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Evaluation of Aluminum Dissolution, Current Density, and Pitting Patterns During Electrocoagulation

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Evaluation of Aluminum Dissolution, Current Density, and Pitting Patterns During Electrocoagulation

by

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A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Environmental Engineering
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Dedication

For my family.
Acknowledgments

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**Abstract**

Electrocoagulation (EC) is a sustainable water treatment process involving the generation of coagulants on-site through the application of a voltage on metal (usually aluminum or iron alloys). The factors that impact EC system performance have been well researched, however further research is needed on the factors that impact anodic dissolution of aluminum electrodes, especially when the technology is transferred to full-scale applications. Electrode fouling is one of the factors that can impact dissolution of the anode during EC due to the formation of a protective oxide/hydroxide layer on the electrode surface. Previous studies have addressed electrode fouling by reversing polarity, however results have been mixed or obtained for shorter timeframes that might not be applicable to full-scale EC systems. In addition, discussion regarding pitting patterns and aluminum production during EC water treatment is limited. In this study, the effect of switching polarity and pitting patterns (pit size, type, and location) on aluminum production and current density were evaluated in a continuously mixed EC batch reactor. The corrosion timeline and the effect of switching polarity versus normal operation on pitting trends over the expected life of the aluminum plates were also evaluated. The results showed that system performance was superior over time when direct polarity was used, due to sustained higher aluminum production and correlation between aluminum and current. Therefore, the use of direct polarity was recommended over the use of reverse polarity within the experimental parameters implemented.
Chapter 1: Introduction

An estimated 200 million people globally are exposed to groundwater with concentrations of arsenic and fluoride above the recommended WHO guidelines. Exposure to these contaminants can result in adverse impacts to human health. For instance, exposure to arsenic has been linked to cancer, skin lesions, cardiovascular diseases and cognitive development impacts, while exposure to fluoride has been shown to cause dental fluorosis and skeletal fluorosis (Indermitte et al., 2014; Nicomel et al., 2015). In many high-income countries, these contaminants are often removed from the drinking water supply using conventional methods that include a coagulation-flocculation step. However, in many rural areas, access and transport of chemical coagulants is a significant barrier that prevents adequate drinking water treatment (Devlin et al., 2019). Electrocoagulation (EC) has been proposed as a sustainable water treatment alternative that can supply the coagulant dose to remove heavy metals such as fluoride and arsenic. In many areas of rural India, the aluminum material is accessible (Mumtaz et al., 2012), and electricity is available in 95.7% of households (Agrawal et al., 2021). In areas where electricity is absent or expensive, solar photovoltaic cells have also been implemented (Mumtaz et al., 2015).

The electrocoagulation process combines principles of electrochemistry and chemical coagulation to produce coagulant ions from metal plates, such as aluminum and iron, on-site through electrolysis. In its most basic form, an EC reactor will have one anode, one cathode, an insulated reactor and a power source supplying direct current (usually a power supply). Even though the use of EC as a water treatment method has been reported as far back as the 19th century, interest in the technology has increased over the last two decades. Several studies have focused on
contaminant removal efficiencies for a wide range of pollutants (Dalvand et al., 2011; Koyuncu & Arman, 2020; López-Guzmán et al., 2019; Uğurlu et al., 2008; Zaleschi et al., 2012) and optimization of parameters to improve removal efficiencies (Bouguerra et al., 2015; Gwala et al., 2011; Kim et al., 2015; Modirshahla et al., 2008). However, fewer studies have addressed the challenges involved in electrocoagulation, including dissolution of the anode, the formation of a passive film on its surface (Ingelsson et al., 2020), and measuring performance, especially in rural settings, over long periods of operation (Alfredo et al., 2018).

The formation of a passive film on the anode’s surface is also known as electrode fouling, electrode passivation, or electrode scale-formation. Electrode passivation describes the formation of a metal oxide/hydroxide film on the surface of the anode. It is a challenge to implementing EC technology as it impedes dissolution of the anode by preventing the passage of ions into the solution. Many techniques have been proposed to prevent and reduce the formation of the passive film, including mechanical cleaning of the electrodes, increasing the flow rate, and the most common which is reversing the polarity (RP) of the electrodes during and in between water treatment batches. Currently, there is disagreement in the literature for how frequently the polarity should be switched for optimum EC system performance. In addition, the polarity switch has often been tested within small time intervals that would be difficult to manually implement in full-scale systems.

Additionally, performance of electrocoagulation treatment plants over long time periods and at the pilot or full-scale is not widely reported (Garcia-Rodriguez et al., 2020). One organization which has reported data for full-scale systems is the National Environmental Engineering Research Institute (NEERI) in Nagpur, India, which has installed almost 200 electrolytic defluoridation plants around India. Performance in these plants has been evaluated
based on defluoridation efficiency and reported positive results (Andey et al., 2013). However, in most of these treatment plants, operators are not able to measure performance through defluoridation efficiency. Operators have reported changing the coagulant metal material every 4-6 months based on pitting and passivation on the electrodes, but there is no data to support this replacement frequency in the EDF plants (Alfredo et al., 2018). In the absence of defluoridation performance data, there is a need for performance indicators which are practical to measure by the operators and can provide a threshold that operators can use to guide maintenance of these plants, such as current measurements and a pitting timeline.

Due to the gap in research regarding how RP-EC could impact the efficiency electrocoagulation in terms of aluminum production and the lack of practical measurable indicators that operators in rural settings can use to measure performance in the field, this research has the following objectives:

1. Determine the effect of reversing the polarity on the electrodes by switching the direction of current at a frequency 24 hours (polarity reversal time = 24 hours) on aluminum production efficiency, current density, and pitting trends on the electrode surface when compared to standard operation (no switch in polarity) during a long-time frame that models the wear of electrodes on full-scale systems (144-168 hours).

   a. Hypothesis: Reversing the polarity will result in decreased electrode fouling which will result in higher current densities, aluminum production, and pit density and volume as compared to standard operation.

2. Evaluate the efficiency of current and a corrosion timeline as practical performance indicators that can be related to aluminum concentration in both standard operation and reverse polarity operation. The corrosion timeline will show trends in pitting patterns, including pit
volume, type, and location on electrode surface and evaluate trends between pitting patterns and aluminum production efficiency and current density.

\textit{a. Hypothesis}: Aluminum production efficiency will decrease over time as the pitting volume increases and the pitting patterns will determine trends in Al production in both standard operation and reverse polarity operation.

To accomplish these objectives, two sets of experiments were performed, the first set received direct current with no polarity change, and the second received direct current with polarity reversal every 24 hours. All other experimental conditions remained constant. After the experiments, the aluminum concentrations were measured using Flame Absorption Spectroscopy and the electrode surfaces were analyzed using a 3D Keyence Scanner Microscope. Scanning of the electrode plates allowed for a pitting volume and distribution analysis that could be compared to the aluminum concentration results. The weights of the electrode prior to and after electrocoagulation were also recorded.

The remainder of this thesis consists of a literature review, chapter 2, which includes a brief history of electrocoagulation, the chemical reactions involved in the process, discussion of the major factors impacting treatment efficiency, and a description of how passivation and pitting of the electrode impacts system performance. The knowledge gaps this research will address are also presented in chapter 2. Next, chapter 3 contains the methodology for experimental assessment of operating bench-scale electrocoagulation treatment units in both direct and reverse polarity electrocoagulation. Chapter 4 contains the results and discussion. Finally, conclusions of the data analysis for the stated research objectives are presented in chapter 5.
Chapter 2: Literature Review

2.1 Water Supply Access

2.1.1 Sustainable Development Goals

In 2015, the United Nations announced the 2030 Agenda for Sustainable Development, which included 17 Sustainable Development Goals and 169 targets. The SDGs build on progress achieved by the Millenium Development Goals (MDGs), which were established by the United Nations Member States in the year 2000. The SDGs expanded on the MDG targets to reduce the number of people without access to drinking water by announcing Goal 6, “Ensure availability and sustainable management of water and sanitation for all” (United Nations, 2015). The SDGs further broke down the MDG definition for improved/unimproved into a five-step ‘service ladder’ ranging from surface water to safely managed drinking water (WHO and UNICEF, 2021) (Table 1).

Even though the MDG to halve the population without sustainable access to safe drinking water and sanitation was met five years prior to the SDGs, two billion people still lacked access to safely managed drinking water services in 2020, including 1.2 billion who have basic water services (WHO, 2021). To reach “safely managed”, the highest category of safe water according to the SDGs, drinking water should be free from fecal and priority chemical contamination (WHO, 2015). These priority chemicals include geogenic fluoride and arsenic, which are found in many areas of the world where groundwater is the main source of drinking water.

