Fate of Conductive Ink Pigments During Recycling and Landfill Deposition of Paper-Based Printed Electronics

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FATE OF CONDUCTIVE INK PIGMENTS DURING RECYCLING AND LANDFILL DEPOSITION OF PAPER-BASED PRINTED ELECTRONICS

by

James Edward Atkinson

A dissertation submitted to the Graduate College
in partial fulfillment of the requirements
for the degree of Doctor of Philosophy
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Printed electronics (PE) are being developed as an alternative to traditional electronics, due to the more efficient use of materials and lower cost of production. The overall goal of this study was to understand how metallic pigments in conductive inks in PE are partitioned during landfill disposal and paper recycling conditions. The purpose is to assess the potential environmental impacts of PE landfilling in terms of metal leaching and to help develop new strategies for sequestering metallic ink components while paper-based PE are subjected to conventional paper recycling methods. The objective of this research is to study the fate of PE metallic pigments by analyzing how metals partition across different streams in the recycled papermaking system, the potential leaching characteristics of the inks, and the ink film characteristics on paper that will help to show whether or not the metallic pigments can be removed from the paper fibers. Three studies were conducted to address each of these specific objectives. In the first study, three conductive inks used to create PE - nickel, silver flake, and nanoparticle inks were printed on label paper substrates simulating PE materials, which were then pulped and screened in bench-scale experiments. Accepts, rejects, and wastewater streams were collected and analyzed using Atomic Absorption Spectrometry (AAS) to measure the metal concentrations in each stream and create a material balance around the pulping and screening process. Results showed that for the nickel and silver flake inks the metallic pigments partitioned mostly into the “accepts” stream, while for silver nanoparticle inks, the metallic pigments were partitioned mostly to the
wastewater stream. The second study involved landfill simulation experiments to evaluate the potential leaching of metal pigments from polymer and paper based PE while subjected to landfilling conditions using EPA methods 1311 (Toxicology Characteristic Leaching Procedure) and Hazardous Waste Test Method - SW 846. Results show that the nickel ink used could potentially form hazardous leachate if landfilled, because it crossed 5 parts per million in the leachate. The silver inks did not cross 5 parts per million threshold named in the Toxicology Characteristic Leaching Procedure (TCLP) test and do not pose a leaching potential in a landfill at the weight fractions tested. The third study involved a qualitative assessment of nickel and silver conductive ink penetration and adsorption/absorption characteristics in paper substrates using scanning electron microscopy (SEM). From these microscopic observations, we can substantiate the findings from the re-pulping and screening test when talking about removing and recovering these pigments from the paper fibers during recycling. Results showed that nickel and silver flake inks do not penetrate the fiber pores and are mostly concentrated in the paper substrate surface, but appear to have become attached or bonded to the fiber surface in some regions. The silver nanoparticle pigments have migrated into the void structure of the sheet, but because they do not appear to become attached or bonded to the fiber surface, re-pulping and screening may readily remove the nanoparticles. Based on these observations, it is likely that nickel and silver flake inks can be removed and recovered more easily than the silver nanoparticle ink. This research shows PE could provide papermakers with an opportunity to innovate their process and potentially create a new revenue stream by recovering metallic pigments. Landfill operators should be aware that metallic pigments could show up at their facility in order to establish the necessary measures for sequestering potentially hazardous materials from leachate streams.
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I would start by thanking my mother and father. You both have been so supportive and encouraging to me over the course of my life and have taught me many lessons that I shall try my best to live up to. I would also like to thank my brother for believing in me and defending me, even when I wasn’t doing the same for him. I would like to thank and acknowledge my committee, both past and present, for all of the guidance, motivation and advice they have given to me over the years. I would thank Dr. Andro Mondala for helping me to organize both this dissertation and all of my publications; I would not be where I am today had it not been for your help and organization. I would thank Dr. Dan Fleming, for your expertise and advice throughout my years at WMU. I also want to thank the other members of my committee, Dr. Jan Pekarovic and Dr. Jorge Rodriguez for their reviews, comments, and advice throughout this process. I would also thank Dr. Thomas Joyce and Dr. Margaret Joyce for their help and encouragement as previous chairs and members of my committee for their reviews, funding, comments, advice, encouragement, and help with presentations both inside and outside the university. The Paper Technology Foundation deserves many thanks for funding and industry support of this work. There are many others to thank, but they shall remain anonymous, for guiding me to a faith in a God of my understanding. I would not have gotten this far in advancing toward and earning my Ph.D. if not for the help, advice, and time spent by many people whom I now have as good friends in fellowship and action.

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CHAPTER I
INTRODUCTION

This dissertation research was conducted to address the potential environmental issues that are expected to arise with increasing, production, use, and eventual disposal of paper-based printed electronics. Recycled papermakers rely on bacteria in the wastewater treatment aspect and the release of toxic metals originating from the printed electronics inks would be detrimental to that system. Landfills could generate leachate that contains these metals, and it is important to understand how these metals attach to the substrate to be able to develop strategies for removal and recovery for beneficial reuse. It is the goal of this research to eventually yield a standard test package for the PE industry to test their inks before release to market to ensure environmental compliance.

Printed electronics (PE) is an emerging technology that can be used to create an electrically functional device by printing with conductive ink, typically silver, copper, or nickel, on various substrates, including paper and film. Examples of this are RFID (radio-frequency ID tags), photovoltaic cells, sensors, displays, resistors, capacitors, paper batteries, and solid-state lighting [1][2][3][4]. Printed electronics are expected to be very useful in the near future for applications that require low-performance, low-cost electronics, such as smart packaging labels and RFID tags [5]. Current PE substrates include polymer films, glass, silicon, and ceramics. Paper is an attractive substrate due to its low cost, sustainability, recyclability, and renewability [6][7], but further research is needed to ensure the functionality of the electronic circuit when printed on paper in RFID tags, paper batteries, and low cost consumer electronics (e-book readers) [3][8][9]. One of the key issues limiting the widespread application of PE is that the
metals used in the inks are known to be toxic to the environment and would probably be scrutinized for regulation. Research suggests that nanoparticle silver can disrupt photosynthesis in in certain types of algae [10]. Even if the heavy metals did not reach the environment, a recycled paper mill processing recovered papers with PE components will still be faced with the task of disposing sludge containing these metals. Most of the current research on PE focus on developing production technologies [1][11][12][13][14]. The exact partitioning and disposal routes will strongly affect the amount of Ag nanoparticles that might be released into the environment [15]. There are some studies about the life cycle analysis of PE [16][17], but the studies on the metallic pigments in reference to recycling and disposal are limited. The above studies also suggest that there needs to be a plan for recovering these metals, due their high cost and also that it is a limited natural resource [18]. The U.S. EPA has identified major benefits of recovering and reusing valuable materials, such as reduced energy usage to manufacture the same product if recycled materials are used instead of virgin material [19]. Conductive inks used in PE should be considered valuable materials and should be treated as such in the context of recycling and reuse. PE inks are very similar to traditional inks, except that they use metallic “pigments” instead of color pigments. The way these inks are applied on the substrate depends on if the inks are solvent-based, water-based, or UV curable [6]. PE inks can be printed through screen-printing, flexography, and rotogravure dry by evaporation, penetration, oxidation, or cross-linking from a liquid to solid by exposure to UV light [20][21]. For PE, it is not desirable for the metallic ink pigments to penetrate the paper fiber pores. This would lead to less conductivity and also make the deinking process very difficult. Furthermore, conventional deinking relies on the ink being washed off the surface of the fiber [22].
According to the IDtechEx 2016-2026 forecast, the utilization of printed electronics for consumer and military uses is expected to expand rapidly in the next ten years [23]. Eventually, the fate of the potentially toxic metal-containing inks printed on paper versus film may become a major concern, as currently no measures are in place to sort these PE containing paper wastes from regular paper wastes. For PE containing paper wastes disposed in landfills, it is important to understand the potential of metal leaching under landfill conditions, which could pose serious environmental hazards. For recovery and reuse of metallic inks in PE inks, it is important to understand how these materials interact with paper substrates so that conventional paper recycling operations can recycle both fiber and metals with minimal process modifications.

Research is needed to understand the effects that disposal or recycling PE materials might have on the environment. Research has been done on the potential environmental problems that could be caused by recycling or landflling traditional electronic materials, and the environmentally toxic metal-containing inks, but the research for printed electronics themselves appears to be lacking. Separation of printed electronic items from the household good waste stream is difficult and therefore should a source of concern [24][25]. Research is being conducted on nanoparticles and there is significant concern about the harmful effects of silver nanoparticles. There is debate about the mechanism by which the silver nanoparticle creates toxicity, but in general it is agreed that releasing silver into the water or waste stream has a great potential for ecological damage [10][26][27][28]. In the printed circuit board industry, there are strict regulatory limits on how much silver and/or nickel can be present in the wastewater effluent from a manufacturing facility. The regulatory limit for silver is 0.43 mg/L silver concentration for any one day and no greater than 0.24 mg/L average for a one-month time
period [29]. Nickel has a limit of 3.98 mg/L nickel concentration on any one day, and an average of no more than 2.48 mg/L in one month [29]. These regulatory limits could be helpful in setting a standard for regulating the effluent from a recycled paper mill.

1.2 Research Goals and Objectives

The overall goal of this research was understand how the metallic pigments in PE inks can be recovered and reused in the recycled papermaking industry. It also proposes to investigate the potential for hazardous leaching if PE is deposited into a landfill.

The specific objectives were the following:

1. To assess the partitioning of the metals when subjected to conventional pulping and screening techniques.
2. To determine the potential of metal leaching if PE is placed into a landfill.
3. To assess the metallic ink pigment penetration and adsorption/absorption characteristics of PE inks.

Chapter III discusses the partitioning of the metal pigments during the paper recycling process in papermaking, specifically the pulping and screening process, which removes contaminants from the fiber stream before the sheet is formed. Chapter III also uses SEM to analyze the penetration and adsorption/absorption characteristics of PE inks. The SEM study helps to further understand the partitioning by visually analyzing the ink-film characteristics to speculate about the ease or difficulty of removal of the metal from the fiber surfaces. Chapter IV looks at the possibility of metal pigment leaching if PE containing wastes are disposed of in a landfill to know whether or not PE poses a risk to the biological system present in said landfills.
CHAPTER II

LITERATURE REVIEW

2.1 Printing Technology

Before talking about the production of PE, it is important understand how printing works and how some of the processes fare better in the manufacturing of PE than others. The five printing processes available to printers are: Lithography (offset), flexography, rotogravure, screen-printing, and digital (non-impact). First, we will discuss how these processes are different and in what ways they can be used to produce PE.

