Seba Songstha (community NGO), STHF, and WIST, Inc.

The tube well for which the system was designed and first connected, had inadequate water flow and the system was reconnected to a nearby deep tube well (August 2015). A "black precipitate" in the treated water was due to significantly higher iron concentrations than the original well. Sodium hypochlorite dosing followed by a packed bed of manganese dioxide-granular activated carbon was later installed and removed the high iron content. However, the period of poor water quality eroded local trust and loyalty in the treated water, which led tens of households to defect from Drinkwell to other local (un)treated water options. The majority of the households who left did not return, but new customers were acquired.

Throughout operation, a paid delivery employee earned BDT 9000/month ($115), or 30% above the BDT ~7200/month national per capita income in Bangladesh. The history of monthly water revenue, expenses and profit are in **Figure 8.10**. Volumetric monthly water sales and means of distribution can be found in **Figure 8.11**. In total, four systems have been installed across Bangladesh, in Manikganj, Kalaroa, Faridpur and Nawabgunj.

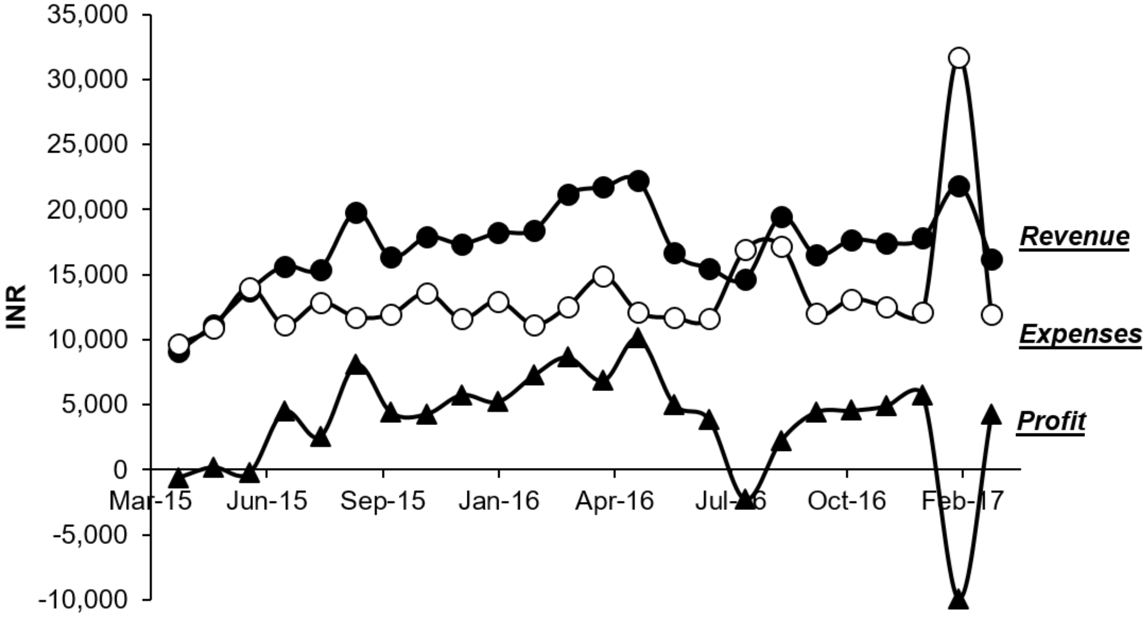


Figure 8.10. Monthly revenue, expenses, and operating profit, HAIX-NanoFe system installation, Manikganj, Bangladesh.

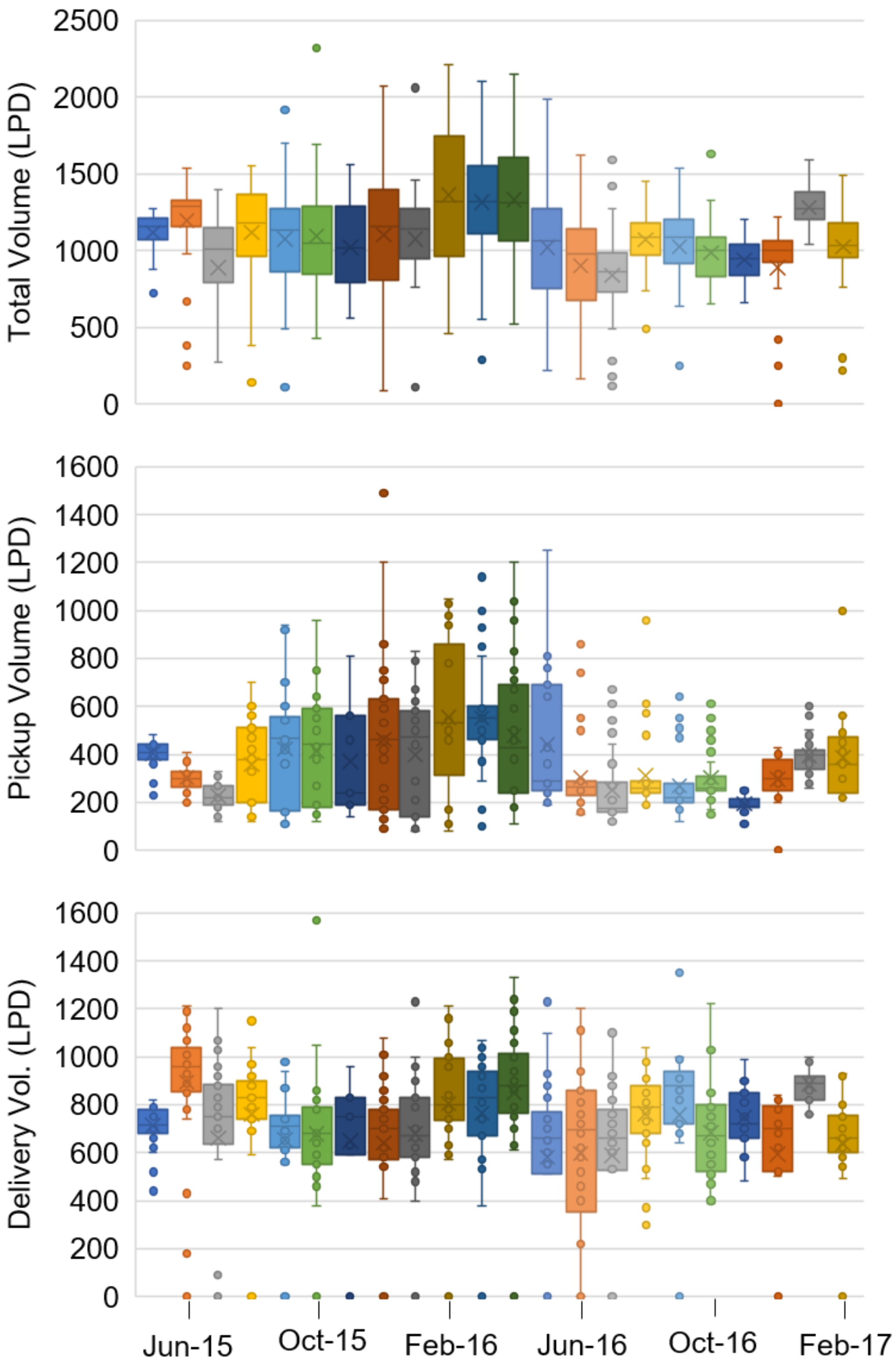


Figure 8.11. Box and whisker plot of daily water consumption at the Betila HAIX installation by month and category (total, pickup, delivery), (top-bottom).

8.1.5 Learnings from Case Studies with HAIX-Nano

Major influences on water sales were water quality (e.g., undesirable precipitation), water aesthetics (e.g., temperature), and seasonality (e.g., seasonal temperature and demand changes, Ramadan fasting). Note that none of these influences include the primary public health concern: arsenic. Yet, such non-arsenic concerns are central if safe water microenterprise operations are to be profitable and self-sustainable. Hardness and iron content must be appropriately managed to ensure the final water quality meets customer aesthetic expectations. Expectations of summertime water usage, e.g., as a refreshing beverage, should influence system design to limit solar radiation and to moderate water temperature. Dates of religious celebrations should influence sales strategies and water delivery planning, e.g., delivery schemes that reduce the burden of water access during fasting, increasing the customer base via variable pricing and short-term discounts.

Initial treatment operations had low customer sales. Supaul was only cash flow positive above Rs. 5,000/month for one month during the first year. Manikganj had ≤100 household customers for over 65% of the first 12 months of operation. Despite having similar numbers of customers and prices (INR 100/month) as Supaul and Manikganj, Ballia was cash flow positive for the entirety of its operation, because the standard monthly fee at Ballia did not include water delivery, eliminating costs for delivery labor and vehicle OpEx. Depending on local conditions, an average of 225 households paying monthly fees would be necessary to make operations cash flow positive.

8.2 HAIX-Nano System: Technical Design and Economic Needs

8.2.1 Financing Options

The upfront CapEx is a principal barrier to centralized water treatment systems for rural communities. **Table 8.3** lists the major CapEx components for different HAIX-Nano systems and approximate costs in India. The main funding options for CapEx of microenterprises are charitable donations (individuals or NGOs), public contracts, or private loans. Many NGO- and government-funded groundwater treatment and sanitation projects have had high rates of failures (15,18,129–133). Key challenges with public contracts have included collusion between bidders and graft in government bidding process in the bidding process, which often foretells poor implementation quality and system performance (134,135).

Table 8.3. Overview of CapEx components for an HAIX-Nano system.

Example Initial Capital Expense Components	New site, full w/ATM pay system (INR)	Existing well & structure	Barebones
HAIX-Nano Media & Commodity Chemicals	1,02,750	1,02,750	1,02,750
Land	2,50,000		
Tube well Drilling	48,000		
Overhead Tank	15,000	15,000	15,000
Resin Reactors	50,000	50,000	50,000
Storage Tank	15,000	15,000	15,000
Water Jugs	36,750	36,750	
Solar Panel	23,850	23,850	
Water ATM	85,000	85,000	
Building Construction	1,40,000		
Sales Tracking & Reporting System	6,400	6,400	
System Installation	32,000	32,000	32,000
Delivery Vehicle	44,800	44,800	
Launch Festival	15,750	15,750	
Total INR	8,65,300	4,27,300	2,14,750
Total USD (@ 68 INR/$, Jan. 2016)	$12,754	$6,298	$3,165

The limited track record of effectiveness and ability to scale for heavily subsidized public/private options requires loan financing of private microenterprises to be considered. Few rural village microenterprises could qualify for traditional bank loans at commercial business rates (~12% APR in the region), given the high risk and unproven nature of the business model (136). However, private investment of $5,000-$10,000 could be supported by the competitive marketplace of microfinance institutions throughout the Indian subcontinent at 20-40% APR, for loan terms up to 3-5 years.

8.2.2 Competitive Benchmarks

Many companies have installed community water kiosks that are operated by local entrepreneurs in rural India. The majority of these systems used reverse osmosis (RO), which has high water reject, is prone to mechanical failure, and requires consistent availability of electricity. A selective adsorbent, e.g., HAIX-NanoZr, avoids these costs and a system operator could charge lower fees, **Table 8.4**.

Table 8.4. Comparison of monthly subscription prices for community water kiosks.

Monthly Subscription Price (INR) for 20 L/day	Description
35	**STHF (N. 24 Parganas, West Bengal) ***
100	**STHF (Ballia, UP) ***
100	**Drinkwell (Bangladesh); SHRI (India) ***
120	Safe Water Network
150	E-Health Point/Naandi Foundation
180	Waterhealth International
200	Waterlife
240	Sarvajal
270	Springhealth

* HAIX-Nano installations

8.2.3 Cash Flow Model Development

8.2.3.1 Background

With detailed cash flow models, multiple simulations of operations can be examined and sensitivity analysis of individual parameters can be performed; similar real life testing would not be possible because of time and resource limitations. A cash flow model of unit economics was developed in Excel by Minhaj Chowdhury, Mike German, and Trisha Chakraborty for microenterprise operations to account for process economics: CapEx [e.g., site preparation cost (S), HAIX-Nano resin (R), system equipment (E), construction (C)]; Wages (W); non-wage OpEx [e.g., quantity of water processed (Q), electricity expense (Z), operation and maintenance (M), delivery (D), marketing (K), overhead (Ov)]; financial expense or FinEx [e.g., amount borrowed (B), loan interest rate (I), amortization term period (T)]; and revenue or REV [e.g., price of water (P) and number of customers (N)].

Net monthly cash flows (CF_{it}), i.e., monthly operating profit or loss, in location *i* during month *t*, were then:

$$CF_{it} = REV(P_{it}, Q_{it}, N_{it}) - \left\{ \begin{matrix} CapEx_{it}(S_{it}, R_{it}, E_{it}, C_{it}) + W_{it} + \\ OpEx_{it}(Q_{it}, Z_{it}, M_{it}, D_{it}, K_{it}, Ov_{it}) + FinEx_{it}(B_i, I_i, T_i) \end{matrix} \right\} \quad (8.1)$$

Three operational sustainability questions for potential system owners or system managers are 1) whether operations can have sustainable economics—with monthly revenues exceeding monthly expenses; 2) when can operations payback their up-front capital equipment investments; 3) the rate of return on their investments. Operations are cash flow positive, i.e., have a monthly operating profit, when $CF_{it} > 0$, and were considered sustainable if $CF_{it} > 0$ more often than $CF_{it} < 0$. From period cash flows, cumulative cash flows (CCF_{it}) through month *t* are

$$CCF_{it} = \sum_{n=0}^{t} CF_{in} \tag{8.2}$$

If it is assumed that early period cash flows are negative due to up front CapEx investments, the breakeven time, if ever, required to pay back the up-front investments, would occur in the first month when $CCF_{it} \geq 0$.

The internal rate of return of an investment over time period k is the interest rate (IRR) at which the sum of discounted cash flows (i.e. net present value) equals zero.

$$0 = \sum_{n=0}^{k} \frac{CF_{in}}{(1 + IRR)^{n}} \tag{8.3}$$

Self-sustaining operations were explored via Monte Carlo simulations (using Palisade's @Risk 7 in Excel 2016, 2000 iterations) under various scenarios to determine period cash flows, operational breakeven periods and internal rates of returns on investments. Mike German coded a Monte Carlo VBA file that was used for initial testing and development of the Excel cash flow model for Monte Carlo. Dr. Watkins ran the presented simulations in January 2016 with access to @Risk 7. Rather than making assumptions about variable parameter distributions, as is typical in Monte Carlo applications, financial data from actual system implementations was used to inform the modeling. Probability distributions for key input variables in the cash flow simulations (CapEx, W, non-wage OpEx, P, N, Q, B, I, T) were best fit distributions from data collected, in some cases for more than a decade, at nine installed village-scale HAIX-Nano-based arsenic treatment systems in India, Bangladesh and Cambodia (a total of 103 observations) or from national surveys (for W, I). The major modeling outputs of interest are monthly operational profitability (CF_{it}), time until breakeven (t when $CCF_{it} \geq 0$) and internal rate of return (IRR).

Various scenarios were considered, in which: 1) the initial CapEx cost was or was not borne by the owner; 2) initial CapEx payment by the owner was complete or partially financed by a loan; and, 3) caretakers did/did not take a salary. In addition to identifying field conditions for operational sustainability and profitability, the simulations explored: 1) the necessity (or not) of capital subsidies from outside groups, such as NGOs or governments; 2) the desirability of microcredit; and, 3) whether operations can create employment opportunities at reasonable wages.