Exposure to geogenic arsenic and fluoride affects millions of people globally. More specifically, the WHO estimates that currently around 220 million people are exposed to drinking water contaminated with high levels of fluoride and 200 million people are exposed to drinking
water contaminated with arsenic (WHO, 2017). Researchers at EAWAG modeled the probability of geogenic fluoride and arsenic contamination exceeding the WHO guidelines of 1.5 mg/L fluoride and 10 ug/L arsenic to determine the risk of exposure from groundwater at a global scale (Amini et al., 2008a; Amini et al., 2008b). The model used geological, chemical, climatic, and soil condition data associated with high fluoride and arsenic concentrations to predict areas with high probability of contamination. The results indicated a high probability of both fluoride and arsenic contamination in many areas in India and China. Other regions estimated to have a high probability of fluoride and arsenic contamination are summarized in Table 2.

The results from the EAWAG study indicate the high global incidence of naturally occurring fluoride and arsenic in groundwater, however, risk of exposure to arsenic and fluoride depends on the area’s reliability on groundwater as a drinking water source, as well as the area’s water treatment capacity to remove these contaminants. In many high-income countries, areas with a drinking water contamination threat are easily managed using traditional treatment technology. For arsenic and fluoride, traditional treatment often involves the use of iron or aluminum chemicals for complexation with these contaminants. Nevertheless, the purchase of chemicals as either adsorption media or coagulation chemicals can be expensive due to the large chemical requirement (Waghmare & Arfin, 2015) or difficult to access in remote or rural locations (Devlin et al., 2019). Therefore, in many rural areas, decentralized water treatment schemes are desirable.

Decentralized water treatment schemes can be designed and adjusted to meet local needs, which consider technology selectivity, cost, and operation as important design parameters. Decentralized treatment could provide an important water treatment alternative to rural communities, who also comprise the majority of the world population who still lack access to the highest water service level (Figure 1), with an estimated 8 out of 10 of the global population who
lack safely managed water access living in these areas (WHO and UNICEF, 2020). Nonetheless, even though decentralized treatment can help overcome site specific issues and provide flexibility in management and operation, all aspects of the technology, from installation to wastewater management need to be carefully considered in the appropriate context to ensure sustainability of the system (Massoud et al., 2009).

As a decentralized treatment system, electrocoagulation treatment plants present several advantages to traditional systems as they require little maintenance, usually have a modular design that can be adjusted, and produce less sludge than traditional coagulation systems. In rural India, the aluminum metal is widely accessible (Mumtaz et al., 2012) and electricity is accessible in 95.7% of these areas (Agrawal et al., 2021). Further, depending on demand, the EC system may be applied in areas where electricity cannot be applied for long time periods or charged using solar photovoltaic cells (Mumtaz et al., 2015). The National Environmental Engineering Research Institute (NEERI) in Nagpur, India has installed almost 200 electrolytic defluoridation treatment plants (EDF) throughout India (NEERI, 2020).

According to NEERI, their electrolytic defluoridation plants commonly use a DC power unit, are able treat fluoride concentrations up to 10 mg/L and have a capacity of 2000 L per batch in 3-3.5 hours (NEERI, 2020). The capacity of these treatment plants ranges from at least 250-4000 L (Cherukumilli & Gadgil, 2014) and they are run in batches ranging from 30-120 minutes (Alfredo et al., 2018). For instance, a solar power based EDF plant in the village of Dongargaon in the Madhya Pradesh state, showed that the current used ranged between 16-20 A depending on the season, with the lowest current corresponding to the rainy season when there was less sunlight available. Initial fluoride concentrations ranged seasonally between 4.05-5.43 mg/L and batch time ranged between 60-90 minutes. Even though a higher batch time was needed during the winter due
to the lower available current, fluoride concentration was still successfully reduced to 0.99-1.2 mg/L, which is below the WHO limit of 1.5 mg/L.

Despite the presence of EDF plants in many areas in rural India, challenges persist related to the technology, many which are related to maintenance and costs. These challenges include the maintenance of plants that are not operated by private vendors in rural areas, difficulty changing behavior to encourage users to buy treated groundwater from the treatment plants, limited reach to other states affected by fluoride, and the potentially high cost for construction of the plant and costs for electrode replacement and maintenance (Cherukumilli & Gadgil, 2014). To address these challenges, community engagement and user-preferences are important factors, especially in situations where EDF treatment plant is handed over to the community from the government or a private vendor (Alfredo & O’Garra, 2020). The identification of practical measurable performance indicators in these EDF plants and other similar electrocoagulation plants could contribute to the sustainability of these systems.

Figure 1. World drinking water service level household data by rural and urban settings

---

1 Data publicly available from WHO/UNICEF Joint Monitoring Programme for Water Supply, Sanitation and Hygiene (JMP) Global Database.
To address the challenges related to decentralized electrocoagulation treatment, further research is required regarding the performance of these systems in the long-term, including social and economic aspects related to operation and maintenance. Even though the studies evaluating the number of pilot and full-scale electrocoagulation plants have increased, most have been conducted for shorter timeframes and smaller volumes (Garcia-Rodriguez et al., 2020) that might not be easily transferrable to rural settings such as the EDF plants in India.

Table 1. Sustainable development goals drinking water service ladder (WHO, 2021).

<table>
<thead>
<tr>
<th>SERVICE LEVEL</th>
<th>DEFINITION</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAFELY MANAGED</td>
<td>Drinking water from an improved source that is accessible on premises, available when needed and free from faecal and priority chemical contamination</td>
</tr>
<tr>
<td>BASIC</td>
<td>Drinking water from an improved source, provided collection time is not more than 30 minutes for a round trip, including queuing</td>
</tr>
<tr>
<td>LIMITED</td>
<td>Drinking water from an improved source, for which collection time exceeds 30 minutes for a round trip, including queuing</td>
</tr>
<tr>
<td>UNIMPROVED</td>
<td>Drinking water from an unprotected dug well or unprotected spring</td>
</tr>
<tr>
<td>SURFACE WATER</td>
<td>Drinking water directly from a river, dam, lake, pond, stream, canal or irrigation canal</td>
</tr>
</tbody>
</table>

Table 2. Global occurrence of fluoride and arsenic (Amini, et al., 2008a; Amini et al., 2008b).

<table>
<thead>
<tr>
<th>Fluoride</th>
<th>Arsenic</th>
</tr>
</thead>
<tbody>
<tr>
<td>• North and East Africa (especially along the rift valley)</td>
<td>• South Asia (Bangladesh, Nepal, Cambodia, and Vietnam)</td>
</tr>
<tr>
<td>• The Middle East</td>
<td>• South America (Brazil, Bolivia, Ecuador, Costa Rica, Chile and Argentina)</td>
</tr>
<tr>
<td>• South and Central Asia (Pakistan, Uzbekistan, Kazakhstan)</td>
<td>• North and Central America (Southwest United States, Mexico, Guatemala, Nicaragua)</td>
</tr>
<tr>
<td>• North America (Mexico and the United States)</td>
<td>• Northern European countries (Ukraine, Poland, Belarus, Estonia, and Lithuania)</td>
</tr>
<tr>
<td>• Argentina</td>
<td>• Taiwan</td>
</tr>
<tr>
<td>• South Africa</td>
<td></td>
</tr>
<tr>
<td>• Australia</td>
<td></td>
</tr>
</tbody>
</table>

2 “SDG ladder for drinking water services” by World Health Organization is licensed under CC BY-NC-SA 3.0 IGO
2.2 The Electrocoagulation Process as a Viable Treatment Option

2.2.1 Electrocoagulation Technology Background

The use of electrochemical methods for water treatment dates back to 19th century England, when Eugene Hermite received a patent for an electrolytic method to bleach sewage (Vik et al., 1984). In the early 20th century, several advances in the technology lead to the development of the first electrolytic water treatment plants in the United States, all of which were abandoned by 1930 (Miller and Knipe, 1965). These water treatment plants were abandoned due to high costs of operation and uncertain treatment efficiencies in comparison to the conventional methods that were available at the time.

Electrochemical technologies were also used for water treatment in the former USSR in 1925, in the United States in 1946, and in England in 1956 (Vik et al., 1984). In the 1925 investigation, an iron electrode was used to purify water in Shature Station, however results were not identified in this study. In both the 1946 and 1956 studies, positive results were reported for turbidity and color removal, but the methods used at the time were still more expensive than for traditional coagulation (Matteson et al., 1995).

However, research on electrocoagulation for wastewater treatment regained interest in the latter half of the 20th century due to the high cost of physical chemical treatment processes and the difficulty of biological treatment due to the slow speed of the process, variations in organic loading, and high maintenance of the system (Poon & Brueckner, 1975). Moreover, in the late 1970s, more promising results for electrocoagulation were being reported than in previous studies, making it a more feasible option (Monica et al., 1980).

