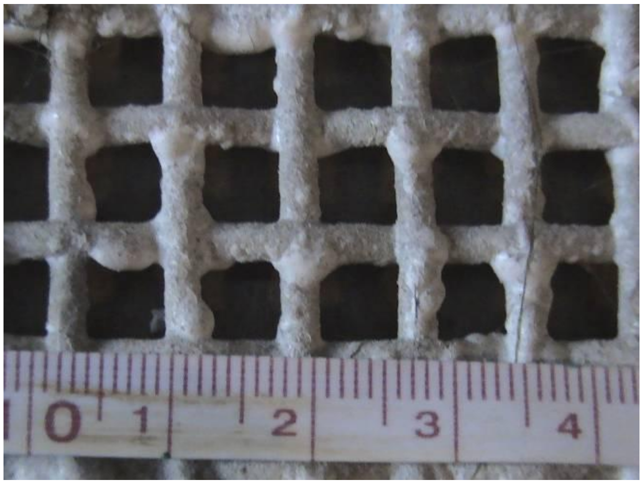
AUTO-ACCRETION POWERED BY MICROBIAL FUEL CELLS IN THE VENETIAN LAGOON



By:
Jessica Balesano
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March 10, 2008

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Executive Summary

Venice, Italy is a city known for its beautiful architecture, culture, and unique lifestyle. What adds to the romance of the city and sets it apart from all of the others are the canals flowing between the different historical buildings. These canals are the natural dividers for the 110 mud flat islands that make up Venice and are the cornerstone for Venetian life. Not only are the canals the main mode of transportation, but they are also the foundation for all of the buildings along the canals. The walls lining the canals are subjected to stresses inflicted due to their location and contact with the canal waters. These walls are deteriorating, leaving weak building structures and an aesthetically unpleasing appearance.

There are many sources of the canal wall damage beyond the mere age of the buildings and materials; one of these sources is moto ondoso, or damage from boat wake. In open waters, the wake from boats can dissipate over a large area. In the canals and narrow waterways in the Venetian lagoon, however, there is less space and opportunity for the kinetic energy of the wave to be reduced before it strikes the canal walls. The impact causes disintegration of the existing wall material and brick mortar. Figure 1 is an example of the damage inflicted by moto ondoso.

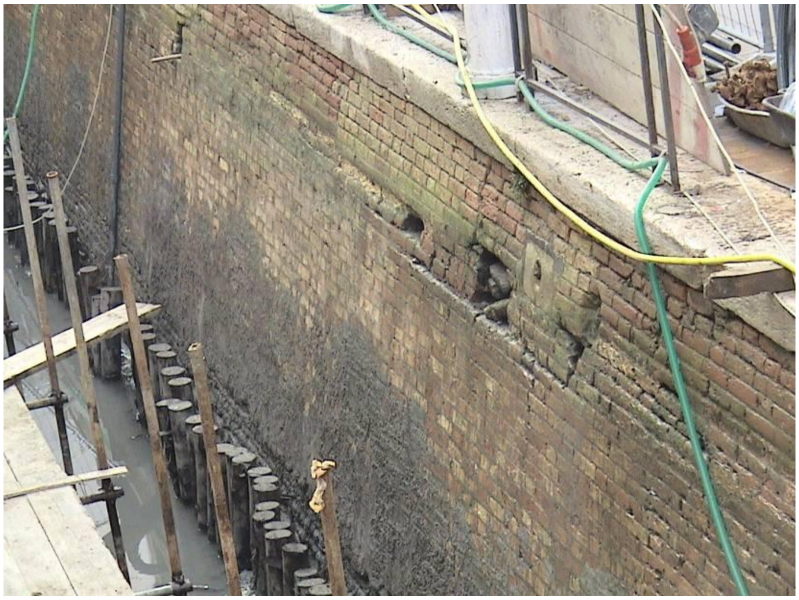

Figure 1: Example of canal wall damage

An ideal solution to the moto ondoso problem would be to form a protective barrier in front of the walls without inflicting damage or alteration in appearance of the canal walls. This protective barrier would absorb the forces from moto ondoso, while ideally, remaining out of eyesight so as to not detract attention from the beauty of the historic city. The Venetian preservation laws require reconstructed walls to mimic the original wall in material and appearance. Therefore, as long as the constructed protective barrier is not part of the original wall, it could be made out of any material and would not add any additional stresses to the wall.

The proposed solution is to form this protective barrier in situ using the minerals present in the seawater flowing through the lagoon and canals. The minerals would precipitate out of the seawater and deposit on a metallic wire mesh, forming a mineral barrier. This wall would be regenerative, meaning that if some of the minerals were removed due to a boat crashing into the barrier, the minerals would build back up in the areas where the thickness was lost. Also, this wall would ideally be a less expensive option to the rigorous and costly maintenance of the canal walls now performed.

Provided there is a medium through which electrons can transfer, such as seawater, there are electron transfer capabilities in all metals. This is due to the galvanic cells, or electrically charged areas, that occur within all metals. When subjected to seawater, the ionic minerals present in the seawater are electro-chemically attracted to these slightly electrically charged areas and form weak ionic bonds with the metal. The minerals are thus precipitated out of the seawater solution as they adhere to the metallic surface. This naturally occurring process is called accretion.

The accretion process can be accelerated by increasing the electrical charge on the metallic surface. This is done by supplying a charge to the metal through an external power supply. Extensive research has been conducted on this topic and many applications are currently in use, such as Seacrete, a producer of artificial coral reefs. Typically, the direct current is supplied to the metal using a battery charger or regulator of some kind that allows the operator to control the amount of current and power that goes to the metal.

The principles of electrodeposition can be used to accelerate accretion by inducing an electrical current. Electrodeposition is the process through which a material, usually a metal, is deposited onto the cathode of a circuit that consists of two electrodes – an anode and a cathode – connected by a power source. The circuit is completed by the electrolyte between the electrodes, as seen in Figure 2. In this case, the electrolyte is the seawater and the seawater minerals are the material that is deposited on the cathode. Additionally, the power supply that drives electrodeposition is a direct current supplier, such as a battery charger.

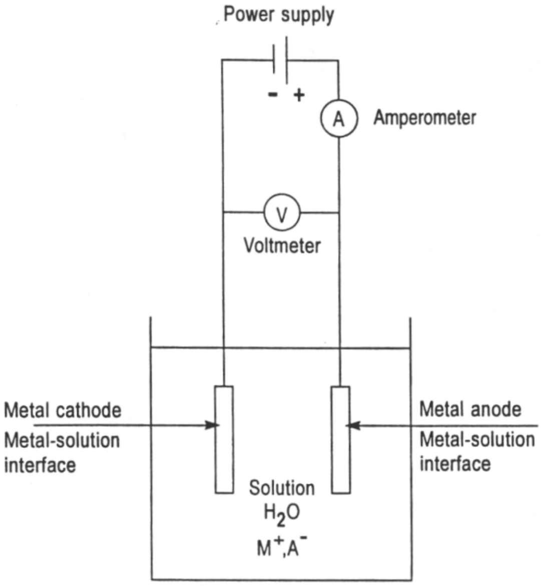

Figure 2: Electrodeposition (From: http://electrochem.cwru.edu/ed/encycl/art-e01-electroplat.htm)

An idea that has not yet been explored is the use of alternative power sources for the acceleration of the accretion instead of the battery charger. This would increase the range of locations where this process could be applied by eliminating the need for a near-by source of electricity. This could also drive the technology of an accelerated accretion process towards the increasingly popular trend of a greener future.

One alternate power source is microbial fuel cells (MFCs). MFCs utilize the naturally occurring process of microbial digestion of organic matter. As microorganisms break down organic matter, such as the wastewater that runs through the Venetian canals, electrons are shuffled through an electron transport chain. These electrons are harvested to induce an electrical current. It is possible to replace the battery charger, which powers electrodeposition, with an MFC to accelerate the rate of accretion. In this case, the current generated by the MFC would be employed to drive the accretion of seawater minerals.

The goal of this project was to determine the feasibility of using MFCs to drive the accretion process to form a protective barrier for the canal walls of Venice. This coupled process, including MFCs and accretion, is referred to as auto-accretion. From this goal, three research objectives were created:

1. Determine the best configuration to maximize the accretion.
2. Determine capabilities of proposed MFC-driven auto-accretion system.
3. Perform an economic analysis on the system.

Methods

To meet these research objectives, a literature review was first done on previously conducted research of electrodeposition, especially that done in seawater, and MFCs. The best configuration for maximizing the accretion of the auto-accretion system was determined based on the limitations of the MFCs. For example, many metals are toxic to the bacteria that drive microbial fuel cells; therefore, only a few metals could be used in close proximity to the bacteria. This is one of the reasons why the anode brush handle was made of titanium. Also, it has been determined that larger anode surface areas yield larger power densities in MFCs, therefore it was important to increase the surface area as much as possible, which was done using anodes in the form of carbon fiber bottle brushes. The distance between the electrodes was also determined through literature review.

To accomplish the second objective, which was to determine the capabilities of the auto-accretion system, we designed and constructed 6 apparatuses, described in Table 1. One apparatus was installed in Connecticut, USA and the other 5 were installed in the Venetian lagoon. There were many controls and validations built into the design of the experiment, which helped to define the six apparatuses. For example, apparatus 2 was a validation for apparatus 1 results, the battery charger and naturally powered apparatuses were controls, and apparatus 5 provided a validation that the results were repeatable in another location. The last apparatus, number 6, was a modified, simplified design that would confirm that the apparatus could not be simplified more than the design of the previous 5.

Table 1: Name and description of apparatuses

Apparatus	Source of Power	No. of bottle brushes	Connection Point of Power	Location
1	MFC	6	Steel plate	Venice, Italy
2	MFC	6	Steel plate	Venice, Italy
3	Battery charger	0	Steel plate	Venice, Italy
4	None (natural accretion)	0	-	Venice, Italy
5	MFC	2	Steel plate	Groton, CT, USA
6	MFC	6	Wire mesh	Venice, Italy

To determine the feasibility of the system, quantifiable data was needed on the accretion and the economics of the project. The monitoring of each apparatus was done by measuring and recording the electrical properties of voltage, current, and resistance. The more important data, however, came from the electrodes, specifically the cathode, when the apparatuses were extracted from the water and analyzed. When this was done, observations about the local environment surrounding and within the apparatuses and about the extensive level of corrosion were made.

The apparatuses' cathodes were analyzed to determine if accretion was produced and to examine the corrosion on the surface. The accretion collected was further analyzed to determine its mass, thickness distribution, elemental composition, and structure. This was done through the use of visual observations, mass balances, scanning electron microscopes, and x-ray diffraction equipment.

An economic analysis was also conducted as one of the final determining factors in the feasibility of running the accretion process off of the power from MFCs. This was important to determine the cost-benefit analysis and to allow comparison with current wall maintenance practices. In order for this auto-accretion powered by MFCs process to be successful and sustainable, the cost had to be less than the current maintenance and the length of time required for the formation of the wall had to be reasonable. The analysis was calculated per square meter using the cost of materials and projected costs of construction and maintenance. These results were compared with those of the current maintenance procedures.

Results & Conclusion

After gathering the data, the analysis was performed and a number of conclusions were drawn. These results included the relationship between the MFCs and voltage, a determination of the accretion composition, and an economic cost-benefit analysis. From the analysis procedures mentioned above, the following data were collected:

- The voltages for the MFC apparatuses shared a general trend, as shown in Figure 3. The difference was in the peak voltage time, in which case, the Connecticut apparatus took approximately 30 days longer to reach its peak value. The difference in water temperature, thus microbial activity, was identified as the likely cause of this.

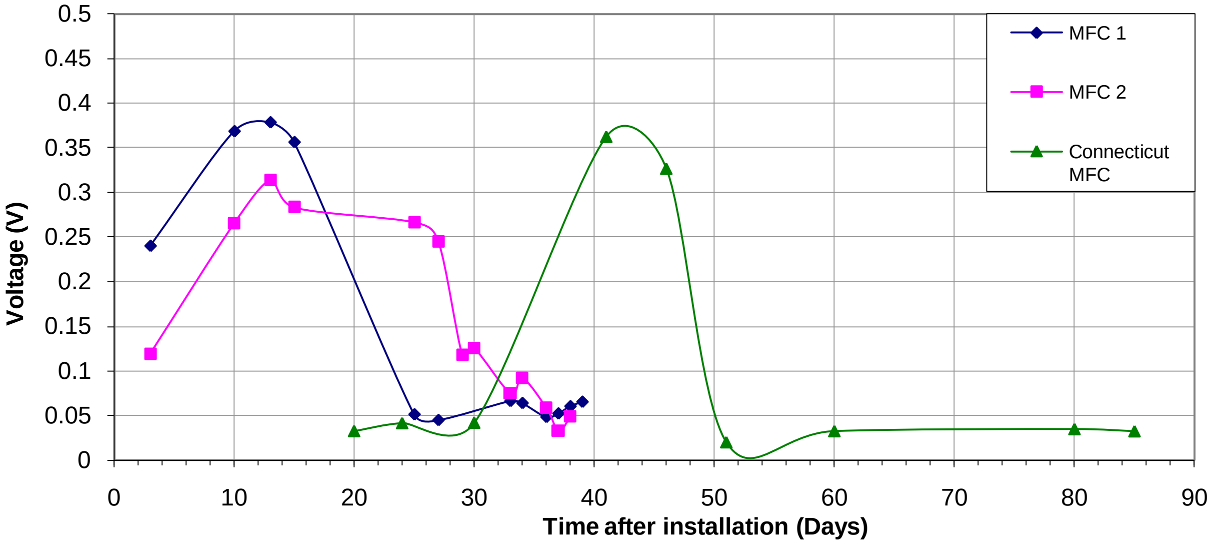

Figure 3: Voltage readings from MFC powered apparatuses

- Accretion thickness was greatest around the edges of the cathode.
- The MFC powered-apparatuses experienced accelerated accretion rates compared to the control and direct connect apparatuses, but were a mere fraction of that of the battery charger powered apparatus.
- The accretion composition differed between samples and apparatus cathodes. Figure 4 summarizes the general trends found.

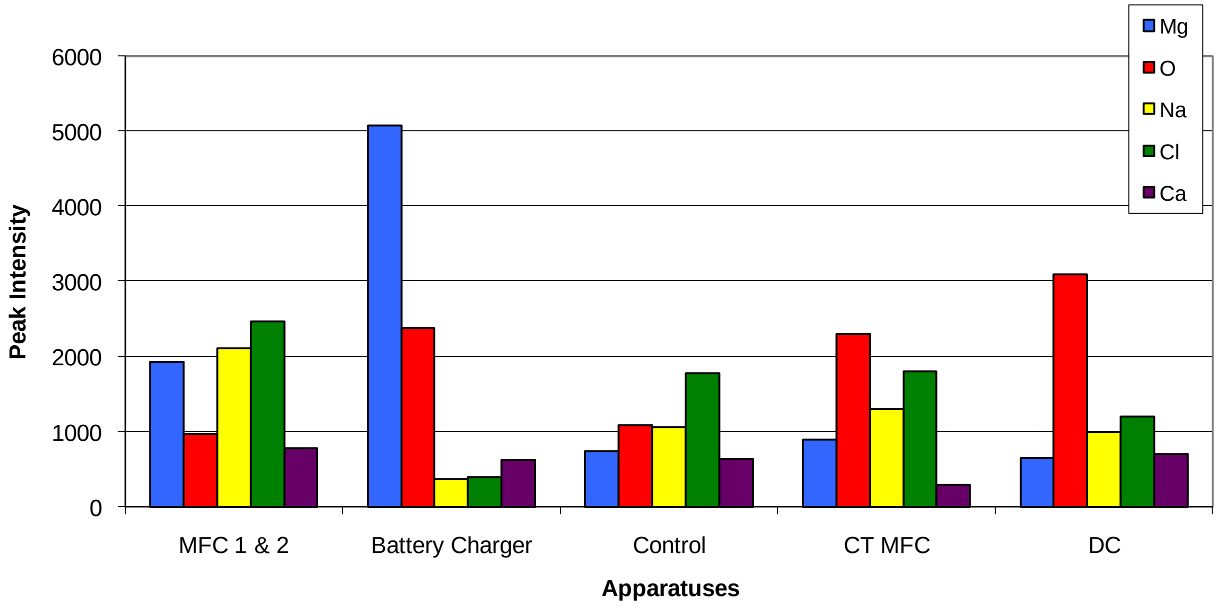

Figure 4: Relative accretion compositions

- Brucite, $Mg(OH)_2$, was the main compound in the accretion sample from the battery charger powered apparatus, as determined by x-ray diffraction.

- The expected relationship between the anode surface area and voltage was not achieved. Voltages achieved in Connecticut and Venetian apparatuses shared the same trends and approximate peak and steady state values. This was hypothesized to result from the surface areas used being too close to the asymptote of the surface area to power density relationship curve.

- Corrosion was a major factor that was extremely underestimated. The design of the apparatus allowed for small galvanic cells to be created at each of the connection points of the electrodes, especially on the anode steel plates, which drew some of the potential current from the cathode. The specific types of corrosion that were faced included the reduction of the stainless steel protection and crevice corrosion, which was a product of water trapped under the silicon that was meant to seal the electrical connections.

- There was an apparent increase in wildlife near and within the apparatuses in Venice, but no clear change in or near the apparatus in Connecticut. It was determined that this was most likely a result of the shelter and protection that the basket frame in Venice provided. Conversely, the more open frame used in Connecticut did not have the same protection, and so did not have a higher density of wildlife surrounding it.

- The economic analysis resulted in the following cost data:

  - Current canal wall maintenance costs - $189 to $4,766 per square meter of wall for small to average sized canals and $11,680 per square meter of wall for large canals
  - Cost of auto-accretion process
    - Capital investment - $698 per square meter of wall
    - Yearly maintenance cost - $240 per year
    - Minimum time required for process – 35 years
  - Battery charger powered option
    - Capital investment – $512 per square meter of wall
    - Yearly maintenance cost – $144 per year
    - Minimum time required for process – 3 months

- Conclusion: While an acceleration in the accretion rate was achieved from the auto-accretion process, the economic analysis clearly defined the need for further technological development before this system can be a feasible option to the moto ondoso problem within the Venetian canals.

Recommendations

From these results and conclusions, 10 recommendations were developed for further research. These include:

1. Validate the high concentration of halite, NaCl.

2. Conduct experiment over a longer period of time which spans a few meteorological seasons in the Venetian waters.

3. Alter anode connections. Suggestions include:

    - Changing the material of the brush handle from platinum to another metal that can be physically connected to the steel plate.

    - Replacing the steel plate with a solid block of carbon fiber.

4. Optimize ratio of anode brush surface area to induced current between electrodes.

5. Optimize distance between electrodes.

6. Optimize shape for force absorption. There are two alterations to the current design's overall shape that should be investigated:

    - Changing the frame supporting the electrodes.

    - Changing the overall shape of the electrodes.

7. Evaluate potential use of other power sources.

8. Evaluate the operation of a jump-started apparatus maintained by a MFC.

9. Determine affects of bio-coating anode brushes pre-installation.

10. Explore issues of cultural acceptance from local citizens.

A full copy of this report can be obtained by contacting Dr. David DiBiasio, WPI – Department of Chemical Engineering, or Dr. Fabio Carrera, WPI – Interdisciplinary and Global Studies Division, or from the WPI website.

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AUTO-ACCRETION POWERED BY MICROBIAL FUEL CELLS IN THE VENETIAN LAGOON

A Major Qualifying Project Report:

Submitted to the Faculty of

WORCESTER POLYTECHNIC INSTITTUE

In partial fulfillment of the requirements for the

Bachelors Degree in Chemical Engineering

by

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March 10, 2008

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Abstract

The canal walls in Venice, Italy are eroding, largely due to moto ondoso, or impact forces from boat wake, and the corrosive seawater. Ideally, a protective barrier would exist in front of the walls to shield them from erosion caused by moto ondoso. The primary focus of this project was to determine the feasibility of using microbial fuel cells to power the acceleration of seawater mineral accretion on metallic surfaces to form a protective barrier for the canal walls. Accretion, or the accumulation of minerals on metallic objects submerged in seawater, is a naturally occurring process which can be enhanced by an induced current. Microbial fuel cells generate current by harnessing the electrons produced by the microbial digestion of organic material. To test the feasibility of driving the accretion process using the current generated by microbial fuel cells, various experiments were performed in the Venetian lagoon and off the Connecticut, USA coast. While accretion was formed despite many of the worst-case conditions, an economic analysis concluded that the process was not yet economically feasible. Further research, however, has the potential to bring the auto-accretion process into an economically beneficial venture for many of the waters even outside of Venice.

Authorship

While both persons were responsible for the material, each had various areas of focus.

Jessica Balesano became proficient in microbial fuel cells, and drafted much of the introduction, background, conclusions, and economical analysis sections of the paper.

Jodi Lowell focused more on the materials and corrosion aspects, executive summary, abstract, results, and recommendations sections, and formatting of the paper.

Both shared the writing of the methodology and the outlines for each of the sections, and were the main editors of each other's work.

Acknowledgements

We would like to acknowledge all of the people who assisted in the success of this project. Without their guidance and support, it would have been impossible to achieve as much as we did. Thanks.

- Professor David DiBiasio – WPI Chemical Engineering Department
- Professor Fabio Carrera – WPI Interdisciplinary and Global Studies Division
- Daniela Pavan – Venetian logistical support
- Boquan Li – WPI Materials Department
- Doug White – WPI Goddard Hall Machine Shop
- Professor Richard Sisson – WPI Director of Material Science and Manufacturing Engineering
- Professor Janine Plummer – WPI Department of Environmental Engineering
- Felicia Vidito – WPI Chemical Engineering Office
- Turner Cabaniss and UCONN-Avery Point campus – hosting an apparatus
- Davide Tagliapietra – Istituto di Scienze Marine
- The faculty, staff, and students of the WPI Chemical Engineering Department
- The various people who were kind enough to help us find our way through Europe to Venice

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Abbreviations

EPV	Electro-potential voltage
MFC	Microbial fuel cell
PVC	Poly-vinyl chloride
SEM	Scanning electron microscope
SS	Stainless steel
UCONN-AP	University of Connecticut – Avery Point campus
XRD	X-ray diffraction

1.0 Introduction

Venice, Italy is a unique city with unparalleled splendor. It is a city known for its beautiful architecture, distinguished culture, and celebrated art; however the characteristic that makes Venice clearly distinct from everywhere else in the world are its canals. Venice is a city that stretches across 110 islands in the Venetian Lagoon. This collection of islands is separated by waterways that are called canals. The canals are vital to the way of life in Venice. To the Venetians, the canals are synonymous with the roads of other cities, serving as the main avenues for transportation.

A major issue the city of Venice is faced with is the degradation of the canal walls. As the canal walls deteriorate, not only is the structural stability of the buildings lining the canals compromised, but the mobility of the city is halted as the major routes for transportation are in dire need of repair. Damage to the canal walls is caused by continual contact with the corrosive seawater, by pollutants in the seawater, and by biological life that feeds on the walls; however, the main cause of erosion to the walls is moto ondoso, or boat wake. As boats move through the canal water, they continually produce wake, or waves that crash into the canal walls causing friction. Over time, this friction leads to erosion of the canal walls. Because the canals are an integral part of life in Venice, it is essential to ensure that the canals are functional and that their condition is satisfactory. Thus, the canal walls constantly require maintenance to protect them from the destructive forces of erosion (Chui, Jagannath, & Nodine, 2002). The mudflats in the lagoon, which are called the barene, also suffer from the effects of moto ondoso, and require protection from erosion. Also, because of the historical preservation laws in place in Venice, there are strict guidelines for the reconstruction and repairs of canal walls. Repairs can be made with the purpose of improving safety; however the overall structure and characteristics of the walls cannot be changed. This puts restrictions on the maintenance of the canal walls (F. Carrera, personal communication, February 28, 2008).

Currently, maintaining and repairing the canal walls is an extremely expensive and time intensive process. This existing method of repairing eroded canal walls is dredging. When canals are dredged, they are drained, or a small section of the canal is drained, and the walls are manually repaired. The maintenance that occurs while a canal is dredged typically takes six months, and thus the canal or a section of the canal cannot be used during that time. This is a serious inconvenience to boat traffic and transportation throughout Venice, and this type of canal maintenance is very costly. The city of Venice spends about thirty million dollars per year on canal repairs (Black, Migdal, Morin, Rene, & Vitello, 2008). Additionally, the barene is protected from erosion by wooden pilings which line the mudflats; they are inserted deep into the lagoon floor directly in front of the mudflats. This process is also time consuming and very expensive for Venice.

Ideally, a protective barrier in front of the canal walls would shield the walls from moto ondoso. The protective barrier would be in the form of a sacrificial wall made of seawater minerals that are readily available in the canal waters. This could be accomplished by combining two processes: accretion and microbial fuel cells (MFCs). Accretion is the accumulation of minerals on metal submerged in seawater. It is a naturally occurring process that can be enhanced by increasing the electric charge of the metal. If metallic wire mesh was inserted into the canals in front of the walls, then slowly, over time, a build-up of seawater minerals would form on the mesh, creating a sacrificial wall. This natural accretion would take an extremely long time, on the order of hundreds of years, to yield a protective barrier that would actually be effective in reducing the erosion of the canal walls. Due to the fact that it is possible to accelerate the rate of accretion by increasing the charge of the metal, a source of electricity could be used to induce a current and charge the wire mesh, thus assisting in the more rapid generation of a sacrificial wall. One source of electricity that is readily available is microbial fuel cells.

A microbial fuel cell has the ability to produce current by converting chemical energy to electrical energy. Microbes are present in abundance in the sediment at the bottom of the canals. As these microbes break down organic matter, or as they digest the wastewater, they produce energy in the form of free moving electrons. An MFC harnesses these electrons, allowing it to generate a current. MFCs are comprised of an anode and a cathode; the anode must be placed in contact with the microbes because it is the component that harnesses the electrons from the microbes. Thus the anode must be submerged in the sediment, and in this system, the cathode is the wire mesh lining the canal wall that receives the electrons harnessed by the anode. The process of using the current generated by MFCs to accelerate the rate of accretion is called the auto-accretion process.

The auto-accretion process could be used in Venice to form a protective barrier in front of the canal walls and barene. Ideally, this process would produce a protective barrier of seawater minerals thick enough to combat the erosion caused by moto ondoso in a reasonable time frame. The sacrificial wall created would be regenerative, so as the wall begins to erode it will automatically repair itself by the accretion of additional minerals. Therefore, this process will require little maintenance and will be a less expensive option for Venice than the current methods of canal wall maintenance. Also, the system would be completely underwater (i.e., not visible), and consequently, would not conflict with any of the preservation laws in place in Venice.

The main goal of this project was to determine the feasibility and practicality of applying the auto-accretion process to Venice to protect the canal walls and barene from erosion. In order to accomplish this goal, it was necessary to determine methods to maximize the rate of material build-up using the auto-accretion process, to establish the capabilities of this process, and to examine the economic impact of this process. To achieve this, small scale auto-accretion systems were designed and installed in the lagoon of Venice, Italy and off of the Long Island Sound in Connecticut, USA.

2.0 Background

In order to determine the practicality of applying the auto-accretion system to protect the Venetian canals from erosion, in depth research has been conducted into relevant subject matters. Thorough research has been conducted on the individual processes that combine to form the auto-accretion process. These processes include accretion, electrodeposition, and microbial fuel cells. Additionally, to determine the scope of the problem, the reasons for the deterioration of the canal walls have been examined, along with the costs of maintaining them.

2.1 Accretion

Accretion is the accumulation of minerals on metallic objects submerged in seawater. This accumulation is a result of salts precipitating onto the surface of the metal caused by the galvanic behavior of the metal. Accretion is a naturally occurring process that is extremely slow; however it can be enhanced by an induced electric current. An example of naturally occurring accretion can be seen when viewing a shipwreck that has been underwater for many years. As seen in Figure 5, a layer of minerals has begun to build-up on the shipwreck.

Figure 5: Example of accretion on a ship wreck (From: http://voyage.pierwisconsin.org/Titanic/Titanic%20bow%20railing.jpg)

The salts that precipitate out of the ocean in the accretion process are comprised of chemicals that are commonly found in seawater. The relative chemical composition of seawater can be seen in Table 2 (Lee, 2001). Table 2 indicates that accreted matter is made mostly of sodium, chlorine, magnesium, oxygen, and calcium. Accreted matter is known to be composed of brucite

($Mg(OH)_2$), aragonite ($CaCO_3$), and sodium chloride or halite (NaCl) (Lee, 2001). Brucite is a mineral with a hexagonal crystal system, density of 2.37 g/cm3, and hardness of 2.5 (on a Moh's scale of 1 to 10 with talc=1 and diamond=10). Aragonite is a mineral with an orthorhombic crystal system, density of 2.83 g/cm3, and hardness of 3.5 on Moh's scale (Lide, 1996).

Table 2: Chemical comprising seawater (Lee, 2001)

Compound	Amount (g /L)
NaCl	23.9849
Na_2SO_4	4.0111
KCl	0.6986
$NaHCO_3$	0.1722
KBr	0.1000
$B(OH)_3$	0.0254
NaF	0.0029
$MgCl_2$	5.0290
$CaCl_2$	1.1409
$SrCl_2$	0.0143

The composition of the ocean is relatively consistent everywhere, varying very little with respect to location (Lee, 2001). The salinity, or relative concentration of salts dissolved in the water, was relatively equivalent for both locations where the experiments were conducted, so that would not be a major factor for any differences in results (Lide, 1996; Aimo, Della Sala, Stradella, Tagliapietra, & Vazzoler, 1999). Both locations of apparatus placement were protected from the open ocean in a lagoon surrounding, but were not subjected to stagnant water. One difference in the locations was the water temperature. For the times that the experiment was conducted, the Connecticut area averaged about 10˚C, whereas the Venetian waters were closer to 15˚C (Aimo et al., 1999; Ltr_1003, 2008; Ltr_1103, 2008; Ltr_1203, 2008; Ltr_0104, 2008).

The ideal current to be used for the formation of accreted matter is considered to be equal to or less than 1.83 A per square meter of anode surface area. There are several reasons for using currents of this magnitude. When matter is accreted using currents above 1.83 A/m^2, the composition of the matter is mostly brucite deposits ($Mg(OH)_2$) rather than aragonite deposits ($CaCO_3$). Aragonite is much harder than brucite and aragonite is therefore desired in the accreted matter. Also with low currents, accreted matter forms more slowly and is denser and stronger than when it is formed quickly (Lee, 2001).

2.2 Electrodeposition

Electrodeposition is the process by which a layer of material is deposited on a cathode through a current-induced electrical attraction. The process requires two electrodes - an anode and a cathode - a source of electricity, and an electrolyte all arranged in a circuit as shown in Figure 6. The electric current necessary to drive the electrodeposition is supplied by an external source connected to the two conductive electrodes. The electrolyte, the ionic fluid between the two electrodes, completes the electrical circuit, thus allowing the electrons to cycle around the open loop creating a current. The current produced by electrodeposition greatly increases the rate of accretion.

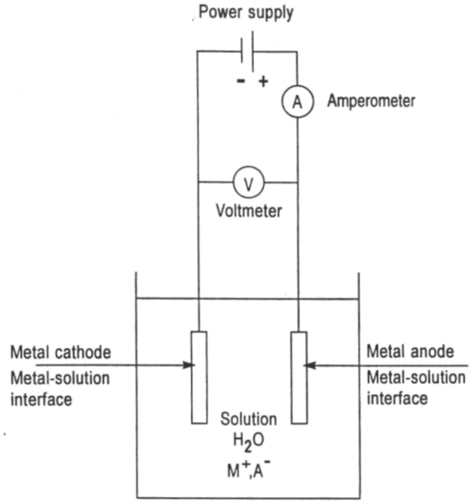


Figure 6: Schematic of electrodeposition set-up (From: http://www.intactlabs.com/index.php?t=applications&x=mfc)

When metal electrodes are submerged in seawater for an extended length of time, corrosion effects must be considered. Corrosion is a product of oxidation-reduction reactions that occur between a metal and a medium. It is caused by the instability of metals in their processed forms, and the natural tendency to revert back to the metal’s natural state. For example, iron is found naturally in various forms of iron oxide. Processed iron metal has the oxide ions extracted from the ore in order to produce more desirable material properties. When exposed to water, however, the iron reverts back to its naturally favorable entropy state of iron oxide (*Corrosion in Action*, 2003).