Lithography, or offset printing, involves the use of a planar surface, to print images onto a compressible blanket, and then onto a substrate. It should not be confused with photolithography, which is essentially the way electrical circuitry is traditionally formed [30]. Lithography relies on the concept of chemical separation between image and non-image areas. This usually involves a two phase process to accomplish printing [31]. There is waterless lithographic ink which uses special plates that only accept ink in the treated areas [32][33]. Offset printing is currently used to manufacture PE, but in modified forms that soften the impression pressure, as lithography relies on a higher impression pressure to create ink transfer, which can cause ink film issues and limits the types of substrates that can be used [34]. Another form of printing is flexography, and it uses a raised image area to transfer ink to the substrate [35]. This form of printing has made large strides for PE, particularly because of its ability to print on virtually any substrate, but it has the limitation that the electronic features must be very small to print PE and flexographic plates are limited in the ability to hold these very thin lines
Rotogravure is a type of printing that uses an engraved cylinder to print directly onto the substrate [4]. It is a very simple, but expensive way to put ink on a substrate, due to the cost on engraving and chrome coating the print cylinder. The use of rotogravure for PE is gaining popularity in use for items such as RFID and integrated circuits, but it cannot print extremely thin lines due to the fact that the image is engraved and is subject to the resolution of the equipment used to engrave the cylinder, and because it is engraved, rotogravure prints also produce a jagged edge, which affects conductivity [4][31]. Laser engraving can now produce cylinders at a resolution of 2,000 or more lines per inch [31]. This has allowed gravure to be used for some PE applications. Screen-printing, however, has made the longest strides in PE production [4]. Screen-printing is a printing process that physically forces ink through a stencil onto the substrate. This process can be done on flat surface, as well as in a rotary configuration to produce PE [20]. Screen printing has made it possible to produce flexible pressure sensors, organic light emitting diodes (OLED), and thin film transistors [4]. Digital printing is usually associated with inkjet printing in reference to PE. It uses very small nozzles configured in an array to form droplets that create the image areas on the substrate [20]. Inkjet is used in PE because of the precise control it provides in reference to drop shape size, drop rate and placement [20]. Inkjet does have the disadvantage of being a low throughput process, but it is being used to form devices such as the front electrode grid for a solar cells and RFID tags, as well as resistors, capacitors and transistors [4][36][37][38]. Research shows that most of the printing processes show some amount of viability for PE production, but this dissertation will focus on flexographic and screen printed PE printing and inks.
2.2 Printed Electronics Technology and Application

Printed electronics (PE) are functional devices that have been printed with an additive process using a printing process and conductive ink [20]. They show potential for use in many different devices such as Radio Frequency Identity tags (RFID), photovoltaic cells, sensors, solid state lighting (LED), paper batteries, transistors, textiles, and even audio amplifiers [3][6][20][25][39][40]. This is different and more efficient than traditional electronics, which utilize a subtractive scheme to produce circuits [20]. PE is being used to create smart packages with RFID that can be used to prevent counterfeiting and to be able to track and send large amounts of data on such packages [2][41]. PE will continue to be used in greater proportions because of their low cost [3]. The low cost of the technology makes it feasible to be used on a high volume scale, such as in packaging. Corrugated packaging is a great candidate for PE technology, and a large proportion is recycled [42]. Amazon began a partnership with Auburn University in 2015 to use RFID technology for supply chain management through order fulfillment [43]. Old corrugated container is a major source for recycled papermaking and therefore creates the possibility of conductive inks being brought to a recycled paper mill. The conductive ink composition is of major importance and will be discussed in the next section.

2.2 Conductive Ink Composition and Toxicity

The conductive inks are made from materials such as silver, nickel, copper, and others [20]. Silver and nickel are known to be toxic to the environment and are therefore highly regulated by the EPA and efforts should be made to prevent their release into the environment [44][45][46]. The use of PE is growing rapidly and within the next decade the market will be
inundated with products that contain PE [23]. There are also many concerns surrounding the use of silver nanoparticles to make the inks as they are difficult to collect and remove [47][48]. Silver nanoparticles have been proven to be toxic to certain algae and small organisms [10][49]. Nickel is also a highly regulated material when it comes to its environmental toxicity [46][50][51]. This makes it important and necessary to study and quantify the potential partitioning of the paper recycling process to assess the end fate of the metallic pigments. The end fate of conductive inks also makes the issue a reality when considering the leaching potential in landfills [52][53][54][55]. Most of the research found by previous research pertained to printed circuit boards (PCBs) [52][53][54][55]. Since PE are produced using similar conductive materials as PCBs, the issues are similar and should be considered. This constitutes a gap in knowledge based on the current research into PE in reference to end fate or potential environmental impact. It is also important to understand the recycled papermaking process so that the metallic pigments do not create issues in the paper mills themselves.

2.3 Recycled Paper Production

The recycled paper industry has become an important part of the paper industry overall because of the fact that it reuses fiber. This reduces landfill loading and lessens the dependency on trees through government legislation which mandated the use of some amount of secondary fiber in certain grades of paper [56]. Recycled fiber has to be pulped and cleaned and screened in order to remove contaminants that cannot be used in papermaking. Contaminant removal involves not only the rejection of things like dirt, rocks, staples, glue, and other non-fibrous material, but it also includes deinking of the fiber that has been printed on, in cases like old newspaper (ONP) or mixed office waste [56]. The deinking process at present involves the
flotation of ink particles with the use of heat, mechanical action, and surfactants to release the inks from the fiber surface and float them to surface for removal [56]. In the case of PE, the pigments used to manufacture the inks have a much higher density and more than likely cannot be removed by flotation. Therefore, the removal of the metallic ink pigments will be the primary responsibility of downstream cleaning actions, such as screening and reverse flow cleaners [56]. The presence of silver and nickel in recycled papermaking may also challenge the effluent treatment within the mill. The treatment process for the effluent water stream at a mill relies on two types of treatments. Primary treatment is a mechanical action, which seeks to remove suspended solids from mill water by screening and flotation [56]. Secondary treatment relies on microorganisms (mostly bacteria and fungi) to consume oxygen to convert organic waste into carbon dioxide and water [56]. Silver and nickel are known to be toxic to many bacteria and microorganisms that are used to treat wastewater [57][58]. As the use of PE in packaging increases, the chances of conductive metallic pigments being present in the recycle stream becomes more and more likely [9][41]. The solid waste stream from recycled paper mills is landfill bound and if the metals are removed to this stream then the metallic pigments through screening and cleaning, the landfill now has to deal with the toxic metals in their system.

2.4 Landfill Deposition of PE Ink Pigment Leaching

Landfills are essentially anaerobic digesters that rely on certain bacteria to create decomposition [59]. New landfill designs are being designed that allow the leachate to be recycled in order to maximize the decomposition rate without affecting the leachate properties in a negative way [60]. The increased use of PE in consumer products could potentially increase the potential for toxic leaching of silver and nickel into the leachate stream at these landfills [61].
Silver is known to be antibacterial, and while the hope is that the metals can be recovered and reused, landfill deposition could be a reality and the leachate from PE might cause issues [62]. Nickel also appears to have antimicrobial effects that could be detrimental to landfill bacteria, as its presence prevents microbial respiration in regular soil [63]. This could potentially create an entirely new set of issues that landfills need to be made aware of if the possibility of toxic leaching exists.

2.5 PE End Fate Research

There is some research about the end fate of PE. Kunnari et al. did a study in which PE are studied in regards to the environmental friendliness compared to traditional electronics [16]. However, the end fate of the inks is discussed only to indicate that more research is necessary [16]. Another study assessed the recyclability of paper containing PE, but only in reference to fiber recovery and not to assess the partitioning of the metals used to manufacture the PE [64]. There are researchers calling for investigations into the possibility of environmental issues arising from the increased use of PE [41][61][65]. It will be important to understand how the conductive metal pigments could affect a recycled paper mill and/or landfills.
CHAPTER III

PARTITIONING OF METAL PIGMENTS IN PULPING AND SCREENING PROCESS STREAMS DURING PAPER RECYCLING

3.1 Introduction

The goal of this study was to assess the pulp screening process through material balancing to determine the partitioning characteristics of conductive metal pigments into the pulping and screening streams. Figure 1 shows the flow diagram of the material balance.

![Flow chart diagram for pulping and screening material balance](image)

During paper recycling, the waste product must be re-pulped and then screened to separate foreign materials (staples, wire, glue, metals, etc.) from the fiber before being fed into the paper machine. The typical screen is a cylinder with a sleeve machined with slots of varying sizes and shapes to remove the objects not desirable for papermaking [66]. As the water and fiber slurry is screened, the individual fibers that have been separated pass through the screen into the “accepts” flow. The fibers that have foreign materials attached to them do not pass into
the accepts, and are therefore rejected (thus called “rejects”) and may end up in the landfill or the incinerator to generate supplemental energy for the mill [67]. The water that goes through with the pulp slurry is then recycled or sent through the approach system to the paper machine. Eventually, the water used in the papermaking process is sent to clarification ponds and is then released back into the environment after treatment. It is important to ensure that environmental contaminants such as metal PE pigments are not released into the environment or landfilled with the paper mill waste stream. At this time, there does not appear to be technology in place that can be 100% effective in removing these contaminants. This could provide the industry with an opportunity to innovate and create profit out of the rejects of the re-pulping and screening process. It is also important to understand the adhesion characteristics of the ink and paper interface.

The second part of this chapter qualitatively analyzed the ink-paper interactions using SEM to help understand and support the findings of the pulping and screening based on how the pigments attached or penetrated the surface of the paper during printing. IDTechEx, a market research group in the PE industry, predicts that the market for conductive inks will grow substantially in the next decade to a $1.7 billion level, which is 15-20% higher than what the forecast was just two years ago [23]. Therefore, it is extremely important to ensure sustainable supplies of nonrenewable metallic elements for conductive inks and conserve these resources due to their high costs. In order for these materials to be recovered and re-used it is necessary to understand how metallic conductive inks materials bind to paper substrates. SEM can be used to visualize and make qualitative assessments regarding the extent of ink penetration and the nature of ink attachment into the substrate surface. Previous research has been done to visualize only
the surface characteristics of conductive ink films for quantification of electrical properties based on print quality of said ink films [68][69]. These studies used nonporous substrates and SEM to analyze particle size and top-down surface profiles of the conductive ink films for electrical property measurement, but not the adhesion characteristics of the metallic pigments themselves. Research on ink adhesion characteristics for the purpose of recycling and recovery is still lacking.