8.2.3.2 Inputs

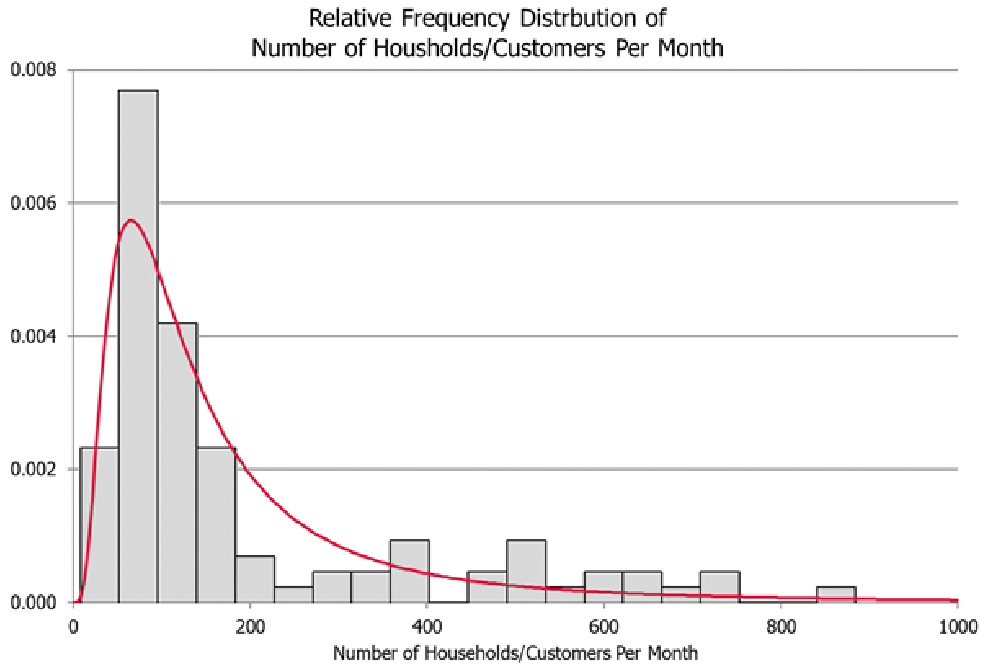
Summary input field data and best-fit distributions for Monte Carlo Analysis of the cash flow model are in **Table 8.5** and **Figure 8.12**, respectively. Filter media or HAIX-Nano resin (R) was a variable separated from the rest of CapEx and varied independently; many potential customers, e.g., local governments and NGOs, have expressed concern about the price of the filter media. Revenue per customer, or water price (P), had three main modes (INR 30, 100, 150 per month for 20 L/day), which represented non-profit vs. for-profit pricing and different delivery distances (0-5km). For operational scale in customers per month (N), newer (< 3 years) and more remote field installations typically had smaller operations with 50-200 households. Upper-end observations (>500 households) are from long-established, well-managed operations. For monthly cash flow modeling over time, N was increased from zero to a variable maximum over 24 months, with faster growth in year 1 than during year 2.

Since locations reported elements of OpEx differently, monthly operating costs (OpEx) were included as a whole, excluding wages. Rural wage (W) distributions were drawn from 2014 surveys by the Labor Bureau, Government of India (137). Microfinance loan interest rate (I) data was sourced from public records that represented 94 different microfinance institutions (MFIs) in India, offering hundreds of different loan products; microcredit interest rates in India have been near 30% APR, and depend marginally on the loan term (T, varied as standard 12, 36, or 60 month loans) (138). Models were also varied on the fraction of CapEx borrowed (B = 0%, 20%, 40%, 60%, 80% or 100%).

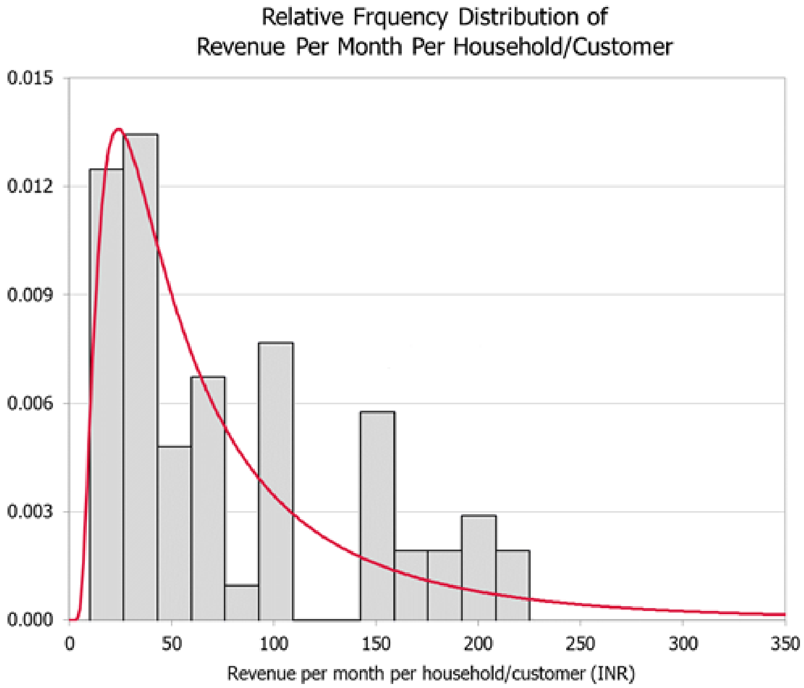
Table 8.5. Field experience data and national data used in modeling, summary statistics.

		Mean	St. Dev.	Min	Max	Skew	Kurt.	Best Fit Distribution
Field Data	Initial Capital Expense, INR (CapEx)	3,59,272	2,49,267	1,55,000	7,18,387	0.895	2.547	LogNorm
	Revenue Per Customer Per Month, INR (P)	79	63	10	225	0.886	-0.431	InvGauss
	Customers per Month (N)	194	195	8	884	1.669	1.941	Pearson6
	Operating Costs per Month (not incl. wages), INR (OpEx)	1,951	2,520	15	11,250	2.218	5.346	LogLogist
National Data	Rural Wages/Month, INR * (W)	5,532	2,105	1,887	13,744	1.070	2.051	LogLogist
	Microloan Interest Rate ** (I)	32.1%	5.7%	13.4%	58.3%	0.973	1.835	LogLogist

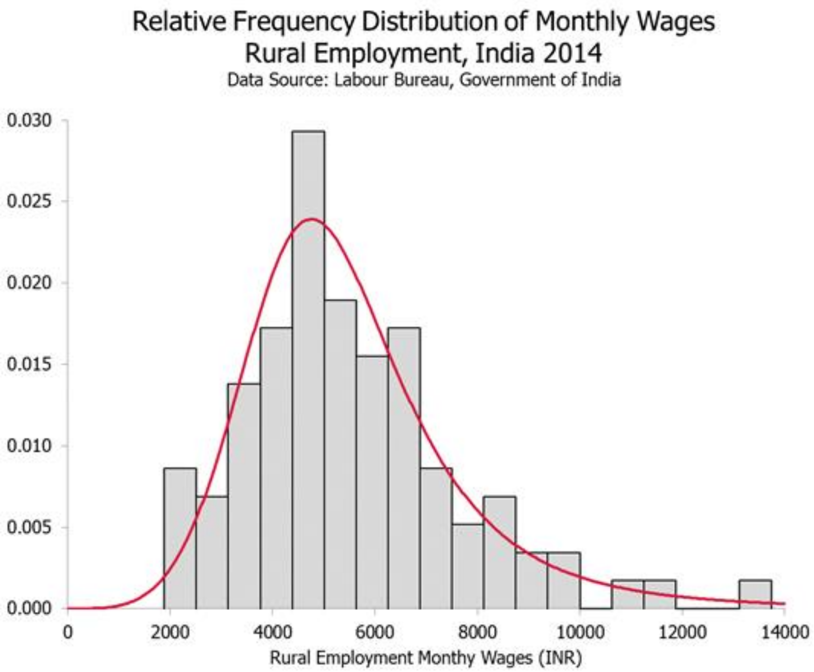
* *Data source*: MFTransparency.org, 2012-2014 (137)
** *Data source*: Labour Bureau, Government of India, 2014. (138)



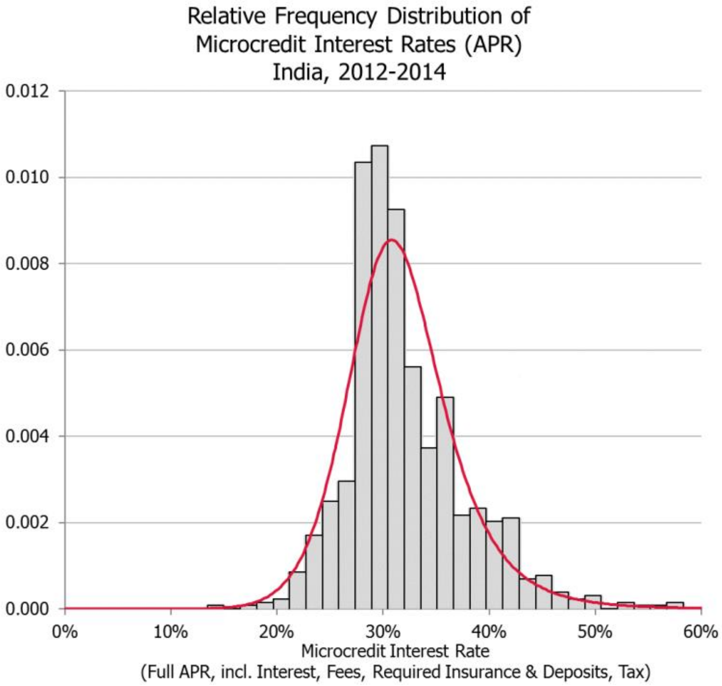
A) Customers per Month (N)



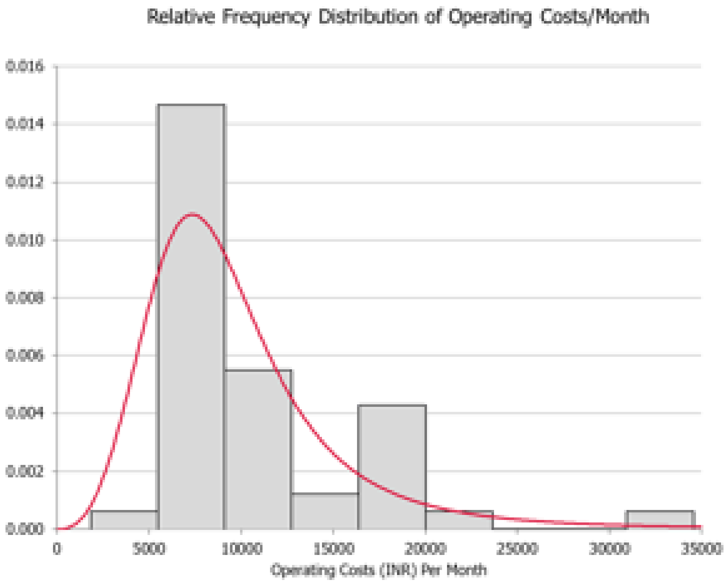
B) Revenue per household per month (water price, P)



C) Average rural wages per month (W)



D) Microcredit interest rates across India (I)



E) Monthly OpEx

Figure 8.12. Relative frequency distributions from field data & best-fit distributions used in the cash flow model: A) Customers per Month (N); B) Revenue per household per month (water price, P); C) Average rural wages per month (W); D) Microcredit interest rates across India (I); E) Monthly OpEx.

8.2.3.3 Outputs

Under the most expensive upfront operating conditions, i.e., financing the entire upfront CapEx (B=100%) with a microfinance rate loan (I) and paying market rate rural wages (W) to a caretaker to operate the system, 90% of scenarios that became cash flow positive (CF>0) did so between N=40 and N=468 household customers, as shown in **Figure 8.13**. Actual treatment systems have had average monthly customers within or above this range. Thus, the operational-scale needed for self-sustainable operations with operators earning above average wages was achieved and can readily be achieved in future systems.

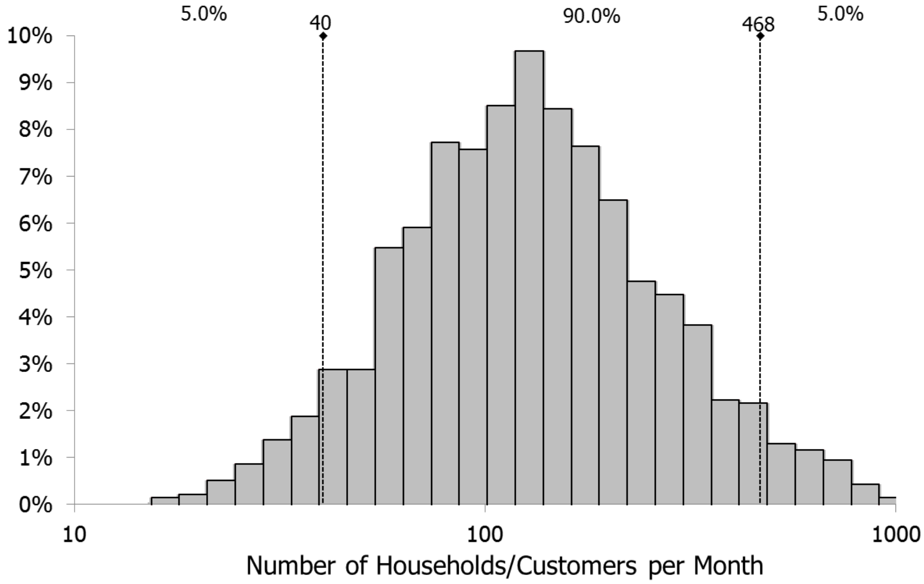


Figure 8.13. Monte Carlo outcome relative frequency distribution for the number of households per month (log scale) at which monthly net operating profit becomes positive (CF>0), in models with a microfinance loan and market-rate wages.

Similar results were produced from simulation results on monthly operating profits (CF), which would represent the monthly take home for any private owner. Two-thirds or more of scenarios, in models with or without a salaried caretaker (W=0 or W_{it}), are cash-flow positive by the end of customer growth (Month 12), **Figure 8.14** and **Figure 8.15**, respectively. **Figure 8.15** is based on operations at many NGO sites and **Figure 8.17** is based on operations at several Drinkwell sites, per **Table 8.4**. About one-third of scenarios, also, enable earning more than India's average per capita income of roughly INR 5500.

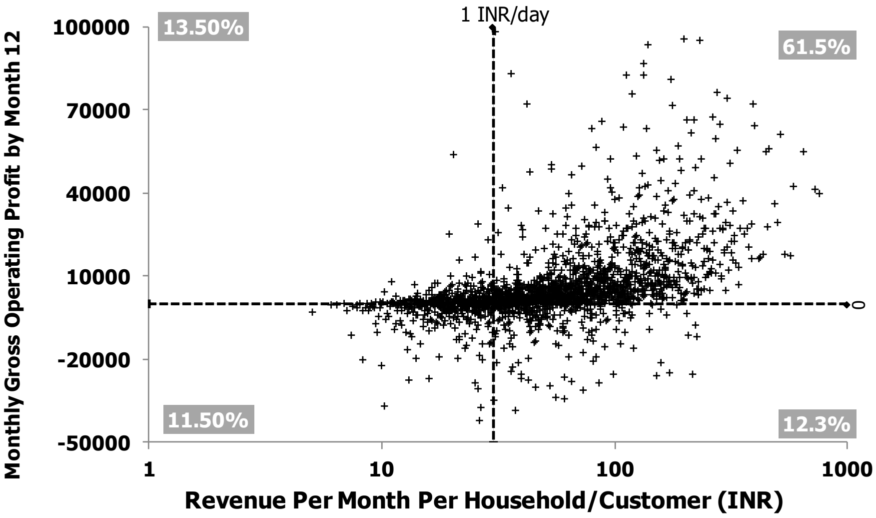


Figure 8.14. Monte Carlo outcome for monthly gross operating profit per month vs. revenue per month per customer (or price), without a salaried caretaker (W=0) and without loan financing (B=0%).

