MINERAL SCALE BUILDUP ON LINED VERSUS TRADITIONAL POLYETHYLENE PIPE MATERIALS SUBJECTED TO MINE INFLUENCED WATERS

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ACADEMIC ABSTRACT

Mine influenced waters (MIW) pose a broad range of potential environmental impacts, which often also carry financial and social consequences. MIWs are often high in both suspended and dissolved solids content, and can have highly acidic or alkaline pH and high contents of metals or other problematic constituents (e.g., traces of chemicals used in minerals processing or water treatment). Acid mine drainage (AMD) is a common type of MIW and generally occurs due to oxidation of fresh sulfide mineral surfaces. Release of untreated MIWs like AMD to surface waters, for example, can lead to problems such as sedimentation and siltation, undesirable changes in pH and/or precipitation of metals and salts, and addition of particular stressors for various aquatic organisms. As such, these waters are frequently captured and treated on-site in systems requiring extensive piping.

Polyethylene (PE) pipes are popular in mining, including MIW, applications because they are chemically inert, and have relatively low costs, low density, and high flexibility. However, PE material is susceptible to abrasion. To combat this problem and offer a single pipe option for a variety of mining applications, Gerodur MPM Kunststoffverarbeitung GmbH and Co. KG.(Gerodur) has developed a novel liner for PE pipes. The liner is made of a rubber-like material that is resistant to mechanical abrasion by slurries or high-solids waters, but its susceptibility to mineral scale buildup has not been specifically evaluated. Scale buildup can occur due to settling or diffusion-driven attachment of particles onto solid surfaces or due to direct precipitation of scale onto surfaces. In AMD capture and treatment systems, water chemistry (i.e., which changes with pH adjustment) and flow conditions may control scale development via different mechanisms.

In order to evaluate scale buildup on the lined PE versus traditional PE pipe material, two studies were undertaken and are reported in this thesis. A short-term field study was conducted in the Reiche Zeche underground mine in Freiberg, Germany – an inactive lead-zinc mine. Water quality varies considerably between different zones in this mine, but is characterized by very high dissolved solids content dominated by iron and sulfates, which is typical for AMD. For this study, the pipe materials were

exposed to waters in six locations for three weeks; and were then analyzed for weight gain and scale composition. Results showed that there was only a marginal difference in the scale build up when comparing the two piping materials. In a follow-up study in the laboratory, the two pipe materials were exposed over a total of 16 weeks to three idealized AMD water qualities: an untreated AMD made to simulate the most extreme condition observed in the field study, the same AMD following passive treatment (i.e., neutral pH), and the same AMD following active treatment (i.e., slightly basic pH). Exposure was done in pipe-loop apparatuses such that samples could be subjected to different flow and sedimentation conditions (i.e., gentle mixing only on the sides of the water reservoir, gentle mixing and sedimentation on the bottom of the reservoir, and constant flow and possible sedimentation within the pipe-loop tubing itself).

Results of this study indicated that factors such as water chemistry and flow velocity had significant effect on the quantity, morphology and chemistry of scale. However, there was very little difference in propensity for scale build up between the two materials. This liner was designed in an effort to resist mechanical abrasion. Because scale build up is not exacerbated by the liner, it may provide a means for uniform applications across mines with contiguous abrasive and scale prone waters. That is, it could eliminate the need to have various specialized piping materials on a site to handle these problems individually, streamlining the pumping and piping network installation and operation.

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GENERAL AUDIENCE ABSTRACT

Mine influenced waters (MIW) are a potential danger to the environment, and a company's financial and social standings. MIW's come in many different varieties, and can contain harmful contaminants from the mine site. One of the most common MIW's is characterized by low pH, and is commonly referred to as Acid Mine Drainage (AMD). In addition to the problematic pH, AMD can have excessive dissolved solids such as metals, salts, and sediment.

Polyethylene (PE) pipes are popular in mining applications because they do not react to most chemicals, and have low costs, low density, and high flexibility. However, PE material is susceptible to losing wall thickness through abrasion caused by slurries and solids in water. Gerodur MPM Kunststoffverarbeitung GmbH and Co. KG.(Gerodur) has developed a liner for PE pipes to address the abrasion problem. The liner is made of a rubber-like material that is resistant to mechanical abrasion, but its susceptibility to mineral scale buildup has not been specifically evaluated.

To study the differences between the new liner versus traditional PE pipe, two studies were completed and are reported in this thesis. The first was a short field study conducted in an underground mine in Freiberg, Germany. Though the water throughout the mine varies, it generally has high dissolved solids as seen in most AMD. In the mine, traditional and lined pipes were exposed to waters in six different locations for three weeks, and weight gain and scale composition were tested. Results showed very little difference in both quantity, and content of scale.

To further test the material, a longer lab study was conducted. The two materials were exposed for 16 weeks to three different simulated waters. One simulated untreated AMD, AMD treated to a neutral pH, and finally AMD treated to a basic pH. Results showed that the water chemistry and flow did have an effect on the quantity and chemistry of the scale. It also supported that there was very little difference in the scale on the two materials when exposed to the same water conditions.

Because the material did not make scale worse, it can be applied to waters with high abrasion and scaling potential. This could be an asset to the mining community because it eliminates the need for

multiple pipe materials. It simplifies the mining process by allowing one pipe material to be applied uniformly across a mine site.

ACKNOWLEDGEMENTS

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CHAPTER 1 : LITERATURE REVIEW

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1. Introduction

The mining and minerals industry provides the raw mineral and energy resources for modern society. Fertilizers for crops, metals for technology, and even rare earths for sustainable energy development all require mined resources. However, to produce these resources, mining and processing operations use huge amounts of water. The United States mining sector alone uses over 5 billion gallons of water per day (Perlman, 2017). Additionally, these operations have the potential to impact even more water resources if mine influenced waters (MIW) are not properly contained and treated. Uncontrolled discharges of waters with high solids contents, altered pH, or significant contaminant levels (e.g., metals) can all be problematic. In addition to environmental impacts, such problems can have financial and social costs. Given these considerations, water collection, treatment and conveyance systems require careful design, operation and maintenance.

Pipe conveyance systems are a crucial part of almost any mining and metallurgical or mineral processing operation. They require significant expanses of piping material in addition to accompanying valves, pumps, and sometimes monitoring systems. As such, they demand a significant research and capital investment from mining companies to optimize the system. One of the most important things to consider in optimizing a conveyance system is the different challenges which MIWs introduce.

2. Challenges in Pipe Conveyance Systems

Mines require water for a variety of purposes within a mine site. These include watering roads for dust control, creating hydrous slurries for metal separation, coal washing, and potable water for mine works (Lottermoser, 2003). Once water is effected by a mine site, whether intentionally utilized by the site, or runoff through the mine site, it is known as a mine influenced water (MIW). The chemistry of MIW are heavily driven by the geology of the mine site. However, there are several common characteristics seen in a large majority of MIWs. High suspended solids loading creates physically abrasive waters; as does the transport of ore or tailings slurries. Abrasion is caused by the gradual removal of the pipe due to physical means; especially particles impacting the pipe. This is most common in

segments with bends, or change in flow direction by which particles collide with pipe walls at angles, maximizing the impact (Fighting Pipe Abrasion, 2011).

Acidity, alkalinity, and various chemicals used in the mining process create chemically abrasive waters. The most common form of chemical abrasion is known as corrosion, by which metallic materials face an electrochemical reaction by which it converts to a more stable form (i.e. oxide, hydroxide) (Mitrofanov et al, 2016). It is possible (especially in metallic pipes) for abrasion to exacerbate abrasion (i.e. remove galvanized layer, etc); a phenomenon known as erosion corrosion. (Hu et al., 2011). In addition, pipes in mine sites can be exposed to degrading UV light regularly, and must withstand the natural elements in the area of installation (i.e. extremely high or low temperatures, freezing and thawing, external abrasion due to dirt and dust, temperature or pressure gradients underground, etc.).

Immediate pressure induced pipe failures (known as bursts or ruptures) are a possibility any time the pipe is under load. This becomes even more likely if there is a surge (i.e. a sudden increase in flow volume creating excess pressure), or if the pipe has previously been compromised through abrasion, thermal, UV degradation, etc. Pipes can also fail through more gradual processes. Two of the more common gradual degradation processes are scaling and sedimentation.

Sedimentation typically describes a process by which suspended solids such as sand, clay, silt, or organic matter deposit onto a surface. The most frequent modes of occurrence are a decrease in the host fluid velocity below the suspension velocity, or collisions with pipe walls due to bends (O'Melia, 2008). Sedimentation, in contrast to scaling, is limited to those particles which are large enough to settle out via gravity (O'Melia, 2008).

The two primary forms of scaling are diffusion, and precipitation. Diffusion occurs as the hydrous solutions concentration gradient shifts to equilibrium. Molecules move toward the pipe wall as the gradient stabilizes, but then adhere to the wall removing them from solution (Whelton et al., 2010). The result is a concentration void in that area, causing other molecules to move toward the wall, and the process repeats (Whelton et al., 2010). In contrast, precipitation is caused by a (previously) soluble substance converting to an unsoluble form. This often displays as the formation of mineral salts. The most common scale salts are carbonates, hydroxides, sulfate/sulfides, phosphates, and oxides (Chilingar et Al, 2008).

In cases of both sedimentation and scale, the build-up results in a decrease in effective pipe diameter, and an increase in resistance. This causes decreased performance of the conveyance network, and excessive strain on the pumping system. In its most extreme case, scaling and sedimentation can create a complete clog in a pipe, preventing flow, increasing pressure, and resulting in a pipe burst (Mandrone, 2015).

With MIWs having the potential to create so many adverse conditions, it is critical for an appropriate piping material to be used. In the case that an inappropriate choice is made, pipe failures and burst become a more likely possibility.

3. Piping Materials

Historically, metallic materials (i.e. alloys or galvanized steel) have been a popular choice for piping material in mines. Steel pipes are a good candidate for transporting tailings, ore, or other slurries due to a high resistance to physical abrasion and relatively low cost. However, metallic pipes are quite susceptible to chemical abrasion, specifically that caused by low pH conditions (i.e. rust) (Chilingar et Al, 2008). This makes making metal piping it a poor candidate for any mine applications in which acidic fluids (e.g., acid mine drainage or AMD) must be transported. Additionally, allowable water leakage (due to joints and fittings) in a steel pipe conveyance is can be as high as 10-20% (The Plastics Pipe Institute, 2008). This loss may exhibit itself as a loss to valuable ore or water, or the need to clean up leaked tailings, untreated water, or waste.

Polyethylene (PE) pipes are relatively new to the mining industry, with some of the first large scale applications in the mid 1950's (Radoszewski, 2014). They are attractive to the mining industry due to their flexibility, resistance to chemical corrosion, low leakage, and relatively low cost (Davis et Al., 2006). PE is flexible in two major ways: it is able to be bent slightly over long distances eliminating the need for joints and fittings in those situation. In addition, it can expand to accommodate pressure surges, decreasing the chance of pipe bursts and extending the life of the pipes. Its light weight (~1/8 the density of steel) allows for easier transportation and maneuvering. PE is chemically inert in a large range of pH and chemical conditions. Acidity, alkalinity, and causticity all have minimal impacts on PE pipes. In addition, PE can be heat fused at the joints. This almost completely eliminates leaking; a significant improvement over metallic and PVC pipes (Handbook of Polyethylene Pipe, 2008). Finally, the service life of PE pipes in 50-100 years. The significantly longer service life decreases cost per time as compared to other piping materials. However, PE is much more susceptible to physical abrasion and UV degradation than its metallic counterparts.

Liners have been used to enhance the performance of pipes in a variety of applications. Elbows and bends face exceptionally harsh conditions when conveying abrasive materials. As such, it is not uncommon for these segments in metallic pipes to be lined with a ceramic wear liner due to its extremely high abrasion resistance (Davis, 1987). Additionally, metallic pipes are sometimes lined internally with PE liners to mitigate chemical abrasion. However, the mining industry is unique in that the pipes are exposed to harsh conditions both internally and externally. Though the mining industry has found

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sufficient materials for pipelines, there is a constant need for a more industry specific material to be developed.

There are several options for piping materials on the market, however none of these are specifically designed for the mining industry. Though some of these materials are sufficient, a material tailored to the needs of the mining and minerals industry would be a tremendous asset. A new rubber-like liner for PE pipes has been developed by Gerodur MPM Kunststoffverarbeitung GmbH and Co. KG. (Gerodur). The liner was designed to address the abrasive nature of fluids in some mining applications. However, in addition to susceptibility to abrasion, propensity to form scale must also be considered in order to use the liner in mining applications.

To test this material, two studies were conducted to compare scale build up on traditional PE pipe material versus PE material with the abrasion-resistant liner. The first was a field study (Chapter 2) in which the pipe materials were exposed to several different water quality conditions in an inactive lead-zinc mine. Due to the nature of the ore body, the study site has typical acid mine drainage-type water conditions of many sulfide mines. The second study was in the laboratory (Chapter 3), where scale build up was evaluated under idealized conditions designed to simulate untreated, passively treated, and actively treated acid mine drainage (AMD).

4. Mine Waters Qualities Specifically Studied in Field and Lab Experiments Here

Both the field study and the lab study tested waters of high suspended and dissolved solids. Suspended and dissolved solids are a crucial aspect of those waters with a propensity to make scale. They are present in almost all mine sites due to comminution. Comminution encompassing blasting, crushing, grinding, and milling, all of which are crucial parts of traditional mining operations (Jeswiet & Szekeres, 2016). It allows a much greater surface area of rock to come into contact with air and water (Brown et al., 2002). Any water flowing through ore piles, tailings heaps, or backfilled workings is likely going to be elevated in suspended and dissolved solids.

In addition to suspended and dissolved solids, both the field and lab studies tested waters with acidic conditions. Many minerals which are stable when underground and intact become unstable due to displacement and weathering. This reaction is often due to a sulfide minerals oxidizing to form sulfate (SO_4^{2-}) with a metal ion (e.g. Pb^{2+},Cu^{2+} ,etc) (Johnson & Hallberg, 2005). Most commonly seen and studied is the oxidation of pyrite (FeS_2) into Fe^{2+} and SO_4^{2-}. Specifically, this reaction happens via the following formula (Singer & Stumm, 1970):

$$2FeS_2(s) + 7O_2(g) + 2H_2O(l) = 2Fe^{2+}(aq) + 4SO4^{2-}(aq) + 4H^+(aq) \qquad \text{(Equation 1.1)}$$
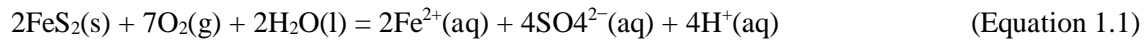
In addition to acidic conditions, the lab study simulated the treatment of AMD. AMD is commonly treated before release to environment due to its environmental concerns. Aquatic organisms can typical tolerate a pH as low as 5.0. In extreme cases, AMD has caused a pH as low as -3.5 making AMD a direct threat to the biota (Nordstrom, 2011). AMD significantly changes and limits the native biodiversity in the area; typically species richness declines as pH decreases (Smucker et al., 2014). Acid mine drainage treatment often causes scale build up. This is because at a low pH, mine waters are likely to dissolve minerals from rock which it has contact with (i.e. aluminum, iron, manganese, etc.) (McLemore, 2008). As pH increases (due to treatment, or natural processes) minerals (e.g., metal hydroxides) will begin precipitating (Matlock et al., 2002). This results in an accumulation of metals and minerals salts, which we refer to as scale.

5. Conclusions

The mining industry places significant strain on the worlds fresh water resources. In addition to a large quantity of water being required for everyday mine operations, MIWs have the potential to create numerous issues in surrounding ecosystems. As such, it is crucial for mines to handle and transport MIW with great caution. At the current, pump and pipe conveyance systems are the transport of choice for many mine operations. Steel and PE are two of the most widely used materials. In addition, liners have been developed to work in conjunction with the primary piping material. However, mine waters have vast diversity, and a number of harsh conditions all which need to be addressed (i.e. acidity, chemical abrasives, physical abrasives, high propensity for scaling, etc). Though the current materials used for mine industry piping have merit, a more suitable material to address some of the industry's most specific co-occurring issues is desired.

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CHAPTER 2 : A FIELD STUDY OF MINERAL SCALE BUILDUP ON LINED AND TRADITIONAL PE WATER PIPES

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Abstract

Pipes are used on mine sites in a variety of applications including transport of slurry, conveying clean and processing water, and in mine dewatering. Mine waters and slurries can cause pipe wear and failures via several mechanisms (or combinations thereof) such as abrasion, scaling, and corrosion. Polyethylene (PE) pipe materials have grown in popularity over the past several decades due to their chemical and mechanical properties (e.g., inertness, flexibility, relatively low density) and low cost. While PE is generally resistant to corrosion, it is subject to abrasion. To combat this, a novel, rubber-like liner is in development. In addition to comprehensive abrasion testing, however, the liner must be evaluated to see how it performs under other conditions. Here, a brief field study is described that tested PE pipes with the new liner against traditional PE pipes to specifically assess mineral scale buildup. The study was conducted in the Reiche Zeche study mine in Freiberg, Germany in six different locations with varying water qualities and flow conditions. Samples were then collected and analyzed by weight change, X-Ray Fluorescent, and Scanning Electron Microscopy. The two pipe materials displayed only marginal differences in scale weight, chemical composition, and morphology making the new liner a competitive candidate.

1. Introduction

Water and slurry conveyance are major operations on and around mine and mill sites, from mine dewatering, to tailings transport, to water treatment processes. Conveyance systems in such applications can include great lengths of pipe materials along with pumps and monitoring instruments, and thus represent significant capital investments. Due to the variability of the physical and chemical properties of water and slurries, pipe materials are subject to a wide range of conditions. These can cause pipe wear and eventually failure leading to serious economic, environmental and social, consequences. While pressure-induced pipe failures (e.g., ruptures or "bursts") can be immediate, most failure mechanisms involve gradual processes. Scaling and sedimentation can present major problems for pipe systems conveying highly mineralized waters.

Sedimentation generally refers to the deposition of suspended solids, such as sand, clay, silt, or organic matter onto pipe surfaces. This phenomenon can occur due to a decrease in water velocity or particle collisions with the pipe wall. Scaling, on the other hand, commonly refers to the deposition of precipitated mineral salts (including oxides and hydroxides) onto pipe surfaces. Mine waters often have extremely high ion concentrations (i.e., high dissolved solids content) due to their interaction with enormous surface areas of minerals, which are exposed during mining and processing operations (Brown and Barley, 2002). As these waters are transported, slight changes in temperature, pressure or chemistry (e.g., pH or ORP) can cause instability with respect to ion solubility such that salt precipitation begins to occur. "Seed" crystals can rapidly grow and attach to pipes, either due to local surface phenomenon near the pipe wall (e.g., which can promote coagulation) or sedimentation of the precipitated solid. Whether due to suspended or precipitated solids, as the solids begin to stick to pipe walls, "aging" or hardening processes can commence; and the build-up of scale can become self-perpetuating as the scale itself provides an attractive "nucleus" for further attachment of particles or crystal growth (Muryanto et al., 2014). Over time, scale-buildup reduces the effective pipe diameter, which can ultimately result in decreased flow velocity, clogging and, in some instances, bursting (Dirany et al., 2016).