During the past two decades, interest in electrochemical water treatment technologies has increased due to the increased demand for environmentally friendly technologies (Moussa et al.,
2017). This can be observed by conducting a simple search in web of science and outputting the number of articles related to the search (Figure 2). The search was constrained to articles published in English. Figure 2 presents the searches for “electrocoagulation” and one of the other sub-category search terms listed in the legend. For example, “water treatment” represents the search ‘electrocoagulation’ AND ‘water treatment’. It is apparent that interest in electrocoagulation has increased in past decade with the percentage of papers dedicated to “drinking water treatment” increasing as well. Nonetheless, several gaps remain, including the lack of an established reactor design, which makes comparing performance between systems with different parameters challenging (Holt et al., 2005).

![Results from Web of Science Search](image)

Figure 2. Results from Web of Science search for number of articles related to electrocoagulation and water treatment published in English.

### 2.3 Electrocoagulation Basics

Several designs for an electrocoagulation reactor have been proposed, but the most basic form usually consists of an insulated reactor or cell, an anode, a cathode, and a power supply. The electrocoagulation process involves a combination of chemical, physical, and electrochemical
mechanisms, including physical adsorption, coagulation, flotation, acid/base equilibrium, metal hydroxide precipitation, metal dissolution, water reduction, and pollutant electro-oxidation or reduction (Hakizimana et al., 2017). Even though variations exist on the reported mechanisms that occur and dominate during electrocoagulation, these mechanisms are frequently summarized into three stages: (1) formation of coagulants (2) destabilization of pollutant charge, and (3) aggregation of particles to form flocs (Mollah, 2000).

1. Step 1: Formation of Coagulants

The first step described by Mollah et al., 2000 is the formation of coagulants, the majority of which occurs as a result of dissolution of the anode (Equation 1) and hydrolysis at the cathode (Equation 2). Due to the generation of \( \text{OH}^- \), the pH of the solution will increase, leading to the formation of various aqueous metal hydroxide species over time (Al-Raad & Hanafiah, 2021). Depending on the pH of the solution, the species formed could include \( \text{Al(OH)}^{2+} \), \( \text{Al(OH)}_2^+ \), \( \text{Al(OH)}_3 \), \( \text{Al(OH)}_4 \), \( \text{Al(OH)}_5^{2-} \), \( \text{Al}_2(\text{OH})_2^{4+} \), \( \text{Al}_6(\text{OH})_{15}^{3+} \), \( \text{Al}_7(\text{OH})_{17}^{4+} \) and \( \text{Al}_8(\text{OH})_{20}^{4+} \) (Lu et al., 2017), though the monomeric species dominate at lower concentrations (Cañizares et al., 2006).

\[
\text{Al} (s) \rightarrow \text{Al}^{3+} + 3e^- (Eq \ 1)
\]
\[
2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^- (Eq \ 2)
\]
\[
\text{Al}^{3+} + \text{H}_2\text{O} \leftrightarrow \text{Al(OH)}^{2+} + \text{H}^+ (Eq \ 3)
\]
\[
\text{Al(OH)}^{2+} + 2\text{H}_2\text{O} \leftrightarrow \text{Al(OH)}_3 + 2\text{H}^+ (Eq \ 4)
\]

Using amorphous aluminum as the solid that forms in solution, the log C-pH diagram was created and is presented in Figure 3. From this we can see that even though there is a wide range of pH where aluminum precipitation would occur, maximum precipitation occurs between pH 6-8. At pH values less than 6, the aqueous species that dominates is \( \text{Al(OH)}^{2+} \) and at higher pH values it is \( \text{Al(OH)}_4^- \). In general, \( \text{Al(OH)}_3 \) is considered the species which is mainly responsible.
for coagulation and pollutant removal (Garcia-Segura et al., 2017). The formation of Al(OH)$_3$ is summarized in Equations 3-4 (Mechelhoff et al., 2013).

2. Step 2: Destabilization of pollutant charge

The destabilization mechanism of pollutants during electrocoagulation due to the produced coagulants can vary with the pollutant type. For instance, for both colloidal particles and soluble ions (such as heavy metals) the produced metal cations will compress the pollutant double layer, which will decrease repulsive forces between particles, resulting in coagulation or adsorption (El-Ashtoukhy et al., 2020; Hakizimana et al., 2017).

For colloidal particles, Hakizimana et al., 2017 described the destabilization mechanism as simultaneous or consecutive adsorption, charge neutralization, physical enmeshment, and adsorption on particles, depending on water composition. This is different than in chemical coagulation because the pH change in this case will drop to acidic levels, changing the dominant aluminum species available and thus the dominant removal mechanism as shown by the logC-pH diagram in Figure 3 (Cañizares et al., 2006).

3. Step 3: Aggregation of particles to form flocs

Following the destabilization of pollutants, bigger particles will form that turn into flocs, which create a “sludge blanket” that traps pollutants they come into contact with (Mollah, 2000). The formation of flocs is largely dependent on the previous step and the collision rate between particles (Harif et al., 2012). This is because the previous step will dictate the strength of the repulsion or attraction of forces between particles in the solution.

Following flocculation, the main removal mechanisms include settling and electroflotation, which can be done through filtration, settling, centrifugation, hydrocycloning and flotation, though the most common of these are filtration and settling (Hakizimana et al., 2017). Managing the
sludge after this step is more practical than in chemical coagulation because its composition is more stable and lower in quantity, thus making it easier to dewater (Kabdaşlı et al., 2012).

Figure 3. Diagram (logC-pH) of equilibrium aluminum speciation with amorphous aluminum hydroxide. Dissociation constants obtained from Benjamin, 2015.

2.4 Many Factors Impact EC Performance

Electrocoagulation efficiency is dependent upon electrode metal material (Jiménez et al., 2012; Sahu et al., 2013; Zhao et al., 2011), surface area of the electrode that is submerged in the solution to the volume of solution in the reactor (S/V ratio) (Bouguerra et al., 2015), distance between the electrode plates (interelectrode distance) (Aoudj et al., 2010; Huda et al., 2017; Mameri et al., 2001), and the current and applied voltage (Chen et al., 2002; Dalvand et al., 2011). Common ranges cited in the literature for the surface area to volume ratio and the interelectrode distance include 6.9-43 m²/m³ (Holt et al., 2002a) and 0.5-3 cm (Aityoub et al., 2020), respectively. These two parameters are important to consider when scaling up an EC technology for optimum removal of the targeted contaminant while minimizing operational costs due to current demands. In general, a high S/V ratio is desirable due to the increase in the available anode area, but might
also require higher applied currents (Martínez-Villafañe et al., 2009). Similarly, shorter interelectrode distances are desirable to enhance mass transfer between the anode and the cathode, but higher current demand has been reported in these cases as well (Aoudj et al., 2010; Huda et al., 2017).

Besides varying with the surface area to volume ratio and the interelectrode distance, the optimum current has also been shown to vary with initial concentration of the contaminant (Mameri, 1998). The current is the most important parameter because it will determine the concentration of aluminum that will dissolve in solution, with higher current densities corresponding to higher aluminum coagulant generated. Faraday’s law has previously been used to predict coagulant dose; however, use of this equation is limited as it has been shown to underestimate coagulant production (Vik et al., 1984). In addition, mathematical models have also been developed to attempt to relate the coagulant dose to the current and the compared to experimental results (Graça et al., 2019; Gu et al, 2009; Matteson et al., 1995), but these studies have been conducted for short time frames that do not encompass multiple days of operation.

Contrary to what might seem intuitive, higher current densities are not always the most efficient for treatment and can also result in a higher treatment cost. For instance, at high current densities, competition between aluminum dissolution and oxygen evolution reactions results in decreased aluminum generation than at lower potentials (Cañizares et al., 2005). In addition, it is widely reported in the literature that the current density also determines the dominant removal mechanisms taking place in the solution. As described by Holt et al. (2002b), the current density will determine the dominant removal mechanism with settling dominating at lower currents and flotation dominating at higher currents. This difference in how the produced solid behaves is extremely important for sludge handling and must be considered during the design phase.
However, high current densities might be required in some cell configurations such as in continuous reactors receiving high flow rates (Emamjomeh & Sivakumar, 2009).

The type of current most frequently used during EC is direct current (DC), during which the electrode assigned as anode and cathode remain the same. However, other methods such as alternating current (AC-EC) or reverse polarity (RP-EC) have also been tested in the literature to determine if these would improve EC performance. In AC-EC and RP-EC methods, the electrodes are alternated as anode and cathode throughout the EC process, with the goal of consuming both electrodes uniformly and reducing the formation of the metal oxide/hydroxide film on the electrodes. During the AC-EC process, the anode and cathode are alternated quickly, while during PR-EC, the polarity reversal time (PRT) intervals that have been implemented vary (Chow et al., 2021); thus RP-EC with lower PRTs are the same as AC-EC. However, while the results from AC-EC have indicated a decrease in the passive film and more uniform dissolution of the anode (Vasudevan et al., 2010), results from RP-EC have been mixed, with different PRTs suggested in the literature.

