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Understanding the Leaching Mechanism for Lead (Pb) Found in Components of Locally Manufactured Handpumps in Eastern Madagascar

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Understanding the Leaching Mechanism for Lead (Pb) Found in Components of Locally Manufactured Handpumps in Eastern Madagascar

by

Nidhi Shah

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Environmental Engineering
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Keywords: Sustainable Development Goals, Self-Supply, Drinking Water, Adsorption, Surface Complexation

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Dedication

To everyone who dares to dream and their parents who support them

To my brother, Pranay
Acknowledgments

This opportunity has laid a foundation to prepare myself for future endeavors. This was possible only because of Dr. James Mihelcic. His constant support, encouragement, and guidance through each step has helped me complete my thesis successfully. He has helped me learn everything from being a novice to reach all the way here. I would like to thank Dr. Katherine Alfredo for her time and efforts while I took class with her as well as for her inputs to solve my doubts during my thesis. I would like to thank Dr. Jeffrey Cunningham for giving suggestions and crucial feedbacks for my thesis. I would like to thank Dr. Abla Zayed for guiding me through the analytical techniques used for this research.

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Abstract

This research sought to determine the lead leaching mechanism impacted by an inorganic scale observed from lead valve weights of the pitcher pump systems used in Tamatave, Madagascar. Based on previous research, these valve weights are considered to be a major source for high lead levels in pump water consumed by the residents. As a part of the study, Raman Spectroscopy, X-ray Fluorescence Spectroscopy (XRF) and Energy Dispersive Spectroscopy with Scanning Electron Microscope (SEM-EDS) were performed to address the objectives of this research. The pump component samples for the analysis were selected based on the amount and visual characteristics of the scale seen on the valve weights. The scale was identified to be hematite ($\alpha$-Fe$_2$O$_3$) and base (uncoated valve weights referred as base) was identified to be lead base mineral, Matlockite (PbClF) by Raman analysis. However, Raman analysis did not seem completely accurate and consistent with the results from other two techniques; XRF and SEM-EDS analysis. The XRF results reported lead and iron to primary elements with its limitation to not detect elements with atomic number below 12. The scale was found to be uneven and thickness of the scale ranged between 35 – 410 μm as analyzed by SEM analysis. The major elements reported in the scale by SEM-EDS analysis were iron, lead, oxygen, and carbon. The lead concentration in the scale by SEM-EDS analysis was reported to range between 4 – 25% with restriction to measure up to the depth of 3 μm which less than XRF penetration depth to detect elements. The lead compound found in the scale was estimated to be in the form of hydrocerussite [Pb$_3$(CO$_3$)$_2$(OH)$_2$] and lead carbonate (PbCO$_3$) from examination of lead solubility diagram. Furthermore, based on the literature review, possibilities of lead adsorption due to surface complexation with hydroxyl
groups present on the scale was estimated to support the presence of lead range (4-25%) detected in the scale by SEM-EDS analysis. This research developed possible explanations for lead adsorption and complexation which can further be confirmed through XRD and ICP-MS analysis and specific complexation modeling. Furthermore, the ability to study the scale at greater depth than 3 μm could confirm the variation in lead concentration observed in the scale.
Chapter 1: Introduction

1.1: Background and Motivation

Madagascar is known to face many challenges related to the equitable provision of safe water. This is important because globally it is estimated that 782,000 annual diarrheal deaths are attributed to inadequate drinking water and sanitation (Prüss-Ustün et al., 2014). As recorded, Madagascar is ranked 3rd in the world for the worst consumable water quality (WHO, 2012). In addition, the United States Agency for International Development (USAID) reported that more than 58% people in Madagascar do not have access to an improved water source (Water, 2020). The rural and peri-urban areas of Madagascar are in fact reported to have least access to improved water sources in comparison to other Sub-Saharan African countries during the period of 2010 - 2015 (Armah et al., 2018).

To overcome the lack of improved water, many rural and peri-urban residents in Madagascar have adopted the self-supply approach to ensure access to water. Self-supply is defined as a method where the user can decide all the aspects of technology to supply water, such as the type of technology, provider of the technology, and required service level (Sutton, 2009). This approach is basically a self-investment for users without any substantial control by the government and is preferred by low-income communities (Butterworth et al., 2013; Sutton, 2009). Examples of self-supply in this context include rainwater harvesting, household dug wells, and hand pumps. Tamatave, a city located on the east coast of Madagascar is estimated to have 170,000 people actively using locally manufactured household pump systems to obtain shallow groundwater (Akers et al., 2015; MacCarthy et al., 2013). In this context, a household pitcher pump
system consists of manual suction pump that contains two check valves in order to procure water from shallow groundwater up to the water lifting limit of 9 to 9.4 meters (Marshall, 2017).

Unfortunately, locally manufactured pitcher pump systems in Tamatave contain lead (Pb) components which has been show to lead to unsafe concentrations of lead in the water. In fact, a study carried out by Akers et al. (2015) on the household pitcher pump systems in Tamatave detected lead concentrations in the water obtained via pitcher pump to be greater than 10 μg/L; which is the drinking water guideline issued by the World Health Organization (WHO) (Barnako, 1972).

In that study, anodic stripping voltammetry was utilized to measure the dissolved lead (particulate lead was not considered significant here because of the slow flow rate and absence of piped distribution system) in water samples collected from pitcher pumps (Akers et al., 2015). Eighteen household pumps were monitored over three different campaigns and water samples from these pumps were collected for both “first draw” (a condition where the pump has been inactive for more than 1 hour) and “flushed” conditions. A statistically significant relationship was only obtained between lead concentration and contact time (i.e. “first draw” and “flushed” condition) (Akers et al., 2015). The water samples obtained from the “first draw” conditions under three different campaign resulted in more than 60% of water samples exceeding a lead concentration of 10 μg/L with a median lead concentration of 13 μg/L. The results from the “flushed” conditions showed significant reduction in the lead concentration of the water, where 35% of water samples exceeded 10 μg/L with a median lead concentration of 9 μg/L.

The pump water was also estimated to result in elevated blood lead levels (BLL) of children utilizing water obtained from the pitcher pump system. The Internal Exposure Uptake Biokinetic Model for Lead in Children (IEUBK model) (EPA, 2006) was applied to this location. The results
showed that 15 to 70% of the children in Tamatave city had risks of elevated BLL (i.e., greater than 5 μg/dL (Brown & Margolis, 2012). To reduce the lead leaching in the water, two pumps out of the eighteen pumps under observation, had their leaded check valve components replaced with the iron components. This intervention resulted in a decrease in the lead concentration in the water samples; around 57 – 89% reduction of the lead concentration in the first pump and 89-96% reduction of the lead concentration in the second pump (Akers et al., 2015).

After, University of South Florida faculty and students observed the construction of one of the pitcher pumps where it was noticed that lead car batteries were melted over a charcoal fire and molded into lead components that became part of the check valves (foot and piston) found in the pitcher pump system. The significant reduction in the lead concentration due to the replacement of the lead components (i.e., the piston and foot valves) in the pitcher pump system led to a 2018 remediation project supported by the University of South Florida and Water Charities with a goal to replace the lead components in the 500 pumps (in actuality, 504 pumps were remediated). In addition, surveys and training sessions were conducted for the pump owners and manufacturers to make them aware of the benefits of replacing the lead components of the pump with iron. Besides measuring the lead concentration in the pump water before and after the intervention took place, detailed water quality analysis was performed on 30 water samples to understand the influence of groundwater and infrastructure properties on lead concentrations (Usowicz, 2019).

After remediation took place, 98% of the 504 pumps showed the lead concentration below the WHO guideline of 10 μg/L and 95% of the remediated pumps showed the lead concentration ≤ 5 μg/L (Usowicz, 2019). During the study there was also an observation of an unknown inorganic coating on the lead components of the pitcher pumps. Accordingly, it was hypothesized that the presence of this coating would impact the lead concentrations in the pump water. Statistical
analysis of the data obtained from Usowicz (2019) suggested the lead concentration in the water obtained from the pitcher pumps was related to the alkalinity of the water and the surface area of the unknown coating found on the check valves (i.e., piston and foot valves). This statistical analysis showed the measured lead concentration in the pump water decreased with an increase in the alkalinity and coated surface area on the check in both first draw and flushed conditions (Usowicz, 2019). The inorganic coating may adsorb the lead or simply serve as a barrier between the water phase and the pure lead components of the pitcher pump systems.

Understanding the mechanism of how the inorganic coating impacts lead leaching may provide opportunities to reduce the risk associated with the lead exposure from the pitcher pump water and potentially help to identify locations where pitcher pump water is less likely to have lead concentrations that exceed WHO lead concentration guidelines. Accordingly, the overall goal of this project is to provide insight on the fundamental mechanism by which the inorganic coating influences the lead concentrations in the pitcher pump water utilized in Eastern Madagascar.

This research is important because for centuries lead has been known to be ubiquitous in commerce and exposure to humans is known to result in severe health effects (Rosen et al., 2020; Tong et al., 2000). Historically, lead was found in manufactured products, water pipes with iron solder, cosmetics, medicine, and certain sources of food and soil (Dignam et al., 2019). The WHO had identified sources of lead exposure in Sub-Saharan Africa and this lead exposure can result in severe neurotoxicity, organ impairment, and adversely affect the behavioral development of the children (Edwards, 2014; Kordas et al., 2018). An effective strategy to reduce the lead exposure is to control and then reduce its sources (Dignam et al., 2019). The Lead Copper Rule (LCR) introduced in 1991 by the Environmental Protection Agency (EPA) has achieved reduction in lead concentration in drinking water consumed in the U.S. (EPA, 2016). Residential homes constructed
before 1970s mostly had lead pipes and leaded solder that have been replaced over time under this EPA regulation. However, even with this regulation in effect there has been several cases of large-scale lead poisoning in U.S. municipal water systems such as Washington D.C water crisis in 2001 (Renner, 2004) and Flint water crisis in 2014 (Pieper et al., 2018; Zahran et al., 2017). Ironically, most of the population of developing countries are not aware of the many uses and health consequences of lead exposure (Kordas et al., 2018). As reported by UNICEF and Pure Earth report, one in three children in the world is reported to have BLL more than 5 μg/dL (Rees & Fuller, 2020). Many people in these countries continue to utilize lead for a variety of activities including the previously mentioned construction of water supply systems like pitcher pumps (Kordas et al., 2018). The easy availability of lead, its malleable properties, and low cost makes lead a primary choice for many people in developing countries without comprehending the long-term adverse effects on children and adults (Chowdhury et al., 2016).

1.2: Research Objectives

Based on the data available from previous research conducted by University of South Florida faculty and students, the following objectives were developed to be addressed as a part of this thesis in order to determine the lead leaching mechanism of the pitcher pump systems.