In contrast to the accumulation of solid scale on pipe walls, abrasion represents another common problem in water and slurry transport systems. Abrasion typically refers to the gradual removal of material from the pipe wall by physical means. While extreme turbulence and other flow phenomena (e.g., cavitation) can certainly contribute to abrasion, it is most often caused by solids impacting the pipe surfaces as flow is conveyed (Fighting Pipe Abrasion, 2011). In straight pipe segments, abrasion can occur along the entire length of pipe as particles effectively drag against the walls; in segments with bends or where flow regimes change, particles can additionally impact walls at angles, often increasing the effects of abrasion (Fighting Pipe Abrasion, 2011).

Like physical abrasion, corrosion also results in gradual removal of material from pipe walls. Corrosion is most often associated with metallic pipe materials where the process is electrochemical in nature, but sometimes the term is also used to describe degradation of other materials (e.g., plastics) due to exposures to chemicals, heat or light (Mitrofanov et al., 2016). Corrosion can affect both the interior and exterior of pipes depending on exposure conditions. With respect to internal corrosion, beyond thinning of the pipe wall and associated loss of structural integrity, this can often lead to increased frictional resistance to flow and related inefficiencies. In many cases, electrochemical and chemical corrosion can be exacerbated by abrasion (e.g., via removal of protective pipe coatings) and/or scale buildup (e.g., via development of areas of localized chemical conditions); these conditions are often referred to as erosion corrosion (Hu et al., 2011).

In mining applications, like in other industry, metallic pipe materials (e.g., carbon steels) have historically dominated due to their relative low-costs and benefits (e.g., resistance to abrasion). However, it has long been recognized that (internal) corrosion represents a predictable wear and failure mode. In addition to high dissolved (and often suspended) solids content, mine-influenced waters and slurries frequently have extreme pH values – and both highly acidic and highly caustic conditions can promote corrosion (Brown and Barley, 2002). Thus, great efforts have been made to provide corrosion protection to pipe materials commonly via galvanization or application of other linings (e.g., high-density polyethylene) (Papavinasam et al., 2008).

In the 1950s, polyethylene (PE) pipes were introduced into the oil and gas sectors (Radoszewski, 2014). The material is effectively inert, meaning it is not generally susceptible to chemical corrosion. Moreover, it is relatively flexible, light-weight and inexpensive, making it an attractive alternative metallic counterparts (Radoszewski, 2014). Given these properties, PE pipes have rapidly gained popularity in the mining and minerals sector too (Radoszewski, 2014). While PE does exhibit some sensitivity to heat and light degradation, as well as pressure changes, these generally do no render it unsuitable for most mine applications (*Handbook of Polyethylene Pipe,* 2008). Similar to metallic pipe systems, waters prone scaling and sedimentation can still present problems for PE pipes. Their major shortcoming in the context of mine applications, however, is that they are much more susceptible to abrasive flows than their metallic counterparts (Zok and Miserez, 2007).

To combat the issue of rapid PE pipe wear due to abrasion, a novel pipe liner is currently in development by Gerodur MPM Kunststoffverarbeitung GmbH and Co. KG. (Gerodur). It is made of a rubber-like material and applied to the entire inner circumference of the pipe. In addition to comprehensive abrasion testing, evaluation of the lined pipe is also necessary with respect to suitability and performance under other commonly encountered conditions for mine waters and slurries. Here, we present results from a brief field study designed to specifically investigate the potential for scale buildup on PE pipes with the

novel liner versus those with no liner.

2. Experimental Details

The study was conducted in the Reiche Zeche underground mine. Three pairs of unlined (termed PE from here) and lined pipes (L) were installed in six different locations in the mine, which varied by water quality and flow conditions. Pairs were removed from each location on one-week intervals and examined for scale buildup based on visual inspection, weight change and elemental analysis.

2.1 Study Mine

The Reiche Zeche mine field in Freiberg, Germany is a collection of approximately 800 year old metal mines, which have been connected to form a single maneuverable mine (Junghans and Tichomirowa, 2009). Started in 1168 as a silver mine, and transformed in 1937 to a lead, zinc, and copper mine, Reiche Zeche finished its last period of production from 1950 to 1969 (Junghans and Tichomirowa, 2009). The mine has an estimated 100 km of adits, over 700m of depth. Levels below about 200m have been flooded since 1969 (Haubrich and Tichomirowa, 2007). Currently, the mine is primarily used as a research and teaching facility by TU Bergakademie Freiberg its partners (Schlösser et al., 1999).

The Reiche Zeche mine contains sulfide ores primarily composed of pyrite, sphalerite, and galena. During mining, valuable high-grade ore was hoisted to the surface, while low grade ore and waste rock were used to backfill completed workings (Haubrich and Tichomirowa, 2007). It is common for water to seep slowly through the backfilled sulfide material. The relatively long residence time within this material allows for oxidation and significant acid mine drainage. Drainage pools and in-situ pore waters have been sampled by several researchers; the pH can be as low 0.8 and the sulfate as high as 160,000 mg/l (Haubrich and Tichomirowa, 2007). Within the mine, there are also areas with relatively high water flows, which have pH values in the 3-8 range (Haubrich and Tichomirowa, 2007). Due to the variability in water qualities and flows, pipe systems in the mine are significantly challenged and can face issues such as clogging and corrosion – but these conditions make the mine an ideal site for related research.

2.2 Test Locations and Pipe Installation

To allow scale buildup testing under a range of conditions, six locations within the study mine were selected for testing based on their historical water quality and typical flow. A control condition was also tested (i.e., using a stagnant tap water bath in the laboratory). Before pipe installation, in situ conductivity and pH were measured with an InLab 738 ISM and an InLab Expert Pro ISM, respectively, by Mettler

Toledo. At the end of the total test period, flow velocity was measured and two bottle water samples (150 mL each) were also taken in each location. These samples were sent to Virginia Tech, where pH and conductivity values were confirmed and sub-samples were prepared for inorganic ion analysis by inductively coupled plasma –mass spectrometer (ICP-MS, using a Thermo Electron X-Series instrument). For this, one filtered sample (i.e., 0.45 µm pore) and one unfiltered sample were taken from each bottle.

The filtered sample corresponds to dissolved constituents and the unfiltered sample corresponds to total acid-soluble constituents (i.e., at 2% HNO_3); and the difference between them should thus indicate the acid-soluble particulates. Table 2.1 shows the water quality and velocity at each test location.

Table 2.1: Water quality at study locations. Ion concentrations are shown for both total and filtered (F) samples.

Location	pH	Cond. (µS/cm)	Velocity (cm/s)	Na	Mg	Al	Si	S	K	Ca	Fe	Zn
				ppb				ppm	ppb			
L1				17990.0	50575.0	11683.8	20126.3	871.5	10417.9	163200.0	13375.0	52850.0
L1-F	3.3	1728.0	0.1	14279.0	43370.0	10055.0	16913.0	661.2	10501.2	137240.0	1090.1	46840.0
L2				55350.0	31710.0	36.3	9065.0	255.0	11210.0	103800.0	17.7	3078.3
L2-F	4.9	1131.0	0.9	52050.0	30250.0	13.9	8609.0	242.3	10654.0	100590.0	0.0	2924.0
L3				8757.0	30760.0	10240.0	11469.0	499.4	1526.0	87130.0	8981.0	27810.0
L3-F	3.2	1204.0	0.1	8322.0	27740.0	9649.0	10612.0	453.0	1495.9	78800.0	1394.4	25980.0
L4				9413.0	18626.0	853.8	11458.0	202.0	2763.0	44930.0	33.0	2961.0
L4-F	5.1	493.0	0.8	8975.0	16662.0	749.2	10664.0	179.4	2659.0	39830.0	0.0	2765.0
L5				34405.0	26947.5	10.1	9582.5	216.7	5247.5	82900.0	15.8	2551.0
L5-F	6.9	976.0	*NR	34020.0	27250.0	5.9	9644.0	212.5	5275.0	80100.0	0.0	2534.0
L6				2605.8	1595750.0	1049250.0	65300.0	23685.0	0.0	434525.0	2438250.0	3248000.0
L6-F	2.5	22000.0	0.0	898.4	1055200.0	689850.0	40585.0	16155.0	0.0	301200.0	1674000.0	2209500.0
Control	8	215	NA	0.0	0.0	0.0	0.0	23.0	0.0	0.0	0.0	0.0

NA = not applicable; NR = not reported; *Value not measured, but by visual inspection velocity in this location is significantly higher than in other locations.

Segments of new PE and L pipes (10 cm in diameter) were donated by Gerodur. The PE pipes were solid PE material (i.e., no coating or liner on either the interior or exterior surfaces); the L pipes were made of the same PE material, but the interior surface was lined. To prepare samples for scale buildup testing, the pipes were cut into sections 10 cm in length. Then, each sample was cut lengthwise to form half pipes. This allowed for better observation of the changes occurring on the samples. A small hole was drilled in each corner of a sample such that it could be anchored in place in its test location.

At test each location in the mine, a catch ditch and dam was constructed to ensure each sample in that location was exposed to a consistent amount and/or flow of water. Then, the pipes were placed (such that the concave interior surface was facing upward) to the natural buoyancy level and anchored. This ensured that there was no variation between the submerged surface areas of each pipe. Figure 2.1 shows examples of the prepared test locations.

2.3 Sample Analysis

Once installed, the pipe samples were observed at one, two, and three weeks. In situ observations

Figure 2.1: Examples of prepared test locations.

included a qualitative analysis of visible scale buildup, and photographs were taken before the samples were removed. Upon removal (i.e., one pair of PE and L samples from each location, each week), the samples were allowed to dry for 24 hours in storage underground before weight change and elemental analyses were conducted. The virtually constant humidity and geothermal conditions in the mine ensured minimal variation in drying conditions for all samples. Immediately after removing from the mine, the samples were weighed and photographed; and within 2 days, elemental concentration data from the pipe scales were obtained by x-ray fluorescence (XRF, using a Niton XL3t980 instrument). Two XRF scans were made on each sample, and results were averaged to produce data for the sample. Finally, samples were shipped to Virginia Tech, where more comprehensive elemental and morphological analysis of pipe scales was completed using scanning electron microscope with energy dispersive x-ray (SEM-EDX).

3. Results and Discussions

Table 2.2 shows the weight change for all pipes at all time intervals, while Figure 2.2 shows a photograph of each pipe at each time interval. In most locations, scale buildup was relatively minor in terms of weight gain over the short exposure time. However, pipes in locations 1 and 3 did gain significant weight – more than 2 g on the roughly 65 cm^2 of total exposed surface area. Importantly, by visual observation, scale buildup was almost completely limited to the interior pipe surfaces (i.e., the concave surfaces shown in Figure 2.2), which suggests that settling of particulates may have been key in at least initiation of scale formation.

Overall, only subtle differences in weight gain could be observed between the lined and unlined pipes – and one material did not consistently gain more weight than the other. The visual appearance of the pipes generally supports the weight change observations. Samples from locations 1 and 3 had significantly more scale buildup than those from other locations at all time intervals. Moreover, no noticeable differences could be discerned between scale development on the L versus the PE pipes.

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Table 2.2: Weight change (g) for all pipe samples at Weeks 1, 2 and 3. The absolute weight change is shown as the top value for each sample, and the corrected weight change is shown in parentheses (i.e., the difference between the absolute value and the control value for the specific pipe type and week). Since the control L pipe in week 3 showed an unexpected weight loss, the average of weight gain measured for weeks 1 and 2 (0.33 g) was used to correct L pipe values in week 3. Bold values indicate instances where all weight gain appears to be due to water absorption (i.e., the corrected weight change is near 0).

Week	Pipe	L1	L2	L3	L4	L5	L6	Control
1	PE	1.31	0.35	0.77	**0.22**	0.29	0.35	0.21
		(1.10)	(0.14)	(0.56)	**(0.01)**	(0.08)	(0.14)	
	L	1.46	**0.31**	0.78	**0.34**	**0.29**	0.42	0.32
		(1.14)	**0.00**	(0.46)	**(0.02)**	**0.00**	(0.10)	
2	PE	1.74	**0.35**	1.47	**0.26**	0.42	0.38	0.29
		(1.45)	**(0.06)**	(1.18)	**0.00**	(0.13)	(0.09)	
	L	2.41	0.44	1.35	0.48	0.61	0.52	0.34
		(2.07)	(0.10)	(1.01)	(0.14)	(0.27)	(0.17)	
3	PE	1.87	0.49	2.81	0.47	0.52	0.26	0.15
		(1.72)	(0.34)	(2.66)	(0.32)	(0.37)	(0.11)	
	L	2.69	0.59	2.73	0.51	0.73	**0.30**	-0.22
		(2.36)	(0.26)	(2.40)	(0.18)	(0.40)	**0.00**	

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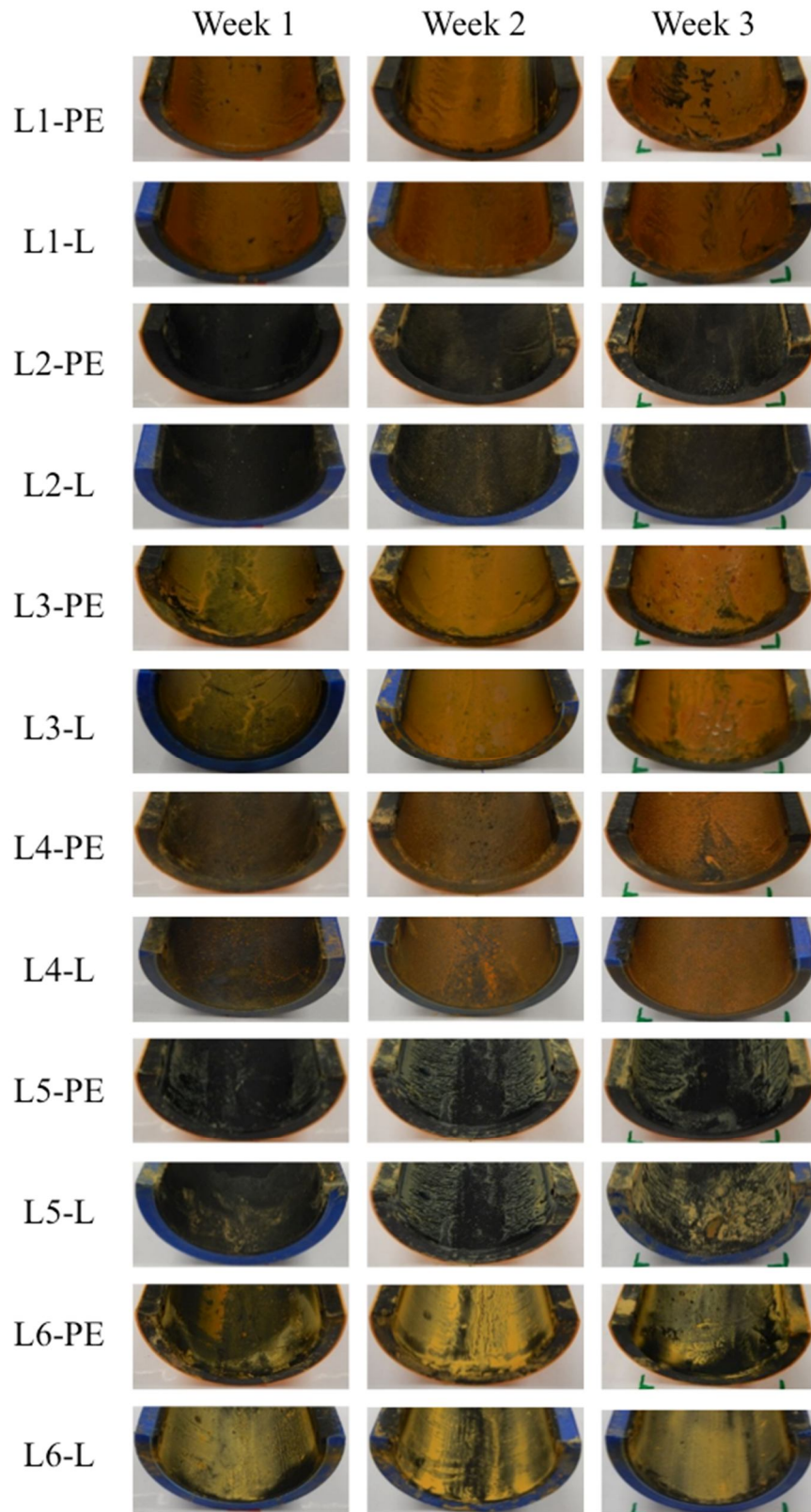|	Week 1	Week 2	Week 3
L1-PE			
L1-L			
L2-PE			
L2-L			
L3-PE			
L3-L			
L4-PE			
L4-L			
L5-PE			
L5-L			
L6-PE			
L6-L			

Figure 2.2: Photographs of pipe scale buildup in each test location by week.

3.1 X-Ray Fluorescent Results

Table 2.3 shows XRF data for aluminum, iron and sulfur, which were generally observed to be the three primary pipe-scale constituents that can be measured by XRF (i.e., relatively light elements like oxygen are not measured). On pipes exposed to mine water, these three elements were consistently elevated above the (low-level) background values measured on new, clean pipe materials. The XRF data presented in Table 2.3 has been corrected to show the elemental concentrations in excess of the background concentrations for a given pipe material. No real differences could be observed between the scale constituents on the PE and L pipe materials; differences were only related to the test locations.

Table 2.3: Corrected aluminum, iron and sulfur concentrations (ppb) measured in pipe scale by XRF.

	Al		Fe		S		Si
Sample	**L**	**PE**	**L**	**PE**	**L**	**PE**	**PE**
L1-Week-1	1994.0	2642.5	15806.6	14641.6	9556.0	9116.7	18316.5
L1-Week-2	956.2	3027.9	19247.7	15155.7	5856.5	10184.2	19186.3
L1-Week-3	910.1	4145.0	28299.6	21399.0	7125.5	13625.1	24967.6
L2-Week-1	515.6	424.0	180.8	0.0	390.3	131.9	523.1
L2-Week-2	1880.9	1016.5	1401.7	81.9	1376.7	535.1	3866.1
L2-Week-3	1308.5	812.5	745.5	0.0	971.8	357.8	2391.7
L3-Week-1	0.0	385.7	5066.5	4228.1	6134.7	7072.1	1262.1
L3-Week-2	0.0	953.9	10979.2	10051.3	10015.7	19322.1	2559.7
L3-Week-3	0.0	708.3	17058.1	18249.3	6715.2	17189.8	2078.6
L4-Week-1	212.9	776.7	1123.7	740.8	1257.1	1226.4	3267.6
L4-Week-2	314.7	484.2	3194.2	1030.8	2570.4	1355.7	2070.2
L4-Week-3	271.2	796.9	3582.4	4627.9	3356.0	4355.5	4601.9
L5-Week-1	1320.9	1140.9	434.2	204.5	426.8	184.0	2716.3
L5-Week-2	163.5	903.6	126.1	62.7	0.0	131.0	2124.8
L5-Week-3	2999.4	1114.4	3414.9	194.9	970.6	337.2	3557.3
L6-Week-1	804.9	918.5	2189.8	4770.5	13068.6	18968.9	3838.6
L6-Week-2	0.0	761.8	2177.8	3077.6	13750.0	16582.2	4612.6
L6-Week-3	576.9	825.4	2712.0	826.9	16951.9	8010.8	3020.6

In addition to aluminum, iron and sulfur, silicon also appeared to be a significant scale constituent in some test locations. In Table 2.3, silicon values are only shown for the PE pipes because this pipe material had only low-level background silicon. The L pipes, in contrast, had relatively high background levels of silicon, and as scale built up on the pipes the measured silicon concentration decreased (i.e., as the background was progressively covered in scale). Thus, even though the scale on these pipes may contain silicon, the relative abundance could not be estimated. Potassium was additionally observed to be a significant scale constituent on pipes from location 1. On week 3, the L and PE pipe scales showed excess potassium concentrations of 1,920 ppm and 2,142 ppm, respectively.