The selection of the anode plate and cathode mesh focused on the material properties of various metals. Stainless steel was deemed the best option for both the anode plate and cathode mesh because of the corrosion resistance provided by the nickel and chromium additives to plain carbon steel. The higher the nickel and chromium concentrations are in the steel, the greater the corrosion resistance. Another consideration involved the Galvanic Series index, which orders various metals according to their electrical potentials and defines which metals will corrode faster than the others.

2.2 Microbial Fuel Cell

A fuel cell is a device that converts chemical energy stored in a fuel into electrical energy. It produces electricity by harnessing electrons as they move from a high energy chemical reactant bonds to low energy chemical product bonds. A microbial fuel cell uses the energy produced by the oxidation reactions of microorganisms, or microbes.

2.2.1 Microbes

Microbes are microscopic organisms, including bacteria, protists, and fungi. They are classified as organisms that are too small to be seen by the naked eye, typically ranging in size from a micron to a few millimeters. Throughout its normal live cycle, a microbe undergoes microbial metabolism, which is the way a microbe is provided with the nutrients and energy it needs to survive. Metabolism occurs through metabolic pathways. A metabolic pathway is a network of reactions that break up or synthesize proteins, biochemical products, and other chemicals. The reactions involved in a metabolic pathway are driven by an enzyme, which serves as a catalysis for the process (Bansal, 2000). The metabolic pathway is the means of producing energy in a microbe by the network of reactions that results in the movement of electrons to a final electron acceptor (O'Malley, 2003).

The most common way energy is produced in microbes is through the break down and resynthesis of adenosine 5'-triphosphate, or ATP. Energy is made available as ATP breaks down to adenosine diphosphate, ADP, and orthophosphate, P_i. It is possible for this energy to be used a chemical work, transport work, or mechanical work. The following reaction shows the breakdown of ATP:

$$\text{ATP} + \text{H}_2\text{O} \rightarrow \text{ADP} + \text{P}_i$$

This reaction is exergonic, which means it has a negative Gibbs free energy (ΔG^o) indicating that the reaction will release energy. In other words, this reaction produces free energy, which can be used to promote the competition of an endergonic (energy using) reaction; in the case of this project, the free energy could be intercepted by the anode of a microbial fuel cell for the purposes of driving accretion (Prescott, Harley, & Klein, 2005)

2.2.2 MFC Structure and Design

A microbial fuel cell usually consists of two electrodes, an anode and a cathode, which are separated into compartments by a semi-permeable membrane. The anode compartment contains a medium comprised of microbes. This compartment also houses the substrate and, if present, the mediators. The compartment that holds the cathode contains a medium of electron acceptors. The electrons given off when the microbes metabolize the substrates are captured by the anode and are then transferred through the electrical circuit to the cathode (Gil et al., 2003). Figure 7 shows a diagram of a general microbial fuel cell. In this diagram, the methylene blue is the medium consisting of microbes, the yeast cells are the microbes, the glucose is the substrate, and the potassium hexacyanoferrate is the medium containing electron acceptors.

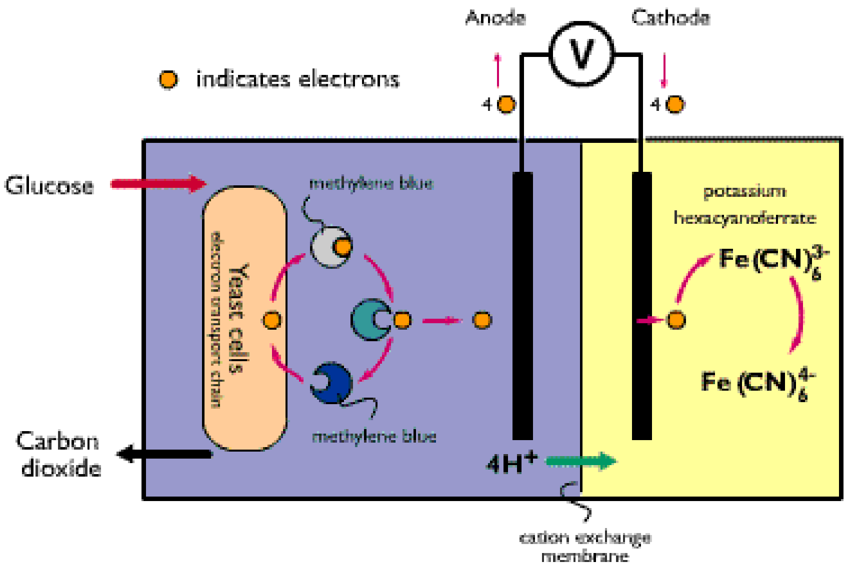


Figure 7: Typical microbial fuel cell (O'Malley, 2003)

2.2.3 Maximizing MFC Current

The amount of current, or flow of electrons, is dependent on the type of microbes and substrates present and more importantly, the configuration and design of the fuel cell, including the materials of the electrodes. For this project, which consists mainly of practical field experiments in Venice, the type of microbes and substrates will not be able to be controlled. Thus, the focus is set more on manipulating the structure and materials of the MFC in order to maximize the current. Although MFCs are a newer technology, some conclusions have been drawn on how to maximize the current potential, including conclusions about electrode surface area, material, and spacing, as well as the temperature of the environment.

Previous experiments have proven that an electric current can be generated through a modified microbial fuel cell with the anode submerged in sediment. These experiments show that about 0.01 Watts of electrical power can be produced per square meter of anode surface area (Bond, Holmes, Tender, & Lovely, 2002). Many previous studies have determined that increasing the surface area of the anode will in turn increase the current produced by the MFC. These studies include those conducted by Logan, Rezaei, and Kim and their colleagues (Logan et al., 2006; Rezaei, Richard, Brennan, & Logan, 2007; Kim et al., 2002). One study done by Kim et al. shows the effects of increasing the anode surface area of an MFC on the Coulombic yield, or the proportion of electrons transferred. Anode surface areas between 0 and 60 cm^2 were examined (Kim et al., 2002). Figure 8 shows the relationship between anode surface area and the Coulombic yield found in this study. It clearly indicates that as the surface area increases, the electron transfer also increases. Therefore a simple way to increase the current potential of the MFCs in this project is to increase the surface area of the anodes. Additional studies have shown that to increase current generation of an MFC, multiple smaller anodes should be used rather than one larger anode. Also the surface area of the cathode should never be larger than the surface area of the anode; the cathode area should be roughly equal to or less than that of the anode (Logan et al., 2006).

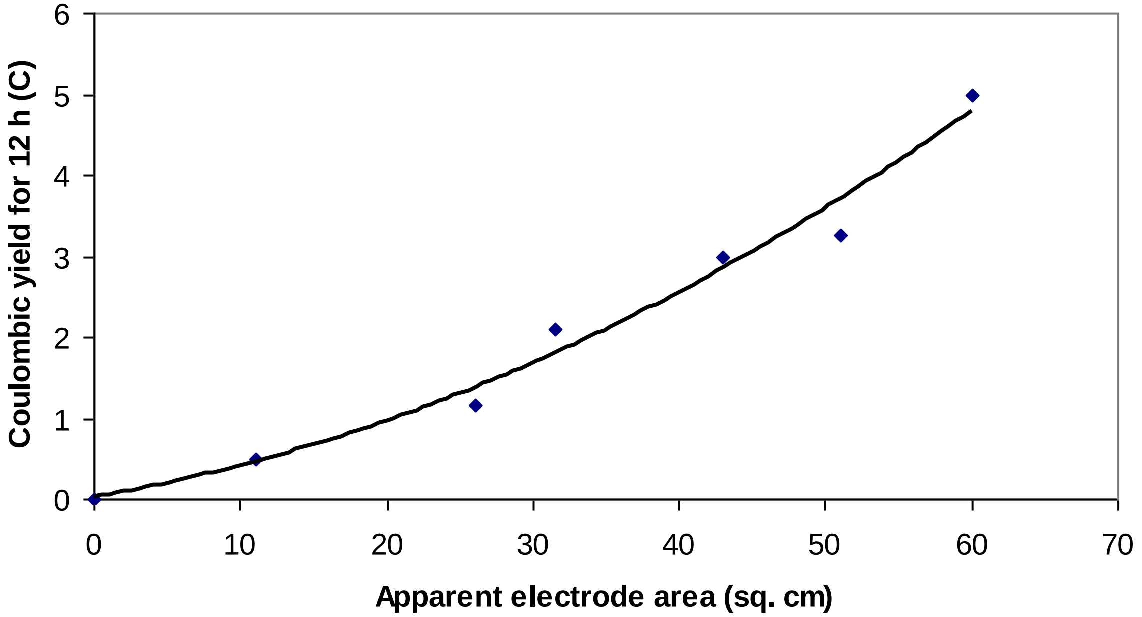


Figure 8: Relationship between electrode surface area and Coulombic yield in a microbial fuel cell (Kim et al., 2002)

The material of the electrodes is an additional design variable that can influence the current produced by an MFC. Other than being conductive and relatively non-corroding, the material used for the cathode has very few limitations. On the other hand, the material selection for the anode is the deciding factor on the rate of accretion and is thus more crucial. The material of the anode is also important because it is the limiting factor of an MFC. It is important for the anode to be conductive, non-corrosive, bio-compatible, have a high reduction potential, and be chemically stable in the reactor solutions, which for the case of this project is seawater. The anode materials used most commonly are carbon, copper, and steel. Copper cannot be used in MFCs because it is toxic to bacteria and would therefore harm the microbes. Of the common anode materials, carbon is the most versatile. Carbon anodes could take the form of graphite plates, rods, or granules, or of fibrous material such as cloth, felt, foam, or fibers. The current potential of a carbon anode increases with the internal surface area of the carbon. Carbon fiber has the greatest internal surface area followed by carbon felt and foam, while graphite has the least (Logan et al., 2006). Therefore carbon fiber bottle brushes were selected as anodes for this project. As previously stated, maximizing the surface area of the anode is an important aspect of this project, and the use of fibrous bottle brushes allows for the area to be maximized within a small volume of space, thus making the design of the MFC more practical. Further justification for this selection can be seen in the research of Logan, Cheng, Watson, and Estadt (2007), who achieved the highest power density produced by an MFC using carbon fiber bottle brushes.

Also certain operating conditions, such as electrode spacing and seawater temperature, can affect the amount of power generated by microbial fuel cells. Changing the operating conditions of an MFC could potentially increase its power density significantly. A decrease in the distance between the anode and the cathode will result in an increase in the power generated by the fuel cell. An experiment conducted by Liu, Cheng, and Logan (2005) on the power generation of microbial fuel cells has shown that as the distance between the anode and cathode decreased from 4 cm to 2 cm, the power generated increased from 720 mW/m^2 to 1210 mW/m^2. Thus to produce the maximum amount of power, the anode and the cathode should be placed as close to each other as possible while still being able to ensure that there is no physical contact between the two electrodes.

The temperature of the seawater where the microbial fuel cell is located, also affects the power generation of the fuel cell. Below 30°C, power generation begins to decrease as the temperature decreases. A temperature decrease from 32°C to 20°C has resulted in a 9% loss of power by the fuel cell (Lui et al., 2005). Therefore, if the MFC is operated at higher temperatures, its capability for producing current would be greater than if operated at low temperatures. This implies that the ideal time to use MFCs to power accretion in the Venetian canals would be during the summer months, when the water is warmest. However due to the time limitations of this project, it was necessary to conduct experimentation during the colder winter months.

2.3 Combining Accretion and MFCs

The goal of this project was to combine the technology of accretion enhanced by the current produced by the technology of MFCs. This process is called auto-accretion, and its principles are similar to that of electrodeposition, with the exception that the source of electricity comes from the MFCs.

A modified microbial fuel cell was used for the purposes of this project. A modified microbial fuel cell is a simpler version of the generic microbial fuel cell. The modified version does not contain any mediators and is used most frequently in seawater or wastewater. When this fuel cell is submerged in seawater, the anode is embedded in sediment containing microbes, and the cathode is placed in the seawater a short distance from the anode. Figure 9 shows a schematic of the microbial fuel cell that has been used in this project. This design allows the current produced by the MFC to drive the accretion of matter on the cathode, instead of solely generating power, which is the purpose of most fuel cells. The goal of this project was to maximize the amount of accretion forming on the cathode. To maximize accretion it was necessary to maximize the current produced by the MFC. This was done by manipulating certain design variables of the MFC, like the distance between electrodes.

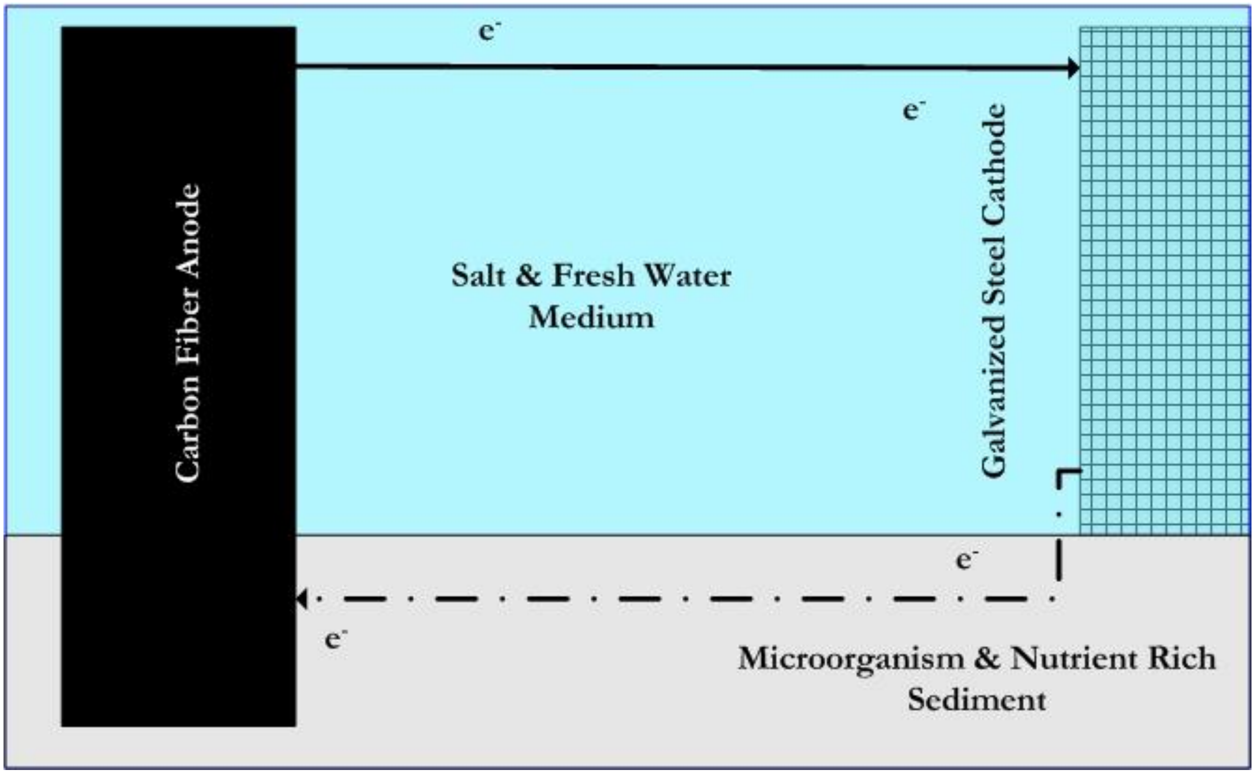


Figure 9: Modified microbial fuel cell (O'Malley, 2003)

2.4 Venetian Canal Walls

Venice is a collection of islands separated by waterways which are referred to as canals. The canals are essential to the way of life in Venice. To Venetians, the canals are equivalent to the roads of other cities, and they serve as the main avenues for transportation. Over time the walls of the canals erode and deteriorate, and since the canals are such an integral part of life, it is necessary to maintain them. Canal maintenance can be very costly, so it would be beneficial for Venice to explore ways to minimize canal wall damage.

The canal walls are made of mainly two different materials: Istria stone and brick. The lower part of the canal walls are constructed of Istria stone and the rest is made of brick. Istria stone does not allow for much corrosion because it is nonporous and thus does not allow water to penetrate it. Brick, however, is porous and corrodes easily. The major damage to the canal wall occurs in the area constructed of brick. When the canal walls are repaired, the damaged areas are filled with concrete. Additionally, concrete is used to reinforce the bottom portion of the canal walls.

When the canals were first built, only the portion of the canal walls constructed of Istria stone was under water. Since 1897, however, the water level in the canals and lagoon of Venice has risen 23 centimeters, and now a brick segment of the wall is submerged in seawater. Therefore, because the porous brick is exposed to the corrosive seawater, damage occurs to the canal walls more frequently. The canal walls serve as a foundation for most of the buildings in Venice. When the canal walls corrode, the structural stability of the buildings is compromised and the buildings' foundations begin to deteriorate upward from the canal walls. This is an additional reason that the maintenance of the canal walls is vital to the city of Venice (www.insula.it).

2.4.1 Canal Wall Damage

Canal wall damage occurs when the physical and mechanical properties of the walls become altered. There are many causes of canal wall deterioration including exposure to the corrosive seawater and the pollutants present in the seawater, biological materials that live in the canals, and boat traffic, and moto ondoso. The erosion caused by exposure to the seawater has been discussed in the previous section, Section 2.4 Venetian Canal Walls. Biological materials present in the canals, such as algae, fungi, and bacteria, eat away at the stone that the canal walls are comprised of resulting in damage to the walls. Also sometimes the boats that travel through the canals collide with the canal walls creating a hole in the wall. These holes allow seawater and pollutants into the walls which further damages the walls. One of the major causes of canal wall deterioration, however, is moto ondoso.

Moto ondoso is deterioration of the canal walls due to boat wake. Wake is the turbulence caused by a solid body moving through water. As a motor boat moves through the water, the spinning of its propellers create turbulence, or wake. The waves generated by the wake collide with the canal walls producing friction and resulting in the erosion of the canal walls. Moto ondoso does not normally create a problem because most bodies of water that experience heavy boat traffic are large enough for the turbulence to disperse. However the canals have limited area for the dispersion of turbulence, and therefore moto ondoso has a considerable impact on the walls. The intensity of boat wake is dependent on the size of the boat, the shape of its hull, the size of the propeller, the load it is carrying, the area of water it is traveling through, and the speed it is traveling at. One of the reasons that moto ondoso is such a large problem in Venice is that the boats traveling through the canals almost never comply with the set speed limits. The speed limit is 5 kilometers per hour; however the average speed of boats is over 12 kilometer per hour. As a result, the wake produced by these speeding boats is greater and much more damaging to the canal walls than it would be if the speed limits were obeyed (Black et al., 2008).

The canal walls of Venice are continuously subjected to the force of water crashing into them. Moto ondoso is the major contributing factor to the erosion of the canal walls, and therefore is a principle reason for the need for constant maintenance of the walls. If the erosion caused by moto ondoso were to be reduced, the total need for continual repairs would also be reduced, which would in turn save the city of Venice a great deal of money.

2.4.2 Canal Maintenance

Canal maintenance has been performed in Venice since before 1797. However with the recent introduction motor boats over the past thirty years, it has become increasingly important to perform more regularly scheduled repairs to the canal walls. In 2006, the Venetian government budgeted 35 million euros ($51.1 million) for canal maintenance. However in 2007, only 5 million euros was budgeted. Thus even though canal maintenance is important, its level of funding changes drastically from year to year. Insula s.P.a is an agency in Venice devoted to ensuring the canals are maintained, and it was formed in 1997 by the City Council for this purpose.

A major project that Insula is currently working on is “The Integrated Canals Project.” All of the canals have been classified as different priority levels, and the main focus of this project is to repair the canals that most urgently need maintenance. The repairs include dredging the canals and restoring and lining the canal walls. Insula has estimated that it will cost approximately 1,213 million Euros to complete this project (Black et al., 2008).

There are two methods of canal wall maintenance used in Venice, as seen in Figure 10. The first is called dry dredging, and it is used to repair smaller to average canals. During dry dredging the canals are completely drained of all water and the walls are manually repaired as the canal is dredged. This process typically takes six months to complete, during which time the canals are unusable. The average cost of dry dredging canals ranges from $189 to $4,766 per square meter of canal wall. The second method of canal wall maintenance is called the vertical maintenance procedure. This procedure is used to repair large and frequently traveled canals because they cannot be dredged all at once without causing extreme delays in transportation. In the vertical maintenance procedure a small portion of the canal is sectioned off relatively close to the wall so that boats are still able to pass. This section is then drained and the canal wall is repaired. The average cost of this procedure is about $11,680 per square meter of canal wall (Black et al., 2008).

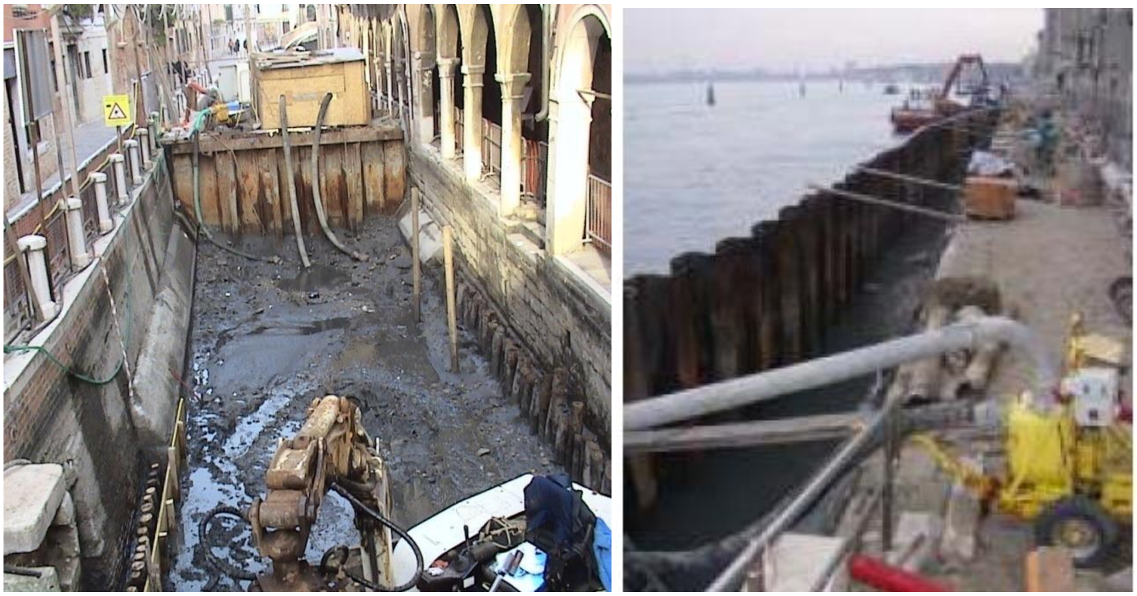


Figure 10: Canal wall maintenance procedures: dry dredging (left), vertical maintenance procedure (right; Black et al., 2008)

Similarly to the canal walls, the barene is facing the problem of erosion due to moto ondoso. The lagoon is comprised of many islands and mudflats called the barene. To protect the barene from erosion, the mudflats have been lined with wooden pilings. The wooden pilings are driven deep into the floor of the lagoon along the outer edge of the barene. This process is very costly and time intensive.

3.0 Methodology

In order to accomplish the goal of determining the feasibility of the auto-accretion system as a solution to the moto ondoso problem, the three research objectives were addressed. First, the best configuration was determined through background research, then field testing was conducted using the best configuration to establish the capabilities of the auto-accretion system, and finally an economic analysis examined the cost-benefit aspect to this process. The field testing included one longer-term experiment conducted in Groton, Connecticut, USA and multiple short-term experiments conducted in the lagoon of Venice, Italy. The materials used and construction procedure differed between the two locations due to the availability of materials.

3.1 Apparatus Construction

A major focus of this project was the materials selection due to the significant effect that it was projected to have on the accretion rate. The materials selected were chosen for their potential optimization of the MFC configuration, relative economic benefit, and practicality. The method for constructing the apparatuses included many accommodations for the various difficulties found along the way.

3.1.1 Material Selection

The materials used for the apparatus construction were chosen for their physio-chemical properties and their availability in the local marketplace. The frame for the Connecticut apparatus as shown in Figure 11, for example, was made from poly-vinyl chloride (PVC) piping due to the wide-availability, low cost, and electrically insulating properties of the PVC piping and fittings. Also, it has high tensile strength properties, relatively no corrosivity in salt water, and was fairly lightweight. A primer and cement specified for PVC applications was chosen to bind the various pipes and fittings together. The dimensions of the frame were determined by the size of the electrodes that were secured inside of it.

Figure 11: Assembled frame for Connecticut apparatus

The material used for the Venetian apparatuses' frames was a common plastic in the form of a laundry basket, see Figure 12. The high-strength plastic laundry basket was also widely available and reasonably inexpensive in Venice, relative to the cost, availability, and irregular angles of the PVC piping and fittings. It also shared the PVC's insulating, non-corrosive, and lightweight properties, yet did not require any assembly or binding agents.

Figure 12: Laundry basket frame for Venetian apparatuses

The electrodes were chosen using the detailed results from various published scientific pieces of literature, as discussed in section 2.0 of this report. The effect of different materials on the accretion rate, amount of accreted matter, or the amount of current produced was studied and compared. It was apparent that the anode material was the most crucial aspect to the electrode design, whereas the cathode material had less impact on the results. The cathode material was often stainless steel, which was a reasonable selection because of its low corrosivity in turbulent-moving salt water, ranging between 4 ("Good. Suitable when superior alternatives are uneconomic") and 5 ("Good to excellent") on a scale of 1 to 6, but not very applicable for slow moving or stagnant water in which the corrosivity of stainless steel ranged between 1 ("Poor to fair") and 2 ("Fair. For mild conditions or when periodic replacement is possible. Restricted use") on the same 1 to 6 scale (Perry & Green, 1997). It was assumed that the water would be turbulent in most canals and waterways in the lagoon, given the daily tides and moto ondoso conditions in the canals. Another option would have been to use Ni-Resist Corrosion resistant cast iron or 14 percent silicon iron, both with corrosivities of 5 (on 1 to 6 scale) for stagnant and turbulent seawater (Perry & Green, 1997). However, these metals were more difficult to obtain and due to the higher costs, not a practical choice given the assumption of turbulent water conditions in the canals and lagoon.

The anode material that produced the highest amount of accreted matter over time was carbon fiber, or graphite. The previous auto-accretion research that was conducted by Christopher O'Malley (O'Malley, 2003) used carbon fiber blocks, and many researchers have documented using carbon fiber sheets (Logan et al., 2007). However, with the advances in MFC technology, Logan and colleagues was able to increase the power density significantly by using carbon fiber in the configuration of bottle brushes, demonstrating the practicality of the bottle brushes versus carbon cloth or graphite granules (Logan et al., 2007). By having strands of carbon fiber strung into a bottle brush, the amount of surface area was maximized, and thus, more electrons could be collected from the degradation of organic waste. The electrons collected by the carbon fibers in the bottle brush would then flow through the titanium brush handle and mechanically connected copper wire to the anode stainless steel plate. Titanium was used for the brush handle because of its low electrical resistance ($39x10^{-8}$ Ωm at standard 20˚C) in comparison to other materials (Lide, 1996), extremely low corrosivity in salt water (rating 6: Normally excellent on 1 to 6 scale), and most importantly, that it one of three metals that does not incur microbiological damage (Perry & Green, 1997). The last property was the most important because the metal would be in constant direct contact with microorganisms.

The stainless steel anode plate was used to provide a more even transfer of electrons from the anode to the electrode. Stainless steel again was chosen for its corrosivity and electro-potential voltage (EPV) properties. The stainless steel plate was connected to the other part of the anode, the bottle brush, by copper wire. Copper has a low internal resistivity (1.7 μΩ cm) (Lide, 1996) and is fairly inexpensive (about $0.25/foot of insulated multi-strand copper wire), making it an optimal choice for the wiring between the anode brush and plate and the testing leads from the electrodes that allowed for measurements to be taken. One point of concern with using copper is the high oxidation rate which is amplified in current-flowing conditions. To overcome this, copper wiring with pre-coated insulation was used and the exposed copper areas on the wires were coated with silicon, a non-conducting insulator.

Finally, all of the smaller components to the apparatus were chosen for their electrically non-conductive properties. For example, for the Connecticut apparatus, two pieces of wood, an insulator material, were used to secure the bottle brushes and were clamped together using plastic (also an insulator) screws and wing nuts. For all apparatuses, plastic zip ties were used to attach the pieces of the electrodes – the cathode wire mesh, anode plate, and wood securing anode brushes (Connecticut apparatus) – to the PVC frame. Lastly, non-conducting sand or rocks were used to weigh the frame down so that it would sink and remain relatively stationary in the water. A non-metallic material was used for the rope that was attached to the frame. All of these non-conducting materials were used so as not to draw any electrons away from the cathode.

3.1.2 Materials and Construction of Connecticut Apparatus

The long-term microbial fuel cell-powered apparatus was placed in the alcove of the University of Connecticut-Avery Point (UCONN-AP)'s dock, seen in Figure 13. The apparatus design was finalized and constructed employing common supplies available in the United States. The construction also occurred prior to the assembly of the Venetian apparatuses, and thus, many design aspects, such as the attachment of the anode bottle brushes, were first attempted on this Connecticut apparatus.

Figure 13: Location of UCONN-AP (Courtesy of Google Earth)

<u>Materials</u>

Apparatus frame
- PVC piping and fittings
- PVC primer and cement

Electrodes
- Carbon fiber bottle brushes
- Stainless steel anode plate
- Stainless steel wire mesh
- Wood
- Plastic bolts and wing nuts
- Metallic bolts, washers, and wing nuts
- Copper wire
- Electrical connector caps
- Silicon

Other
- Zip ties
- Sand
- Rope

Procedure

Apparatus frame

1) Obtained PVC pipes and cut to appropriate lengths:
   a) 2 x 17.5” (44.45 cm) Bottom long pieces
   b) 2 x 24” (60.96 cm) Top long pieces
   c) 4 x 9” (22.86 cm) Bottom and top short pieces
   d) 4 x 13.5” (34.29 cm) Vertical pieces
   e) 2 x 1.5” (3.81 cm) Compensation for different fittings not aligning

Figure 14: Dimensions for Connecticut apparatus frame

2) Obtained the proper fittings:
   a) 6 x 90-degree elbows
   b) 10 x Ts
   c) 2 x removable caps

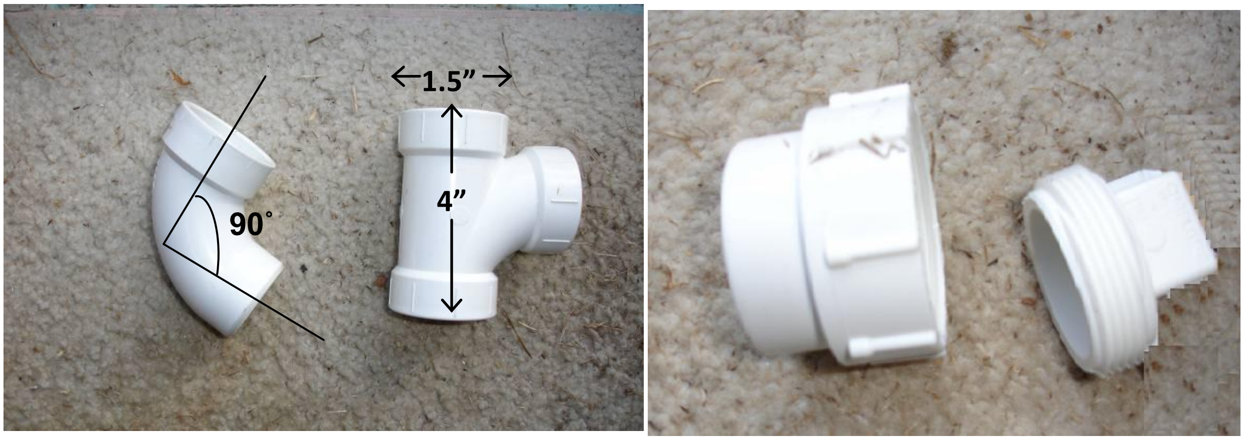


Figure 15: Fittings for Connecticut apparatus frame (from left to right: 90-degree elbow, T, removable cap)

3) Assembled apparatus as shown in Figure 16, making sure to apply primer and cement to the PVC pipes and fittings that made contact with each other.

Figure 16: Final PVC piping frame for Connecticut apparatus

Electrodes – Anodes

4) Obtained two carbon fiber bottle brushes, copper wire, electrical connector caps, pieces of wood, bolts, washers, and nuts (plastic and metallic), silicon, and a 12” x 18” (30.48 x 45.72 cm) stainless steel plate of a known mass.

