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Exploring a decision-trigger for maintenance of remotely monitored arsenic-remediation system planned for low-income community in Central Valley, CA

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# **Exploring a decision-trigger for maintenance of a remotely monitored arsenic-remediation system planned for low-income community in Central Valley, CA**

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## **Abstract:**

Arsenic is one of the most toxic elements found in groundwater, and in terms of maximum allowable concentration, poses the highest carcinogenic risk of all drinking water contaminants. The brunt of arsenic-related challenges is faced by low-income communities, as there is currently very limited technology that can filter arsenic on a community-wide basis in a scalable and cost-effective manner, forcing individuals to resort to point of use technologies that prove ineffective in the long run. In the following paper, the premise of providing clean drinking water to rural and impoverished communities in the Central Valley, California is discussed in the lens of a novel technology being developed by the Gadgil Lab for Energy and Water Research. The solution proposed is a disposable iron cartridge that makes use of External Oxidizer Assisted Iron Electrocoagulation (EOAIEC), utilizing ex situ hydrogen peroxide to filter out arsenic in a large scale plant. The usage of EOAIEC is to be monitored remotely via a cell phone network connecting to a smart phone app. The prior implementation of similar technology, Electrochemical Arsenic Remediation (ECAR), in West Bengal, India is discussed in the following paper. The socio-economic circumstances of the Central Valley, including higher labor costs for the maintenance of the technology and higher water sanitation standards has prompted significant modifications to the operating protocol. The feasibility of monitoring the efficiency of the cartridge remotely and prompting timely replacement when each cartridge is utilized to its maximum is currently being tested. The preliminary results of observing the change in resistance of the cartridge as it undergoes electrochemical decomposition will potentially help determine a cut-off warning period at which the current through the system drops significantly, indicating that the cartridge should be replaced. Future steps for the research are outlined, including the expansion of current work to supplement field trials of the prototype.

## 1. Introduction

Access to clean water is 6th of the 17 Sustainable Development Goals (SDGs) identified by the United Nations (United Nations). In rural areas of developing countries, the lack of access to water sources safe for consumption is a huge problem. As shown in Figure 1, in West Bengal, India and Bangladesh, arsenic contamination in groundwater is widespread (Chakraborti et al., 2003; Maity et al., 2010; Chowdury et al., 2000). Moreover, a study that spatially mapped and modeled the arsenic contamination of groundwater in Bangladesh found that, “the average arsenic concentration in groundwater is found to be 22.5 times the maximum permissible limit ([i.e., 0.01 mg/L as set by the World Health Organization (WHO 2011)]), and at places, it crosses even 50 times of the said limit” (Ghosh, Merina et al., 2020). This is concerning as such high concentration of arsenic in drinking water is extremely dangerous to human health. An eight year study on the health effects of arsenic contamination in the Eruani Village of Bangladesh documents several negative impacts including arsenical skin lesions (many of which were suspected to be skin cancer), mild to severe cases of peripheral, motor, and/or sensory arsenical neuropathy, and an increase in spontaneous abortions and stillbirths (Sad et al., 2006). Furthermore, arsenic is a known carcinogen associated with a variety of cancers, and it can have noticeable dermatological, developmental, neurological, respirator, cardiovascular, immunological, and endocrine effects (Naujokas et al., 2013).