1. To determine the chemical composition of the base area of the valve weights used in the pump.
2. To determine the chemical composition of the scale area observed on the valve weights used in the pump.
3. To determine the presence of lead in the scale observed on the valve weights used in the pump.
4. To determine the thickness of the scale observed on the valve weights used in the pump.
To determine possible interaction between the elements in the surface of the scale observed on the valve weights.
Chapter 2: Literature Review

2.1: Health Concerns Caused by Lead in Drinking Water

Amongst common chemical contaminants found in drinking water, lead is considered to have long lasting impairments (Rees & Fuller, 2020). Lead has been utilized by humans since 3000 B.C and is considered one of the earliest metals. In 1800s lead was only used in plumbing and today in modern age, lead is introduced into a variety of products such as gasoline, paint, aviation fuel, and solder and also its pollution is identified with mining and metal smelting (Jean Brown et al., 2011; Rees & Fuller, 2020). With increasing usage, there are several routes of lead exposure to humans. Common known routes of exposure are through oral and nasal route from food, drinking water, and breathing air (Rees & Fuller, 2020). Lead exposure through drinking water is common in developed countries and low-income countries (LICs) (Attina & Trasande, 2013; Kordas et al., 2018). This is because lead is present in parts of the material used for some water pipelines and plumbing fixtures (Kordas et al., 2018).

The presence of lead in human bodies has toxic and permanent effects (Edwards, 2014). It primarily affects the cognitive capacity and neurological defects of children depending on blood lead level (BLL) (Caravanos et al., 2013). Women with high lead exposure will experience impairment of reproductive organs (Edwards, 2014). Almost 90% children from developing countries are reported to show BLL greater than 5 µg/dL (Gidlow, 2015; Rees & Fuller, 2020). In Asian countries like India, Indonesia, and Philippines lead is major toxic element found in soil and water. These locations are reported to have children with BLLs greater than 10 µg/dL (Dignam, et al., 2019; Rees & Fuller, 2020). Peru and Mexico are known for its smelting activities and
witnessed environmental and ecological hazards due to lead in soil which is affecting the BLL of children and women living in the nearby regions (Calzada et al., 2017). Asia and Africa have shown lead toxicity to be a major health concern amongst people living in rural as well as urban areas for decades (Chowdhury et al., 2016; Dignam, et al., 2019).

Figure 1: Health Concerns Related to Different BLL (Tong et al., 2000)\(^1\).

Figure 1 provides a general overview of different BLL and related human health impairments. In developing countries people rely on community-supply, self-supply, or household water treatments to obtain potable water (Harvey & Reed, 2007; Rosa & Clasen, 2010; Smits & Sutton, 2012). These water systems do not guarantee contamination free water. These systems have their own socio-economic impacts depending on the geography, distance to travel to obtain required water, class of gender putting majority of efforts on daily basis, employment and awareness about improved drinking water (Attina & Trasande, 2013; Grönwall & Danert, 2020; Whittington et al., 2009).

In a developed country like the United States (U.S.), lead exposure was noticed back in 1970s and since then constant efforts were executed to reduce lead exposure. Prior to 1970s in the U.S., around 74% of adults and 88% of children below the age of 5 recorded to have BLL 10 µg/dL or more (Cornwell et al., 2016; Dignam et al., 2019). This was alarming which led to federal regulations and public health activities to ardently spread awareness about the lead exposure. With constant efforts, the U.S. reported 93% reduction in BLL for the overall population during the span of 1970 to 2016 (Dignam et al., 2019). In 1970, the U.S. created the Occupational Safety and Health Administration (OSHA) in order to control the lead exposure through mining and smelting activities, construction work including renovation and lead paints, and manufacturing companies (Dignam et al., 2019; Huang., 2019). The U.S. Environmental Protection Agency (EPA), defines the limit to lead concentration in water under Safe Drinking Water Act (SDWA) passed in 1974 (EPA, 2016). Under Lead Copper Rule (LCR), regulation to control lead release from pipes and service lines were modified. This includes water utilities all over U.S. to comply with EPA’s decided lead concentration i.e. lead action level of 15 µg/L (California Water Boards, 2018;
Dignam et al., 2019; EPA, 2016). Despite well-structured plan to reduce lead exposure via water by EPA, houses in U.S. still experience adverse levels of lead in drinking water.

2.2: Guidelines by EPA, WHO, and CDC for Lead in Drinking Water

In this modern era, access to safe and improved water, sanitation, and hygiene (WaSH) is recognized as a bare minimum requirement for human needs (Gizaw & Worku, 2019; McMichael, 2019). Yet, many developing countries are not yet successful to provide basic WaSH services, especially in rural areas. The United Nations (UN) initiated the Millennium Development Goals (MDGs) in 2000 followed by Sustainable Development Goals (SDGs) that resolved to solve multiple global problems related to human rights and healthy life (Johnston, 2016; Pizzi et al., 2020; United Nations, 2015). Goal 6 of the SDGs focuses on providing clean water and improved hygiene and sanitation (Johnston, 2016; United Nations, 2015). Today, more than 90% people have access to improved drinking water. (WHO/UNICEF, 2015; WHO and UNICEF, 2017).

Safe drinking water is defined based on the quality of water consumed by the group of people in particular region or community. In the U.S., limits for drinking water contaminants (chemical & microbiological) are determined by the EPA (Dignam et al., 2019; EPA, 2016). Under the Safe Drinking Water Act (SDWA), EPA has defined standards for water quality to be followed by all nation-wide water systems (SDWA, 2000). The U.S. population now experiences a majority of lead exposure through drinking water sources affecting infants as well as adults. The control of lead exposure through drinking water, was enhanced under Lead Copper Rule (LCR) (Cornwell et al., 2016; EPA, 2016). Under the LCR, the EPA set strict rules for water distribution system to promote replacement of lead service lines (LSLs) with a priority for houses built before 1980s (Cornwell et al., 2016; EPA, 2016). One of the recent modifications of LCR, aims to reduce lead exposure to children at schools and child care facilities (EPA, 2016).
The water utilities are responsible to control lead levels in tap water due to corrosion and provide necessary remedies including water treatment and corrosion control. However, it is important to know that water utilities are responsible to control corrosion within water system and are not responsible to provide lead service line replacement that are located on personal property. One of the effective corrosion control methods actively used is treating the utility water with addition of orthophosphate (Cornwell et al., 2016; Dignam et al., 2019). The old houses have most of their water pipelines, faucets, fixtures, solders and other plumbing materials made up of primarily lead or copper or mixture of lead, copper, brass, and zinc (AWWA, 2014). Lead corrosion in these old plumbing systems may be responsible for high lead levels reported in drinking water distributed in U.S. houses. Even after continuous efforts for three decades, more than 6 million U.S. houses require lead service-lines replacement and on average 500,000 infants are recorded to suffer from impairments due to lead exposure (AWWA, 2014; Cornwell et al., 2016).

With a combined effort from EPA, WHO, and CDC constant progress is made to control lead exposure through drinking water in the U.S. and other parts of the world. Table 1 summarizes the regulations and guidelines from these three organizations.

<table>
<thead>
<tr>
<th>EPA</th>
<th>WHO</th>
<th>CDC</th>
</tr>
</thead>
<tbody>
<tr>
<td>• The action level recommended by EPA is 0.015 mg/L and MCLG is 0.00 mg/L (or ppm) due to toxicity causing harmful health effects ranging from stomach disorder to brain impairment.</td>
<td>• The latest WHO acceptable lead in water limit is 0.01 mg/liter as mentioned in drinking water guidelines published in 1993.</td>
<td>• The Centers for Disease Control and Prevention (CDC) follows the EPA guidelines for lead limits owing to lead’s impact on infant, children as well as adults.</td>
</tr>
<tr>
<td>• EPA introduced Lead Copper Rule (LCR) in 1991 under the Clean Water Act (CWA) with a goal to control lead level in US potable water. Lead regulation is also carried out under Safe Drinking Water Act (SDWA) in 1986.</td>
<td>• Lead leaching mainly occurs because of plumbing systems, fittings and connections. It is also affected by temperature, pH, dissolved oxygen, water standing time, acidity of water.</td>
<td>• In 2012, 5 μg/dL was decided as acceptable Blood Lead Level (BLL) for reference to understand the severity of lead exposure affecting the IQ, memory and other neurological disorders.</td>
</tr>
<tr>
<td>• Under the LCR by EPA, four requirements need to be under control to maintain lead level. They are as follows – A) Optimization of Treatment system to control corrosion. B) Check tap water lead levels in houses that has lead service lines or lead parts in plumbing system. C) Removing the source water due to significant lead levels. D) Incase of exceeding the EPA action level for lead, spread awareness amongst the customer and suggest plans to reduce their lead exposure.</td>
<td>• New homes having solder connections with copper would have high level of lead in water.</td>
<td>• National Health and Nutrition Examination Survey (NHANES) decided the reference value based on the survey result of blood lead in children in US. The CDC will check this survey result every four years.</td>
</tr>
<tr>
<td>• Suppliers will need to take actions to replace the parts of plumbing systems to control lead exposure in area exceeding the lead action level.</td>
<td>• Corrosion control is recommended using the lime and adjusting the pH to be between 8 to 9.</td>
<td>• In adults, BLL greater than 40 μg/dL shows higher chances of cardiac disorder, cancer and higher mortality.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• CDC claims lead exposure can cause neurological damage, reduced overall development, behavioral disorders, as well as chances of speech and listening impairments in children.</td>
</tr>
</tbody>
</table>
2.3: Self-Supply Systems in Madagascar

Self-supply water systems are preferred in areas where public water systems or government organizations are unable to provide drinking water services (Foster et al., 2020). Even though the majority of self-supply systems are preferred by people in developing countries, it is observed to also be used in rural areas of developed countries like the U.S. (Sutton, 2009). In rural areas of low-and middle-income countries such as India, Madagascar, Zimbabwe, and Ethiopia there has been constant difficulty faced by communities to obtain safe drinking water for their daily needs (Butterworth et al., 2013; Sutton, 2009). It is observed that African countries are increasingly facing difficulty to obtain safe water to meet their daily needs (WHO & UNICEF, 2017). These communities thus resort to suitable self-supply water systems. Examples of self-supply water systems are hand dug wells, drilled and manual wells, boreholes, rope and pitcher pumps, and tube wells, in-house treatments like biosand filters, filtration and disinfection as well as rainwater harvesting (Sutton, 2010; Sutton et al., 2004). Furthermore, it is estimated that more than 2 billion people depend on self-supply systems and groundwater to obtain safe water (Grönwall & Danert, 2020).

Few reasons for communities and households not being able to obtain sufficient and safe water required for multiple purposes are due to low income, lack of government support, high cost from private suppliers, unavailability of water and supply sources, community remoteness, and lack of management (MacCarthy et al., 2013; Sutton, 2009). Therefore, a self-supply approach has been recognized as a method that can improve their water services and not suffer from unavailability of potable water (Chávez García Silva et al., 2020; Smits & Sutton, 2012). Self-supply is defined as a user oriented, improvised, customized method, where a user primarily plans and invests in technologies to obtain water that can serve his multiple needs (Sutton et al., 2004).
It usually implies a low-cost technology without involvement of government or private sectors (though more expensive technologies such as solar powered pump could be characterized under self-supply) (Butterworth et al., 2013; MacCarthy et al., 2013; Sutton, 2009). One major drawback of self-supply systems is a higher risk of contaminants in the source water and susceptibility to waterborne diseases (Sutton, 2010; Smits & Sutton, 2015; Sutton et al., 2004).