Paper-based PE will most likely be subject to recycling, especially if utilized as Radio Frequency Identification (RFID) tags in paper packaging materials and thus the metallic conductive inks need to be separated from the paper fibers. A significant portion of packaging used in industry is recycled, and more than 65% of consumer waste is recycled through community recycling programs [70]. Currently, recycled paper is mostly de-inked by flotation. This process is based on density differences between the ink particles, which are floated out of the flotation cell, and the paper fibers which settle out of the flotation cell [71]. There are other emerging methods, such as enzymatic deinking and ultrasonic treatments, but usually those treatments eventually end with flotation de-inking in order to separate the detached inks from the paper fibers [22][72][73][74]. The flotation method is most effective if the density of the ink particles is approximately 1.0-1.5 g/cm³ [71]. If the ink particles have a higher density, these will settle out with the fiber. Nickel and silver-based ink particles have densities ranging from 7.8-8.9 g/cm³, and 9.3-10.5 g/cm³, respectively depending on environmental conditions. Thus, traditional flotation methods are not expected to be effective at separating nickel and silver ink particles from paper fibers. If the conductive ink materials are actually separated from the usable fiber using flotation deinking, it has the potential to be disposed along with paper mill sludge, which is
currently mostly disposed of in landfills. Furthermore, releasing silver or nickel as effluent in the deinking/recycling process is not desirable. For instance, silver is known to possess antibacterial properties and would be detrimental to the bacteria needed in an effluent pond to perform Biological Oxygen Demand (BOD) removal [15][57]. Therefore, silver should not be released into the environment as solid waste into landfills or in paper mill effluents where the process relies on certain bacteria to complete the water cleaning process [15][57][75].

Despite this, there is little research on the topic of potentially being able to remove the metallic conductive inks based on the amount of adsorption or absorption into the substrate. Mechanisms of ink attachment to substrates include solvent evaporation, oxidation, penetration, or cross-linking in the case of UV inks [21]. The possibility of metallic ink removal and recovery depends on which drying method is utilized and to what extent the ink dries and adheres to the substrate. This study sought to determine the extent of this penetration on paper substrates to determine if mechanical or existing chemical removal is possible without negatively impacting the physical properties fiber to be used for papermaking. Paper substrates rely on some amount of penetration for ink adhesion. It is anticipated that the metallic pigment particles will stay on the paper substrate surface while the binder penetrates the pores of the sheet to adhere the ink film to the substrate [21]. In this study, scanning electron microscopy (SEM) was used to visualize and qualitatively analyze the adsorption/absorption characteristics and the extent of penetration of PE metallic ink pigments on the paper substrates. This was done in order to assess the potential for recovering and recycling not only the paper substrate fibers but also the costly, nonrenewable, and potentially environmentally harmful metallic ink pigments used to create printed electronics. Knowledge of the metallic ink adhesion characteristics on a printed
electronics paper substrate will enable the development of recycling, deinking, and repulping strategies for sustanably recovering metallic ink pigments for beneficial reuse to supplement conventional paper recycling processes.

3.2 Materials and Methods

3.2.1 Sample Preparation

Paper-based PE samples were prepared by printing conductive inks on paper substrates using laboratory scale proofing techniques. The paper used was a 50# EDP 92 brightness label face stock for printing PE. Domtar, Inc. (Benton Harbor, MI) donated the paper used in these experiments. The paper substrate has an average surface roughness of 3.02 ± 0.12 microns at a clamping pressure of 1000 kPa. The porosity of the paper is has an average value of 83.85 ± 6.45 ml/min at a clamping pressure of 1000 kPa. The surface energy of the paper as measured by contact angle using water and methylene iodide as polar and dispersive components was approximately 73 dynes/cm². The dispersive component was approximately 31 dynes/cm², and the polar component contributed around 42 dynes/cm². The 8.5 x 11-inch paper sheets were cut in half lengthwise to form a 4.25 x 22-inch sheet to fit the flexographic proofing equipment. The screen-printed samples were printed on the full 8.5 x 11-inch sheets. The nickel ink was purchased from NovaCentrix (Austin, TX). The nickel ink is a water based developmental product. It has a solids content of 62% as measured. It has a Brookfield viscosity of 8,200 centipoise at 60 rpm with a #4 spindle. The silver flake ink used is manufactured by Sun Chemical (Parsippany, NJ). It is a water-based PE ink with a particle size of 1-3 microns. This silver flake ink has a solids content of 62.2% according to the MSDS, which was confirmed by
measurement. It has a low viscosity as required by flexographic printing. The silver nanoparticle ink used was manufactured by InkTec (NEUNGAN-RO, Korea). It is waster based functional ink with a particle size of 10-100 microns. According to the MSDS, and the ink has a viscosity of 10-300 centipoise. This silver nanoparticle ink has a measured solids content of 34% The nickel inks were screen-printed while the silver flake and silver nanoparticle inks were printed using the flexographic process. The printed patterns for the nickel and silver inks are shown in Figure 2.

![Printed patterns for PE samples: A - nickel ink, B - silver inks (right)](image)

The printed samples were cured using the NovaCentrix (Austin, TX) PulseForge 1200 photonic sintering unit. The silver and nickel inks have different atomic properties and therefore need to be cured using different voltages to be sure not to over-energize the ink film and burn up the binder, therefore preventing ink adhesion. The nickel ink was treated with 300 volts at 20 feet per minute with a 1.0 overlap. This sheet was treated with this condition 3 times to effectively cure the ink in order to achieve a measured (on scale for the meter) amount of electrical resistance on the sheet, somewhere in the range of 10-100 ohms. The silver inks were treated
with 400 volts at 20 feet per minute with 1.0 overlap. These sheets were also treated three times to achieve electrical resistance. The next step was to re-pulp and screen the samples.

### 3.2.2 Re-pulping and Screening

The printed samples were weighed before and after printing to determine the ink weights. Table 1 shows the weights deposited for each re-pulping and screening test. It is important to note the solids contents of the inks. The nickel ink contains 62% metal pigment. The silver flake ink has 62% metal loading. The silver nanoparticle is loaded with 34% metal pigment. Table 1 also shows the calculation of the actual weight of pigment in the inks as printed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total weight (g)</th>
<th>Ink weight (g)</th>
<th>Metal content of inks (%)</th>
<th>Pigment weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>63.8</td>
<td>5.11</td>
<td>62</td>
<td>3.17</td>
</tr>
<tr>
<td>Silver flake</td>
<td>64.0</td>
<td>0.77</td>
<td>62</td>
<td>0.48</td>
</tr>
<tr>
<td>Silver nanoparticle</td>
<td>63.4</td>
<td>0.30</td>
<td>34</td>
<td>0.10</td>
</tr>
</tbody>
</table>

The samples were then pulped in the FORMAX MicroMaelstrom Laboratory pulper (Adirondack Machinery Corporation Queensbury, NY) at 6% consistency according to TAPPI T-240 [76]. Approximately one liter was added based on the printed sample weight to pulp at 6% solids in the pulper.
Table 2 Ink/fiber and water weights added to pulper

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ink fiber weight to pulper (g)</th>
<th>Water to pulper (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>63.8</td>
<td>998.9</td>
</tr>
<tr>
<td>Silver Flake</td>
<td>63.9</td>
<td>1001.8</td>
</tr>
<tr>
<td>Silver nanoparticle</td>
<td>63.4</td>
<td>993.5</td>
</tr>
</tbody>
</table>

The samples were re-pulped at room temperature (no heating) with water only (neutral pH) for 20 minutes. Figure 3 shows a picture of this equipment.
The samples were then collected and prepared for screening. The screening step was conducted according to TAPPI T-275, with the use of a 0.15 mm slotted screen by Allis Chalmers Manufacturing Company (Appleton, WI), shown in Figure 4.

![Figure 4 Allis Chalmers MFG. Co. slotted screen used in screening step with modification for water collection](image)

The method was slightly modified to collect the water from the accepts stream to be used as the wastewater water stream for material balance, but it could also be called process water as it would be in the system and recycled over and over through the approach system [76]. The accepts stream was collected using a no. 200 (75 micron) sieve placed over a bucket as shown in
Figure 4. The fiber and ink slurry from the re-pulped PE samples were then fed into the screening process until approximately 38 liters (10 gallons) of process, or wastewater was collected. The accepts, rejects, and water samples were collected and the streams were then weighed and tested for solids to attain fiber/ink weights in the accept and reject streams.

Only one experimental replicate was run for each ink/paper combination. Three sample replicates were taken from each stream. These sample replicates were digested and tested by atomic absorption spectrometry. Each sample replicate was read five times by the spectrometer and those values were then used to calculate the average of the ppm concentration in the sample (see Appendix 4). The average ppm concentrations were then used to calculate the weight fraction of metal recovered for each sample replicate. The average and standard deviation of the weight fraction of metal recovered in the material balance was calculated. The weight fraction averages and standard deviations were then multiplied by the weight of ink/fiber in each stream to calculate the total weight of metal recovered in each stream (see Appendix 1).

The silver nanoparticle rejects stream only had two sample replicates, and the nickel rejects only had one sample replicate because the weight of the rejected material was low and a mistake was made in the digestion of the nickel rejects, so only one sample was correctly digested.

3.2.3 Analysis of Metal Pigment Levels in PE Pulping and Screening Streams

Samples of the accepts and rejects stream were dried, weighed and digested with nitric acid until all solids were dissolved using heat and curved watch glasses as lids to retain the acid in the beaker. This procedure was done according to EPA method 7760A [77]. The samples were then diluted to 100 mL with reagent water for Atomic Absorption Spectrometry (AAS) testing.
The ppm concentrations that were interpolated by the AAS software based on a calibration curve of known standards were used to calculate the weight fraction of metal in the digested sample, and then the total weight is back calculated based on solids in the accepts and rejects stream. Wastewater, or process water, samples (100 mL) were digested with nitric acid according to EPA method 7760A [77]. When the solids in the wastewater/process water samples were dissolved, it was the diluted back to 100 mL with reagent water and tested by AAS. This concentration was calculated into weight fraction of metal in the measured sample and then multiplied by the weight of the process water collected, in this case 37.85 L (37,850 grams).

### 3.2.4 Atomic Absorption Spectrometry (AAS)

The Varian AA240FS Flame Atomic Absorption spectrometer (Mulgrave, Victoria Australia) was used to analyze the acidified fiber and water samples for part per million concentration readings for the respective streams in order to calculate the material balances. The Varian AA240FS uses acetylene and nitrous oxide as the flame agents to vaporize the atoms for analysis. Flame AAS can be used to determine the concentration of the metals in each stream by plotting the atomic absorption values against a calibration curve and interpolating the values. AAS is a spectroanalytical procedure for the quantitative determination of chemical elements using the absorption of optical radiation (light) given off by free atoms in the gaseous state [78]. It uses a spectral filter to measure the radiation levels given off by the vaporized sample in order to measure the spectral absorbance. AAS has become a well established method for trace metal analysis [79][80]. The standard samples of known concentration were made from a 1000-ppm solution purchased from Fisher Scientific (Waltham, MA). The standard solutions were made at 1, 5, 10, 20, 50, 100, and 500 ppm concentrations, respectively. Figures 5, 6, and 7 show
calibration curves for nickel, silver flake, and silver nanoparticle created with Agilent Technologies Inc. (Santa Clara, CA) SpectrAA software for the AA240FS software. The silver flake calibration curve included the 1,000 ppm standard in the calibration curve. The ionization and absorption ratios differ based on the concentration of the analyte to be tested. This creates a calibration curve instead of linear representation. There are optimum working conditions indicated by the analytical methods for each element. However, the software can still interpolate analyte concentrations even if the absorption value is above the linear region of the calibration. The red lines on the graphs indicate the end of the linear region of absorption.