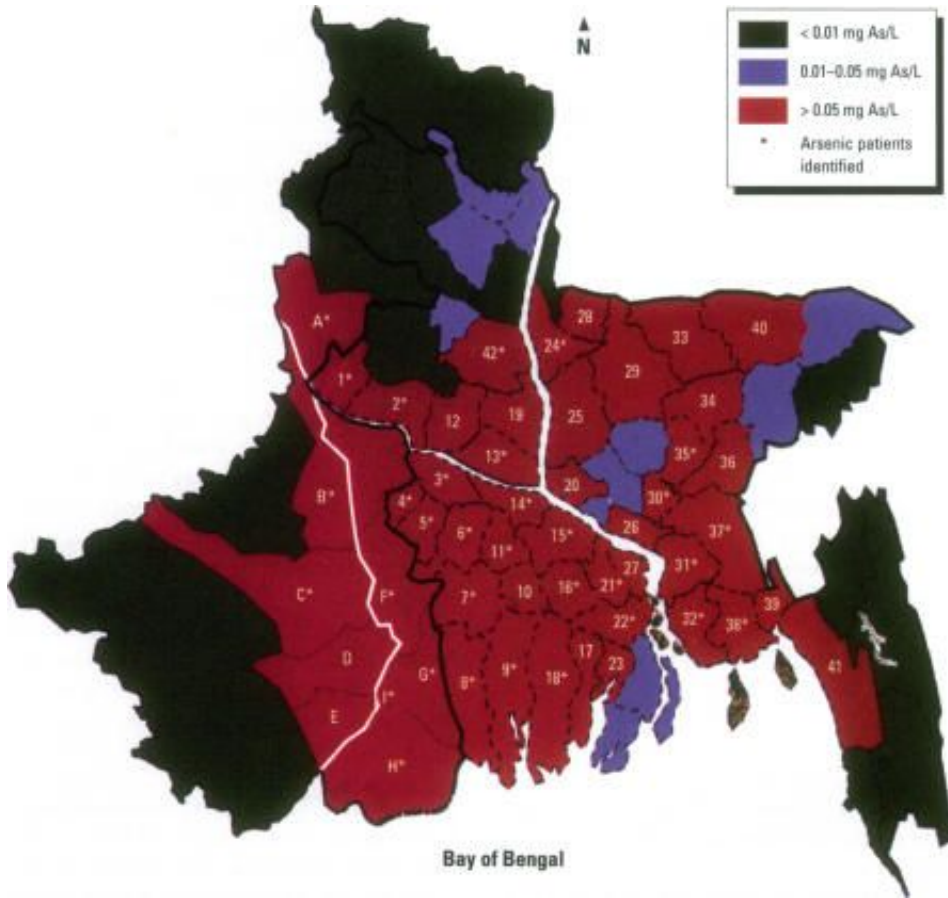


Figure 1: Map of West Bengal and Bangladesh displaying the concentration of arsenic in groundwater by area.

Sourced from: Uttam K. Chowdhury, et al. (2000)

Not only is this a huge problem abroad in developing countries, parts of the United States, including Utah, Nevada, Arizona, and California, also suffer from high concentrations of arsenic in groundwater (Balazs et al., 2012). In California, almost 300 public water systems concentrated in the Central Valley deliver water that contain unsafe levels of arsenic (Gadgil and Hernandez, 2020). The devastating impacts arsenic consumption has on human health, which in turn affect the livelihood of these communities, demand an effective and sustainable implementation of water remediation technology.

## 2. Introducing ECAR as the solution

An effective technological solution to removing arsenic from groundwater is known as Electrochemical Arsenic Remediation (ECAR) and was developed by researchers in the Gadgil Lab for Energy and Water Research at Lawrence Berkeley National Laboratory (LBNL). The chemical mechanism of ECAR is described as follows:

A small voltage is applied to steel plate electrodes immersed in the contaminated water. This applied voltage leads to the dissolution of iron (Fe) into Fe(II) ions at the anode. These aqueous Fe(II) ions are oxidized by the dissolved oxygen in the water via an oxidation pathway to form insoluble oxyhydroxides of Fe(III). This oxidation pathway also leads to a highly reactive intermediate oxidant that oxidizes the arsenic in the contaminated water (which is in the form of As(III)) to an arsenic oxyanion (As(V)). This step is important, as the arsenic oxyanion readily binds to the insoluble oxyhydroxides of Fe(III) that were produced. Thus this insoluble oxyhydroxide of Fe(III) essentially removes arsenic from the water due to its high binding affinity for the arsenic oxyanion. Since it is insoluble, it is essentially a precipitate and forms a floc. This floc can be removed from the water via flocculation and sedimentation, therefore successfully leaving behind water with an arsenic concentration below the allowable limit. (Hernandez et al., 2019; Amrose et al., 2013)

The arsenic free water would then undergo subsequent sanitation steps to remove other impurities before it is safe for consumption. As shown in Figure 2, ECAR has been proven to successfully lower the arsenic concentration in water to below the WHO guideline of 10 ppb.

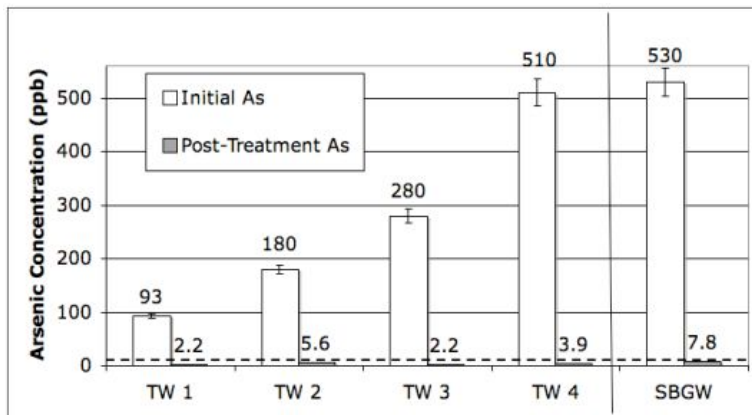


Figure 2: Initial and post-ECAR treatment arsenic concentrations for groundwater taken from four contaminated tube wells in Bangladesh (TW 1 - 4) along with synthetic Bangladesh groundwater (SBGW) for comparison.