2.5 Pitting and Corrosion of Electrodes as a Measure of Plate Health

The rate of dissolution, or corrosion, of aluminum anodes during EC, as well as the pitting patterns observed on the plate surface can potentially provide information about the service life of the electrode. During EC, uniform corrosion is desirable as it will lead to longer service life of the electrodes than localized pitting corrosion (Wellner et al., 2018). The rate of corrosion can be determined using methods such as electrode weight loss measurements, measuring the concentration of aluminum on solution, and potentiostatic or galvanostatic tests (Mansouri et al., 2011; Mouedhen et al., 2008; Wellner et al., 2018). On the other hand, the pit distribution on the
The electrode surface has been analyzed using Scanning Electron Microscopy (SEM), X-ray Diffraction, or optical microscopy (Chow & Pham, 2021; Hu et al., 2003; Vasudevan et al., 2010).

The corrosion rate and mechanism will vary with the electrolyte composition, as an increase in conductivity will usually lead to a higher corrosion rate. For instance, it has been often demonstrated in the literature that solutions containing aggressive anions such as Cl\(^-\), lead to pitting corrosion and destruction of the passive film that forms during EC (Abodi et al., 2012; Mansouri et al., 2011; McCafferty, 2010). In addition, solutions containing phosphate ions have shown to lead to lower corrosion rates as these encourage formation of the passive film (Mansouri et al., 2011). The effect of other particles, such as NH\(_3\) has also been reported to lead to crevice corrosion in an electrolyte solution containing F\(^-\) ions (Hu et al., 2003).

The pit distribution can also vary during Al-EC, as shown by optical micrograph analysis performed by Mansouri et al. 2011, where localized pits were observed during Al-EC in a NaCl solution, while uniformly distributed pits were observed during Al-EC in a NaH\(_2\)SO\(_4\) solution. However, uniform dissolution of the cathode has been observed in other studies, even when Cl\(^-\) ions were present (Mouedhen et al., 2008).

The corrosion and pitting behavior may also vary with the type of current that is used. For example, Vasudevan et al. (2010) showed that when AC current was used, the electrode surface was smoother, which was determined by the authors to suggest more uniform dissolution. On the other hand, when DC current was used, the electrode surface was rougher and various pits were observed on the surface which were thought to be due to consumption of the anode at those sites due to oxygen evolution. Even though interest in research evaluating the effect of different electrolytes and current types on the pitting behavior of aluminum alloys has increased, the long-term pitting behavior of aluminum alloys during electrocoagulation and how this relates to...
operation in the field has not been evaluated. The potential for visual evaluation of performance based on the pitting of the electrode surface over time is not reported in the literature.

2.5.1 Electrode Passivation

As the electrocoagulation process continues, another reaction at the plate surface other than corrosion is scale formation. This scale formation is often referred to as electrode fouling or passivation. Passivation is described by the formation of a protective film on a metal surface, usually consisting of metal oxides and hydroxides (Ingelsson et al., 2020). The formation of a passive film on the surface of the anode is one of the biggest constraints in water treatment via electrocoagulation, as it can prevent further dissolution and formation of coagulants in the bulk solution and lead to higher potential requirements, leading to increases in operation costs.

Aluminum alloys form a protective oxide film when exposed to air and water at neutral pH between 4-9 (Schmuki, 2002). This layer acts as an insulating layer that can be thick at high potentials. During EC, besides this oxide film, the layer composition also includes metal hydroxides, usually in the form of excess Al(OH)₃ other metal species such as aluminum phosphates, and cations and anions in the solution, such as Ca²⁺ or Mg²⁺ which are attracted to the oppositely charged electrode surface and precipitate or adsorb to it (Ingelsson et al., 2020).

The species that accumulate in the passive layer have been analyzed through SEM or XRD studies (Chow & Pham, 2021; Mouedhen et al., 2008; Zheng, 2019) and have also been shown to vary according to the type of current applied. For instance, in Chow and Pham (2021) it was noted that during when DC current was applied, SEM analysis revealed that the anode was covered with aluminum hydroxide precipitates, while the cathode was covered with Ca-Mg-CO₃ precipitates. On the other hand, when PR-EC was applied at PRTs of 0.5 and 10 min., calcium, carbon, oxygen, and aluminum hydroxides elements were found on the pits of the electrodes.
As mentioned in the previous section, PR-EC is a common technique to remove scale formation, but the reported results and PRTs are mixed, which suggests that optimum PRTs are based on other factors specific to the treatment such as electrolyte composition, current density, and hydraulic retention time (Ingelsson et al., 2020). In addition, it is important to note that experimental techniques to determine the effectiveness of PRT method vary between studies, as some focus on contaminant removal efficiencies (Betancor-Abreu et al., 2019) others on the passive layer build-up and coagulant production (Chow & Pham, 2021; Fekete et al., 2016).

Further, while Betancor-Abreu et al. (2019) found that for three PRTs tested of 0.5, 1, and 2 minutes, the 1-minute PRT resulted in higher fluoride removal efficiencies in the larger reactors tested (368 mL and 2000 mL) and similar removal efficiencies in the smaller reactor (168 mL) but at a longest HRT of 15 min. This was attributed to increased passivation and surface roughness at the cathodic surface at longer polarity change periods. On the other hand, Chow & Pham (2021) found higher removal efficiencies for the highest PRT tested of 10 minutes. There seems to be little consensus in the literature regarding the optimal polarity reversal time that should be applied to achieve a decrease in the thickness of the passive layer.

2.6 Knowledge Gaps and Research Objectives

As noted from the previous studies, RP-EC is usually done in time increments that are not realistic for field operations, especially if the change in current direction has to be performed manually. In central India, these systems are typically operated daily for 30-120 min, once to twice a day. The current applied in the field is DC current, thus requiring manual switching of applied charge to achieve RP-EC configurations. Automation of this process is possible, but cost increases must be considered in this case. As such, the identification of a polarity reversal time that is both efficient at removing the passive film and practical to implement in the field could be beneficial
to performance of EDF plants in India. Previous research in the area has revealed that most full-scale systems are not regularly checked for treatment efficiency. Instead, generalized timelines for plate replacement due to pitting, corrosion, and film development are often quoted by operators (Alfredo et al., 2018). Given the lack of research into how RP-EC could impact the efficiency of aluminum production and the lack of practical measurable performance indicators that could be used by operators to evaluate system performance, this research has the following objectives:

1. Determine the effect of reversing the polarity on the electrodes by switching the direction of current at a frequency 24 hours (PRT = 24 hours) on aluminum production efficiency, current, density and pitting trends on the electrode surface when compared to standard operation (no switch in polarity) during a long-time frame that models the wear of electrodes on full-scale systems (144-168 hr.).

   a. Hypothesis: Reversing the polarity will result in decreased electrode fouling which will result in higher current densities, aluminum production, and pit density and volume as compared to standard operation.

2. Evaluate the efficiency of current and a corrosion timeline as practical performance indicators that can be related to aluminum concentration in both standard operation and reverse polarity operation. The corrosion timeline will show trends in pitting patterns, including pit volume, type, and location on electrode surface during both standard operation and switched polarity operation and evaluate trends between pitting patterns and aluminum production efficiency and current density.

   a. Hypothesis: Aluminum production efficiency will decrease over time as the pitting volume increases and the pitting patterns will determine trends in Al production in both standard and reverse polarity operation.
Chapter 3: Methods

3.1 Electrocoagulation Reactor Set-up

Design of the electrocoagulation cell was based on the optimum parameters discussed in the literature review section and the general design of the EDF plants installed in India by NEERI. The implementation of the optimum parameters discussed in the literature review section have been implemented in at least one EDF plant in India (Mumtaz et al., 2012). As such, the electrocoagulation experiments were conducted in a continuously stirred batch reactor with an electrolyte solution consisting of 1.1 L of deionized water and 0.272 g NaHCO₃ to provide an alkalinity of 150 mg/L as CaCO₃ which is within the range of alkalinity found in groundwater. The anode and cathode were composed of Al 6061 alloy with dimensions of 3 x 6 x 0.125 inches. The submerged area of the electrodes was 16.5 in², the interelectrode distance, 0.19 inches (0.5
cm), and the S/V ratio was 9.6774. Dimensions can be seen in Figure 4. The interelectrode distance was maintained constant by using nylon rod spacers between the plates (Figure 5).