Figure 5 Calibration curve for nickel ink AAS sample concentration calculation

Figure 6 Calibration curve for silver flake ink AAS sample concentration calculation
3.3 Results and Discussion

3.3.1 Nickel Ink Results

Table 3 shows the calculation of the material balance at the screen. Figure 8 shows a diagram of the material balance.

<table>
<thead>
<tr>
<th></th>
<th>Fiber/ink weight in stream (g)</th>
<th>Weight fraction</th>
<th>Standard deviation of weight fraction</th>
<th>Total weight recovered in stream (g)</th>
<th>Percent recovery of stream (%)</th>
<th>Standard deviation of total weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input - Screen</td>
<td>63.8</td>
<td>0.0497</td>
<td>-</td>
<td>3.17</td>
<td>-</td>
<td>n/a</td>
</tr>
<tr>
<td>Accepts</td>
<td>42.0</td>
<td>0.017</td>
<td>0.014</td>
<td>1.14</td>
<td>35.9</td>
<td>0.22</td>
</tr>
<tr>
<td>Rejects</td>
<td>4.10</td>
<td>0.005</td>
<td>n/a</td>
<td>0.21</td>
<td>6.6</td>
<td>n/a</td>
</tr>
<tr>
<td>Wastewater</td>
<td>minimal</td>
<td>3.0x10^{-6}</td>
<td>1.5x10^{-7}</td>
<td>0.13</td>
<td>4.1</td>
<td>0.01</td>
</tr>
</tbody>
</table>
In the case of the nickel ink re-pulping and screening, the material balance ended up with a 46.6% recovery rate for the screening process. The system recovered 1.48 g of nickel back from the operation out of 3.17 g. The accepts recovered 35.9% of the total, the rejects held 6.6% of the recovered metal, and the wastewater contained 4.1% of the total input. This can be somewhat explained by the inherent variation in ink film thickness and the fact that even though the ink weight deposited was measured by analytical balance, the amount of pigment can vary depending on printing conditions and ink film thickness variation. It is believed that the rest of the nickel was lost within the screening equipment or when the equipment was turned off and drained. These data indicate that most of the metal travels with the fiber in the papermaking stream. The material balance diagram show a fiber recovery for the system of 81.7%. The wastewater is likely to have lots of fines and small fibers due the 150 micron sieve used to collect the accepts and could account for a portion of the lost fiber. The rest of fiber was likely
lost when the screen was turned off and drained. Figure 9 shows an SEM electrograph of the ink/paper interface. Figure 9 shows the nickel particles appearing to embed themselves into the fiber surface. It is believed that this action is what keeps the nickel with the fiber through the screening step. This implies that some amount of metal will probably be formed into the sheet with the fibers themselves. If a large enough amount is carried through, it may cause rejects in folding carton inspections due to metal content. It may also cause premature failure of the paper machine clothing due to abrasion and contamination of these materials as they come into contact with it during the papermaking process.

Figure 9 SEM electrograph of nickel ink/paper interface at 8,000x magnification – the lighter regions indicate nickel and the darker regions indicate paper fiber.
3.3.2 Silver Flake Results

Table 4 shows the material balance calculation around the screen. Figure 10 shows the material balance in a diagram.

<table>
<thead>
<tr>
<th></th>
<th>Fiber/ink weight in stream (g)</th>
<th>Weight fraction</th>
<th>Standard deviation of weight fraction</th>
<th>Total weight recovered in stream (g)</th>
<th>Percent recovery of stream (%)</th>
<th>Standard deviation of total weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Input - Screen</strong></td>
<td>64.0</td>
<td>0.0075</td>
<td>-</td>
<td>0.48</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><strong>Accepts</strong></td>
<td>42.0</td>
<td>0.0034</td>
<td>0.002</td>
<td>0.14</td>
<td>29.2</td>
<td>0.01</td>
</tr>
<tr>
<td><strong>Rejects</strong></td>
<td>3.32</td>
<td>0.0088</td>
<td>0.006</td>
<td>0.03</td>
<td>6.3</td>
<td>0.001</td>
</tr>
<tr>
<td><strong>Wastewater</strong></td>
<td>minimal</td>
<td>1.3x10^6</td>
<td>8.9x10^-7</td>
<td>0.05</td>
<td>10.4</td>
<td>0.03</td>
</tr>
</tbody>
</table>

This system shows a silver weight recovery of 0.22 g. This is only about 46% of the total metal put into pulping and screening. The accepts accounts for 29.2% of the total, the rejects recovered 6.3% of the total, and the wastewater held 10.4% of the total that was recovered from
the input. It is believed that the remainder is attached to the machine parts and piping of the screening equipment, or lost when after the screen was stopped and emptied to collect the rejects. Some of the loss can also be attributed to the variation in ink film thickness and the inherent variation in solids content within the ink film itself. It cannot be assumed that the pigment is 100% evenly distributed within the printed film on the sheet. This can cause variation in pigment solids within the ink film. The fiber recovery rate is 74.4%. There was some loss when the screen was turned off and drained. Much of the finer loss is due to creation of fines during re-pulping that then drained through the sieve into the wastewater. Downstream stock preparation equipment would be responsible for removal of silver contaminants, assuming they have been detached from the fiber surface. The wastewater partition would also need to be further treated in order to prevent the silver from getting into the effluent stream of the paper mill to prevent the biocide effect from destroying the system. Scanning electron microscope micrographs were taken and Figure 11 shows the ink/paper interface.
As can be seen in the SEM electrograph in Figure 11, the flakes appear to embed themselves into the fiber surface. This most likely leads to the metal particles being retained during the screening step. This implies that some amount of metal will probably be formed into the sheet with the fibers themselves. If a large enough amount is carried through, it may cause rejects in folding carton inspections due to metal content. It may also cause premature failure of the paper machine clothing due to abrasion and contamination of these materials as they come into contact with it during the papermaking process.

3.3.3 Silver Nanoparticle Results

Table 5 shows the material balance calculation around the screen. Figure 12 shows the material balance in a diagram.
Table 5 Silver nanoparticle material balance for screening step

<table>
<thead>
<tr>
<th></th>
<th>Fiber/ink weight in stream (g)</th>
<th>Weight fraction</th>
<th>Standard deviation of weight fraction</th>
<th>Total weight recovered in stream (g)</th>
<th>Percent recovery of stream (%)</th>
<th>Standard deviation of total weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input- screen</td>
<td>63.4</td>
<td>0.0016</td>
<td>n/a</td>
<td>0.10</td>
<td>-</td>
<td>n/a</td>
</tr>
<tr>
<td>Accepts</td>
<td>53.1</td>
<td>0.00048</td>
<td>0.00038</td>
<td>0.026</td>
<td>26</td>
<td>0.018</td>
</tr>
<tr>
<td>Rejects</td>
<td>3.19</td>
<td>0.0011</td>
<td>0.0014</td>
<td>0.004</td>
<td>4</td>
<td>0.003</td>
</tr>
<tr>
<td>Wastewater</td>
<td>minimal</td>
<td>1.5x10^-6</td>
<td>4.5x10^-7</td>
<td>0.057</td>
<td>57</td>
<td>0.013</td>
</tr>
</tbody>
</table>

Figure 12 Silver nanoparticle ink material balance

This material balance indicates a total weight of 0.087 g silver recovered from the system. This illustrates approximately 87% total recovery of the silver nanoparticle pigment. The accepts stream represents 26% of the recovered weight. The rejects stream is 4% of the total weight and the wastewater accounts for 57% of the silver recovered in this test. It is very likely that the particles are stuck inside the screening equipment itself on any surface that is available, or were lost when the screen was stopped and emptied to collect the rejects stream. The
nanoparticle ink appears to partition mostly with the wastewater in this case. Figure 13 below shows the SEM electrograph of the ink/fiber interface at 2,000x magnification.

![SEM electrograph of silver nanoparticle ink/paper interface at 2,000X magnification – the lighter regions are the metals and the darker regions indicate fiber surface](image)

It was difficult to determine where the nanoparticles are in this electrograph. Another image is shown at a much higher magnification to show one single fiber surface in Figure 14.
Figure 13 shows that even though the pigment particles penetrate well into the voids of the sheet, that the silver nanoparticles do not become embedded in the fiber surface (Figure 14) and can therefore be released into the wastewater with relative ease during pulping and screening. Some kind of filtration step should be put in place to prevent silver from contaminating the effluent stream. If the downstream cleaning and filtering steps does not separate the metallic pigment from the wastewater, it will end up as effluent and may be detrimental to the bacteria within the clarifying ponds.
3.4 SEM Visualization of Ink/Paper Interface

3.4.1 PE Sample Imaging

The prepared PE printed sheets were imaged and analyzed using a JSM-7800F Extreme-Resolution Analytical Field Emission Scanning Electron Microscope (SEM). This SEM, located in the Electron Microscopy Analysis Lab (EMAL) at the Department of Earth and Environmental Sciences at the University of Michigan (Ann Arbor, MI). Samples of the PE printed sheets were attached to the sample holders (Ted Pella Inc., Redding, CA) in the cross sectional direction in order to visualize the ink-paper interface. The samples were then sputter-coated with gold and placed into the SEM for analysis. The magnifications and settings are shown in the figures in the results and discussion section. It was found that the electron beam tended to negatively impact the fiber surface of the sample at higher levels, so the beam energy was lowered to allow for image collection without damaging the samples.
3.4.2 Nickel Ink-Paper Substrate Interactions

For nickel-based PE samples, Figure 15A shows a clearly defined interface between the nickel ink pigments and the paper substrate fibers. The nickel pigments do not appear to fully penetrate the paper sheet pores and only gets adsorbed onto the paper surface. Further magnification of this interface (Figure 15B) shows some shallow penetration of the nickel particles into the surface voids but still demonstrates a clearly defined separation from the paper.
fibers. In PE, it is desirable for the metallic ink particles to be held close to the surface for optimum electrical conductivity properties, but some absorption appears inevitable due to the capillary properties of the paper. At 8,000x magnification (Figure 15C), the interface between the nickel ink and paper fibers is still fairly well delineated as indicated by Arrow 1, but this could be nickel particle stacked on top of one another. However, it appears that some of the metal particles have become embedded in the fibers, as indicated by Arrow 3. This could lead to some difficulty in nickel ink removal. At 30,000x magnification (Figure 15D), there still appears to be a definite gap between the nickel particle and the fiber. This shows promise for the removal and recovery of nickel PE ink pigment. Based on these observations, we conclude that for nickel-ink based paper PE, the nickel ink particles appear to be mostly adsorbed on the paper substrate surface with some metal particle embedding. Nearly all recycled paper mill re-pulping operations include some chemical treatment to encourage the deinking process. Surfactants are used to separate inks from fiber surfaces, and since PE ink formulations are very similar to traditional inks, it should allow them to be removed. Future studies should be done to closely simulate the chemical treatment in order to assess the partitioning of the metal during pulping and screening. If the ink can be removed from the fibers, the metals will likely be partitioned to the water stream and can be removed with specific gravity cleaners and filtration. Being able to remove and recover the metallic pigments should be the goal, and this research indicates that there are still some challenges that need to be overcome, but they are not out of reach. Downstream cleaners are specific gravity based, and as long as the fiber and metal particles are separated, these equipment should possess the ability to remove the metallic pigments to prevent them from being put into the sheet.