Different countries in Sub-Saharan Africa have been using the low-cost self-supply technologies for decades to meet their requirements for water and sanitation due to above mentioned reasons (MacCarthy et al., 2013; Rosa & Clasen, 2010). A pitcher pump is an example of a water lifting technology used for self-supply. Madagascar for example, is known for its adaptation of pitcher pump systems for several decades. With a population of more than 20 million, there is constant lack of administration to arrange provision for potable water (Annis & Razafinjato, 2012; MacCarthy et al., 2013; Ram et al., 2007). The city of Tamatave (Madagascar) which is the focus of this research, is known for its local pitcher pump manufacturing industry. Malagasies residing in Tamatave rely on these pitcher pumps to meet their daily potable water requirements (Akers et al., 2015; MacCarthy et al., 2013). The low cost and local availability of pitcher pump systems contributes towards existence of the industry (MacCarthy et al., 2013). The price of these pitcher pumps can be as low as $35 and as high as $100, depending on the requirements of every owner (MacCarthy et al., 2013). Figure 2 shows detailed construction of pitcher pump system used in Madagascar. The components of the pitcher pump system (as mentioned in Akers et al, 2015) includes a piston and foot valve, a primary source of lead contamination. The piston and foot valve are made from a piece of leather and lead obtained from old lead acid car batteries. (Akers et al., 2015). The secondary source of lead contamination is the brass well screen which is soldered using lead-tin solder. The pitcher pump is manually attached
to the rising main. The rising main is connected to the well screen. The well screen, through manually boring, sits below the ground surface at an average depth of 12 meters to be able to connect to groundwater level (Marshall, 2017). The use of lead containing components in the pitcher pumps have increased the chances of lead exposure above WHO guidelines (Akers et al., 2015; MacCarthy et al., 2013).

Figure 2: Construction of Pitcher Pump System and Possible Location of Lead Components (Akers et al, 2015)\(^2\). The figure shows four locations for lead components; a) piston valve, b) foot valve, c) brass well screen, and d) lead-tin solder along the screen.

2.4: Lead Release from Water Pipes and Water Supply Components

The harmful effects of lead leaching from water pipes and plumbing components such as plumbing fittings, fixtures, faucets, and solders were noticed in U.S. during 1970s. By 1986 in the U.S., production and use of lead pipes in water distribution systems was banned and by 1991 replacement of lead pipelines was introduced as a remediation measure under the LCR (AWWA, 2011; Ng et al., 2018). Since 1991, continuous reforms have been made in the LCR to expedite replacement of lead pipelines to reduce the lead exposure from drinking water. The public water utilities did not have lead contamination issue in their main water distribution system. The lead leaching problem however persists primarily through the service-lines and pipe connections present in the private areas of consumers and communities that deliver water to them (Edwards & McNeill, 2002; Hosseinibalajadeh, 2018; Ng et al., 2018).

Water pipe and associated components are produced using metals such as copper, steel, iron, and galvanized metal as a substitute to lead pipes with limited use of lead because of its properties. Lead being adaptable and malleable, was historically added to water pipes at levels up to 8% by weight (EPA, 2016). Later, due to health implications related to lead in the drinking water, this allowance was reduced to 0.25% in 2011 under SDWA guidance by EPA (EPA, 2016; Levin, 2014).

Lead release from the lead pipes or lead alloys occurs primarily through the process of corrosion when in contact with water (Kim & Herrera, 2010). Corrosion is defined as an electrochemical or chemical process that occurs when any metal or metal surface comes in contact with water or its surrounding environment (Beccaria et al., 1982). It is a natural process that occurs to convert the metals into a more stable state. Different metals in contact with each other that undergo corrosion is referred to as galvanic corrosion. Metals have range of corrosive resistance.
but in theory, all metals are susceptible to corrosion. The amount of corrosion is characterized by factors like acidity of water, temperature, pressure, pH, total alkalinity, contact time with water, flow rate in the pipelines, and the concentration of dissolved oxygen and carbon dioxide (Schock, 1989, 2018). To control corrosion, water utilities strategize to add corrosion control chemicals or corrosion inhibitors in the distribution system (Pieper et al., 2017, 2018). Another approach is to galvanize the pipes and plumbing materials with a metal more reactive than the material used for manufacturing pipes and plumbing materials. The most commonly used corrosion inhibitor is orthophosphate (H$_2$PO$_4^-$, HPO$_4^{2-}$, and PO$_4^{3-}$) (Ng et al., 2018; Wasserstrom et al., 2017). In fact, the use of orthophosphate in public water treatment increased by 10 times between 1994 to 2001. It is reported that orthophosphate is also effective in reducing lead release from aged pipe. (Cartier et al., 2012; Pieper et al., 2017). Though, the use of orthophosphate is only useful to control the release of soluble lead and not total lead (i.e., soluble and particulate lead) (Edwards & McNeill, 2002). Furthermore, a study has shown elevated lead release while using orthophosphate in new pipes because of a high concentration of chloride and reduced alkalinity in the treated water (Wasserstrom et al., 2017; Willison & Boyer, 2012).

Lead being impacted by corrosion forms compounds such as lead oxides (PbO), lead dioxides (PbO$_2$), lead hydroxycarbonates [Pb(HCO$_3$)$_2$], lead carbonates (PbCO$_3$), and lead hydroxyphosphates (PbHPO$_4$), (Edward, 2004; Santucci & Scully, 2020). Apart from corrosion control additives and corrosion inhibitors, formation of a passivating layer has shown reduction in lead release in water. The process of passivation protects the pipe surfaces from exposure to water creating a barrier to oxidation and thus in turn prevents corrosion of pipelines and plumbing materials. Though, disruption of this layer can however result in high lead release in water (Edwards & McNeill, 2002; McNeill & Edwards, 2001).
2.4.1: Impact of Lead Release in Drinking Water in U.S.

Under the SDWA and LCR, the EPA has consistently taken steps to maintain standards of drinking water at public water utilities keeping public health in mind. Despite this, the U.S. has experienced state of emergency in cities like Flint, and Washington D.C. Furthermore, cities like Chicago, Newark, Durham, Greenville, and Pittsburgh have reported high lead levels in their drinking water over short span of time (Edwards et al., 2009; Pieper et al., 2018).

The Flint (MI) water crisis revolved around absence of corrosion control chemical (i.e., orthophosphate) which caused lead concentrations in the public water supply to reach hazardous levels. This started in 2014 when the city of Flint moved their water source from the Detroit Water System to the Karegnondi Water System (Pieper et al., 2017, 2018). In this transfer process, the city’s water source was changed to local Flint river water. Residents immediately noticed a change in water color, taste, and odor after the change in source water. Flint river water was unstable and corrosive by nature (Pieper et al., 2018) and officials opted to not add a corrosion inhibitor and simultaneously used ferric chloride as the coagulant to control disinfectant by products (DBPs) along with bacterial contamination (Pieper et al., 2017, 2018). Use of ferric chloride thus increased the chloride-to-sulphate mass ratio to greater than 2 (Baum et al., 2016; Zahran et al., 2017). The existing insoluble, protective scale layer on the water pipe began to break in absence of orthophosphate. As a result, corrosion of lead and galvanized iron pipes increased and caused exponential lead release in the drinking water for several months (Hosseinibalajadeh, 2018; Roy & Edwards, 2019). Flint switched back to its original water source but this incident has left long lasting health impact on the residents. Figure 3 provides a detailed explanation of corrosion inhibitor, orthophosphate ($\text{PO}_4^{3-}$) and its action of mechanism in inhibiting corrosion of lead and galvanized pipes.
Figure 3: Action of Mechanism of Orthophosphate (Pieper et al., 2017). The figure shows formation of insoluble phosphate compounds developed on the pipe surface in presence of phosphate group (PO$_4^{3-}$). The presence of phosphate group prevents release of soluble lead and other metals like iron, zinc, and cadmium in the flowing water. b) The figure shows water chemistry in the water pipes in absence of phosphate group (PO$_4^{3-}$). In absence of phosphate group, pipe surface comes in contact with water resulting in oxidation reaction. The oxidation of lead or galvanized pipes will increase release of soluble lead and other metals like iron, zinc, and cadmium in the flowing water.

Prior to Flint, Washington D.C. experienced a lead water crisis in the year 2001 primarily because of the violation of LCR regulations in order to be in compliance with DBP regulations by EPA (Renner, 2004; Roy & Edwards, 2019). In 2000, the D.C. water utility decided to change their disinfectant from chlorine to chloramine (Renner, 2004; Edwards & Dudi, 2004). The change successfully reduced the level of carcinogenic DBPs below the EPA limit but caused an alteration

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in the water chemistry (Renner, 2004). The change in water chemistry increased the lead in water consumed by people in D.C. Alteration of the disinfectant and existing lead-brass pipes and plumbing material together increased lead release into the water (Edwards, 2014; Edwards et al., 2009). This incident resulted in increases in BLL to levels greater than 10 μg/dL in children below the age of for three consecutive years (Edwards, 2014; Pieper et al., 2018).

It was reported for children older than 6 years to have irreversible neurological and developmental defects in span of 2 years after 2001 (Edwards, 2014; Renner, 2004). The number of deformities in new-born babies and cases of miscarriage increased also because of high lead levels in the water. It was stated by Marc Edwards that the D.C. water crisis was 20 times more harmful when compared to Flint case (Edwards, 2014). In fact, the D.C. crisis is still not completely resolved because of presence of existing old lead pipelines and plumbing materials (Edwards et al., 2009).

2.4.2: Corrosion in Galvanized Steel Pipes

As a replacement to pure lead pipelines, galvanized plumbing materials have been used since the 20th century (Clark et al., 2015). A metal surface coated with another metal which is more reactive to form a protective layer against corrosion is known galvanization. Zinc is frequently utilized for galvanization on steel, copper, and iron pipes. Zinc naturally consists of less than 1% concentration of lead which holds potential for lead leaching in water from pipelines (Ng et al., 2018; Wasserstrom et al., 2017). In fact, galvanized steel pipes installed for years are considered as direct or indirect sources of lead in drinking water. Studies in U.S. as well as in other countries have reported cases of galvanic corrosion resulting in lead release between galvanized pipes replacing the old lead pipes (Ng et al., 2018).
Galvanized steel pipes contribute to lead release less because of the zinc coating and mainly due to use of brass in faucets, solder and other plumbing materials (Li et al., 2020). One study by Clark et al. (2015) used cadmium to detect lead in galvanized steel pipe. The study analyzed water pipes in D.C., Chicago, and two other cities and showing lead level to exceed 100 μg/L (Clark et al., 2015). Cadmium was used as a fingerprint to detect lead release from zinc coating on the old steel pipes. The water flow rate through these pipes also contributes to the amount of lead release (Cartier et al., 2012). The lead pipelines are partially replaced with galvanized pipes as well as other pipes like copper pipes along with the presence of brass materials (Schock, 2018; Xie & Giammar, 2011). This combination of multiple pipes leads to different mechanism causing lead release in water one way or the other (Cartier et al., 2012; Wang et al., 2012).