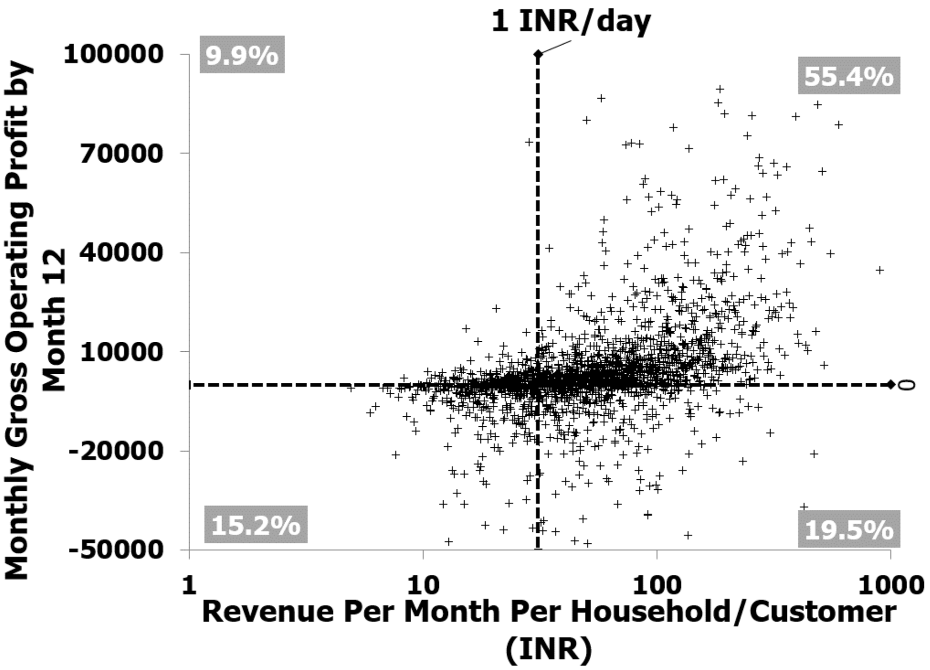


Figure 8.15. Monte Carlo outcome for monthly gross operating profit per month vs. revenue per month per customer (or price), with a salaried caretaker (W_{it}) and without loan financing (B=0%).

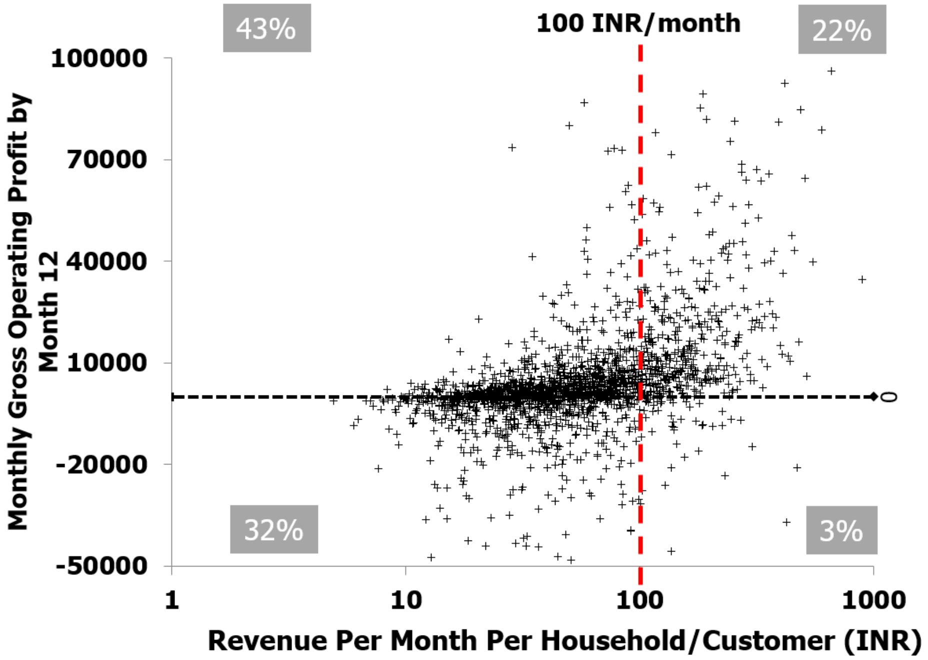


Figure 8.16. Figure 8.15 with quadrant percentages for monthly revenue of 100 INR.

Self-sustaining ongoing operations (CF>0) were modeled to be relatively achievable under a wide range of field settings. However, thin operating margins, e.g., wages being paid to system caretakers (W>0), caused long payback periods (>5 years for CCF>0). Long expected payback periods would make access to traditional financing for capital investments difficult for private owners without subsidization. In models without caretaker wages (W=0) nor loan payments (I=0%), capital breakeven (CCF>0) in two years (20%) was half as probable as capital breakeven in over five years (>40%), **Figure 8.17**. Including caretaker wages (W=) and full loan payments (I= %), decreased the probability did not significantly decrease the probability of payback within five years, **Figure 8.19**. Thus, only locations that accurately forecast several hundred paying households within 18 months would be amenable to financing the majority of CapEx through a standard 3- or 5-year loan without defaulting.

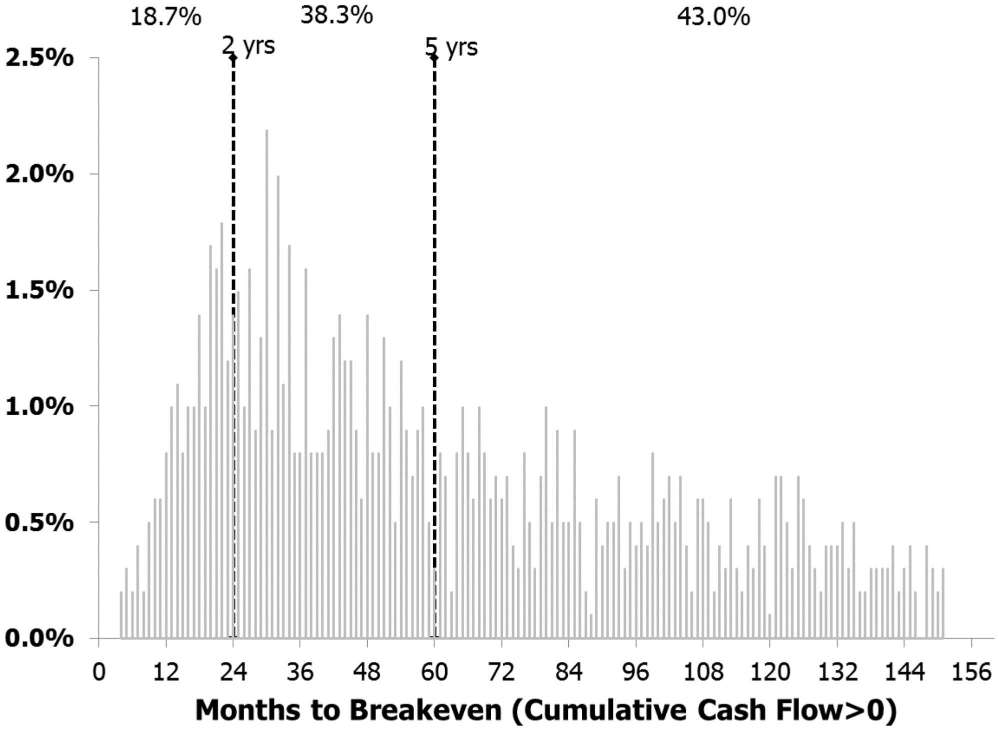


Figure 8.17. Monte Carlo outcome frequency distribution of time (months) until the cumulative cash flow was positive, if ever, including CapEx. (B=0%, W=0).

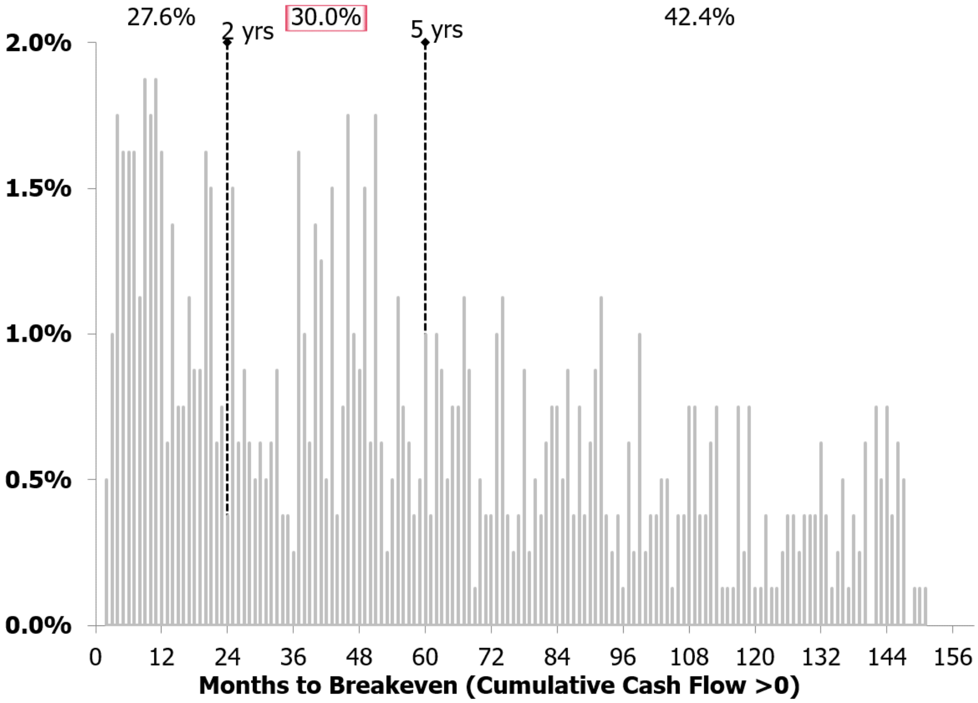


Figure 8.18. Monte Carlo outcome frequency distribution of time (months) until the cumulative cash flow was positive, if ever, including CapEx. (B=100%, W_{it}).

The relative importance of key economic variables to the modeled 5-year CCF is presented in **Figure 8.19**. Overall, the main drivers of water treatment self-sustainability were achieving scale in 1) numbers of customers served and 2) fees charged for water—i.e., perhaps not surprisingly, what mattered most for sustainable operations was the price of the product and quantity sold, like the Economics 101 total revenue equation TR= P x Q. Simulation results were not very sensitive to the initial cost of HAIX-Nano filter materials (R), compared to existing alternatives. However, the high performance of HAIX-Nano was key to significantly lower ongoing operating costs and long-term profitability.

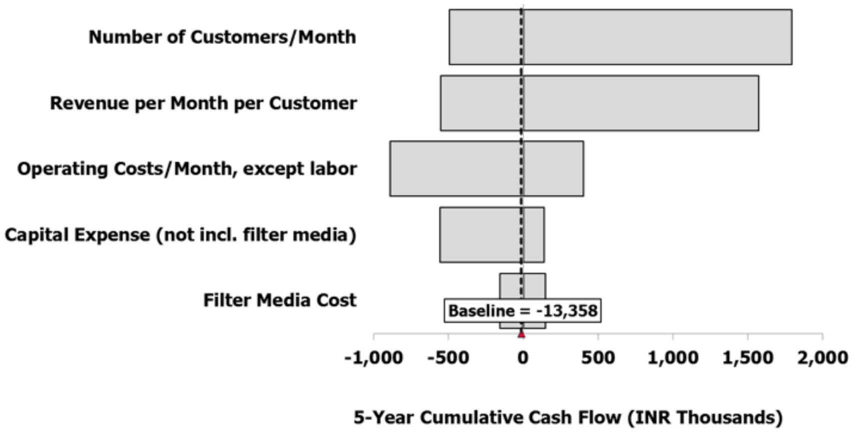


Figure 8.19. Sensitivity analysis of multiple input parameters on the cumulative cash flow over 5 years when there is no loan nor wages.

For individuals or private/public organizations who don't require a loan, the value of treatment systems is derived significantly from the public health benefit or regulatory compliance, but the financial benefit and local job creation could also be significant. The likelihood of positive IRR on the upfront investment over 5 years was significant (>25%) and dependent on the same factors that influence CCF. Model scenarios indicated the importance of minimizing capital expense, or loan amount, in order to achieve a positive IRR, where a positive IRR was 3x more likely (21% vs. 8%) if the capital expense was below the expected bare bones system cost, **Figure 8.20**. However, a pure IRR calculation should not be the only consideration for water treatment installations because of the indirect value to health, community and productivity.

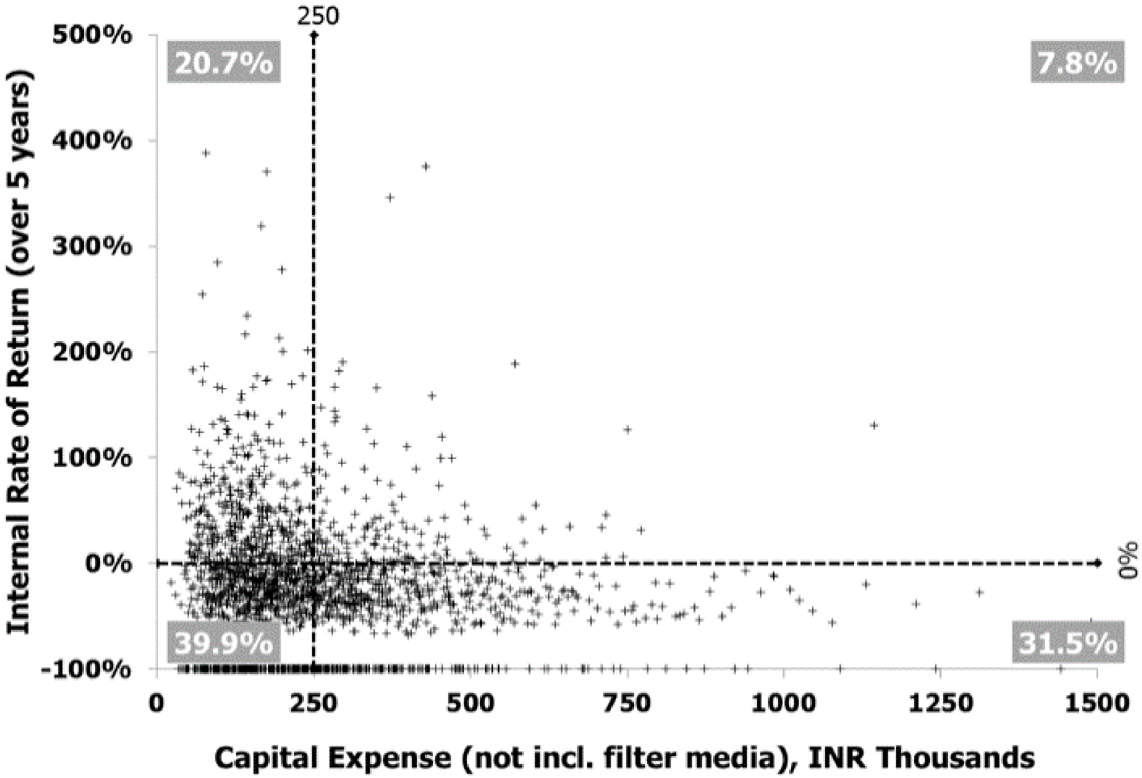


Figure 8.20. Internal rate of return (over 5 years) vs. CapEx. Model without loan or wages.

8.2.4 Insights

The past 15 years of development and implementation of HAIX-Nano technology with holistic business models created arsenic and fluoride treatment ecosystems that have effectively provided safe water for rural communities. Success was seen in multiple countries in South/Southeast Asia and new efforts will shortly bring HAIX-Nano supported fluoride treatment to East Africa; pilot-scale testing is underway in Kenya as of Spring 2016. Using a detailed cash flow model and input distributions drawn from field experience, Monte Carlo simulation analysis found 1) total number of households served; 2) water prices; 3) and recurring expenses to be the most significant factors to reach self-sustainability, in agreement with empirical experience in the field.