![Nylon spacers dimensions](image)

Figure 5. Nylon spacers dimensions. Plate height, not shown, was 3 inches.

All glassware and materials used in the study were subjected to an acid bath procedure. A magnetic stirrer was used to maintain constant mixing of the solution at a slow speed. The pH was measured by placing the pH meter both close to the cathode and anode outer, to account for local differences in pH that result from oxidation/reduction reactions near the positively and negatively polarized electrodes in the reactor. A voltage of 10 V was maintained constant using a Gamry Interface 1000 instrument in potentiostatic mode. This allowed for periodic measurements (set at 10 seconds) of current (A) at a constant voltage over time as the passive layer accumulated on the anode. The complete set-up can be seen on Figure 6.

### 3.2 Electrocoagulation Experiments

#### 3.2.1 Preliminary Experiments

Prior to the electrocoagulation experiments, preliminary experiments were performed to evaluate the effect of voltage on current density and aluminum production. The voltages tested
were 10 V and 15 V, to generate a current similar to that applied in rural EDF systems in India. The preliminary experiments were conducted using the set-up described in the previous section, with the difference that current measurements were performed using a Klein Tools MM300 multimeter. Due to the rapid development of a passive film observed when a voltage of 15 V, a voltage of 10 V was selected.

![Figure 6. Electrocoagulation set-up including 1) Batch reactor, 2) Magnetic stirring plate, 3) Potentiostat, and 4) Gamry software.](image)

3.2.2 Electrocoagulation Experiments

The effect of reversing polarity on aluminum production, current density, and pitting patterns was evaluated in two sets of experiments with a duration of 6-7 days each (144-168 hours). In both sets of experiments, the potentiostat was reset and the batch solution changed every 24-hours. At the start of each new batch, samples were collected at 0, 15, 30, 45, 60 and 120 min to evaluate changes over the duration of a batch treatment session (Alfredo et al., 2018). The batch
reactor continued to operate for 24 hours prior to starting a new batch to simulate electrode wear before the next sample collection period. The 24-hour period relates to the day of plate operation based on the duration of batch in the field. For example, a batch system using 30-minute batches would have the equivalent of 48 days of use after 24-hours in my reactor. Similarly, a batch system using 60-minute batches would have the equivalent of 24 days of use after 24-hours in my reactor (Table 3).

Table 3. Time equivalence between lab scale and full-scale reactor.

<table>
<thead>
<tr>
<th>Plate (hrs.)</th>
<th>30 min.</th>
<th>60 min.</th>
<th>120 min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>48 days</td>
<td>24 days</td>
<td>12 days</td>
</tr>
<tr>
<td>48</td>
<td>96 days</td>
<td>48 days</td>
<td>24 days</td>
</tr>
<tr>
<td>72</td>
<td>144 days</td>
<td>72 days</td>
<td>36 days</td>
</tr>
</tbody>
</table>

Figure 7. Inner face of anode from direct polarity experiments A) before and B) after cleaning procedure.

In the first set of experiments, the polarity was kept unchanged, allowing the passive layer to keep building on the anodic surface over time. In the second set of experiments, the polarity
was reversed every 24-hours with the change of batch solution. Theoretically, this polarity reversal would allow for dissolution of the passive layer through reversal of the chemical reactions taking place on the electrode interfaces (Chow & Pham, 2021). The effect of forward and reverse current could then be analyzed by comparing the batches receiving current in each forward and reverse directions.

The samples were collected in 5-10 mL aliquots at 15-min intervals for the first 2 hours of operation per new batch solution. The pH of the solution was also monitored in this manner. The procedure was repeated until the system exceeded 200 hours of operation. The samples collected from the experiments where polarity remained unchanged were labeled as “Direct Polarity”, while the samples collected from the experiments where the polarity was reversed were labeled as “Reverse Polarity” (see Table 4 for label examples). At the end of each 24-hour run, pictures of the electrode outer faces were taken to construct a corrosion timeline. This would allow to make visual observations that could be related to performance based on aluminum concentration. Since operators of EDF plants in India often use visual observation of pitting and passivation to guide electrode replacement (Alfredo et al., 2018), evaluation of the timeline would allow for the determination of whether this current method is an efficient performance indicator.

After the entire electrocoagulation period, the plates were gently scrubbed with a soft bristle brush and submerged in nitric acid in 1-minute intervals until most of the corrosion products had been removed (Figure 7), then rinsed with DI water and dried, according to the ASTM-G1 Standard (ASTM Committee G-1 on Corrosion of Metals, 2017). The electrodes were weighed after the first 1-min cleaning cycle to account for mass loss due to the procedure.
3.3 Analytical Methods

The total aluminum concentration resulting from electrolytic aluminum dissolution was quantified in samples from the direct and alternating polarity experiments using Flame Absorption Spectrometry (Agilent 240FS AA) direct nitrous oxide-acetylene flame method (Baird, 2017). Prior to analysis, the samples were acidified with 67-70% nitric acid until a pH of less than two was reached and stored at room temperature. The volume of acid required for acidification varied with alkalinity of the sample and fell in the range between 0.7-2.0 μL/mL sample. Three replicates were taken of each sample with relative standard deviation (RSD) below 5. A linear calibration curve was fit using concentrations from 0 m/L Al to 200 mg/L. Finally, the electrodes were weighed for comparison to the initial weight to account for mass loss due to corrosion.

Table 4. Example sample nomenclature and description.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Sample ID Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPD1_0</td>
<td>Direct Polarity Day 1, t= 0 minutes</td>
</tr>
<tr>
<td>DPD2_30</td>
<td>Direct Polarity Day 2, t= 30 minutes</td>
</tr>
<tr>
<td>DPD6_90</td>
<td>Direct Polarity Day 6, t= 90 minutes</td>
</tr>
<tr>
<td>RPD1_0</td>
<td>Reverse Polarity Day 1, t= 0 minutes</td>
</tr>
<tr>
<td>RPD3_90</td>
<td>Reverse Polarity Day 3, t= 90 minutes</td>
</tr>
<tr>
<td>RPD4_120</td>
<td>Reverse Polarity Day 4, t= 120 minutes</td>
</tr>
</tbody>
</table>

The distribution and size of pits formed on the electrode surface were analyzed using a Keyence VR series One Shot 3-D Scanner Microscope. In the direct polarity experiments, the electrodes were labeled as anode and cathode and both the inner and outer sides were scanned (see
Figure 4 for electrode face labels). Since the electrodes in the reverse polarity experiments both functioned as an anode and cathode throughout the experiments, the electrode that was originally the anode was labeled as original anode and the remaining electrode as original cathode for analysis purposes. Both sides of the electrodes were scanned as well.

During scanning, all electrodes were divided into three sections of equal size to obtain an optimum resolution. After scanning, the images were processed using Keyence software to set the measurement reference area and exclude the area where the plates were perforated. A pitting location and size analysis was then performed with the software which summarized the data into an exportable table. The data in this table was collected to compare pitting in standard operating conditions (direct polarity) to reverse polarity conditions.
Chapter 4: Results and Discussion

4.1 Aluminum Concentration as a Function of Cumulative Plate Time

The aluminum concentrations at each batch time were also plotted as a function of cumulative plate time (Figure 8). In general, as expected, Figure 8 shows an increase in aluminum concentration with batch time in both sets of experiments, with the exception of the last day in the reverse polarity experiments, where the highest aluminum concentration was reached in 30 minutes. The 30-minute batch time and the 120-min batch time are highlighted in pink and red, triangles respectively, for both sets of experiments. As observed in the 120-min batch time in Figure 8, the aluminum concentration decreased rapidly in both experiments after only the first day of operation. Decreases in aluminum concentration over time at 120-min batch time were also observed from Day 2 to Day 3, and from Day 3 to Day 4 but at much slower rates than the previous days. After Day 4, the aluminum concentration seemed to level off, which could indicate that passive film formation was complete.

It is important to note that Day 4 is equivalent to 96 hours of plate operation time in the lab-scale system. If a system was operated in 30 min batches, this would equal 192 days of operation. Similarly, if it was operated as 120 min batches, this would equal 48 days of operation. Focusing on the 120-minute batches, this would mean that in a full-scale system, the electrodes would be fully covered in the passive layer after 48 days (Table 3), which is shorter than the time at which electrodes have been quoted to be replaced in EDF systems in India which is between 121 and 182 days or 4-6 months (Alfredo et al., 2018). However, while more aluminum is expected
in the longer duration batches, Figure 8 does indicate a more rapid decline in total aluminum over time for the longer batches.