Deposition and galvanic corrosion plays an important role in increasing the lead release (Clark et al., 2015). Galvanic connection between lead and copper pipes has shown positive result for increase in lead leaching. Galvanic corrosion is combined with deposition corrosion especially at the joint areas (Clark et al., 2015; Wang et al., 2012; Xie & Giammar, 2011). Results show deposition corrosion causes long-term lead release in water. Certain factors that can impact the rate and efficiency of corrosion are flow rate, water chemistry, pipe age and arrangement, solubility, and species of copper (Gonzalez et al., 2013; Pisigan & Singley, 1985). Lead release from pure lead, pure copper and partial replacement of both lead and copper pipelines has also been reported to have no significant change in the amount of lead release. In fact, lead release from partial replacement pipes has shown long-term corrosion; both galvanic and deposition corrosion (Clark et al., 2015; Wang et al., 2012). The flowrate is an important factor to know which type of lead is present. The soluble lead release would slow down over time when the flow rate of water
is fast due to short contact time with water. The reverse effect is observed in presence of particulate lead (Cartier et al., 2012).

2.4.3: Corrosion in Lead-Iron Pipes

The use of iron pipes was wide-spread before World War II in plumbing materials, joints, premise plumbing and as galvanized iron pipes (Pipe, 2001). Redox reactions are the fundamental cause of iron pipe corrosion. Iron in water undergoes oxidation reaction resulting in rust and iron compounds. Iron has evidently increased lead release in water either by development of iron scale deposits on galvanized steel and copper pipes or by corrosion from galvanized iron pipes (McFadden et al., 2011; Morgan, 1991). The majority of iron pipes were replaced by copper pipes. Lead release from iron pipes is largely affected by factors like pipe age, pipe length, formation of scale, exposure period (Hosseinibalajadeh, 2018; Xie & Giammar, 2011). Galvanized steel pipes along with lead pipes tend to develop iron layer over the years when zinc coating scraped off (Wasserstrom et al., 2017). The iron layer has a tendency to adsorb the lead from the lead pipes in upstream. As a result, this iron layer contributes to lead release in the absence of a zinc coating (McFadden et al., 2011). The partial replacement of lead pipes causes formation of iron deposits in upstream and downstream piping. Iron deposits are found to be a major contaminant in many lead pipes (Morgan, 1991; Xie & Giammar, 2011). These deposits act as a reservoir of lead release from partial replacement and galvanized pipes (McFadden et al., 2011). The galvanized iron pipes cause particulate lead release in water which can also be converted into soluble lead (McNeill & Edwards, 2001). The soluble lead is found trapped on iron scales in older pipes and is considered a major source of lead in water. In fact, Washington D.C. reported exacerbation of lead release in the houses with iron plumbing material and galvanized iron pipes (McFadden et al., 2011). The study reported the long-term impact of iron deposits contributing in lead release even after making
substantial changes like replacement of full lead pipes (McFadden et al., 2011; Morgan, 1991). Thus, iron in any form, as deposits or galvanized pipes has been contributing to lead release in drinking water.

2.4.4: Role of Chloride Sulphate Mass Ratio

The chloride-to-sulphate mass ratio (CSMR) plays an important role during oxidation-reduction reaction for pure lead pipes and lead-copper pipes (Ng et al., 2018; Nguyen et al., 2010). There are different redox reactions occurring in pure lead and lead-copper pipes. In pure lead pipe, where the anodic reaction is on lead and the cathodic reaction is on oxygen, the pH either remains constant or can increase due to presence of some non-neutralized hydroxyl group (-OH) (Alfredo et al., 2015; Hosseinibalajadeh, 2018; Edwards & Dudi, 2004; Nguyen et al., 2010). In lead-copper pipes, lead undergoes an anodic reaction and copper surface undergoes cathodic reaction. Here due to low pH and a high corrosion rate, lead release will increase and the formation of a passivating layer to protect the lead surface will be obstructed (Nguyen et al., 2010; USEPA, 2016). The chemistry of chloride and sulphate is shown with both the pipes (lead pipes and copper-lead pipes) (Edwards & Triantafyllidou, 2007). Chloride for lead pipes showed protective behavior whereas for copper-lead pipes, chloride enhanced corrosive behavior. Sulphate, in both pipe cases, acted as an inhibitor towards corrosion and supported formation of passivating layer. The mathematical calculation for CSMR was first proposed by Gregory in 1985 (Edwards & Triantafyllidou, 2007; Reiber, 1991). When the CSMR was over 0.5, lead release was reported to increase due to an increase in galvanic corrosion. Therefore, utilities tend to either maintain the ratio at 0.5 or keep the sulphate concentration high (Ng et al., 2018; Reiber, 1991). The presence of sulphate will also promote formation of insoluble lead sulphate (PbSO₄) whereas chloride will form soluble, corrosive lead chloride (PbCl₂) (Nguyen et al., 2010).
2.4.5: Removal of Lead via Adsorption by Using Metal Oxides

Removal of metals such as lead can be done through several processes like precipitation, adsorption, filtration and extraction, complexation, and electrochemical treatment (Tilley et al., 2010; Verdugo et al., 2016; Wang et al., 2020). Adsorption is a process where an adsorbate (usually solid, liquid, or gaseous phase) is adhered to an adsorbent (usually liquid or solid phase). Adsorption can be categorized as bulk phase, film phase, or pore phase physiochemical treatment (Grover et al., 2012). Figure 4 shows mechanism of basic adsorption process between adsorbate and adsorbent (Wang et al., 2020). Adsorption out of all the treatment is cost-effective, efficient, and easily operative making it favorable method to remove lead and other heavy metals from drinking water (Cao et al., 2012; Wang et al., 2020). The use of metal oxides as adsorbents has been shown since the 1950s because of its properties like stability, large surface area, chemical properties and performance rate (Wang et al., 2020). The other metal oxides that demonstrate an efficiency in removing heavy metals are aluminum oxide (Al₂O₃), manganese dioxide (MnO₂), magnesium oxide (MnO), titanium oxide (TiO₂), zinc oxide (ZnO), zirconium oxide (ZnO₂) (Chen et al., 2019; Grover et al., 2012; Wang et al., 2020). Challenges faced while using metal oxides for environmental remediation are instability, biocompatibility and mass production (Wang et al., 2020).
Figure 4: Fundamental Mechanism of Adsorption (Wang et al., 2020). The adsorbate can pass through three phases of diffusion and enter the active sites present on the surface of the adsorbent. The adsorbate undergoes mono-layer adsorption forming single layer on the adsorbent surface and multi-layer adsorption forming multiple layers on top of each layer on the adsorbent surface.

Both iron oxides (Fe$_2$O$_3$ and Fe$_3$O$_4$) [(II, III (hematite) and III (magnetite))] have been extensively studied for their efficiency in removing lead and other heavy metals from drinking water (Chen et al., 2019; Wang et al., 2020). Chen et al (2018) reported enhanced efficiency of iron (III) oxide (Fe$_2$O$_3$) to remove lead ions when doped with metals like nickel (Ni) and cobalt (Co)(Chen et al., 2019). The experiment reported an increase in adsorption due to an increase in hydroxyl groups leading to multilayer adsorption. The adsorption capacity was also enhanced due to an increased metal-oxygen bond. Doping iron oxide with cobalt and nickel has been shown to increase adsorption from 93.9 mg/g (Fe$_2$O$_3$) to 136 mg/g (Co-Fe$_2$O$_3$) and from 97.5 mg/g (Ni-Fe$_2$O$_3$) (Chen et al., 2019). Removal of lead and copper ions was also analyzed using hematite (Fe$_2$O$_3$) and magnetite (Fe$_3$O$_4$) as adsorbents (Tamez et al., 2016). That study reported optimal

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lead adsorption at pH 4 and above. The lead adsorption onto Fe₂O₃ was noted to be 47.62 mg/g and that on Fe₃O₄ was noted to be 166.67 mg/g in presence of other metal ions like potassium (K⁺), sodium (Na²⁺), calcium (Ca²⁺), and magnesium (Mg²⁺) (Tamez et al., 2016). The lead adsorption from another experiment using iron-based water treatment residues reported adsorption capacity of 40.20 mg/g with pH 4.5 and above (Castaldi et al., 2015). A comparative study of adsorption of lead between hematite (Fe₂O₃), goethite (FeOOH) and manganese oxide (MgO) reported hematite to be efficient for lead adsorption up to a concentration of 10⁻⁴ M lead in solution at pH 3 and above (McKenzie, 1980).
Chapter 3: Materials and Methods

3.1: Sample Selection

In 2018 University of South Florida (USF) directed a program to replace lead components used in locally produced handpumps (pitcher pumps) at Tamatave city of Madagascar. The handpumps consist of check valves (piston and foot) and a well screen made of brass and lead solder. The replacement of lead components was initiated to reduce the lead concentration in the handpump water below the lead level recommended by World Health Organization (WHO). The recommended lead level by WHO is below 10 μg/L.

Below is a summary of the 2018 intervention. Further details can be found in Usowicz report published in 2019 (Usowicz, 2019).

As a part of this project, 504 handpump lead components were replaced with unleaded components (replaced with iron components). The analysis of 418 water samples after the intervention reported 98% samples had lead concentrations below 10 μg/L, 95% of the samples had lead concentrations below 5 μg/L and 80% samples had lead concentrations below 2 μg/L.\(^5\) Furthermore, in-depth water analysis was performed on 30 water samples before the intervention. For those 30 water samples, parameters like lead concentration, pH, conductivity, temperature, and total dissolved solids (TDS) were tested. Additional testing of nitrate, iron, nitrite, manganese, fluoride, sulphate, chloride, ammonia, arsenic, water hardness, total alkalinity and a microbiological test for Enterococcus were performed. The testings were done to obtain a basic

\(^5\) All 418 water samples analyzed for lead concentration after intervention were collected after flushing in order to maintain consistency. Some of the users consumed water directly from first draw water without flushing.
understanding of groundwater chemistry and possibly provide insight to the lead leaching mechanism and resulting lead concentrations. In all the pumps remediated, an unknown inorganic coating was observed on the surface of the lead components (piston and foot valve) which were later replaced. The surface area of the coating was measured and statistical analysis showed that a greater surface area of coating on the lead component resulted in a lower lead concentration present in handpump water (Usowicz, 2019). This result for the statistical analysis for the assumption of this study is shown in Chapter 4 (Section 4.1).

The analytical methods used in this study are Raman Spectroscopy, X-Ray Fluorescence (XRF), and Energy Dispersive X-Ray Spectroscopy with Scanning Electron Microscope (SEM-EDS). These methods were utilized to determine the surface characterization of the unknown coating. Raman Spectroscopy and XRF analysis were performed in the laboratories of Dr. Peter Vikesland and Dr. Marc Edwards respectively, at Virginia Tech University. The SEM-EDS technique was performed by Dr. Yusuf Emirov at USF. Samples that were used for these analyses were selected from the subset of 30 lead weight samples that were removed from pumps that had the in-depth water analysis. The selection of lead weights to perform this analysis of the coating was based on them being representative of other lead components and the visual determination of a large amount of coating.

The samples selected to perform the analyses are 5F, 12F, 16F, 17F, 18F, 20F, 25F.6 The samples were selected based on visual characteristics, appearance, and amount of scale present. All the samples were maintained in plastic bags in the laboratory at room temperature. Samples were weighed and images were taken before and after every analysis. An example of what sample 17F looks like appears in Figure 5 followed with 3 other samples i.e., sample 14F, sample 16F,

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6 F stands for foot valve lead weights.
and sample 25F, respectively. Samples were kept in desiccator 24 hours before performing the SEM EDS analysis.

Figure 5: The Check Valve Weight (Foot) Samples Considered for Analysis. a) Sample 17F b) Sample 14F c) Sample 16F and d) Sample 25F.