Figures 2.3 and 2.4 give a comparison of weight gain to pH and conductivity (respectively) of the water at each location. This, in conjunction with the XRF results gave a basis for evaluating the chemical and mechanical behavior of the scale.

Figure 2.3 shows that the relatively high rate of scale buildup in locations 1 and 3 is consistent with the water quality in these locations. Both had relatively high conductivity (i.e., 1,728 and 1,204 µS/cm, respectively) and very low velocity, and they also had high levels of iron, aluminum, and sulfur – all of which were evident in the XRF results. Additionally, in location 1, more than half of the aluminum and sulfur appeared to be present as particulates; and this was the case too for potassium and (acid-soluble) silicon, which were found to be significant scale constituents in this location per the XRF analysis. These findings further suggest that some mineral scales formed in this study are likely associated with settled particles. Interestingly, particulate zinc was also high in location 1, yet it was not observed in the pipe scales.

Figure 2.4 shows that location 6 actually had, by far, the highest conductivity (i.e., 22,000 µS/cm), and the water in this location was virtually stagnant. However, very little scale buildup occurred during the test period. It can be observed in Figure 2.3 that in addition to the highest conductivity, location 6 also had the lowest pH (i.e., 2.5). Because solubility increases as pH decreases, this likely inhibited significant precipitate formation, and scale that did form was probably due to settled solids. Like location 1, the water analysis and XRF indicates these included iron, aluminum, sulfur and silicon.

Locations 2 and 4 also showed minimal scale buildup. As seen in Figure 2.4, Location 4 had the lowest conductivity of all test locations, and accordingly low concentrations of iron, aluminum and sulfur. Further, it had a low velocity. The pH in this location was somewhat higher than in most others (i.e., 5.0, as seen in Figure 2.3), resulting in precipitation of significant mineral salts being unexpected. However, the water constituents with the highest concentrations in this location were calcium and magnesium, which are generally quite soluble at low pH (i.e., as compared to iron or aluminum, for example). Additionally, Figure 2.3 and 2.4 show that Location 2 had a similar pH (i.e., 4.9) and velocity to location 4, but much higher conductivity (i.e., 1131 µS/cm, similar to location 3). Concentrations of iron, aluminum and sulfur, however, were relatively low and water analysis indicated that all iron and about half of the aluminum were particulate.

Visibly, pipe samples in location 5 did not appear to form much scale, but marginal weight gain was observed by week 3. This location had the highest pH (i.e., 6.9, seen in Figure 2.3), which could have promoted some scale precipitation. However, the very high velocity likely prevented significant settling of solids.
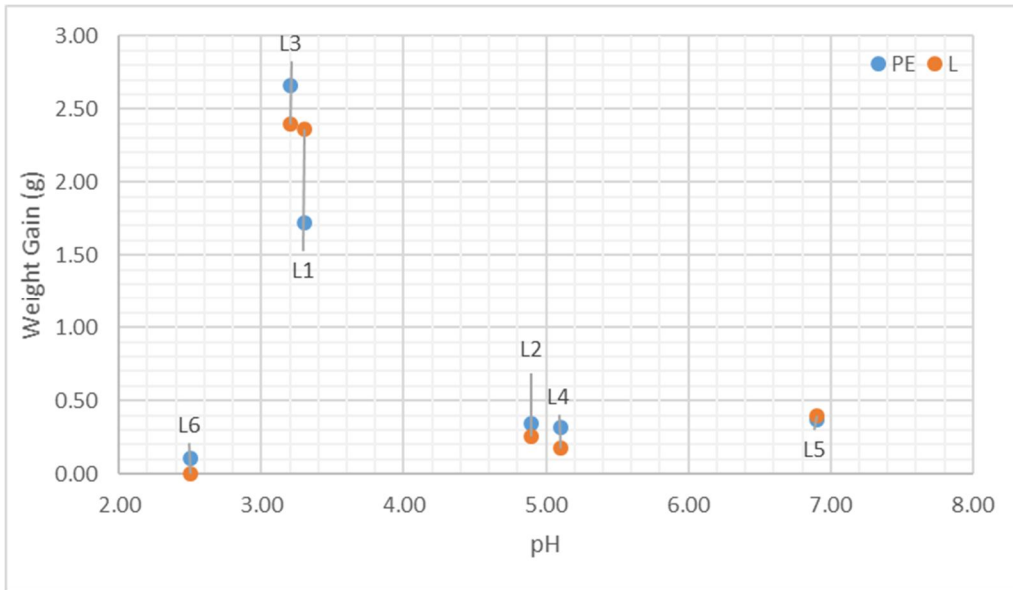
Figure 2.3: pH versus total weight gain after week 3.
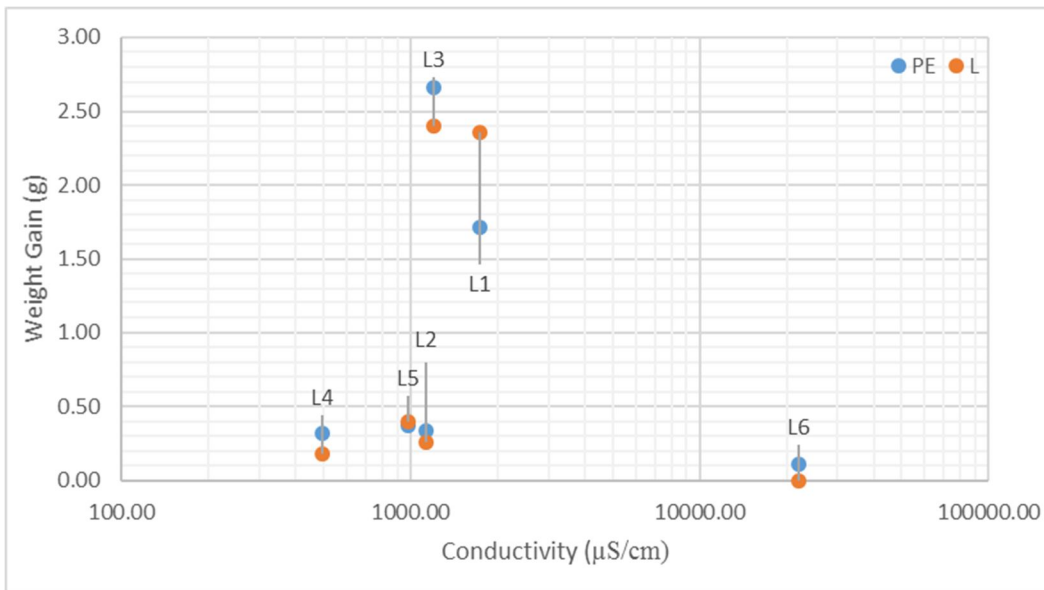
Figure 2.4: Conductivity versus total weight gain after week 3.

Figure 2.5 shows ratios of iron, aluminum and sulfur concentration in week 3 pipe scales to their respective (total) concentrations in the mine water at each test location. Figures 2.6, 2.7, and 2.8 show concentration in week 3 pipe scale to concentration in each water for to aluminum, iron, and sulfur, respectively, versus the pH in each location. In this comparison of relative abundance, values above 1.0

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indicate that an element is being concentrated in the pipe scale (versus the water). As seen in Figures 2.6 and 2.7, the aluminum and iron results tend to correlate strongly with water pH. That is, test locations with higher pH (i.e., locations 2, 4 and 5) produced higher scale to water ratios of these elements than locations with lower pH (i.e., locations 1, 3 and 6). Higher-pH locations also concentrated much more iron (and generally aluminum) into the pipe. However, this correlation was not seen with sulfur. That is, the sulfur ratio was similar in all samples, regardless of pH. Based on this observation, it is likely that sulfur on the pipes was largely acid residue.
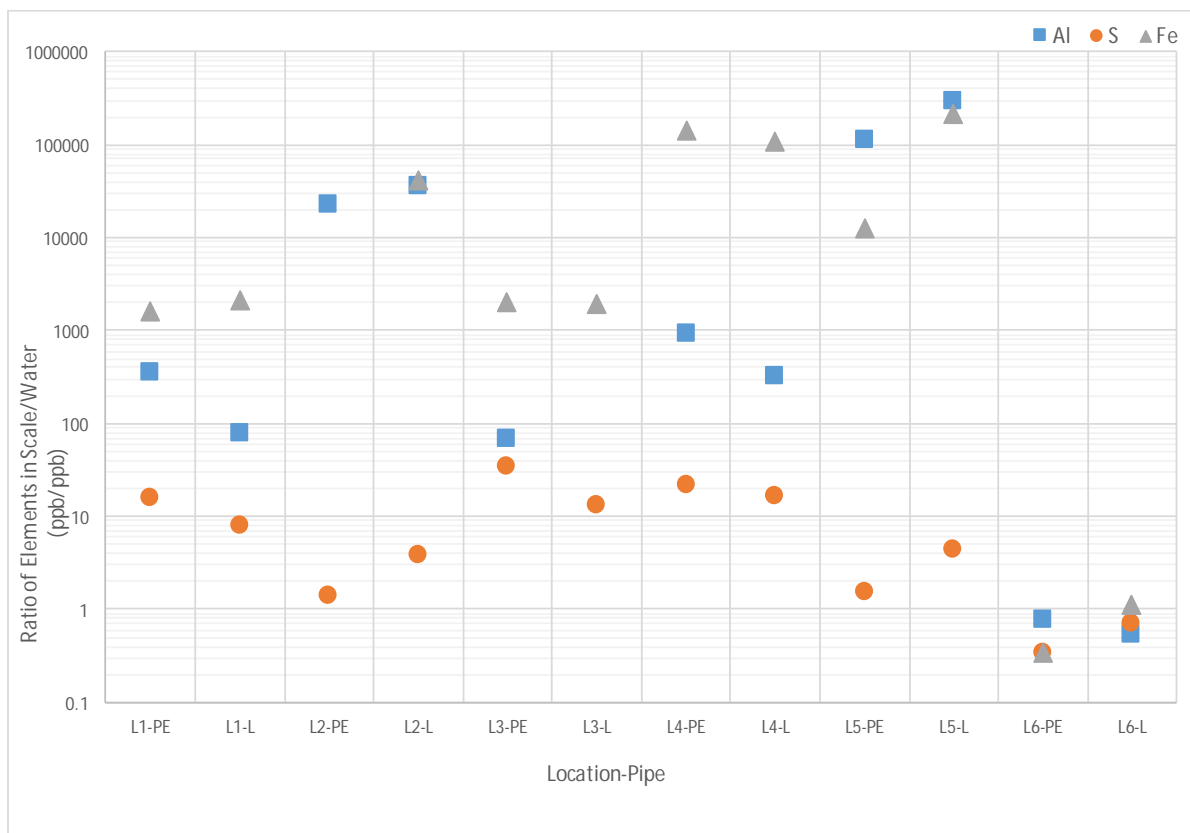

Figure 2.5:Ratio of sulfur, aluminum or iron concentration (ppb) in pipe scale to total concentration in water (ppb).
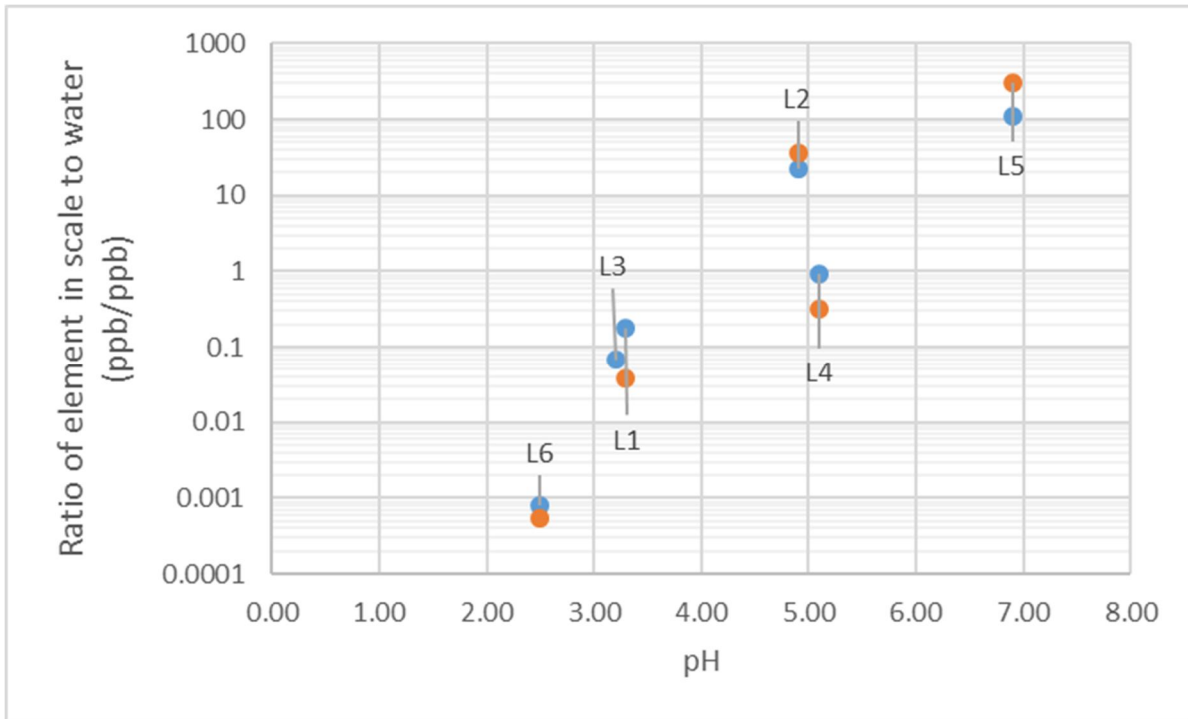
Figure 2.6: Ratio of aluminum concentration (ppb) in pipe scale to total concentration in water (ppb) versus pH.
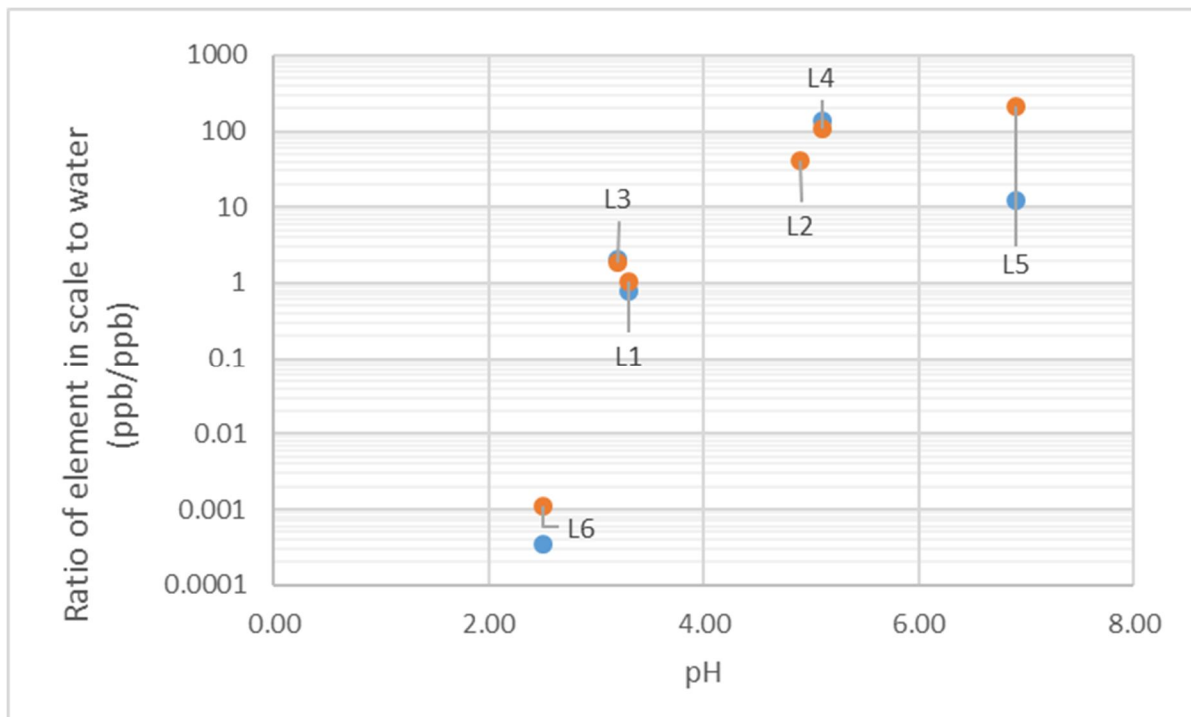

Figure 2.7: Ratio of iron concentration (ppb) in pipe scale to total concentration in water (ppb) versus pH.
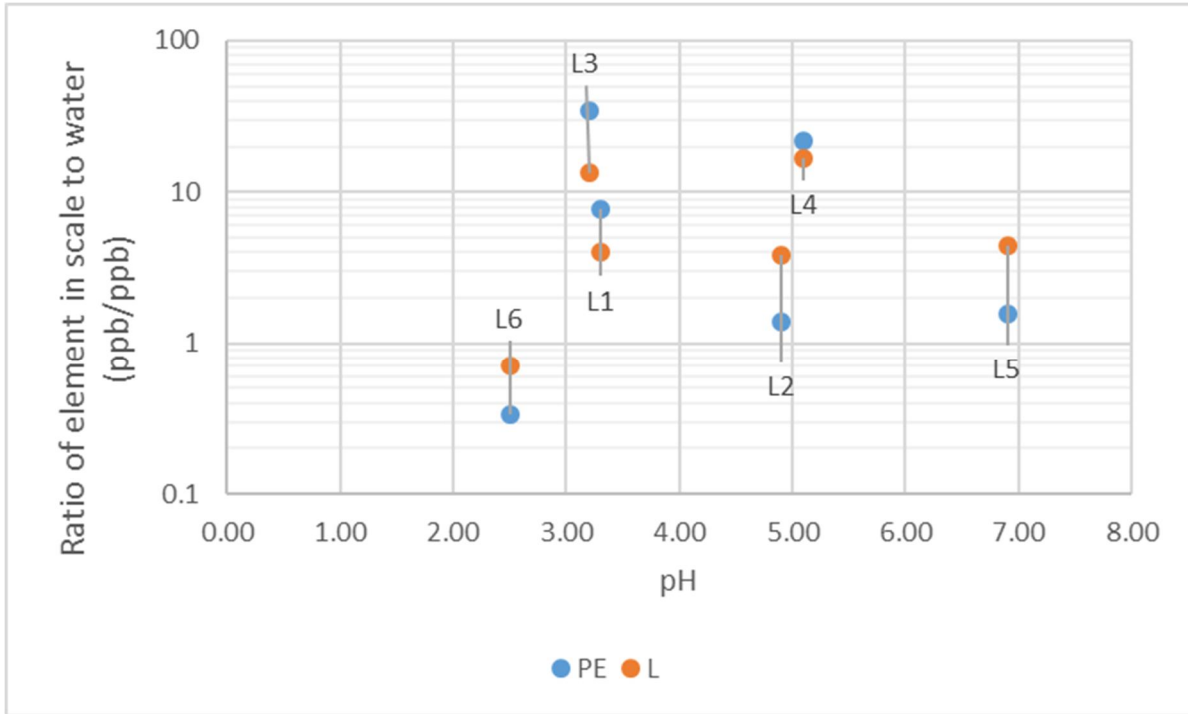
Figure 2.8: Ratio of sulfur concentration (ppb) in pipe scale to total concentration in water (ppb) versus pH.