5) Connected copper wire to titanium end of bottle brush by removing some of the insulation on the wire to expose the copper. Wrapped the copper around the brush handle starting at the tip of the handle and wrapping in the direction towards the carbon fibers and with the direction of the connector caps screws. Screwed on electrical connector caps. Filled cap and exposed copper wire with silicon.

6) Obtained slender, approximately 17” (43.18 cm) long piece of wood and sliced it approximately in half in the long direction. Clamped two pieces of wood together as if the wood was not sliced apart and bored two ¾” (1.91 cm) in diameter holes in the middle of the split. The depth of these bored holes correlated with the distance between the bottom of the carbon fibers on the brushes and the tops of the electrical connector caps. Unclamped pieces of wood and inserted 1 brush into each hole with the electrical caps within the bored out area and carbon fibers resting flush on the whole pieces of wood. Secured pieces of wood together by screwing plastics bolts and wing nuts together as tightly as possible.

7) Drilled 12 holes into stainless steel (SS) plate – 4 for connection to frame, 2 for wire connection from anode brushes, 1 for measurement leads that run to the surface, and 5 for electrode spacers. See Figure 17 for location of holes.

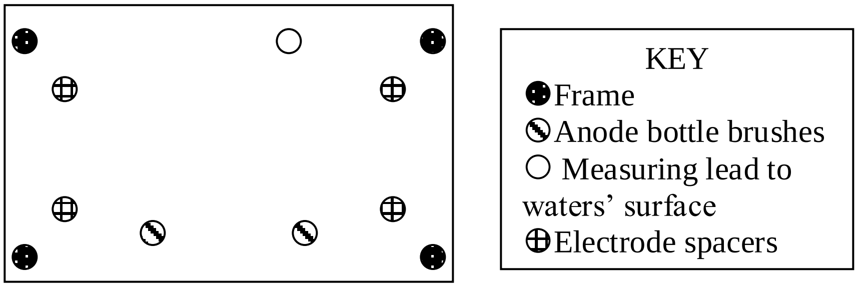
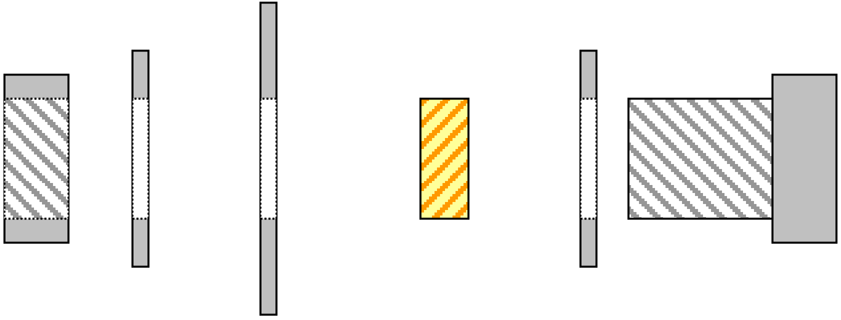


Figure 17: Anode plate holes and connection points for Connecticut apparatus

8) Connected copper wire from bottle brushes and measuring lead to the waters’ surface to anode plate using metallic bolts, washers, and wing nuts according to Figure 18.



Nut – Washer – SS plate – Copper wire – Washer – Bolt

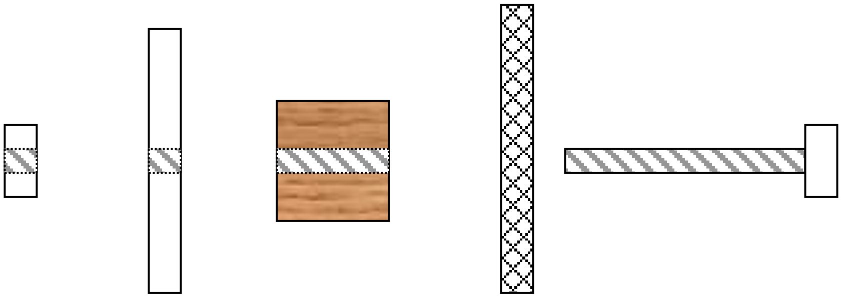
Figure 18: Configuration of wire connections to anode plate

Electrodes – Cathodes

9) Connected copper wire from the measuring lead to the waters’ surface to cathode wire mesh using metallic bolts, washers, and wing nuts according to Figure 18 but with the wire mesh instead of the SS plate. This connection was not directly next to an electrode spacer but was towards the top of the wire mesh. The bolt was short enough that just a little was beyond the nut and was wide enough that it would not slip through the openings in the mesh.

Electrodes – Electrode connection

10) For construction of spacers, cut 1” (2.54 cm) thick spacers from wooden dowel. Drilled a pilot hole through the center. Connected electrodes according to Figure 19.



Plastic nut – SS plate – Wood spacer – Wire mesh – Plastic bolt

Figure 19: Configuration of electrode connection

Assembly of components

11) Drilled holes large enough for zip ties to pass through into the middle of the horizontal frame pieces. Then connected zip ties from the frame to the electrodes in a way such that the electrode plates were suspended approximately in the center of the frame.
12) Connected the pieces of wood supporting 2 brush anodes securely to the frame using zip ties.
13) Up-righted and supported the frame so as to not damage the brushes dangling off of the bottom of the frame. Funneled sand into the pipes through the opened caps.
14) Securely tied rope around the top face of the frame.
15) Slowly lowered the apparatus into the water, keeping it as level as possible while allowing it to sink naturally as the air trapped inside the frame slowly escaped through the holes drilled for the zip tie connections. Exercised caution so as to not drop the measuring leads from the electrodes.
16) Noted that the apparatus sat on a hill, probably with some rocks nearby it. Secured ropes to dock in a manner that held the apparatus upright. The following day, a diver removed rocks from nearby area, repositioned apparatus so it laid flat on sea floor, and ensured brushes were submerged in the sediment.
17) Secured measuring leads to dock and ensured that the measuring leads were not in contact with each other.

3.1.3 Materials and Construction of Venetian Apparatuses

When beginning to obtain the materials necessary to build the apparatuses in Venice according to the original design, a few problems arose. These problems led to slight variations in the design of the Venetian apparatuses. The largest change in the configuration was the frame to which the plates and wire meshes were attached. In Venice, PVC pipes were sold either with fittings built onto the ends of the pipes and required adapters for all fittings-to-fittings connections, or the PVC pipes had straight ends and required an expensive tool to melt the plastic pieces together. The use of the PVC pieces that required the tool to melt the pieces together was eliminated as an option early in the deliberation stage of obtaining equipment due to the high expense of the tool and the piping that it accompanied. Another problem that arose was that all of the angles of PVC pipes found in Venice were 87.5˚, not 90˚ like the standard in the United States to which the design was based upon. Due to the difficulty of forming a cubic structure using 87.5˚ angles, the high expense of the piping, and the need for more and expensive fitting-to-fitting adapters, the use of local Venetian PVC piping and fittings was impractical. Although it was considered, the option of ordering the needed parts and having them shipped to Venice was both economically impractical and time-consuming. Therefore, other alternatives were explored and laundry baskets were deemed acceptable replacements.

Five apparatuses were placed in the Venetian lagoon off of a dock on the island of Lazzaretto Nuovo, located at the pinpoint in Figure 20. All five were different according to the functions of the apparatus. As discussed later in the methodology section, the five Venetian apparatuses included two MFC powered, one battery charger powered, one non-powered, and one MFC powered apparatus with a direct connection between the anode brushes and the cathode plate, thus eliminating the electro-deposition aspect. The arrangement and configuration was as similar between the five apparatuses and that of the one in Connecticut as possible.

Figure 20: Location of Lazzaretto Nuovo (Courtesy of Google Earth)

<u>Materials</u>

Apparatus frame
- Large laundry Basket

Electrodes
- Carbon fiber bottle brushes
- Iron-steel anode plate
- Stainless steel wire mesh

- Rubber stoppers
- Metallic bolts, washers, and wing nuts
- Zip ties
- Copper wire
- Electrical connector caps
- Silicon

Other
- Rope
- Zip ties

Procedure

Apparatus frame

1. Obtained 5 laundry baskets, as shown in Figure 12.
2. Determined and marked location for anode brushes, electrode plates, and rope attachments.
3. Drilled holes into ends of laundry baskets to allow for more flow throughout the basket.
4. Drilled holes for anode brushes and rope attachments.
5. Removed an equal amount of the bottom of the laundry basket from each of the apparatuses directly beneath the electrode plates and as far to the ends of the basket as possible to allow for the movement of water and sediment underneath the baskets. The parts of the bottom of the laundry basket that remained were the end with the anode brushes and a small part on the opposite end in order that rocks could rest on it to weigh the apparatus down. For consistency, all of the baskets were modified identically. See Figure 21.

Figure 21: Modified laundry basket

Electrodes – Anodes

6. Obtained 18 carbon fiber brushes, copper wire, rubber stoppers, electrical connector caps, bolts, washers, nuts, silicon and silicon gun, and four 30 cm x 30 cm iron-steel plates.
7. Rubber stoppers of approximately 1 cm in thickness were pushed onto the end of the titanium handle of the brushes. This was to compensate for the approximately 0.5cm lip on the bottom of the basket and to decrease the amount of movement the brushes could do once they were attached to the bottom of the baskets.

8. Holes were drilled into the four steel plates as shown in Figure 22. The measurements are to the center of the drilled holes.

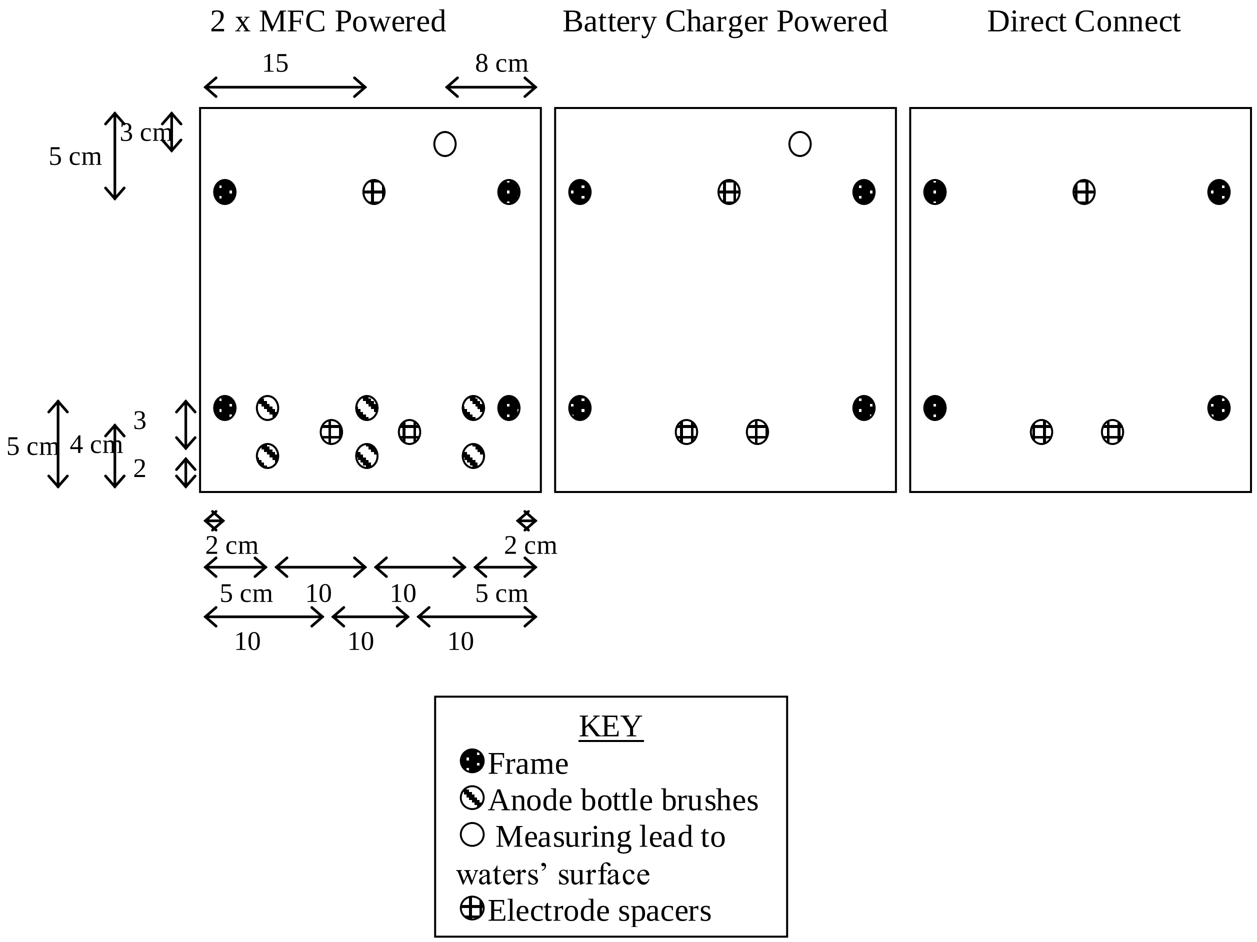


Figure 22: Anode plate holes and connection points for Venetian apparatuses

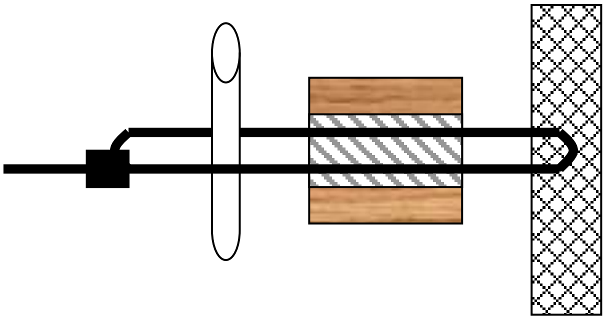
9. Determined masses of the 4 plates.

Electrodes – Cathodes

10. Obtained 5 cathode wire mesh plates of known individual masses from the United States.

Electrodes – Electrode connection

11. Cut twelve 3cm spacers - 3 spacers for each of the 4 anode plates. Drilled a pilot hole through the center and connected the anode and cathode plates using zip ties as shown in Figure 23.



Zip tie around: Plastic tubing – Wood spacer – Wire mesh

Figure 23: Configuration of electrode connection for Venetian apparatuses

Assembly of components

The final assembly occurred on-site on the dock of Lazzaretto Nuovo due to the complications of carrying 5 completed apparatuses around the streets of Venice.

12. Divided the 18 anode bottle brushes evenly among the two MFC and one direct connect apparatuses, equating to 6 brushes for each of those three apparatuses. Attached the brushes to the apparatus baskets as shown in Figure 24.

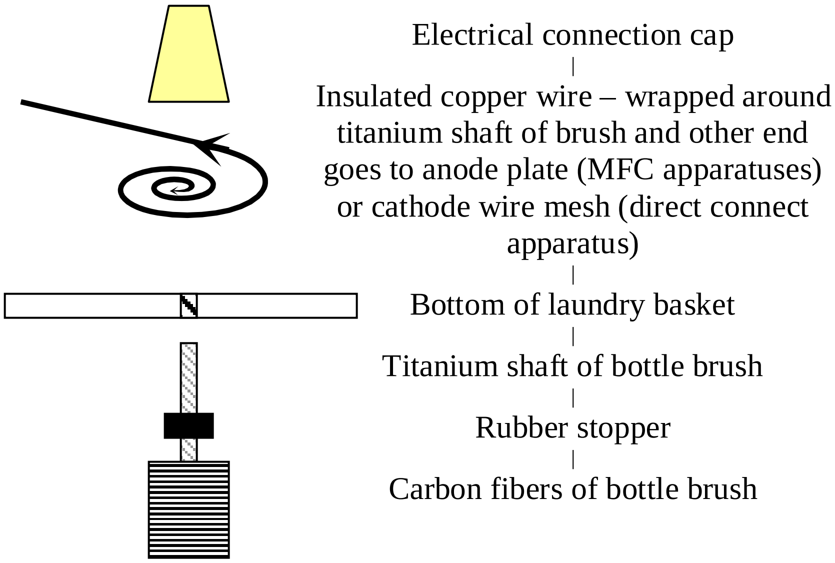


Figure 24: Connection of anode brushes to basket

13. Secured the electrode plates to the baskets using the pre-fabricated holes on the sides of the baskets and zip ties. All of the plates were secured to the same holes in the different baskets for consistency.
14. Attached the insulated copper wires connected to the anode brushes to the anode plate using bolts, washers, and nuts as shown in Figure 18.
15. Attached separate insulated copper wire to the test connections on both of the electrode plates on the MFC and electricity-powered apparatuses.
16. Applied a thick layer of silicon wherever there was a metal-metal connection, especially all wire connections.

17. Threaded rope through the pre-drilled holes of the baskets and formed a loop on either side of the basket. Tied a single rope between the two loops with enough rope left on the end to ensure it would be long enough at the unknown depth. Burned the ends of the ropes to prevent fraying and unraveling of the strands.
18. Obtained bricks with one hole off to one end of the brick from around Lazzaretto Nuovo. Drilled another hole at the other end of the brick.
19. Secured brick to the insides of apparatuses using zip ties, as shown in Figure 25.

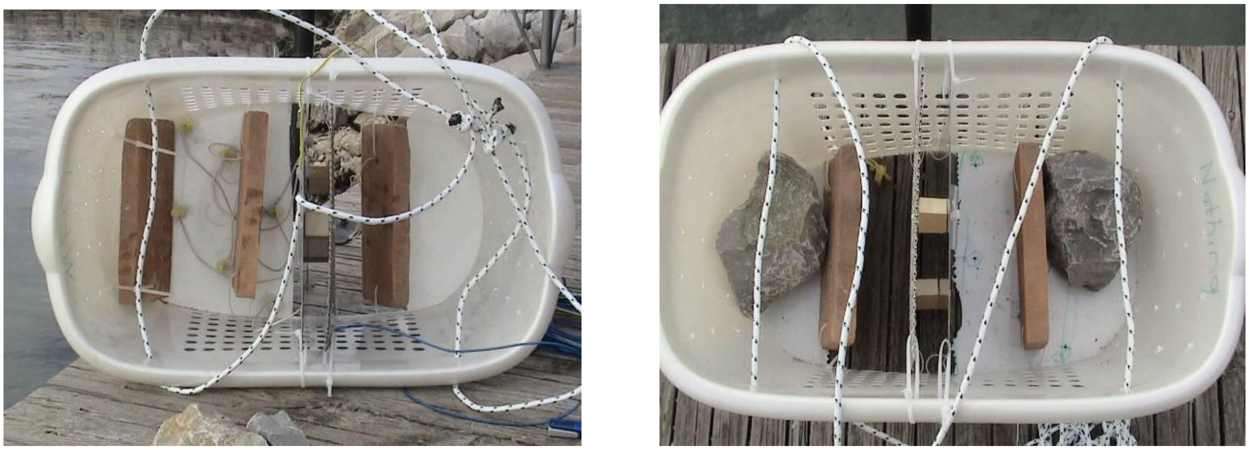


Figure 25: Bricks secured inside MFC & direct connect apparatuses (left) and control & electric apparatuses (right)

20. Acquired rocks to ensure the apparatuses sank and remained stationary once dropped in the water.
21. Placed rocks in between the bricks and the ends of the laundry baskets, taking care not to damage the bottle brushes attached to the MFC and direct connect apparatuses.
22. In Venice, divers could not be used to reposition apparatuses if they did not lie flat on sea floor due to the unsanitary conditions of the water. Thus, we lowered a crate of similar size to the laundry baskets and filled with rocks down to the sea floor in the location and orientation of the apparatuses prior to the actual apparatuses being set into position. This determined if the floor was flat enough and void of rocks.
23. Slowly lowered each apparatus into the water, allowing it to sink as naturally as possible. It was ensured that the apparatuses landed in the appropriate configuration of having the electrode plates parallel with the flow of the water as much as possible. Caution was exercised not to drop the measuring leads from the electrodes into the water.
24. Ropes and measuring leads were secured to the nearest piling as inconspicuously as possible. Caution was taken to ensure that the ends of the measuring leads were not in contact with each other.

3.2 Maintenance Procedure

The apparatuses installed in the Venetian lagoon went through an overhaul maintenance period once, except twice in the case of MFC 1 apparatus. The maintenance was performed when there was evidence of a problem with the apparatuses, as noted by the undesirable an inexplicable change in the electrical readings. The second maintenance was performed only on the MFC 1 apparatus because the others were taken out of the water as the experiment was deemed complete. It was considered unnecessary to re-run the other apparatuses since sufficient data was recorded on these during the first experiment. However, to obtain more MFC powered auto-accretion results, the apparatus was restarted with a fresh wire mesh cathode. The first maintenance overhaul, from time the apparatuses were taken out of the water to the time they were re-lowered into the water, was completed within 3 days. The second maintenance overhaul on MFC powered apparatus 1 was completed in 2 days due to an increase in maintenance proficiency and that it was the only apparatus that was repaired, instead of 5 as done in the first overhaul.

The first step in completing all of the repairs was to clean out all of the sediment and sea life that had accumulated in the apparatuses, making observations about the condition of the electrodes and local environment within each of the apparatuses. The next step was to remove all of the silicon from the various electrical connecting points. Then, for the MFC powered apparatuses including the direct-connect apparatus, the electrical caps were unscrewed and the debris inside removed. The copper wires were stripped to reveal untarnished copper. The silicon was removed from the other end of the copper wire that was attached to the anode plate, in the case of the MFC powered apparatuses, or the wire mesh cathode, the direct-connect apparatus. The corroded washers, nuts, and bolts were removed and replaced with new equivalents. The copper wire on that end was also stripped to reveal fresh, non-corroded copper. Next, the corroded washers, nuts, and bolts from the test wires were replaced, and the copper wire testing lead was also stripped to the point of revealing fresh copper. The apparatuses were then reassembled as described in the assembly procedure. All of the electrical connecting points were then resiliconed and the apparatuses were set aside, covered for protection from the elements, for approximately 24 hours to allow the silicon to dry. The apparatuses were then re-lowered into their original locations and the electrical readings continued.

The MFC powered apparatus in Connecticut was not repaired due to a few factors. The foremost factor being that this experiment occurred simultaneously to the Venetian experiment and the human inability to be in two places at one particular time. While readings were recorded from the Connecticut apparatus by a third party, it was impractical for this party to make the repairs. Also, as noted when the apparatus was finally taken out of the water, the corrosion was not significant enough to warrant the repairs done on the Venetian apparatuses.

3.3 Installation

The primary objective of this project was to determine the feasibility of applying an auto-accretion process to form protective barriers for the canal walls in Venice, Italy. To accomplish this, five apparatuses were installed relatively close to each other off of the island Lazzaretto Nuovo in the lagoon of Venice and one apparatus was installed in the waters in Groton, Connecticut, USA. These apparatuses had varied configurations and were run off of different power sources.

3.3.1 Experimental Setup

Six apparatuses were used in this experiment. Table 3 summarizes those apparatuses.

Table 3: Name and description of apparatuses

Apparatus	Source of Power	No. of Bottle Brushes	Connection Point of Power	Location
1	MFC	6	Steel plate	Venice, Italy
2	MFC	6	Steel plate	Venice, Italy
3	Battery charger	0	Steel plate	Venice, Italy
4	Nothing (natural accretion)	0	-	Venice, Italy
5	MFC	2	Steel plate	Groton, CT, USA
6	MFC	6	Wire mesh	Venice, Italy

Apparatus 1 and apparatus 2 were powered by microbial fuel cells. They were constructed according to the procedure outlined in Section 3.1 Apparatus Construction. Apparatus 3 was powered by a 12-Volt battery charger located out of the water and was constructed in a similar manner to the Venetian MFC powered apparatus. While the frame, wire mesh cathode, and steel plated were constructed and configured in the same way for both apparatuses, the battery charger powered apparatus did not have any carbon fiber anodes attached to it. Instead, the battery charger with insulated copper wires connected to it at both the positive and negative ends powered the accretion process. The wire attached to the positive end of the charger was mechanically connected to the anode, or steel plate, with a screw, two washers, and a nut, as detailed in Section 3.1. The wire attached to the negative end of the battery charger was mechanically connected to the cathode, or the wire mesh. The mechanical convention was chosen to describe the electrical connections. In this convention electricity flows from the positive to the negative end. Apparatus 4 was powered by nothing but the natural accretion process. The design of this apparatus was similar to the design of the previous three apparatuses. All of these four had the same frame, wire mesh, and steel plate configuration; however, apparatus 4 was not connected to a battery charger and did not utilize carbon fiber anodes. The construction of apparatus 5 is explained in Section 3.1.2 Materials and Construction of Connecticut Apparatus. Apparatus 6 had the same frame as the apparatuses 1-4, however the configuration of electrodes differed. The design of apparatus 6 had the six carbon fiber anodes connected directly to the wire mesh cathode by insulated copper wires and did not incorporate a steel plate anode.

Apparatuses 1 through 4 and apparatus 6 were installed in the Venetian lagoon off of the island Lazzaretto Nuovo and apparatus 5 was installed in the waters of Groton, Connecticut, USA. The MFC 2 and direct connect apparatuses installed in the Venetian lagoon remained submerged for a duration of 36 days, the battery charger powered and control apparatuses for 35 days, MFC 1 for 28 days, while the apparatus in Groton remained under water for a period of 85 days – more than twice as long as any of the Venetian apparatuses. Data about the voltage, current, accreted matter, and the surrounding water conditions of the apparatuses were measured and recorded in the manner described in Section 3.3.2 Data Collection Method.

3.3.2 Data Collection Method

In order to assess and analyze the information generated by this project, it was necessary to establish a specific data collection method to monitor and record the activity of each apparatus and its environment.

3.3.2.1 Determining Environmental Properties

The environment, including both the water and sediment surrounding the apparatuses, directly impacted the accretion rate. The environmental properties that had the greatest affect on the auto-accretion process included the temperature, pH, and the dissolved oxygen levels of the water. Also, the bacterial concentration in the sediment was an important indication as to the approximate energy that could be expected from the microbes. Therefore, it was important to determine these properties in order to accurately identify their affect on the project as well as to better understand and explain the yielded results.

Data of the temperature, pH, and dissolved oxygen levels of the water were obtained from literature review. Extensive research was previously performed on the Venetian canals and lagoons, and a great deal of data documenting the yearly trends of the properties of interest was available. This existing data was deemed sufficient for the analysis required by this project. However, previously conducted research has determined that the microbial species and the concentrations that are found in the lagoon vary greatly even within close proximities (F. Carrera, personal communication, September 26, 2008). Therefore, this knowledge was not determined for the apparatuses locations since the apparatuses slightly shifted in their location due to tides and raising and lowering of apparatuses.

3.3.2.2 Measuring Electrical Properties

In order to gauge the progress of the experiments, as well as to help draw conclusions about the effectiveness of the project, it was essential to measure the voltage and current flowing through the apparatuses. A multi-meter was used to make the required electrical readings.

To take the readings for the apparatuses powered by MFCs, it was necessary to mechanically connect two insulated copper test wires each to apparatuses 1, 2, and 5. One wire was connected to the wire mesh cathode and the other wire was connected to the steel plate anode. To make electrical measurements the negative wire of the voltmeter, the black wire, was attached by an alligator clip to the end of test wire which was connected to the cathode and the positive wire, the red wire, was attached by an alligator clip to the test wire which was connected to the anode. After all necessary connections were made, the voltmeter was then used to measure the voltage and current produced by the microbial fuel cell, along with the resistance of the electrons to flow from the anode to the cathode. All data was then recorded and when finished, the exposed ends of the copper test wires were completely covered by electrical tape. Current, voltage, and resistance measurements were made on a regular basis.

The apparatus powered by a battery charger, apparatus 3, had two insulated copper wires; one wire connected the positive end of the battery charger to the anode while the other wire connected the negative end of the battery charger to the cathode. To take electrical readings for apparatus 3, the negative wire of the voltmeter was attached by an alligator clip to the exposed part of the copper wire connected to the negative end of the battery charge. The positive wire of the voltmeter was attached by an alligator clip to the exposed part of the wire connected to the positive end of the battery charger. After the necessary connections were made, the voltage, current, and resistance of the system were recorded. Then all exposed sections of copper wire were covered by electrical tape. As with the MFC powered apparatuses, current, voltage, and resistance readings for apparatus 3 were taken on a regular basis.

Due to an oversight, there was initially no way to take electrical readings on apparatus 4, the control apparatus with no induced current. It was quickly realized that electrical data about this apparatus was important to the analysis of this project and the situation was promptly rectified. Eleven days after the initial installation in Venice, all five apparatuses were pulled out of the water to check there progress and inspect any electrical connections for corrosion. At this time two insulated copper test wires were mechanically connected to apparatus 4; one wire was connected to the steel plate, the other to the wire mesh. The connections were thoroughly covered in silicon to prevent corrosion of the copper wires. All of the apparatus were then returned to their original location underwater in the lagoon.

From that point on, it was then possible to take electrical readings for the control apparatus. To accomplish this, the negative wire of the voltmeter was attached by an alligator clip to the end of test wire which was connected to the wire mesh and the positive wire was attached by an alligator clip to the test wire which was connected to the anode. As with the other apparatus, the current, voltage, and resistance of the control apparatus was recorded regularly. After readings were taken, the exposed ends of the copper test wires were completely covered by electrical tape to prevent corrosion.

3.3.2.3 Measuring Accretion

A major goal of this project was to determine the feasibility of applying an auto-accretion system to Venice. Therefore, it was imperative to establish a way to evaluate the auto-accretion process tested in this experimentation. To do this it was necessary to measure the amount of matter accreted by the apparatuses powered by MFCs. Additionally it was crucial to measure the matter accreted by the apparatuses powered by electricity and nothing. This data severed as a comparison and was used to help assess and analyze the practicality of the auto-accretion system.

The amount of matter accreted by each of the six apparatuses was predominately determined by mass. The intended site of accretion was the wire mesh cathode. Therefore the wire mesh of each apparatus was weighed on an analytical balance prior to the inception of this project. The mass was measured in grams and the precision of the balance was to the thousandth decimal point. At the end to the experiment, after the apparatuses were removed from the water and the wire mesh was allowed to thoroughly dry, the wire mesh was weighed again. The difference between the final and initial mass was equal to the total mass accreted throughout the duration of the experiment.

Additional observations were made about the accreted matter on the wire mesh. For example the thickness was measured and notes were recorded about the structure of the accreted matter (i.e. if the matter was uniformly distributed or localized to one area, etc.). Also samples of the accreted matter were brought to the laboratories at Worcester Polytechnic Institute for further analysis.

3.4 Analysis of Data

In order to assess the experimental setup of the auto-accretion system and determine the practicality of its application to Venice, six apparatuses were installed in the Venetian and Connecticut waters as described in Section 3.3.1 Experimental Setup. These apparatuses varied in configuration and had different sources of induced current. They were used to verify that the configuration and design of the microbial fuel apparatuses were correct, as well as establish the feasibility and sustainability of large scale installations of an MFC system in the canals of Venice. The following sections detail the approach of analysis of the obtained results, with particular emphasis on the feasibility and practicality, largely including economic analysis, of a large scale application of the auto-accretion process to Venice, Italy.

3.4.1 Validity and Feasibility

Apparatuses with three different power sources - microbial fuel cells, battery charger, and no supplied power - were tested in this project. Also, apparatuses were installed in two locations; the Venetian lagoon and an alcove of Groton, Connecticut. All of these apparatuses were used as to establish the validity and feasibility of the auto-accretion process.

Two MFC powered apparatuses, apparatuses 1 and 2, were installed in the Venetian lagoon to validate the experimentation. It was important to install two MFC powered apparatuses to ensure that the results yielded by one were repeatable. The use of two apparatuses also made certain that data was actually collected by this experiment. If significant damage was inflicted on one apparatus or if it was not properly installed, the other apparatus would still be able to provide data.

The data collected from the MFC powered apparatuses, apparatuses 1 and 2, were used to establish the feasibility of installing this system throughout the Venetian canals on a large scale. The total accretion of this apparatus was measured and the rate of accretion was determined. This information helped form conclusions about the accretion potential, along with the practicality, of installing this MFC powered system in Venice. The specific questions that were answered included:

- Did the MFC powered apparatus accrete enough matter to support its large scale installation in the canals?
- Was the accreted matter distributed evenly across the wire mesh or was it localized to one area? Was the matter distributed in a way that would allow for the protection of the entire canal wall?
- Was the accreted matter thick enough to shield the canal walls from boat wake?