Sourced from: Genuchten et al. (2009)

### 3. Implementation of ECAR technology in West Bengal, India

#### 3.1 Water plant installation and mechanism

Recently, LBNL in collaboration with researchers from Jadavpur University (JU) successfully implemented ECAR in Dhapdhapi village in West Bengal, India. A 1400 ft<sup>2</sup> water plant was installed at Dhapdhapi High School (as pictured in Figure 3), which is located at a central point within the village thus making it an ideal location among other considered factors.

The plant functions as following, and a schematic of the process is provided in Figure 4:

Groundwater is pumped from the school's shallow tubewell into two 1250 L tanks that contain the steel plates. The ECAR process then takes place when a programmed voltage is applied. The "iron-dosed" water is then transferred to a holding tank in which a flocculation chamber helps with the floc formation and a tube settler aids in settling the floc so that the floc-free water can be treated for other impurities now that arsenic has been removed. These include a rapid sand filter, micron filters, and UV disinfection. After treatment, the water is then transferred to overhead tanks to automatic dispensing units, ready for consumption. (Hernandez et al., 2019)



Figure 3: Pictures of the reactor tank and removal tube settler.

Sourced from Wangchuk, 2018.

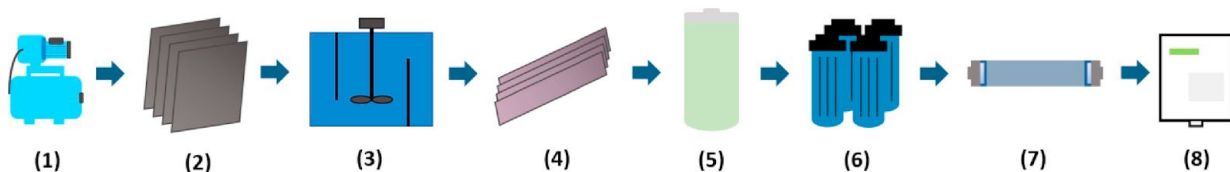


Figure 4. Schematic representation of the treatment process at the Dhapdhapi pilot plant: 1) raw water pump, 2) ECAR reactors, 3) flocculation chamber, 4) tube settler, 5) rapid sand filter, 6) micron filters, 7) ultraviolet disinfection system, 8) automatic dispensing unit.

Sourced from: Hernandez et al. (2019)

### *3.2 Sustainable implementation process*

While the ECAR mechanism itself is robust, the success and longevity of this project was ultimately due to developing this technology to function within the socio-economic constraints of the village, the formation of active communication with villagers, and the long term monitoring and testing of the treated water from the plant (Hernandez et al., 2019). The design process of this technology within the socio-economic and technical constraints are further discussed.

From an economic standpoint, Dhaphdhabi village experiences extreme poverty, therefore the plant requires minimal costs once in use so that the price of the water that is sold to villagers is affordable. This was accommodated via a slow kinetic ECAR mechanism, and a large reactor size meant to produce a labor-intensive maintenance design (Hernandez et al., 2019; Gadgil and Hernandez, 2020).

The oxidation pathway from ECAR in which Fe(II) ions are oxidized to an insoluble iron oxyhydroxide by the dissolved oxygen is a relatively slow process. Since this slow oxidation pathway is also responsible for oxidizing arsenic into a form that is readily removable once adsorbed to the iron oxyhydroxide precipitate, it takes about 1-2 hours for arsenic to be removed (Gadgil and Hernandez, 2020). While the process can be sped up by using another oxidant, such as hydrogen peroxide instead of dissolved oxygen, access to these types of chemicals in India is not readily available and would therefore be an unnecessary extra expense (Gadgil). For this reason, the plant's capacity of producing 10,000L of water per day allowed for the slow kinetic design of the mechanism to meet the requirements of the village while operating within the inherent economic constraints.

Secondly, the reactors were 2500 L in size and required consistent maintenance. The plates were to be cleaned everyday using a hard-wired brush, and were to be deep cleaned semi-annually. This model was economically suitable as it was more feasible to train and employ skilled workers to perform these tasks instead of developing a low-maintenance, high-cost version. This economic feasibility is due to India's low labor costs. India's current minimum wage is 176 rupees for an eight hour work day which translates to approximately \$3 for an eight hour work day (Srivastava, 2019). The company managing the Dhapdhapi plant after its implementation by LBNL and JU, pays the workers more than double of the minimum wage at \$10 per day (Gadgil).