3.1.1: Raman Spectroscopy

The Raman analysis was performed on 17F, 18F, 20F, and 25F samples to identify the scale area and on 5F, 12F, 17F, 20F, and 25F samples to identify the base area. The uncoated, bare metal is referred to as the base area and the coating is referred to as scale. The instrument used for this analysis was a WITec alpha 500R Raman spectrometer. Single point spectra with an exposure time of 10 seconds and 10x magnification was used to obtain clear images of scale and base area.

Raman analysis is considered to be highly sensitive and both a qualitative and quantitative method. It helps to identify the chemical composition of the sample. Raman focuses on the molecular level such as vibrational, rotational and several other low frequency modes of the sample instead of elemental level (Bugay & Brittain, 2006; Halvorson & Vikesland, 2010; Sivakumar et al., 1978). Its working is based on the interaction between light and chemical composition of the samples and the corresponding wavelengths of the scattered light. The scattered light with different intensity and wavelength is compared to the incident light and provides information regarding the
chemical composition, chemical structure, and chemical bonds of a sample (Bugay & Brittain, 2006; Halvorson & Vikesland, 2010; Lindfors & Ivaska, 2007; Sorb et al., 2013). It is preferred for microscopic analysis and to identify impurities or contamination present at the molecular level (Halvorson & Vikesland, 2010; Sorb et al., 2013).

As an example, a study used Raman analysis to analyze the chemical composition and molecular behavior of zinc, copper, and brass present in artificial tap water in the presence of phosphate ions (Yohai et al., 2011). Lead oxide (PbO₂) and other lead pigments were identified using Raman spectra showing its efficiency in identification of lead and other metal products (Burgio et al., 2001). Another study used Raman analysis to detect qualitative and quantitative presence of lead chrome green, a harmful substance, used in tea to enhance its quality (Li et al., 2015). Raman micro-spectrometry has also been used to study solid surfaces. For example, it has been used to study corrosion on steel pipes that had zinc coating on it (Etienne et al., 2014). Another study used Raman spectroscopy to study graphene present on the surface of nickel and cobalt (Usachov et al., 2017).

Raman analysis is used in compliment with XRF analysis in order to identify structure composition, element composition and the molecular behavior of any material (Baslak, 2019; Morgan et al., 2017; Sivakumar et al., 1978; Skougstad & Fishman, 1965). ⁷ XRF analysis was used to identify the presence of trace elements in the samples (check valve weights).

3.1.2: X-Ray Fluorescence Spectrometry

X-Ray Fluorescence (XRF) spectrometry was performed using an Innov-X Alpha 8000 LZX XRF instrument. XRF was performed on both the scale and base area of 5F, 12F, 17F, 18F, 20F, and 25F samples. XRF is an effective analytical technique to quantify and characterize

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⁷ XRF cannot identify metal with atomic mass below 40. SEM-EDS was preferred in order to obtain accurate and sensitive information about surface elements.
elemental composition of any solid or liquid material emphasizing on its wide-spread applications (Chen et al., 2008; Nasrazadani & Hassani, 2016; Streli et al., 2017). XRF is based on the principle where the respective sample is excited by external x-ray radiation (Chen et al., 2008; Oyedotun, 2018). This radiation excites the sample and emits secondary rays with a specific wavelength from the sample. Specific wavelength of the secondary rays from the sample are then counted in order to identify and quantify the sample. The intensity of the wavelengths from the sample provides information regarding the concentration of the elements or trace metals present in the sample (Barreiros et al., 1997; Chen et al., 2008; Nasrazadani & Hassani, 2016; Oyedotun, 2018). In comparison to other techniques, XRF can be sensitive, economical, and efficient (Barhoum et al., 2018). A study for example detected the concentration of metals like cadmium (Cd), copper (Cu), nickel (Ni) and lead (Pb) present in trace amounts in drinking water samples using XRF along with solid-phase extraction disks (Barreiros et al., 1997). Another study focused on the polluted and salt-impacted waters which used XRF in order to identify the elemental data such as soil and sediments responsible for it (Pearson et al., 2017). A recent study by Tighe et al (2020) reported sensitivity and cost effectiveness of using XRF in detecting lead present in tap water. The method reported to have detection range of 1 to 150 μg/L (Tighe et al., 2020).

3.1.3: Scanning Electron Microscope – Energy Dispersive X-Ray Spectroscopy

The Energy Dispersive X-Ray Spectroscopy with Scanning Electron Microscope (SEM-EDS) technique was performed on samples 17F and 16F to determine the in-depth surface characterization of the elements present on the scale area. The technique measured the thickness of the scale itself and gap present between the scale and base area. The SEM-EDS instrument at USF can scan the surface up to the depth of 3 μm. The instrument used for this experiment was a
Hitachi SU-70 with 500x magnification and 30 kV accelerating voltage and is located at the USF Nanotechnology Research & Education Center.

Energy Dispersive X-Ray Spectroscopy (EDS), combined with Scanning Electron Microscope (SEM), can identify presence of the surface elements and provide information regarding its approximate concentration of elements present in the surface (Moro et al., 2021; Nasrazadani & Hassani, 2016; Ngo, 1999). SEM-EDS cannot detect elements like hydrogen and helium because of its electron configuration. The difference between XRF and SEM-EDS is the source of the beam and its sensitivity to detect elements present in concentration less than 1%. SEM-EDS uses an electron beam for the analysis (Ngo, 1999; Zohar et al., 2018) and EDS is combined with SEM in order to obtain high resolution images of the sample surface and its topographic information (Goldstein et al., 2012; Ngo, 1999). The information obtained from this technique can be viewed as visual maps and as scanned lines (also known as an EDS spectra). In this technique electron beam is incident on the sample surface of interest. The incident electron beam hits an electron in an inner shell of an atom creating a positive charged electron hole (Moro et al., 2021; Ngo, 1999). The electron from the inner shell is pushed out and an electron with higher energy from the outer shell takes the position in the inner shell. The shift from higher energy level to lower energy level causes release of secondary electrons captured in the form of x-rays captured by EDS detector (Goldstein et al., 2012; Corbari et al., 2008; Ngo, 1999). These x-rays are unique to every element based on the specific number of electrons present the atoms. SEM-EDS images are produced from secondary electrons backscattered electrons. The backscattered electrons are produced due to different atomic number of all elements present in the sample surface and due to inelastic interaction within the sample surface. The secondary electrons give information regarding
the elements present and backscattered electrons gives topographic information of the sample surface (Godelitsas et al., 2003; Moro et al., 2021; Ngo, 1999; Goldstein et al., 2012).

SEM-EDS along with other surface characterizing techniques has been used to detect the presence of lead, lead compounds, and other heavy metal compounds. Elemental Characterization in suspension with SEM-EDS indicated lead ion removal mechanism (Nuspl et al., 2004; Sharma et al., 2018). The study confirmed that lead ion present in concentration less than 1,000 mg/L will be primarily removed by electrostatic interaction method and in case of lead ion present in concentration greater than 1,000 mg/L, it will be primarily removed by lead crystallization (Sharma et al., 2018). Leaching effects have also been studied using lead and zinc doped cements. In this case, SEM-EDS was used to obtain the surface morphological information of two types of cement. The results showed adsorption efficiency of divalent ions and elements present in leached and unleached area indicating the impact of each element concentration on the process of leaching (Cocke et al., 1992). An interaction between aqueous lead solution and calcium carbonates was analyzed using SEM-EDS along with ICP-AES and XRD. SEM-EDS results showed active formation of lead carbonates in minutes because of lead sorption from aqueous solution on calcium carbonates (Godelitsas et al., 2003).
Chapter 4: Results and Discussion

4.1: Water Analysis

An overview of the in-depth water analysis reported for 30 water samples obtained before the replacement of lead components is provided in Table 2. The pH influences behavior of all the compounds in aqueous solution and therefore it may help interpret behavior of lead leaching mechanism in the handpump (Usowicz, 2019). From the suite of water quality analyses performed (discussed in Chapter 3), two parameters showed a statistical correlation with the concentration of lead in the pump water. Based on the stepwise multiple linear regression, lead concentration in the pump water was related to alkalinity and the uncoated surface area present on the check valves. The uncoated surface area showed a maximum influence on the lead concentration in the pump water with standardized coefficient of 0.706. Table 2 also provides information on the water analysis specific to samples 16F, 17F, and 20F as these samples are discussed in greater detail later.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>pH</th>
<th>Conductivity</th>
<th>TDS</th>
<th>Temperature</th>
<th>Before Intervention Lead Concentration</th>
<th>After Intervention Lead Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analysis of all 30 samples</td>
<td>5.7-7.9</td>
<td>58 to 1,820 μS/cm</td>
<td>30 to 1,080 ppm</td>
<td>Average of 26°C</td>
<td>Up to 100 μg/L</td>
<td>&lt; 10 μg/L</td>
</tr>
<tr>
<td>Sample 16-foot</td>
<td>6.0</td>
<td>524.0 μS/cm</td>
<td>277.0 ppm</td>
<td>24.8 °C</td>
<td>19.0 μg/L</td>
<td>11.0 μg/L</td>
</tr>
<tr>
<td>Sample 17-foot</td>
<td>6.6</td>
<td>307.0 μS/cm</td>
<td>167.0 ppm</td>
<td>25.3°C</td>
<td>100 μg/L</td>
<td>56 μg/L</td>
</tr>
</tbody>
</table>

8 After intervention of 504 lead weights, 98% water from the remediated handpump reported lead level below 10 μg/L. Brief information can be found in Chapter 3 and detail information can be found in Usowicz report of 2019.
Table 2 (Continued)

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>pH</th>
<th>Conductivity</th>
<th>TDS</th>
<th>Temperature</th>
<th>Before Intervention Lead Concentration</th>
<th>After Intervention Lead Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 20-foot</td>
<td>6.4</td>
<td>429.2 μS/cm</td>
<td>227.1 ppm</td>
<td>24.5°C</td>
<td>65.0 μg/L</td>
<td>11.0 μg/L</td>
</tr>
</tbody>
</table>

4.2: Raman Spectroscopy Analysis

Raman analysis was performed to identify the chemical composition (compound composition) of the base area and scale area of the lead valve weights used in the pitcher pump systems. The Raman peaks are specific and identification is based on the vibrational mode of the molecules present in the sample. Raman analysis for samples 5F, 12P, 17F, 20F, and 25F showed 120 and 150 cm\(^{-1}\) peaks for the base area as shown in Figure 6. The peaks 120 and 150 cm\(^{-1}\) indicate the base area to be the lead-based mineral, Matlockite (PbClF) from the reference data of Raman database, RRUFF project as shown in Figure 7. Note that this specific identification is contested in this thesis discussion that occurs later in this chapter. Raman analysis for four samples (17F, 18F, 20F, and 25F) showed 224, 292, 407, 493, and 607 cm\(^{-1}\) peaks for the scale area as shown in Figure 8. These peaks indicate the scale to be hematite (α-Fe\(_2\)O\(_3\)). The reference for identification of peaks observed for the scale area was obtained from the Lassoued et al. (2017) study on hematite. Figure 9 shows the reference image for identification of peaks for scale area. Furthermore, a study by Faria et al. (1997) and Xu et al. (2009) reported similar Raman peaks for identification of hematite.
Figure 6: The Raman Spectra for Base Area of Lead Component. The result shows Raman shift for the base area of samples 5F, 12F, 17F, 20F, 25F. The figure shows two peaks at 120 and 150 cm⁻¹.