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3.4.3 Silver Flake Ink – Paper Substrate Interactions

![Image of Silver Flake Inks on Paper Substrate]

Figure 16 Silver flake ink-paper interactions in sample printed electronics. Silver pigments are displayed as the lighter regions while the paper fibers are displayed as the darker regions. Magnification levels: A – 550x, B – 3,500x, C – 4,000x, D – 25,000x

Figure 16A shows that silver flake inks penetrate much farther into the fiber matrix than the nickel ink. A higher magnification image view of the silver flake ink-paper interface (Figure 16B) further confirms this observation, which is most likely the result of silver flake fusion to the fiber surface by the sintering process. Sintering, in this case is the process of using a pulsed xenon light source to create localized compaction and fusion of particles to create continuous
pathways for electricity to flow [81]. This will make removal of the silver ink particles during the recycling process difficult. Higher magnification (Figure 16C) shows that while the silver flake ink penetrated further into the paper surface fiber matrix, the silver particles appear to attach mainly on the surfaces of the individual fibers and not into the fiber pores. Further magnification in Figure 16D shows what appears to be a silver particle sitting on top of the fiber (Arrow 1), but there also appears to be some embedding of the silver flake particle in the fiber surface pores in other areas (Arrow 2). These observations indicate that traditional methods of contaminant removal prior to papermaking might not be effective for silver flake inks, as the ink-paper bond strength due to sintering and adsorption in the pores could be greater than the force applied by the process used to remove contaminants in the papermaking process. As stated above, the recycled process does include use of surfactants to separate inks from fibers, and as long as the metal particles can be released from the fiber surface, removal and recovery by downstream cleaning operations should be possible.
3.4.4 Silver Nanoparticle Ink – Paper Substrate Interactions

Figure 17 Silver nanoparticle ink-paper interactions in sample printed electronics. Silver pigments are displayed as the lighter regions while the paper fibers are displayed as the darker regions. Magnification levels: A – 950x, B – 2,000x, C – 2,700x, D – 3,000x

In Figure 17A, it is immediately apparent that the silver nanoparticle phases are difficult to distinguish from the paper fibers or even paper filler particles. Due to their small particle size, it is likely that the silver nanoparticles have been able to penetrate the fiber surface pores and voids and absorbed into the fiber matrix (Figures 17B-17D). In order to confirm these
observations, elemental composition analysis of selected regions in the SEM image was conducted (Figure 18). Regions were selected within the fiber matrix pores, in which silver nanoparticles are expected to be found in large quantities, as well as on the paper substrate surface.

![SEM image of silver nanoparticle ink/paper interface at 950x magnification with regions of interest for spectral element composition analysis. B - spectral element analysis for spectrum 1 (Arrow 1) in Figure 18A. C- Spectral element analysis for spectrum 2 (Arrow 2) in Figure 18A](image)

**Figure 18** Spectral Element analysis of silver nanoparticle ink/paper interface A – SEM image of silver nanoparticle ink paper interface at 950x magnification with regions of interest for spectral element composition analysis, B - spectral element analysis for spectrum 1 (Arrow 1) in Figure 18A. C- Spectral element analysis for spectrum 2 (Arrow 2) in Figure 18A

Elemental spectral analysis in Region 1, indicated by Arrow 1, is representative of pores and voids within the paper sheet. This indicates the penetration of silver nanoparticles within the paper substrate voids and pores due to high silver content. Spectral analysis of all the other regions showed low silver contents relative to carbon, which confirms the absorption/penetration of the silver nanoparticle into the substrate. This seems to imply that detachment and recovery of silver nanoparticle inks from paper substrates will be a critical challenge during conventional
paper recycling and reprocessing operations. The size of the particles appears to prevent the silver from embedding or fusing to the surface of the fiber. However, when the pulping and screening operations were carried out it was found that the majority of the silver nanoparticles partitioned to the wastewater stream. This indicates that the nanoparticles were not embedded or fused to the surface of the fibers. It appears that even though the metal essentially penetrated every pore and void, they are not bonded with the fiber surface. This nonbonding is the primary reason why the majority of the silver nanoparticles were found in the process water stream after the screening step. Silver nanoparticles will continue to be problematic, because of the fact that they are so small. Filtration would need to be so fine that the costs would be very high. It appears that some form of chemical coagulant would need to be applied in order to agglomerate the nanoparticles together for traditional removal methods to be effective. There is research that suggests increasing the pH to 8.5 and then using coagulants such as poly-aluminum chloride (PAC), polyferric sulfate or ferric chloride to flocculate the silver nanoparticles [82]. This group had success with PAC at a pH of 7.5. This condition could realistically be achieved inside of a paper mill, which could help the papermaker to remove these materials if and when they are introduced through the recycled stream.

3.5 Conclusions

In this experiment, the nickel and silver flake inks appear to have affinity for the fiber through the screening step. This could potentially be manifest in these metals being formed into sheet and sold. In the folding carton market, there is a zero metal requirement for the packaging to ensure that there is no metal in the food in the next step of creating food packaging and selling said food and packaging to the customer. This could create reject for papermakers and converters
alike, which costs both time and money. The silver nanoparticle inks travels in a greater proportion with the process water. This has implications for both the papermaking process and the effluent water stream. If silver accumulated in the whitewater system in a paper mill, it will kill the bacteria in the recirculation loop and cause issues with machine runnability. It is possible that the presence of silver might help the biocides placed into the system, but the presence of silver in any stream of the papermaking process would be less than desirable. If the silver gets into the effluent stream and pumped into clarifier ponds, the antibacterial effect of silver could potentially destroy the bacteria that is crucial to removal of BOD from the water before discharge to the environment. SEM was also used with spectroscopic elemental composition analysis was used to visualize and qualitatively assess the adsorption/absorption characteristics and the extent of penetration of metallic ink particles on paper substrates in printed electronic assemblages. The results indicate that nickel and silver flake ink have lower extents of penetration through the surface pores and voids compared to silver nanoparticles. However, the metal particles appear to be embedded in the fiber surface. This embedding then causes the nickel and silver flake ink to partition to the “accepts” stream, but the silver nanoparticles are being released from the fiber surface. Based on the qualitative analysis, the silver nanoparticles do not become embedded in the fiber surface. The nanoparticles do tend to penetrate into the sheet matrix during printing and curing. However, during re-pulping and screening, it is much easier for the nanoparticles to be released from the fiber surface, therefore concentrating the silver nanoparticles in greater proportion to the wastewater stream. Sedimentation and filtration might be a useful method for the removal and recovery of all three metallic pigments studied in this experiment. It is not known how deinking surfactants might aid in the removal of the metal
particles during pulping, but knowing that the inks are made of similar materials when compared to traditional inks shows that traditional methods could be successful in separating the metallic ink pigments from the fiber surface.

Further studies should include SEM analysis of the PE paper substrate fibers during and after re-pulping to understand how metallic inks and paper fiber interact during the paper recycling process. The goal is to prevent and/or minimize the partitioning of the metallic ink particles into paper mill sludges, which are typically disposed of by landfilling as well as recover and recycle these inks for reuse in PE manufacturing. The silver that travels with the rejects is assumed bound for a landfill. In the later study, it is not proven that silver nanoparticle ink should be considered a potential for toxic leaching. However, if a high enough concentration gets into a landfill, the bacteria within the landfill could be detrimentally affected, especially if the leachate material is recycled to maximize decomposition rates. This reject stream could potentially be diverted to a reclamation group so that the silver can be recovered and reused. This could give the mill an opportunity to create profit off the waste stream in the future as opposed to having to pay for landfill services to remove and dispose of the rejects from papermaking.

Another possible study would again carry out re-pulping and screening, but include the use of pulping surfactants to again assess the partitioning of the metals under conditions similar to recycled paper mill operations to further understand the end fate of the metallic ink pigments used to create PE. The water temperature, re-pulping time, pulp slurry consistency, and pH variables that exist within a mill could also be researched in order to maximize the release of the metals from the fiber surface to ensure recovery.
CHAPTER IV

A LANDFILL SIMULATION STUDY TO ASSESS POTENTIAL FOR METAL LEACHING FROM PE METALLIC INKS

4.1 Introduction

The goal of this research is to assess the potential of metal leaching from PE materials that are deposited into a landfill. Separation of PE items from the household goods waste stream is difficult and therefore should be a source of concern [24][25]. Research is being conducted on nanoparticles and there is significant concern about silver nanoparticles. There is debate about the mechanism by which a silver nanoparticle creates toxicity, but in general it is agreed that releasing silver into the water or waste stream has a great potential for ecological damage [10][26][27][28]. The exact disposal route will strongly affect the amount of silver nanoparticles that might be released into the environment [15]. Another study also suggests that there needs to be a plan for recovering these metals, due to their high cost and also that it is a limited natural resource [18]. Silver nanoparticles have been found to be toxic and readily released depending on variables such as pH, presence of natural organic material, and presence of ocean salts [83].