Other methods of ensuring longevity of the plant's implementation included adapting the technology to the technical restraints unique to the area. For instance, power outages and intermittent power supply in the village were accounted for by installing storage capacity for the product water from ECAR. Intense heat which caused calcium carbonate precipitates to form in the water was managed by moving water pumps underground and placing storage tanks over the exposed automatic dispensing units to reduce direct sun exposure (Hernandez et al., 2019). Working closely with the community by addressing all of their concerns and educating them about the dangers of arsenic, was another key component in ensuring harmony between the villagers and the plant implementation project (Hernandez et al., 2019).

The water quality was continuously monitored after installation and was only distributed to villagers after six months of testing. While there were a few spikes in arsenic concentration that were addressed and fixed as aforementioned in the discussion of technical constraints, the



plant consistently produced water with an arsenic concentration below the WHO permissible limit. The accompanying data is shown in Figure 5.

With ECAR and the water plant’s successful implementation in India, a similar approach was taken recently to address the arsenic contamination issue in the Central Valley. However due to differences in circumstances, appropriate accommodations were made to the ECAR process and are discussed further.

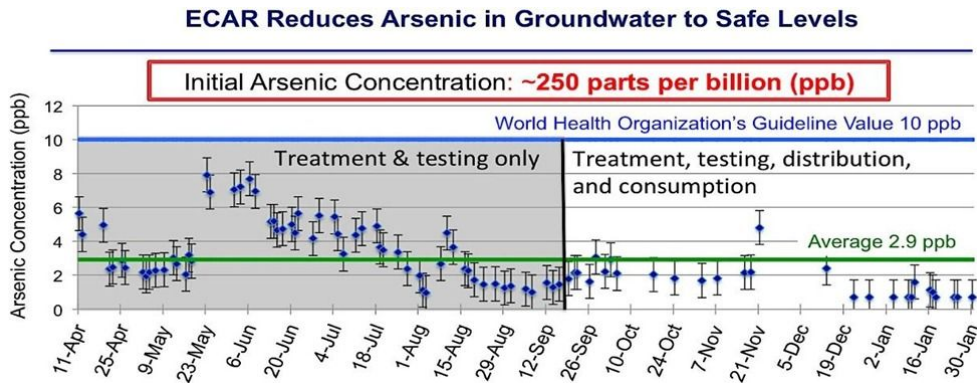


Figure 5: Results from the plant in West Bengal, India, from April 2016 to January 2017, depicting continuous effective arsenic removal to less than 10 ppb during both pilot and distribution phases. Sourced from: Hernandez et al. (2019)

#### 4. Central Valley - Inequities in Drinking Water Access

To address how ECAR will be implemented in the Central Valley, it is important to be situated in California’s current water system and understand the inequalities it creates between rural and urban municipal water systems. As seen in Figure 6, there is a high concentration of water systems with arsenic levels above the maximum allowed concentration (labelled “high”) of 10 ppb/litre.

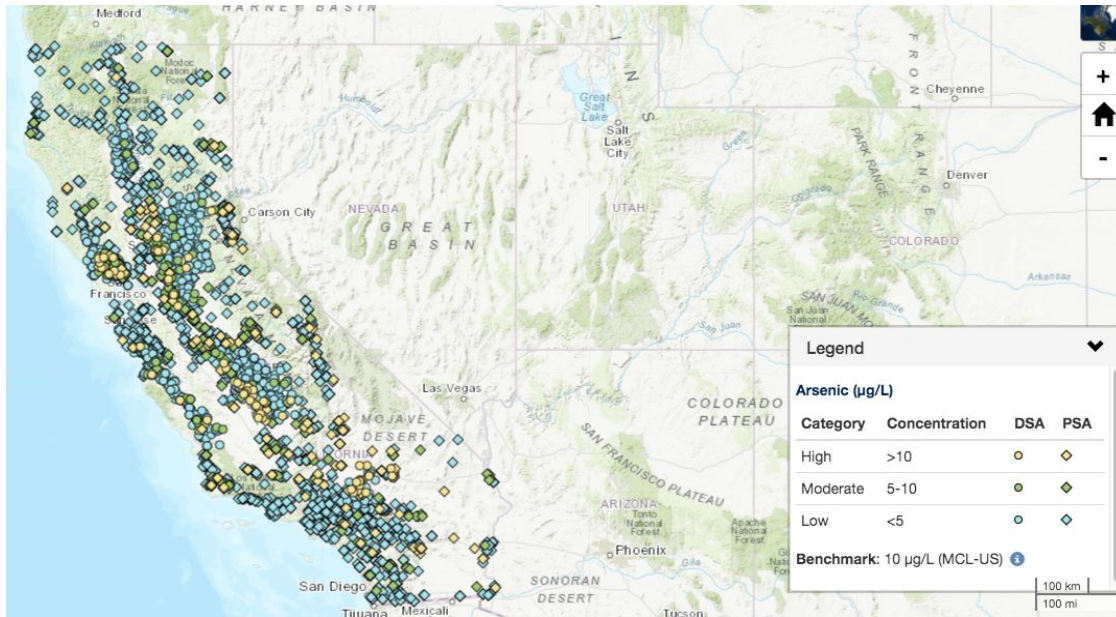


Figure 6: Map of arsenic concentrations in public water systems in California. This demonstrates that water sources with low to moderate arsenic concentrations are often concentrated along the coast of CA while sources with high arsenic concentrations are situated in Central California.