Identification: Matlockite (PbClF)

Figure 7: The Raman Reference for Identification of Base Area. The link for Raman Database used to identify base area is as follows http://rruff.info/about/about_general.php. The peaks for Matlockite as shown in the Raman database are 120 and 150 cm⁻¹.
Figure 8: The Raman Spectra for Scale Area of Lead Component. The result shows Raman shift for the scale area of samples 17F, 18F, 20F, 25F. The figure shows 5 peaks that are 224, 292, 407, 493, and 607 cm\(^{-1}\).

Identification: \(\alpha\)-Fe\(_2\)O\(_3\)

Figure 9: The Raman Reference for Identification of Scale Area (Lassoued et al., 2017)\(^9\). The reference to identify the Raman peaks 224, 292, 407, 493, and 607 cm\(^{-1}\) as reported for the scale observed on the check valve weights of the pitcher pump.

Sample 17F was selected for further image scanning and is believed to be representative of all samples. For sample 17F, 400 single spectra were collected by image scanning and a bitmap image with different intensities was created. The image of sample 17F is 200 µm x 200 µm (400 points) in size. The result from the bitmap image of sample 17F showed high intensity for peaks of the base and scale area. Figure 10 shows an image obtained from image scanning of sample 17F. This was done to check different intensity peaks obtained from Raman analysis and were specific to base and scale area.

4.3: X-Ray Fluorescence Analysis

Table 3 shows elements identified and quantified in the X-Ray Fluorescence (XRF) analysis of the base and the scale area on the check valves used in the pitcher pump system. The XRF analysis was performed on samples 5F, 12P, 17F, 18F, 20F, and 25F. The comment column in this table shows whether the scale or base of a particular sample was analyzed. The XRF results for the base area reported similar results as that of Raman analysis results with lead being the
primary element. The lead concentration reported in the base area of the check valve weights ranged from 93.39 – 96.91%.

The XRF results for the scale area reported that the primary elements in the scale area are iron and lead. XRF is not able to accurately detect light weight elements; i.e., analysis of elements with atomic number less than 12 (MW less than 24) (Melquiades & Appoloni, 2004; Brand & Brand, 2014). Therefore, it does not provide information to support the conclusion from Raman analysis that the scale is specifically hematite. The iron and lead concentration in the scale area is reported to range from 1.92 – 90.79% and 7.86 – 88.94%, respectively. Therefore, the scale area is found to be either iron almost completely or mixture of iron and lead. The XRF results also detected trace amounts of Chromium (Cr), Copper (Cu), Nickel (Ni), Tin (Sn), Vanadium (V), Zinc (Zn), Zirconium (Zr), and Antimony (Sb). The concentration of these trace elements is less than 5%. The presence of trace elements is most likely because the lead required to make lead pump components (foot and piston) is obtained from lead acid batteries. Lead acid batteries are made from lead alloys in which the above-mentioned elements can be found (King et al., 2000; Zhang et al., 2016).
Table 3: XRF Analysis Results. The results reported primary distribution of iron and lead concentration in the scale area of all the samples selected for XRF analysis.

<table>
<thead>
<tr>
<th>Reading</th>
<th>ID</th>
<th>Comment</th>
<th>Cr</th>
<th>Cu</th>
<th>Fe</th>
<th>Pb</th>
<th>Ni</th>
<th>Sn</th>
<th>V</th>
<th>Zn</th>
<th>Zr</th>
<th>Sb</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>17 foot</td>
<td>bare metal</td>
<td>ND</td>
<td>0.12</td>
<td>1.37</td>
<td>95.58</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>2.94</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>17 foot</td>
<td>scale</td>
<td>ND</td>
<td>ND</td>
<td>82.18</td>
<td>16.69</td>
<td>ND</td>
<td>ND</td>
<td>0.19</td>
<td>0.09</td>
<td>0.02</td>
<td>0.83</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>20 foot</td>
<td>bare metal (back side)</td>
<td>ND</td>
<td>ND</td>
<td>0.81</td>
<td>96.91</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>0.32</td>
<td>2.16</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>20 foot</td>
<td>scale</td>
<td>ND</td>
<td>ND</td>
<td>8.24</td>
<td>88.9</td>
<td>ND</td>
<td>ND</td>
<td>0.77</td>
<td>ND</td>
<td>ND</td>
<td>2.09</td>
<td>100</td>
</tr>
<tr>
<td>6</td>
<td>20 foot</td>
<td>scale (different spot)</td>
<td>ND</td>
<td>ND</td>
<td>8</td>
<td>88.94</td>
<td>ND</td>
<td>ND</td>
<td>0.75</td>
<td>ND</td>
<td>ND</td>
<td>2.31</td>
<td>100</td>
</tr>
<tr>
<td>7</td>
<td>5 foot</td>
<td>mostly bare metal</td>
<td>ND</td>
<td>0.12</td>
<td>2.13</td>
<td>93.39</td>
<td>ND</td>
<td>1.49</td>
<td>ND</td>
<td>0.08</td>
<td>ND</td>
<td>2.79</td>
<td>100</td>
</tr>
<tr>
<td>8</td>
<td>5 foot</td>
<td>mostly scale</td>
<td>0.23</td>
<td>0.24</td>
<td>1.92</td>
<td>87.45</td>
<td>0.07</td>
<td>3.95</td>
<td>ND</td>
<td>0.19</td>
<td>ND</td>
<td>5.95</td>
<td>100</td>
</tr>
<tr>
<td>9</td>
<td>25 foot</td>
<td>bare metal (back side)</td>
<td>ND</td>
<td>0.04</td>
<td>0.74</td>
<td>96.84</td>
<td>ND</td>
<td>0.27</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>2.11</td>
<td>100</td>
</tr>
<tr>
<td>10</td>
<td>25 foot</td>
<td>scale</td>
<td>ND</td>
<td>ND</td>
<td>14.41</td>
<td>83.91</td>
<td>ND</td>
<td>0.29</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>1.4</td>
<td>100</td>
</tr>
<tr>
<td>11</td>
<td>12 piston</td>
<td>coated nail-like piece</td>
<td>ND</td>
<td>ND</td>
<td>0.6</td>
<td>91.77</td>
<td>ND</td>
<td>7.27</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>0.37</td>
<td>100</td>
</tr>
<tr>
<td>12</td>
<td>12 piston</td>
<td>washer?</td>
<td>ND</td>
<td>ND</td>
<td>4.53</td>
<td>1.65</td>
<td>ND</td>
<td>0.06</td>
<td>0</td>
<td>ND</td>
<td>6*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>12 piston</td>
<td>metal surface</td>
<td>ND</td>
<td>ND</td>
<td>2.98</td>
<td>94.85</td>
<td>ND</td>
<td>0.48</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>1.68</td>
<td>100</td>
</tr>
<tr>
<td>14</td>
<td>18 foot</td>
<td>scale</td>
<td>ND</td>
<td>ND</td>
<td>90.79</td>
<td>7.86</td>
<td>ND</td>
<td>0.18</td>
<td>0.27</td>
<td>ND</td>
<td>0.9</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

ND = 'not detected'
('*94% light element')

4.4: Scanning Electron Microscope-Energy Dispersive X-Ray Spectroscopy Analysis

Energy Dispersive X-Ray Spectroscopy in conjunction with Scanning Electron Microscope (SEM-EDS) was performed on the scale surface of sample 17F and 16F. The SEM analysis was performed to study the characteristics of the developed scale and SEM-EDS was performed to identify and quantify elements present in the developed scale on the check valves used in the pitcher pump system. The SEM imagery analysis showed that base and scale area are not completely attached and that the scale surface is highly uneven. The thickness of the scale area was measured through SEM analysis. The measured thickness of scale area for sample 17F and 16F ranges between 176 μm – 410 μm and 35 μm – 50 μm, respectively. The gap between base and scale area for sample 17F and 16F was measured by SEM analysis and ranges from 40 μm – 75μm and 13 μm – 30 μm, respectively. Figure 11 shows the visual of scale surface of sample 17F and Figure 12 shows the scale surface of sample 16F as captured by SEM analysis. Figure 13 for sample 17F, Figure 14 for sample 17F, and Figure 15 for sample 16F show the thickness of the
scale and the distance between the base and the scale area on both the samples as mentioned in the text above.

The SEM-EDS analysis performed to identify elements in the scale was measured up to the depth of only 3 μm. The SEM-EDS mapping provides a visual idea about the identification of elements and SEM-EDS spectra gives quantitative information of all the elements present in the scale surface. Figure 16 shows SEM-EDS mapping and Figure 17 shows SEM-EDS spectra for elements in the scale of sample 17F. Figure 18 shows SEM-EDS mapping and Figure 19 shows the SEM-EDS spectra for elements in the scale of sample 16F. The major and minor elements detected in the scale of both the samples (sample 17F and 16F) are the same as shown in Figure 16 for sample 17F and Figure 18 for sample 16F. The major elements as shown in the SEM-EDS mapping and spectra are oxygen, carbon, iron, and lead and minor elements detected are calcium, and mercury. The concentration of primary elements in sample 17F as shown in Figure 17 in descending order (by weight) is iron – 44.3%, oxygen – 38.5%, carbon – 11.5%, and lead – 4.25%. These results support the presence of some type of iron oxide though the reported weight percentages do not always support the Raman result that the oxide is hematite. The concentration of both minor elements identified, calcium and mercury are less than 1%. The concentration of primary elements in sample 16F as shown in Figure 19 in descending order is iron – 33.5%, oxygen – 30%, lead – 25%, and carbon – 8.6%. The concentration of both minor elements, calcium and mercury was found to be same as sample 17F; less than 1%.
Figure 11: The Visual of Scale Surface of Sample 17F Determined by SEM Imaging.

Figure 12: The Visual of Scale Surface of Sample 16F Determined by SEM Imaging.
Figure 13: The Thickness of Scale of Sample 17F Determined by SEM Imaging. The thickness of scale as shown in this figure is uneven and ranged from 176.55 – 406.71 μm. The space between the scale and base area ranged from 41.78 – 45.90 μm.

Figure 14: The Thickness of Scale of Sample 17F Determined by SEM Imaging. The thickness of scale as shown in this figure is uneven and ranged from 150.50 – 353.04 μm. The space between the scale and base area ranged from 45.75 – 72.11 μm.
Figure 15: The Thickness of Scale of Sample 16F Determined by SEM Imaging. The thickness of scale as shown in this figure is uneven and ranged from 36.61 – 48.81 μm. The space between the scale and base area ranged from 14.03 – 28.67 μm.

Figure 16: The SEM-EDS Mapping of Sample 17F. The figure shows visual quantification of all elements detected in the scale area of sample 17F.
Figure 17: The SEM-EDS Spectra of Sample 17F. The major elements detected in the scale area of sample 17F are iron, oxygen, carbon, and lead. The atomic percent provides the proportion of element based on number atoms of each element while the weight percent provides the proportion of element based on mass of each element.