3.2 Scanning Electron Microscopy Results

To further explore the scale build-up on the pipe samples (from Weeks 1 and Week 3), scanning electron microscopy with energy dispersive x-ray (SEM-EDX) was used. Specifically, a Quanta 600 Field Emission Gun (FEG) by FEI Company was used on the Virginia Tech campus. Thus, samples were shipped to Blacksburg from Freiberg. Images were captured to explore surface morphology, and then elemental composition was examined. An image comparison of samples at 1000x magnification can be found in Figure 2.4, while elemental maps can be found in Figure 2.5. It should be noted that the elemental maps in Figure 2.5 are taken at various magnifications, as was required for the clear visibility of mineral constituents in each sample.

	Week 1		Week 3	
	Unlined	Lined	Unlined	Lined

Control

Location 1

Location 2

Location 3

Location 4
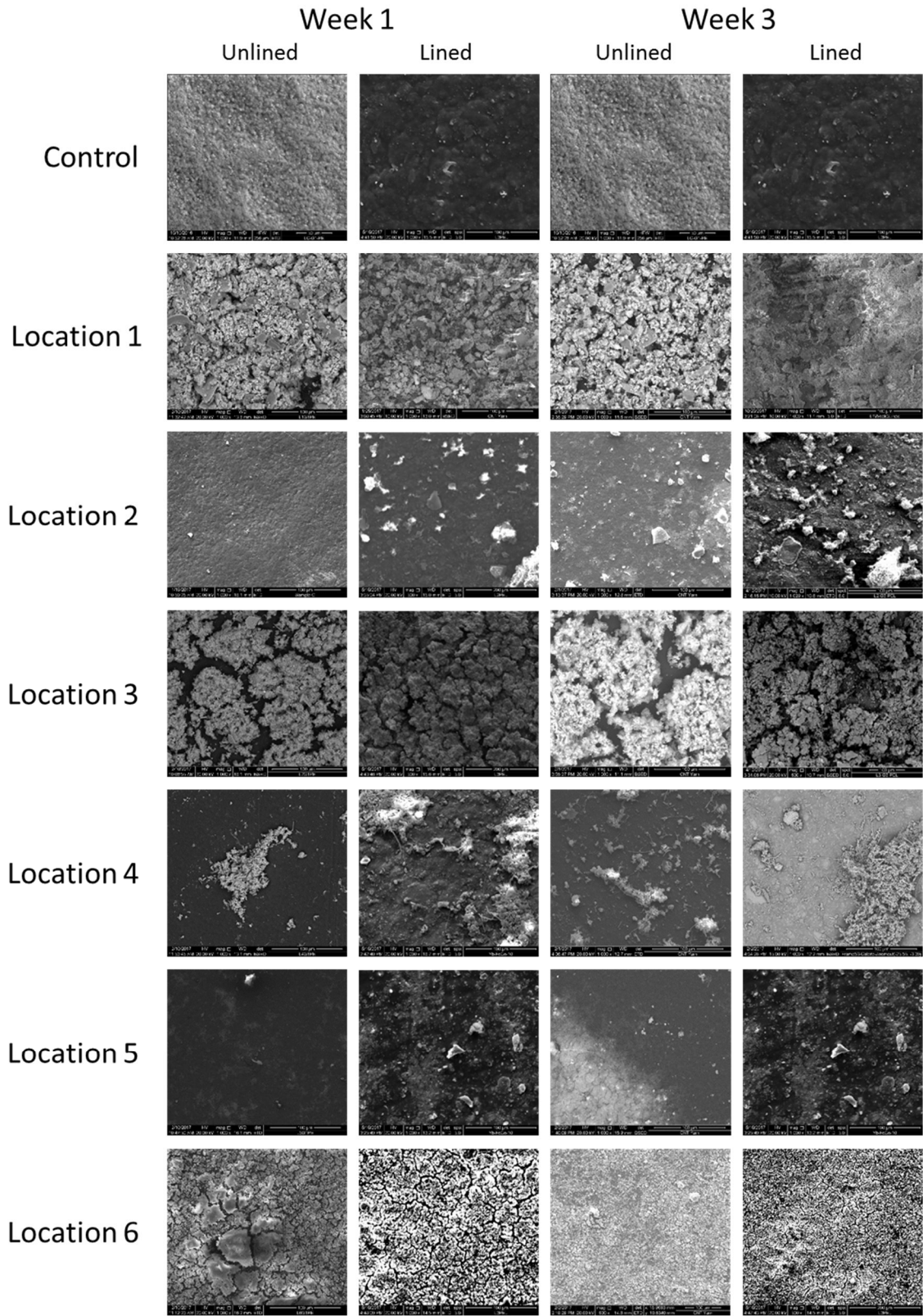
Location 5

Location 6

Figure 2.9: Image comparison of each location and pipe type. Taken at 1000x magnification.
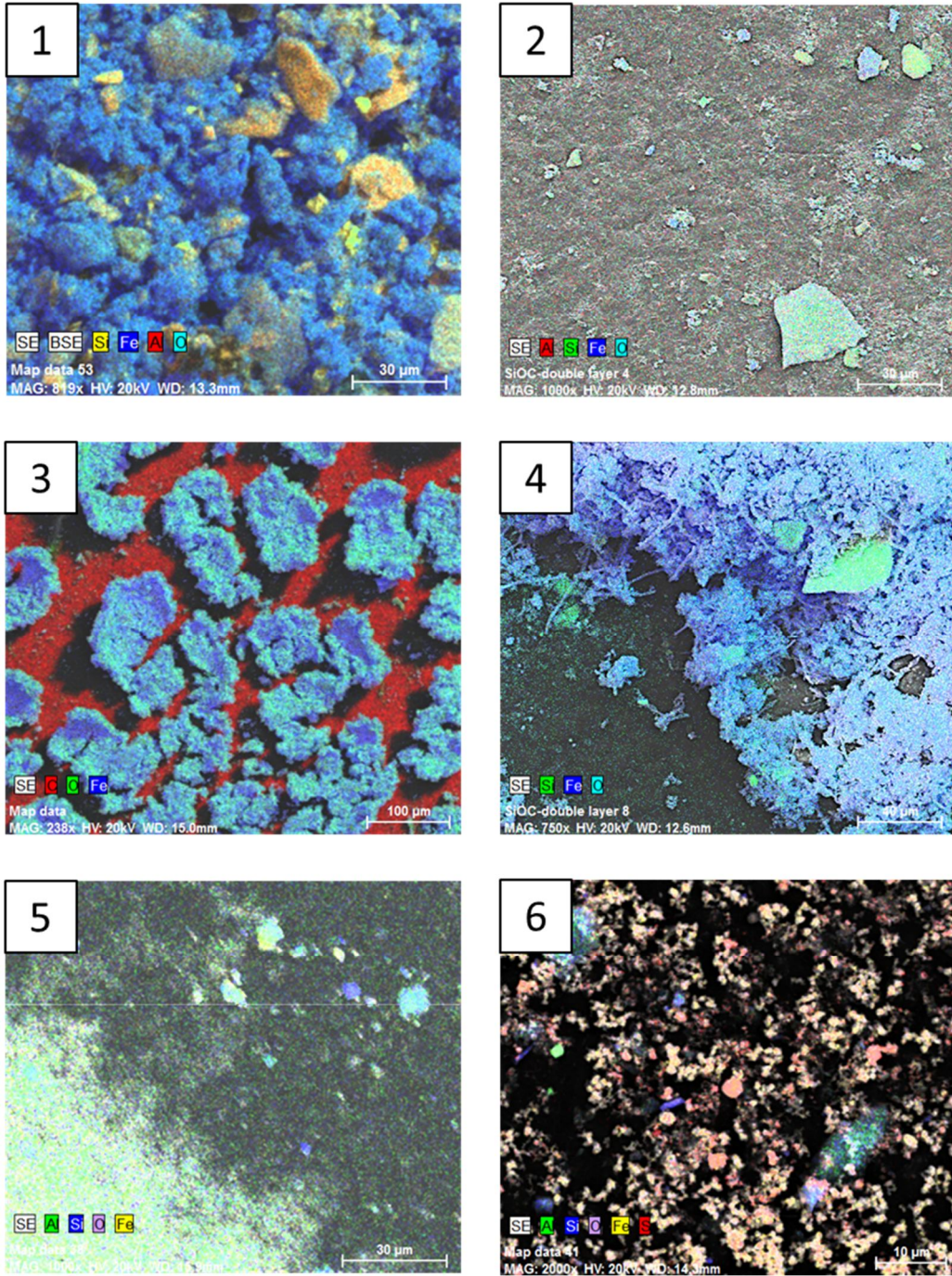
22

Figure 2.10: Elemental maps of each location.

Location 1 was characterized by a conglomeration of many individual particles varying in size in the range of 1 micron to 40 microns covering a large majority of the pipe surface (observable in Figure 2.4). Elemental analysis of the samples showed two primary constituents. Smaller particles were composed of large amounts of iron, and oxygen likely in the form of iron hydroxides. Larger particles showed aluminum, silica, and potassium indicating an aluminum silicate ($xAl_2O_3*ySiO_2$), possibly in the form of a potassium aluminum silicate ($KAlSiO_2$). This is confirmed by the co-occuring elements in map in Figure 2.5(a). Additionally, a sample spectra analysis for location 1 can be found in Figure 2.6.
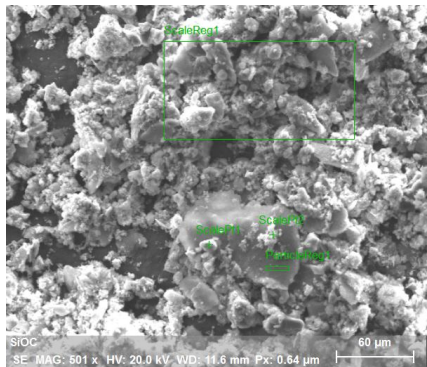

```
Atomic percent (%)
Spectrum          O    Mg    Al    Si    S     K     Fe
-------------------------------------------------------
ParticleReg1 65.96 1.01 13.80 14.23    -  4.21  0.78
ScaleReg1    65.59    -  3.88  4.94 2.92 1.30 21.36
ScalePt1     59.22    -  3.84  3.84 2.62 1.02 29.46
ScalePt2     67.34    -  8.26  8.30 2.18 2.54 11.37
```
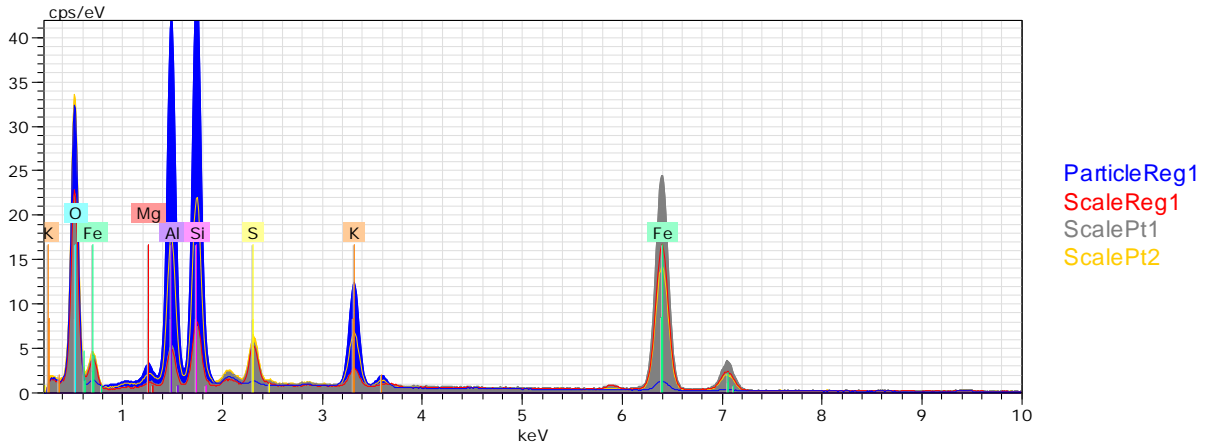

Figure 2.11: Spectra Analysis for Location 1.

As seen in Figure 2.4, Location 2 showed scattered coverage of individual particles around 25 microns with little coverage of the pipe surface. All particles had very similar chemical compositions rich in silica, iron, and some potassium. These are likely similar to those found in location 1: aluminum silicate ($xAl_2O_3*ySiO_2$), possibly in the form of a potassium aluminum silicate ($KAlSiO_2$). Chemical composition can be verified in the map in Figure 2.5(b), and a sample spectra analysis can be found in Figure 2.7.
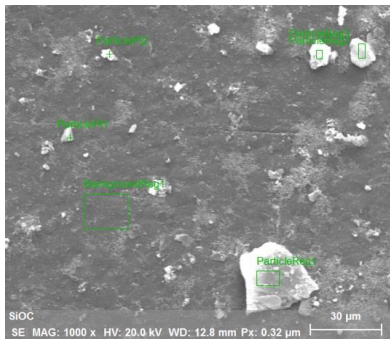

```
Atomic percent (%)
Spectrum              C      O     Mg    Al    Si    S     K     Fe
------------------------------------------------------------------
ParticleReg1       24.54  57.21  2.83  4.38  6.23    -  1.56  3.25
BackgroundReg1     92.80   7.08  0.01  0.02  0.02    -  0.00  0.06
ParticleReg2       46.56  40.71  0.75  1.86  2.14    -  0.27  7.69
ParticleReg3       30.05  53.69  0.71  6.55  6.98    -  1.56  0.46
ParticlePt2        47.41  45.36  0.94  1.22  1.02  0.35 0.07  3.63
ParticlePt1        52.74  40.93  0.36  2.58  2.23    -  0.58  0.58
```
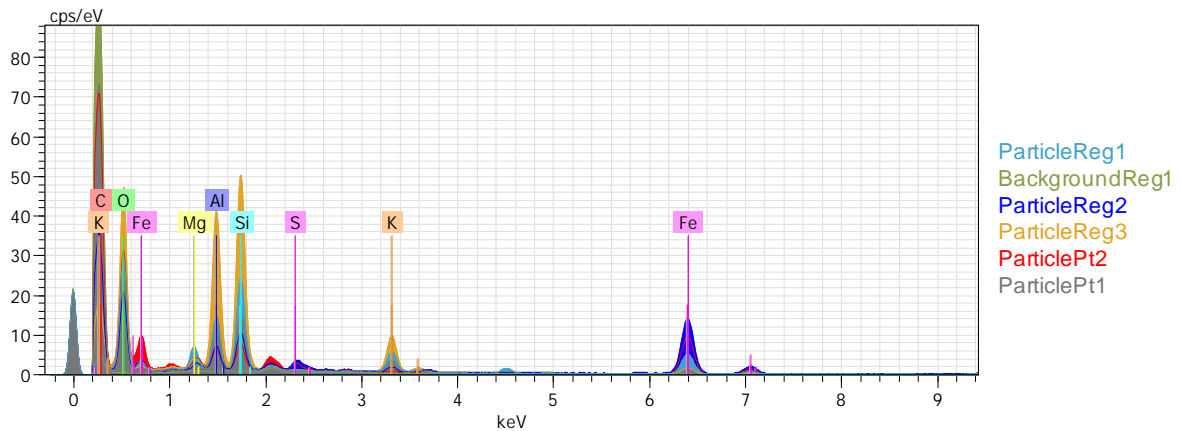
Figure 2.12: Spectra Analysis for Location 2.

Location 3 was heavily covered with scale in large patches. As seen in Figure 2.4, the morphology across the entirety of the pipe was quite similar, without any large particles of silicates as those found in the other locations. Because of the uniformity, it is likely that the scale in this location was formed exclusively through the precipitation of iron oxides. The elemental map in Figure 2.5(c) further supports the formation of iron oxides. A sample spectra analysis for this location can be found in Figure 2.8.
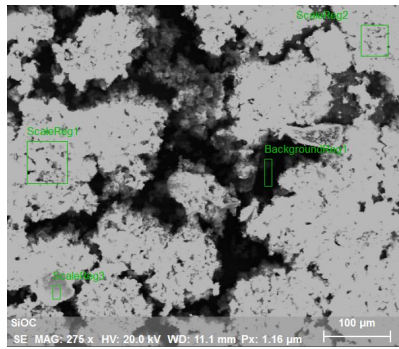

```
Atomic percent (%)

Spectrum                  O    Al   Si    S    Fe
-----------------------------------------
ScaleReg1            65.12 0.49 0.36 4.47 29.56
ScaleReg2            66.97 0.65 0.96 3.68 27.74
ScaleReg3            76.23 0.06 0.01 2.31 21.39
BackgroundReg1 30.69 1.25 1.82 7.43 58.81
-----------------------------------------
```
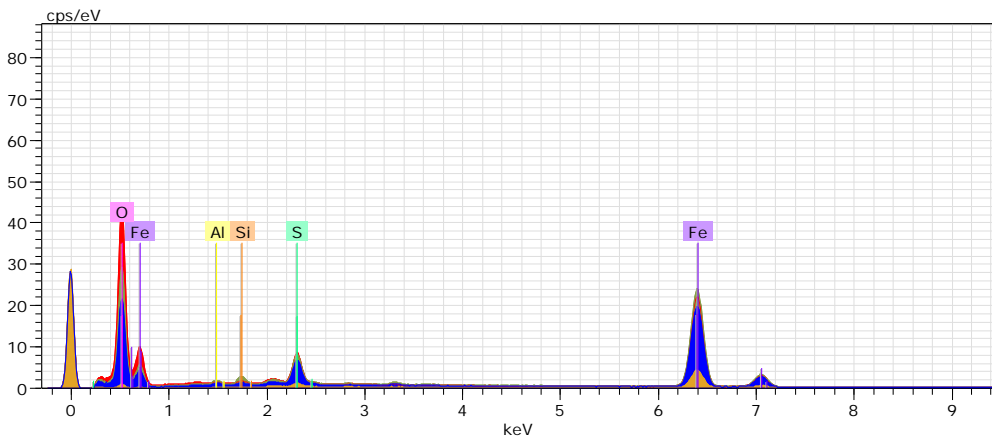

Figure 2.13: Spectra Analysis for Location 3.