Research on PE suggests that the study of potential leaching in landfills is not known and should be carried out [61][84]. Another study says that unfortunately most of the products that project to be using RFID technology in the future will end up in the trash and into municipal solid waste streams [62]. It makes the case that PE materials should be tested to assess the potential for metallic pigment leaching.
4.2 Methods and Materials

4.2.1 Sample Preparation

Paper-based PE samples were prepared by printing conductive inks on paper and Polyethylene terephthalate (PET) substrates using laboratory scale proofing techniques. The paper used was a label facestock adequate for printing PE. Domtar, Inc. (Benton Harbor, MI) donated the paper used in these experiments. It has an average surface roughness of 3.02 ± 0.12 microns at a clamping pressure of 1000 kPa. The porosity of the paper has an average value of 83.85 ± 6.45 ml/min at a clamping pressure of 1000 kPa. The surface energy of the paper as measured by contact angle using water and methylene iodide as polar and dispersive components was approximately 73 dynes/cm². The dispersive component was approximately 31 dynes/cm², and the polar component contributed about 42 dynes/cm². PET used in the experiment had an average surface roughness of 1.11 ± 0.19 microns at a clamping pressure of 100 kPa. The average porosity at 1000 kPa clamping pressure is 8.57 ± 0.56 ml/min. The surface energy of the PET used in the experiment is approximately 46 dynes/cm² as calculated by the First ten angstroms software using water and methylene iodide as the polar and dispersive components for measurement by contact angle. The dispersive contribution is approximately 39 dynes/cm², while the polar component contributes about 7 dynes/cm². For flexographic printing, the 8.5 x 11-inch paper sheets were cut in half lengthwise to form a 4.25 x 22-inch sheet. The screen-printed samples were printed on the full 8.5 x 11-inch sheets. The PET was cut into approximately 4.25 x 17inch for flexographic printing, and the screen-printed samples were cut to approximately 8 x 8 inches. The nickel ink was purchased from NovaCentrix (Austin, TX). The nickel ink is a water based developmental product. It has a solids content of 62% as measured. It has a
Brookfield viscosity of 8,200 centipoise at 60 rpm with a #4 spindle. The silver flake ink used is manufactured by Sun Chemical (Parsippany, NJ). It is a water-based PE ink with a particle size of 1-3 microns. This silver flake ink has a solids content of 62.2% according to the MSDS, which was confirmed by measurement. It has a low viscosity as required by flexographic printing. The silver nanoparticle ink used was manufactured by InkTec (NEUNGAN-RO, Korea). It is water-based functional ink with a particle size of 10-100 microns. According to the MSDS, and the ink has a viscosity of 10-300 centipoise. This silver nanoparticle ink has a measured solids content of 34%. The printed samples were cured using the NovaCentrix (Austin, TX) PulseForge 1200 photonic sintering unit. The silver and nickel inks have different atomic properties and therefore need to be cured using different voltages to be sure not to over-energize the ink film and burn up the binder, therefore preventing ink adhesion. The nickel ink was treated with 300 volts at 20 feet per minute with a 1.0 overlap. This sheet was passed treated with this condition 3 times to effectively cure the ink and achieve a measurable electrical resistance. The silver inks were treated with 400 volts at 20 feet per minute with 1.0 overlap. These sheets were also treated three times to achieve electrical resistance. Substrate samples were weighed prior to and after printing in order to quantify the weight of ink transferred onto the substrate. Table 6 shows the average amount of ink transferred to the sheet for each substrate/ink combination.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average ink weight deposited-g</th>
<th>Ink weight into extraction-g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel Paper</td>
<td>0.24</td>
<td>1.68</td>
</tr>
<tr>
<td>Nickel PET</td>
<td>0.26</td>
<td>0.78</td>
</tr>
<tr>
<td>Silver Flake –Paper</td>
<td>0.09</td>
<td>0.58</td>
</tr>
<tr>
<td>Silver Flake – PET</td>
<td>0.04</td>
<td>0.18</td>
</tr>
<tr>
<td>Silver Nano – Paper</td>
<td>0.06</td>
<td>0.37</td>
</tr>
<tr>
<td>Silver Nano - PET</td>
<td>0.01</td>
<td>0.06</td>
</tr>
</tbody>
</table>
4.2.2 TCLP Testing Procedures

EPA method 1311 is a landfill simulation. SW 846 is a hazardous solid waste testing method analysis procedure. These two standards were used in combination to create the testing parameters. The Toxicology Characteristic Leaching Procedure (TCLP) uses a mixture of acetic acid and sodium hydroxide as the solvent in the extraction. The samples were shredded in a standard office shredder to reduce the size of the material to less than one square centimeter. The material and solvent was placed into a jar sealed and placed into a rotary mixer as recommended by EPA 1311. The printed samples were arranged in three sets for TCLP extraction. The paper extraction samples used seven sheets. The PET samples used four printed sheets to achieve the weight indicated as minimally acceptable by SW 846, which is 30 grams of solid waste for each sample to be tested. The ink weights are significantly different between paper and PET. The weights are also different between inks as well. PE are concerned with small features, so the low ink weights are an artifact of creating representative PE samples to analyze for toxicity. The average ink weight deposited for TCLP extraction is listed in Table 6. The EPA method 1311 procedure calls for the extracted liquid to be tested for metal concentration. The concentration level of this liquid determines whether the waste material should be considered hazardous waste or not.

This experiment utilized a modified version EPA test method 1311. This method is used to quantify the amount of hazardous waste in both the liquid fraction and the solids fraction of potentially hazardous waste. For liquid wastes that contain less than 0.5% dry solids, it is filtered through a 0.7 micron glass fiber filter from Whatman Specialty Products (Clifton, NJ). The solid
waste (greater than or equal to 0.5% solids) is separated from the liquid fraction. The particle size is reduced and then the extraction is carried out with the amount of extraction fluid being equal to twenty times the weight of the solid phase. The fluid used is determined by the alkalinity of the waste. Following extraction, the liquid phase was separated by filtration through a Whatman 0.7 micron glass fiber filter. When they are compatible, i.e. will mix together and not form multiple phases, the two liquid extracts were then combined for analysis. If they are not compatible, they are analyzed separately and the results are then combined mathematically to yield a volume-weighted average. Since this extraction is performed on samples containing mostly water, it is only necessary to use a vessel capable of holding the sample and extraction fluid. The extraction vessel should be made of a material that will not absorb any of the hazardous material. Glass flasks were used. Filtration was performed under a hood. The filter apparatus was made of a non-porous material. In this case, a ceramic filter with a glass Buchner funnel flask was used to collect filtrate for analysis.

The evaluation of mobility of metals requires the filters to be acid washed prior to sample filtration. The filter is washed with 1N nitric acid, and then rinsed three times with reagent water. A pH meter is needed that has an accuracy of ± 0.05 units at 25°C. A lab balance with accuracy of ± 0.01 grams was used to make all measurements. A magnetic stirrer and a watch glass to cover the flask are also needed. There are two extraction fluids to be used in this process. Extraction fluid #1 is made in the following manner: Add 5.7 mL glacial acetic acid to 500 mL reagent water. Next, add 64.3 mL of 1N sodium hydroxide, then dilute to 1 L. The pH of this solution should be 4.93 ± 0.05. The second extraction fluid uses only glacial acetic acid in the ratio of 5.7 mL in total with reagent water to 1 L. These extraction fluids should be maintained at
the proper pH and if they are found to be out of pH range they should be disposed of and remade. Sample collection for the TCLP procedure for metals requires that the sample be treated with nitric acid to a pH below 2, unless precipitation occurs. If precipitation occurs, the sample should not be acidified with nitric acid, and should be analyzed as soon as possible after extraction. Refrigeration of samples it is only allowed if it does not physically change the samples. If the samples are greater than 0.5% solids, it needs to be determined whether or not the samples require particle size reduction. If the sample has greater than 3.1 cm$^2$ area per gram of material, then it must be reduced in size before analysis. Crushing, cutting, and grinding are all acceptable forms of particle size reduction. Care must be taken to prevent loss of material as well. It is not necessary to actually measure the surface area. This step has been put in place for fibrous materials such as paper and cloth. In this case paper and polymer film were used and will likely require particle size reduction before extraction. The solids for extraction were placed into the extraction bottle with the filter used to separate the liquid phase from the solid phase. The weight of extraction fluid was calculated by multiplying 20 times the solids of the sample (in this case 100%) times the weight of the waste to be filtered after extraction divided by 100. In this case, since the samples are 100% solids, the weight was simply multiplied by 20 to exact the amount extraction fluid to be added. Table 7 shows the weights of sample and extraction fluid added.
<table>
<thead>
<tr>
<th>Experimental replicate</th>
<th>Total ink/fiber weight (g)</th>
<th>Weight extraction fluid (g)</th>
<th>Ink weight added (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel paper #1</td>
<td>33.2</td>
<td>664</td>
<td>1.6</td>
</tr>
<tr>
<td>Nickel paper #2</td>
<td>33.2</td>
<td>664</td>
<td>1.7</td>
</tr>
<tr>
<td>Nickel paper #3</td>
<td>33.4</td>
<td>668</td>
<td>1.8</td>
</tr>
<tr>
<td>Nickel PET #1</td>
<td>32.5</td>
<td>645</td>
<td>0.70</td>
</tr>
<tr>
<td>Nickel PET #2</td>
<td>33.7</td>
<td>674</td>
<td>0.78</td>
</tr>
<tr>
<td>Nickel PET #3</td>
<td>33.3</td>
<td>666</td>
<td>0.87</td>
</tr>
<tr>
<td>Silver Flake paper #1</td>
<td>32.1</td>
<td>642</td>
<td>0.61</td>
</tr>
<tr>
<td>Silver Flake paper #2</td>
<td>32.1</td>
<td>642</td>
<td>0.57</td>
</tr>
<tr>
<td>Silver Flake paper #3</td>
<td>32.2</td>
<td>644</td>
<td>0.57</td>
</tr>
<tr>
<td>Silver Flake PET #1</td>
<td>35.0</td>
<td>700</td>
<td>0.21</td>
</tr>
<tr>
<td>Silver Flake PET #2</td>
<td>34.9</td>
<td>698</td>
<td>0.16</td>
</tr>
<tr>
<td>Silver Flake PET #3</td>
<td>34.9</td>
<td>698</td>
<td>0.17</td>
</tr>
<tr>
<td>Silver nano paper #1</td>
<td>31.8</td>
<td>636</td>
<td>0.35</td>
</tr>
<tr>
<td>Silver nano paper #2</td>
<td>31.8</td>
<td>635</td>
<td>0.37</td>
</tr>
<tr>
<td>Silver nano paper #3</td>
<td>31.8</td>
<td>636</td>
<td>0.38</td>
</tr>
<tr>
<td>Silver nano PET #1</td>
<td>34.1</td>
<td>682</td>
<td>0.07</td>
</tr>
<tr>
<td>Silver nano PET #2</td>
<td>34.7</td>
<td>694</td>
<td>0.05</td>
</tr>
<tr>
<td>Silver nano PET #3</td>
<td>34.5</td>
<td>690</td>
<td>0.05</td>
</tr>
</tbody>
</table>

The experimental replicates shown in Table 7 were all extracted and collected for AAS testing. Only the first set of replicates (#1 for each ink/substrate combination) was tested by First Analytical Labs. The waste sample was added first, then the extraction fluid. The criterion in the standard states that samples greater than 0.5% solids with no volatile substances should use extraction fluid #1. This extraction fluid is made by combining 5.7 mL of glacial acetic acid combined with 64.3 mL of 1N sodium hydroxide, which is then diluted to one liter. This mixture yielded a pH of 4.93 ± 0.05. The extraction vessel should be sealed with Teflon tape to ensure that no liquid is lost during the extraction process. The vessels were loaded with sample and extraction fluid and agitated by rotation at 30 ± 2 rpm for 18 ± 2 hours. This should occur at an
ambient room temperature of 23 ± 2 degrees Celsius. After the extraction, the samples were filtered through a new glass fiber filter. Since metals are being analyzed, the filters need to be acid washed prior to filtration. The samples were filtered through the acid washed glass filters and the analyte was collected and stored until they could all be measured by AAS.