The main other extrapolations of community-based arsenic treatment systems from the Monte Carlo simulations, include:

1) Filter media cost is of low importance to overall cash flows and profitability;
2) Rapid user acquisition, i.e., entrepreneurial acumen, should be emphasized for maximum impact and long-term sustainability;
3) Once capitalized, self-sustaining operations were relatively achievable under a wide range of scenarios;
4) Systems can generate monthly income for an owner-caretaker, or a wage employee, near or above average rural income in India (~INR 4500-5500, or several times the poverty line), while simultaneously reducing arsenic well below WHO standards;
5) Reimbursing and financing capital costs will likely remain a problem for all but the best managed operations without subsidies or unconventional loan terms.

9. Conclusions and Future Work

9.1 Conclusions

Global water quality issues are complex and multi-faceted. Many stakeholders are required to work in tandem for making long-term change. An important part of this change is the proper technological solution that is implemented through a proper business model. Aquifers with high concentrations of trace toxic ligands (e.g., arsenic, fluoride) in combination with high TDS were a poorly-addressed technological challenge.

Novel HAIX-NanoZr adsorbents were synthesized with high zirconium oxide content (~15%). As a hybrid ion exchanger, HAIX-NanoZr retained the individual properties of both the polymeric and metal oxide phases: anion exchange capacity and Lewis acid-base interactions. The zirconium oxide had high affinity for arsenic, fluoride, phosphate, and silica. The fluoride capacity of HAIX-NanoZr was directly correlated to the zeta potential. To maximize fluoride capacity, passive influent acidification without addition of TDS was required. Through proton-cation exchange, the pH of influent water was decreased and hardness was removed. Additionally, with proton exchange, alkalinity was eliminated as carbon dioxide was degassed. Under proper operation, the fluoride capacity of HAIX-NanoZr per regeneration cycle increased 10x from 300 BVs to 3500 BVs. Fluoride capacity was constant over several cycles of regeneration and the zirconium oxide remained in the amorphous phase. Partial desalination with concurrent defluoridation was achieved.

After successful lab testing at Lehigh University, synthesis was modified and re-developed over many iterations in the laboratory space of STHF in Kolkata, India. Past field work success in arsenic treatment and new development of HAIX-NanoZr spurred the founding of a start-up company to scale-up a high capacity, sustainable arsenic and fluoride treatment system using HAIX-NanoZr across the Indian subcontinent. Through grant funding awarded by the US-India government to the tart-up and a partner local company, multiple community-scale test systems were installed and monitored across multiple states of India. Lessons learned from early operational and installation errors, led to improved system design and operational practices. Third-party evaluations by the governmental organizations in charge of water treatment certified HAIX-NanoZr as an effective treatment process for arsenic, fluoride, and partial desalination. With certification, HAIX-NanoZr earned government contracts through the local partner company.

Cash flow and operational data from entrepreneurially-operated HAIX-based treatment systems were analyzed from multiple sites in India and Bangladesh. Multiple locations had seasonal trends in water consumption correlated with the average temperature. Well operated systems tended to have water sales grow over time. Anecdotally, different unquantified point events impacted water consumption and sales over the short- and long-term. Cash flow models were developed based on real-world experiences and operations. Monte Carlo simulations reinforced field understandings:

1) The cost of the adsorbent or treatment scheme does not play a significant role in the overall cash flows and long-term profitability;
2) Market rate wages can be afforded by typical operations;

3) Profitability is most sensitive to the number of customers and cost of water (i.e., TR=PxQ);
4) The majority of operating scenarios are able to afford operating expenses, after the capital expenses have been met;
5) Financing capital costs through MFIs or traditional financial institutions is unlikely, except for the systems with maximum number of customers.

9.2 Future Work

9.2.1 On-going Work in India and Bangladesh

As of March 2017, the production of HAIX-NanoZr continues to expand in Kolkata. Export of HAIX-NanoZr has not occurred for fluoride removal, but import of HAIX-NanoFe(/Zr) to Bangladesh may occur in the near future for arsenic treatment work. More community-scale pilot systems are being planned and installed in partnership with an Indian partner company across multiple states in India as part of work with governmental agencies and non-profit foundations. General water treatment enquiries involving cooling water, desalination, iron removal, microbiological treatment, and reverse osmosis have been presented and considered at different points. But, the priority for the Indian start-up company is increase revenue and profit in order to meet all budgetary requirements.

9.2.2 Data Mapping

Community-operated HAIX-NanoZr systems similar to the developed model will be installed and tested in collaboration with large non-profit foundations. An assumption that was inherent in the model was that site and entrepreneur selection was easily accomplished. The selection process arose as a major difficulty and time requirement in recent efforts. Datasets of water quality, socioeconomics, water-related news events, and on-going governmental projects are being compiled into an interactive heat map that guides site selection to avoid future delays. Such a tool may be useful for other development projects for pre-screening locations.

9.2.3 Other Uses for HAIX-NanoZr: Phosphate and Silica Removal

Besides arsenic and fluoride capacity, HAIX-NanoZr has high selectivity for phosphate and silica. Phosphate is a significant concern for the prevention of eutrophication. Multiple other phosphate adsorbents and treatment methods exist, but in work by Dr. Sukalyan Sengupta (UMass), Chelsey Shepsko (Lehigh), and Jinze Li (Lehigh), zirconium showed greater capacity than other adsorbents at certain water chemistries. Shepsko is using HAIX-NanoZr as part of her PhD dissertation research on nutrient reuse.

Silica removal from influent water is important to eliminate fouling on heating surfaces and membranes. Warm lime softening is one of the standard treatment methods for industrial processes, but is operationally complex and generates large volumes of sludge for disposal. Currently, there are no high efficiency, easy to operate silica removal processes. With high silica selectivity, HAIX-NanoZr could be the first packed-bed option for silica removal, based on preliminary work by Hang Dong, Mike German, and Jinze Li. However, silica removal did not behave like either an ion exchange or sorption process.

More research on silica removal by HAIX-NanoZr will be necessary to understand the mechanism behind removal.

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11. Appendix

11.1 Chapter 2 Appendix

11.1.1 Comparing strength of Lewis acidity/basicity

Hard-hard interactions are well described by RG Pearson in his 1983 paper (Parr, Pearson 1983):

> For hard acid-hard base combinations, since there is little electron transfer from base to acid, the bonding electrons must, on the average, remain on the base. Thus, ionic bonding will usually be favorable. The characteristics of a hard acid, high positive charge and small size, favor electrostatic interaction with B, which retains most of its negative charge, and which presents a favorable dipole interaction with a lone pair of electrons pointing at A.

Experimentally, comparisons of the enthalpy of complexation between Lewis bases to a reference Lewis acid (e.g., BF_3, CH_3Hg^+) can be used to define and compare the strengths of Lewis basicity (Laurence, et al. 2009): reactants with more exothermic reactions are stronger Lewis bases, i.e., greater enthalpy. The hardness of a Lewis acid was well correlated with β-values for the Edwards equation. For measuring Lewis acidity, the current best practice was only developed in the mid-1990s: the Gutmann-Beckett method (Beckett et al. 1996). In this method, a Lewis acid is reacted with triethylphosphine oxide (TEPO) and the reaction is monitored under ^{31}P NMR. Both of these scales of measurement are quite labor and resource intensive to develop, and generally unknown/unused by people in the field. As applied to surfaces, further difficulty arises versus the solution-based tests.

11.1.2 Ion Exchange Induced Precipitation

Solids precipitation via ion exchange can be used to remove: (1) chloride via precipitation after passing a solution through a cation exchange resin in silver-form; (2) divalent cations (e.g., Ca^{2+}, Ba^{2+}, Sr^{2+}, Ra^{2+}) via an anion exchange resin in sulfate-form; (3) sulfate via a cation exchange resin in barium-form. But, salts of silver, sulfate, or barium are either less available, expensive, and/or toxic, and their potential trace leakage into effluent water would be a health concern.

11.2 Chapter 3- Appendix

11.2.1 Bone Char

Below is a series of photographs depicting the bone char production process at NDC

Figure 11.1. Example of bones from a variety of animals, especially cows, that might be used in the synthesis of bone char.

Figure 11.2. A worker sorting bones before grinding and crushing them into smaller pieces.

Figure 11.3. Barn-sized furnace where bones were placed for controlled charring/activation.

Figure 11.4. Steel tubes used for spacing the bones inside the furnace for more uniform air flow.

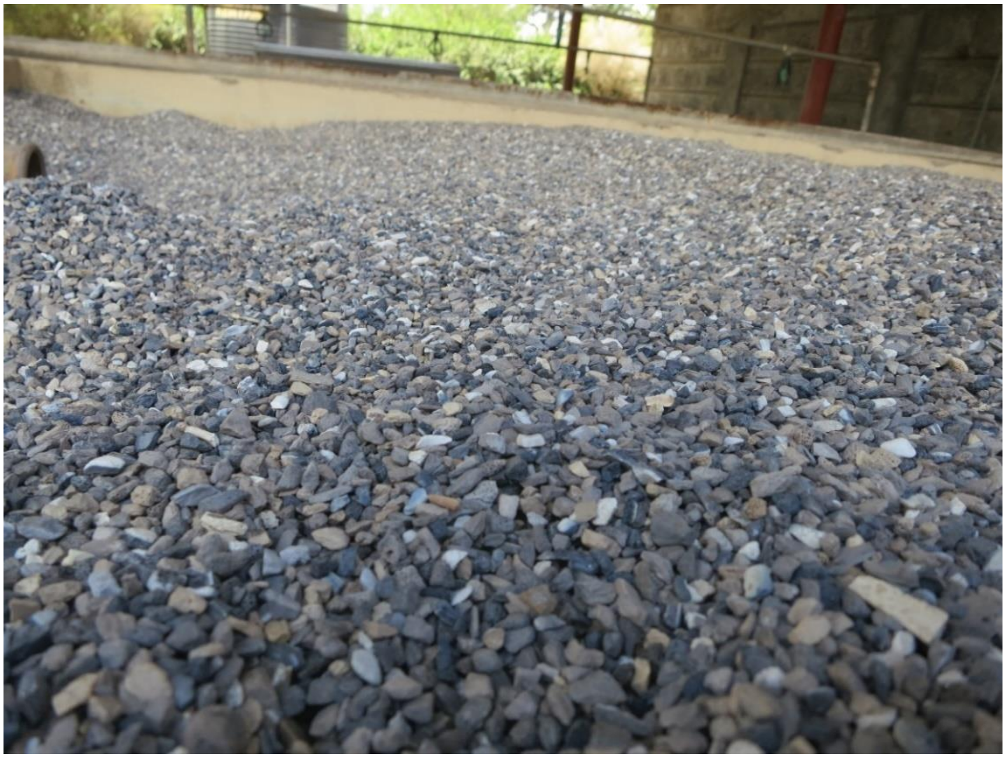
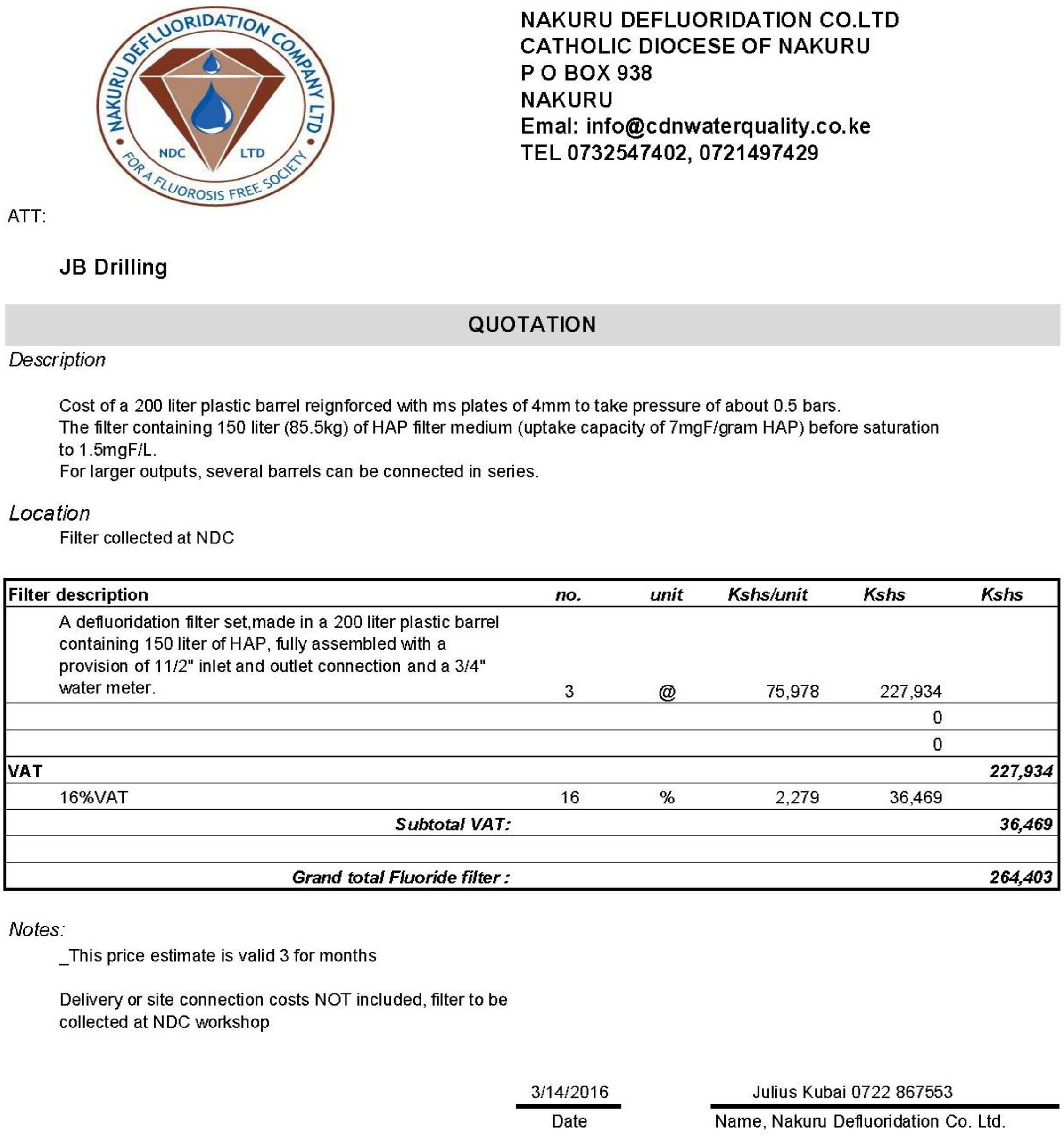


Figure 11.5. Charred bone pieces in the washing tank where charred-on organics are removed with a dilute acid wash.

11.2.2 Hydroxyapatite (HAP)

Figure 11.6. Trailer-mounted HAP production system.

Figure 11.7. HAP filters installed by JB Drilling in a treatment system outside Nakuru.



NAKURU DEFLUORIDATION CO.LTD
CATHOLIC DIOCESE OF NAKURU
P O BOX 938
NAKURU
Emal: info@cdnwaterquality.co.ke
TEL 0732547402, 0721497429

ATT:

JB Drilling

QUOTATION

Description

Cost of a 200 liter plastic barrel reignforced with ms plates of 4mm to take pressure of about 0.5 bars.
The filter containing 150 liter (85.5kg) of HAP filter medium (uptake capacity of 7mgF/gram HAP) before saturation to 1.5mgF/L.
For larger outputs, several barrels can be connected in series.