Sourced from: U.S. Geological Survey, 2018, CA GAMA-PBP Groundwater-Quality Results: Assessment and Trends: U.S. Geological Survey database available online at <https://ca.water.usgs.gov/projects/gama/water-quality-results/>. (Accessed April 15 2020)

California’s decentralized water system has been used as a model for the United States. In terms of legislation, the California Safe Drinking Water Act, 1986 divides public water systems based on the number of connections and people served into Small Community Systems, Local Small Systems, Noncommunity Systems and Non-transient Non-Community Systems (United States Environmental Protection Agency, 2004). Drinking water quality is monitored by these public drinking water systems and data is reported to the State Water Resources Control Board and are evaluated based on the Maximum Contaminant Levels. In 2006, the scope of the Safe Drinking Water Act was expanded to state that “every citizen in California has the right to pure drinking water” (Marshall, 2013). However, there does not appear to be a clear distinction between rural and urban municipal water systems.

Multiple factors have been observed in the unequal access to drinking water seen in the Central Valley. These include unequal enforcement of drinking water regulations, noncompliance with federal standards, inequities in access to funding, and the absence of a community’s political power in accessing a safe water supply (Balazs and Ray, 2014). There is a direct correlation between the percentage of the population living below the poverty line (depicted in Figure 7), and the ability to utilize these resources. (Balazs and Ray, 2014).

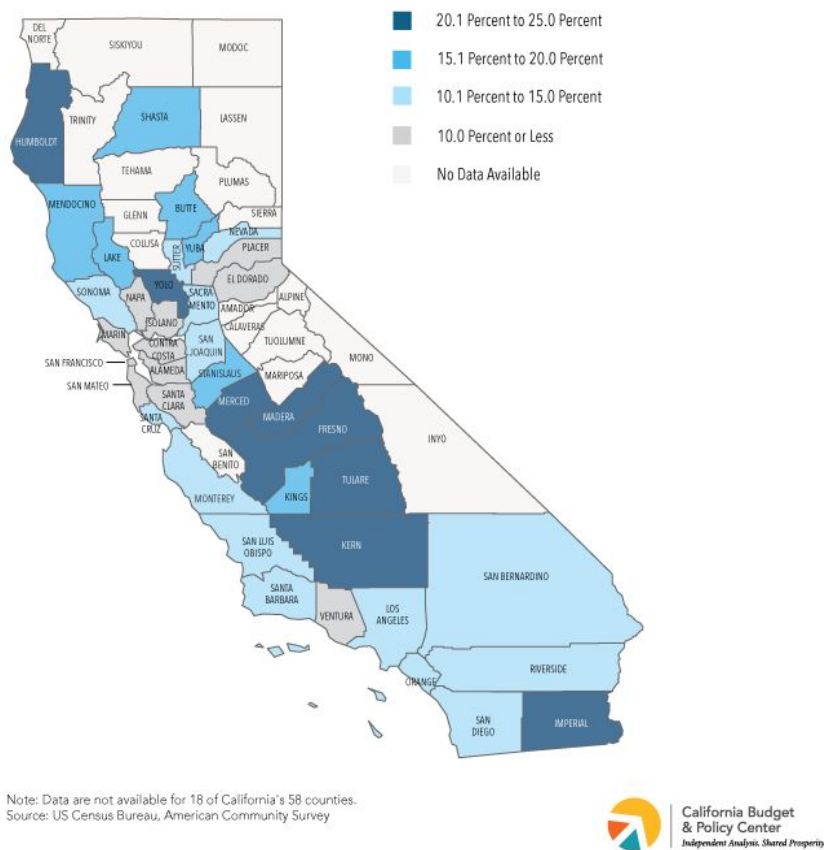


Figure 7: Percentage of people living in poverty in 2018 based on official poverty measure  
Sourced from: Kimberlin, 2018

This inequality is furthered as the effects of arsenic contamination in water has unequal effects across race, and disproportionately affects low-income communities of color. This is

visible in the demographics of the Central Valley, where 64% of the population is Hispanic or Latino (Hernández-Nieto, Gutiérrez, 2017).