Additionally, the apparatus powered by the battery charger, apparatus 3, served as a control for the experimentation conducted in Venice. The main purpose of apparatus 3 was to ascertain the effectiveness of the MFC powered apparatus. It has been proven through many experiments, especially those of Lee (2001) and Hilbertz (1979), that accretion driven by a battery charger actually yields a substantially amount of accreted matter. Therefore, if the battery charger powered apparatus in Venice failed to accrete matter, there must have been a flaw in the configuration of the apparatus. This would in turn indicate that there were problems with the configuration of the MFC powered apparatuses and that accreted matter should not be expected to form on the cathode. On the other hand, if the battery charger powered apparatus was configured correctly and successfully accreted matter, the configuration of the MFC powered apparatus must have also been correct. Therefore, if the MFC powered apparatus did for some reason fail to work, then a faulty configuration could have been eliminated as a possible of the cause of failure.

The battery charger powered apparatus was also used to help determine the feasibility and practicality of installing the MFC powered systems throughout the Venetian canals on a large scale. The battery charger powered apparatus was expected to drive the accretion of matter at a higher rate than that powered by MFCs. This was primarily due to the fact that MFCs involved biological processes which were comparatively slower. This project determined the relationship between the rate of accretion powered by a battery charger and the rate of auto-accretion, which is accretion powered by MFCs. This information assisted in determining the feasibility, based both on practicality and economics, of applying auto-accretion to Venice. While it was expected that the rate of auto-accretion would be less than the rate of accretion powered by a battery charger, analysis was conducted to ascertain if the rate of auto-accretion was so significantly lower that it was deemed an impractical process.

The apparatus with no induced power, apparatus 4, was an additional control for this project. The principal function of this apparatus was to help determine the driving force behind the accretion of matter by the MFC powered apparatus. Apparatus 4 was designed like the MFC powered apparatus, with the steel plate directly across from the wire mesh, except it did not have a source of power. The reason for this was to identify the amount of accretion that was driven by the electric potential difference between the steel plate and the wire mesh instead of by the current produced by MFCs. This data established the extent that accretion was actually driven by MFCs, which in turn helped determine the importance, effectiveness, and the practicality of using MFCs to power auto-accretion in Venice. If the accreted matter accumulated on the control apparatus was comparable to the amount of matter accreted by the MFC apparatuses, then it was probable that the best action would be to do nothing or to insert wire mesh or steel plates by themselves into the canals.

Apparatus 5, the one installed in Groton, Connecticut, served as both a control and a validation test of the usefulness and sustainability of auto-accretion. The other five apparatuses were installed in one localized area of the lagoon off of the island Lazzaretto Nuovo. It was critical to test the auto-accretion process in an additional location to ensure that it would work outside of that one specific environment. Also, apparatus 5 was left operating in the water for a much longer period of time than the apparatuses installed in Venice (85 days versus 28, 35, or 36 days). The observations made and the data generated by apparatus 5 allowed conclusions to be drawn about the long term sustainability of the auto-accretion process. Analysis was conducted particularly to determine the limiting design variable and the required maintenance of this process as well as if the process continues to drive accretion as time passes.

The purpose of the direct connect apparatus was to simplify the design and configuration of the MFC powered apparatus. Apparatus 6 was the apparatus in which the carbon fiber bottle brushes were directly connected to the wire mesh with insulated copper wire. It was expected that apparatus 6 would accrete less matter than apparatuses 1 and 2, which were designed with the carbon fiber brushes connected to a steel plate anode that was orientated parallel to the wire mesh cathode. Even though it was predicted that the rate of accretion of apparatus 6 would be less than that of apparatuses 1 and 2, it was important to determine the relationship between the different rates of accretion. This was due to the fact that the design of apparatuses 1 and 2 was relatively complex and would be more difficult to install into the Venetian canals. The design of apparatus 6 is much more simplistic and would be more practical to install and maintain in the canals. Therefore, if it was found that the rate of accretion of apparatus 6 was comparable to the rate of the other two apparatuses, than the design of apparatus 6 would present a more feasible option for a large scale installation into the canals of Venice.

3.4.2 Accretion Analysis

After the completion of the experiment in Venice, the apparatuses were taken out of the water and disassembled and the electrodes were allowed to air dry indoors to reduce contamination sources. The electrodes were further disassembled into the individual wire mesh and stainless steel plates, which were then carefully wrapped in plastic wrap to contain all matter on the surfaces. The electrodes were packaged well and shipped to WPI where much more extensive study could have been done on the metallic surfaces and accreted matter.

3.4.2.1 Mass

The first analysis was the determination of the mass of accreted matter, or ideally, the change in the electrodes' masses. This was done by weighing each individual electrode still wrapped in plastic wrap on a balance, then subtracting the weight of the plastic wrap and any silicon, nuts, bolts, or washers that were attached to it during the first mass determining step. To do this, the silicon was scraped off of the steel plates and wire meshes and the nuts, bolts, and washers were removed.

3.4.2.2 Composition

The composition of the accretion was determined using a scanning electron microscope (SEM). This machine shot a thin, condensed beam of high energy electrons at a sample, which interacted with the electrons from the atoms on the sample's surface. These interactions were detected using various sensors and then "counted". Each element has a known set of interactions, so the detected interactions were compared with those of the samples, and the intensity of the resulting graph was representative of the number of interactions (http://www.unl.edu/CMRAcfem/semoptic.htm).

Among the various interactions were backscatter electrons which were electrons that hit almost normal to the sample and were repelled 180° "backward", and these electrons provided the visual pictures of the sample surface. The energy from the high energy electrons was also passed on to the lower-energy electrons in the sample, and as this happened, the electrons from the sample, called secondary electrons, had enough energy to leave the sample. These secondary electrons were collected and "counted". After a secondary electron, originally a lower energy electron, left the atom in the sample, a physical atomic imbalance was formed. To alleviate this, a higher energy electron from the atom reduced its energy to fill the spot of the lower energy electron, which bumped another electron, called the Auger electron, off of the atom to regain the balance. These Auger electrons had energies specific to each element and helped determine the relative composition of the sample. Also, as the higher energy electron filled the spot of the lower energy electron that left as a secondary electron, an imbalance in the atom's overall energy was created. X-rays with energies specific to each element were then emitted to regain the energetic balance, and these were collected and analyzed (http://www.unl.edu/CMRAcfem/interact.htm). Therefore, by utilizing all of these interactions, the elemental compositions of each of the accretion samples were determined.

From the results of previously conducted research, it was expected that the samples would consist of mainly brucite, $Mg(OH)_2$, and aragonite, $CaCO_3$. Hilbertz (1979) conducted a similar experiment powering the accretion process off of a constant direct current (DC) power supply, and these were the two main minerals in his samples. Since the SEM was unable to detect hydrogen atoms, the main elements that were expected to be seen, in order of their expected peak intensities were: Mg, O, C, and Ca.

3.4.2.3 Structure

To determine the structure of the accretion, X-ray diffraction (XRD) was used. This test involved a machine that shot X-rays of known wavelength at a known angle at the accretion sample. Depending on the interactions the X-ray had with the electron densities of the particular atoms in the sample, their path changed, or diffracted. The diffracted X-rays were then received at different intensities (a measure of the number of X-rays received), thus indicated by the difference in peak sizes and locations (two times the diffraction angle) on the resulting graph. The intensity in the peaks indicated the interplanar spacing in the lattice, and each compound had its own unique XRD pattern of these peaks (Mitchell, 2004). Therefore, the structural make-up of the sample was identified by aligning the peaks found in the sample with the empirically determined and well-published peaks of known compounds suspected to be present in the sample. Suspected compounds were drawn from previously conducted research like Hilbertz's (1979), as previously discussed, and from the SEM test results. Unfortunately, the XRD analysis requires a much larger sample than the SEM so only the battery charger powered apparatus wire mesh had enough accreted matter to analyze. Accreted matter was scraped off of two places on this wire mesh – one from near the electrical connection to the battery charger and one on the opposite end from that connection – and then pulverized into a fine powder to allow for a clearer reading. Samples from two locations on the wire mesh were taken to determine if there was a difference in the spatial distribution of the compounds. Another sample was taken from the top layer of accretion from the entire surface of the wire mesh for a representative account of the overall sample mineral make-up.

3.4.3 Corrosion

While the numerical support for this proposed system was interesting, the unquantifiable conclusion of whether matter was accreted on the wire mesh cathode was the most important result. It was believed, however, that the apparatuses did not have ample chance to accrete the matter, largely due to corrosion. The apparatuses were regularly monitored and when the measured electrochemical properties were not as were expected about 30 days after installation, the apparatuses were hauled out of the water. The readings were not completely consistent up to that point, however, the fluctuations were attributed to a change in other uncontrollable variables, such as the tidal level. It was not until the readings continued to decrease dramatically that the apparatuses were lifted out of the water for closer inspection. That inspection led to the discovery of the worst case scenario: the copper wires and the nuts, bolts, and washers that were located at each of the wire connections suffered much damage from corrosion. Figure 26 shows the damage that one nut and washer withstood, as the silicon only provided a buffer to the corrosive seawater for less than 3 weeks.

Figure 26: Corroded bolt, nut, and washers

After the inspection and determination that the corrosion of the Connecticut apparatus was different than that of the Venetian apparatuses, further analysis was completed. An SEM analysis was completed to confirm the hypothesis that the steel plate was in fact not stainless steel as originally believed. Further analysis was conducted on the two leading corrosion sources: the reduction in the stainless steel coating and crevice corrosion.

3.4.4 Environmental Impact

This was not technically necessary for the completion of this project, but an ethical responsibility required consideration of the environmental impact this project would have on the local Venetian and Connecticut ecosystems. Throughout the duration of the experiment, observations about the wildlife populations and interactions with the apparatuses were made. This was coupled with literature review about the impact of induced electrical currents on various wildlife species. It was important that this system peacefully cohabitate with the local environment to prevent more devastating problems than that of the moto ondoso problem, such as the application of stresses on local wildlife.

3.4.5 Economic Analysis

To assist in establishing the feasibility of the auto-accretion process, an economic analysis was conducted on the various methods to protect the canal walls and barene from erosion. Even if the auto-accretion system and the system powered by a battery charger both successfully produce the accretion of seawater minerals, it is still necessary to examine the economic impact of these systems. If the systems succeed, and yet it is found that the cost will be significantly more than the current methods of canal and barene maintenance, then it is not practical to apply either of these systems to Venice.

The economic analysis was performed by comparing the total cost of the current method employed by the city of Venice to maintain and repair the canal walls and the barene with the total costs of building, installing, and maintaining both the auto-accretion system and the system powered by a battery charger. In theory, these two systems once installed in the canals and lagoon should accrete a sacrificial wall made of seawater minerals directly in front of the canal walls or mudflats. This sacrificial wall would then intercept the force of the boat wake, and this wall would erode in place of the canal wall or barene. Also the accreted wall would be self-regenerating, and therefore the erosion of the accreted wall would be automatically repaired with time.

The cost to build the auto-accretion system was determined by summing the costs of all the materials used to build the microbial fuel cell powered apparatus necessary to protect one square meter of canal wall. The installation cost was found by estimating the total time required to install this system per square meter, along with the hourly wages of Venetian canal maintenance workers. The total time required for installation was approximated based on the time need to build and install the MFC powered apparatus and an assumed efficiency of workers, as well as an assumed availability of all materials of construction. The yearly maintenance cost was based on the time required to make repairs to the MFC powered apparatus throughout the duration of this experiment, along with the hourly wages of canal maintenance workers.

The costs to build, install, and maintain the system powered by an external source of electricity was determined in a manner similar to that of the auto-accretion system described above. The building cost was based on the costs of all the materials necessary to construct the apparatus powered by a battery charger per square meter of canal wall. The installation cost was based on the time required to install this apparatus into the lagoon of Venice. As with the auto-accretion system, the yearly maintenance cost was estimated based on the time required to repair the apparatus powered by a battery charger, however this cost also includes the yearly cost of electricity needed to sustain this system. In Italy, the average cost of electricity per kilowatt-hour in 2007 was found through background research.

The current methods utilized to maintain and repair the canal walls and the barene include dredging and the lining of mudflats with wooden pilings, respectively. Costing estimations for both of these methods were determined through extensive background research. After the cost data for all four of these options for protecting the canal walls or barene from erosion was ascertained, a detailed comparison was completed to determine the feasibility of applying either the auto-accretion system or a similar system powered by an external source of electricity to the city of Venice. For this comparison to be complete, it was also necessary to take into account the time required for these two systems to accrete a sacrificial wall that would effectively provide protection from erosion. The money invested in these systems before they begin to yield results increases proportionally with time. Therefore it is essential to investigate the amount of time required accrete a sacrificial wall, in addition to the costs associated with each system.

3.5 Summary

The development of this experiment progressed in multiple stages. The first stage was the research of a collage of research areas, including electrodeposition, MFCs, and material properties. Using the latest technologies and developments, an apparatus design was formulated, though modified for the Venetian apparatuses due to unforeseen material apprehension problems. The apparatuses were constructed according to the designs with provisions to account for the feasibility and validity of the experiment. The apparatuses were then constructed and installed in the appointed locations. Maintenance procedures were created and executed when the need for repairs was discovered. Plans for experimental results analysis were devised and also performed, including the major feasibility determining factor – the economic analysis of this process.

4.0 Results and Discussion

The assessment of the proposed MFC powered auto-accretion system was based on the field experimentation conducted in Venice, Italy and Connecticut, USA. The electrical properties of the system, which were recorded throughout the experiment, were analyzed to find general trends. Also, the accretion produced on each wire mesh cathode, was analyzed to determine the chemical composition and structure. This section details the results of the experiments, which includes the direct results, consisting of electrical measurements and analysis of the matter accreted during the experiment's duration, and indirect implications of the economical analysis of the proposed system.

4.1 Determined Environmental Properties

The environmental properties of the Venetian lagoon and the Connecticut waters were determined through literature review. It was not necessary to measure these for this project since more in-depth studies had already been conducted and the data made available. From these studies, data within the time frame in which this project was conducted was used for comparisons. The data that was used, therefore, was within the span of the middle of October to the beginning of January; however, since the data was not available for the current year, properties were extrapolated. Data collected in 1999 was used for the Venetian properties and data from the winter of 2003 into 2004 was used for the Connecticut properties with no extrapolation necessary (Aimo et al., 1999; Ltr_1003, 2008; Ltr_1103, 2008; Ltr_1203, 2008; Ltr_0104, 2008). For ease of visualization, the results were compiled into Table 4.

Table 4: Environmental properties of Venice and Connecticut waters

	Venice	Connecticut
Average water temperature (˚C)	15	10.6
Average pH	8.05	-
Average salinity	32	29.6
Average dissolved oxygen (mg/L)	5	7.9

Note: The dissolved oxygen levels varied greatly between testing sites, so this is a rather rough estimate. The average seawater pH for the Connecticut apparatus' location was undetermined at the time of this paper's submission.

4.2 Measured Electrical Properties

The system's electrical properties of current, voltage, and resistance readings were recorded periodically throughout the experiment, with the exception that only the voltage of the MFC powered apparatus in Connecticut, USA was measured. The compiled table of these readings can be seen in Appendix B: Tabulated Results. Trends, either a pattern or lack thereof, drawn from the charted results led to a greater understanding of the progressing process. It was these readings that indicated the electrical activity in the system and provided the red flags of trouble that led to the discovery of corrosion's disastrous effects on the system.

4.2.1 Electrical Current

Originally, one of the major focuses of this experiment was the amount of current that was induced between the electrodes of the apparatuses. The difficulty of measuring this electrical property, however, was severely underestimated. The electrical current readings were unexplainably inconsistent, even with the large affect that the tidal conditions has on the readings taken into consideration. It was possible that such a small current was being read by the multi-meter, that a reasonably accurate measurement was not possible.

4.2.2 Voltage

The voltage was a reading of the electrical differences between the wire mesh and steel plate. The greater the amount of electrons flowing from the sediment to the steel anode plate, the greater the electrical potential difference. However, as the accretion accumulated on the cathode, an increase in the resistance and therefore decrease in voltage should have been measured. The voltage readings were recorded at various times of day at different tidal conditions. The results of the readings, see Appendix A: Apparatus Maintenance Schedules for readings schedule, were as shown in Figure 27.

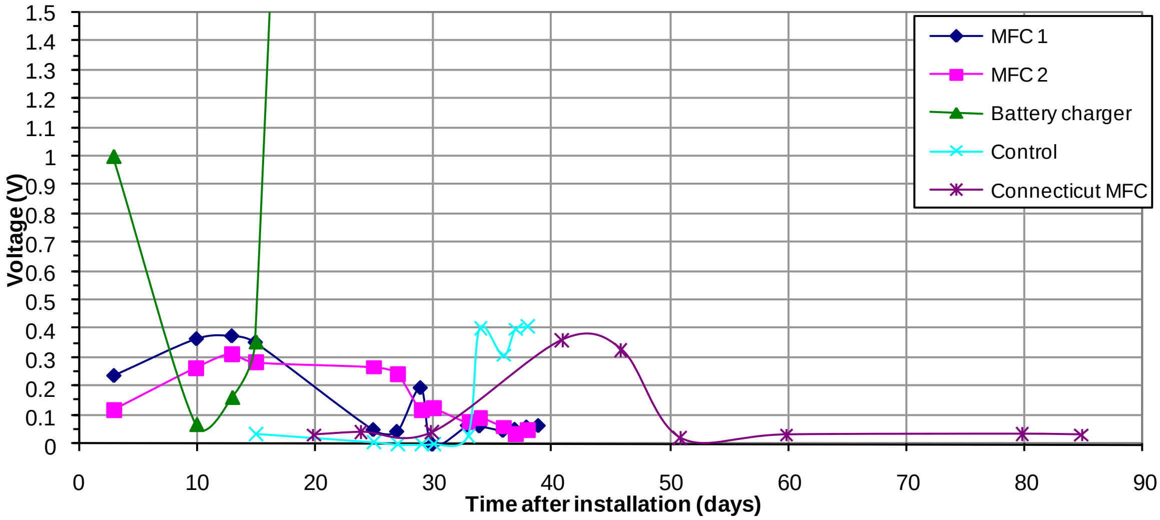


Figure 27: Recorded voltages as a function of time
Note: battery charger voltage peaks at 18V, but steadies at 12V (not shown)

As seen in Figure 27, the voltage readings were not consistent. The battery charger powered apparatus not only started at only 1V opposed to the 5-10V it was supposed to, but it soon plummeted to less than the voltage measured across the MFC apparatuses. This indicated that the battery charger was not operating properly and that it was necessary that it be replaced. Once the battery charger was replaced with a functioning charger, the voltage shot up to 18Vand settled at about 12V of induced voltage difference (not shown on graph).

When the voltages in the MFC powered apparatuses are compared, as seen in Figure 28, a similar trend can be noted. There was a peak in the voltage early in the experiment and then the voltage tapered off to about a tenth of the size of the peak. It is also important to note that the amplitude of peak voltage was nearly identical for the MFC 1 from Venice and the Connecticut apparatus, with the MFC 1 from Venice only achieving about a 4 percent higher peak voltage. The interesting difference in the trend was when the spike in voltage occurs. For the Venetian MFC powered apparatuses, the peak occurred at about 13 days after installation, versus after about 42 days for the Connecticut apparatus. This could be due to many factors, including the 5˚C on average colder water temperatures in Connecticut, which, as previously discussed, would significantly decrease the amount of microbial activity, or the anode brush surface area (Aimo et al., 1999; Ltr_1003, 2008; Ltr_1103, 2008; Ltr_1203, 2008; Ltr_0104, 2008).

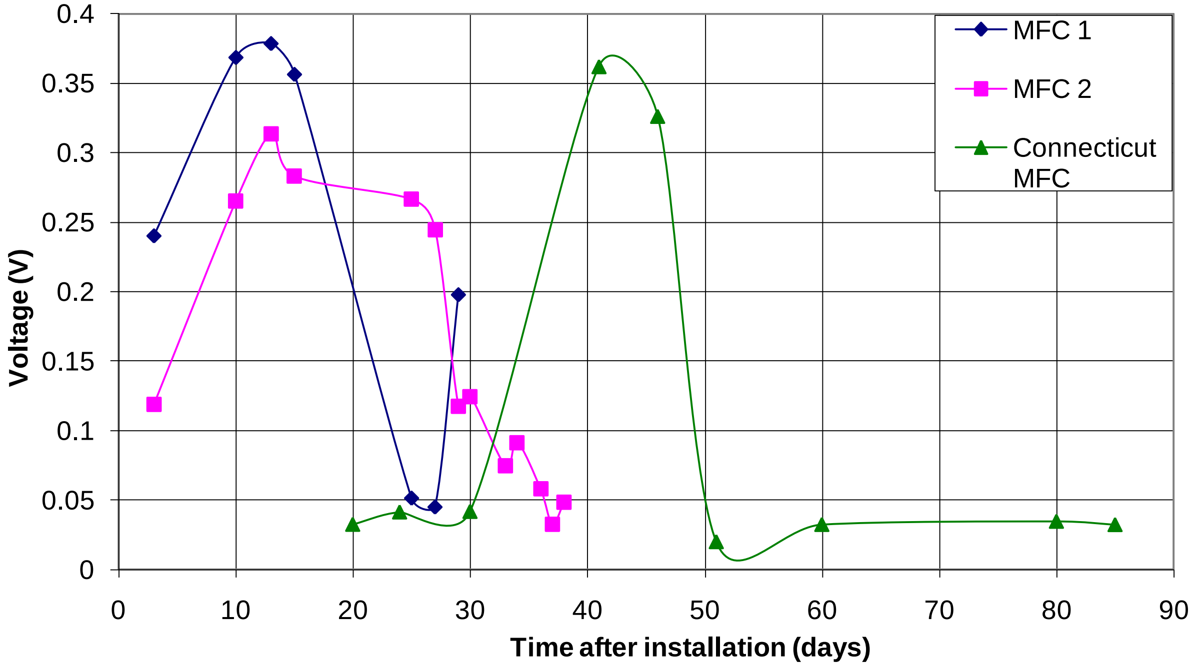


Figure 28: Voltages from MFC powered apparatuses

The more likely cause for the difference in the peak voltage timing was the approximate 5˚C difference in the water temperature (Aimo et al., 1999; Ltr_1003, 2008; Ltr_1103, 2008; Ltr_1203, 2008; Ltr_0104, 2008). This is because the anode brush surface area remained constant through the experiment, so that variable should only affect the amplitude of peak voltage, not the timing. As previously described, the rate of this process is greatly affected by the microbial activity, which is enhanced at higher temperatures. Since the temperatures were on average higher in the Venetian lagoon, the amount of microbial activity was greater than that in Connecticut, and thus, the experiment proceeded at a greater rate.

4.2.3 Internal Resistance

Similar to the voltage readings, the recorded resistances seemed to be quite sporadic, as seen in Figure 29. The resistances for the Connecticut and direct-connect apparatuses were not recorded, but there was no clear trend that could be drawn from the data that was recorded, even with tidal conditions taken into consideration.

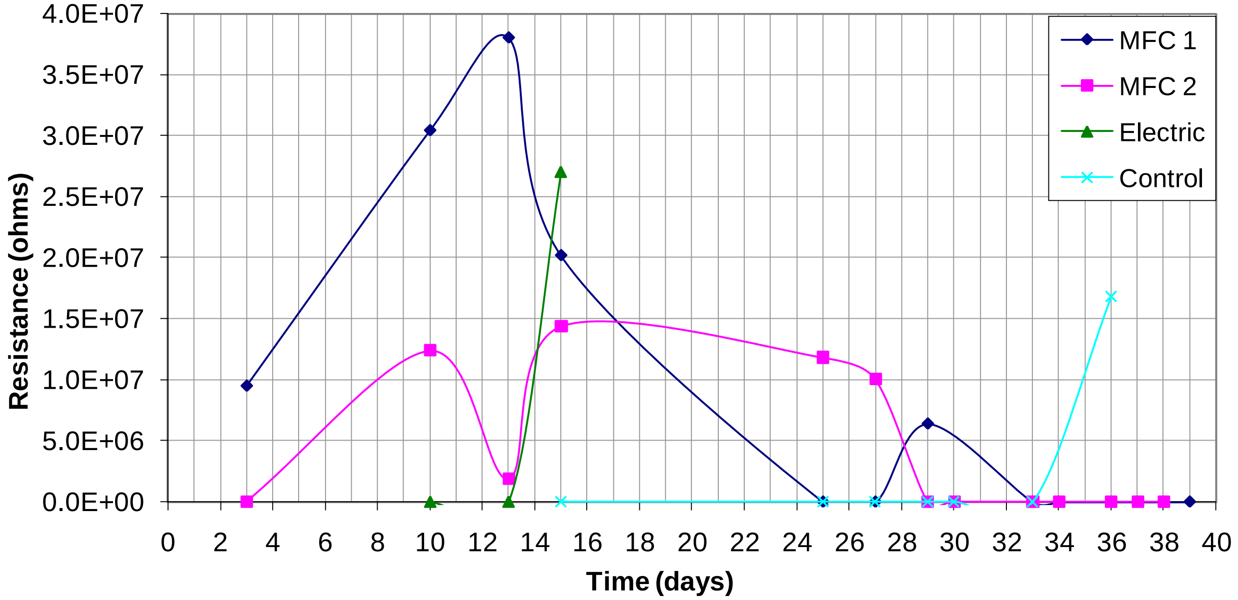


Figure 29: Recorded resistances as a function of time

4.3 Accretion Mass

The change in masses of the wire meshes and steel plates can be seen in Table 5 and Table 6 respectively. The differences in masses were considered to only be approximations and were unable to be linked solely to the amount of accreted matter. This was due to the oxidation of the metal surfaces, some impurities like algae stuck on the wire mesh, and the inability to remove all of the silicon that was added after these were initially weighed. In the end, it was determined that this was not an extremely useful method for determining the overall accretion mass due to all of these uncontrollable factors.

There was a general trend that the higher current apparatuses – the two Venetian MFC powered apparatuses and the battery charger powered apparatus – had an increase in the masses of wire mesh, which, especially in the case of the battery charger wire mesh, was largely due to the mineral accretion. The control and Connecticut apparatuses had a slight decrease in mass which was attributed mainly due to error in the weighing process, and some corrosion. It was unknown why the direct connect wire mesh was so drastically reduced, other than due to potential weighing and data recording error.

Table 5: Change in mass of wire mesh cathodes

	Before (g)	After (g)	Difference (g)
MFC 1	357.39	362.08	4.69
MFC 2	355.79	357.39	1.60
Battery charger	354.50	539.71	185.21
Control	355.22	353.19	-2.03
Connecticut	106.10	104.09	-2.01
Direct Connect	363.13	350.44	-12.69

As seen in Table 6, only three steel plate measurements could be compared. This was due to an oversight in collecting a reasonable weight of the Connecticut steel plate prior to installation, and the steel plate from the MFC 1 apparatus in Venice was still unavailable for measurements at the time of this paper's submittal. Also, the direct connect apparatus did not have a steel plate, as the anode brushes connected directly to the steel wire mesh. The general trend for these apparatuses was that more mass was lost with greater induced currents. The loss of mass was especially seen in the battery charger apparatus in the form of crevice corrosion, where the metal was completely corroded through at parts.

Table 6: Change in mass of steel plate anodes

	Before (g)	After (g)	Difference (g)
MFC 2	1033.49	1020.0	-13.5
Battery charger	1042.00	985.5	-56.5
Control	1042.19	1034.71	-7.48

4.4 Accretion Distribution

Unfortunately, only the battery charger powered apparatus accreted enough matter for the sample to be visually assessed without the assistance of a microscope. The distribution of the accretion was visible only on that apparatus. Figure 30 shows how the accretion thickness appeared to be relatively equal across the interior of the wire mesh, only slightly thicker than the interior near the electrical connections, and much thicker around the edges of the wire mesh. This was not the same result that Hilbertz (1979) achieved with his experiment of accretion powered by a DC current in the waters off of St. Croix. In his experiments, the accretion was thickest at the top of the wire mesh where the DC power was connected and then the thickness tapered off slightly as the distance to the power connection increased (Hilbertz, 1979). However, since his experiments had a full layer of accretion and the accretion achieved in Venice did not even close the gaps of the wire mesh, it was hypothesized that the Venetian apparatus may have achieved the same results with more time.

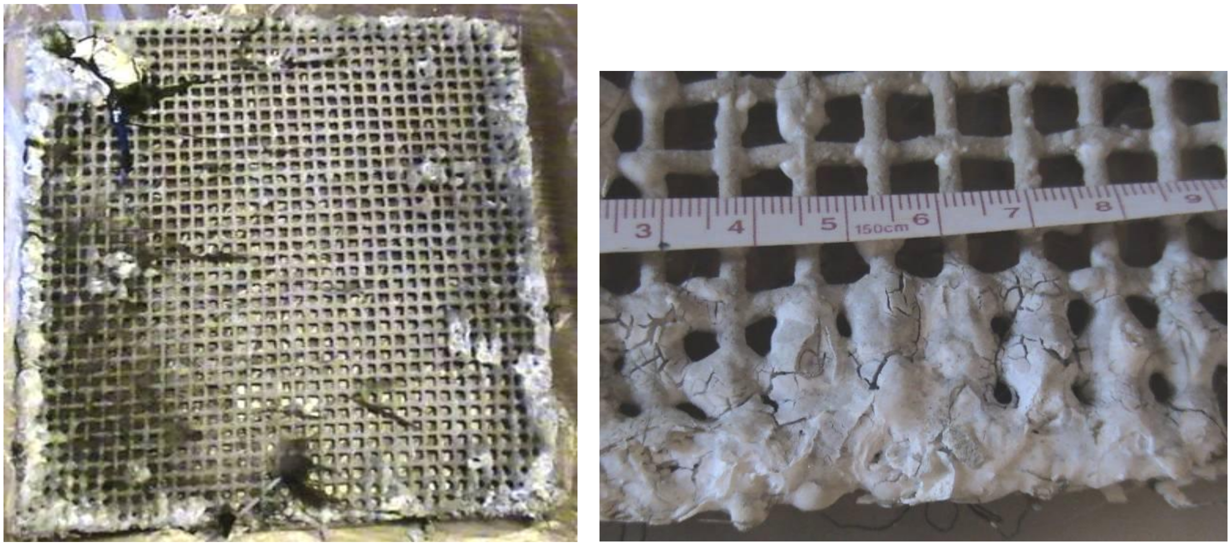


Figure 30: Accretion on battery charger powered apparatus: accretion distribution on wire mesh (left) and magnitude of accretion difference of interior versus mesh edges (right)

4.5 Accretion Composition

With the assistance of microscopes, the accretion obtained from all of the samples was able to be analyzed. The first microscopic analysis was done using a scanning electron microscope (SEM) to determine the elemental composition and relative contributions. As previously discussed, the minerals expected to be accreted on the wire mesh consisted of mostly brucite ($Mg(OH)_2$) and aragonite ($CaCO_3$).

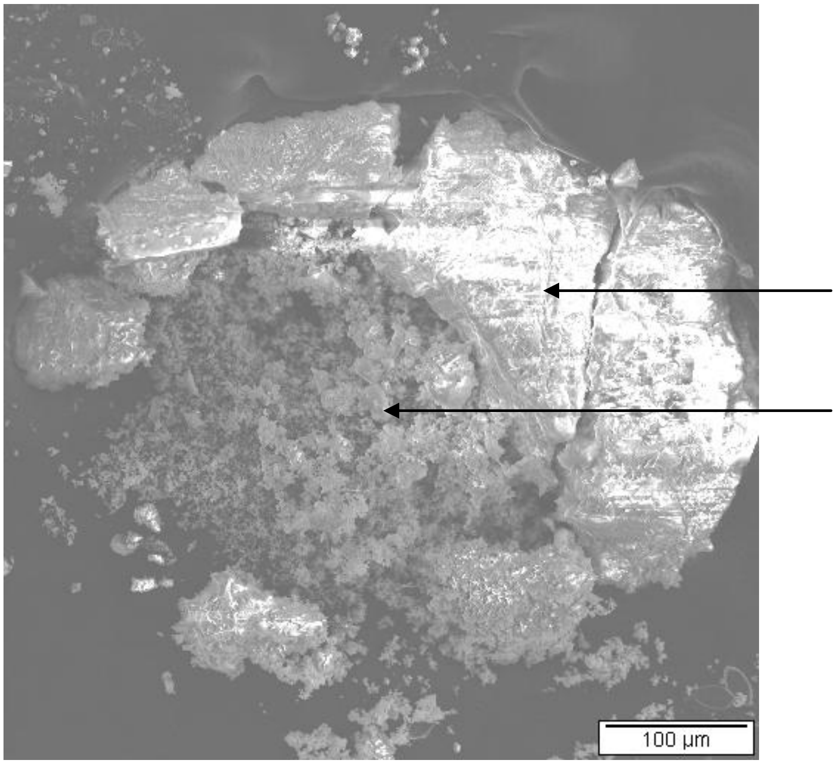
A fair amount of silicon, Si, however, was found in the samples, and this has been attributed to the use of an inappropriate type of Si to seal the electrical connections during the overhaul maintenance procedures. It was noted that when the apparatuses were pulled out of the water at the end of the project, this silicon was still tacky, meaning that it was still not set. This caused the Si to migrate while underwater. It was assumed that this was the source of the silicon in the SEM results.