Location

Filter collected at NDC

Filter description	***no.***	***unit***	***Kshs/unit***	***Kshs***	***Kshs***
A defluoridation filter set,made in a 200 liter plastic barrel containing 150 liter of HAP, fully assembled with a provision of 11/2" inlet and outlet connection and a 3/4" water meter.	3	@	75,978	227,934	
				0	
				0	
VAT					***227,934***
16%VAT	16	%	2,279	36,469	
Subtotal VAT:					***36,469***
Grand total Fluoride filter :					***264,403***

Notes:

_This price estimate is valid 3 for months

Delivery or site connection costs NOT included, filter to be collected at NDC workshop

3/14/2016
Date

Julius Kubai 0722 867553
Name, Nakuru Defluoridation Co. Ltd.

Figure 11.8. A quote for HAP filters from NDC to JB Drilling.

6.3.1.4. Cycle 1-4 Full Figures

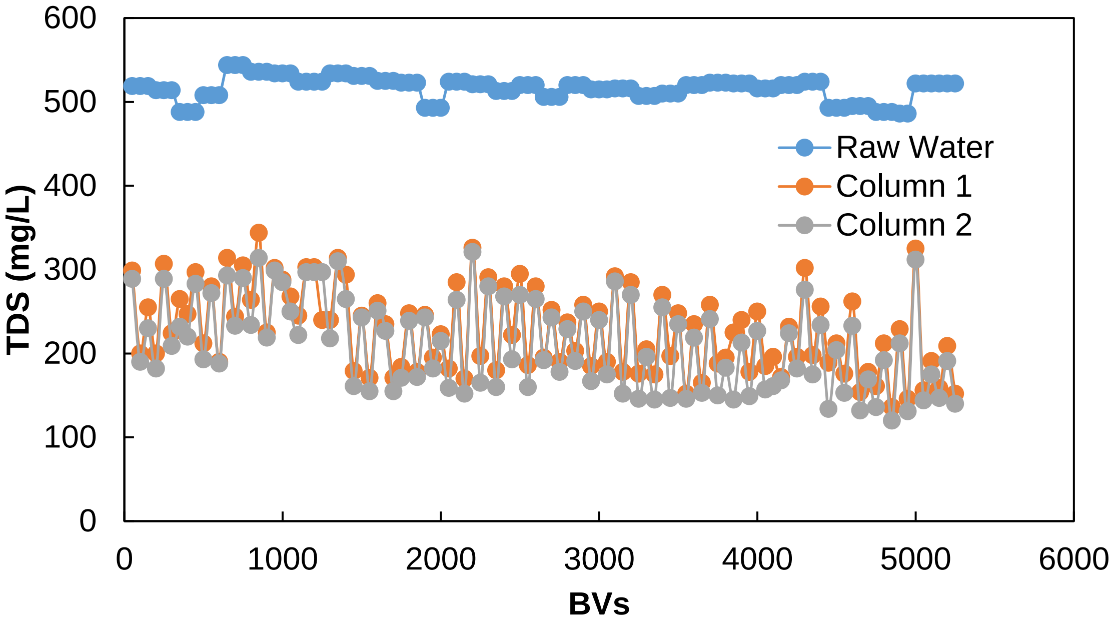


Figure 11.9. TDS history from HAIX-NanoZr system during Cycle 1 at Piraya.

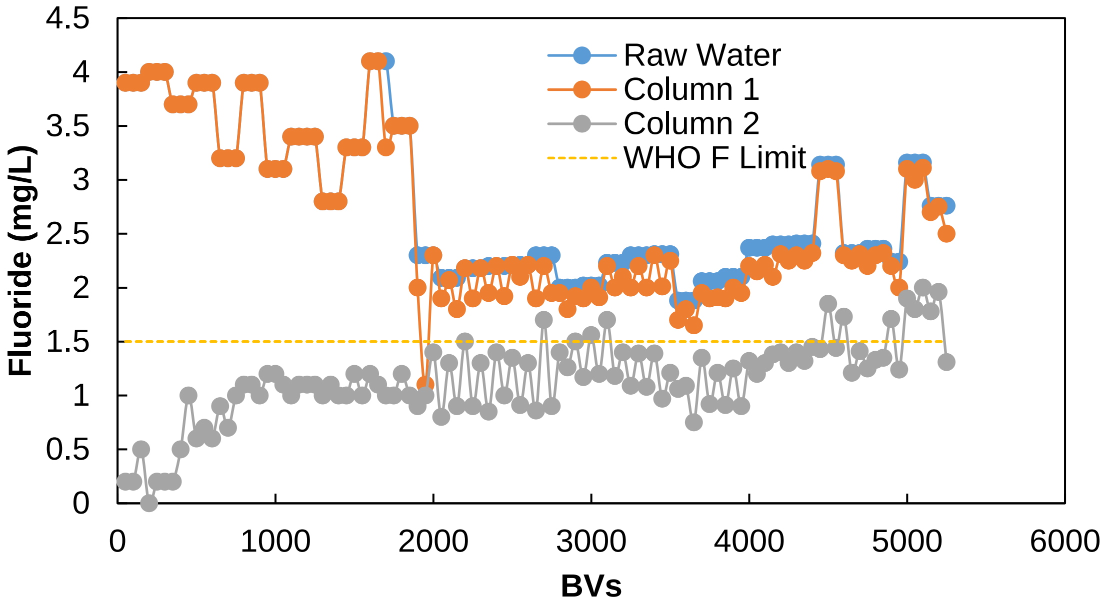


Figure 11.10. Fluoride history from HAIX-NanoZr system during Cycle 1 at Piraya.

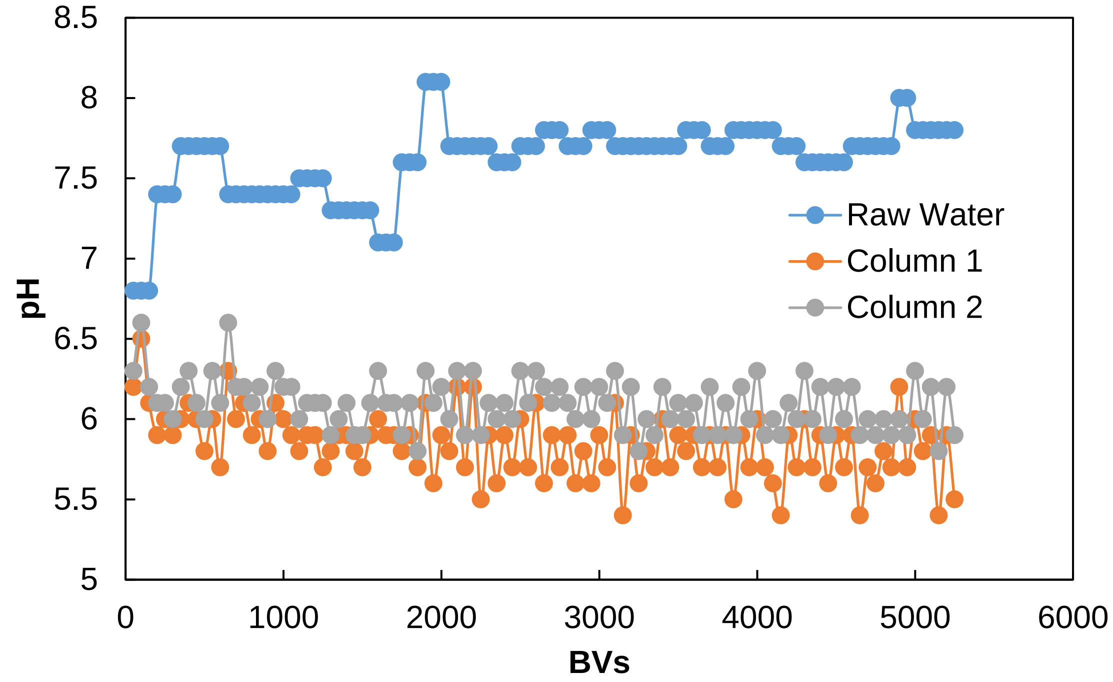


Figure 11.11. pH history from HAIX-NanoZr system during Cycle 1 at Piraya.

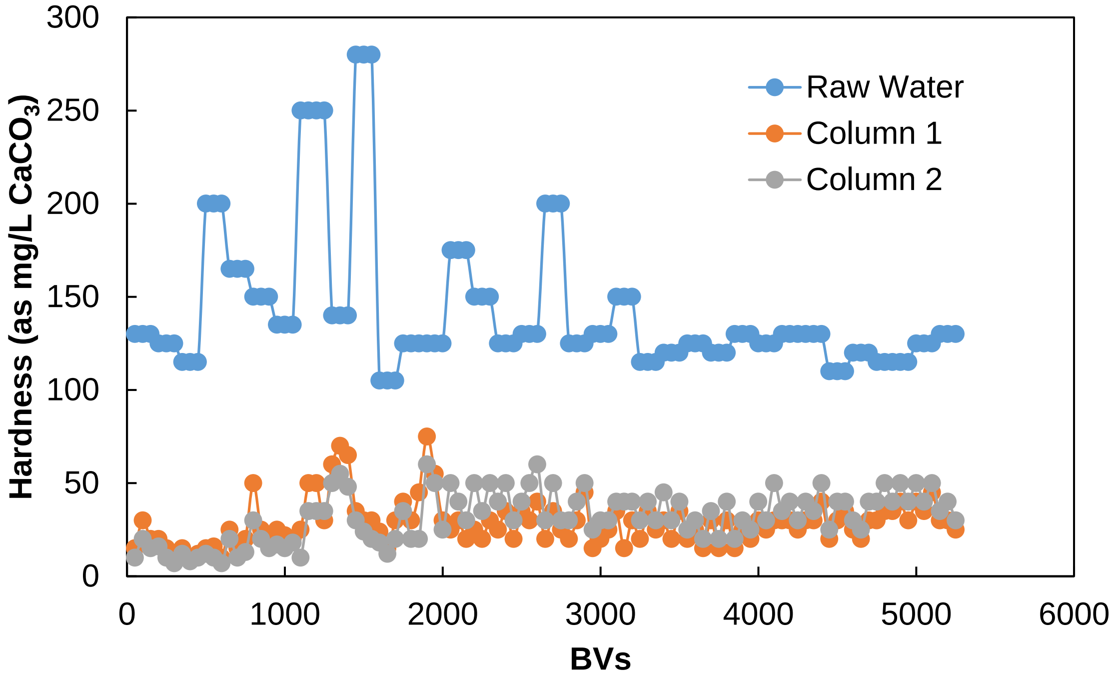


Figure 11.12. Hardness history from HAIX-NanoZr system during Cycle 1 at Piraya.

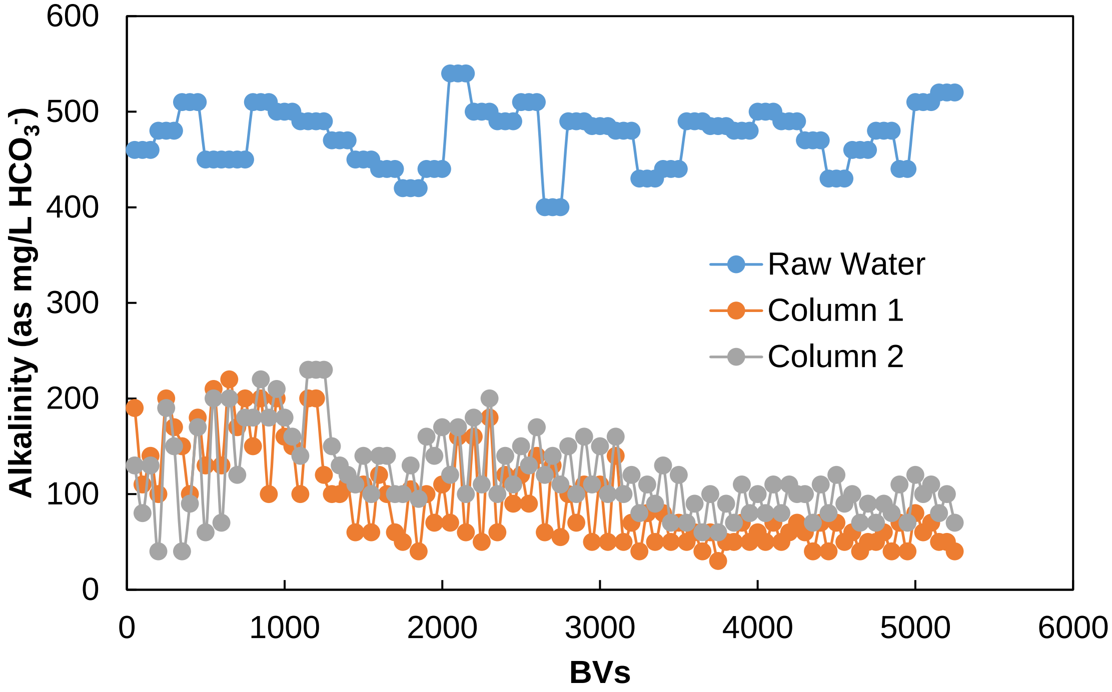


Figure 11.13. Alkalinity history from HAIX-NanoZr system during Cycle 1 at Piraya.

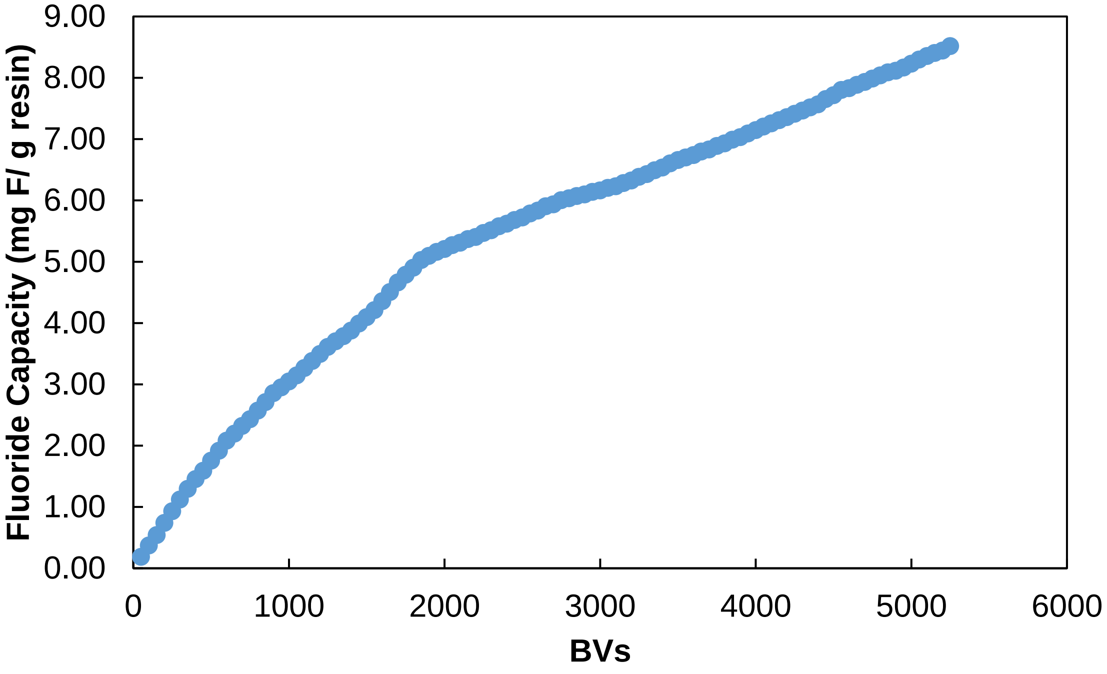


Figure 11.14. HAIX-NanoZr fluoride capacity history during Cycle 1 at Piraya.