4.2.3 Atomic Absorption Spectrometer Analysis

The TCLP samples were collected and stored at 4°C until analysis. Each sample was acidified with 70% nitric acid in order for pH to be below two. In this case, a 2% v/v of the nitric acid was sufficient to acidify the samples for analysis. Concurrently, standard samples of known concentration were made from a 1000-ppm solution purchased from Fisher Scientific. The standard solutions were made at 1, 5, 10, 20, 50, 100, and 500 ppm concentrations, respectively.

The Varian AA240FS Flame Atomic Absorption spectrometer (Mulgrave, Victoria Australia) was used to analyze the acidified TCLP samples. Flame AAS can be used to find the concentration of the silver by plotting the Atomic Absorption absorbance against a calibration curve and interpolating the values. AAS is a spectroanalytical procedure for the quantitative determination of chemical elements using the absorption of optical radiation (light) by free atoms in the gaseous state. Basically, the instrument vaporizes the sample into atoms and then uses a spectral absorbance filter to quantify which atoms are which in the vapor. For Nickel, the other two experimental replicates for each substrate were measured five times to calculate average and standard deviation (see Table 8). For silver flake and silver nanoparticle, all experimental replicates were tested by AAS. However, the concentrations were found to be lower than the detection limits of the equipment, so only the First Analytical Labs experimental replicate data is presented.
4.3 Results and Discussion

4.3.1 Nickel Ink Results

4.3.1.1 Visual Observations

The extractions were done and the next step was to filter the extraction fluid through a 0.7 micron borosilicate glass fiber filter. The PET samples appeared to readily release the metal into the extraction fluid. The paper samples did not show a ready release of the metal into the extraction fluid. Figure 19 shows the glass filter fiber pads after filtration. The PET sample filter is on the left and the paper sample filter is on the right. The initial observation was that the PET sample would definitely have a significantly higher amount of metal in the extraction fluid. This was based on the observation that the PET releases the ink quite readily. This could correlate to the release into the environment if PE printed with nickel ink was placed into a landfill. It is not to say that the leachate will be more or less concentrated based on these observations, it is just to point out that paper seems to be a better candidate for holding onto the ink and not releasing it to the environment.

![Figure 19 Nickel ink TCLP extraction filters: A – PET sample filter and B – paper sample filter](image)
3.3.1.2 AA Spectrometer Analysis

The TCLP extracts were collected and analyzed. Nickel ink appears to have surpassed the regulatory limit for hazardous material. The TCLP extract contained a nickel concentration of 6.46 ± 0.001 parts per million (ppm) on paper, and 6.82 ± 0.001 ppm on PET in the first experimental replicate in Table 7. The data reported above was measured by First Analytical Labs (FAL) (Raleigh, NC). The AA spectrometer at WMU did verify the measurements taken at WMU for Nickel only. Table 8 show the results of the two other replicates measured at WMU. Each experimental replicate was measured five times by AAS to calculate averages and standard deviations in Table 8.

<table>
<thead>
<tr>
<th>Experimental replicate</th>
<th>Average-ppm</th>
<th>St. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel paper #2</td>
<td>6.40</td>
<td>0.48</td>
</tr>
<tr>
<td>Nickel paper #3</td>
<td>7.49</td>
<td>0.30</td>
</tr>
<tr>
<td>Nickel PET #2</td>
<td>9.68</td>
<td>2.36</td>
</tr>
<tr>
<td>Nickel PET #3</td>
<td>8.23</td>
<td>0.95</td>
</tr>
</tbody>
</table>

The TCLP regulation for nickel is 5 ppm [85]. This means the nickel ink used in this experiment presents a hazard if placed into a landfill. It is important to note that 5% of the total weight placed into the extraction vessel was nickel ink. This represents a high number compared to how much might actually end up in a landfill. Nickel inks are still largely in the developmental stages for use in PE, so it will be important to formulate these inks in the future to prevent the release into the environment, or should not be used for PE due the potential for environmental damage.
4.3.2 Silver Flake Ink Results

4.3.2.1 Visual Observations

The silver flake ink samples were collected, extracted and filtered. The filter papers for the PET samples appeared to release a more significant amount of metal into the extraction fluid. This observation led us to believe that the PET potential for environmental damage was more significant than that of the paper PE samples. The filter papers are shown in Figure 20 below. Again, the visual observations were not used to speculate on the results of the TCLP testing, just a comparison between the substrates.

![Silver flake TCLP extraction filters: A - PET sample filter and B – paper sample filter](image)

Figure 20 Silver flake TCLP extraction filters: A - PET sample filter and B – paper sample filter

4.3.2.2 AA Spectrometer Analysis

The AA spectrometer in the lab at WMU has detection limits of approximately 500 parts per billion (ppb). The absorption numbers appeared inconsistent, so First Analytical Labs (Durham, NC) was contacted and agreed to carry out the analysis by Inductive Coupled Plasma Mass Spectrometry (ICP-MS). This spectrometer has a much lower detection limit,
approximately 0.5 ppb. The silver flake samples were analyzed by FAL and the concentration levels are presented from the first experimental replicate (#1) for each ink and substrate combination in Table 6. The paper sample had a silver concentration in the extraction fluid of 0.054 ± 0.001 mg/L. (see appendix 2 for FAL analysis certifications) The PET sample had a silver concentration of 0.117 ± 0.001 mg/L. This translates to less than 1 ppm for both of the samples. The maximum concentration limit for TCLP method 1311 for silver is 5 ppm [85]. Both of these samples are below the limit, but it is important to note that PET sample had more than double the amount of silver in the extraction fluid. It is also important to note that the weight of ink placed into the extraction vessel was quite low. For the PET samples, the ink only accounted for approximately 0.6%, and around 2% of the total weight for paper. This artifact is a result of the thin ink films printed and the nature of PE having small features.

4.3.3 Silver Nanoparticle Ink Results

4.3.3.1 Visual Observations

The nanoparticle ink printed PE samples were extracted and filtered. The filter papers appeared to have much more ink released from the PET sample than from the paper sample, but the paper sample filter had much more ink on it than either the nickel or silver flake ink PE samples on paper. The nanoparticle silver seemed to be more readily released from the paper due to its smaller particle size. The filter papers are shown below in Figure 21. It was thought that the silver nanoparticle ink would probably have a greater concentration in the TCLP extraction fluid based on these observations. But the visual analysis is only to compare substrates and inks to each other. The results from the spectrometry are separate from these observations. The particles
of this ink are 10-100 times smaller than the other silver and nickel inks, but we cannot speculate on the leachate concentration through this method.

![Figure 21 Silver nanoparticle ink TCLP extraction filters: A - PET sample filter and B – paper sample filter](image)

4.3.3.2 AA Spectrometer Analysis

The AAS readings obtained did not appear consistent so the single sample measured by First Analytical Labs (Durham, NC) will be presented. The silver concentration level for the nanoparticle ink printed on PET is 0.361 mg/L, and the silver concentration for the paper PE sample is 0.144 mg/L (see appendix 2 for FAL analysis certifications). These are both well below 1 ppm. The maximum concentration limit for the analytes extracted using EPA method 1311 for silver is 5 ppm [85]. It is important to note again that the ink weight to total weight ratio placed into the extraction vessel was quite low, about 0.2% for the PET samples and about 1% for the paper samples. However, the concentration levels for the nanoparticle ink is significantly higher than the flake ink, even at the lower weight percentages. This holds true for both PET and paper PE samples.
4.4 Conclusions

EPA method 1311 and SW 846 were utilized to perform this landfill simulation. It appears that paper as a substrate retains more metal than PET. AAS and ICP-MS analyses seem to indicate that silver flake concentrations are at very low levels, below 1 ppm for both paper and PET substrates with the weight proportions at approximately 2.0 wt.% for paper and 0.6 wt.% for PET. Silver nanoparticle ink shows a level below 1 ppm for PET, and for paper, even at the low ink/substrate weight proportions added to the TCLP extraction vessels (approx. 0.2 wt.% for PET and 1.0 wt.% for paper). The nickel ink has a much higher concentration in the TCLP extract. At approximately 5.0 wt.% for nickel on paper and 2.5% for nickel on PET, the concentration levels are above 6 ppm for paper and for PET. However, the TCLP filter pads tell a different story. The filter pads for the PET substrate samples are completely covered with metal, whereas the paper substrate sample filter pads have little or no metal present on them after filtration. This tells us that even though most of the metal can be filtered out, the PET substrate still releases the metal more readily into the environment, while the paper substrate retains it. There should be some concern over landfilling printed electronics, especially if large quantities of printed electronic material are being landfilled. Nickel inks are a cause for concern. The concentration level for regulation of nickel for industrial semiconductor producer wastewater effluent is 3.98 mg/L on any one day, with a monthly average of 2.38 mg/L as a discharge concentration [45]. Printed electronics with nickel conductive inks should be highly regulated if and when they are produced.

For silver, the concentration level for regulation of nickel for industrial semiconductor producer wastewater effluent is 0.43 mg/L on any one day, with a monthly average of 0.24 mg/L
This would put the nickel TCLP extracts above the standard for wastewater effluent, and all of the silver ink TCLP extractions except for the flake ink on paper. There is a definite need for more extensive research in this area. The PE industry does not want to be responsible for an environmental issue, as abatement is very costly and can be avoided by employing measures to prevent these materials from being dumped into a landfill. These measures should include product labeling, consumer education and possibly incentives for recycling PE products to prevent landfill deposition. Another study suggests equipping the curbside containers with a device that could sense RFID technology in the bin and notify the collector which items contain the devices [62]. Other solutions could include RFID readers at the collection facility in order to facilitate stream separation during sorting [62]. Other solutions provided by this study include requiring the RFID tag to be placed on the product instead of the packaging, having dedicated recycling facilities for PE products, or smart trash cans in homes that can tell that person whether or not the product contains RFID [62].
CHAPTER V

CONCLUSION AND RECOMMENDATIONS FOR FUTURE WORK

In this dissertation, three metallic conductive inks used to manufacture PE have been studied in order to determine the end fate characteristics in reference to recycled papermaking and disposal. Chapter I established the basis for this research. It was found that environmental research on PE was lacking but being called for, especially in reference to the conductive inks. The inks are made with metallic pigments, known to be toxic to the environment, such as silver and nickel. These metals are highly regulated in the electronics industry, and probably should be in the PE industry as well. The literature review in Chapter II established the novelty of this dissertation by showing that end fate research is being called for, but has not been carried out on the conductive inks themselves. In Chapter III, the pulping and screening processes were studied as a material balance to quantify the partitioning of the metals through the screening process on a lab scale, and also by using SEM to visualize and further understand what happened in the study and why.