## **5. Deployment of arsenic remediation technology in the Central Valley**

Different circumstances in the Central Valley, primarily the higher demand of water quantity required and high labor costs, are what account for the need to modify the ECAR technology.

First, unlike in India where each household only requires on average 2L of water per day, households in the Central Valley require at least 100 gallons per day (Gadgil and Hernandez, 2020). Therefore, the slow kinetics of the ECAR mechanism used in the Dhaphdapi water plant is not at all suitable for producing the quantity of water required in the Central Valley. As mentioned prior, the rate limiting step of this mechanism is the oxidation pathway. Thus, to increase the kinetics of the reaction, an appropriate oxidizer must be used.

Secondly, in the case of California, high labor costs with a minimum wage of \$12/hour, and a labor shortage in the skilled and semi-skilled sector, with the United States expected to face a labor shortage of 7.5 million workers by 2020, makes the labor-intensive maintenance model used in India economically impractical (Corchado, 2018). Thus, the long-term success of the project depends on the degree of autonomy it can operate with, indicating that the Central Valley would benefit from a reactor designed to accommodate a remotely monitoring system.

The need for a faster oxidant and new reactor model first led to the development of Air-Cathode Assisted Iron Electrocoagulation (ACAIE). The in-site production of hydrogen peroxide as a non-toxic, powerful oxidant led to its use. Subsequently, the research group developed a novel concept, External Oxidizer Assisted Iron EC (EOAIEC) for use in the

industrial world, where in-site production of hydrogen peroxide in ACAIE was replaced with externally added, easily available dilute hydrogen peroxide, as an external agent in this mechanism (Gadgil).

Second, in EOAIIEC, a compact spiral reactor is used, in which the anode and cathode are thin iron sheets separated by plastic meshes and rolled to form a tight spiral (similar to the sketch in Figure 9). This reactor does not require cleaning or maintenance, but rather a cartridge replacement. This is because electrolytic dissolution occurs at the thin iron sheet making up the anode when Fe is oxidized to Fe(II), thus the “sacrificial” anode is designed to disintegrate via dissolution at the end of its life (Hernandez and Gadgil, 2020; Hernandez, Bandaru, et al., 2019). In reality, both the steel sheets disintegrate at the end of the cartridge life, since programmed shifts in polarity of the mechanism will alternate the function of any given sheet from cathode to anode and back periodically, so as to consume both the iron sheets (Gadgil). This cartridge can be replaced on a weekly basis. With this sacrificial reactor, the system can be implemented with just cartridge replacement and remote monitoring. The external addition of hydrogen peroxide as an oxidizer increases the kinetics of the reaction 10,000 fold, producing 2400 L of water per hour (Hernandez and Gadgil, 2020; Hernandez, Bandaru, et al., 2019).

The solution hence proposed is a remotely monitored spiral iron reactor cartridge, and when it is close to its end of life, can be replaced (roughly on a weekly basis) by a local caretaker. From here, we need to determine how the decomposition of the sacrificial iron anode can be monitored so that the caretaker can be notified when the cartridge needs to be replaced.

## 6. Conducted Research

### 6.1 Purpose

A study was undertaken to simulate on the bench-top, the operation of the External Oxidizer Assisted Iron EC reactor as shown in Figure 8. By observing the change in current as the iron electrodes undergo electrochemical decomposition upon application of a constant voltage, the experiment aims to plot the change in resistance with time. Repetition of the outlined procedure is intended to eventually identify the time at which there is a steep rise in measured resistance and a corresponding decrease in the current, at which time the dissolution of iron electrode sheet begins to cease as does the capture and removal of arsenic in water. By determining a safe cut-off period at which the reactor is operating at around 80% efficiency, arrangements can be made for the replacement of the cartridge.

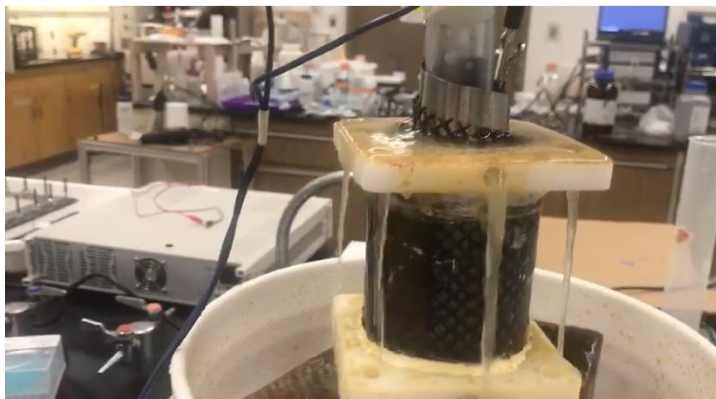


Figure 8: Experimental set-up, February 21, 2020

### 6.2 Theory

#### Key equations

#### 1. Faraday's law

The theoretical amount of  $\text{Fe}^{3+}$  or  $\text{Fe}^{2+}$  ions dissolved into solution at current  $i$  in current processing time  $t$  is given by Faraday's law

$$w = \frac{i \cdot t \cdot M}{nF}$$

w = weight of iron (mg)

i = Operating current (A)

t = Time of operation (s)