Figure 18: The SEM-EDS Mapping of Sample 16F. The figure shows visual identification of all elements detected in the scale area of sample 16F.
Figure 19: The SEM-EDS Spectra of Sample 16F. The major elements detected in the scale area of sample 16F are iron, oxygen, lead, and carbon. The atomic percent provides the proportion of element based on number atoms of each element while the weight percent provides the proportion of element based on mass of each element.
4.5: Summary of Results

Table 4: Summary of All Analytical Techniques Performed on Sample 16F and 17F.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Sample Type</th>
<th>Sample Description</th>
<th>Analysis Name</th>
<th>Analysis Perform By</th>
<th>Lead Content</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>Foot</td>
<td>Scale is rust like, light reddish brown in color. Scale is present on the top. It is does not cover the base area completely.</td>
<td>Raman Spectroscopy</td>
<td>Virginia Tech University</td>
<td></td>
<td>This technique identified the base area as lead-base mineral called Matlockite (PbClF) and scale to be $\alpha$-$\text{Fe}_2\text{O}_3$. Note that this specific identification of Matlockite is contested in this thesis discussion that occurs later in this chapter. The technique does however support the conclusion that the base area consists primarily of lead.</td>
</tr>
<tr>
<td>17</td>
<td>Foot</td>
<td>Scale is rust like, light reddish brown in color. Scale is present on the top. It is does not cover the base area completely.</td>
<td>X-ray Fluorescence</td>
<td>Virginia Tech University</td>
<td></td>
<td>The base area was reported to be 95.58% lead and the scale was reported to have a solid-phase lead content of 16.69%. The iron content in the base area was 1.37% and in the scale was 82.18 %. Negligible (&lt; 5%) antimony, copper, zinc and vanadium was detected.</td>
</tr>
<tr>
<td>17</td>
<td>Foot</td>
<td>Scale is rust like, light reddish brown in color. Scale is present on the top. It is does not cover the base area completely.</td>
<td>SEM-EDS</td>
<td>Universit y of South Florida by Dr Yusuf Emirov</td>
<td></td>
<td>The scale surface was analyzed up to a depth of 3 μm. Two points opposite to each other, near the edges were analyzed. The lead content detected at these two points was determined to be 4.23% and 6.27%. The iron content detected at these two points was 44.33% and 37.10 %. The oxygen content at both points ranges from 34 – 39%. Results support the presence of some iron oxide though the wide difference in reported percent weight of iron and oxygen does not consistently support the presence of hematite. The remaining metals detected were carbon (&gt; 5%), calcium and mercury (&lt; 5%).</td>
</tr>
<tr>
<td>16</td>
<td>Foot</td>
<td>Scale is rust like, reddish brown in color. Scale covers the base area completely at top and bottom.</td>
<td>SEM-EDS</td>
<td>Universit y of South Florida by Dr Yusuf Emirov</td>
<td></td>
<td>The scale surface was analyzed up to the depth of 3 μm. Two points, one near the center and one near the edge were analyzed. The lead and iron content near the center point was 25.72% and 33.53% respectively. The oxygen content at the center point was 30.14%. The edge point showed lead and iron content to be 3.97% and 71.87 % respectively. The oxygen content at the edge point was 17.87%. Results support the presence of some iron oxide though the wide difference in reported percent weight of iron and oxygen does not consistently support the presence of hematite. The remaining metals detected were carbon (&gt; 5%), calcium and mercury (&lt; 5%).</td>
</tr>
</tbody>
</table>
Based on the results summarized in Table 4 from all analytical techniques performed to analyze lead components (foot and piston) of the Madagascar handpumps, the following research objectives were answered. 1) The base area of the lead component of the handpump was identified to be lead based mineral, Matlockite (PbClF) by Raman analysis; however, this specific identification is contested later in this chapter. 2) The unknown scale area of the lead component of the handpump was identified to be Iron Oxide ($\alpha$-Fe$_2$O$_3$) by Raman analysis. The XRF results showed the scale to be primarily iron or iron and lead both. This finding was not supported by Raman analysis for scale identification. 3) The thickness of the scale as measured by SEM analysis was identified to be in the range 35 $\mu$m – 410 $\mu$m. 4) The elements present in the scale surface as analyzed by SEM-EDS analysis apart from iron and oxygen, were identified to be lead, carbon, calcium, and mercury. 5) The lead concentration on the scale surface of the lead component was reported to range from 4 – 25 %.

4.6: Further Discussion Using Selected Samples as Examples

In this study, three non-destructive chemical techniques, Raman Spectroscopy, XRF, and SEM-EDS were used to detect and understand the presence of lead in the scale developed on the lead check valves (i.e., piston and foot) used in the pitcher pump system in Madagascar. The techniques were used to determine the composition of valve weights. The samples 16F, 17F, and 20F are further selected for interpreting the results obtain from each technique. The XRF and Raman analysis was performed on 17F and 20F and SEM-EDS was performed on 16F and 17F.

It is known that the recycled lead used to manufacture the lead check valve components are obtained from old automobile lead acid batteries. Lead acid batteries are made from lead alloys. The lead alloys consist of elements like antimony, tin, copper, nickel, cadmium, calcium, and zinc (Jullian et al., 2003; Rocca et al., 2006).
Raman analysis provides information only on the chemical composition of a sample from its molecular vibrations and does not give information related to individual elements in the sample. The Raman analysis suggests that the base was Matlockite (PbClF) for samples 17F and 20F and other samples tested. However, Raman analysis is reported to be suspect in identifying a specific compound compared to other techniques (personal communication between Dr. James Mihelcic and Dr. Marc Edwards, September 10, 2020). Furthermore, this mineral is not expected to be present in the lead alloys that make up an automobile battery. In addition, the XRF analysis, which does provide elemental identification and quantification, showed lead to be the primary element of the base with 95.58% reported in the base of sample 17F and 96.91% reported in the base of sample 20F. XRF also didn’t show the presence of Cl and F in both samples 17F and 20F along with other analyzed samples. Therefore, it is concluded that the Raman analysis supports the conclusion that the base area primarily consists of lead but did not confirm the base to Matlockite.

The scale observed on the check valve weight was studied using all three techniques in order to interpret characteristics of the scale responsible for impacting the lead concentration in the pump water. The Raman analysis of the scale observed on sample 17F and 20F showed Raman peaks associated with hematite. The identification of Raman peaks is supported based on three different studies as shown in Section 4.3. The Raman peaks implied the scale to be only iron oxide without presence of any other chemical compound. However, XRF results for the scale of sample 17F and 20F showed wide range in elemental quantification as well as showed lead and iron to be primary elements. The scale of sample 17F reported iron to be 82.18% and lead to be 16.69% and that of sample 20F reported iron to be 8.24% and lead to be 88.9%.

The scale of sample 17F and 16F was analyzed by SEM-EDS to obtain more elemental information of the scale. SEM-EDS is a surface analyzing technique that suggested the presence
of carbon, oxygen, iron, and lead primarily and mercury and calcium in less than 1% concentration. The detection of carbon and oxygen in the scale by SEM-EDS confirmed the inability of XRF to detect light weight elements. In general, analysis of elements with atomic number less than 12 (MW less than 24) is not detectable or is inaccurate if detected using XRF (Melquiades & Appoloni, 2004; Brand & Brand, 2014).

The concentration range reported by weight percentage of lead associated with the scale by SEM-EDS analysis is 4 – 25%. In comparison to the XRF analysis, the analysis by SEM-EDS is limited up to the depth of 3 μm while the analysis from XRF can be performed to a depth of up to a millimeter (Hutton et al., 2014; Brand & Brand, 2014). The scale thickness as reported by the SEM analysis is as large as 410 μm; unfortunately, the analysis only provided information on the elemental composition up to 3 μm. Therefore, while the scale identification and quantification results from the three analytical techniques does support the scale being some type of iron oxide, it is not with certainty that the scale is specifically hematite as the Raman analysis indicated.

Furthermore, there can be two possible mechanism for occurrence of lead in the scale as shown by XRF and SEM-EDS analysis. The pH range of all 30 samples is considered to be an important factor for two possible mechanisms that explain the presence of lead in the iron scale – formation of insoluble lead compounds and adsorption due to surface complexation.

Regarding the formation of insoluble lead compounds, elemental lead is soluble in drinking water at pH 6.5 – 8.5 and ambient temperature. To control the release of lead, formation of insoluble lead compounds at these conditions is preferred (Beccaria et al., 1982; Wasserstrom et al., 2017). Lead compounds can occur with two forms of lead (Pb); Pb^{2+} and Pb^{4+} ions. The compounds associated with Pb^{4+} are primarily formed in highly acidic or alkali conditions. Therefore, the majority of lead compounds in engineered and natural water systems are formed.
with Pb$^{2+}$ ions (Willison & Boyer, 2012; Xie & Giammar, 2011). Lead can form insoluble compounds by reacting with carbonates, phosphates, sulphates, chlorides, and oxides depending on parameters like pH, temperature, soluble lead concentration, and alkalinity (Wasserstrom et al., 2017; Willison & Boyer, 2012). The pH and soluble lead concentration influences lead compound formation that ultimately impacts the rate of lead release in water. These lead compounds form a film on the surface of lead or galvanized pipes contributing to lead release (Edwards & McNeill, 2002; EPA, 2016; Xie & Giammar, 2011).

The WHO guideline and EPA action level for soluble lead in drinking water is 10 μg/L and 15 μg/L, respectively (EPA, 2016; Levin, 2014; WHO, 2015). The pH of drinking water ranges between 6.5 to 8.5 (Cornwell et al., 2016; Jurgens et al., 2019). Figure 20 provides information about the solubility of lead as Pb$^{2+}$ in aqueous solution and formation of various insoluble lead compounds. In the drinking water pH range, as shown in Figure 20, water treated with phosphate forms lead phosphate film (Pb$_3$(PO$_4$)$_2$) at a soluble lead concentration of 10$^{-3}$ μg/L, approximately falling in the acceptable concentrations provided by WHO and EPA. Carbonate in water forms carbonate films [lead carbonate (PbCO$_3$) and hydrocerussite [Pb$_3$(CO$_3$)$_2$(OH)$_2$]] at a soluble lead concentration of approximately 10$^3$ μg/L in the absence of phosphate. The water analysis of 30 pumps for this study reported soluble lead with a maximum concentration up to 10$^2$ μg/L and pH that ranged between 5.7 – 7.9 before the intervention of replacing the lead components (Usowicz, 2019). Furthermore, the results from XRF and SEM-EDS analysis of these lead components reported primarily the presence of iron, lead, oxygen, carbon. The presence of lead was detected on both the base and scale area. The water analysis of pump water also reported the presence of chloride, sulphate, iron, and carbonate in the groundwater along with other tested parameters. The results from the pump water analysis for 30 pumps reported detection range of chloride from 5 –
255 mg/L, sulphate from 0 – 43 mg/L, iron from 0 – 3.3 mg/L, and carbonate from 0 – 268 mg/L. The presence of lead on the scale could possibly occur due to complexation with other elements. These results and additional detail of the water quality analysis associated pumps can be found in Usowicz (2019). The detection of these chemical parameters suggest the possibility of formation of insoluble lead compounds like lead oxides, lead sulphate, and lead carbonate, or and soluble lead chloride.