The 30-min batch data points depicted by pink triangles in Figure 8, show that in general, the aluminum concentration decreases less quickly for this batch time in both the direct and reverse polarity cases. In the DP experiments, the concentration in the 30-minute batch increased after the first day, which was not observed for other batch times except for 15-minutes. After the second day, the Al concentration at 30 min batch time started to decrease, but at what appears to be a much slower rate than the 120-minute batch. On the other hand, on the RP experiments, the aluminum concentration decreased after Day 1 and then decreased with time until the last day. Similar to the DP experiments, aluminum concentration declines also occurred at a much slower rate for the 30-minute batch than the 120-minute batch.

As such, systems treating water for 30-minute batch times would have lower aluminum production but less decrease in aluminum production efficiency over time. This is important to consider when implementing to full-scale and could provide an advantage as less treatment time could be required per batch. However, this will depend on the coagulant dose needed and whether enough coagulant would be generated in 30-minutes.

In addition, it has been theorized that reversing the polarity has the potential to increase aluminum production as the switch in current could allow for displacement of the deposits on the passive film (Chow & Pham, 2021; Ingelsson et al., 2020). However, when aluminum concentration is compared between the first four days of the DP and RP experiments, a lower loss in aluminum within the same batch time data point, after each 24-hour period, is observed in the DP experiments (Figure 8). Again, in the conditions used in this research, reverse polarity does not present an advantage to standard operation.
4.2 Current as a Function of Cumulative Plate Time

The current at all batch times measured was also plotted as a function of the cumulative time for both sets of experiments (Figure 9). A decrease in the current with cumulative plate time was observed in both the direct (Figure 9A) and reverse (Figure 9B) polarity experiments. In the direct polarity experiments, with the exception of the first two days, the current was observed to increase consistently with batch time within the same day. However, the drop in current observed within the same day was less consistent in the reverse polarity experiments (Figure 9B). As demonstrated in Figures 8-9, both current density and aluminum production decrease as the plates age with time. A close relationship between aluminum and current density could serve as a helpful indicator of plate health for operators in rural areas where EC systems are used.
Figure 9. Current (A) as a function of cumulative plate time (hrs.) in A) direct polarity and B) reverse polarity experiments.

### 4.3 Aluminum Concentration as a Function of Current

The current was observed to drop over time during both the direct and reverse polarity experiments as the plates began pitting and accumulating a passive film. These drops in current were plotted against aluminum concentration (mg/L) to determine whether aluminum concentration decline corresponded to the observed current decline. The batch times selected for analysis included 30, 60, and 120 minutes for days 1-7 when polarity was not reversed and days 1-6 when polarity was reversed (Figures 10-11). These batch times were selected for analysis because these are the most common batch times used in rural India EDF systems (Alfredo et al., 2018). A linear regression analysis was performed, which resulted in $R^2$ values of 0.68, 0.976, and 0.992 for batch times of 30, 60, and 90 minutes, respectively for the experiments where polarity was not reversed.

Unlike the DP experiments, aluminum production was less consistent with current in the reverse polarity experiments as shown by the $R^2$ values (Figure 11). This could be due to the long
polarity reversal time implemented during this research, which might have resulted in accumulation of a passive film in both electrodes as they were switched between anode and cathode, which has been observed in other studies (Betancor-Abreu et al., 2019). In other words, the accumulation of the passive film on both electrodes could be preventing metal cations to pass through the metal when the current is applied. This is undesirable as it could also indicate loss of efficiency in coagulant production with the applied current.

![Graph showing aluminum concentration (mg/L) as a function of current (A).](image)

Figure 10. Direct polarity: Aluminum concentration (mg/L) as a function of current (A).

The close relationship between current and aluminum in the DP experiments could provide a promising performance indicator for operators of decentralized EC systems in rural India. The relationship between current and aluminum concentration could still be helpful in the RP experiments but would not be recommended as the relationship in the DP experiments is stronger. Even though the polarity reversal frequency as implemented in this study could be practically
implemented in the field, it might not present an advantage to maintaining constant polarity throughout the experiment.

![Graph showing aluminum concentration as a function of current (A).](image)

Figure 11. Reverse polarity: Aluminum concentration as a function of current (A).

### 4.4 pH as a Function of Cumulative Time

The pH at points next to the anode and cathode outer faces as a function cumulative time for the direct polarity experiments is shown in Figure 12. A larger change in pH in the areas next to the anode and cathode occurred from the first day to the third day of operation. After Day 3, the pH remained in the range between 8-10 for the anode and 7-8 for the cathode. If all conditions are kept constant, the trend in pH change is expected to follow the change in measured aluminum production between days according to Equations 2-4. This trend can be observed by comparing Figure 12 with Figure 8, where aluminum production efficiency decreases more rapidly during the first three days.
In addition, Figure 12 also demonstrates that the pH in solution did not always increase with batch time, as the batch times with the highest pH measured per day vary at both the anode and cathode sampling points. This same variation is observed in the reverse polarity experiments, even though the overall pattern in pH changes was different (Figure 13). For instance, in Figure 13A, pH changes much faster than in the direct polarity set in the first two days when polarity was reversed. Then, when polarity was reversed again on Day 3, aluminum concentration had decreased from Days 2 to Day 3 according to Figure 8, but there is an increase in pH in Day 3. This could indicate that additional reactions could occur when the polarity is reversed that could make changes in pH harder to predict. Additionally, the pH by the anode increased between days when the polarity was reversed to the original anode (Days 1, 3, and 5).

Figure 12. Direct polarity: pH changes by the A) anode and B) cathode as a function of cumulative time in direct polarity experiments.

It is also important to mention that the localized pH observed near the anode and cathode described in Figures 12 and 13 also suggests that adequate mixing of the solution is important to
the EC system design for minimization of these localized pH zones observed. While full-scale systems are often implemented without a mixing mechanism in place, this might not allow for adequate mixing of the coagulant in the solution as it is produced. This could also encourage additional reactions by the anode and cathode due to zones of very alkaline or acidic pH near the electrodes (Cañizares et al., 2005) which could encourage localized wear of the electrodes at those points.

Figure 13. Reverse polarity: pH by the A) anode and B) cathode as a function of cumulative time (hrs.) for both reverse polarity experiments.

4.5 Aluminum Concentration as a Function of pH by the Anode

The variation of aluminum concentration as a function of pH by the anode for the direct polarity experiments is shown in Figure 14. As mentioned earlier, even though the changes in pH follow a similar trend to the changes in aluminum concentration over time, at the batch time scale within the same experimental day, aluminum concentration increased with batch time duration, but the pH did not. Even though the pH appears to follow a linear trend with aluminum concentration with batch time, the variability in pH observed in these experiments would make it
difficult to use pH to predict aluminum concentration. As such, predicting aluminum concentration from measuring the pH would not be recommended.

![Graph showing aluminum concentration as a function of pH measurements by the anode in direct polarity experiments. Most of the aluminum concentration measurements fell in the range of 0-50 mg/L and most pH changes fell in the range of 8-10.](image)

Figure 14. Aluminum concentration as a function of pH measurements by the anode in direct polarity experiments. Most of the aluminum concentration measurements fell in the range of 0-50 mg/L and most pH changes fell in the range of 8-10.

Nevertheless, Figure 14 show that most of the aluminum concentration produced in these experiments was in the range of 0 to 50 mg/L and most of the pH was in the range of 8-10. Higher aluminum concentrations and pH changes corresponded to the longer batches for the first 1-3 days of operation. This is important to consider as keeping the pH in the range of 8-10 would be most beneficial to treatment, as pH changes above this level might require additional chemicals to adjust the pH of the solution after treatment, resulting in an increased cost to maintain the EC system. In addition, the high pH values observed in Figure 14 could cause chemical corrosion of the electrodes in addition to electrochemical corrosion, as dissolution of aluminum metals increases at alkaline pH levels (Jimenez et al., 2012).
4.6 Pitting Distribution Analysis

The pitting distribution, size, and volume analysis was conducted through both quantitative and qualitative methods. The quantitative analysis included comparing the weight of each electrode before and after the entire electrocoagulation period and a 3D surface scan of both sides of all plates for each electrode to analyze the total pit volume, average pit depth, and maximum pit depth. The electrodes with a higher pit volume loss should have released more aluminum into the solution and lost more mass. The magnitude of the pit depths can also provide information on how the current delivery method (direct or reverse polarity) impacts aluminum dissolution on the surface of the electrode. Uniformly distributed pits are preferred to localized pits for longer service life of the electrode material (Wellner et al., 2018).