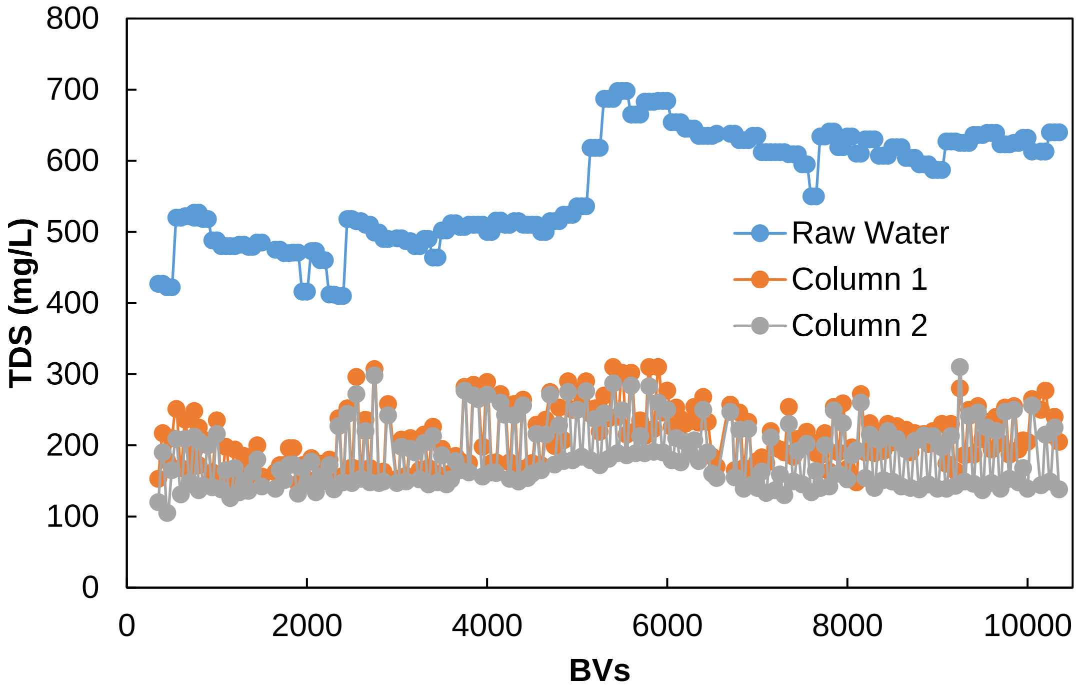


Figure 11.15. TDS history from HAIX-NanoZr system during Cycle 2 at Piraya.

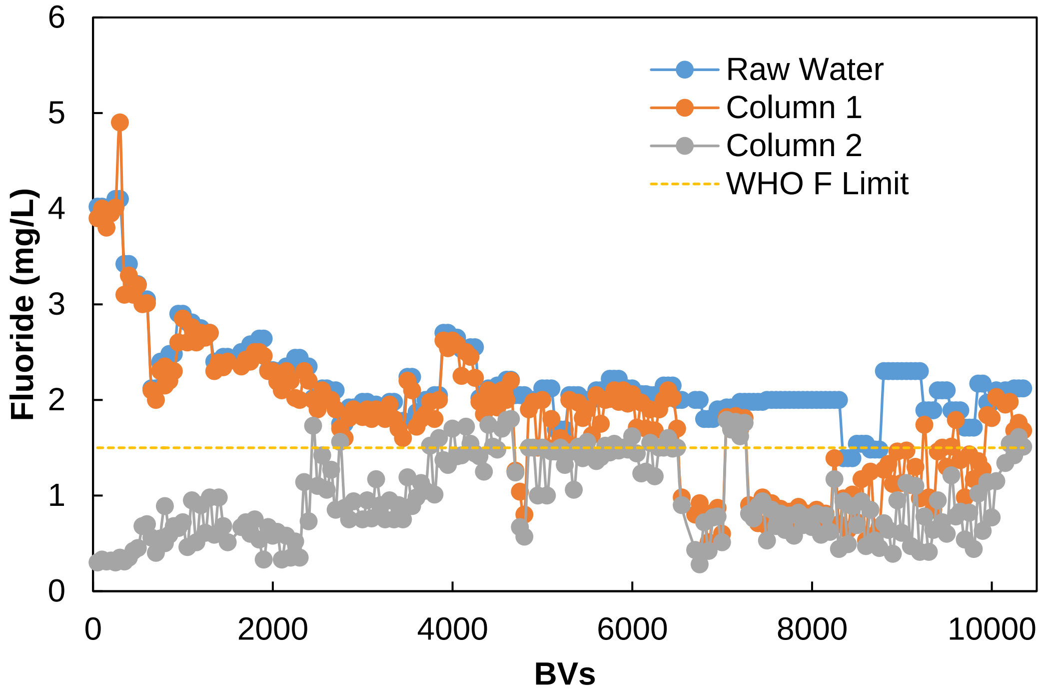


Figure 11.16. Fluoride history from HAIX-NanoZr system during Cycle 2 at Piraya.

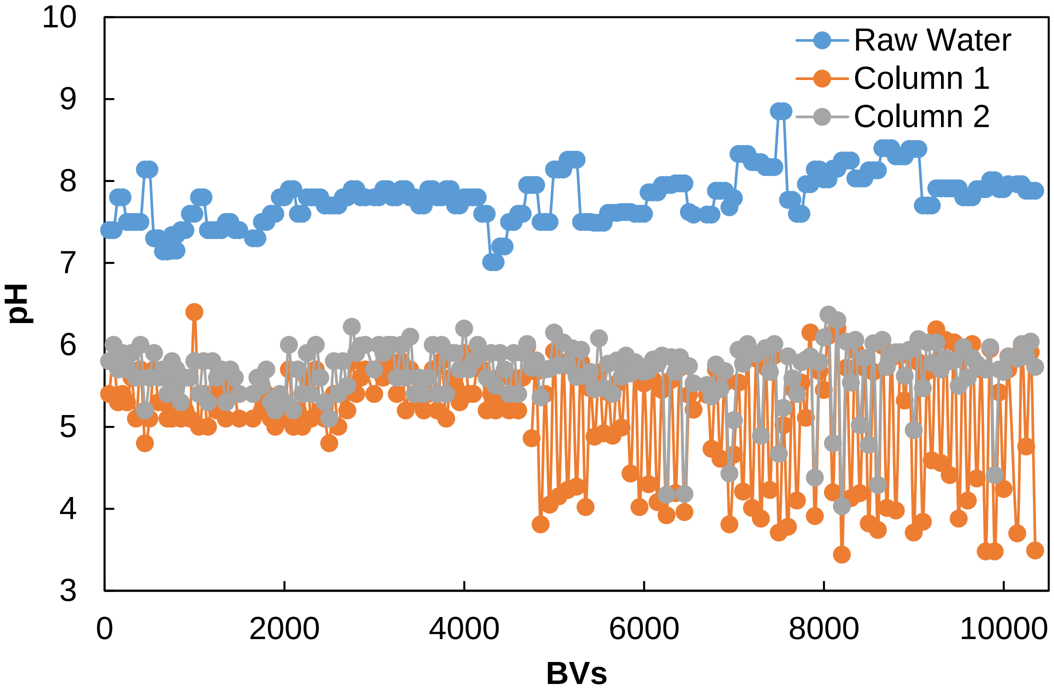


Figure 11.17. pH history from HAIX-NanoZr system during Cycle 2 at Piraya.

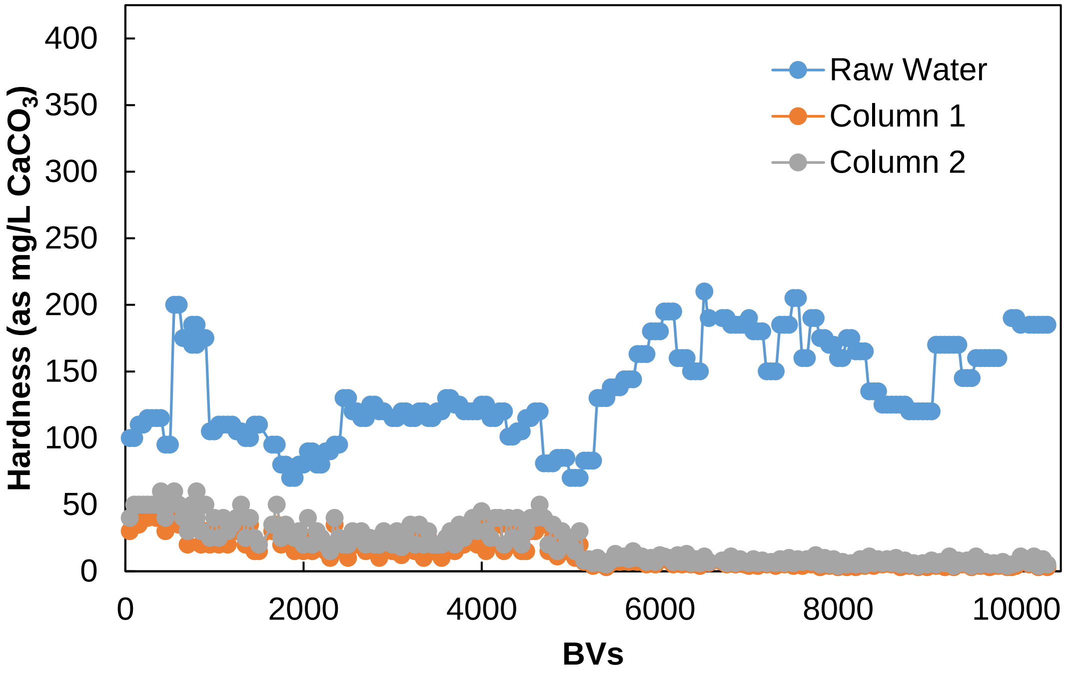


Figure 11.18. Hardness history from HAIX-NanoZr system during Cycle 2 at Piraya.

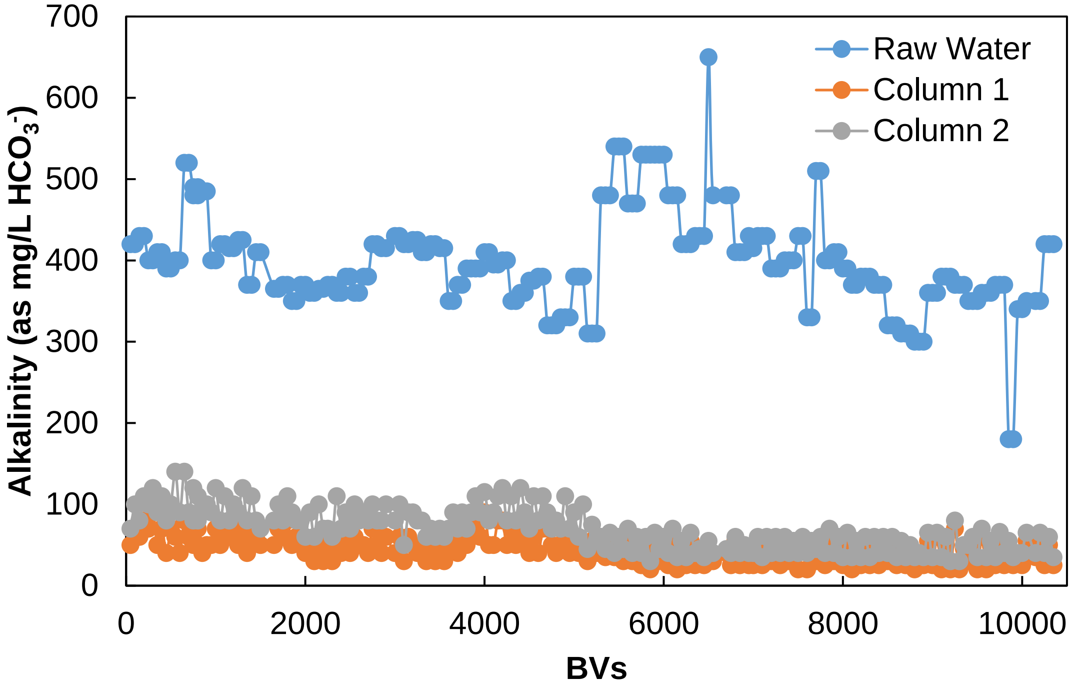


Figure 11.19. Alkalinity history from HAIX-NanoZr system during Cycle 2 at Piraya.

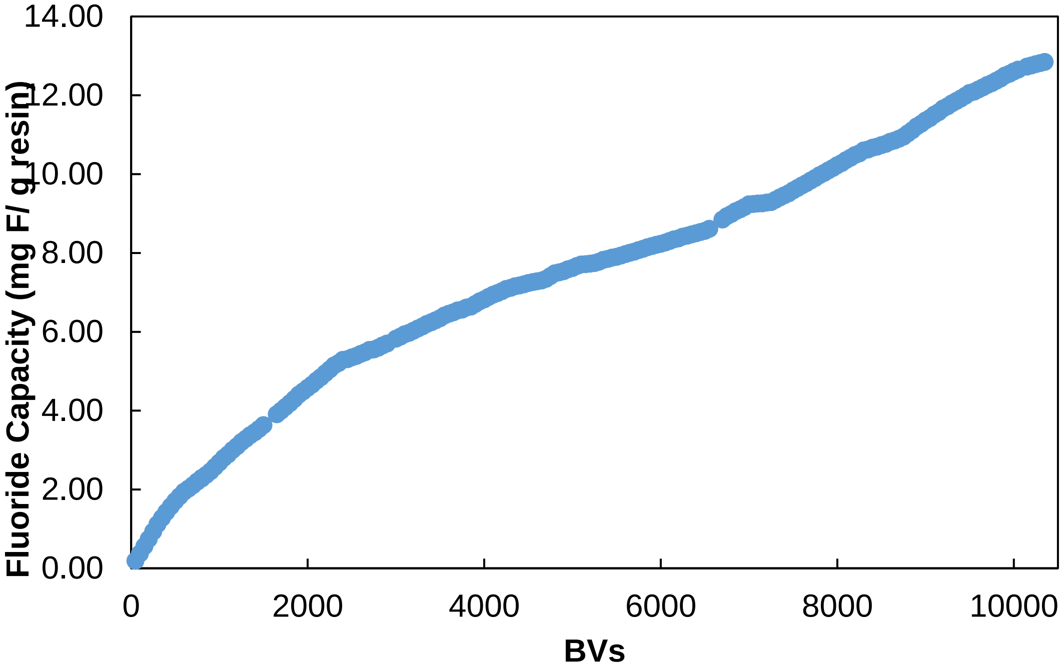


Figure 11.20. HAIX-NanoZr fluoride capacity history during Cycle 2 at Piraya.

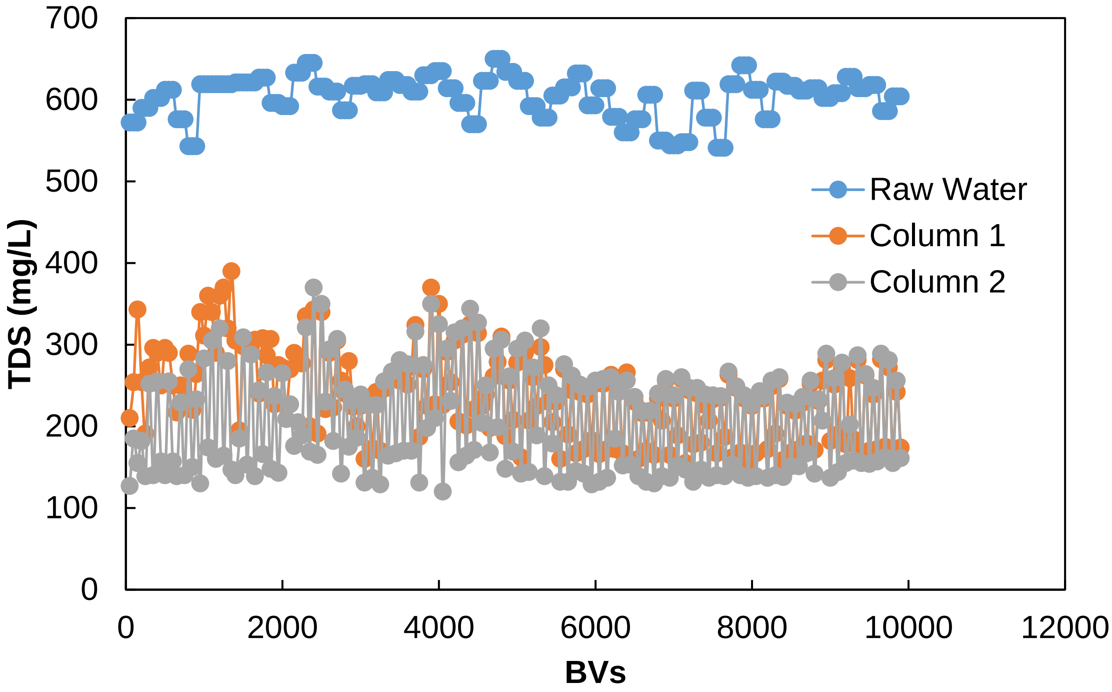


Figure 11.21. TDS history from HAIX-NanoZr system during Cycle 3 at Piraya.