Location 4 showed the most variation in morphology. As seen in Figure 2.4, in addition to rounded particles, it contained rod and helix structures seen in both lined and unlined samples. When analyzed, these rod and helix structures both gave chemical compositions of ~30-50% iron, ~40-70% oxygen, consistent with an iron oxide. Iron oxides can be manipulated into these shapes in a laboratory setting via magnetism and co-precipitation (Ankamwar, 2013). However, because this is a field study it is more likely that these are foreign particles that have been covered in iron oxides. In addition, particles rich in aluminum and silicon indicate the presence of some aluminum silicates. A sample spectra analysis can be found in Figure 2.7, and an elemental map in Figure 2.5(d).


```
Atomic percent (%)

Spectrum         O     Mg    Al    Si    S    K     Fe
-------------------------------------------------------
ParticleReg1  70.55  1.41 10.91 11.86    - 3.05   2.23
Point1        74.08  0.00  1.73  2.51    - 0.84  20.84
Point2        69.95  0.06  0.86  0.89    - 0.04  28.20
Point3        37.91  0.11  2.34  2.56    - 0.46  56.62
ScaleRegion1  67.15  0.00  0.97  1.39 1.63 0.17  28.69
-------------------------------------------------------
```
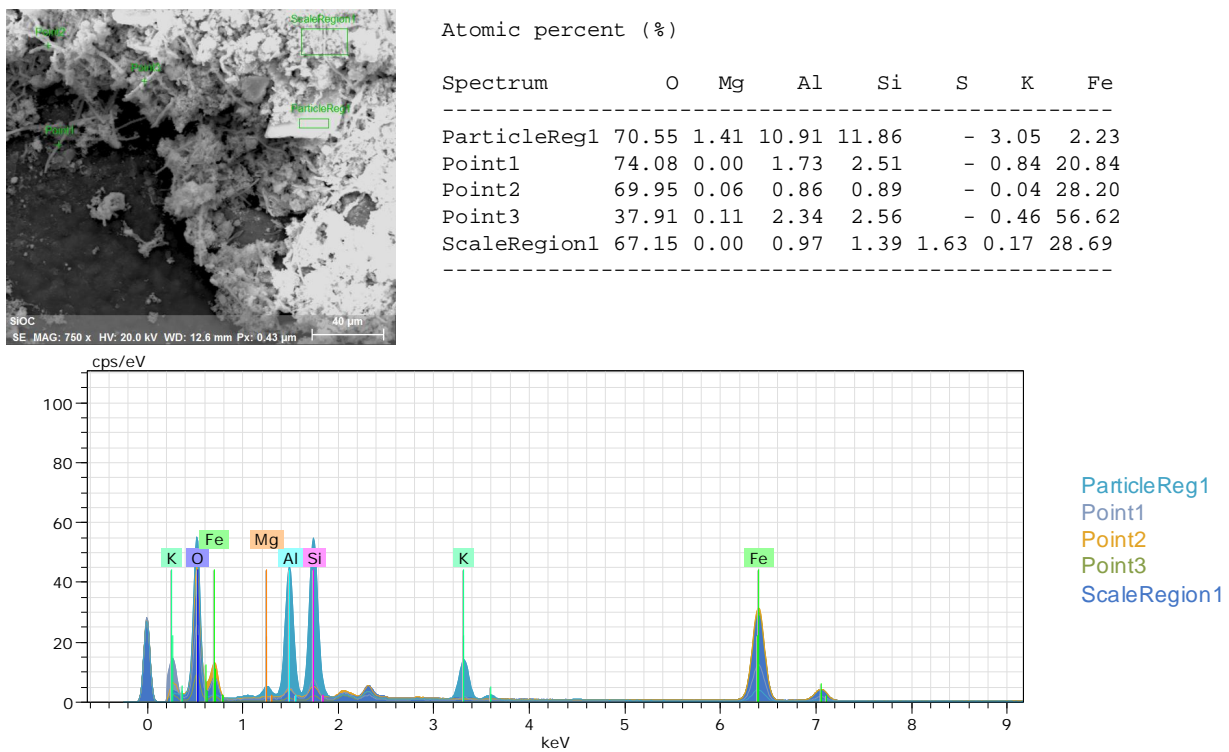

Figure 2.14: Spectra Analysis for Location 4.

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Location 5 had relatively small particles, with a range of about 5-10 microns. The round particles covered only very little of the pipe surface. In addition, there was light patches of scale. As seen in Figure 2.5(e) both the particles and scale patches showed high levels of iron, and moderate amounts of aluminum, silicon, and sodium. A sample spectra analysis can be found in Figure 2.10

.


```
Atomic percent (%)
Spectrum            O     Na     Al    Si    Mn    Fe
------------------------------------------------------
ScaleReg1         74.26  3.04   6.25  4.71  0.02  11.72
BackgroundReg1    49.44 16.85  11.99  9.43  0.08  12.21
ParticlePt1       70.04  3.19   4.26  4.39  3.57  14.56
```

Figure 2.15: Spectra Analysis for Location 5.

Location 6 showed small conglomerations of ~1 micron round particles, in addition to larger particles of between 10 and 20 microns. The smaller conglomerations showed significant amounts of aluminum and silicon, likely in the form of aluminum silicate ($xAl_2O_3*ySiO_2$). Additionally, this location showed large particles with high levels of sulfur, iron, and magnesium occurring together. This could be iron sulfates, and magnesium sulfide occurring concurrently as these elements do not typically occur in a single compound together. A sample spectra analysis can be found in Figure 2.11, and an elemental map in Figure 2.5(f).


```
Atomic percent (%)
Spectrum          O    Mg    Al     Si     S     K     Fe
--------------------------------------------------------
Particle1Reg 56.53 3.89 12.50 14.18  5.38 3.07  4.44
ScaleReg1    54.58 6.13  6.12 10.42  7.71 1.03 14.00
Particle2Reg 68.41 6.84  2.86  2.73 10.82 0.43  7.90
```
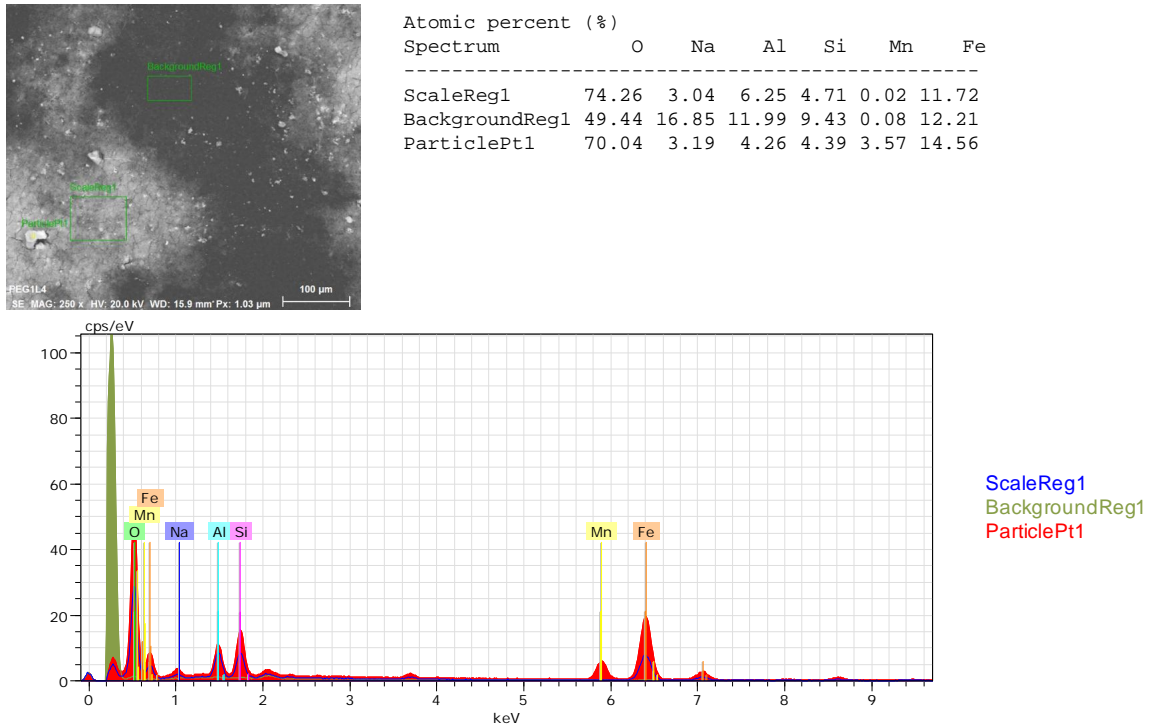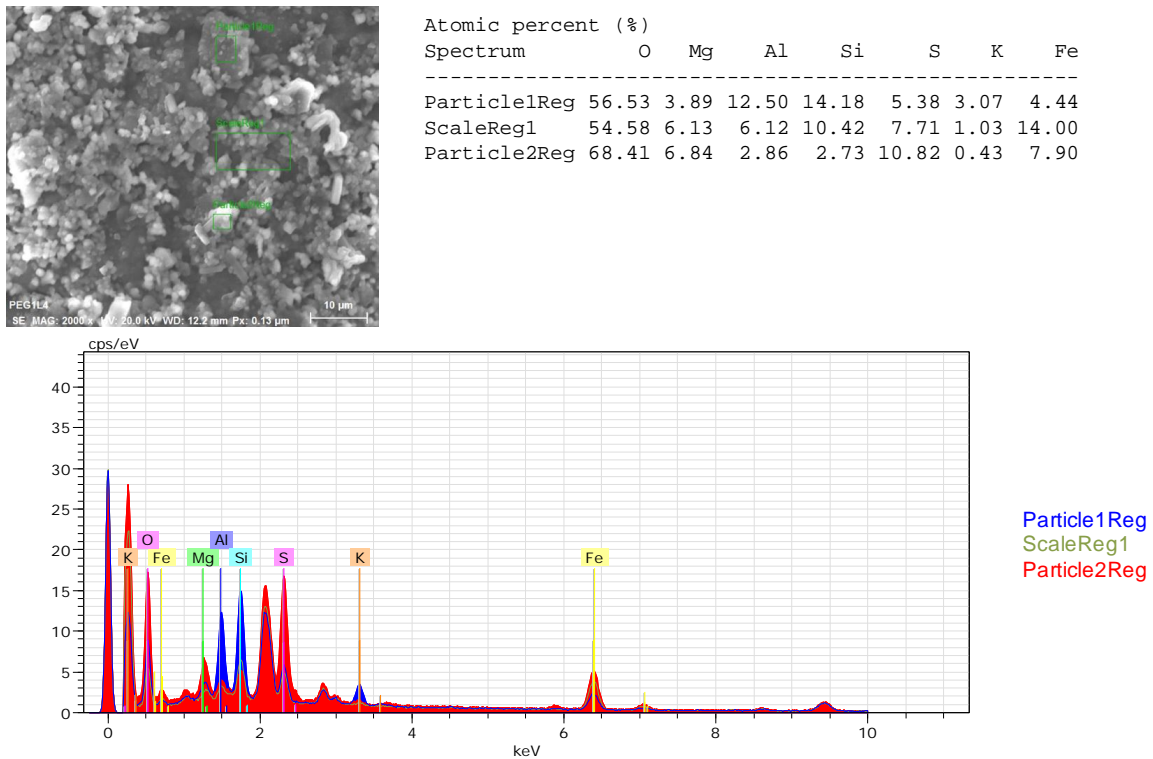
Figure 2.17: Spectra Analysis for Location 6.

The SEM images and analysis reinforce what was observed from the weight change measurements; irrespective of the pipe type, locations 1 and 3 clearly had the highest amount of build-up across the entire test period. In contrast, those locations with only marginal weight gain (2, 4, and 6) showed intermittent coverage in week 3 samples (Figure 2.2). This is verified by the comparison of each pipe type and location can be found in Figure 2.4.

In addition, the EDX spectra analysis reaffirmed the XRF data that aluminum, iron, silicon and sulfur are primary constituents in all locations. Elemental peaks aside from the four primary elements

present in each location correlate with water measurements in each location. The water in locations 1, 2, and 5 show high levels of potassium. Elemental spectra show peaks of potassium for scales in those locations, which do not exist in the spectra for 3 and 4. Similarly, water in location 6 shows the highest sulfur concentration, corresponding with it displaying the largest sulfur peak on spectra analysis.

Finally, surface morphology and chemical composition varied very little among the lined and unlined pipes in identical locations. However, the morphology and composition were significantly different between locations. This is consistent with the unique water conditions in each location being of much more importance to the scale composition and quantity than the pipe material.

4. Conclusion

A novel liner is in development to combat abrasion on PE water and slurry pipes. In order to ensure optimal performance in the field, however, the liner must be tested under a variety of conditions that commonly present problems for pipe wear and failure. In a short field study, the potential for mineral scale buildup was investigated to compare pipes with the novel liner to traditional PE pipes. Weight gain was measured, and surface morphology and chemical composition of the scale was analyzed utilizing SEM and XRF. All analysis varied very little among the lined and unlined pipes in identical locations. However, the morphology and composition were significantly different between locations. This is consistent with the unique water conditions in each location being of much more importance to the scale composition and quantity than the pipe material. Based on all evidence presented here, the two pipe materials behaved similarly in terms of scale accumulation, morphology, and chemical composition. Therefore, the new liner remains a competitive candidate to combat abrasion in mining applications. It is important to note that the field conditions (i.e., water quality, flow) in this study represent only a small range of conditions that may be possible in mining and minerals processing applications. Thus, further investigation is required under other conditions frequently associated with scaling (e.g., elevated pH and hardness).

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CHAPTER 3 : A LAB STUDY OF MINERAL SCALE BUILDUP ON LINED AND TRADITIONAL PE WATER PIPES IN ACID MINE DRAINAGE TREATMENT APPLICATIONS

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Abstract

Plastic, especially polyethylene (PE), pipe material is increasingly used in mining applications due to its inert nature, flexibility, low density, and low cost. Though resistant to chemical corrosion, it is susceptible to abrasion. To combat this problem, an abrasion-resistant liner is in development. It is not yet known how the liner will perform with regards to other common problems that affect pipe systems, such as mineral scale buildup. In mining applications, scale buildup occurs due to the very high suspended and dissolved solids contents in water or slurry. For example, in systems transporting raw or treated acid mine drainage (AMD), scale can form on pipe surfaces due to sedimentation or diffusion of particles onto the surface, or precipitation of solids directly onto the surface. In this study, pipe loop experiments were conducted in the laboratory to under three idealized AMD treatment scenarios (i.e., untreated, passively treated and actively treated) to compare mineral scale buildup on traditional versus lined PE pipe materials.

1. Introduction

Acid mine drainage (AMD) is a common problem across metal, nonmetal, and coal mining operations. This problem primarily arises due to oxidation of sulfide minerals (e.g., pyrite, FeS_2, and other metal sulfides) in contact with water. The following equation describes the oxidation of pyrite by oxygen (Singer & Stumm, 1970).

$$FeS_{2(s)} + \frac{7}{2}O_{2(aq)} + H_2O \rightarrow Fe^{2+} + 2SO4^{2-} + 2H^+ \qquad \text{(Equation 3.1)}$$
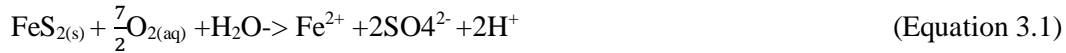
Though this process also occurs in unaltered land, rock breakage and comminution are fundamental to mining operations. This significantly increases surface area of mineral readily available to react with water, thereby accelerating the oxidation process significantly (McLemore, 2008). This reaction can occur in a variety of places in the mine site: water running through waste heaps or fills, runoff from ore or waste piles, and processing water can all be impacted by oxidation reactions. This oxidation in extreme cases can result in pH conditions as low as -3.5 (Nordstrom, 2011). In addition to low pH, acid mine drainage is often elevated in manganese, aluminum, iron, and silicates due to the ability of acidic waters to dissolve surrounding minerals (McLemore, 2008).

In the case that the acid mine drainage meets surrounding surface waters, impacts on aquatic ecosystems can be significant. Beyond immediate consequences such as fish kills (e.g., see Nordstrom, 2011), the survival and productivity of macroinvertebrates, phytoplankton, and zooplankton can all be detrimentally affected by low pH conditions (Cherry et al, 2001). Additionally, if these dissolved metals precipitate, the biota can be flooded with solid metal hydroxides (Luis et Al., 2008). These conditions result in the elimination of more sensitive organisms, and sometimes allow more tolerant organisms to flourish (Luis et Al., 2008). For instance, ferro- and sulpho-oxidising acidophilic organisms tend to thrive in such impacted environments (Olias et Al., 2004). However, the native biodiversity is substantially diminished, and higher level organisms (i.e. vertebrates) tend to suffer (Gross, 2000). Even once the acidity is neutralized, discharges of AMD often result in the surrounding water being undrinkable, unfishable, and unsuitable for purposes of irrigation due to high metal and/or salt content (Cravotta, 2008 & Skousen, 2016).

Apart from ecosystem impacts, AMD can also create problems on-site for mining operations. As water resource sustainability becomes an increasing global concern, many operations are beginning to focus largely on recycling water as a way to decrease consumption (Mudd, 2008). However, AMD must be treated and discharged within acceptable standards before it can be reused. In addition, AMD can

accelerate corrosion in mining equipment or metal roof support compromising the safety of an operation. It can also can corrode the slope rock, damaging the structural integrity of the mine (Zhao, Ju, & Li, 2011). Because of the broad range of potential impacts both on site and to the surrounding ecosystems, it is critical to identify AMD generation potential and mitigate this either through prevention or treatment.

Both active and passive treatment schemes for AMD are common. Active treatment generally entails addition of soluble neutralization agents such as calcium oxide (i.e., lime) in a fixed plant (Younger et al., 2002). The benefits of active treatment include is its effectiveness in treating a wide variety of severe water conditions, relatively small space requirement, and short treatment times (Younger et al., 2002). However, active treatment systems can be energy and cost intensive due mechanical requirements (i.e., pumps, mixers), capital investments and chemical supplies; and treatment facilities generally have a non-trivial environmental footprint and carry risk with the additional input of chemicals (Skousen, 2016).

In contrast, passive treatment typically involves allowing a carbonate mineral (e.g., limestone or dolomite) or other neutralization agent to dissolve into the affected water in a flow through system designed for adequate reaction time (Taylor et al., 2005). Limestone ponds or drains are a common design scheme (Taylor et al., 2005). The main benefit of passive treatment is that the process is less cost and energy intensive (Taylor et al., 2005) since it is largely autonomous; thus, fewer environmental impacts are usually associated with passive versus active treatment systems too (Hengen et al., 2003). However, passive AMD treatment is normally only practical in lower acidity scenarios, where metal concentrations (e.g., Fe and Al) are relatively low (Rakotonimaro et al., 2017)

In either treatment scenario, acid neutralization and the associated increase in pH often leads to the precipitation of metal salts (Al et al., 2000). In some cases, this precipitation is desirable, as it allows the removal of excess metals (e.g., to meet allowable water standards for discharge). In this instance, a pH above neutral is generally desired. For example, manganese requires a pH above 8.5 to appreciably precipitate (Balintova & Petrilakova, 2011). Though passive treatments utilizing limestone self-buffer above about pH 6.5, active treatments can be used to attain higher pHs (Watzlaf et al, 2000).

Undesirably, as pH increases the precipitated minerals can lead to buildup and on inert surfaces such as pipes and pumps used for conveying AMD (Rötting et al, 2008). This buildup is frequently referred to as "pipe scale". Scale can buildup either due to precipitation of solids directly onto the surfaces, or by settling/diffusion of solids to the surfaces. Excess pipe scale can restrict flow and result pump failures, and in some cases it can cause actual pipe failure (i.e., leaks or bursts). Such outcomes can have significant financial impacts, and potentially pose environmental hazards. Inert pipe materials, such

as plastics, generally promote less scale buildup than most metal materials, but they are subject to other problems such as abrasion.