Using the information from Figure 20 combined with the measured pH range and soluble lead concentration reported for 30 pump water samples, suggests the lead found on the scale area could exist primarily as hydrocerussite [Pb₃(CO₃)₂OH₂] and with minor possibility as lead carbonate (PbCO₃). From Figure 20, formation of lead oxides (PbO and PbO₂) would only take place at soluble lead concentration of ≥ 10⁷ µg/L in the pH range of 5.7 – 7.9. This could suggest there could be less chances for lead to form oxides in large amount given that the lead concentration in the water from the handpump is much less (≤ 10² µg/L).

The presence of sulphate can control lead release in water by formation of insoluble lead sulphate (PbSO₄) whereas presence of chloride in higher amount would result in formation of soluble lead chloride (PbCl⁺ and PbCl₂) (Ng et al., 2018). The average concentration of sulphate and chloride in the water analysis of 30 samples was found to be 8.6 mg/L and 44.7 mg/L, respectively. Therefore, the average CSMR would be more than 0.5. In order to control lead release, CSMR ratio is maintained below 0.5 (Edwards & McNeill, 2002; Edwards & Triantafyllidou, 2007). This suggests lead could also form complexes with chloride depending on chloride concentration and creating a possibility for lead release in the handpump water.
The concentration of lead can be altered in water through adsorption due to surface complexation. Hematite ($\alpha$-Fe$_2$O$_3$) has been well studied for removal of heavy metals like lead from aqueous solution because of its stable nature. For example, Ali et al. (2020) reported increase in lead adsorption capacity above pH 4.5 due to slow increase in active surface complexation sites of negatively charged OH$^-$ group. Therefore, the adsorption capacity (mg Pb per gm of $\alpha$-Fe$_2$O$_3$)
measured at pH range 4.5 and above at normal temperature (25°C) was 24 mg/g, 25 mg/g and 27 mg/g for three synthesized hematite nanoparticles (Ali et al., 2021). Tamez et al (2016) reported lead adsorption capacity on hematite nanoparticles of 47.63 mg/g at pH 4 and above at normal temperature (25°C) in order to avoid interference with lead hydroxides formation above pH 6 (Tamez et al., 2016). Hashemzadeh et al (2019) reported maximum capacity of lead adsorption on hematite nanorods to be 111 mg/g. The adsorption was found to be dependent on pH, lead ions concentration, hematite nanorod’s weight and contact time (Hashemzadeh et al., 2019). He et al (2011) reported lead ions adsorption on hematite nanoparticles in aqueous solution and at room temperature to be 12.5mg/g (He et al., 2011). Table 5 provides information regarding optimal adsorption capacity of hematite as an adsorbent and lead ion as an adsorbate based on previous studies. Note that synthesized nanoparticles are expected to have a higher surface area and thus a higher adsorption capacity than naturally occurred iron oxides.

Table 5: Binding Capacities of Lead Ions on Synthesized Hematite Nanoparticles.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorbate</th>
<th>pH Range</th>
<th>Binding capacity (mg/g)</th>
<th>Binding capacity (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesized Hematite</td>
<td>Lead ions</td>
<td>pH 4.5 and above</td>
<td>24 mg/g</td>
<td>2.4%</td>
<td>Ali et al., 2020</td>
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<td>12.5 mg/g</td>
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<td>He et al., 2011</td>
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The results from SEM-EDS analysis reported lead present in the scale of the pitcher-pump component to be 4.23% and 6.27% for sample 17F and 3.97% and 25.72% for sample 16F, respectively. The pH of the water from the handpump was in a pH range above 6. Considering the effect of pH, there could be a possibility of combined effect of adsorption and formation of insoluble lead compounds responsible for increase in lead concentration reported in the scale present on the lead components of the pitcher-pump. Furthermore, with increasing pH, active sites of hydroxyl group (OH\(^-\)) on the scale of the lead component increases, enhancing binding of lead ions (Pb\(^{2+}\)) on the scale. Therefore, the lead components with more scale present on its surface will have more hydroxyl groups available for lead ions with increasing pH. Therefore, the reduction in lead release in pump water could be an outcome of surface complexation of lead ions with hydroxyl group causing adsorption on the scale and lead ions forming insoluble hydrocerussite and lead carbonate.
Chapter 5: Conclusions and Recommendations for Future Research

5.1: Conclusions

This research was performed to provide information on the fundamental mechanism(s) that lead to elevated lead levels found in the pump water consumed by peri-urban communities of Madagascar. The pitcher pump system, a type of self-supply, has been the only reliable source of water for communities in the city of Tamatave. The water obtained from the handpump is consumed for drinking as well as cooking. The components of pitcher pump system are locally manufactured using recycled lead acid batteries. The two check valves (foot and piston) of the pump contain lead weights that were found in previous research to be a potential source of lead contamination in the water. An observation of an unknown coating (termed as scale) on the base material of these valve weights (termed as base) was shown to be correlated with lead level in the water (Usowicz, 2019) The following objectives (and associated results) were accordingly developed and addressed as part of this thesis.

1) To determine the composition of valve weights used in the pump.

The composition of based material of the weight that is part of the pitcher pump check valve was confirmed to consist primarily of lead. This confirms the observation made in the field where our research team observed technicians melting down automobile batteries to manufacture the weight component of the pump check valve. Though the Raman results suggested the base to consist of the lead-based mineral, Matlockite (PbClF), more reliable XRF analysis and knowledge of the lead alloy used to manufacture an automobile car battery leads to the conclusion that base
area primarily consists of lead but does not confirm the base to specifically be the lead mineral Matlockite.

2) To determine the chemical composition of the scale observed on the valve weights used in the pump.

The chemical composition of scale on the valve weights was determined using Raman analysis that showed the scale to be hematite ($\alpha$-Fe$_2$O$_3$). The results from XRF and SEM-EDS supported the conclusion that scale was some type of iron oxide though it did not support in all cases that the scale was hematite as concluded from the Raman analysis. Results also supported the presence of some solid phase lead associated with the iron scale.

3) To determine the presence of lead in the scale observed on the valve weights used in the pump.

The XRF analysis of the scale reported variation in concentration of lead in the samples tested. The XRF results reported the presence of solid phase lead associated with the scale that ranged from 7.86 – 88.9%. For example, sample 17F reported 16.69% (by weight) of lead in the scale while sample 20F reported 88.9% (by weight) of lead in the scale. It was also observed that the development and thickness of the scale was not consistent on all samples.

4) To determine the thickness of the scale observed on the valve weights used in the pump.

The SEM analysis was performed to determine the thickness of the observed scale and SEM-EDS analysis was performed to determine elemental composition up to 3 μm. The scale thickness was determined to be uneven on sample 17F and 16F. The scale thickness ranges from 35 (lowest) – 410 (highest) μm.

5) To determine possible interaction between the elements in the surface of the scale observed on the valve weights.
The SEM-EDS analysis reported major elements on the scale to be carbon, oxygen, iron, and lead and minor elements to be mercury and calcium. The presence of lead with the scale is determined to be based on two possibilities. Lead present in the scale is estimated to exist primarily with insoluble hydrocerussite [Pb$_3$(CO$_3$)$_2$(OH)$_2$] and minorly with lead carbonate (PbCO$_3$) based on the reported lead levels in the pump water and examination of solubility diagram for the formation of lead compounds. There is also a possibility of lead adsorption to the iron oxide due to surface complexation with hydroxyl groups present on iron oxide surfaces.

5.2: Recommendations for Future Research

Based on the current and previous studies, the possible presence of a hematite (α-Fe$_2$O$_3$) or some other iron oxide coating on lead valve weights is believed to be important in reducing lead concentrations in pump water. A new study can help to determine the causes and factors affecting natural development of the hematite coating. While previous work has identified the relationship between the scale surface area and lead levels in the pump water, there is a possibility to study the impact of scale thickness on lead leaching found in multiple pitcher pumps. The SEM analysis showed that the scale thickness varied and was measured to be more than 35 μm. In addition, the SEM-EDS analysis performed here was only done to a depth of 3 μm. Therefore, a study to analyze the scale in full profile at a depth greater than 3 μm can be helpful to determine the role of scale thickness and its efficiency to reduce lead leaching. This research has laid foundation to better understand the exact mechanism for the presence of lead associated with the iron scale. That can be further analyzed using analytical methods such as X-Ray Powder Diffraction (XRD) and Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) to confirm the formation of possible solid phase lead compounds associated with the scale (i.e., hydrocerussite and lead carbonate). Furthermore, this research focuses only on soluble lead leaching mechanism and still has a window
to explore if there can be presence of particulate lead in the pump water based on the estimated presence of insoluble lead compounds. In areas where replacement of lead weights is not possible, research on development of iron oxide (e.g., hematite) scale would be helpful to reduce lead in the water obtained from the pitcher pump system. There is further possibility to determine point of zero charge of the iron oxide specific for the water system. This could be helpful to confirm the adsorption capacity of the scale developed on the lead valve weights if surface adsorption is found in later studies to be an important mechanism for lead removal from the aqueous phase.
References


Attina, T. M., & Trasande, L. (2013). Economic costs of childhood lead exposure in low- and middle-income countries. Environmental Health Perspectives, 121(9), 1097–1102. https://doi.org/10.1289/ehp.1206424


https://doi.org/10.1001/jama.1972.03200130065016


https://doi.org/10.1177/1070496517734020

Cao, C. Y., Qu, J., Wei, F., Liu, H., & Song, W. G. (2012). Superb adsorption capacity and...


Chowdhury, S., Mazumder, M. A. J., Al-Attas, O., & Husain, T. (2016). Heavy metals in
drinking water: Occurrences, implications, and future needs in developing countries.  

*Science of the Total Environment, 569–570, 476–488.*  
https://doi.org/10.1016/j.scitotenv.2016.06.166

https://doi.org/10.1089/ees.2015.0073

https://doi.org/10.5942/jawwa.2015.107.0150

https://doi.org/10.5194/bg-5-1295-2008

https://doi.org/10.5942/jawwa.2016.108.0086

https://doi.org/10.1002/(sici)1097-4555(199711)28:11<873::aid-jrs177>3.0.co;2-b

https://doi.org/10.1097/PHH.0000000000000889


green in tea by Raman spectroscopy. *Scientific Reports* (Vol. 5).

https://doi.org/10.1038/srep15729


https://doi.org/10.1002/j.1551-8833.2011.tb11437.x


https://doi.org/10.1071/SR9800061


Sivakumar, T. C., Rice, S. A., & Scéats, M. G. (1978). Raman spectroscopic studies of the OH stretching region of low density amorphous solid water and of polycrystalline ice Ih. *The


https://www.who.int/water_sanitation_health/dwq/fulltext.pdf


https://apps.who.int/iris/bitstream/handle/10665/177752/9789241509145_eng.pdf?sequence=1

World Health Organization. (2012). *Combined global and African ranking -25 country populations with the least sustainable access to improved / clean water sources.*


http://apps.who.int/iris/handle/10665/200168

water, sanitation and hygiene: 2017.


https://www.unicef.org/media/55276/file/Progress%20on%20drinking%20water,%20sanitation%20and%20hygiene%202019%20.pdf


https://doi.org/10.1016/j.watres.2012.02.010


https://doi.org/10.1016/j.watres.2011.09.050


https://doi.org/10.1016/j.envres.2017.05.028

lead-acid batteries. *Procedia Environmental Sciences, 31*, 873-879.

https://doi.org/10.1016/j.proenv.2016.02.103


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