Table 5. Electrode weight before and after electrocoagulation.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Weight Before EC (g)</th>
<th>Weight After EC (g)</th>
<th>Mass loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP Anode</td>
<td>44.9</td>
<td>40.8</td>
<td>9.1</td>
</tr>
<tr>
<td>DP Cathode</td>
<td>45.0</td>
<td>43.1</td>
<td>4.2</td>
</tr>
<tr>
<td>RP Original Anode</td>
<td>44.5</td>
<td>43.4</td>
<td>2.4</td>
</tr>
<tr>
<td>RP Original Cathode</td>
<td>45.1</td>
<td>44.8</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Analysis of Table 5 reveals that both electrodes in the direct polarity experiments experienced the highest percentage of mass loss when compared to the reverse polarity electrodes. This result follows trends in aluminum production discussed in previous sections, where higher aluminum production efficiency was observed when direct polarity was used, as this electrode experienced the highest loss in mass. In addition, the mass loss was higher for the electrode that
was the original anode than the original cathode in the reverse polarity experiments. As such more pitting is expected on the original anode on experiments with reverse polarity operation.

The qualitative analysis included evaluation of the surface of all electrodes in Figures 15-16 for comparison with Tables 5 and 6 and the construction of a corrosion/passivation timeline Figures 18-21). Using the labels established in Figure 4, the “outer face” of either plate refers to the outward face of the plate and the “inner face” is the one directly across and facing the opposite plate. In the direct polarity experiments, both faces of the anode had uniformly distributed pits on the surface. Nevertheless, the side of the anode facing the cathode (the inner face of the anode) (Figure 15A) appeared to have a higher quantity of pits than the other side that was facing the reactor (the outer face of the electrode) (Figure 15B). This could be due to the closer proximity of this side of the anode to the cathode, allowing for faster mass transfer and hydrogen evolution between the anode and cathode faces. In addition, the proximity of the electrodes could encourage pitting due to the pH changes taking place by the oppositely charged electrode.

Pitting was also observed on the cathode for the direct polarity experiments, but in a much lower quantity than in the anode which is consistent with Table 5. Due to accumulation of deposits on the pits in the inner face of the cathode (Figure 15C) and the formation of a black and white film on its outer face (Figure 15D), pits on the cathode were harder to analyze. These deposits were not removed after the plates were subjected to the nitric acid cleaning procedure several times. Previous studies have also observed the accumulation of deposits on the cathode, especially in solutions containing high alkalinity or carbonate ions (Fekete et al., 2016), however, the influence of sodium bicarbonate to passivation is not well known (Wellner et al., 2018). Dissolution of the cathode has also been reported and explained by chemical corrosion due to
exposure to an alkaline solution, as pH increases to more alkaline levels throughout EC operation (Fekete et al., 2016; Gu et al., 2009).

Conversely, pitting in the reverse polarity experiments appeared to be more localized and the pitting distribution was not the same on the two sides of the same electrode. Even though the outer the side of the original anode electrode (Figure 16B), appeared to have somewhat uniform pitting corrosion, the scanning analysis revealed corrosion was localized due to the appearance of deep localized pits (Table 6). Pitting on the inner face of the original anode was also localized and seemed to be inhibited by the formation of a thicker passive film that had accumulated on a few sites on the surface (Figure 16A). On the other hand, the electrode used as the original cathode exhibited more signs of corrosion on the side facing the anode (Figure 16C) than the side facing the reactor (Figure 16D). Similarly, a thicker passive layer accumulated on cathode side facing the anode, leading to localized corrosion. Nevertheless, the surface of the original anodic electrode seemed to have lost more mass, also consistent with the results from Table 5.

This discrepancy in pitting behavior between the direct polarity and reverse polarity experiments could suggest that when polarity is reversed, the passive layer is removed in some, but not all, areas of the surface when a polarity reversal time of 24 hours is used. This could be leading to localized corrosion in the areas where it is removed and further accumulation of a passive layer in the areas where it is not removed. In the literature, de-passivation by reversing polarity has been attributed to hydrogen evolution which dissolves this layer (Chow & Pham, 2021), but the mechanisms have not been well explained (Ingelsson et al., 2020).

In addition, the electrode that is used as the anode on the first day would show more uniform corrosion on the first day, which could make it susceptible to an accumulation of deposits on the pits when polarity is switched. This can be observed by looking at Figure 16A, which shows
that a thick passive layer remained on the electrode’s surface. Similarly, the electrode which is the original cathode will have formed a black oxide film on the first day that is difficult to dissolve when polarity is reversed to anode. Thus, the pitting volume in this electrode was lower.

The pitting volume loss was the highest in the direct polarity anode when compared to both electrodes used in the reverse polarity experiments (Figure 17). In the qualitative examination of the anode, it had been determined that one side was more corroded than the other, which is also confirmed in Table 6. In addition, a volume loss was also observed on the cathode in the direct polarity experiments, but to a much lower extent. Overall, the volume loss was still higher when direct polarity was used, which was expected based on the mass loss results, aluminum dissolution results, and the qualitative observations of the plates (Figure 17).

In a similar manner, observing the total pit volume on the reverse polarity experiment plates in Table 6 corroborates the results from Table 5 and Figures 15-16, that the original anode in the reverse polarity experiments experienced more pitting than the original cathode. In addition, in general, higher pitting depths were observed in the reverse polarity experiments which is consistent with localized corrosion. This would not be convenient in a full-scale system where reverse polarity was attempted at the same frequency and conditions used in this work, as it is likely that one electrode would stop producing sufficient aluminum before the other. Instead, using direct polarity would be expected to lead to a longer system service life. The total pitting volumes per electrode were plotted in Figure 17.

Results from the quantitative and qualitative pitting analysis suggest that pitting appears more uniform when direct polarity is implemented. On the other hand, pitting appears more localized when polarity is reversed every 24 hours. The more uniform corrosion in direct polarity operation, as well as the higher pitting volumes and lower drops in aluminum concentrations,
suggest that direct polarity operation was more efficient. This suggests that a greater surface area was available to react with the solution when polarity remained the same, as inhibition of the active surface was not deterred in the same manner by the formation of a thick localized passive film.

A corrosion timeline was constructed to qualitatively evaluate the progress in pitting and formation of the passive film after every batch and determine its efficiency as a performance indicator (Figures 18-21). Through visual evaluation it seemed that the passive layer was thicker when direct polarity was used and that the layer was dissolving when reverse polarity was used. While measuring the thickness of the passive layer was beyond the scope of this study, this observation was interesting because removal of the passive film required fewer cleaning cycles in the direct polarity anode than in both the electrodes used in reverse polarity, indicating the layer was more persistent in the latter. In addition, the pitting analysis showed a localized passive layer in the reverse polarity electrodes that was not visible before the nitric acid cleaning procedure. This is important because it suggests that the current use of visual inspection of the electrodes by operators in India might not be sufficient to determine aluminum production and service life.

The corrosion timeline for the DP experiments is shown in Figures 18-19. In Figure 18, even though the pictures of the electrodes correspond to the end of a 24-hour cycle, the aluminum concentrations shown were measured after each 120-min batch (the longest batch time). This was done to help visualize the aluminum decline in aluminum concentration after the electrodes had been worn out from the previous day. The passivation and pitting trends seemed to correspond to aluminum concentration during the first four days, however the same trends were not identified after the fifth day. For example, even though more pitting was observed on the electrode on Day 7, aluminum generation was similar to that of Day 5. The accumulation of different film was observed on the DP Cathode, but this did not vary much throughout the seven days (Figure 19).
For the RP experiments, since both electrodes served as anode and cathode for the same amount of time, the aluminum concentrations are shown in both Figures 20-21. Similar to the DP experiments, pitting in the RP Original Anode seemed to correspond to the decline in aluminum concentration until Day 4, as more pitting was observed on Day 6 even though the concentration measured in Day 4 was lower. On the other hand, the RP Original Cathode in Figure 21 did not show a lot of pitting and looked more similar in appearance to the cathode in the DP experiments. These results, together with the results from the weight loss and pitting analysis, suggest that the electrode that functioned as the anode initially in these experiments was favored for pitting and corrosion over the one that served as the cathode originally.

Figure 15. Aluminum plates after direct polarity electrocoagulation experiments and corrosion product cleaning procedure, including A) Anode inner face (side facing cathode), B) Anode outer face (side facing reactor), C) Cathode inner face (side facing anode), and D) Cathode outer face (side facing reactor).
Figure 16. Aluminum plates after reverse polarity electrocoagulation experiments and corrosion product cleaning procedure, including A) Anode inner face (side facing cathode), B) Anode outer face (side facing reactor), C) Cathode inner face (side facing reactor), and D) Cathode outer face (side facing anode).