There was a good amount of aluminum in all of the accretion samples except those from the MFC apparatus 1 and battery charger. This was, at first, a quite perplexing issue since there was no aluminum in the wire mesh or the steel plates, and aluminum is not a metal typically found in salt water. Also, there was a good concentration of it in the Venetian accretion samples, with the exception of those previously mentioned, as well as the Connecticut accretion sample, so it could not be attributed to being localized lagoon pollution. There was a good deal of boat traffic in both locations, however, especially by small, fast motorboats. Many of these boats have an aluminum hull which could, over time, erode into the salt water. Also, the Connecticut apparatus was located about six feet from a large boat that stayed dormant on the dock for a significant period of time. The MFC apparatus 1 and battery charger apparatuses were located closest to the shore, furthest from the boats moored on the dock and boats passing in the channel, allowing the aluminum to dissipate more before reaching those apparatuses. Therefore, the proposed source of this element was from the aluminum-hulled boats.

Some of the carbon, C, that was present in the graphs was a product of the analysis. In order to process the samples, particles were removed from the wire mesh cathodes using double sided carbon tape, which was tape made with an extremely thin layer of carbon atoms with an adhesive coating both sides. Therefore, some of the carbon that was being read by the SEM was from the tape to which the analyzed particle was adhered.

4.5.1 MFC powered Apparatus 1

A few approximately 1-2mm flakes found on the surface of the MFC- powered apparatus 1 were analyzed using a SEM. There were flakes about this size scattered around the wire mesh, but the flakes picked up by the carbon tape and analyzed were found slightly off-center of wire mesh. Two flakes were analyzed by the SEM, one of which was analyzed in two locations on the same flake. This was done because of a visual difference seen using the SEM at 100X, also seen in Figure 31.



SEM analysis of light section

SEM analysis of dark section

Figure 31: Accretion particle 1 from MFC 1

As seen in the SEM results in Figure 32, the major peaks, or elements, found in the dark section were mostly magnesium (Mg) and oxygen (O) as expected. The SEM analysis in the lighter-colored section of the same particle, however, revealed that the major elements in this portion of the particle were not Mg and O, but were sodium (Na) and chloride (Cl) with a large amount of Mg still present.

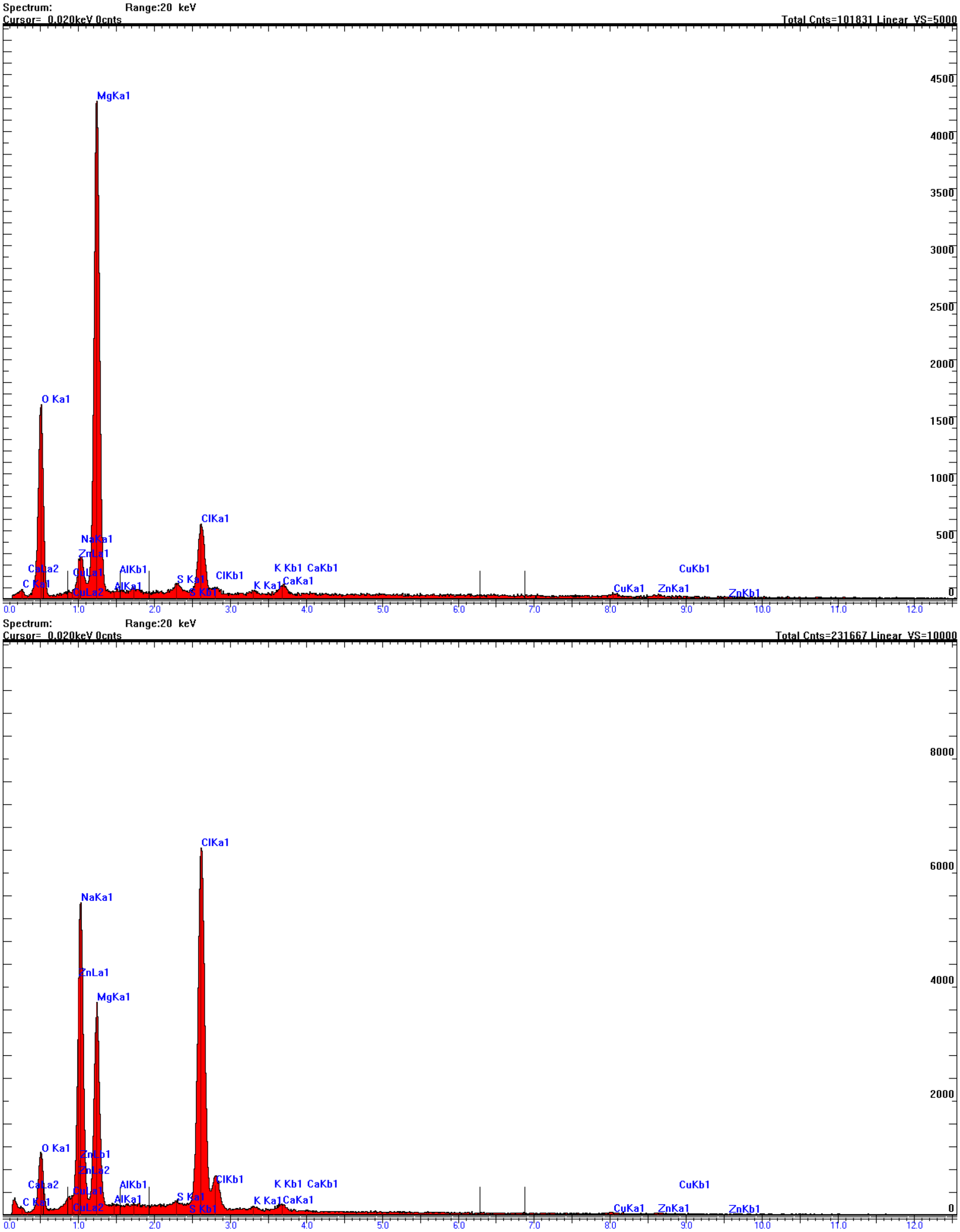


Figure 32: SEM analysis results of dark section (top); SEM analysis results of light section (bottom)

Another particle from the MFC 1 apparatus wire mesh was also analyzed using the SEM technique and, as seen in Figure 33, the elements and their relative amounts in the particle were similar to that of the lighter colored, Na and Cl-rich sample. The possible reason for this was Hilbertz's (1979) hypothesis about very slight variations in temperature and pH changing the mineral that is most favorably accreted to the wire mesh. Since not as many free protons were pushed out of the metal and later forming H_2 gas in the non-battery charger powered experiments, the pH of the seawater directly next to the wire mesh would have been slightly higher than Hilbertz's experiment. It was possible that these conditions were slightly more favorable for NaCl to accrete onto the wire mesh. The possibility of contamination was ruled out due to fact that the NaCl and Mg were found in large concentrations on the same particle or at least found so close together, which can be especially be seen in Figure 31. There was no explanation for the two minerals to be on the same particle or located so close to one another without having been accreted in the same place, as the bonding would have had to have occurred where both minerals were present in decent concentrations. At the same time, the second particle sample consisting of the same elements as the questioned Na- and Cl-rich part of the first particle validated the results of the high concentration of the unexpected mineral.

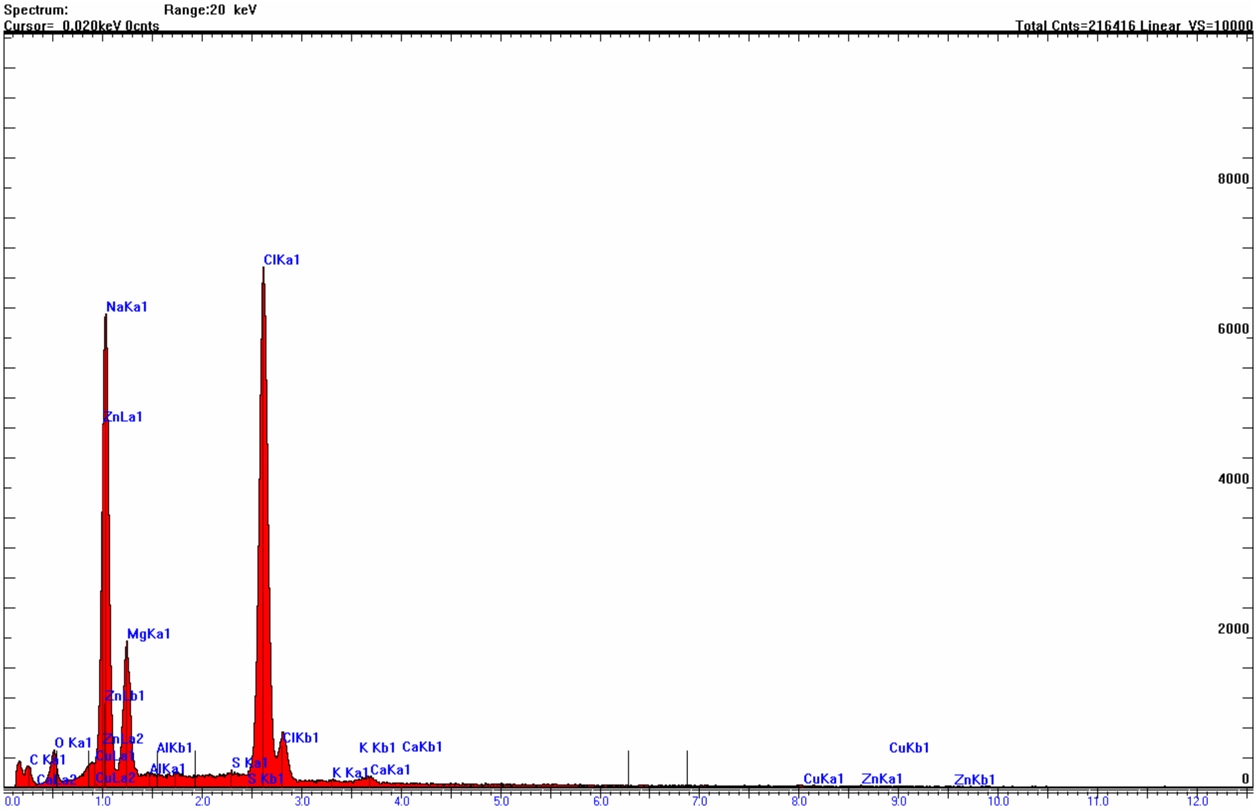


Figure 33: SEM analysis results for accretion particle 2 from MFC 1

It is hypothesized that the Na and Cl ions were forming the mineral halite, NaCl. One disadvantage to accreting the halite, NaCl, however, was the unfortunate weakness of the mineral. On the Mohs' scale of hardness (range of 1 to10), it ranks a 2, which is softer than brucite (2.5) or aragonite (3.5), the expected minerals (Lide, 1996). This indicated that if halite was the main mineral to accrete onto the cathode, then the resulting wall would be weaker and would therefore need to be thicker than one mainly consisting of elements like brucite or aragonite. The self-limiting component of the natural accretion process, or the point at which the resistance between the two anodes becomes so great that little to no current flows between the electrodes, would also have serious implications to whether the wall could get thick enough to overcome the mineral hardness difference.

4.5.2 Battery Charger Powered Apparatus

Using the SEM, the accretion from two locations on the battery charger powered apparatus – near and far from the electrical connection were analyzed, as seen in Figure 34 and Figure 35 respectively (*Note*: figures on different scales on y-axis due to constraints of computer software program). It was important to compare this analysis with similar previously conducted experiments. Hilbertz (1979), in particular, conducted a lot of research in this field from the end of the 1970's and on, but instead of using the accreted minerals to form a breakwater wall like this experiment was designed to do, his application was the formation of artificial coral reefs. His experiments, however, were similar enough to validate the results of this experiment.

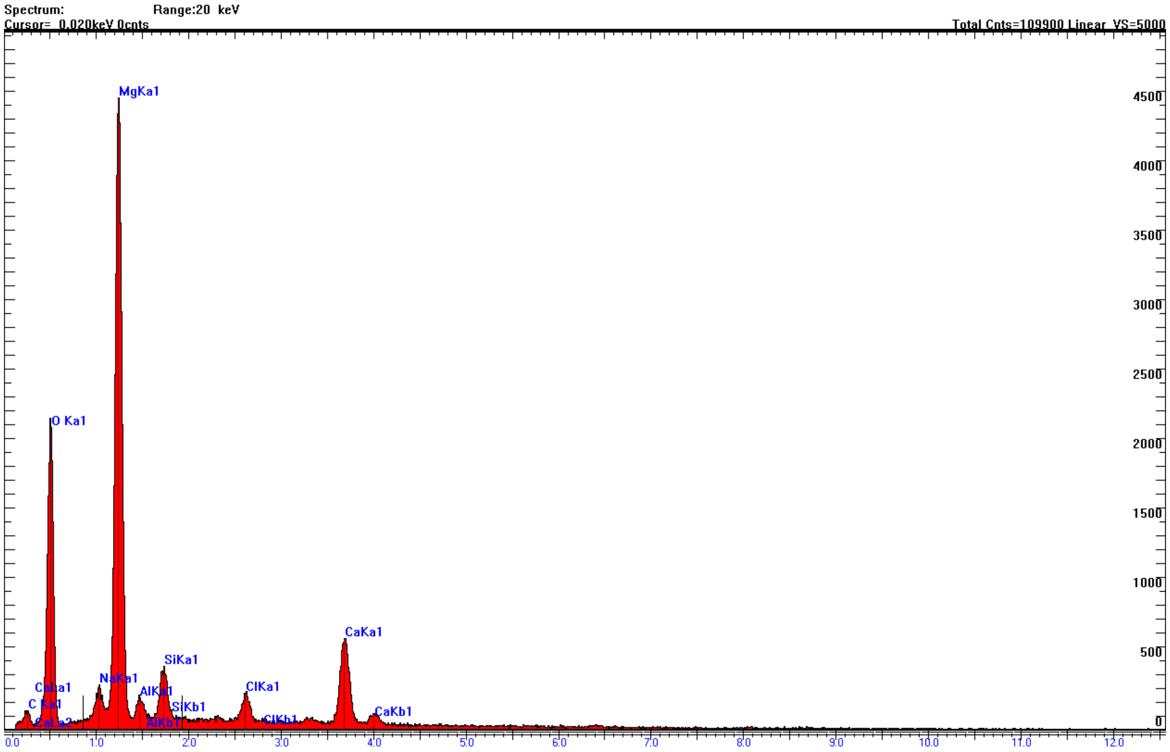


Figure 34: Accretion composition near the electrical connection to battery charger

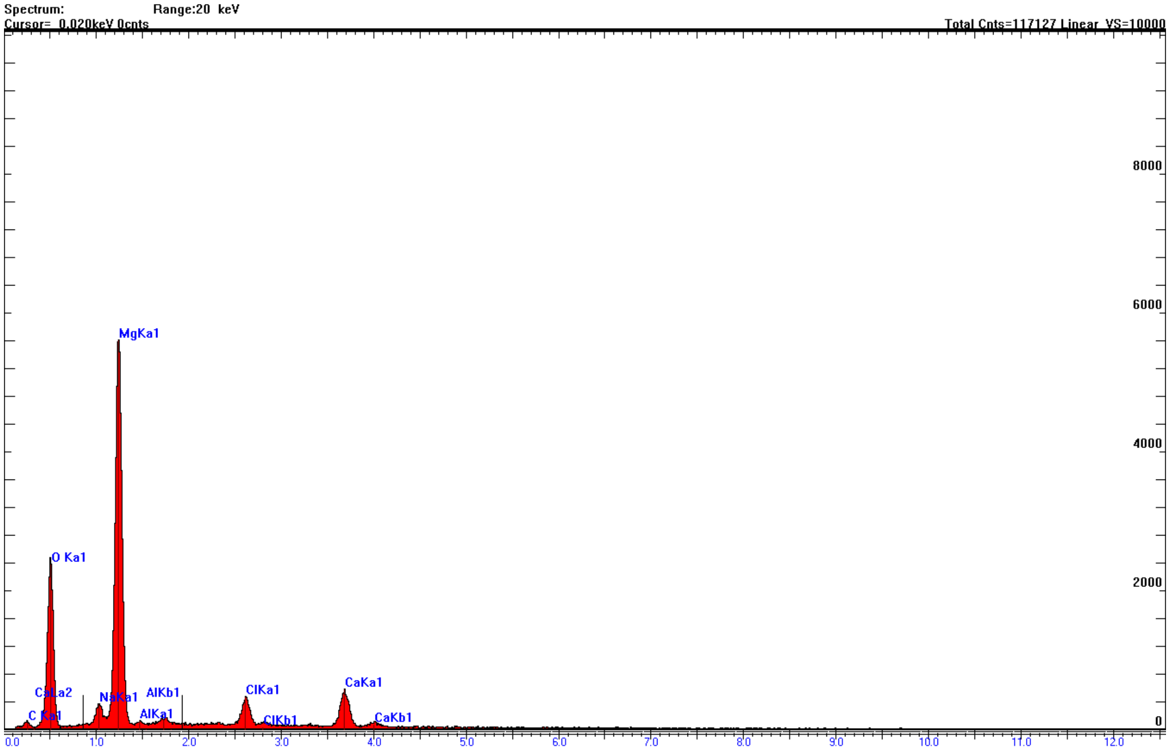


Figure 35: Accretion composition far from electrical connection to battery charger

For the battery charger powered apparatus, the results of the SEM indeed showed that the majority of the mineral accretion was magnesium, which is consistent of with brucite ($Mg(OH)_2$), and calcium, consistent with aragonite ($CaCO_3$). This was comparable to Hilbertz's (1979) research of the accretion he named Seacrete; Hilbertz's results showed that the accretion he generated using a DC power supplier consisted of an average of 60 to 80 percent brucite. His research also suggested that there was a difference in the accretion composition, as well as the amount of impurities trapped within the crystalline matrix, depending on the placement of the cathodes in relation to the cathode surface. However, we tested accretion from near the power connection as well as on the opposition end of the wire mesh and determined that the composition did not differ significantly as a function of location from the point of power supply. Hilbertz hypothesized that the composition difference was due to the mineral's preference to accrete as a function of temperature, resulting from a difference in internal resistance, and pH in the surrounding area. It was hypothesized that for this experiment, however, the cathode was too small to measure the same effect that Hilbertz obtained. Since the results of this apparatus produced similar results to Hilbertz's research, like the high concentration of Mg, it was determined that this project's results were valid.

4.5.3 Elemental Comparison

Of the expected elements, the ones that were of the most importance were Mg, O, Na, Cl, and Ca since they comprised of the expected and unforeseen minerals in the accretion. Figure 36 showed the relative amounts of these elements found in the apparatuses. From this figure, it can easily be noted that the battery charger apparatus had a significantly greater amount of Mg than the other apparatuses, but the Venetian MFC apparatuses also had more than double the amount of Mg than the other apparatuses. The battery charger powered apparatus also had a significant amount less of halite, or NaCl, which corresponds to the expected results and previously conducted research. Interestingly, with the exception of oxygen, the control, Connecticut MFC, and Venetian direct-connect apparatuses had very similar compositions. It was proposed that this was because the control and Connecticut apparatuses were low current systems; the direct connect apparatus was not expected to accrete matter more than control since there was no electro-potential between two plates that would drive the accretion process. In other words, the wire mesh became the anode instead of the cathode since the electrons were being fed there from the MFC. Also, it was interesting that all of the apparatuses consisted of relatively the same amount of calcium, which was supposedly, according to previously conducted research, in the form of aragonite ($CaCO_3$).

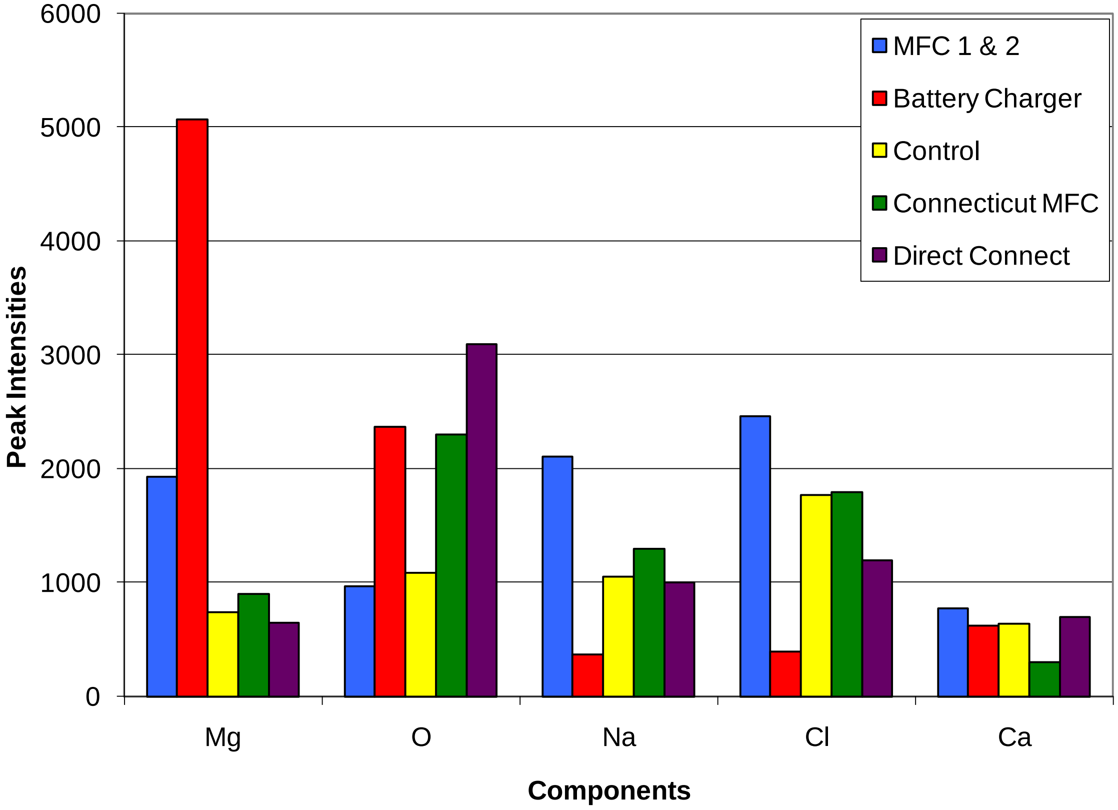


Figure 36: Relative comparison of accretion components by apparatus

The previous comparison displayed trends in the relative amount of particular elements that comprised of the accretion for each apparatus. Figure 37 used the same SEM results but are plotted to better show the relative composition of each of the apparatuses' accretion.

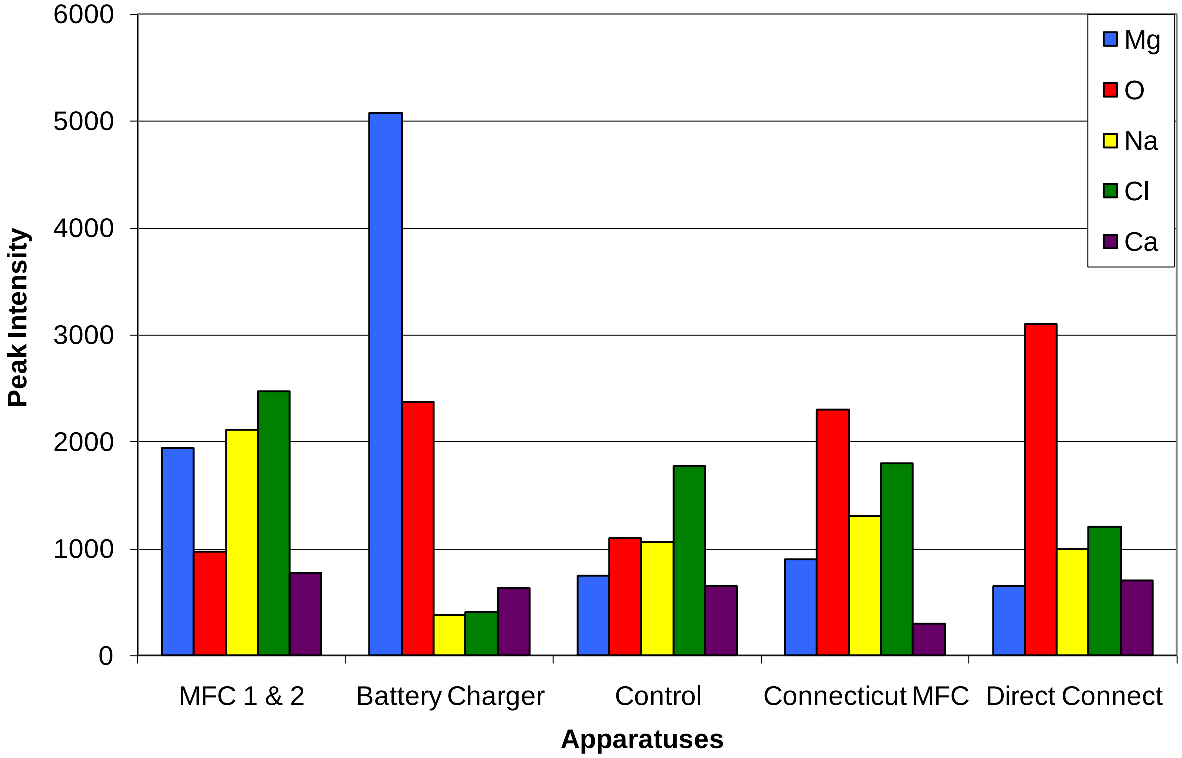


Figure 37: Comparison of relative composition of each apparatus

As seen in the above figure, the composition of the Venetian MFC powered apparatuses consisted of almost even amounts of Mg, Na, and Cl, whereas the Connecticut MFC powered apparatus had much greater amounts of those elements and a lot more oxygen. The control and direct connect apparatuses had similar amounts of Mg, Na, and Ca, but the direct connect had significantly more oxygen and less chloride. This representation of the results also allowed for clear visualization of the battery charger to the other apparatuses, since that accretion is comprised mainly of Mg and very little, especially compared to the other accretion samples, Na and Cl. This, again, agreed with previously conducted research. All of the SEM results can be found in Appendix C: SEM Accretion Results.

4.6 Accretion Structure – Battery Charger Powered Apparatus

The SEM was beneficial in identifying the elements in the accretion; however, it did not determine the structure of the element. To do this, x-ray diffraction (XRD) was used. This test analyzed two samples from differing ends (see Appendix E: XRD Results) and an overall collection of accretion from the battery charger powered apparatus' wire mesh and produced the results seen in Figure 38.

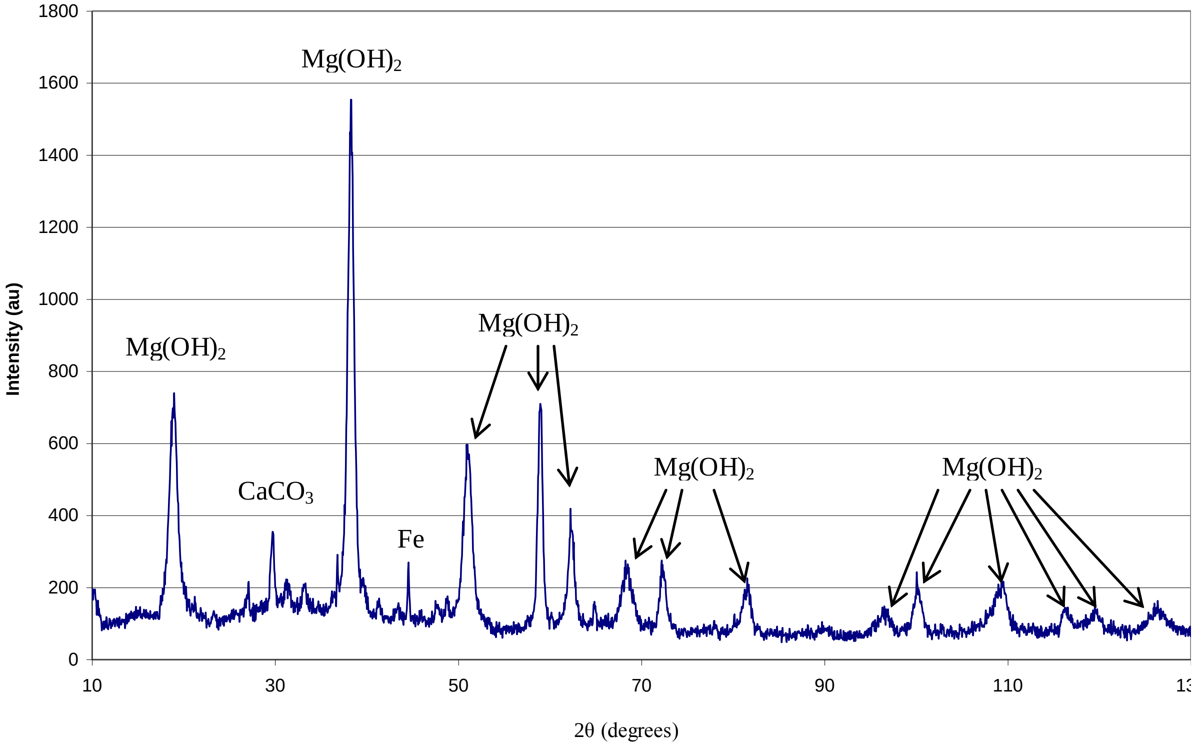


Figure 38: XRD analysis of general accreted matter from battery charger powered apparatus's wire mesh

The intensity, or height, of the peaks in Figure 38 identified the relative amount of the compound in the sample, with the larger peaks indicating a greater composition within the tested sample. In the sample of accretion taken from all over the wire mesh, it was apparent that brucite, or $Mg(OH)_2$ was a major contributing factor to the sample's composition, which was expected. Many of the smaller peaks, called background, that did not match the expected minerals resulted from the impurities trapped within the mineral matrix. This was also expected due to the practical application since very few things in nature are found in a completely pure form, as well as the polluted nature of the Venetian lagoon. Also, some of the small peaks could have indicated some forms of the other elements that were found in the SEM results to be present in the battery charger powered apparatus. In the case of the accretion from the two different areas on the wire mesh cathode, the XRD patterns were nearly identical. This showed that the compound distribution was uniform across the wire mesh, contrary to Hilbertz's (1979) findings.

4.7 Anode Surface Area

It was evident from the amount of accretion normalized by the length of time the apparatuses were in the water and the size of electrodes, the apparatuses powered by the microbial fuel cells in Venice were no more fruitful than the Connecticut apparatus. From the literary review, it was hypothesized that an increase in surface area would induce an increase in the current and thus, accretion rate. However, this was not the case. The voltage measured from the Connecticut apparatus was only 4 percent lower than that of the Venetian MFC powered apparatuses. The results, therefore, supported that the surface area was independent of the voltage, and thus indirectly, the rate of accretion. Nonetheless, this was not believed to be correct. All previous research on the surface area-rate of accretion relationship was conducted on a much smaller scale. It is theorized that the relationship asymptotes and that the two surface areas used in this experiment were too close to the asymptote to achieve a large change in the amount of voltage or current achieved by the system.

4.8 Corrosion

It was apparent that at the time of the overhaul, many of the nuts and bolts were corroded to the point that very little contact was made between the plate or wire mesh and the copper wires. This meant that the circuit was essentially disconnected for an undeterminable length of time. The trend in the voltage, current, and resistance measurements allowed for a reasonable approximation of when the contact was lost, but nothing was certain. Therefore, the electrons that the bottle brushes were harvesting, were not delivered to the anode plate, and thus, not delivered to the wire mesh cathode. As a result, the maximum amount of accreted matter was not achieved in this experiment and the voltage, current, and resistance readings can only be credited as approximations. Rather, this experiment identified the impact that corrosion could have on a large scale system implementation. The corrosion is detailed further in the following section.

4.8.1 Reduction of Stainless Steel Coating

One cause of the high corrosion from the Venetian apparatuses was the elimination of the protective coating on the stainless steel. This was not the problem for the Connecticut apparatus, however, because the steel which was believed to be stainless steel was, after a microscopic evaluation, determined to be plain, basic steel, see Appendix D: SEM Steel Plate Results. The protective coating on the Venetian stainless steel plates was a thin film of weak ionic interactions that increased the surface's passivity to the surrounding medium. This deterioration of the coating resulted from the deprivation of oxygen in connection areas of the plain carbon steel screws, washers, and nuts to the stainless steel plate. The connection of these two non-identical materials caused a localized area of ionic activity with large voltage potential differences, essentially creating individual galvanic cells where ever the two different materials touched. Without the film coating, the material properties of the stainless steel were reduced to those of plain carbon steel. This led to the creation of active-passive cells, or localized areas of intensely active corrosion, which exposed previously protected steel surfaces to the corrosive seawater (*Corrosion in Action*, 2003). The corrosion on the unprotected surfaces was further complicated by crevice corrosion.