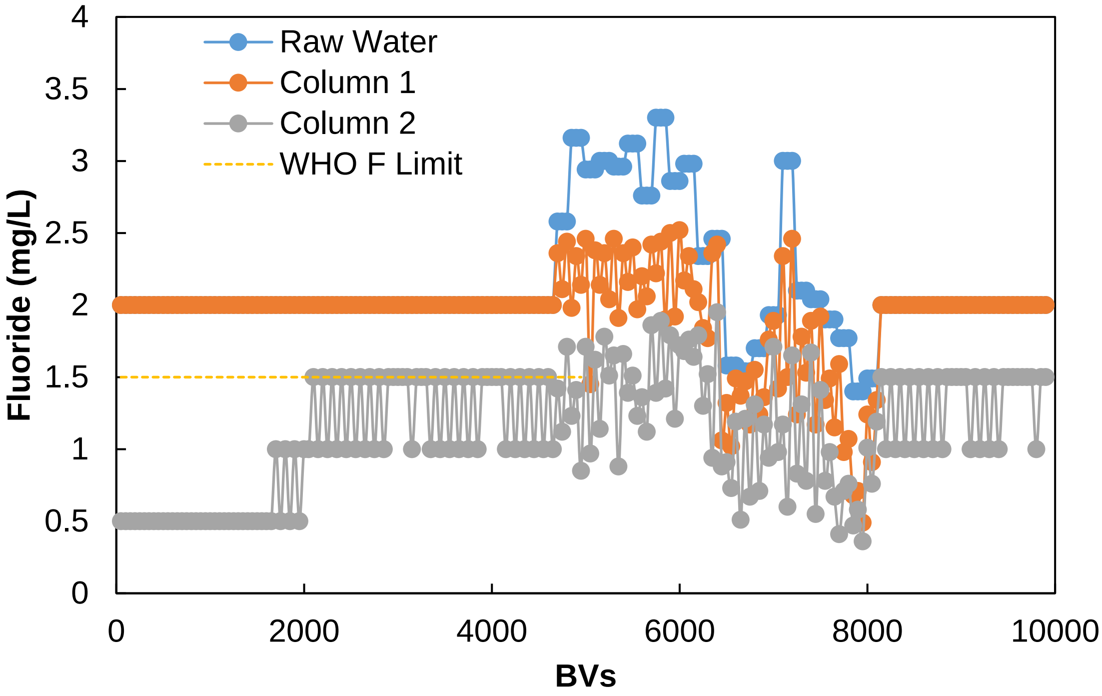


Figure 11.22. Fluoride history from HAIX-NanoZr system during Cycle 3 at Piraya.

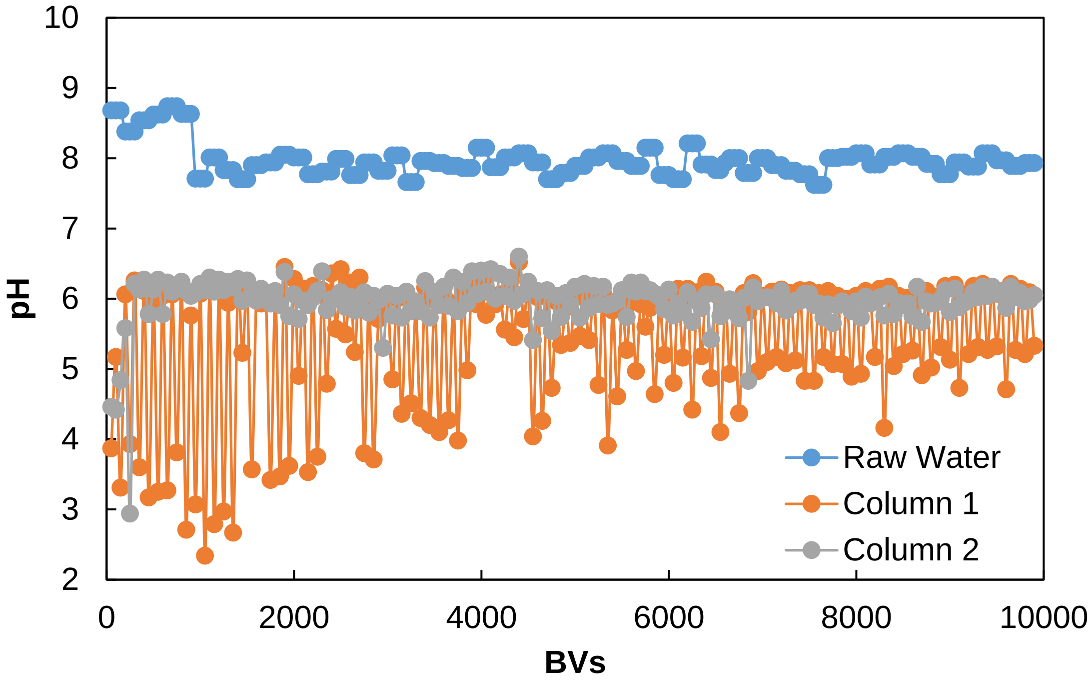


Figure 11.23. pH history from HAIX-NanoZr system during Cycle 3 at Piraya.

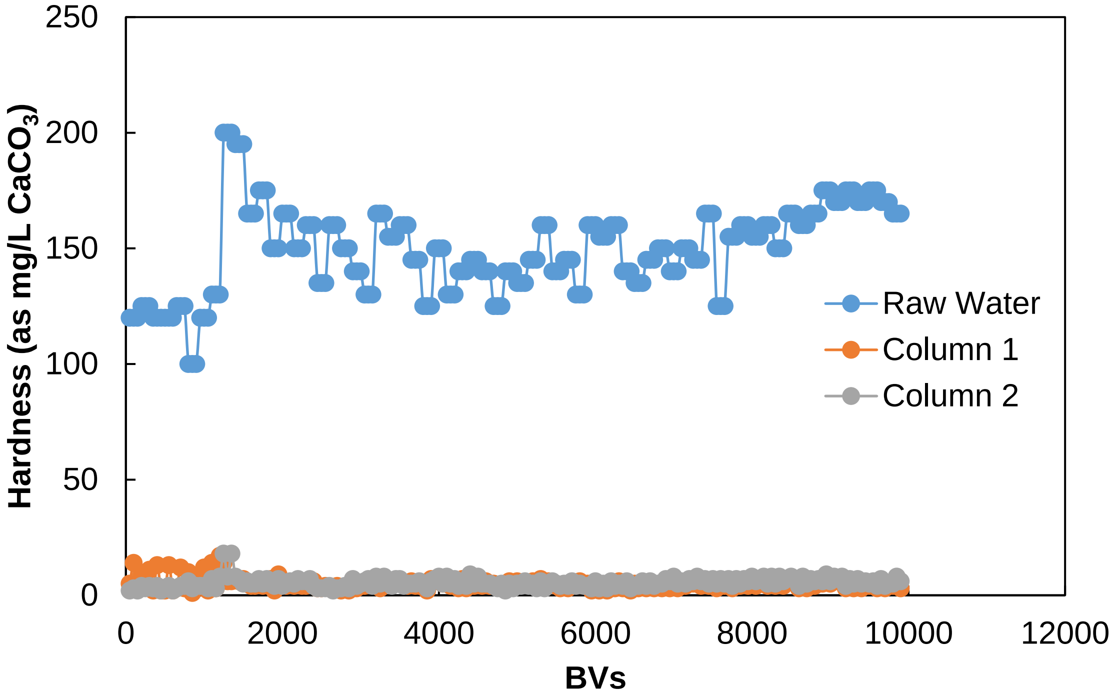


Figure 11.24. Hardness history from HAIX-NanoZr system during Cycle 3 at Piraya.

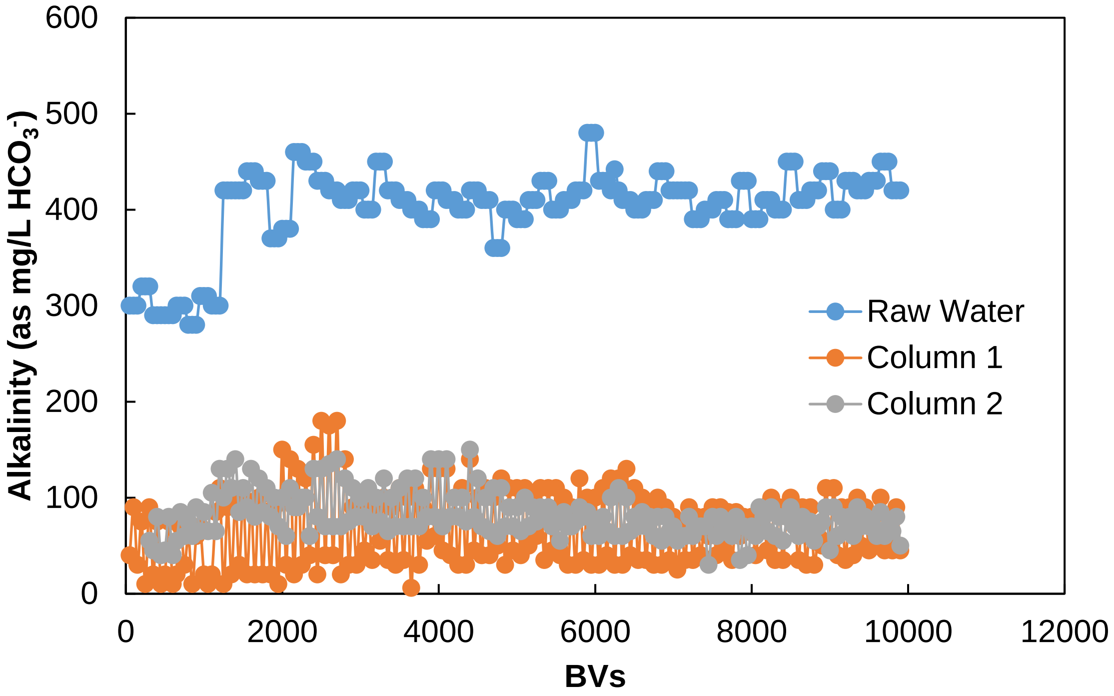


Figure 11.25. Alkalinity history from HAIX-NanoZr system during Cycle 3 at Piraya.

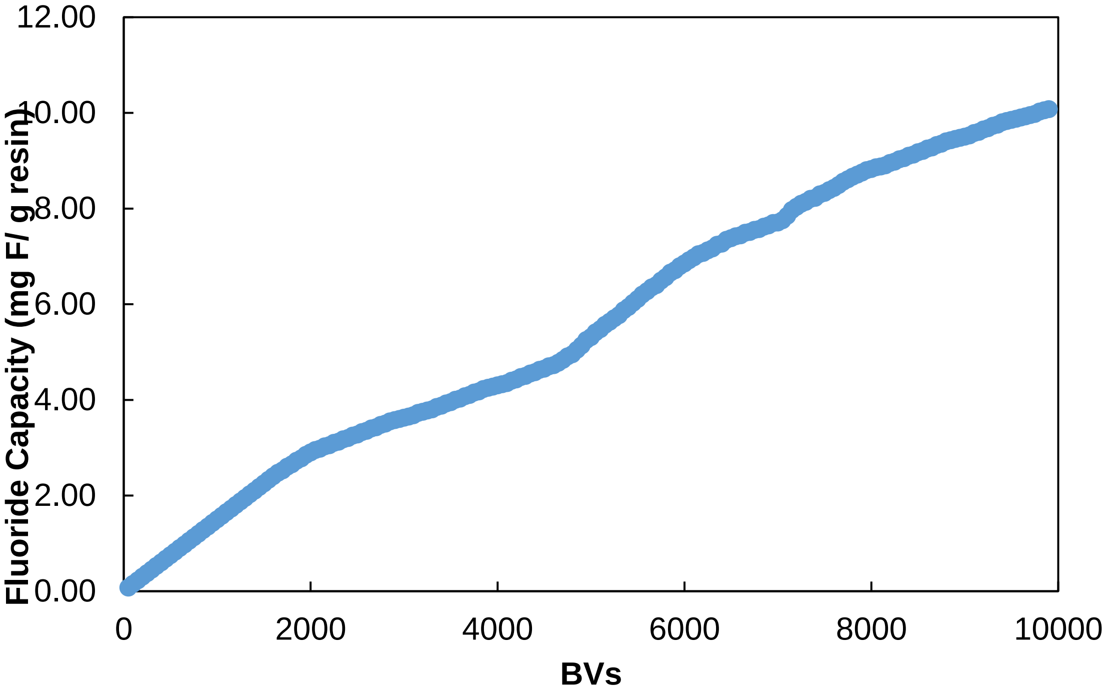


Figure 11.26. HAIX-NanoZr fluoride capacity history during Cycle 3 at Piraya.

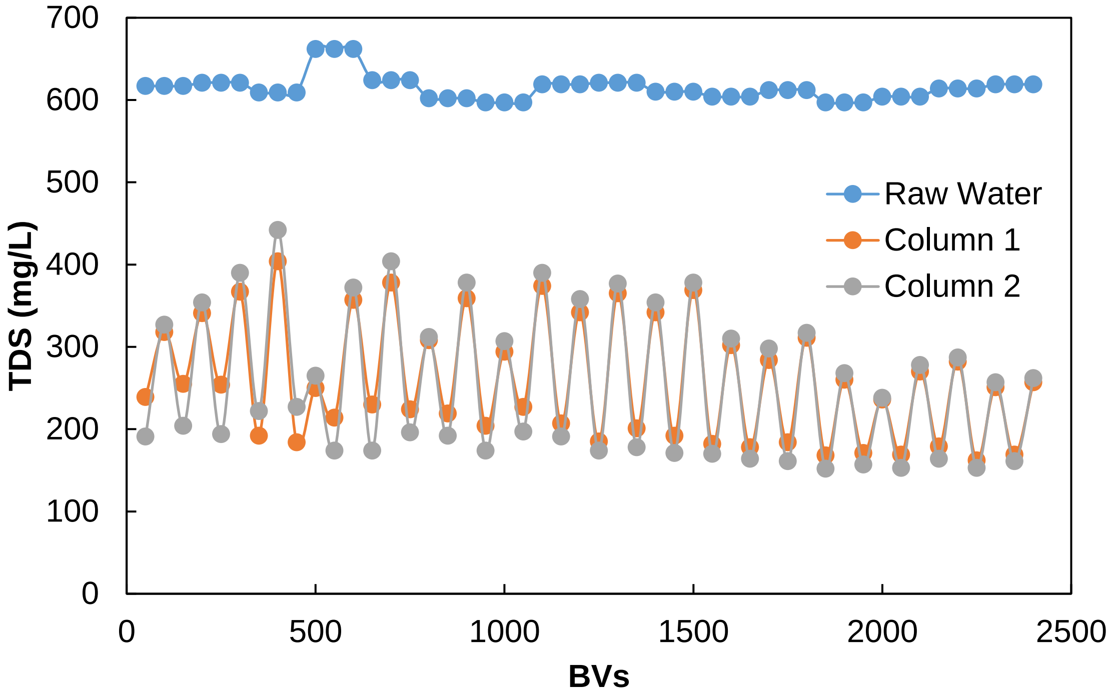


Figure 11.27. TDS history from HAIX-NanoZr system during Cycle 4 at Piraya.