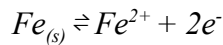
M = Molecular mass of Fe (mg/mol)

n = number of electrons per mol of iron involved in the oxidation or reduction reaction

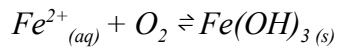
F = Faraday's constant, taken as 96,485 C/mol

## 2. Decomposition of Fe

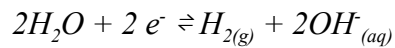
Anodic:



Bulk:

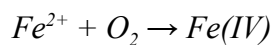


Cathodic:



## 3. Bulk solution:

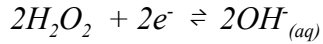
The arsenic removal process occurs in the bulk solution:



In this process, As(III) is oxidized to As(V). Following this, As(V) is irreversibly adsorbed onto the surface of Fe(III) precipitates (Li et. al, 2012) and can be removed via physical methods of separation.

#### 4. Addition of H<sub>2</sub>O<sub>2</sub>

One of the key implications of the ACAIE method is the use of in-site H<sub>2</sub>O<sub>2</sub> in order to speed up reaction kinetic by about 10,000 times. EOAIEC achieves the same goal more simply with external addition of H<sub>2</sub>O<sub>2</sub>.



### 6.3 Experimental Procedure

#### Materials used

##### 1. Synthetic groundwater:

Synthetic groundwater was generated using a variety of concentrations of salts to demonstrate the efficacy of the EOAIEC process. While concentration of As was set to zero, since it is irrelevant to the dissolution of iron electrodes, the water samples as given in Table 1 were intended to represent the constituents of “standard” water for a scoping study. More sophisticated study using synthetic groundwater could not be completed owing to COVID-19 causing the shut-down of all research labs on the campus.

Sample	Constituents	Concentration (mM)
1	NaCl	10
2	NaCl H <sub>2</sub> O <sub>2</sub>	10 9.8
3	NaCl H <sub>2</sub> O <sub>2</sub>	10 9.8
4	NaCl Na <sub>2</sub> SO <sub>4</sub>	2.5 5
5	NaCl Na <sub>2</sub> SO <sub>4</sub>	2.5 5
6	NaCl Na <sub>2</sub> SO <sub>4</sub>	2.5 5

Table 1: Water sample concentrations



## 2. Cell model:

The spiral reactor was built with a pair of iron sheets. The cathodic plate was 46.5 cm. in length and 8.7 cm in width and had a mass of 56.63 g. The anodic plate was 46.7 cm in length and 8.95 cm in width, with a mass of 58.06 g. The coil was enclosed in a mesh-like plastic sheath with openings for the entry of water. A closed tube was inserted into the middle of the spiral reactor setup. A pipe attached to a water pump was connected to the bottom of the cell model. A power source was set up, and connected to the respective electrodes. The cell model rested on blocks in a bucket. The bucket had a hole drilled on the side in which a pipe was securely fastened. Thus, when water was pumped into the cell, the iron-dosed water would spill out into the bucket and drain out into a sink via the pipe fastened to the bucket.