To reduce abrasion effects, a new liner for polyethylene (PE) piping is being developed and considered for use in mining applications. However, the relative susceptibility of the liner to scale buildup has only received some preliminary investigation in a short term field study. That study was conducted in an inactive lead-zinc and silver mine, where mine-influenced waters were dominated by high sulfate (i.e., due to contact the sulfide ore) and high solids contents. Samples of both lined and traditional PE pipe materials were placed in six test locations in the mine, each having somewhat different water conditions with respect to pH and flow. The samples were exposed over a three-week period, and then compared for scale buildup by weight gain and chemical and morphological analyses. Results showed that the lined PE developed only marginally more scale than the PE pipes with no discernable difference in the scale type; the scale characteristics did vary by exposure conditions.

Given the short duration of the field study, a longer study has also been conducted in the laboratory and is presented in this paper. For this, pipe loop experiments were run using three idealized AMD conditions: untreated, passively treated, and actively treated AMD. Pipe loops have been established as a reliable way to test the performance of piping materials under realistic flow conditions (MacKoul, 1995). Here, scale buildup was evaluated on the pipe material samples subjected to constant flow within the loops, and also on samples mounted to the side (minimal flow and mixing conditions) and bottom (subject to gentle flow and water mixing).

2. Materials and Methods

To conduct the experiments, four reservoirs (57 L) were used, each having two pipe loops (i.e., one to expose lined PE samples and other to expose unlined PE samples). Three reservoirs contained active loops, while the forth was a control exposed to deionized water to ensure there was no change in the samples due to water exposure alone. Loops were constructed using 64 cm lengths of acrylic pipe (2.54 cm diameter) with vinyl tubing on either end to complete the flow path from and back into the reservoir (Figure 3.1). Six identical submersible pumps were used with flow rates 7.5-7.7 L/min. Stir plates were placed underneath each reservoir to ensure that the water remained well mixed, though mixing was gentle. Samples were mounted in 3 different locations in each reservoir as shown in Figure

3.1: within the pipe-loop "tube", on the "bottom" of the reservoir, and on the "side" of the reservoir. Sample preparation and placement, and analysis of scale buildup are described in more detail below.
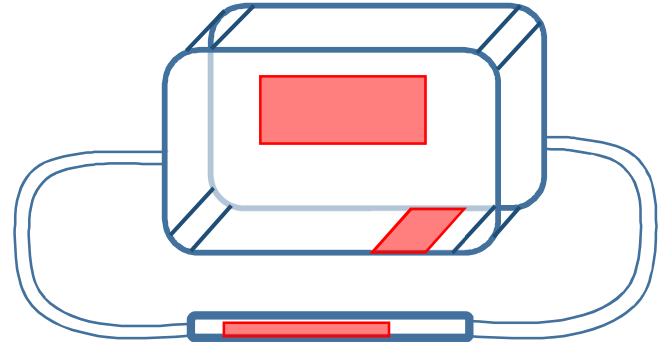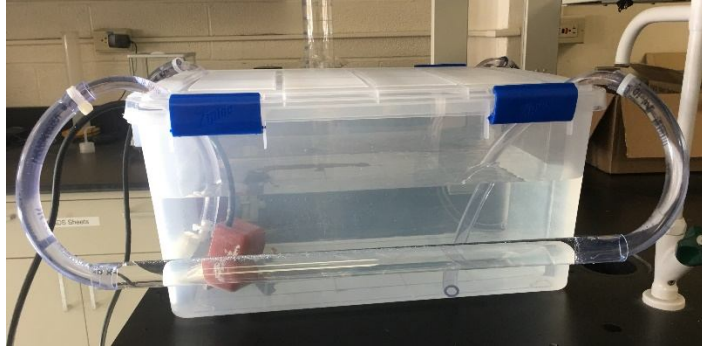

Figure 3.1: Pipe Loop Schematic.

Reynolds number was calculated to determine the flow type within the pipe tubes (Equation 3.2).

$$R = \frac{\rho V D}{\mu} \hspace{3cm} \text{(Equation 3.2)}$$

where ρ is fluid density (1000 kg/m^3), V is fluid velocity (0.247 m/s), D is tube diameter (2.54 cm), and μ is fluid viscosity ($8.9*10^{-4}$ Pa-s). A Reynolds number of 7050 indicates laminar flow in the pipes – though flow right next to the pipe surfaces where scale is forming could be turbulent times.

To simulate different treatment conditions for AMD (i.e., untreated, passively treated and actively treated), three water qualities were tested. All waters had the same initial target concentrations (Table 3.1) for iron (dosed as $Fe_2(SO_4)_3$), aluminum (dosed as $Al_2(SO_4)_3$), silicon (dosed as $Na_2SiO_3*9H_2O$), calcium (dosed as $CaCO_3$ and $CaSO_4*2H_2O$) magnesium (dosed as $MgSO_4*7H_2O$), and sulfate (balance was added H_2SO_4). However, the pH was adjusted in each water: Reservoir 1 (untreated AMD) had pH 4.5, Reservoir 2 (passively treated AMD) had pH 6.5, and Reservoir 3 (actively treated AMD) had pH 8.5.

For the first week, water in all three reservoirs was also tested every day for aluminum, iron, sulfates, alkalinity, to establish how quickly the chemistry was changing. During the second week, alkalinity, pH, and sulfates were measured every day, and the remaining parameters were measured every 3 days. By the end of two weeks, aluminum, iron, and calcium showed a significant decrease, prompting a bi-weekly water change schedule. Before and after each water change, inductively coupled plasma-mass spectroscopy (ICP-MS) samples were taken to measure the suite of elements of interest in the aged and fresh waters. For this, both total and filtered water samples were collected to determine total and soluble elements. Table 3.1 shows the ICP results for the first 8 weeks of the experiments. The pH in each

reservoir was measured every 3 days and adjusted using H_2SO_4 or CaOH; values were generally maintained within 0.5 pH units. This only minimally impacted total sulfate and calcium (Table 3.1).

Table 3.1: Average ICP Data for first 8 weeks.

Element (target conc. in mg/L)		Reservoir 1 4.0-4.5		Reservoir 2 6.0-6.5		Reservoir 3 8.0-8.5	
		Unfiltered	Filtered	Unfiltered	Filtered	Unfiltered	Filtered
Al (10)	fresh	12.4	1.9	10.7	0.1	9.9	0.8
	aged	6.0	0.2	6.4	0.1	9.1	0.3
Ca (100)	fresh	373.0	376.2	447.1	406.1	468.3	377.9
	aged	407.0	413.0	441.4	416.6	515.7	403.2
Fe (20)	fresh	24.9	0.1	20.6	0.1	18.3	0.1
	aged	14.1	0.1	13.0	0.1	16.7	0.2
Mg (10)	fresh	5.8	5.9	5.9	5.8	5.5	4.4
	aged	6.0	6.1	5.9	5.9	6.0	5.2
Na (30)	fresh	29.1	30.2	27.7	28.8	26.2	27.5
	aged	30.1	31.3	28.4	29.8	27.8	28.8
SO_4 (1000)	fresh	960.0	998.1	872.3	941.3	863.0	959.9
	aged	1019.9	1084.1	902.0	986.3	904.1	953.5
Si (15)	fresh	14.4	11.7	13.6	5.7	12.1	3.5
	aged	10.6	8.0	9.6	4.3	11.5	2.8
Zn*	fresh	4.7	4.7	2.5	0.3	0.8	0.0
	aged	28.4	26.6	5.0	0.9	4.4	0.5

* no target established; Zn was present in the water due to corrosion of wire mesh used to mount samples in the pipe-loop reservoirs.

Samples were prepared utilizing 10 cm diameter pipes provided by Gerodur MPM Kunststoffverarbeitung GmbH and Co. KG. (Gerodur). They were cut into approximately 1 cm by 1 cm squares; at this size, the samples were nearly flat (i.e., very little curvature). In addition, wall thickness was sanded from the outside to accommodate the size of the pipe loop tube. Bottom and side samples were mounted onto wire mesh before being adhered to their respective locations. The tube samples were mounted onto a nylon ties which then were adhered to the bottom of the tube. There were 9 samples of each pipe type (i.e., lined and unlined) placed along the bottom and sides, allowing for removal of samples in triplicate for measurements of weight change. In addition, 4 samples were placed in the tube

Samples were taken at 3 weeks, 9 weeks, and 16 weeks and analyzed for weight gain, surface morphology, and elemental composition. In the tube, first and last samples were removed and weighed. Then, the first sample was placed back in the tube while the last one was removed permanently for SEM analysis. This was to ensure that the location in the flow pattern did not appreciably affect how scale built up on the sample. Because water was mixed in the reservoirs, the samples were removed during water

changes. This ensures that samples were not affected by the intermediate water chemistries (i.e., before all constituents were dosed and mixed in each reservoir). An OHaus Explorer EX423 balance was used to measure weight with an accuracy of 1 mg. To map surface morphology, and elemental composition a scanning electron microscopy with energy dispersive x-ray (SEM-EDX) was used. Specifically, a Quanta 600 Field Emission Gun (FEG) by FEI Company was used on the Virginia Tech campus at the Nanoscale Characterization and Fabrication Laboratory. Images were captured at magnification of 500-4,000x to examine the surface morphology of the scaling on the samples. In addition, elemental spectra and maps were generated to visualize which elements occur concurrently in order to gain insights on the constituent minerals of the scale.

3. Results and Discussion

3.1 Weight Gain

To determine the relative mass of scale buildup on the samples, weight measurements were made after samples were collected at 3, 9 and 16 weeks of exposure time. Before weighing, samples were dried for two hours at 50°C, which was determine to be sufficient for removing all moisture. It should be noted, that as the weeks progressed white powder accumulated on the control samples. When analyzed under SEM, this powder was shown to be zinc which dissolved off of the wire mesh. The corrosion of the wire mesh is further reinforced by the increase in zinc as seen in the ICP data in Table 3.1. Unfortunately, this rendered the controls unusable for further comparison to the active samples.

There are four main bases for comparison of sample weight changes: between the different water qualities (i.e., reservoirs 1-3), the location of the sample exposure within a reservoir (i.e., sides, bottom, or tube), the time at which samples were collected (i.e., at 3, 9, or 16 weeks of exposure), and between the two sample materials (lined versus traditional PE). Photos displaying representative samples for each collection can be found in Figure 3.2. Because all samples were not exactly identical in size, the weight gain was normalized per mm^2 of sample. Graphs showing weight gains for the samples removed from the tube, reservoir side and reservoir bottom locations can be found in Figures 3.3(a), 3.3(b), and 3.3(c), respectively.

This experiment was developed to determine the relative susceptibility of the newly developed PE pipe liner versus traditional PE pipe material. In the samples mounted in the

bottom, the lined samples gained more weight than the PE samples in all cases. However, the sides and tubes showed mixed results, with some reservoirs having more weight gain on the PE material, and some on the lined material. However, in all cases the difference in weight gain between the two samples types were marginal. This is further reinforced by observing the photos collected; scale on both materials is similar in color and quantity.

Within each reservoir, the samples mounted to the reservoir sides gained the smallest amount of weight. This was expected because unlike the bottom and tube samples, no particles could settle onto these samples. Rather, these samples only gained weight due to particle diffusion and attachment and/or precipitation of scale onto the surface. This is further seen in Figure 3.2; the scale on the side samples formed in small patches, likely where small particles were diffused onto the sample and then served as a nucleus for further scale growth (Muryanto et al., 2014).

In general, samples in the reservoir tubes gained the most weight, while the samples on the bottom of the reservoir were intermediate in weight gain. Both the bottom and tube samples were able to gain scale via particle settling, as well as diffusion and attachment of small particles and precipitation of solids directly onto the sample surfaces. The slightly higher weight gain on the tube samples is likely a result of higher diffusion potential versus on the bottom samples. Due to the flow through the tube, the concentration of small particles and ions near the sample surfaces should have been continuously replenished – driving more attachment and precipitation to occur. Near the bottom samples, the water was only being gently mixed, which likely resulted in lower diffusion rates.

The three water qualities varied exclusively by pH (i.e., the target pHs were about 4.5, 6.5, and 8.5 for reservoirs 1, 2, and 3, respectively). The varying pH conditions produced scales different in quantity and composition. The lowest pH had significantly less scale than the other two reservoirs. This was expected, as most minerals seen in the simulated mine water precipitate at a pH higher than 4.5 (e.g. Ca above 6.3, Al above 5.0, etc.) (Balintova and Petrilakova, 2011). There was very little difference in the weight gains in the pH 6.5 reservoir, and the pH 8.5 reservoir. This is because the metal which formed the bulk of the scale (i.e Ca, Al, Ferric Iron) precipitate at 6.5, with only a handful of minerals requiring a higher pH to precipitate (i.e. Ferrous Iron, Mg) (Balintova and Petrilakova, 2011).

Scale buildup appears to have occurred over the duration of the experiments. However, the samples did not gain weight linearly over time. From Figure 3.3, it is clear that samples gained weight more quickly in the first 3 weeks. This trend was strongest in the tube and bottom samples. This is surprising, because often once scale buildup has been initiated, it accelerates (Muryanto et al., 2014). However, because it is more strongly noticed in samples with more scale (i.e. tube and bottom, but not on the sides) it may be that the sample surfaces did not stably support scale accumulation beyond a certain point. That is, scale that was only weakly adhered may have started to detach at some point due to water flow or disturbance of the samples when they were removed for measurements. Importantly, this does not seem to have affected one pipe material more significantly than the other.
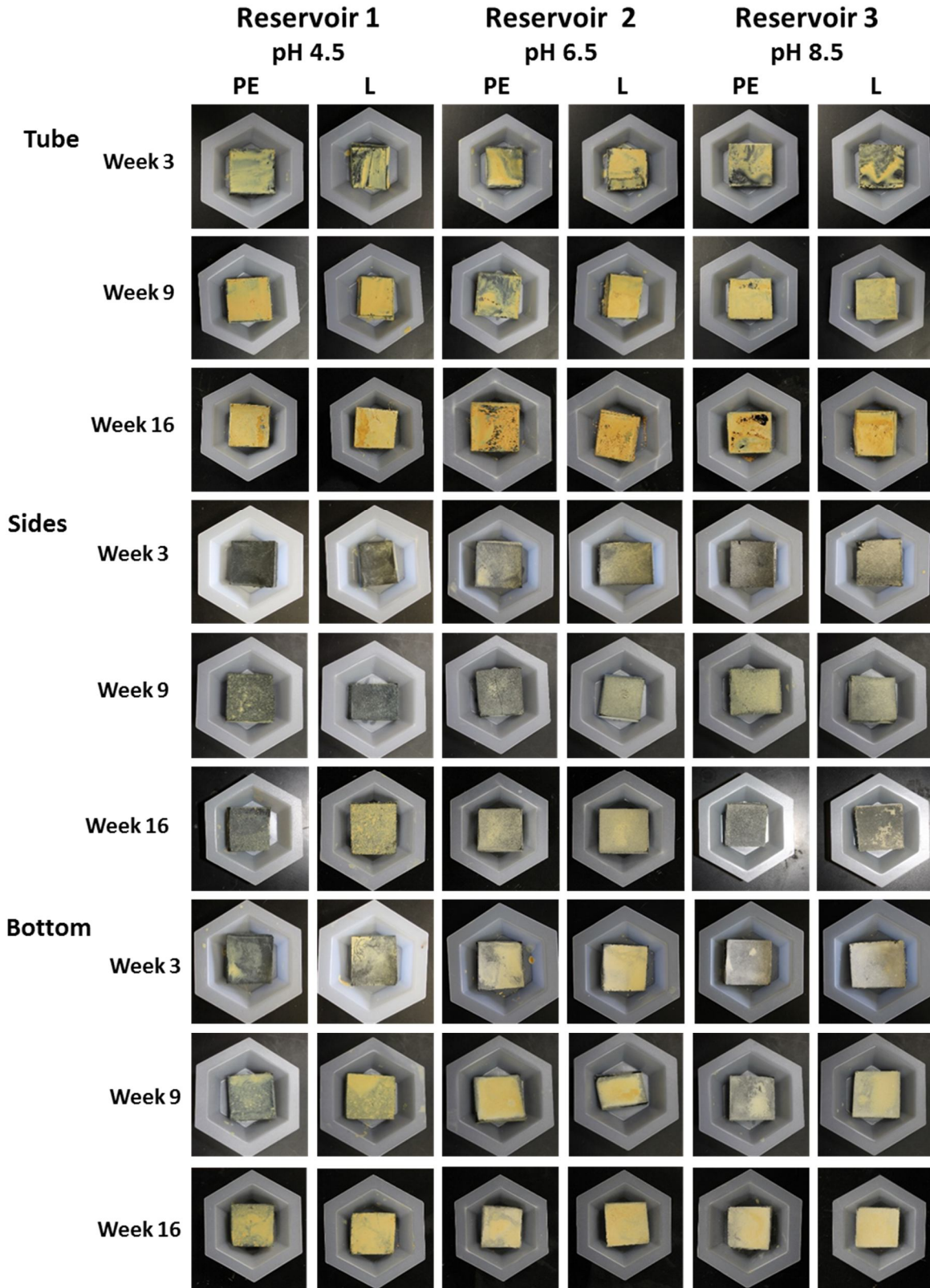
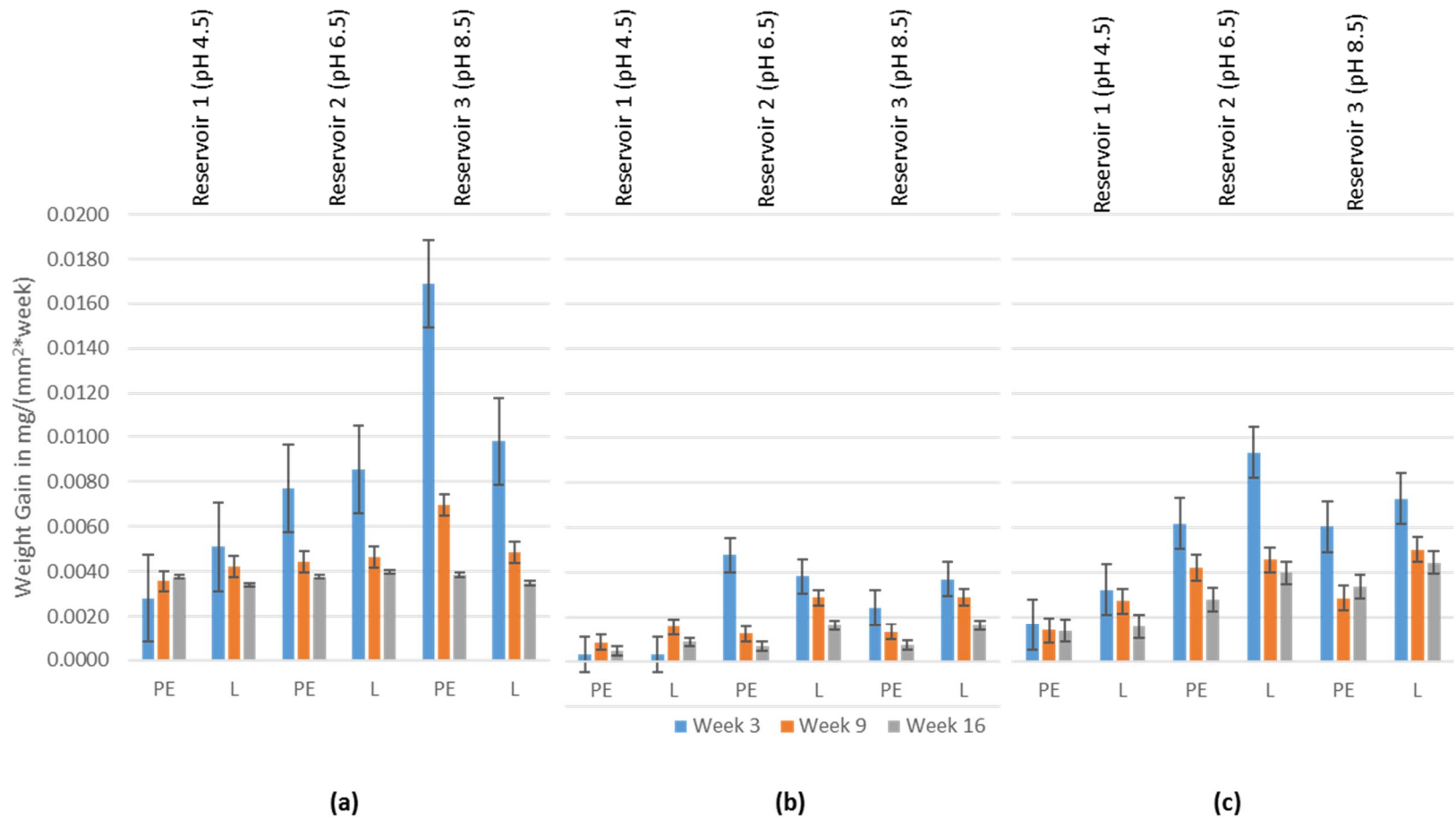*Figure 3.2: Photographs of scale buildup each week collected.*

Figure 3.3: Normalized weight gain on PE and lined-PE samples in mg/mm³ per week taken from (a) within the pipe loop tubing, (b) the side of the reservoir, and (c) the bottom of the reservoir. Results are show for samples collected after exposure times of 3, 9 and 16 weeks.