Table 6. Total pit volume, average pit depth, and maximum pit depth on all electrode faces.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Total pit volume (mm³)</th>
<th>Average pit depth (µm)</th>
<th>Max. pit depth (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP Anode Side 1</td>
<td>90.4</td>
<td>-18.0</td>
<td>-39.2</td>
</tr>
<tr>
<td>DP Anode Side 2 (facing cathode)</td>
<td>230.0</td>
<td>-21.9</td>
<td>-38.9</td>
</tr>
<tr>
<td>DP Anode Total</td>
<td>320.4</td>
<td>-19.9</td>
<td>-39.1</td>
</tr>
<tr>
<td>DP Cathode Side 1</td>
<td>52.6</td>
<td>-2.7</td>
<td>-4.1</td>
</tr>
<tr>
<td>DP Cathode Total</td>
<td>83.7</td>
<td>-15.8</td>
<td>-19.2</td>
</tr>
<tr>
<td>DP Cathode Both Sides</td>
<td>136.4</td>
<td>-9.2</td>
<td>-11.7</td>
</tr>
<tr>
<td>RP Original Anode Side 1</td>
<td>58.5</td>
<td>-35.9</td>
<td>-61.3</td>
</tr>
<tr>
<td>RP Original Anode Side 2 (facing orig. cathode)</td>
<td>98.9</td>
<td>-10.8</td>
<td>-18.6</td>
</tr>
<tr>
<td>RP Anode Total</td>
<td>157.4</td>
<td>-23.3</td>
<td>-39.9</td>
</tr>
<tr>
<td>RP Cathode Side 1</td>
<td>76.1</td>
<td>-9.9</td>
<td>-16.6</td>
</tr>
<tr>
<td>RP Cathode Side 2 (facing orig. anode)</td>
<td>6.5</td>
<td>-54.2</td>
<td>-78.3</td>
</tr>
<tr>
<td>RP Cathode Total</td>
<td>82.7</td>
<td>-32.0</td>
<td>-47.4</td>
</tr>
</tbody>
</table>
Figure 17. Total pit volume loss per electrode (mm$^3$). The reverse polarity plates are labeled using the initial orientation (cathode v. anode) prior to the first polarity switch.

Figure 18. Corrosion timeline for anode outer face in direct polarity experiments after each day of operation. Concentrations are in Al mg/L at 120 min batch.
Figure 19. Corrosion timeline for outer cathode face in direct polarity experiments after each day of operation.

Figure 20. Corrosion timeline for original anode outer face in reverse polarity after each day of operation. Concentrations are in Al mg/L at 120 min batch.
Figure 21. Corrosion timeline for original cathode outer face in reverse polarity experiments after each day of operation. Concentrations are in Al mg/L at 120 min batch.
Chapter 5: Conclusions and Recommendations

5.1 Conclusions

The first objective of this research was to evaluate the relationship between aluminum, current density, and pitting trends on an electrocoagulation system when operated in direct polarity and reverse polarity modes. Previous studies in which the effect of reversing the polarity on EC system performance has been tested have obtained mixed results. One of these areas of disagreement is the optimum time period at which polarity should be reversed. These values typically range in the scale of seconds to minutes, which would not be possible to implement in a full-scale EC system requiring manual switching of the polarity applied to the plates. In this research, a longer polarity reversal frequency of 24 hours was evaluated. These 24 hours were equivalent to 12-24 days of operation assuming either a 60 min or 30 min batch reaction respectively. It was hypothesized that reversing the polarity would help improve aluminum production efficiency, current density, and pit distribution through dislodging of deposits on the passive film and equal utilization of both metals as sacrificial electrodes.

However, while aluminum concentration increased with batch time and declined more rapidly in the higher batch times during both sets of experiments, aluminum concentrations and current measurements were higher in the experiments where polarity remained constant. This suggested that operating the EC system at a polarity reversal frequency of 24 hours did not help reduce the formation of the passive film and rather was harmful to optimum system performance. However, it is important to note that in this research, aluminum dissolution was evaluated in a buffered matrix that did not include the presence of contaminants. This presents a limitation in this
research, as changes in electrolyte composition are known to affect the rate of accumulation and dissolution of the passive film during electrocoagulation.

The distribution and size of pits were also measured and compared to aluminum concentration in both experiments as part of the first objective. It was determined that both sides of the anode in the direct polarity experiments exhibited more uniformly distributed corrosion than in the reverse polarity experiments. On the other hand, the results from the pitting analysis in the reverse polarity experiments showed that pitting was more localized. It was noted that the passive film accumulated on random areas on inner faces of the electrodes in the RP experiments. This suggested that some of the deposits may have been dislodged when polarity was switched, resulting in localized pitting on the sites where dislodging had occurred. In general, the largest average size of pits corresponded to the reverse polarity electrodes than the direct polarity electrodes, supporting that a localized pitting attack had occurred.

The second objective included the evaluation of two parameters, current and a corrosion timeline, as performance indicators in decentralized EC systems. First, a close relationship identified between the applied current and aluminum production over the long timescale tested in this research. The linear regression analysis for the direct polarity operation suggests current is a promising indicator that could be used to measure performance of decentralized electrocoagulation systems in the field. While a relationship was also identified between current and aluminum when polarity was reversed, this relationship was not as strong. Therefore, the use of direct polarity would be recommended for full-scale systems to help operators determine system performance based on current measurements. It is important to reiterate that the absence of contaminants, such as fluoride, also presents a limitation to this conclusion as the relationship between current and
aluminum could be influenced through additional complexation or adsorption reactions that occur when a contaminant is present.

The general corrosion timeline required analysis of the pitting and passivation patterns throughout operation (t= 168 hrs. for direct polarity, t= 144 hrs. for reverse polarity). It was hypothesized that visual observation of the surface of the electrodes over time would correspond to trends in the measured aluminum concentrations, current density, and pitting volumes. After each 24-hour batch, fouling and pitting on the surface of electrodes did not always correspond to periods of high and low aluminum dissolution. As such, the current visual examination of electrodes used during EC in the context of the corrosion timeline would not be recommended as a parameter to measure performance in the field under the experimental conditions in this research.

An additional parameter, the pH of the solution by the anode and cathode was also measured as an additional performance parameter to relate to the chemical and electrochemical corrosion observed in this research. The results in the direct polarity experiments indicated that changes in pH were greater during the first two days of operation when the pH reached more acidic and alkaline levels. On the anodic side, it was found that while changes in pH decreased over time with a new batch as aluminum production dropped, pH changes in the same batch did not always increase linearly with time. Similarly, on the cathodic side, while the pH appeared to stabilize quicker with new batches, pH within a single batch varied with time.

Unlike the direct polarity experiments, the reverse polarity experiments did not experience pH decreases by the anode at the start of a new batch. Instead, pH increased when polarity was switched back to the original anode. The pH measured by the cathode did not vary in the same manner. Due to the variation in pH within every batch for both direct and reverse polarity experiments, it was determined that solution pH would not be a good indicator of aluminum
production. Nevertheless, observing the trends in pH change can provide an opportunity to optimize system performance by ensuring the range is optimum for production of aluminum hydroxide precipitates and reducing the need for additional chemicals for pH adjustments.

In summary, this research identified that the use of direct polarity would be more beneficial than the use of reverse polarity at a frequency of 24 hours based on higher aluminum production and current densities, as well as more uniformly distributed pitting trends. The use of direct polarity is also beneficial due to the positive relationship recorded between aluminum and applied current, which has potential to serve as an indicator for operators to evaluate system performance. The corrosion timeline presented also appeared more consistent in the direct polarity experiments, thus providing a more accurate reference to performance. It is possible that testing reverse polarity at much shorter frequencies would yield different results, but evaluation of an optimum polarity reversal time that considers removal of the passive layer as well as practicality would be required for application rural settings.

5.2 Recommendations

Based on the results and limitations from this research, future research should attempt to implement polarity reversal at a shorter polarity reversal frequency than the one used in this study. An optimum polarity reversal frequency must both efficiently improve performance through removal of the passive film and be realistic to implement in full-scale settings such as the EDF plants in India. In the design of future electrocoagulation systems, the use of AC current could also be evaluated as an alternative to RP.

In addition, further research should include the addition of a water matrix with a composition that is similar to that found in the areas of rural India where electrocoagulation is implemented. This would allow for the evaluation of the same parameters of aluminum
concentration, current, and pitting patterns in the presence of other ions such as fluoride. The current and corrosion timeline indicators could then be re-evaluated as viable performance indicators. Further research should especially pay close attention to the corrosion timeline as visual observations are a common method used by operators when replacing electrodes in EDF systems.

Finally, convection of the reactor could be improved to reduce localized pH measured by the anode and cathode. Improving convection of the reactor could help reduce chemical corrosion due to local acidic and alkaline pH and improve interactions between aluminum cations and metal hydroxides. Improved convection could be achieved through recirculation of the solution or a more rapid mixing mechanism than the one used in this research.
References


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Tom Slaymaker <tslaymaker@unicef.org>
To: Monica Castro Carías <info@washdata.org>

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Tom

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MF, Francesco <mitsil@who.int>
To: Monica Castro Carías

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Francesco