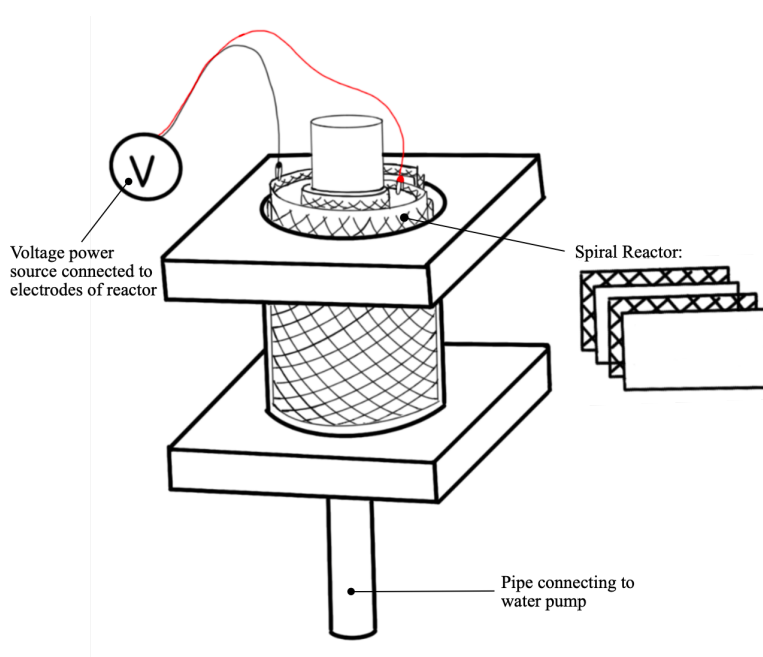


Figure 9: Experimental set-up schematic

#### 6.4 Predicted values

Using Faraday's law, the average time for the complete electrochemical process was estimated at 168 min when a constant current of 20 A was applied to the cell set up. The voltage was varied as needed (because the resistance of the reactor would steadily increase as the electrodes degraded from anodic dissolution).

#### 6.5 Experimental observations

Over a period of approximately 120 minutes, changes in current and voltage were monitored and the resistance was recorded every 5 minutes by hand. This 120 minute period was spread over multiple weeks due to scheduling restraints. The red vertical lines marked on the observed data in Figure 10 correspond to the break-points in time.

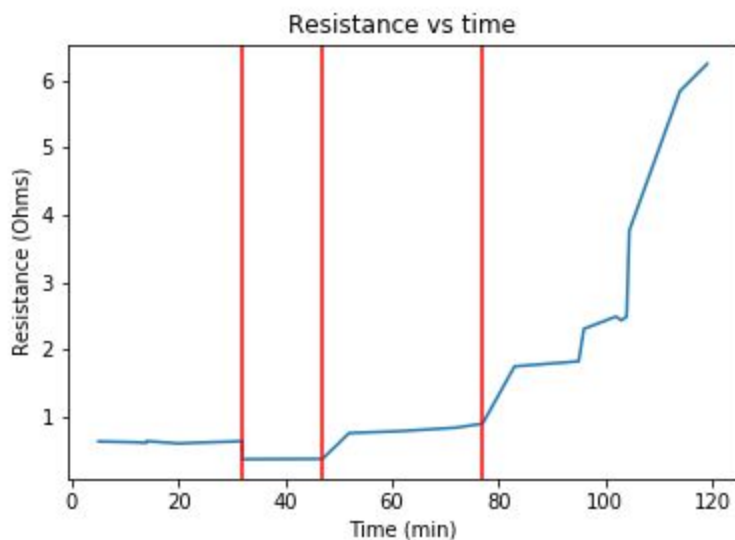


Figure 10: Sample Resistance vs time curve, with marked time intervals indicated by red vertical lines

#### 6.6 Modifications to experimental set-up

This experimental set-up was largely limited by time constraints. Future iterations of the experiment would include setting up a circulation system for the water so that the breaks in

between subsequent samples could be avoided. Additionally, the data points for voltage and current were recorded at 5 minute intervals, and hence, only inferential slopes could be determined for the remaining duration. Further experimental set-ups will utilize a constant voltage monitoring system, possibly using Arduino, that regularly updates values of voltage and current and records the resistance at a set time interval, eliminating the need for recording data by hand. The experimental procedure was largely focused on understanding the mechanics behind the electrochemical breakdown process, and consisted of rough estimates of tap water. Therefore in future setups, we will create more accurate synthetic groundwater samples. More iterations of this process need to be carried out to provide sufficient data that can be used to develop a remote monitoring system.

#### *6.7 Conclusion and further work*

Access to clean drinking water is a fundamental right with complex ramifications. In the search for a community-driven, sustainable solution, multiple factors of socio-economic and cultural significance need to be considered. While the underlying technology component of ECAR using iron reactors remains conceptually similar in its implementation in West Bengal and the Central Valley, the unique considerations made to the technical, managerial and financial (TMF) capacity has resulted in the development of a parallel, remotely monitored EOAIEC solution better suited to the labor market in the Central Valley.

The graph obtained suggests that a suitable cut-off period would be at approximately 80-100 min after the start of the electrochemical breakdown process for the sample iron electrodes . By obtaining more relevant curves for electrodes with suitable dimensions, the exact

time at which the reactor ceases operating at an optimum efficiency can be determined. This is a vital step required for the remote monitoring of the iron cartridges.

The software component required for the monitoring of the reactor, a cellular application, is currently under development. The app will be programmed to have a live monitoring system that will notify the caretaker when it is time to replace the cartridge.

Future work in this technology is primarily aligned towards field trials and gathering an increased contextualization of the conditions under which this technology is to operate on an extended basis. Through fieldwork, it is hoped that the crucial community engagement angle to implementation can also be solidified.

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