3.2 SEM Results

Of the three locations within the reservoir, the tube samples showed the most similar morphologies across the water chemistries. Finely grained scale appeared in large (over 100 µm length) patches with very few distinguishable particles. However, these patches likely developed as cracking as the scale dried (as opposed to be a characteristic of the scale itself). The fine grains of the scale further indicates that diffusion played a large part in the scale buildup on these samples. Scale which precipitates, or samples which settled would likely be larger, and less uniform in size.

In all three reservoirs, the samples on the sides of the reservoir showed 10-100 µm diameter euhedral crystals of calcium sulfate. In addition, the sides showed a conglomeration of cubic to round particles of calcium hydroxide and/or carbonates. More of these particles were present in the middle and high pH location than the low pH condition. Finally, the bottom samples showed very similar morphology to those on the sides, with the primary difference being total mass of scale. That is, the bottom samples had significantly more scale than the sides, thought the morphology was similar.

As the weeks progressed, the SEM images showed a morphologically similar scale. That is, all else being equal with respect to the water quality and sample location, the scale buildup only seems to vary by amount. Figure 3.4 shows representative SEM images for each collection. Despite similar morphology, the chemical compositions of the scale in each reservoir were distinct. Table 3.2 shows an outline of major observations on each type of sample collected.
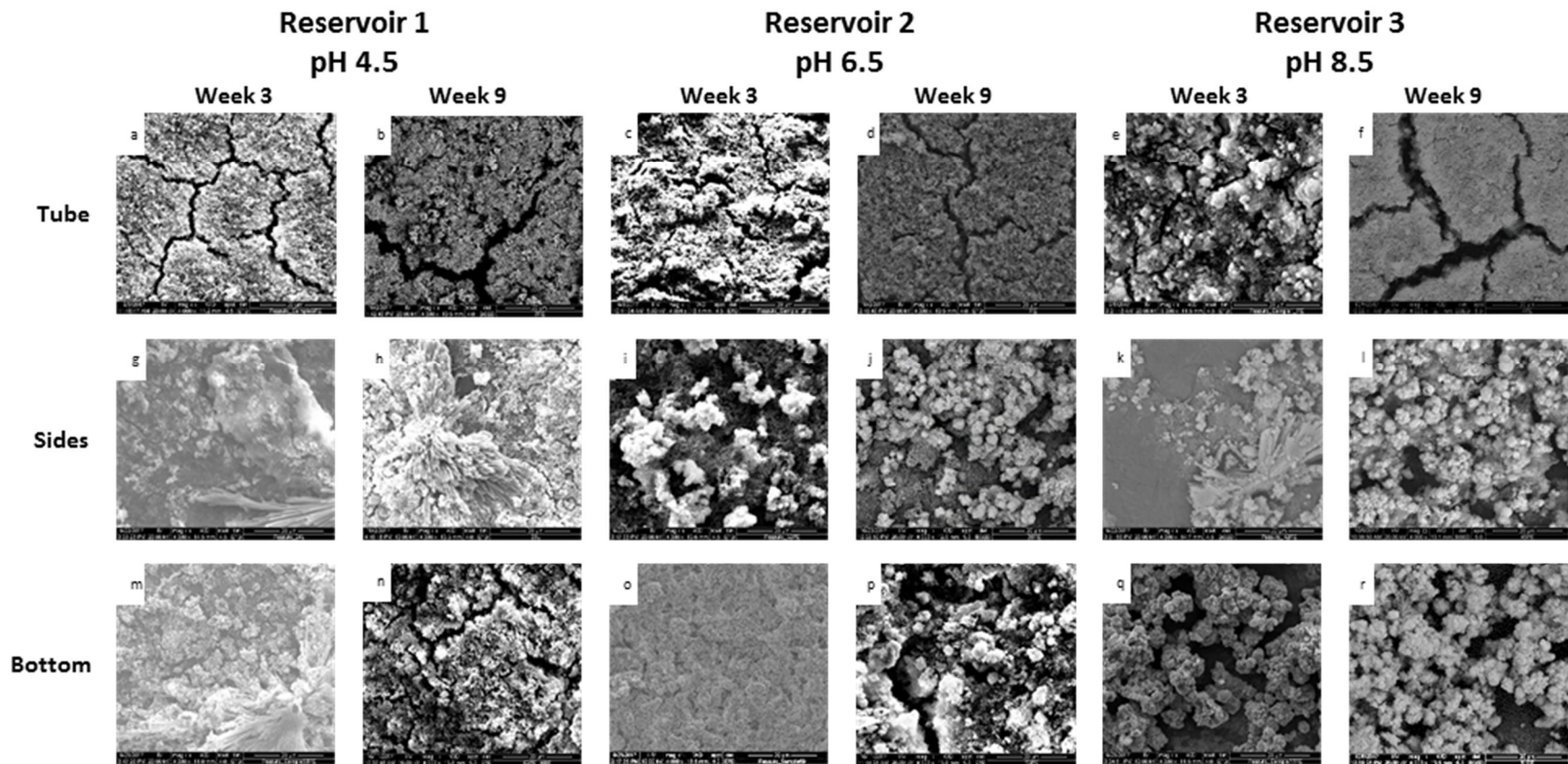
Figure 3.4: : SEM images for each reservoir, location, and week at 4000x magnification.

Table 3.2: Major SEM Observations (percentages given in atomic %).

|	Tube	Sides	Bottom
Reservoir 1 pH 4.5	~20% Fe 9-10% Al 4-5% Si 2-3% S Ca ~0.5%	calcium sulfate particles Mixed scale of: ~20% Fe 9-10% Al 5% Si 3-4% S Ca not detected	calcium sulfate particles Mixed scale of: ~20% Fe 9-10% Al 5% Si 3-4% S Ca not detected
Reservoir 2 pH 6.5	calcium oxide/hydroxide particles Mixed Scale: Si 9-11% Fe 8-10% Al 6-8% Ca 6-7% S not detected	calcium sulfate particles Mixed Scale: Ca 10-15% Fe 8-10% Al 2-4% S 1-4% Si 1-4%	Mixed Scale: Ca 20% Al 1-2% Fe 1-2% Si 1-2% S 0.5%
Reservoir 3 pH 8.5	mixed Scale: Ca 13-17% Fe 3-4% Si 2-4% Al 2-3% S <0.5%	calcium sulfate particles Mixed Scale: Ca 15-20% Al 0-2% Si 0-2% S 0-1% Fe 0-1%	calcium sulfate particles Mixed Scale: Ca 20-25% S 0-2% Si 0-1% Fe 0-1% Al 0.5%

As seen above, the scale in all three locations within each reservoir (i.e. tube, side, bottom) maintained similar atomic ratios. The scale within the lowest pH condition was dominated by iron. Interestingly, as seen in Table 3.1, the iron never appeared abundantly in the filtered samples. This indicates that iron sulfate never dissolved, or it was almost instantaneously converted to an insoluble form upon dissolution. Because iron sulfate is highly soluble in water, it is likely the latter; specifically, the iron likely formed ferric/ferrous hydroxides insoluble in water. The first reservoir also had the highest sulfur and aluminum by atomic percentage. This remained true by total mass for iron, and aluminum but the mass of sulfur was similar in all three reservoirs. This may be because (as demonstrated by the ICP data in Table 3.1) the majority of the added sulfur remained dissolved in the water in all three reservoirs, and was left on the pipe as residue after the water was dried out resulting in an equal amount on all samples. Calcium was added as calcium carbonate, which is highly soluble below a neutral pH, but less soluble moving toward more basic pH. In the pH 4.5 reservoir, calcium carbonate likely remained dissolved resulting in the undetectable levels seen in the SEM data. In contrast, in the higher pH locations, calcium carbonate may have only dissolved partially or may have contributed to precipitation of calcium

hydroxides; both forms are poorly soluble with the propensity to contribute to scale (Chilingar et al., 2008; Mackie & Walsh, 2012).

The sides of the reservoirs likely gained scale via diffusion and precipitation. All three reservoirs displayed thin and intermittent but widespread regions of scale with aluminum, sulfur, silicon, and iron on the sides, as seen in Figures 3.5-7. Aluminum, similar to iron, likely almost immediately formed hydroxides due to the high solubility of aluminum sulfate, but low dissolved aluminum as detected by ICP. In addition, silicate was added as sodium silicate. However, sodium was not consistently detected in the scale. This indicates that the silicate seen in the scale was not in its dosed form; rather, it dissolved and then combined with another element to precipitate (i.e. aluminum silicates). The mid and high pH also showed round to square particles of calcium hydroxide and/or calcium carbonates which was not as abundantly seen in the low pH condition, as seen in Figures 3.5-7. Calcium carbonates or hydroxides likely formed via precipitation. They would have remained dissolved until a pH of 6.3, explaining why they were not present in the lowest pH condition. This is further reinforced by the filtered versus unfiltered measurements of Ca in Table 3.1 which show equal values for Ca in reservoir 1, but notably less Ca in the filtered samples as compared to the unfiltered samples for reservoirs 2 and 3.

In the bottom samples, settling appears to be a major driver in addition to precipitation and diffusion. Samples in this location showed intermittent calcium sulfate crystals, as illustrated by Figures 3.8-10. These crystals may have settled before being dissolved. The scale on the bottom appeared as a more well-defined conglomerate than was seen on the side samples, though composition was similar. It had the highest atomic percentage of calcium, indicating that in addition to the precipitation as was seen on the sides, some calcium carbonate and hydroxides may have settled onto the samples.

In the tube samples, diffusion probably caused significant weight gain in addition to that caused by settling and precipitation. In all three reservoirs, aluminum hydroxides/silicates and iron hydroxides were more prominent in the tube scale than in any other location, as illustrated in Figures 3.5-13. This may be explained by the relatively large impact of diffusion in the tube samples as compared to the bottom and sides. Additionally, the tube samples also show the lowest levels of calcium. This can be explained due to the higher prominence of other elements. That is, because other elements were pushed to precipitate more due to diffusion, calcium was a smaller overall percentage.
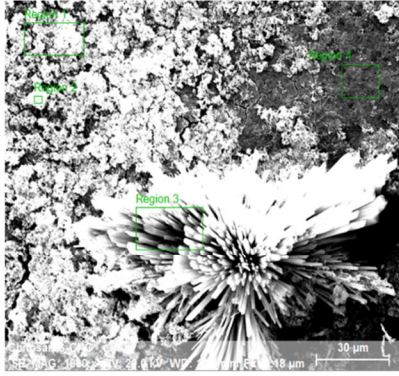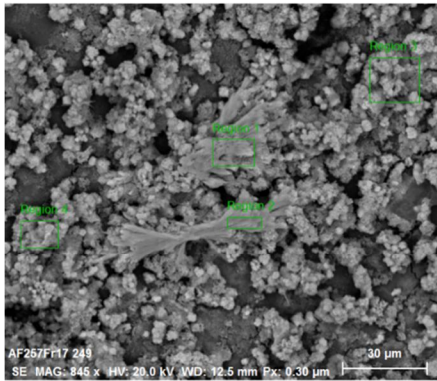
Atomic percent (%)

Spectrum	O	Al	Si	S	Ca	Fe	Zn
Region 1	58.83	9.46	5.01	3.85	0.31	19.34	3.19
Region 2	58.19	11.63	5.79	3.96	0.25	17.49	2.70
Region 3	60.98	0.09	0.09	14.46	23.92	0.40	0.05
Region 4	60.75	10.97	7.36	3.84	1.36	14.43	1.28
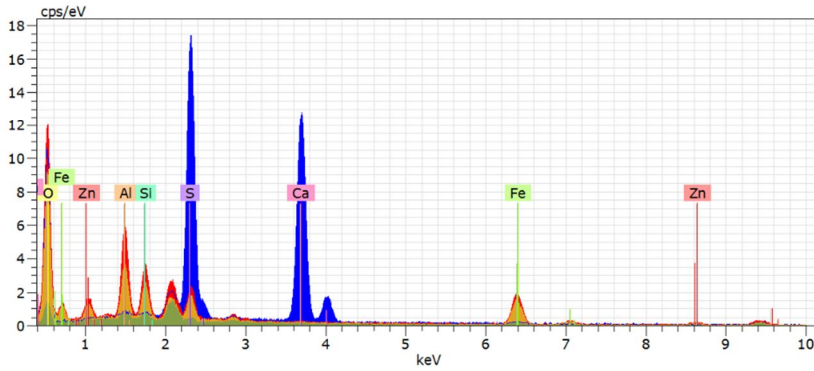
Figure 3.5: Reservoir 1 Side Sample Spectra.

Atomic percent (%)

Spectrum	O	Na	Al	Si	S	Ca	Fe
Region 1	74.37	0.53	0.73	0.60	10.09	13.25	0.44
Region 2	70.67	0.26	0.27	0.30	10.52	17.53	0.46
Region 3	75.79	2.45	3.31	3.06	0.57	11.98	2.84
Region 4	76.40	1.63	2.14	1.49	0.42	16.84	1.09
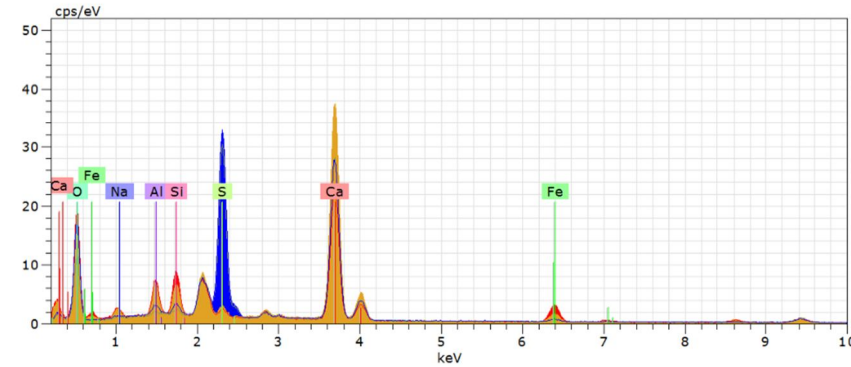
Figure 3.6: Reservoir 2 Side Sample Spectra.

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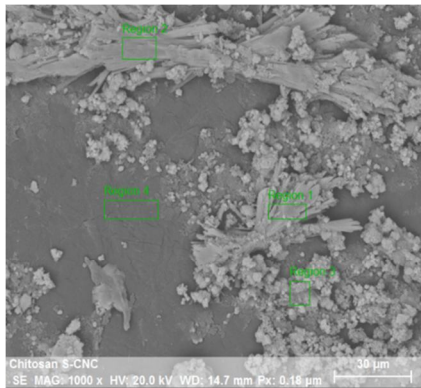
Atomic percent(%)

Spectrum	O	Al	Si	S	Ca	Fe
Region 1	56.09	0.37	0.26	13.22	29.44	0.62
Region 2	56.96	0.30	0.12	13.65	28.72	0.25
Region 3	55.85	2.13	3.07	0.96	26.51	11.48
Region 4	0.00	0.00	2.75	28.94	46.01	22.30
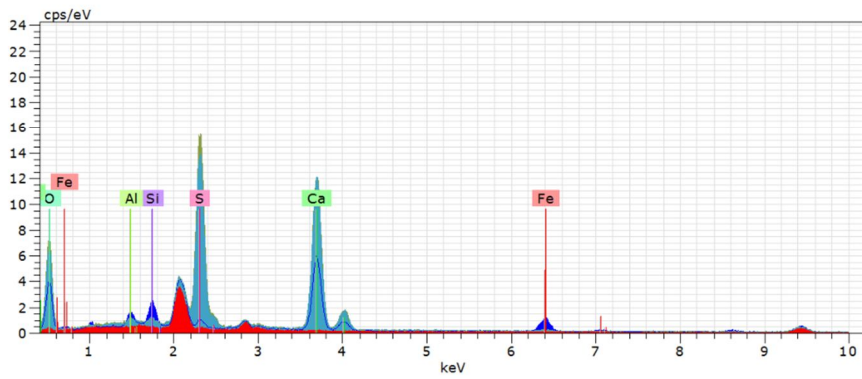
Figure 3.7: Reservoir 3 Side Sample Spectra.
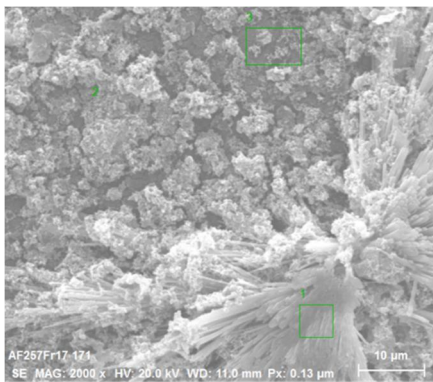
Atomic percent (%)