4.8.2 Crevice Corrosion

A major site of corrosion was under all of the areas to which silicon was applied to the stainless steel plates. Figure 39 showed the area that was underneath the silicon sealing the electrical connection to the battery charger powered apparatus. While it was originally believed that the silicon would protect the metals from corrosion, it in fact caused a much larger problem than solution. In theory, the silicon should have bonded to the steel plate so tightly that it would have formed a water-tight seal around the connection of the nuts, bolts, washers, and copper wires.

However, this was not the case; seawater got underneath of the silicon and was essentially trapped due to little water movement underneath the silicon. Then, as the oxidation-reduction reactions occurred between the water and the metals, the dissolved oxygen in the trapped seawater became depleted. Once this occurred, there was an abundance of hydroxide ions that created a highly active and exposed area of corrosion, which increased the rate of corrosion (*Corrosion in Action*, 2003).

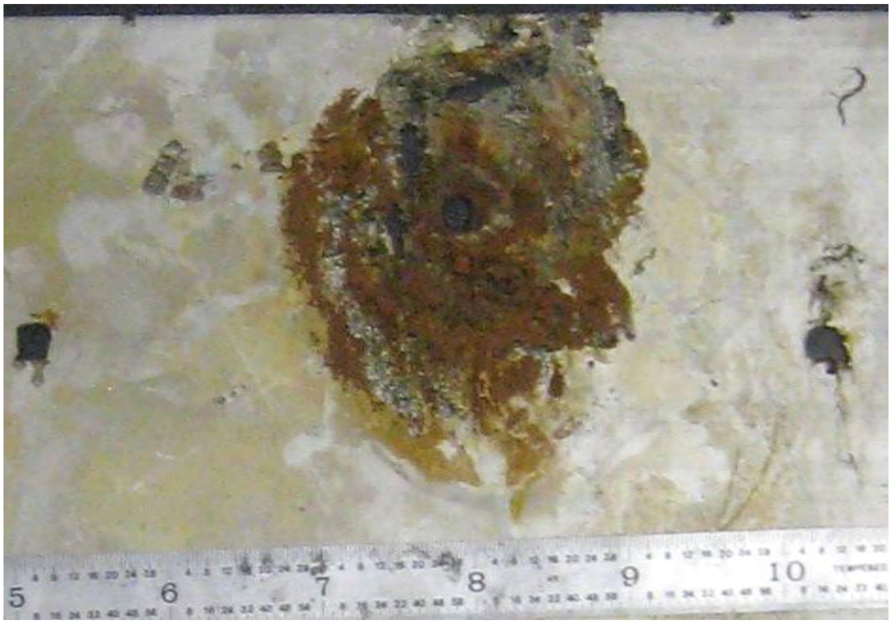


Figure 39: Crevice corrosion at electrical connecting point on battery charger powered apparatus

4.9 Environmental Impact

While it was not at the fore-front of this experiment, observations of the environmental impact were noted. What was particularly unexpected was the amount of wildlife found within the apparatuses located in the Venetian lagoon. There were almost always large schools of fish circling the apparatuses, and during low tide, it was observed that many fish were swimming within the apparatuses. It was interesting to note that the fish were highly concentrated near the apparatuses, but were seldom found swimming near the opposite end of the dock from where the apparatuses were located. When the apparatuses were taken out of the water, the amount of sea creatures that were found within the sediment that rested at the bottom of the apparatuses was astonishing. In most cases, there were starfish coating the inside of the baskets, especially on the wire mesh. There were a few fish and many small shrimp found trying to bury into the sediment to escape the fact that they were out of the water. There was also a high concentration of crabs found in the apparatuses. For example, in the over-haul of the apparatuses, 12 crabs were found in MFC powered apparatus 1.

It is hypothesized that the accumulation of wildlife in the apparatuses was a product of the shelter that the apparatuses provided from the tidal current and many potential predators, especially the very small shrimp. Another yet less realistic hypothesis was that the wildlife was drawn to the electrical current that the apparatuses were generating. There are weakly electric fish that rely on electrolocation, or their own electric signals, for information about their immediately surrounding environment and depth perception (von der Emde, 1999). There has also been a study conducted with electrodes submerged in body of water with fish that, as the researchers concluded, followed the electrical signals to their sources (the electrodes), thus suggesting an induced current may attract certain fish species (Schluger & Hopkins, 1987). While it is unlikely that the species in the Venetian lagoon are such fish, the concept that some aquatic species are affected by this was enough to wonder what other fish have similar electrical signaling mechanisms that have not yet been examined. However, this hypothesis is less credible since there was no significant difference in the wildlife found in the battery charger powered (high electrically induced current) or control (no electrically induced current) apparatuses. If the current truly attracted or repelled the wildlife, a higher concentration of the wildlife would be expected in one of these two apparatuses. The varying amount of sea creatures within the apparatuses could have also been random; a factor of location. Perhaps MFC powered apparatus 1 happened to be located at a place of high concentrations of crabs. It was indeed the apparatus closest to the island and protection of the rocks piled up to the retention wall against the island shores.

This finding was not the same, however, for the MFC powered apparatus in Connecticut. There was little to no difference in the observable sea creatures surrounding the apparatus. For example, there were no fish within sight of the apparatus or surrounding waters. The starfish concentration in the immediate vicinity was seemingly the same as the nearby area. This finding supports the first hypothesis that the large amount of sea creatures in the Venetian apparatuses was due to the protection that the more enclosed electrode frames (baskets) provided. The frame in the Connecticut apparatus was nearly completely open, and therefore, provided essentially no location or shelter advantage for any wildlife. Nonetheless, this project did not observably harm the wildlife in the local waters, but the effect on the ecosystem, especially if this project were to be scaled-up, remains unknown.

4.10 Economic Analysis

In order to further determine the practicality of successfully applying the auto-accretion process in Venice, Italy, was is necessary to examine its economic impact. The purpose of this project was to explore alternate methods of preventing the erosion of canal wall and the barene, or mudflats in the lagoons, in addition to those methods currently available. The new methods explored were to construct a sacrificial wall in front of the canal walls and lagoon mudflats using two different methods of construction; electrodeposition powered by a battery charger and electrodeposition powered by microbial fuel cells. The sacrificial wall would erode from boat wake, one of the major causes of erosion, thus protecting the canal walls and the barene from this type of erosion. The sacrificial wall is self-regenerating, resulting in minimal maintenance in comparison with that now required for the canal walls and barene. It is possible to create these sacrificial walls in the two methods previously stated; however before it can be claimed that this is a practical solution to the problem of erosion faced in Venice, its economic implications must be established. If it is not economically advantageous to construct sacrificial walls using either power source, than these systems should not be applied to Venice.

4.10.1 The Do Nothing Option (Base Case)

To completely and effectively conduct an economic analysis, the “do nothing” option must be considered as the base case for comparison. The “do nothing” options literally refers to the current cost of a process if no changes are added. In this case the “do nothing” option refers to the cost to maintain the canal walls and the barene using only the methods currently employed.

4.10.1.1 Current Canal Wall Maintenance

There are two methods of canal wall maintenance and repairs presently used in Venice, both include dredging. One is the method used to dredge large, frequently used canals, such as the Grand Canal, and the other is that used to maintain smaller to average sized canals. To repair smaller to average sized canals, the canals are totally drained and the walls are manually repaired as the canal is dredged. This process typically takes six months to complete. The average cost for maintain these canals ranges from $189 to $4,766 per square meter of canal wall (Black et al., 2008).

Large, frequently traveled canals cannot be dredged all at once because boat traffic within Venice would essentially shut down if they were. Therefore large canals are dredged in accordance with the vertical maintenance procedure. In this procedure a small portion of the canal is sectioned off relatively close to the wall so that boats are still able to pass. This section is then drained and the canal wall is repaired. The average cost of the vertical maintenance procedure is $11,680 per square meter of canal wall (Black et al., 2008). This cost figure, along with the average cost to maintain smaller and average sized canals, is based on data from 2006. The cost data for the MFC powered option and the electrically powered option, however, were obtained from 2007. For the purposes of this analysis it has been assumed that no significant change has occurred to the costs of canal maintenance from 2006 to 2007, and that subsequently this cost data can be compared as is to the data from 2007 without be scaled with respect to time. Also all cost data is represented in U.S. dollars.

4.10.1.2 Current Barene Maintenance

The existing method for protecting the barene from erosion is by lining the mudflats with long wooden pilings driven deep into floor of the lagoon. Although the purpose of the wood pilings are to prevent the erosion of the barene, the pilings end up eroding and it is necessary that they be replaced on a regular basis. This can be a costly and time consuming process. The pilings are cylindrically shaped. Their average diameter is 25 cm to 30cm and their required length is about 5 meters.

The estimated perimeter of many of the islands located in the lagoon of Venice can be viewed in Table 7. The total perimeter represents the distance that must be lined with pilings, which is information needed to calculate the total number of pilings used in the lagoon. The estimated perimeter of the barene is 138.98 miles. This estimation was obtained from Google Earth, and it does not include every single island in the lagoon. Additionally, due to the limitations of Google Earth, the estimated perimeter is not representative of the exact coast line of every island. However based on the roughly estimated perimeter of the barene, which is about 140 miles, or

22,530,816 cm, and the average piling diameter of 27.5 cm, the total number of pilings required to line the barene is approximately 819,300 (http://books.google.com/images/cleardot.gif).

Table 7: Perimeter of major islands in the lagoon of Venice

Island	Perimeter (mi)	Island	Perimeter (mi)
Sant'Erasmo	6.76	Cavallino	33.34
Murano	5.43	Lazzaretto Nuovo	1.33
Chioggia	2.53	Lazzaretto Vecchio	0.46
Giudecca	3.75	Lido	19.34
Mazzorbo	4.52	Pellestrina	16.16
Torcello	7.74	San Clemente	0.69
La Certosa	2.12	San Francesco del Deserto	0.65
Burano	1.24	San Giorgio Maggiore	0.95
Tronchetto	1.47	San Lazzaro degli Armeni	0.54
Sacca Fisola	1.61	San Servolo	0.72
Isola Di San Michele	1.09	Sottomarina	7.17
Sacca Sessola	1.01	Vignole	4.71
		Island of Venice	13.65
Total			**139.92**

The average cost of a wood piling with a diameter of 10 to 12 inches, or about 25 to 30 centimeters, is 10 to 30 cents per linear foot. Because the pilings are required to be a length of 5 meters, or about 16.4 feet; the total cost of one piling would be about $1.64 to $4.92. Additionally it is necessary to drive the pilings into the floor of the lagoon. The average cost of driving is about $2.50 per piling. Therefore, because approximately 819,300 pilings will be need to line the mudflats, the total cost of protecting the barene from erosion would be about $3,391,900 on the low end of the spectrum. This cost is representative of both the raw material cost and the installation, or driving, cost. The raw materials, which are the wooden pilings, cost $1,343,650 based on the minimum price of 10 cents per linear foot of piling. The installation cost is $2,048,250.

4.10.2 MFC Powered Option

One option to reduce erosion caused by boat wake is to construct a sacrificial wall in front of the barene and canal walls. This sacrificial wall would be built by accreting seawater minerals onto wire mesh, and this process would be driven by an induced current produced by microbial fuel cells. This option would be ideal for preventing erosion in Venice because it requires less maintenance than existing methods and the sacrificial wall is self-repairing as long as the MFC continues to generate current. Also this MFC powered system would be completely contained within the canal or lagoon waters. There would be no need for an external power source outside of the water as with the electrically powered option.

To complete a detailed economic analysis, it is necessary to define all costs associated with each option of maintaining the canal walls and the barene, along with the amount of time it will take the option to be effective. The costs associated with the MFC powered option include an initial capital investment and a yearly maintenance cost. These costs can be viewed below in Table 8 and Table 9 (see Appendix F: Economic Analysis Calculations for detailed calculations). The initial capital investment was estimated per square meter of sacrificial wall. This estimation was determined by summing the costs of all of the materials required to create one square meter of sacrificial wall and the cost of installation. The installation fee is based on the hourly wages for the canal maintenance workers and the total number of hours required for installation. The amount of time needed for installation was estimated to be 5 hours. This estimation was based on the time necessary to install the experimental MFC powered apparatus and an assumed efficiency of canal maintenance workers. The overhead cost includes small items such as silicon and incorporates structural costs, such as the cost of attachment to the canal wall or mudflats. The initial capital investment totals $698 per square meter. This investment only needs to be made once; however eventually the anode will corrode making its replacement necessary. The replacement of this system would coincide with the canal dredging scheduled, and thus there would be no addition fees to replace the system.

The yearly maintenance cost of the MFC powered option is $240 per square meter. This value was obtained by estimating the total number of hours per year that would be spent maintaining this system and multiplying by the average hourly wage of canal maintenance worker in Venice. It was estimated that 12 hours per year would be spent maintaining this system. Once again this estimation was based on the time necessary to maintain and repair the experimental MFC powered apparatus and an assumed efficiency of canal maintenance workers.

Table 8: Initial capital investment for the MFC powered option

Initial Capital Investment per m^2			
Item	**Unit Cost**	**Quantity (per m^2 accreted wall)**	**Cost**
Carbon Fiber Bottle Brush (anode; 1.06m^2)	$31	6	$183
Wire Mesh (cathode, 30cmX30cm)	$14	11	$150
Steel Plate (30cmX30cm)	$22	11	$242
Copper Wire (per m^2)	$0.30	3	$0.90
Bolt, Nut, Washer (1,1,2)	$1.20	6	$7.20
Installation Fee (man hrs.)	$20 per hr	5 hr	$100
Overhead (per $m^{2)}$	$17	1	$17
Total Capital Investment (materials & installation)	**-**	**-**	**$698**

Table 9: Yearly maintenance costs for MFC powered option

Yearly Maintenance Cost			
Item	**Unit Cost**	**Quantity (per m^2 accreted wall)**	**Cost**
Labor Costs (man hrs.)	\$20 per hr	12 hr (1hr/month)	\$240
Total Yearly Cost (maintenance)	**-**	**-**	**\$240**

In order for the accreted wall to effectively reduce the erosion of the canal walls, it is necessary for the accreted wall to obtain a minimum thickness of one centimeter. However a two to three centimeter thick wall would be more successful in completely preventing the erosion of the canal walls or barene. According to the data collected by this project it would take approximately 35 years to accrete a wall of this thickness using MFCs as a power source. This estimation is based on the fact that a total of 4.69 grams of seawater minerals were accreted by the first MFC powered apparatus during the 28 operational days of the apparatus. Also it is important to note that the mass of the accreted matter was determined by total weight difference of the wire mesh from the MFC powered apparatus. A portion of this weight difference could therefore be attributed to elements other than accreted matter, such as algae.

After SEM composition analysis, it was determined that the matter accreted by the first MFC powered apparatus was comprised primarily of brucite, or $Mg(OH)_2$. The density of brucite is 2.39 g/cm^3, and because the accreted matter was mostly brucite, the accreted matter was assumed to have a density of approximately 2.39 g/cm^3. The 4.69 grams of seawater minerals was accreted on a section of stainless steel wire mesh with a cross sectional area of 900 cm^2 (30 cm by 30 cm). Assuming the accreted matter was uniformly distributed across the wire mesh, a thickness of $2.18 x 10^{-3}$cm of matter was achieved in the 28 day duration of this experiment. The rate of accretion was assumed to be constant, and therefore it was determined that a thickness of $1.45 x 10^{-4}$ cm could be accreted per day. This constant was scaled to estimate the time necessary to attain an accreted matter thickness of one centimeter, and it was found that it would take approximately 35 years to obtain the desired thickness. In this calculation, the increase of internal resistance due to the accumulation of accreted matter was neglected. The increase in resistance would actually increase the total amount of time necessary to accrete a 1 cm thick wall because as the resistance increases the current decreases, causing the rate of accretion to also decrease.

The MFC powered system would have to be positioned in the canals or lagoon for 35 years before the city of Venice would experience any of its benefits. Before the accreted wall could begin to prevent the erosion of the canal walls or the barene, a total of \$8,400 would be spent on maintenance costs in addition to the initial capital investment. This means that before the auto-accretions system even partially begins to work, a minimum of about \$9,098 would have to be invested. However once the accreted wall has been formed, in theory the MFCs could generate enough current to continually maintain a protective wall even in spite of erosion. Additionally, following the same estimation procedure described above, it would take approximately 70 years to accrete a 2 cm thick wall of seawater minerals and 106 years to achieve a thickness of 3cm.

4.8.3 Electrically Powered Option

An additional way to protect the canal walls and the barene from erosion due to boat wake is to accrete a sacrificial wall using local electricity as the source of power. The electricity that drives the accretion would be supplied from a source, such as a battery charger or another direct current power supplier.

The cost data for the electrically powered option can be viewed in Table 10 and Table 11. The initial capital investment per square meter of accreted wall would be $512. This cost is based on the costs of all the materials used to create this system, as well as the installation fee of this system. The installation fee is based on the hourly wages for the canal maintenance workers and the total number of hours required for installation. The installation time was estimated to be 5 hours, based on the time necessary to install the experimental apparatus powered by a battery charger and an assumed efficiency of canal maintenance workers. The overhead cost includes small items such as silicon and incorporates structural costs, such as the cost of attachment to the canal wall or mudflats.

The yearly maintenance cost for this system would be $144. This cost includes the yearly cost of labor and electricity. Due to problems with the battery charger, the experimental electrically powered apparatus was successfully operating for only a total of 144 hours, or 6 days for 24 hours a day. During this time, the apparatus was receiving an average of 60 watt-hours, or 0.06 kilowatt-hours (kWh), of electricity. In order for the accreted wall to reach a minimum thickness of about one centimeter, the system must obtain 0.06 kWh of electricity, twenty-four hours a day for 67 days or approximately 10 weeks. Also, in order to combat erosion of the sacrificial wall and to prevent the accreted matter from dissociating, the system should receive 0.06 kWh of electricity for an additional periodic increments of time throughout the year. The system should initially spend 10 weeks connected to an electricity source, then for the remaining duration of its operation, the system should spend one month disconnected and then the next month connected to an electricity source, and this pattern should be continued for the duration of the year. In Italy the cost of electricity per kilowatt-hour is $0.09 and because 0.06 kilowatts of electricity is required for 6 months per year, or 4368 hours per year, the total cost of electricity totals $24 per year (0.06kW x 4368h x $0.09/kWh).

Table 10: Initial capital investment for battery charger powered option

<table>
<tr><th colspan="4">Initial Capital Investment per m^2</th></tr>
<tr><th>Item</th><th>Unit Cost</th><th>Quantity (per m^2 accreted wall)</th><th>Cost</th></tr>
<tr><td>Wire Mesh (cathode, 30cmX30cm)</td><td>$13.60</td><td>11</td><td>$149.60</td></tr>
<tr><td>Steel Plate (30cmX30cm)</td><td>$22</td><td>11</td><td>$242</td></tr>
<tr><td>Copper Wire (per m^2)</td><td>$0.30</td><td>10</td><td>$3</td></tr>
<tr><td>Bolt, Nut, Washer (1,1,2)</td><td>$1.20</td><td>2</td><td>$2.40</td></tr>
<tr><td>Installation Fee (man hrs.)</td><td>$20 per hr</td><td>5 hr</td><td>$100</td></tr>
<tr><td>Overhead (per m$^{2)}$</td><td>$17</td><td>1</td><td>$17</td></tr>
<tr><td>Total Capital Investment (materials & installation)</td><td>-</td><td>-</td><td>$512</td></tr>
</table>

Table 11: Yearly maintenance costs for battery charger powered option

<table>
<tr><th colspan="4">Yearly Maintenance Cost</th></tr>
<tr><th>Item</th><th>Unit Cost</th><th>Quantity (per m^2 accreted wall)</th><th>Cost</th></tr>
<tr><td>Labor Costs (man hrs.)</td><td>$20 per hr</td><td>6 hr (1hr/ 2 months)</td><td>$120</td></tr>
<tr><td>Electricity (per kWh)</td><td>$0.09</td><td>0.06kW for 4368hr</td><td>$24</td></tr>
<tr><td>Total Yearly Cost (maintenance)</td><td>-</td><td>-</td><td>$144</td></tr>
</table>

In order for the accreted wall to effectively reduce the erosion of the canal walls, it is necessary for the accreted wall to obtain a minimum thickness of one centimeter. As stated previously, it would take 10 weeks for an electrically powered system to accrete a wall with this desired thickness. This estimation is based on the fact that a total of 185.21 grams of seawater minerals were accreted on a wire mesh with a cross sectional area of 900 cm^2 by the apparatus powered by a battery charger during the six operational days of this apparatus. The accreted matter on this apparatus was also determined to be primarily brucite, and therefore it was assumed that its density was approximately 2.39 g/cm^3. Assuming the accreted matter was uniformly distributed across the wire mesh, a thickness of about 0.09 cm of matter was achieved in the 6 day duration of this experiment. The rate of accretion was assumed to be constant, and therefore it was determined that a thickness of 0.015 cm could be accreted per day. This constant was scaled to estimate the time necessary to attain an accreted matter thickness of one centimeter, and it was found that it would take approximately 67 days, or 10 weeks, to obtain the desired thickness. To attain a thickness of 2 cm, the system would need to be connected to a source of electricity for 133 days, and for 200 days to reach a thickness of 3 cm.

4.8.4 Comparison of Methods

Even though seawater minerals did accrete on the apparatus powered by microbial fuel cells during this project, the economic analysis indicated that in its present state the auto-accretion system cannot be feasibly applied to the city of Venice. The economic analysis showed that the benefits of the auto-accretion system were outweighed by the overall cost of the system, as well as the length of time required for the system to yield results.

The current cost of maintenance to small or average sized canals is $189 to $4,766 per square meter of wall. The auto-accretion system would cost a minimum of $9,098 per square meter of wall and take at least 35 years before the system even began to protect the canal walls from erosion. It is evident that the costliness of this system prevails over its benefits, and therefore the auto-accretion process could not be applied to small or average sized canals until significant advances in technology our made.

The current cost of maintaining large canals is $11,680 per square meter of wall. When dealing with larger canals, the auto-accretion process does cost less; however the amount time required for the process to effectively and completely prevent erosion of the canal walls due to moto ondoso, is far too much to make the auto-accretion process a viable option for canal maintenance.

5.0 Conclusions

The analysis of this experiment was a detailed process involving multiple tests and evaluations. There was difficulty extracting solid general trends from the electrical readings, due to the highly sporadic measurements. However, the voltage recordings for the MFC apparatuses were consistent enough in the overall process to determine that the voltage peaked after different lengths of time being underwater, which was possibly a results of water temperature and other localized environmental factors. Also, the intensity of the voltage peaks was independent of the anode surface area, as demonstrated by the Connecticut versus Venetian apparatuses.

The analysis conducted on the wire mesh cathodes established that an accelerated rate of accretion was produced by the MFC powered auto-accretion process when compared to that of the natural accretion process; however the rate of accretion driven by MFCs was still significantly less than that driven by the battery charger. From the in-depth analysis of the accretion from the wire mesh cathodes, it was determined that the minerals accreted best to the outer perimeter of the wire mesh and near the electrical connections. Through an SEM, it was concluded that the chemical composition of the Venetian MFC 1 apparatus was very similar to that of the Venetian battery charger powered apparatus, containing mostly Mg and O, which, according to previously conducted research, would most likely be in the form of brucite ($Mg(OH)_2$). However, the composition of all of the other apparatuses had, for the most part, a lot of silicon, Si as well as Na and Cl (most likely in the form of NaCl). This most likely was a result of contamination from or migration of the silicon oxide that was used as the water sealant around the electrical connections, and also the natural affinity for minerals to accrete at very slight condition differences. Also, an XRD analysis was completed on the accretion from the battery-powered apparatus, which confirmed that the most abundant compound in the accretion was brucite.

Although the relationship between the amount of matter accreted and the anode surface area could not be determined at this large of a scale, it was determined that corrosion was a much larger factor to the success or failure of the experiment. The corrosion encountered on the stainless steel plates, nuts, bolts, and washers was significant enough to greatly affect the experiment results. One source of the corrosion could have been caused by the reduction of the thin film protective coating on the stainless steel, which resulted from contact between materials with different electrical potentials. The extremely corroded localized areas underneath the siliconed areas were caused by crevice corrosion, in which seawater trapped under the silicon increased the local rate of corrosion.

An environmental analysis based on observations was noted mostly when the apparatuses were taken out of the water. The results of the analysis were inconclusive and require further study. The project's impact on the local underwater ecosystem is necessary to make an ethical decision on the future success and implementation of the auto-accretion system.

The major deciding factor as to whether this system could be a feasible solution to the Venetian wall erosion problem, however, stemmed from the economical analysis of the process. According to this analysis, the current system is not yet cost-effective enough to justify its implementation. A minimum of 35 years is too great of a time since the system would probably have to have major repairs, if not be replaced, before it accreted the desirable thickness. Therefore, further research must be done to enhance the auto-accretion process to the point at which it becomes an economically feasible solution to the Venetian boat wake problem.

6.0 Recommendations

While this project provided conclusive evidence that MFCs can power the auto-accretion process, much research is required for taking this technological development further. There are many aspects that could be applicable for further research, including repeating this experiment under different conditions to work towards increasing the efficiency of the system. Also, there are many details that can be expanded upon as possible solutions or replacements for certain aspects to the system, such as an alternative energy source. The following are 10 recommendations for the furthering of this research:

1. **Validate the high concentration of halite, NaCl.** The results of the Venetian accretion analysis showed a high concentration of halite, NaCl, which is known to be present in salt water, but was not expected to be a major component of the accretion sample. Repeat experiment to determine if this was a valid finding.

2. **Conduct experiment over a longer period of time which spans a few meteorological seasons in the Venetian waters.** This would allow for a better estimation in time and cost figures since the data would be extrapolated from a larger set of data at the non-worst case scenario. One plausible explanation for the high projection in time and costs of the proposed auto-accretion system from this project was that the data was extrapolated from a very minute amount of data that spanned only a brief stint, relative to length of time necessary for the process, of underwater exposure. Allowing the apparatuses more time in the water would allow a greater opportunity for minerals to accrete onto the cathode surface. Also allowing the process to occur when the water temperature is warmer, the microbial activity would be greater and the rate of accretion faster. This would provide more solid estimates for the whole economic analysis, and would provide further data from which expected future results could be extrapolated, possibly drawing a different conclusion about the overall feasibility of the auto-accretion system.

3. **Alter anode connections.** With the high corrosivity of seawater and the significant inhibition of the experiment due to corrosion, an alternate method of attaching the copper wires to plates must be determined for the auto-accretion system to become a feasible solution. The best alternative would be to avoid having to use copper wires, especially in the connection of the anode steel plate and bottle brushes. Suggestions include:

    - <u>Changing the material of the brush handle from platinum to another metal that can be physically connected to the steel plate</u>. This would eliminate the need to use wires at all with the exception of the testing leads. More research would need to be done on the effects of corrosion at the connection points and the replacement material’s compatibility with microorganisms.

    - <u>Replacing the steel plate with a solid block of carbon fiber</u>. Then, as shown in Figure 40, drill holes into the bottom slightly larger than the width of the bottle brush handle. Insert bottle brush handle into the hole. Fill remaining space with graphite and pack tightly. Then possibly find a way to chemically or physically bind the carbon atoms from the graphite to the block of the carbon. Research would need to be done on the impact of this proposed configuration, especially on the effects at the brush-carbon block connection point. Also, it would need to be evaluated whether or not the solid block of carbon fiber would clog, as previous research suggests may occur.

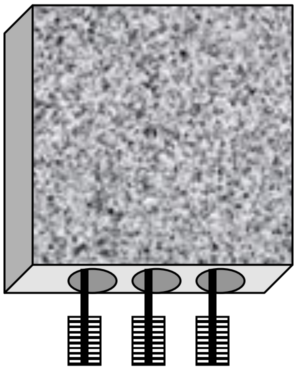


Figure 40: Proposed alteration to anode brush-to-plate connection

4. **Optimize ratio of anode brush surface area to induced current between electrodes**. In previously conducted research, the amount of anode surface area had a clear relationship with the amount of current, or induced electro-chemical potential, (Kim et al., 2002) which in this project was measured in voltage. This trend, however, was not valid according to this experiment's results, and it was hypothesized that it was because the relationship of the surface area to the current between the electrodes asymptotes and that the surface areas used were too close to the asymptote to note the difference. Therefore, it is possible that smaller surface areas, or fewer brushes, could be used to accrete relatively the same amount of matter, making this venture more economical.

5. **Optimize distance between electrodes.** The distance between the electrodes was chosen to be about 3cm for this experiment since this was an approximately average distance according to other MFC experiments that have been done. It is possible, though, that this distance was not optimal considering the increase in the current induced and the field conditions (versus stacked laboratory conditions). Therefore, a change in the distance between the electrodes, either greater or smaller, could induce a greater current flow or accretion rate.

6. **Optimize shape for force absorption**. There are two alterations to the current design's overall shape that should be investigated:

   - <u>Changing the frame supporting the electrodes</u>. The experiment, as is, required a frame, which in the case of the Venetian apparatuses was rather large and spatially inefficient. It is supposed to be the wall of accretion on the wire mesh that breaks the forces of the boat wake in the Venetian canals, not the frame to which the wall is attached. The way the apparatus is currently designed, the laundry basket frame would assume the majority of the impact. Investigations should be made about different configurations that could still provide ample support for the electrodes while allowing the water's pathway to the mineral-accreted cathode wall to remain uninhibited.

- Changing the overall shape of the electrodes. This would require information about the relationship between the absorption of forces from the boat wake on the shape of the electrodes. For example, would a rippled cathode absorb the forces better than a flat cathode? The further the shape moves away from a flat form, however, a possible increase in manufacturing cost could occur. Therefore, a balance must be struck between the absorption force capability and overall cost.

7. **Evaluate potential use of other power sources**. This experiment evaluated the use of MFCs as the power source that would accelerate the accretion rate. This seemed like a logical power source considering the bacteria and wastewater concentrations in the seawater within the lagoon and canals. However, the accelerated accretion process could also be powered by other alternative energy sources, such as solar panels or arrays, small-medium wind turbines, or by utilizing the natural current and tides. Further analysis would need to be done to determine the economical and logistical benefits or disadvantages of each of these sources, as well as some experiments to determine the maintenance that would be required of these systems.

8. **Evaluate the operation of a jump-started apparatus maintained by a MFC**. For this project, the MFC was assumed to start with no accreted matter on the cathode and accumulate the minerals on the surface over time. The economical analysis, however, showed that this would be a very time-consuming process. It is possible that the accretion process could be jump-started either by using a direct-current (DC) battery charger power supply in the apparatus' final location or possibly in a laboratory and then transported to the desired location. If the cathode was coated with mineral accretion in a laboratory, then the desired thickness and composition could be achieved since it would be possible to control the conditions under which it is formed on the cathode. The only difficulty would then be the transportation of the accretion-crusted cathode to the desired location without losing too much of the accretion.

   Once the apparatus was jump-started, the MFC aspect would maintain the equilibrium of the system. The MFC induced current would preserve the self-repairing characteristic that auto-accretion offers, which would be important in reducing the amount of maintenance needed on the system. Also, the small amount of current would ensure that the accreted ions do not dissociate back into the salt water, keeping the thickness at its desired level or slowly increasing to the maximum potential of the configuration.

   This idea of jump-starting the accretion process either using a DC power supply or the formation of accretion in a laboratory and then using a MFC to sustain the process, would need further analysis. This idea has not yet been tested and would need an extensive economic and practicality analysis to determine its feasibility. For example, the practicality analysis would need to consist of best transportation methods for moving the accretion-covered cathode from the laboratory to its final destination, the amount of accretion that can be expected to be lost in that process, as well as the possible need for the laboratory to be close to the final destination. This idea, however, definitely holds a great deal of potential and should be researched much further.

9. **Determine effects of apply bio-coating anode brushes pre-installation**. Since this was a field experiment with many uncontrolled parameters, such as the particular species of bacteria and substrate present in the medium, and considering this to be a base-case scenario, the anode brushes were attached to the apparatus without any pre-installation treatment. In previously conducted research, however, like that done by Logan et al. (2007), it has been shown that a greater current density can be achieved by pre-treating the anode brushes with various electron mediators, such as coating carbon cloth with ammonia-gas for air-cathode MFCs (Logan et al., 2007). Due to experimental constraints, this was not performed, but evaluations should be made to determine the degree to which the pre-treating of the anode brushes could increase the current, and therefore power density, in a field experiment.