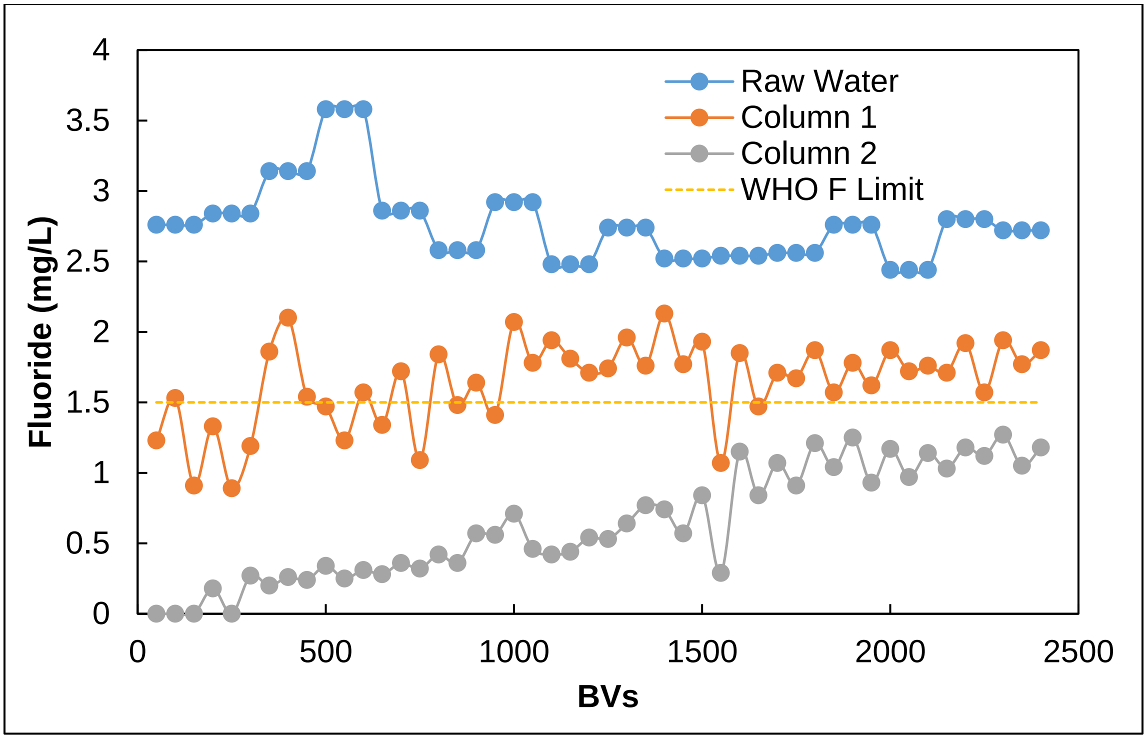


Figure 11.28. Fluoride history from HAIX-NanoZr system during Cycle 4 at Piraya.

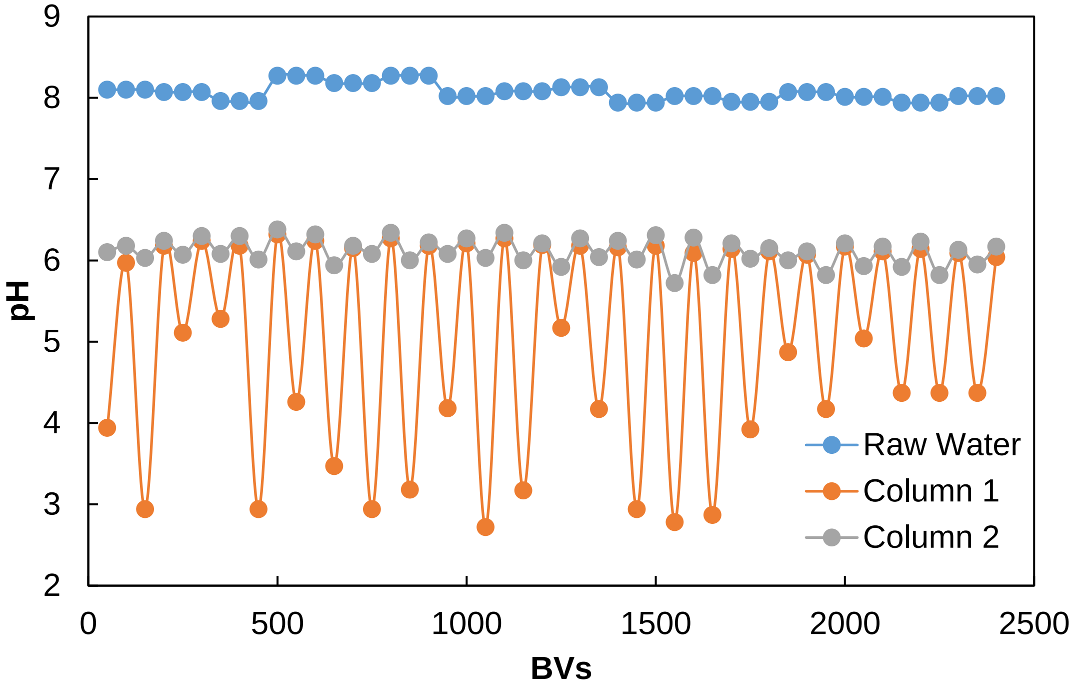


Figure 11.29. pH history from HAIX-NanoZr system during Cycle 4 at Piraya.

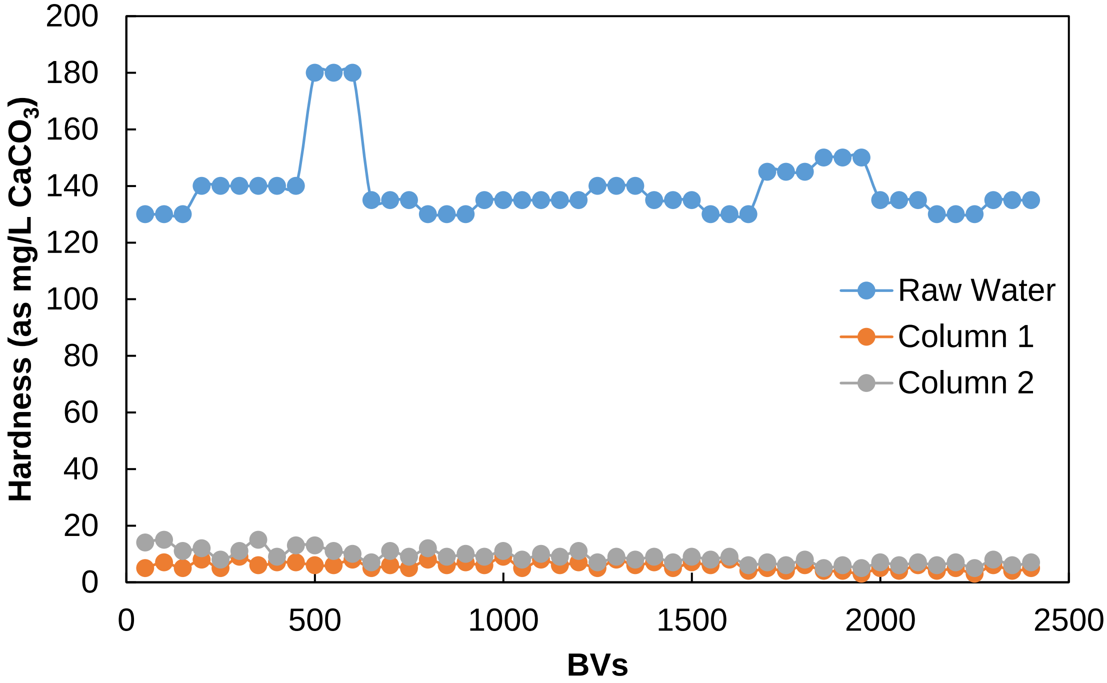


Figure 11.30. Hardness history from HAIX-NanoZr system during Cycle 4 at Piraya.

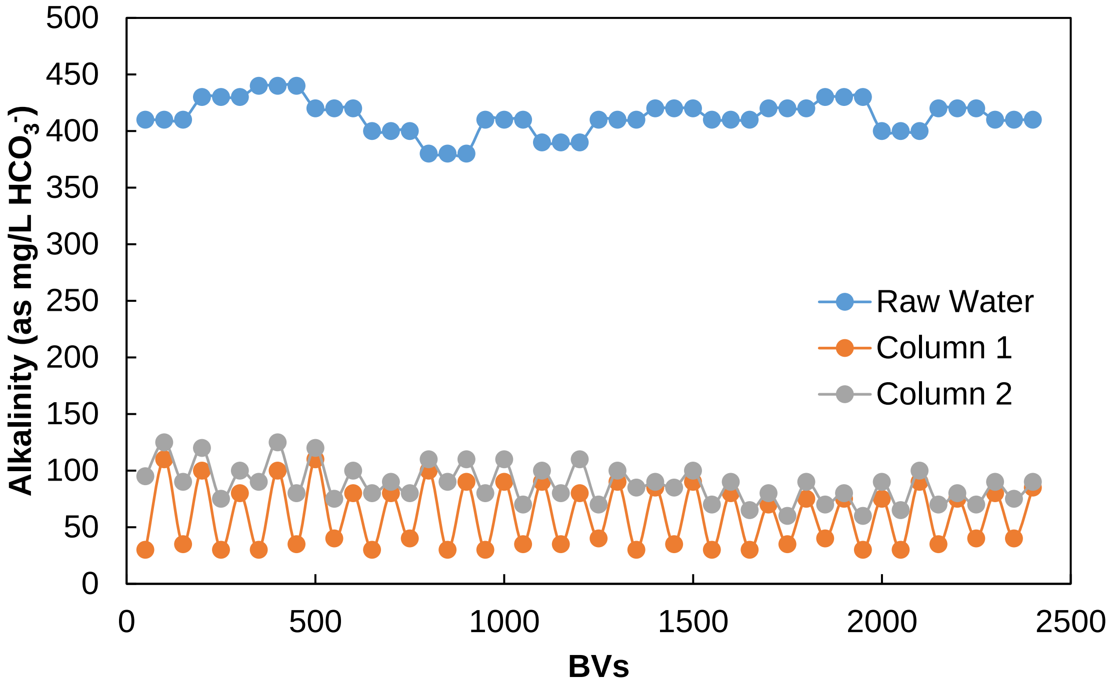


Figure 11.31. Alkalinity history from HAIX-NanoZr system during Cycle 4 at Piraya.

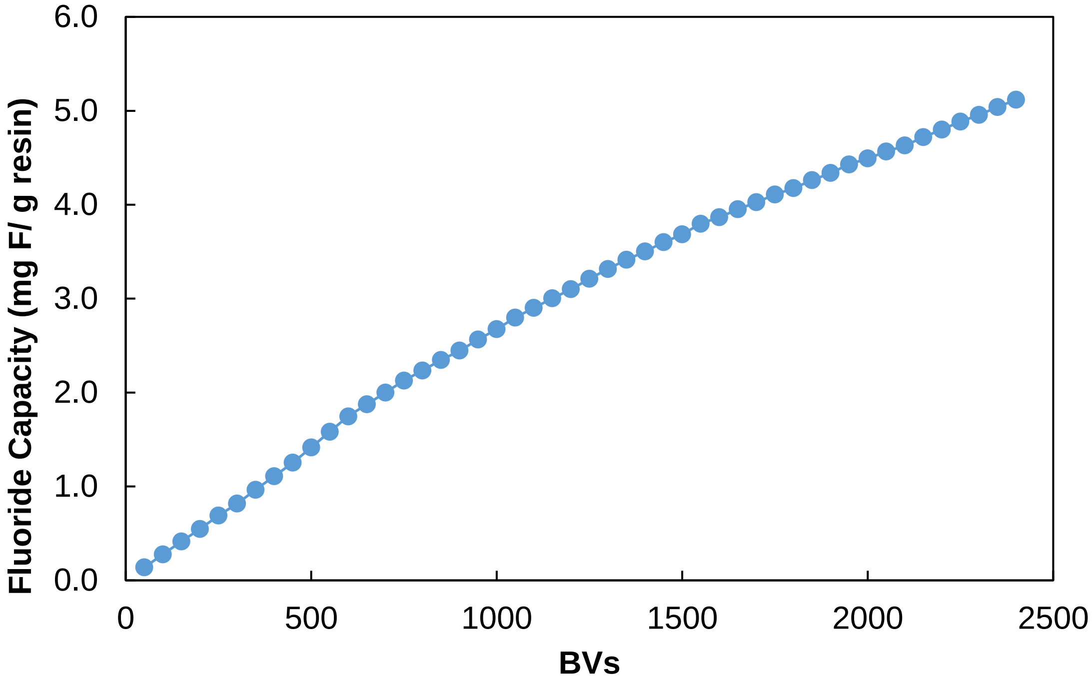


Figure 11.32. HAIX-NanoZr fluoride capacity history during Cycle 4 at Piraya.

11.4 Chapter 7 Appendix

Table 11.1. Physico-chemical analysis of water samples from Nuapada, Odisha (Dec. 29. 2014).

Village Name	**Code**	**pH**	**Turb NTU**	**TDS**	**T. Hard. $CaCO_3$**	**Alk. as $CaCO_3$**	**Cl^-**	**Na^+**	**K^+**	**SO_4^{2-}**	**NO_3^-**	**F^-**
Dhumabhata	RW	7.5	25	388	192	320	18	82	7	10	2	4.1
	TW	7.7	0.7	361	168	300	18	87	7	9.8	2	0.1
Kandetara	RW	7.5	5	1440	272	540	290	400	38	96	189	6.4
	TW	6.7	0.3	1662	280	296	500	410	28	77	152	0.51
Musapali	RW	7.4	4	359	188	276	60	69	5	4	1.6	3.4
	TW	6.4	0.7	200	32	60	70	65	3	1	1.3	0.43
Haripur	RW	7.3	5.3	285	200	120	96	31	1	1	3.7	2.7
	TW	6.5	0.4	288	188	100	120	33	1	1.6	1.2	0.1

12. Vita

Michael Scott German was born on November 15, 1987 in Baltimore, MD to Cathy and Bruce German. Mike German earned his B.S. Chemical Engineering and Honors Certificate from the University of Maryland, Baltimore County in May 2009, magna cum laude. Mike entered Lehigh University in Fall 2010 and earned his M.S. Environmental Engineering in 2012 under Dr. Arup K. SenGupta on “Waste acid as a means to desalinate brackish water”. From November 2012-February 2014, Mike was a Fulbright-Nehru Research Fellow (A.N. College, Patna, Bihar) on “Empowering Women to Transform a Water Crisis into Water Business in the Indian Sub-Continent”. Besides being in India as part of his PhD research, Mike spent significant time in Cambodia, Kenya, and China in development of HAIX materials and systems. Mike co-founded WIST, Inc. (Drinkwell) to commercialize HAIX-Nano to produce safe water to communities of the Indian subcontinent.

During his time at Lehigh, Mike published multiple articles first author on two peer-reviewed publications (Environ. Sci. & Technol. and Sci. Tot. Environ., 26 citations), second author on one peer-reviewed publication (React. Funct. Polym.) and two viewpoints (ES&T), and third author on two peer-reviewed publications (ES&T and Environ. Eng. Sci.). He was a co-inventor on three US patents (20160272511, 20150251928, 62/475,575). He gave three oral presentations at ACS conferences, nine oral presentations at other conferences, posters at eight conferences. Mike peer-reviewed four manuscripts for Environ. Eng. Sci. Mike was, also, responsible for proposals and awards that earned $590,000 between Drinkwell, Lehigh University, and the Tagore-SenGupta Foundation.