Spectrum	O	Al	Si	S	Ca	Fe
1	72.38	0.57	0.14	12.08	14.43	0.40
2	71.20	7.37	3.48	2.28	0.00	15.67
3	73.19	9.57	4.17	2.47	0.00	10.60
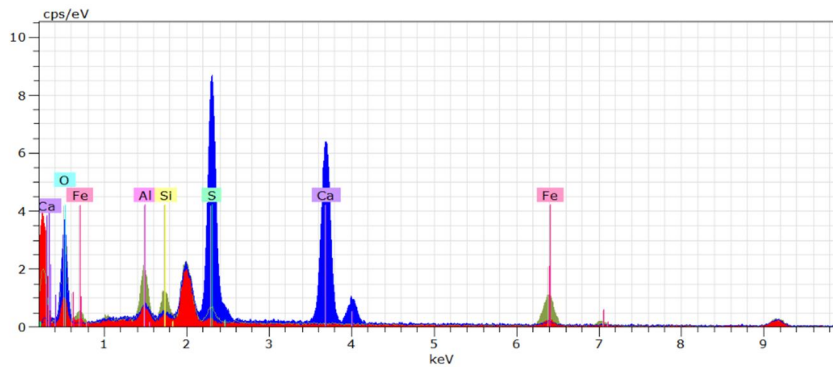
Figure 3.8: Reservoir 1 Bottom Sample Spectra.
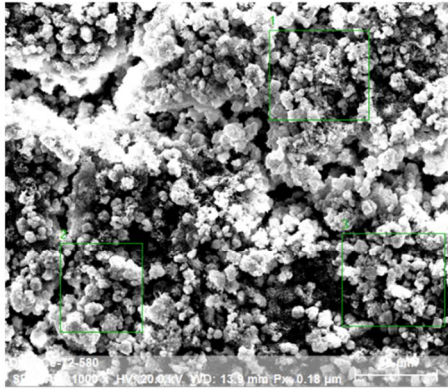
```
Atomic percent (%)
Spectrum      O    Al   Si    S    Ca   Fe   Zn
-------------------------------------------------
1          75.11 0.98 0.84 0.49 20.63 1.47 0.48
2          74.16 1.47 1.22 0.59 19.96 2.00 0.60
3          71.35 1.35 1.25 0.51 22.66 2.43 0.45
```

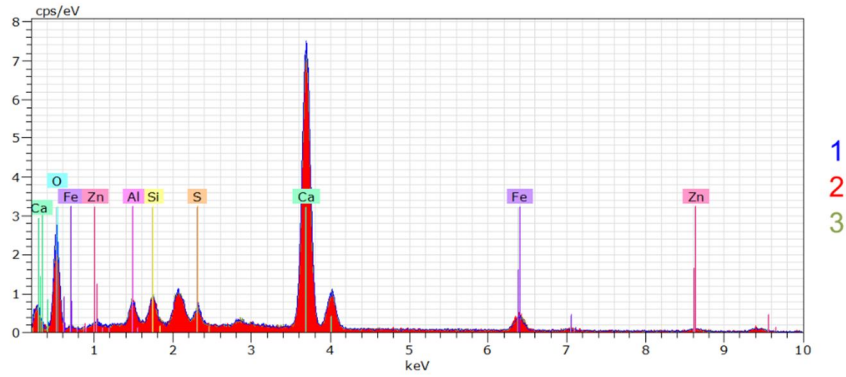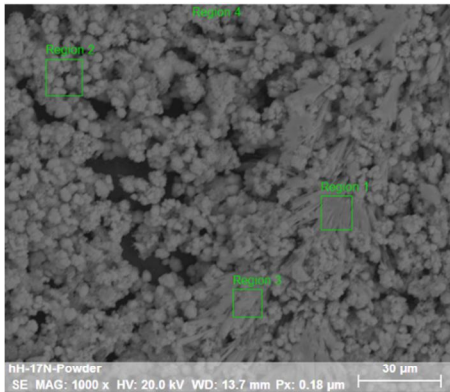*Figure 3.9: Reservoir 2 Bottom Sample Spectra.*


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Atomic percent (%)
Spectrum         O    Al   Si    S    Ca   Fe
-------------------------------------------------
Region 1      77.38 0.05 0.03 8.20 14.24 0.11
Region 2      76.28 0.40 0.43 0.55 21.82 0.53
Region 3      73.07 0.67 0.71 9.30 15.62 0.62
Region 4      73.08 0.29 0.37 1.54 24.23 0.49
```
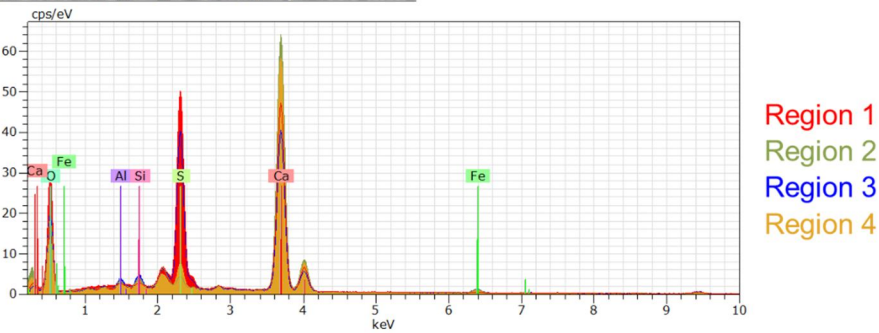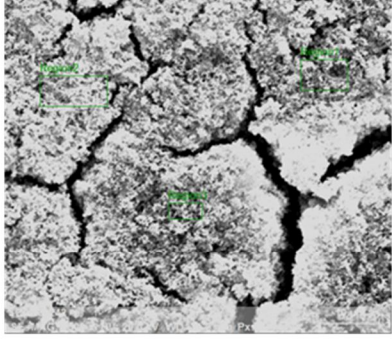
Figure 3.10: Reservoir 3 Bottom Sample Spectra.

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Atomic percent (%)

Spectrum          O     Al    Si    S     Ca    Fe
------------------------------------------------------
Region1        62.80  9.19  4.52  2.35  0.57  20.58
Region2        63.86  9.86  4.88  2.37  0.60  18.43
Region3        62.49  9.52  4.65  2.42  0.65  20.26
```
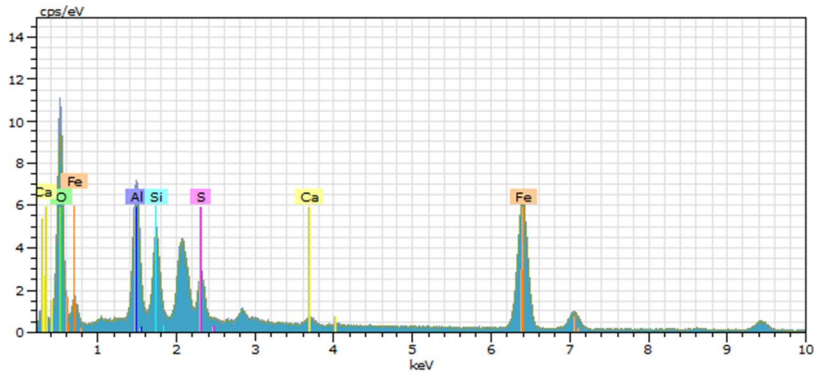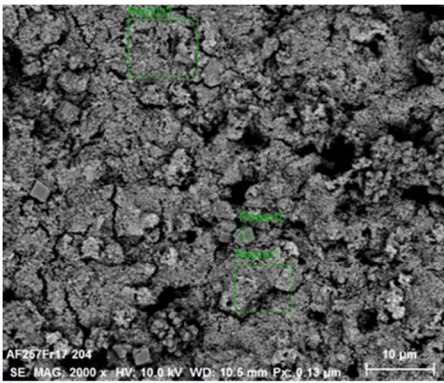
Figure 3.11: Reservoir 1 Tube Sample Spectra.


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Atomic percent (%)

Spectrum         O     Al    Si     S     Ca     Fe    Zn
------------------------------------------------------------
Region1       65.75  6.55   9.27  0.00   6.42  10.08  1.92
Region2       78.68  0.32   0.00  0.46  20.53   0.00  0.00
Region3       64.68  7.22  11.21  0.00   6.13   8.46  2.30
```
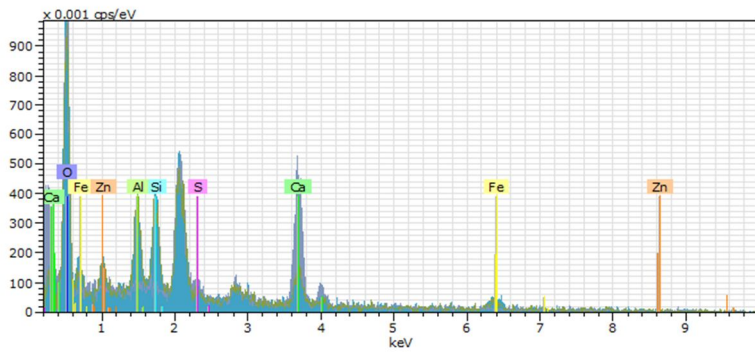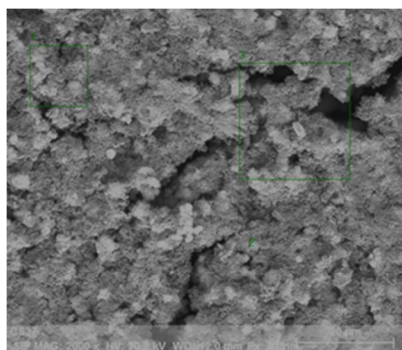
Figure 3.12: Reservoir 2 Tube Sample Spectra.

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Atomic percent (%)

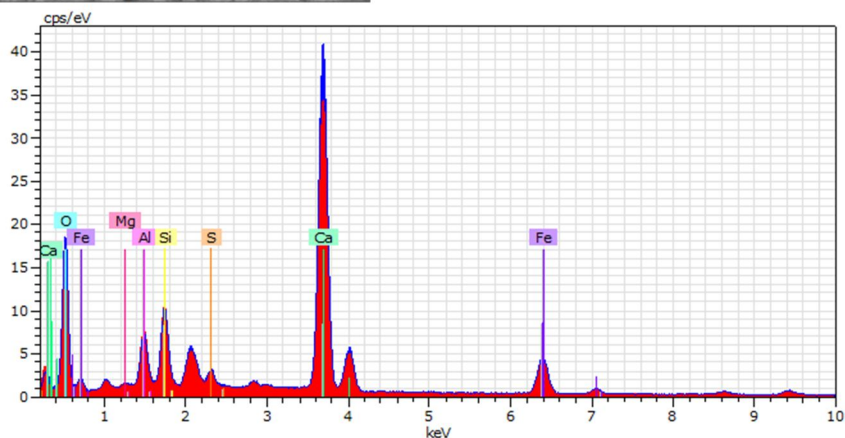| Spectrum	O	Mg	Al	Si	S	Ca	Fe
1	74.07	0.14	2.29	2.56	0.47	16.97	3.50
2	76.60	0.32	2.86	4.13	0.41	12.51	3.18
3	73.83	0.22	2.79	2.91	0.51	16.14	3.61

Figure 3.13: Reservoir 3 Tube Sample Spectra.

4. Conclusions

To enhance PE performance against abrasion, a novel liner has been developed by by Gerodur. However, to determine if the liner may be a candidate for widespread use in mining applications, the performance of the liner against other common problems that affect piping systems must also be evaluated. One such problem is the issue of scale buildup on pipe surfaces. In this laboratory study, the lined PE material was tested against traditional PE to determine the relative susceptibility to scale buildup under three idealized AMD and treated AMD conditions.

The mass and characteristics (i.e., morphology and chemical makeup) of scales varied greatly amongst the water quality conditions (i.e., pH 4.5, 6.3, and 8.5), and depending on the primary mechanisms of scale buildup. Specifically, the lowest pH condition had the least amount of scale, which was dominated by iron hydroxides. The mid and high pH conditions had more similar scales, which were dominated by calcium minerals. Samples exposed to relatively higher flow had the greatest weight gain, consistent with scale buildup due to settling, precipitation, and diffusion. In the water qualities and

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conditions tested, scale continued to buildup over the entire test period, but the growth rate appeared to slow and become limited over time; this may have been due to a weak scale structure which allowed material to detach. Most importantly, in all three water quality conditions, the novel PE liner performed similarly to the traditional PE with respect to scale buildup. Furthermore, SEM analysis showed very similar scale morphology between the two materials. As such, if the liner performs significantly better than the traditional PE with regards to abrasion, it might be a good candidate for MIWs.

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CHAPTER 4 : CONCLUSIONS AND RECOMMENDATIONS

The preceding chapters reported two studies aimed at determining the performance of a newly developed liner for polyethylene pipes. The liner was tested against traditional polyethylene in several mine water conditions to establish if the new material was more susceptible to scale build up. Synthesizing the lessons learned from those studies, some overarching conclusions and final recommendations are offered here.

In considering the field and lab samples together, several commonalities can be found. Figure 4.1 shows a compilation of the weight gain (in $\frac{mg}{week*mm^2}$) of field samples and the in-lab loop samples at week 3. In all cases, the lined (L) and polyethylene (PE) pipes gained similar amounts of weight in their respective location or loop; this is clearly seen by the closely stacked points at each aforementioned loop or location. In contrast, there is much more variation in weight moving horizontally across the graph from one loop or location to another. This indicates that the waters elemental compositions, pH, and velocity have a much greater effect on scale build up than the material utilized.

The loop samples most similarly resembled water qualities in the lab samples were most similar to the water qualities found in locations 1 and 3 in elemental composition (i.e. Al, Mg, Na, Fe content). Locations 1 and 3 had a pH of 3.3 and 3.2, respectively, while the loops Loops 1, 2 and 3 had pH values's of 4.5, 6.5, and 8.5, respectively. Interestingly, despite the similar composition, the lab samples had significantly less weight gain in week three than the field samples. This was surprising, as typically a higher pH is more conducive to scale buildup. This discrepancy may be because the velocity was significantly lower in the field samples than the lab samples (0.1 cm/s vs 0.25 cm/s, respectively). It may also be because while the field samples were kept in larger pieces retaining their curvature, the lab samples were cut in small squares resulting in them being effectively flat. This curvature may allow more settling via preventing particles from moving horizontally off of or away from the sample.
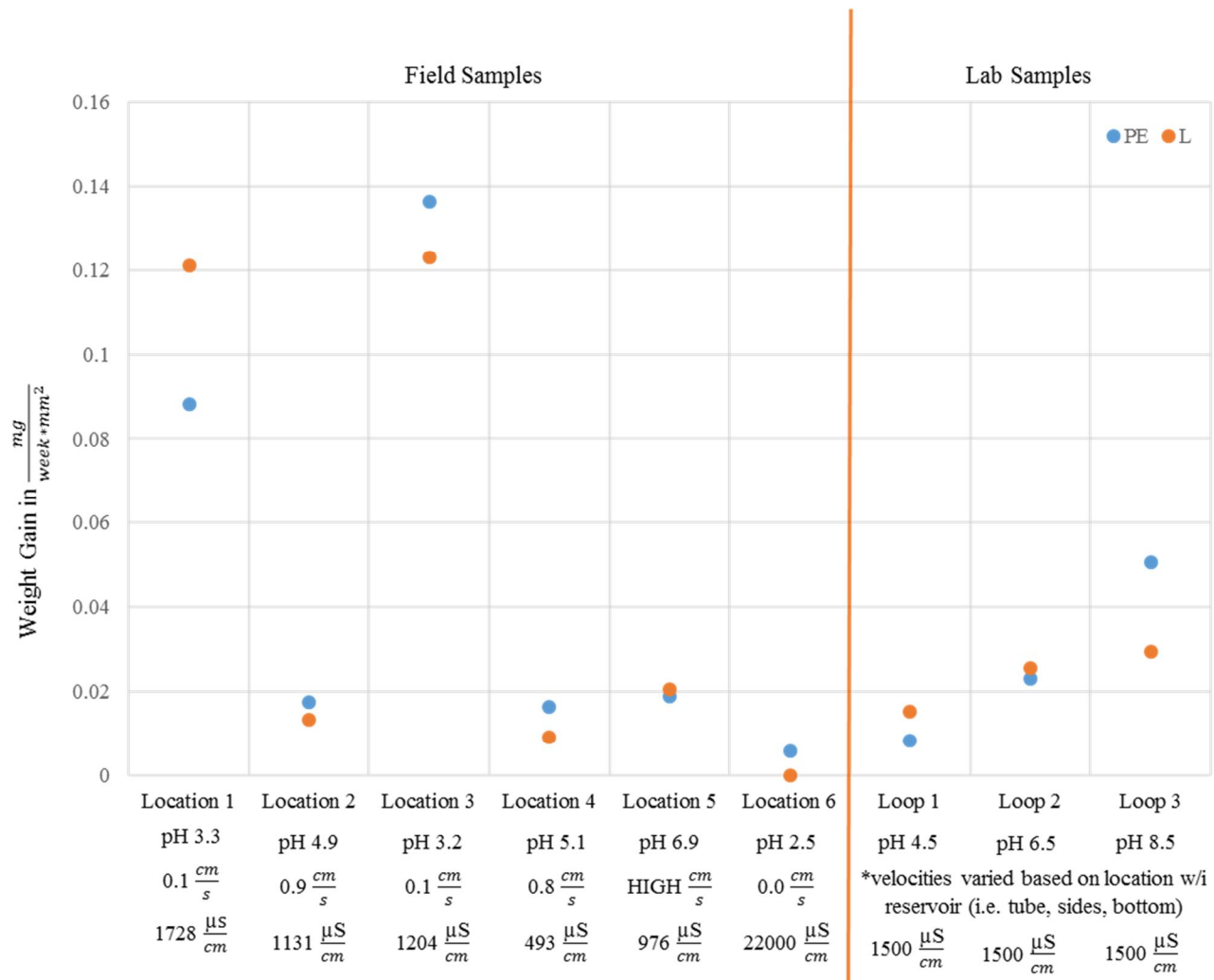
Figure 4.1: Weight gain on traditional (PE) and lined (L) polyethylene pipe material samples following three weeks of exposure in the field and laboratory studies.

Furthermore, some mineral constituents consistently appeared in both the lab loop and field location samples. Specifically, iron, silicon, and aluminum appeared in every one of the samples, proving them to be elements of great important in scale buildup. Calcium, though appearing in significant quantities in all of the water (as measured by ICP), was only a constituent of the pH 6.5 and 8.5 lab samples. This is likely because all of the field samples were below a neutral pH, and most calcium minerals (i.e. calcium carbonates or calcium hydroxides) require a pH of neutral or above to precipitate appreciably (Chilingar et al., 2008; Mackie and Walsh, 2012). This is also consistent with the ICP results for filtered and unfiltered water samples, which show that almost all of the calcium was dissolved in each of the field locations and in loop 1, while loops 2 and 3 had a significant amount of suspended calcium (Tables 2.1 and 3.1 respectively).

Despite these subtle differences in elemental composition, the field and lab studies were in agreement for the most important observation of this study. The novel liner developed by Gerodur MPM Kunststoffverarbeitung GmbH and Co. KG. preformed quite similarly to the traditional PE pipes with regards to propensity toward scale buildup. So from this particular perspective, the liner may represent an attractive piping option in situations where abrasion is a significant concern and scaling may also be problem.

In order to conclusively determine if this liner will be an improvement over traditional polyethylene in MIW applications, further testing is required. The scope of these preliminary test was quite limited. Specifically, these experiments were only a few weeks long while the mining industry typically works on the time scale of years to decades. Though the studies did indicate that scale buildup slows as time progresses, longer term testing could provide more concrete evidence. In addition, only limited water qualities were tested (i.e. only the waters found in one specific mine site, or in the three lab water qualities). A broader scope of testing in various mines, or with different target mineral compositions in the lab would give a better basis to deduce conclusions regarding the overall behavior of the material.

Pipes utilizing the new liner are currently more expensive to produce than traditional polyethylene (though a specific market price has not been established). Because the material seems to perform similarly with regards to scale build up, undisputable evidence proving its superiority with regards to another condition (i.e. abrasion) must be established to determine if this increase in price is a worthwhile investment. In the case that abrasion testing was promising, it is possible that this material could be implemented universally across mine sites with both abrasive and scale-prone waters.