10. **Explore issues of cultural acceptance from local citizens**. When it comes to matters of their city, the citizens of Venice are resistant to the idea of change. Venice is a beautiful place, why alter that appearance with concrete walls instead of the beautiful and original marble, stone, and brick stairways leading out of the canals that have drawn visitors here for hundreds of years? Though the canal walls are in desperate shape, the Historic Preservation Law of 1939 includes a policy that the walls must be repaired in such a manner as to not alter their traditional appearance (F. Carrera, personal communication, February 28, 2008). Therefore, it must be explored whether an improved version of the auto-accretion system would be accepted as a means of protecting the canal walls. If not, it should be determined what other alternatives, such as thick wooden planks or slabs of concrete, would be acceptable. It is possible that this system will not be an applicable solution to Venice's problem with the boat wake and crumbling walls. However, that is not to say that the system is a failure, but that it would not be the correct application for this new technology.

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Appendix A: Apparatus Maintenance Schedules

A.1 Maintenance Schedule of MFC 1 Powered Apparatus

Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday
Oct 28	29	30	31 On-site assembly	Nov 1	2	3
4	5 Installation	6	7	8	9	10
11	12	13	14	15	16	17 Inspected
18	19 Inspected	20	21	22	23	24
25	26	27	28	29	30	Dec 1 Lifted out for visual inspection – determined maintenance needed
2	3 Removed	4	5	6	7	8
9	10	11	12	13	14	15

A.2 Maintenance Schedule of MFC 2 Powered Apparatus

Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday
Oct 28	29	30	31 On-site assembly	Nov 1	2	3
4	5 Installation	6	7	8	9	10
11	12	13	14	15	16	17 Inspected
18	19 Inspected	20	21	22	23	24
25	26	27	28	29	30	Dec 1
2	3	4 Lifted out for repairs; Replaced corroded parts	5 Replaced corroded parts; resiliconed	6 Dropped back in	7	8 Lifted out to check on but dropped back in
9	10	11	12 Removed	13	14	15

A.3 Maintenance Schedule of Battery Charger Powered Apparatus

Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday
Oct 28	29	30	31 On-site assembly	Nov 1	2	3
4	5 Installation	6	7 Inspected	8	9	10
11	12	13	14	15	16	17 Inspected/lifted out for visual inspection
18	19 Confirmed problem was with battery charger	20	21	22	23	24
25	26	27	28 Bought new battery charger	29	30	Dec 1 Pulled out & fixed & resiliconed
2	3 Dropped back in	4	5 Pulled out; resiliconed	6 Dropped back in	7	8 Plugged in
9	10	11	12 Removed	13	14	15

A.4 Maintenance Schedule of Control Apparatus

Sunday	**Monday**	**Tuesday**	**Wednesday**	**Thursday**	**Friday**	**Saturday**
Oct 28	29	30	31 On-site assembly	Nov 1	2	3
4	5 Installation	6	7	8	9	10
11	12	13	14	15	16	17 Installed test leads
18	19 Inspected	20	21	22	23	24
25	26	27	28	29	30	Dec 1
2	3	4 Lifted out for repairs; Replaced corroded parts	5 Replaced corroded parts; resiliconed	6 Dropped back in	7	8
9	10	11	12 Removed	13	14	15

A.5 Maintenance Schedule of Direct Connect Apparatus

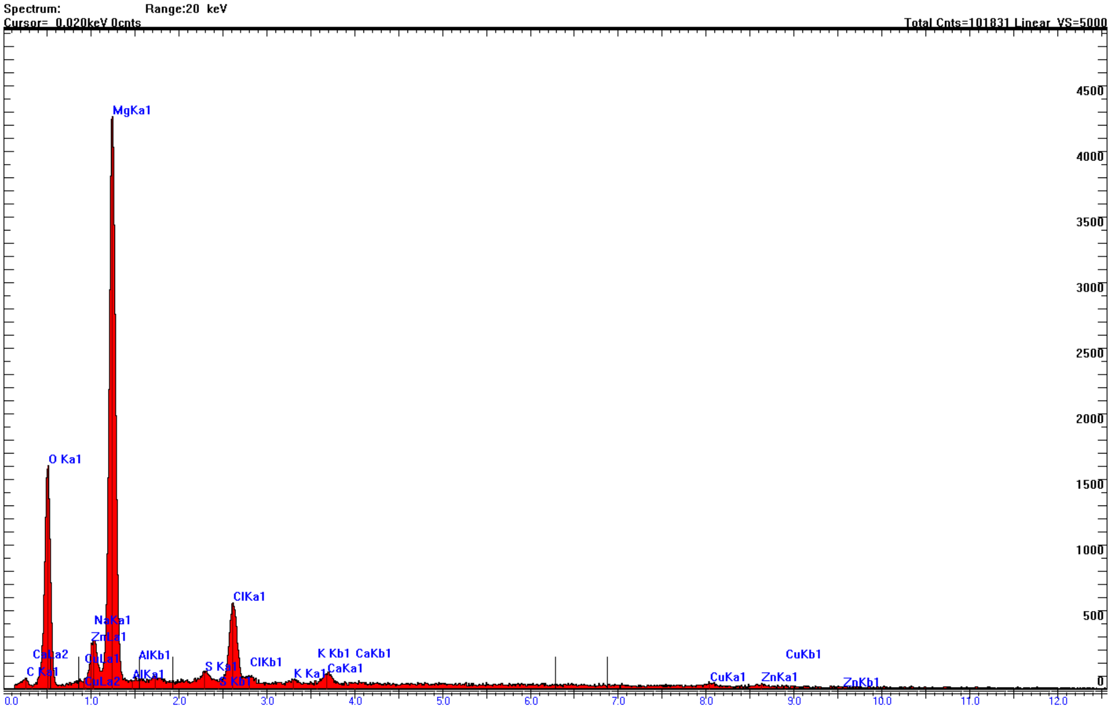
Sunday	**Monday**	**Tuesday**	**Wednesday**	**Thursday**	**Friday**	**Saturday**
Oct 28	29	30	31 On-site assembly	Nov 1	2	3
4	5 Installation	6	7	8	9	10
11	12	13	14	15	16	17 Inspected
18	19 Inspected	20	21	22	23	24
25	26	27	28	29	30	Dec 1
2	3	4 Lifted out for repairs; Replaced corroded parts	5 Replaced corroded parts; resiliconed	6 Dropped back in	7	8
9	10	11	12 Removed	13	14	15

Appendix B: Tabulated Results

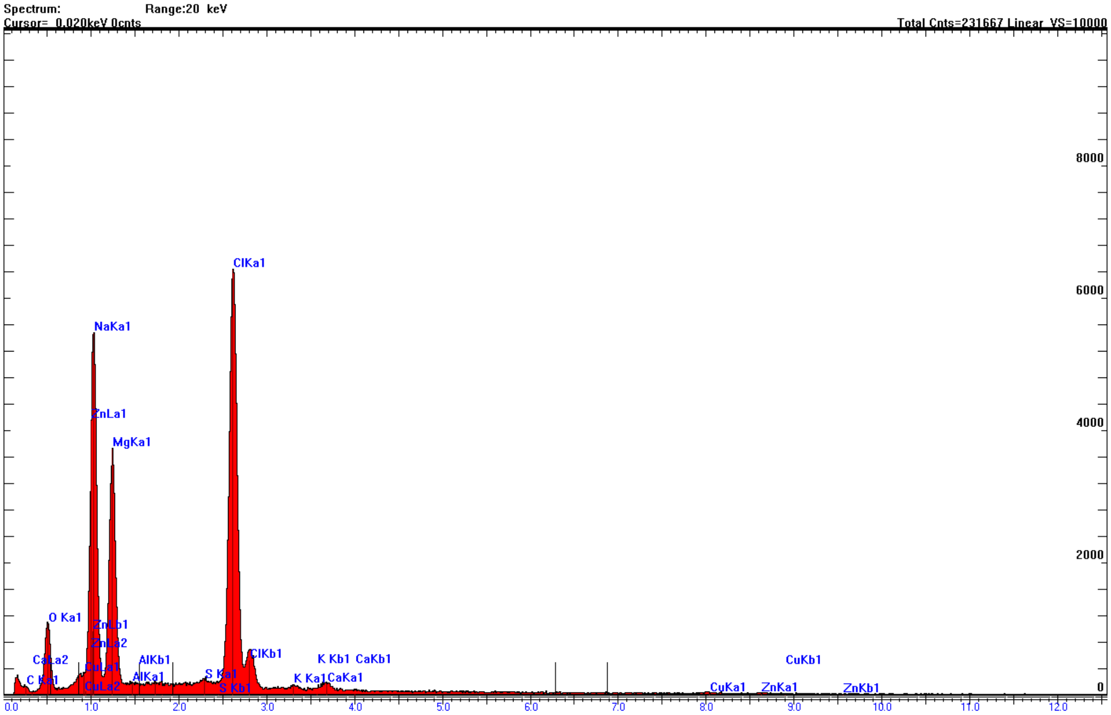
		MFC 1				MFC 2				Electric				Control				CT apparatus
Time (days)	Tide	V (V)	R (Ω)	I (A)	P (W)	V (V)	R (Ω)	I (A)	P (W)	V (V)	R (Ω)	I (A)	P (W)	V (V)	R (Ω)	I (A)	P (W)	V (V)
3	med/high	0.2403	9.50E+06	2.113E-03	5.078E-04	0.119	5.45E+03	8.480E-04	1.009E-04	1	-	1.000E-01	1.000E-01	-	-	-	-	-
10	-	0.3688	3.04E+07	2.830E-02	1.044E-02	0.2653	1.240E+07	2.164E-03	5.741E-04	0.0686	1.430E+02	5.000E-04	3.430E-05	-	-	-	-	-
				3.009E-03	1.140E-03			2.133E-03	6.685E-04			7.310E-04	1.189E-04			-	-	-
13	high	0.3788	3.80E+07	2.56E-02	9.697E-03	0.3134	1.876E+06	1.26E-02	3.949E-03	0.1627	4.400E+03	1.80E-03	2.929E-04	-	-	-	-	-
				2.875E-03	1.025E-03			1.950E-03	5.519E-04			1.073E-03	3.816E-04			2.430E-04	9.283E-06	-
15	low	0.3566	2.02E+07	2.56E-02	9.129E-03	0.283	1.44E+07	1.14E-02	3.226E-03	0.3556	2.71E+07	2.40E-03	8.534E-04	0.0382	1.05E+02	5.0E-04	1.9E-05	-
20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.0324
24	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.0413
				5.51E-04	2.832E-05			1.837E-03	4.892E-04			-	-			2.400E-02	2.160E-04	-
25	high	0.0514	1.26E+02	2.30E-03	1.182E-04	0.2663	1.184E+07	8.5E-03	2.264E-03	-	-	-	-	0.0090	1.759E+03	0.0E+00	0.0E+00	-
				2.24E-04	1.008E-05			1.587E-03	3.883E-04			-	-			1E-06	9E-10	-
27	low	0.0450	1.172E+02	1.4E-03	6.300E-05	0.2447	1.006E+07	6.1E-03	1.493E-03	-	-	-	-	0.0009	1.386E+03	0.0E+00	0.0E+00	-
				1.487E-03	2.943E-04			7.72E-04	9.063E-05			-	-			1E-06	4E-10	-
29	med	0.1979	6.40E+06	8.2E-03	1.623E-03	0.1174	5.55E+02	2.1E-03	2.465E-04	-	-	-	-	0.0004	1.419E+03	0.00E+00	0.000E+00	-
				-	-			8.02E-04	1.001E-04			-	-			0.000E+00	0.000E+00	-
30	-	-	-	-	-	0.1248	4.01E+03	2.0E-03	2.496E-04	-	-	-	-	0.0025	1.575E+03	0.0E+00	0.00E+00	0.0417
				-	-			5.20E-05	3.884E-06			-	-			1.34E-04	4.07E-06	-
33	low	-	-	-	-	7.47E-02	7.97E+02	0.00E+00	0.00E+00	-	-	-	-	3.04E-02	7.49E+02	2E-04	6.08E-06	-
				-	-			0.000E+00	0.000E+00				0.000E+00			0.000E+00	0.000E+00	-
34	high	-	-	-	-	9.17E-02	8.89E+02	0.00E+00	0.00E+00	18.53	OL	5.23E+00	9.69E+01	0.401	OL	0.00E+00	0.00E+00	-
				-	-			0.000E+00	0.000E+00							0.000E+00	0.000E+00	-
36	high	-	-	-	-	5.81E-02	2.799E+02	0.00E+00	0.00E+00	12.00	OL	4.84E+00	5.81E+01	3.08E-01	1.69E+07	0.00E+00	0.00E+00	-
				-	-			2.53E-04	8.298E-06							5.24E-04	2.075E-04	-
37	low	-	-	-	-	3.28E-02	1.400E+03	0.00E+00	0.00E+00	11.79	OL	4.96E+00	5.85E+01	0.396	OL	6E-04	2.38E-04	-
				-	-			3.4E-05	1.646E-06									-
38	high	-	-	-	-	4.84E-02	2.51E+02			11.72	OL	5.43E+00	6.36E+01	0.408	OL	5.04E-04	2.06E-04	-
				-	-			-	-			-	-			-	-	-
39	med	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
41	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.3622
46	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.3264
51	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.0199
60	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.0323
80	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.0346
85	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.0322

Appendix C: SEM Accretion Results

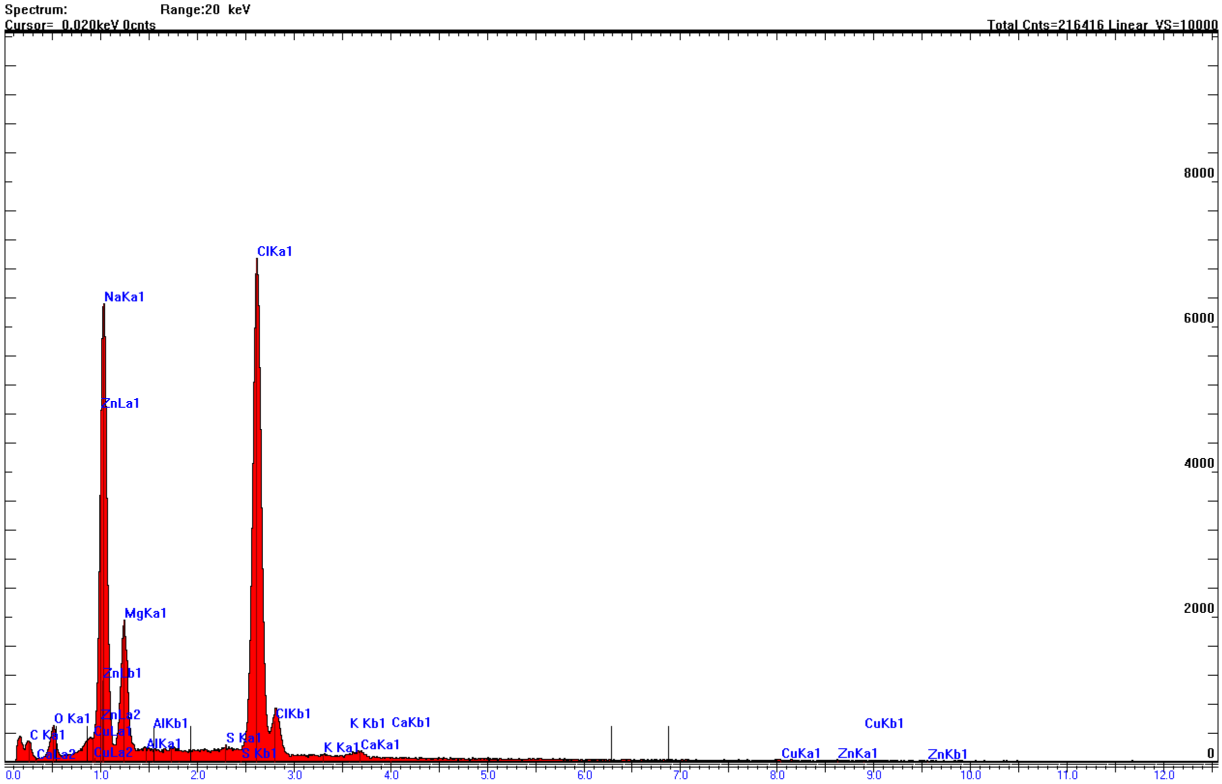
C.1 SEM Results from MFC Powered Apparatuses



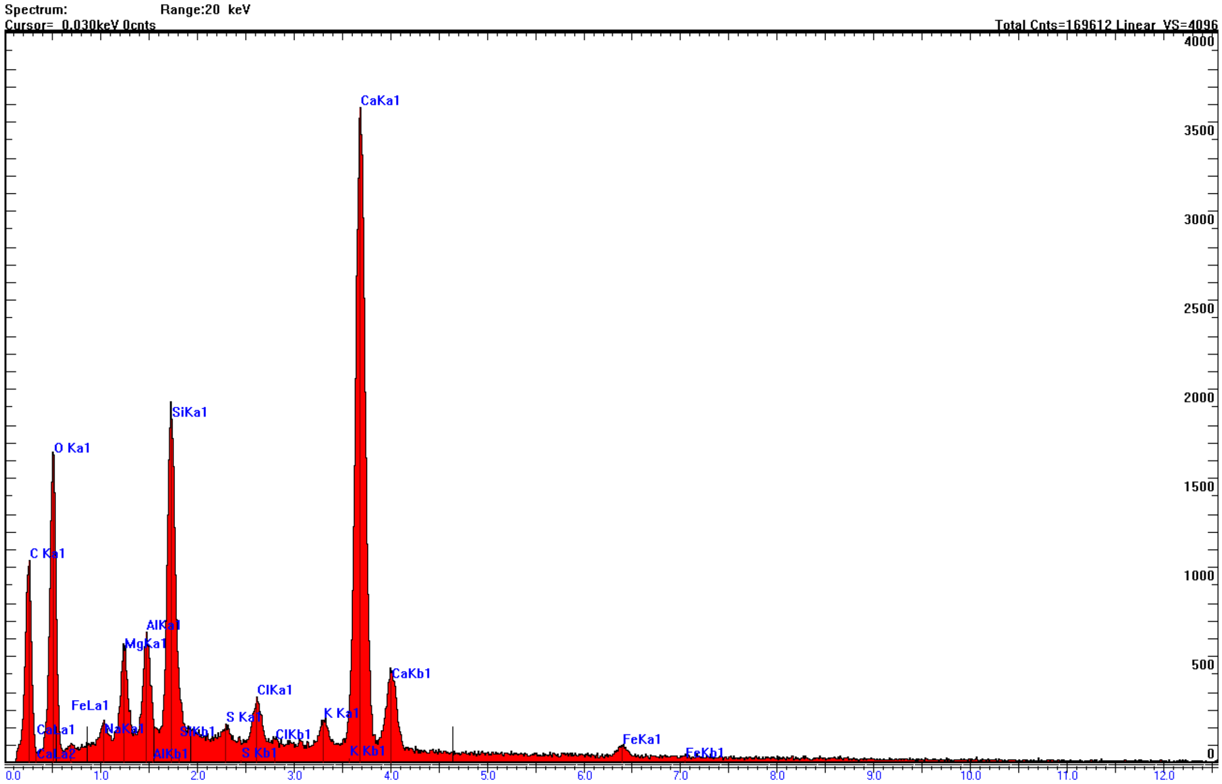
MFC powered apparatus 1 – dark section of particle 1 – February 11, 2008



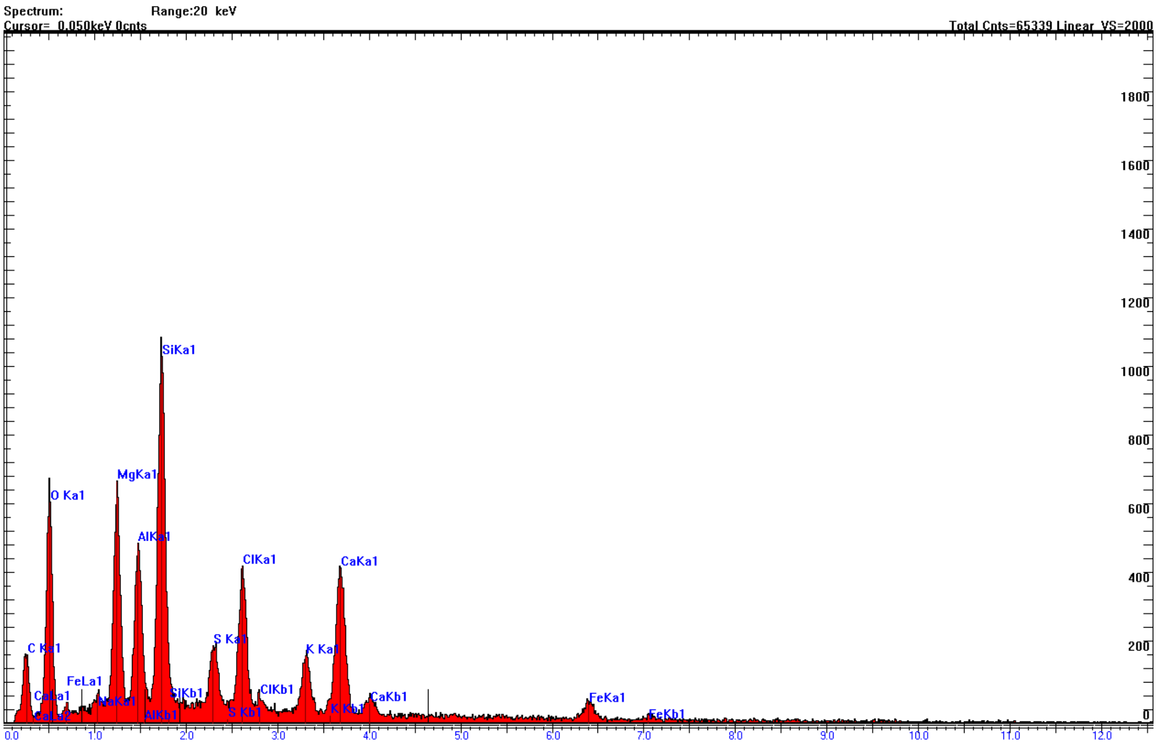
MFC powered apparatus 1 – light section of particle 1 – February 11, 2008



MFC powered apparatus 1 – particle 2 – February 11, 2008

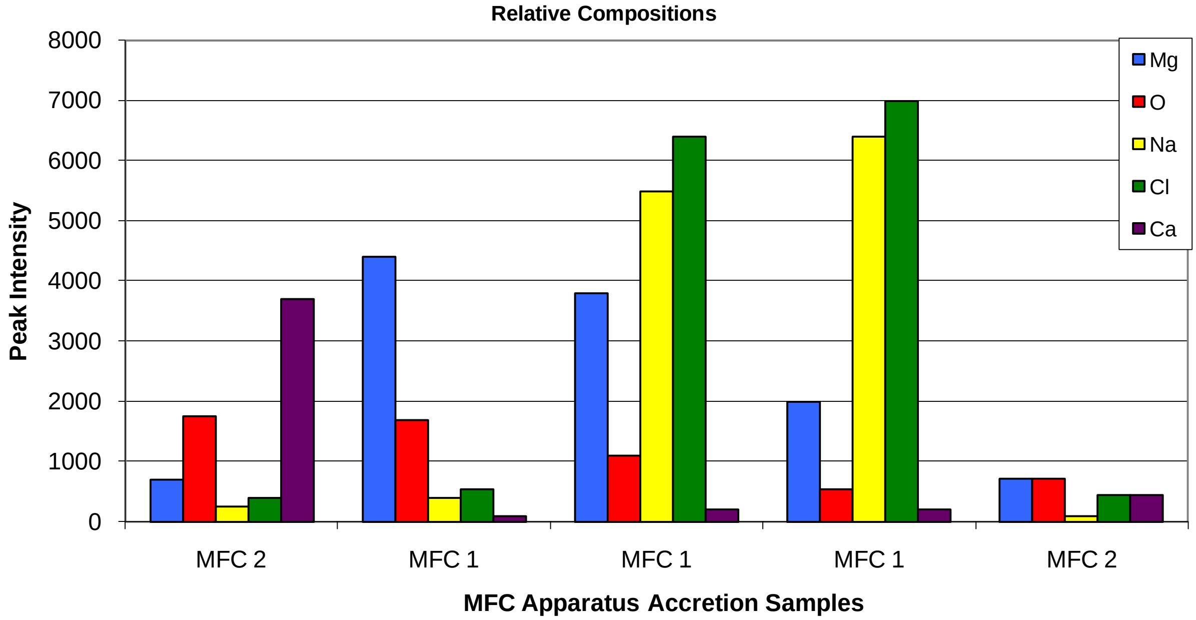


MFC powered apparatus 2 – February 18, 2008

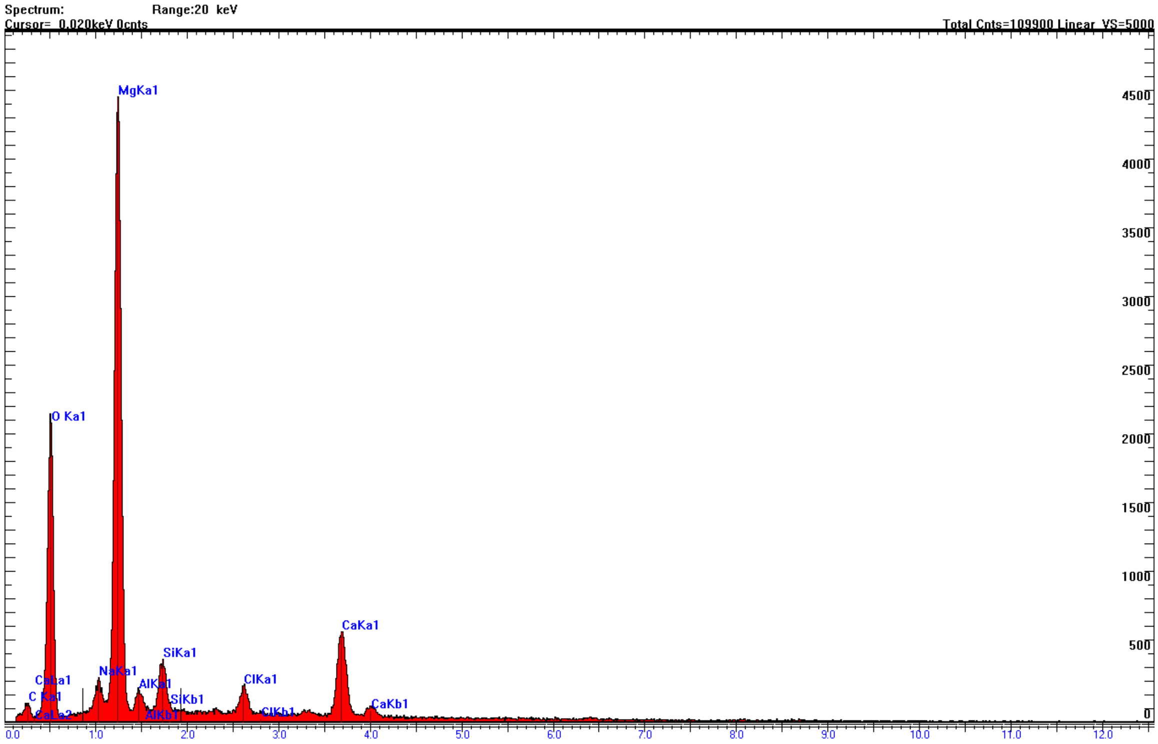


MFC powered apparatus 2 – February 26, 2008

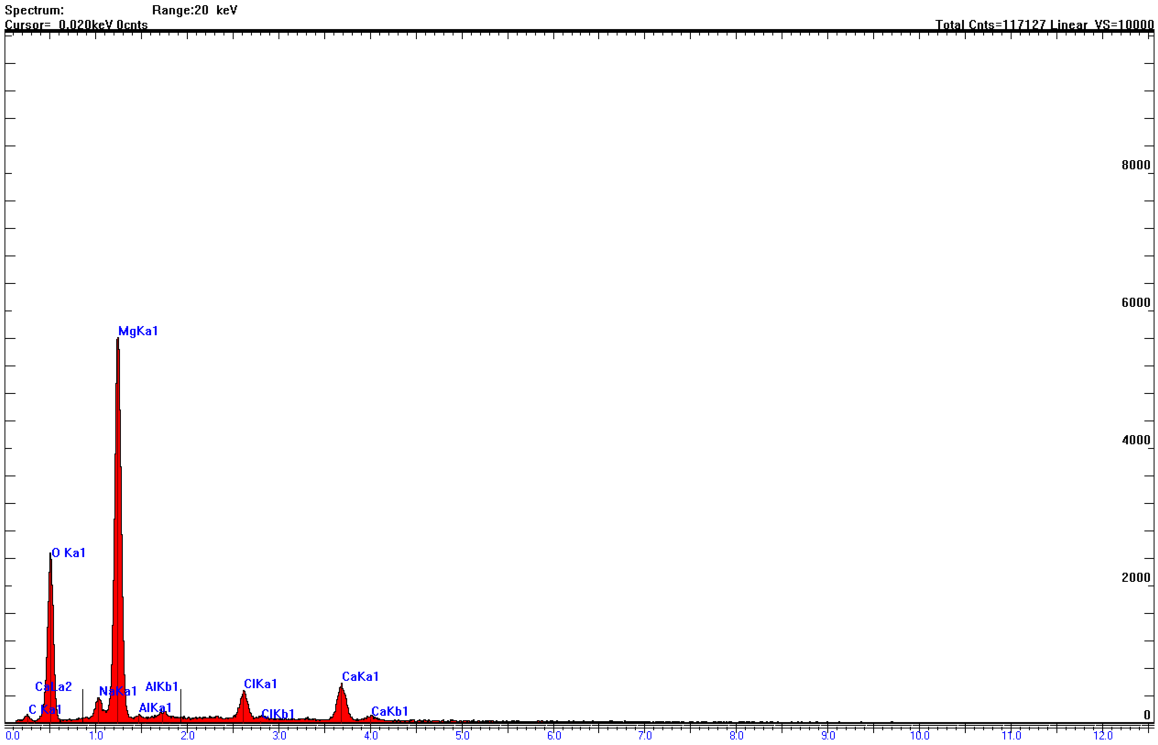
Comparison of all of these samples:



C.2 SEM Results from Battery Charger Powered Apparatus

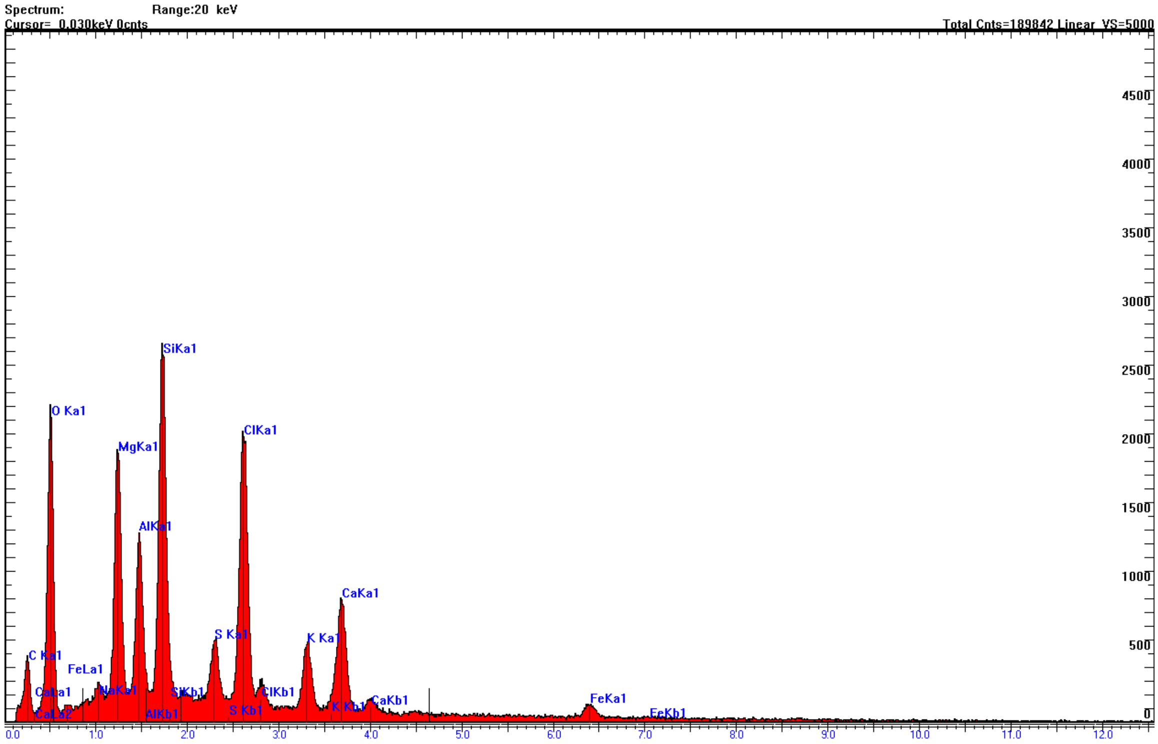


Battery charger – near electrical connection point – February 11, 2008

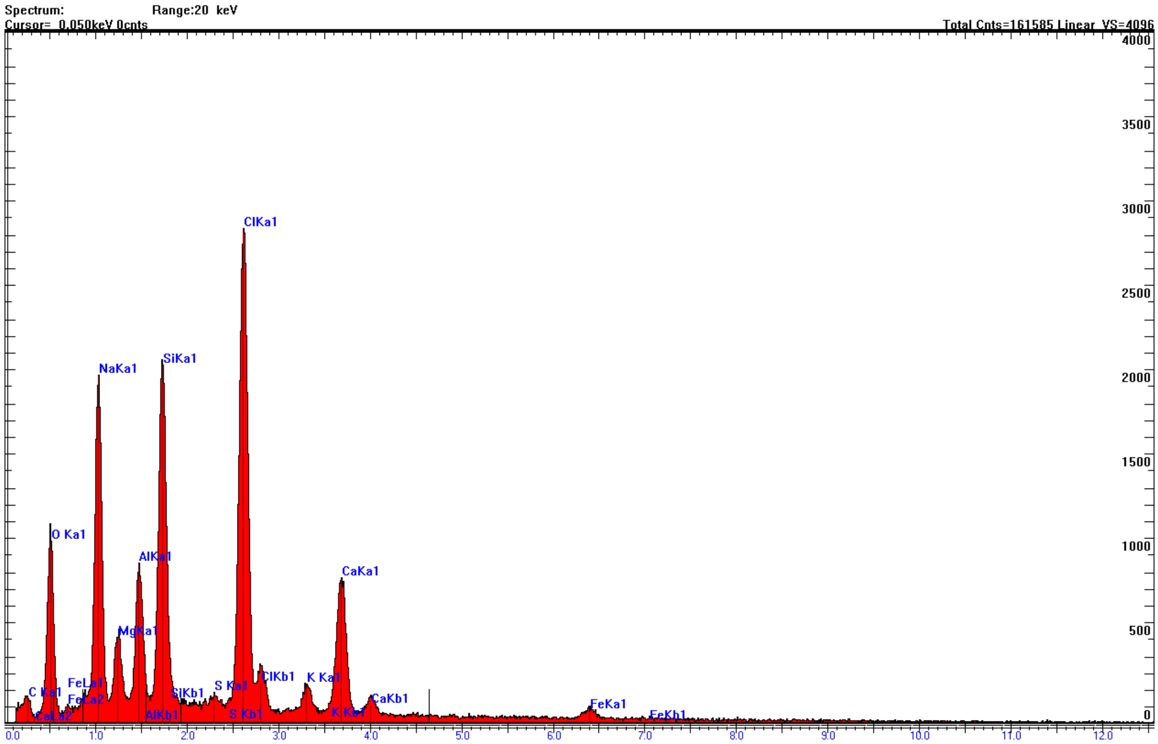


Battery charger – far from electrical connection point – February 11, 2008

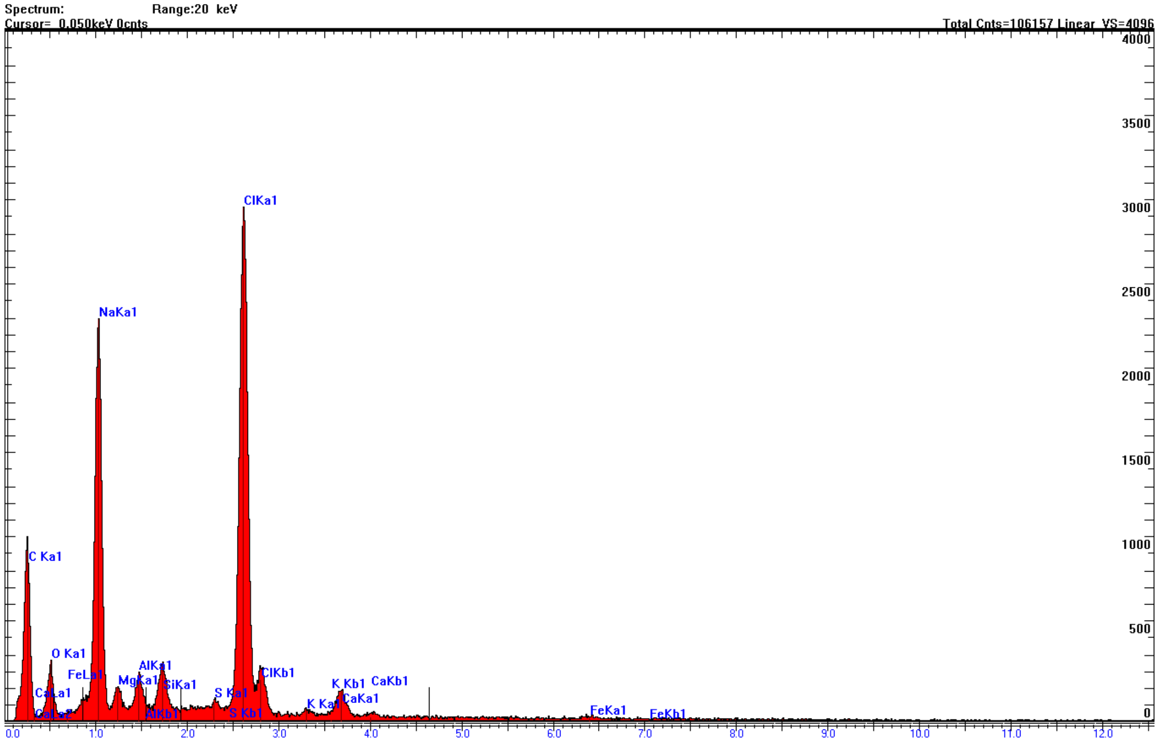
C.3 SEM Results from Control Apparatus



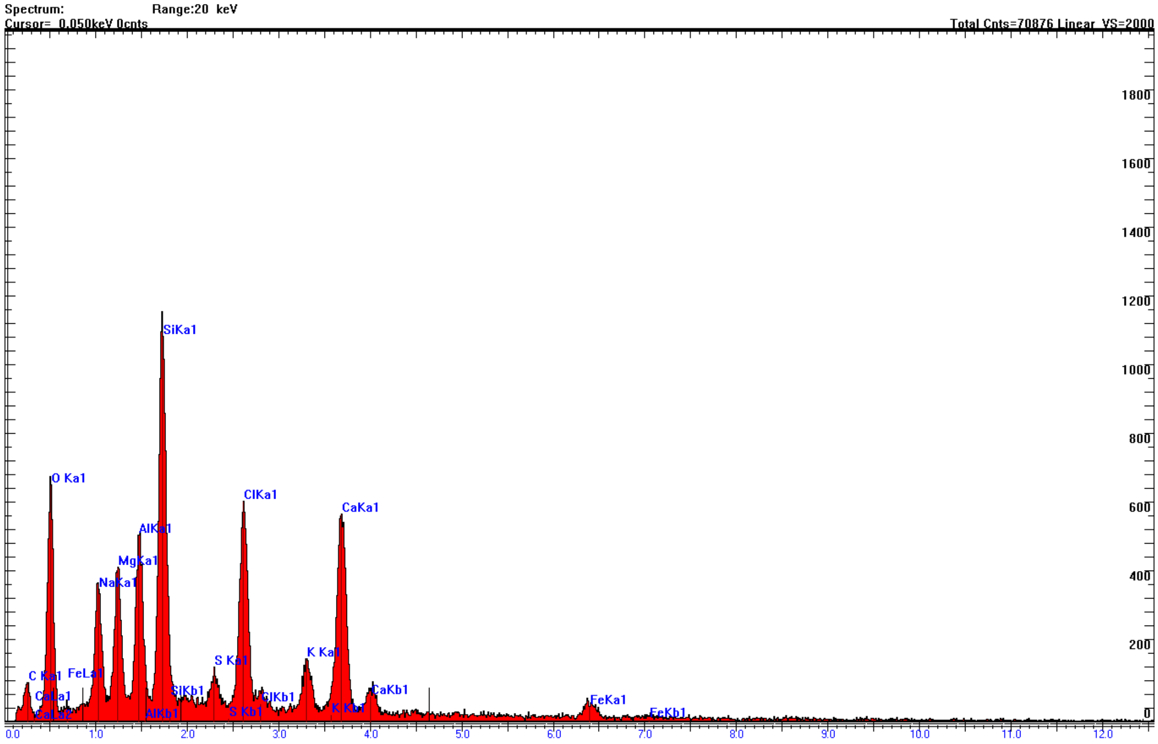
Control – February 18, 2008



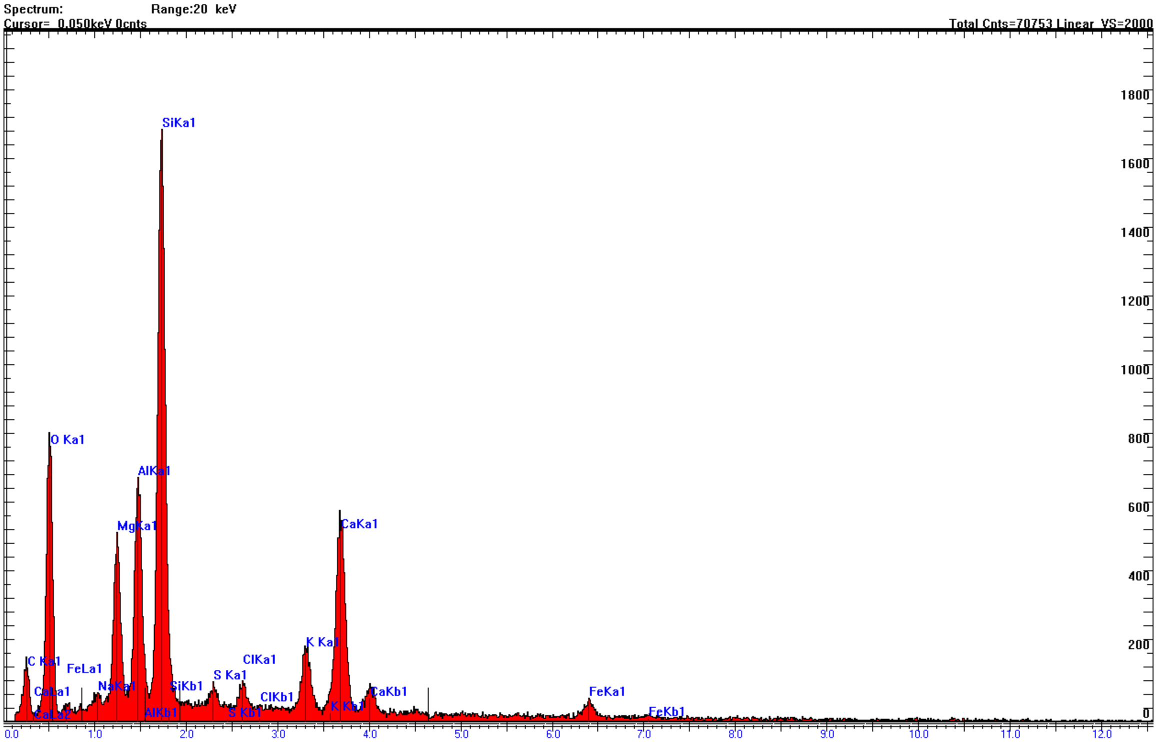
Control – February 26, 2008



Control – February 26, 2008

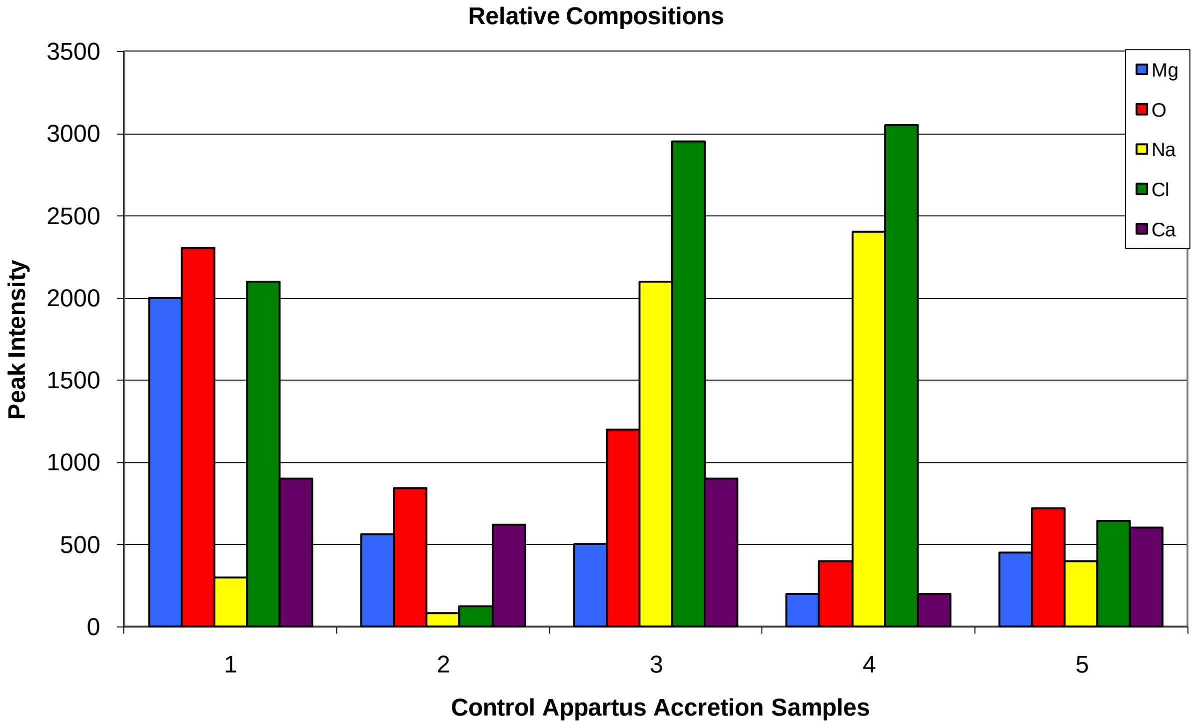


Control – February 26, 2008

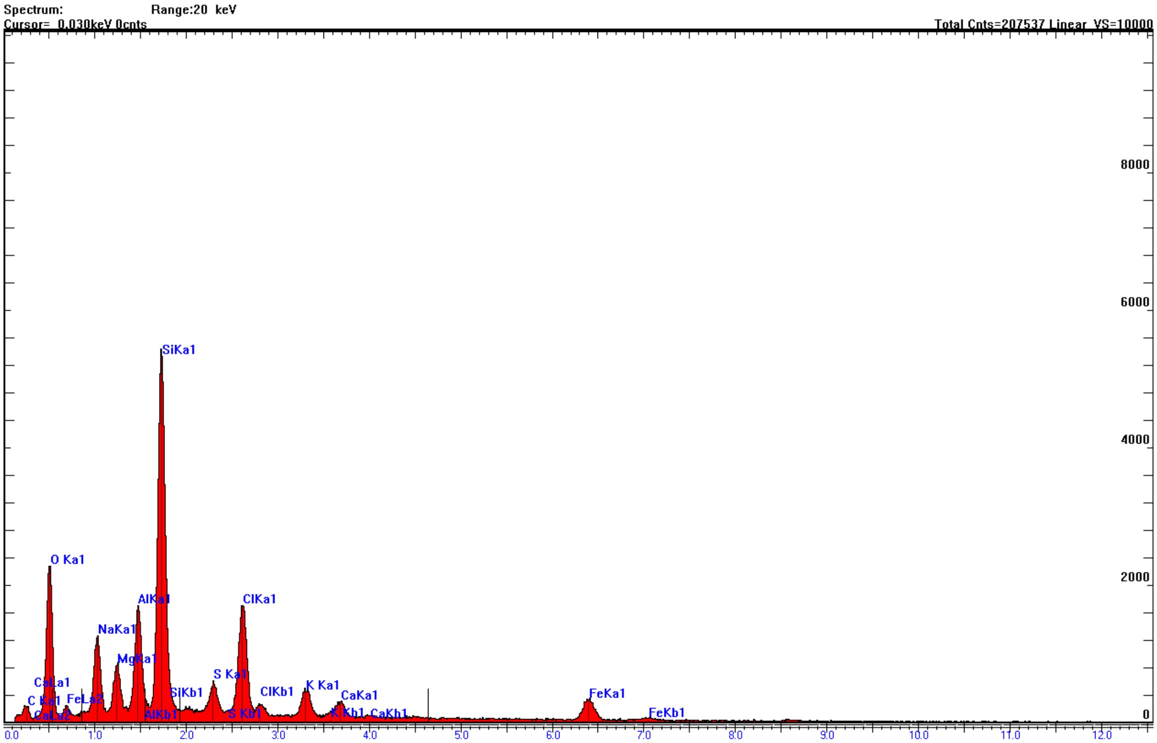


Control – February 26, 2008

Comparison of all of these samples:

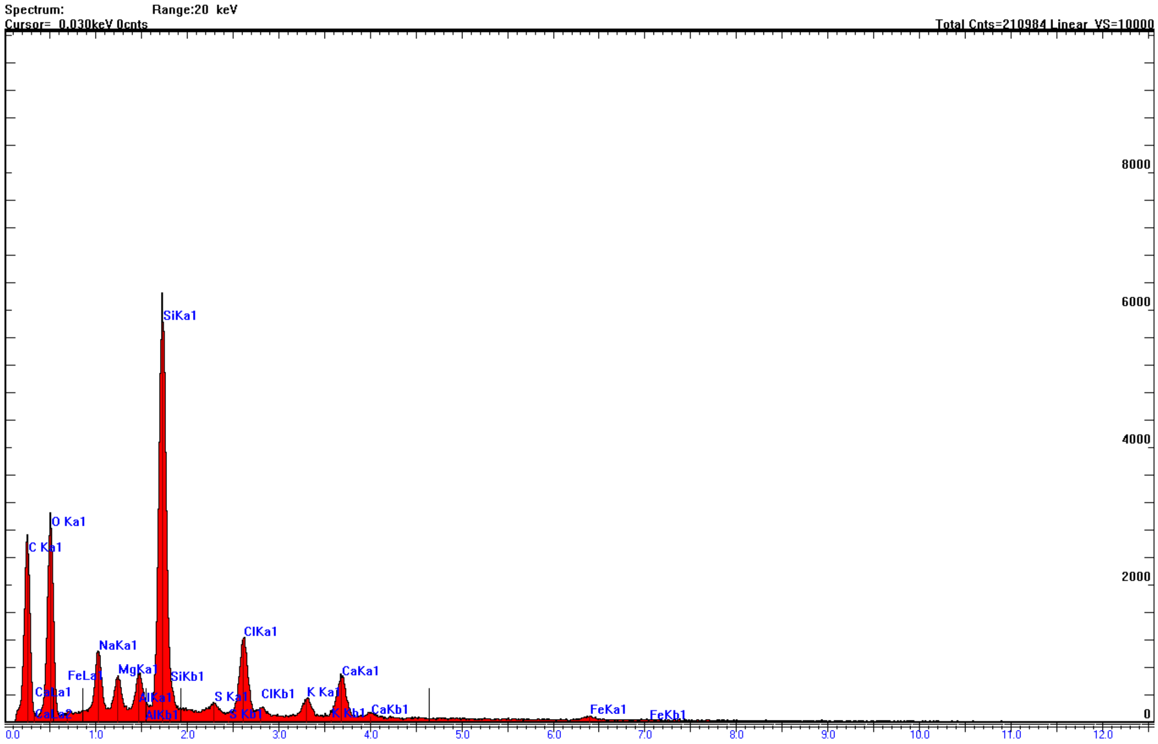


C.4 SEM Results from Connecticut MFC Powered Apparatus



Connecticut MFC powered apparatus – February 18, 2008

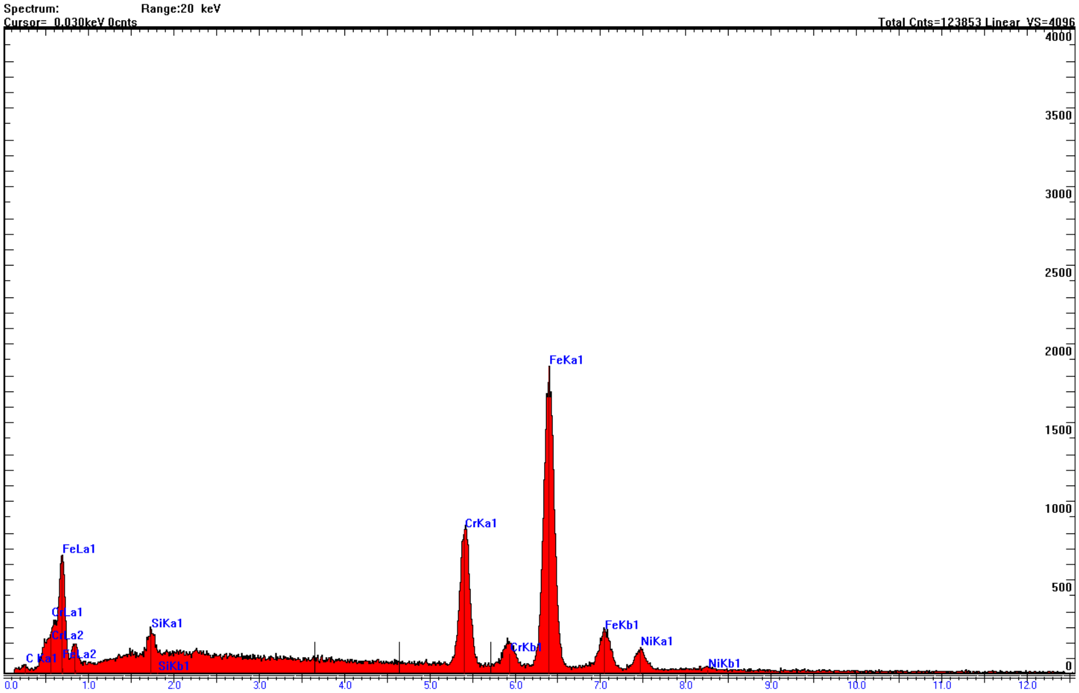
C.5 SEM Results from Direct Connect Apparatus



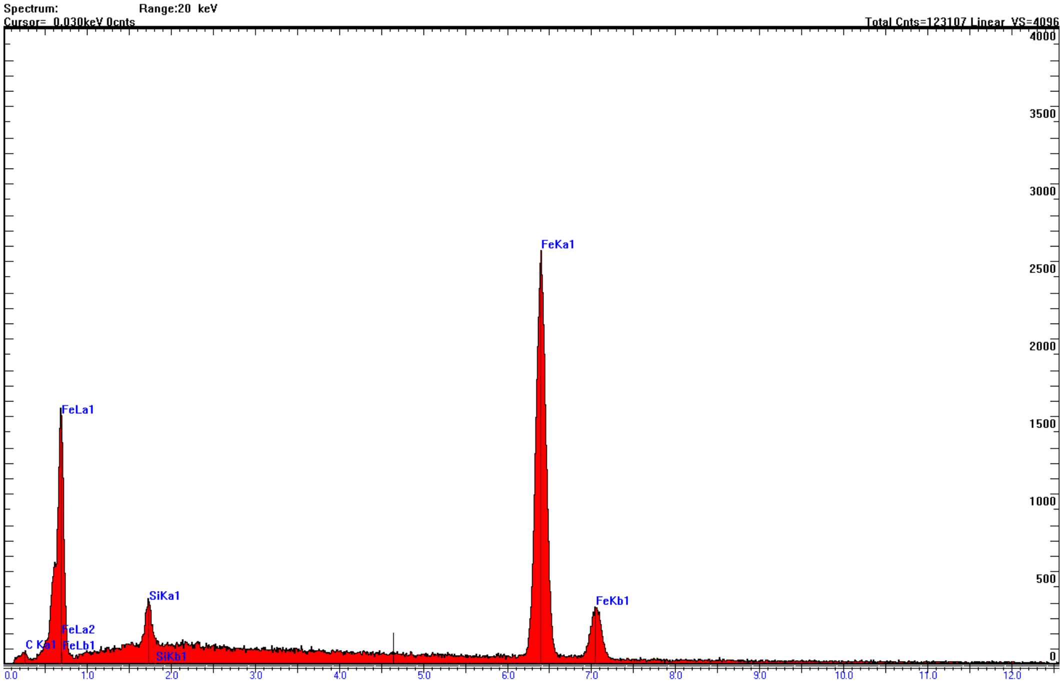
Direct connect apparatus – February 18, 2008

Appendix D: SEM Steel Plate Results

Comparison of Venetian stainless steel plate to Connecticut plain steel plate:



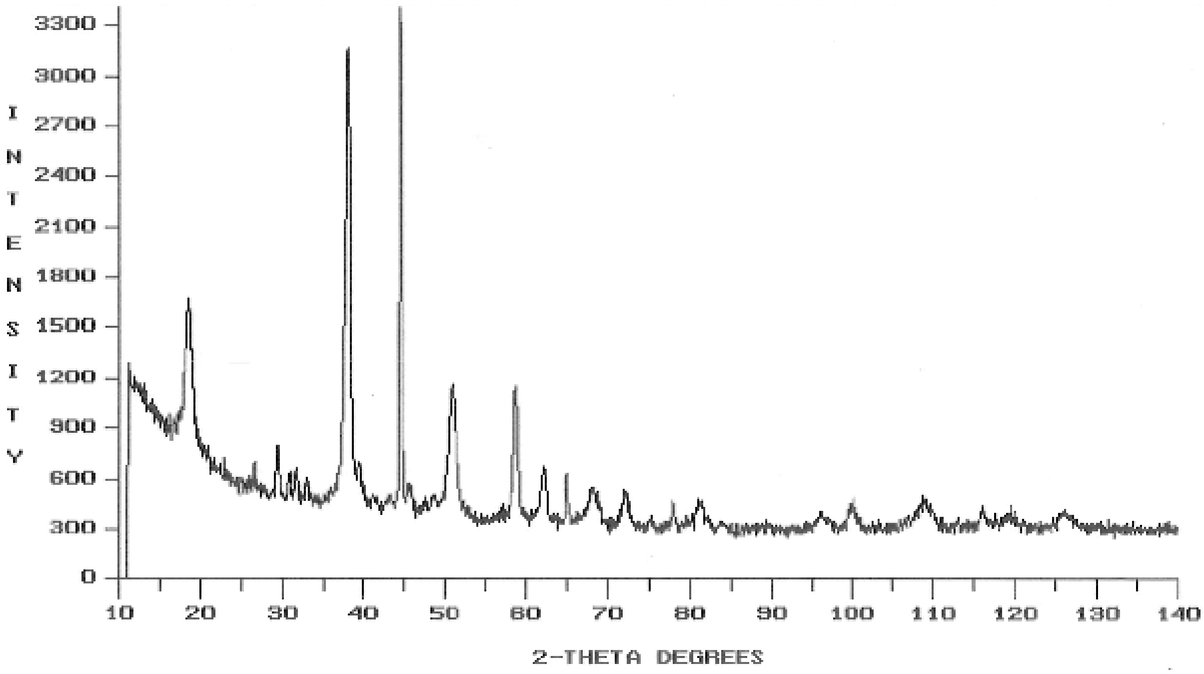
Control steel plate, surface ground with 600 and 400 grit SiC paper – February 18, 2008



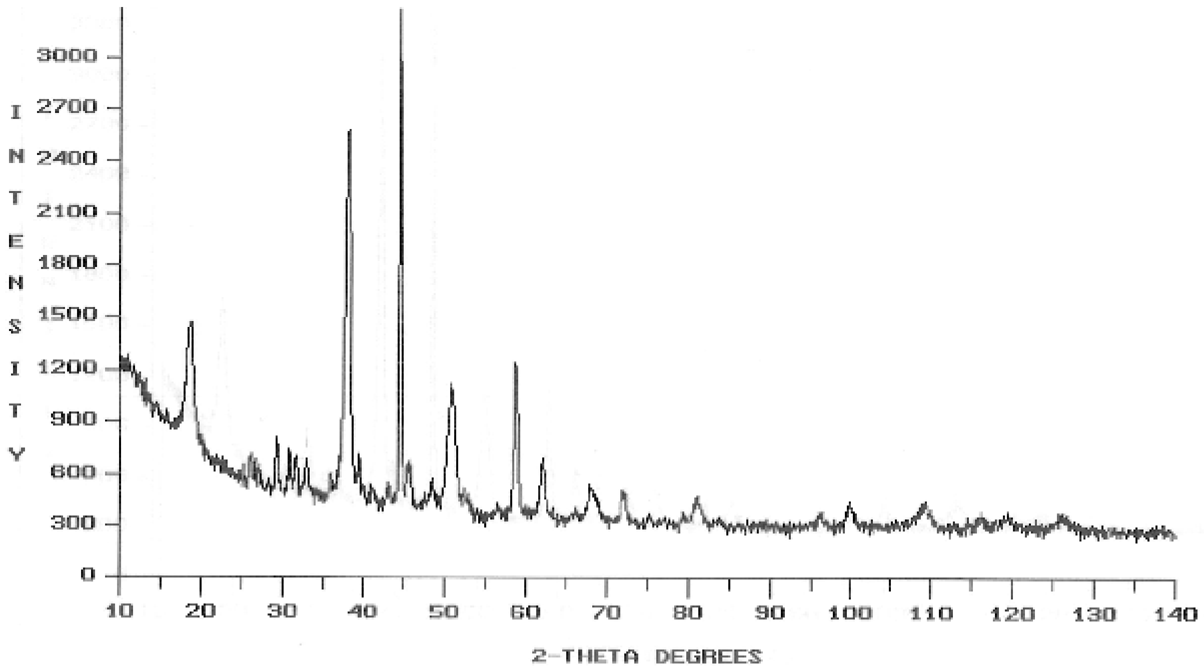
CT steel plate, the surface prepared the same way as the Control sample – February 18, 2008

Appendix E: XRD Results

Accretion far from electrical connection on battery charger powered apparatus



Accretion near electrical connection on battery charger powered apparatus



Appendix F: Economic Analysis Calculations

Multiplication factor – conversion to unit cost per square meter.

Costing Data for the Auto-Accretion Process (using 6 anodes)

Initial Capital Investment

Item	Unit Cost	Unit Area	Multiplication Factor	Total Cost
bottle brush (1.06 sqm)	$30.51	1.06 m^2	6	$183
wire mesh (1'by1')	$13.60	0.093 m^2	11	$150
steel plate (30cmX30cm)	$21.88	0.09 m^2	11	$241
copper wire (per sq meter)	$0.29	1 m	3	$1
bolt, nut, washers (1,1,2)	$1.17	-	6	$7
installation fee (man hrs.)	$20 per hr	-	5 hr	$100
overhead	$17.00	-	1	$17
TOTAL				**$698 per m^2**

Costing Data for the Auto-Accretion Process

Yearly Maintenance Cost

Item	Unit Cost	Unit Area	Multiplication Factor	Total Cost
Labor Cost	$20 per hr	-	12 hr per yr	$240
TOTAL				$240

Costing Data for the Battery Charger Powered Process

Initial Capital Investment

Item	Unit Cost	Unit Area	Multiplication Factor	Total Cost
wire mesh (1'by1')	$13.60	0.093 m^2	11	$146
steel plate (30cmX30cm)	$21.88	0.09 m^2	11	$243
copper wire (per sq meter)	$0.29	1 m	10	$3
bolt, nut, washers (1,1,2)	$1.17	-	2	$2
installation fee (man hrs.)	$20 per hr	-	5 hr	$100
overhead	$17	-	1	$17
TOTAL				**$512 per m^2**

Costing Data for the Battery Charger Powered

Yearly Maintenance Cost

Item	Unit Cost	Unit Area	Multiplication Factor	Total Cost
Labor Cost	$20 per hr	-	6 hr per yr	$120
Electricity	$0.09 per kWhr	60 W	4368 hr per yr	$24
TOTAL				$144