TAPPI standards were used for the pulping and screening process and EPA 7760-A was used to prepare the respective streams from the screen for AAS analysis. The main findings of the study indicate that the metal partitioning is dependent on the ink being used. The nickel ink and silver flake ink appear to show affinity for the fiber and are found mostly in the “accepts” stream. If the downstream processing does not remove these metals, they will be formed into the sheet. SEM analysis showed embedding of the metal particles in the fiber surface. The embedding makes for difficult removal of the metallic ink pigments, as shown by the material balance.
The silver nanoparticle ink SEM analysis showed that even though the metals tended to penetrate into the paper sheet matrix, the particles themselves stayed only in contact with the fiber surface, but did not embed into those fiber surfaces, and hence ended up in the wastewater stream in a greater proportion than the nickel and silver flake inks. The recycled paper industry may have an opportunity to innovate in order to remove and recover the metallic pigments. There are known methods for coagulation of the metallic particles to make recovery easier to accomplish within the mill.

Traditional deinking methods seem to show promise in separating the metallic ink pigment from the fibers during pulping, and if the metals can be partitioned fully into the reject stream by traditional screening and cleaning methods, there is an excellent chance that the metallic ink pigments can be removed and therefore will not travel with the accepted fiber stream. This should be possible with the nickel-based ink and the silver flake based PE inks. The silver nanoparticle ink will continue to be a challenge due to its small particle size. However, the material balance indicates that the majority of the nanoparticles travel with the water. This indicates that the fibers release the nanoparticle and that the methods for removal of both types of silver may need to be tailored to both the fiber and the process water systems in order to be efficient and effective in the removal and recovery of silver and other metals once they arrive at the mill.

Conventional deinking methods might be effective in separating the ink from the fiber, but it may be necessary to customize the equipment in order to create a settling effect in the flotation cells that can then be filtered and sent out for reclamation. There are also chemical
coagulation methods that can be used separately on the process water before it is discharged to
the effluent ponds. This could in turn help the clarifiers be more efficient as well.

As the use of PE increases, the chance for potential issues also increases. Silver and
nickel are both bio-accumulators and every effort should be made to recover these materials for
re-use, either in PE again, or in some other application.

This testing contributes knowledge that previously did not exist but has been called for by
experts, because of the increase in use of PE technology [41]. The cited reference tells that the
materials used to make RFID are known to be toxic, and while the advantages of using RFID are
many, the drawbacks are also numbered as well and should be researched. This research does
utilize existing collection, testing, and analysis procedures, however, it uses them in a manner
not previously carried out. The SEM testing carried out successfully imaged the cross section of
the ink/paper interface without embedding the paper sample in resin as previously done [86].
This is a significant set of results not only because it was accomplished as never before, but also
that the adhesion/interaction characteristics supported the results measured and found in the re-
pulping and screening test.

In Chapter IV, a landfill simulation was conducted using several EPA methods in
combination. This chapter was accepted as a stand alone publication by the Journal of Solid
Waste Management and Technology [87]. EPA method 1311 was used as the basis for the
leaching procedure, for the equipment and solutions used in the extractions. SW 846 was used
for solids handling and analysis methods in the experiment. Method 7760-A was used as the
basis for the AAS readings. This method was used to prepare the analyte samples for AAS
testing. The main findings in this paper seem to indicate the commercially available silver inks,
both flake and nanoparticle inks do not qualify as hazardous waste in the weight proportions used in the experiments if landfilled. The nickel ink tested is still a developmental PE conductive ink product, but it would have qualified as hazardous waste in the TCLP method. Landfill deposition of these materials should be avoided, not only to prevent possible leaching issues in the future, but also to maintain the sustainability of PE. Several methods described above can prevent landfill deposition of PE metallic inks such as smart trash cans and RFID readers at collection facilities, but these are not safeguards and facilities should be made aware of the introduction of these materials due to the predicted increase in usage in the next decade and into the long term future.

This research will serve to create an awareness to landfill operators that these materials will likely appear at their facilities. This testing contributes to science knowledge that was previously known or collected, but needs to be carried out due to the imminent increase in PE production and usage in the near future. It is important because if too much PE material enters a landfill, the toxic materials may negatively impact anaerobic decomposition, which could have long term negative affect on the landfill operation.

In future work, it is recommended that this testing be done on all commercially available inks currently used in PE manufacturing. There should also be a possible certification test package made available to manufacturers as part of a consortium to prevent any future issues from arising without warning. There should also be a major push to educate the consumers of these products to ensure that PE materials are treated properly both during and after use. If the consortium is formed, it should be part of its job to create the educational campaign for the industry with support for the manufacturers of PE, as well as the suppliers. There are many types
of inks being used in the production of PE that have not been tested. This should be considered important not only by the manufacturers of inks, but also the suppliers of the material for the inks.

The recycled paper industry should definitely be made aware of the use and probable introduction of PE metallic pigments into the recycled stream. This awareness should also be passed on to landfill operators and recycling plants that deal with packaging of any kind in order to create the ability to recover and reuse the metallic ink pigments to ensure the sustainability of PE in the future. This could be done through education through future research of a wider variety of the inks, but also potentially through the creation of regulations that suggest the use of resources to ensure the recovery of PE materials. The thought of a new standard to certify any and all PE inks could become a reality in future.

The testing and research should focus on the variables not tested during the re-pulping and screening testing. The pH should be adjusted using chemistry that closely simulates mill conditions (either acid or alkaline depending on process). There should also be a testing standard that varies water temperature to simulate different mills in different parts of the country. The water conditions also vary depending on where in the country the mill operates. There could be testing and research to quantify the effect of conductivity, sand and grit content of the incoming water stream, and also the amount of dissolved solids in that water, which may affect the water quality or uptake of chemicals.

The effluent regulatory limits stated in the introduction as applied to printed circuit board manufacturers could serve as the starting point for a regulatory limit for wastewater effluent. The regulatory limit for silver is 0.43 mg/L silver concentration for any one day and no greater than
0.24 mg/L average for a one-month time period [29]. Nickel has a limit of 3.98 mg/L nickel concentration on any one day, and an average of no more than 2.48 mg/L in one month [29]. The landfill simulation testing should also be worked into the standard to ensure PE disposal is safe, even though it is not desirable to landfill these materials based on the thoughts about sustainability, recovery and re-use. Research should also be conducted to assess the bioaccumulation aspects of silver and nickel if the leachate is recycled through the landfill over and over to ensure that the anaerobic decomposition bacteria are not negatively impacted be a potential increase in toxicity. This dissertation is a starting examination into the possible end fate issues and paths that PE could take in the near future and the industry should definitely want to explore these tests in more depth and width to ensure that industry does not have a negative impact on the environment as PE is used increasingly in the future.
**APPENDIX A**

Sample calculation of material balance:

<table>
<thead>
<tr>
<th>Silver flake</th>
<th>tray -g</th>
<th>Ink/tray/fiber g</th>
<th>Ink/fiber g</th>
<th>Parts per million from AAS</th>
<th>weight fraction average</th>
<th>Fiber/ink weight in stream g</th>
<th>total weight g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured on scale</td>
<td>Measured on scale</td>
<td>Measured on scale</td>
<td>Calculated by software based on calibration curve</td>
<td>=ppm average * dilution factor/1000/weight in sample</td>
<td>Weight fraction* fiber ink weight in stream</td>
<td></td>
<td></td>
</tr>
<tr>
<td>accepts</td>
<td>1.31</td>
<td>2.54</td>
<td>1.23</td>
<td>58.98</td>
<td>0.005</td>
<td>42.0</td>
<td>0.21</td>
</tr>
<tr>
<td>rejects</td>
<td>1.32</td>
<td>2.96</td>
<td>1.64</td>
<td>153.63</td>
<td>0.009</td>
<td>3.3</td>
<td>0.03</td>
</tr>
<tr>
<td>waste-water</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>1.24</td>
<td>1.3 x 10^-7</td>
<td>37850</td>
<td>0.05</td>
</tr>
</tbody>
</table>
APPENDIX B

First Analytical Labs - Certificate of Analysis
# EPA Method 200 Analysis Report

**FAL Project #:** 141049.1  
**Report Date:** 10/29/2014  
**Client:** WMU - James Atkinson  
**Date Received:** 10/15/2014  
**Client Project ID:** TCLP Evaluation

**Sample Name:** Silver Flake Ink on Paper Substrate

## Concentration in Original Sample

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<th>Conc. (mg/L)</th>
<th>RL (mg/L)</th>
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<td>Nickel (Ni)</td>
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</tr>
<tr>
<td>Silver (Ag)</td>
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<td>0.001</td>
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Approved by:  
Matt Loftis, Laboratory Manager
EPA Method 200 Analysis Report

FAL Project #: 141049.2                    Report Date: 10/29/2014
Client: WMU - James Atkinson              Date Received: 10/15/2014
Client Project ID: TCLP Evaluation

Sample Name: Silver Flake Ink on PET Substrate

Concentration in Original Sample

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<td>Silver (Ag)</td>
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Approved by: Matt Loftis, Laboratory Manager
EPA Method 200 Analysis Report

FAL Project #: 141049.3  
Client: WMU - James Atkinson  
Client Project ID: TCLP Evaluation

Sample Name: Silver Nanoparticle Ink on Paper Substrate

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Approved by: Matt Loftis, Laboratory Manager
EPA Method 200 Analysis Report

FAL Project #: 141049.2  
Report Date: 10/29/2014
Client: WMU - James Atkinson  
Date Received: 10/15/2014
Client Project ID: TCLP Evaluation

Sample Name: Silver Flake Ink on PET Substrate

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Approved by:

Matt Loftis, Laboratory Manager
EPA Method 200 Analysis Report

FAL Project #: 141049.1  Report Date: 10/29/2014
Client: WMU - James Atkinson  Date Received: 10/15/2014
Client Project ID: TCLP Evaluation

Sample Name: Silver Flake Ink on Paper Substrate

Concentration in Original Sample

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FAL Project #: 141049.1
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Report Date: 10/29/2014
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Sample Name: Silver Flake Ink on Paper Substrate

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EPA Method 200 Analysis Report

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Sample Name: Silver Flake Ink on Paper Substrate

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</table>

Approved by:

Matt Loftis, Laboratory Manager
APPENDIX C

Glossary of Acronyms

AAS: Atomic Absorption Spectrometry
EPA: Environmental Protection Agency
PE: Printed Electronics
PPM: Parts Per million
RFID: Radio Frequency Identification
SEM: Scanning Electron Microscopy
TAPPI: Technical Association of the Pulp and Paper Industry
TCLP: Toxicology Characteristic Leaching Procedure
APPENDIX D

Raw Data for Material Balance

Silver Flake AAS readings

<table>
<thead>
<tr>
<th>Ag flake acc 1</th>
<th>concentration ppm</th>
<th>Ag flake rej 1</th>
<th>Concentration ppm</th>
<th>Ag flake ww-1</th>
<th>concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.233 g fiber/ink</td>
<td>64.498</td>
<td>1.637 g fiber/ink</td>
<td>155.19</td>
<td>100 ml dilution</td>
<td>2.903</td>
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<tr>
<td>100 mL</td>
<td>59.453</td>
<td>100 mL</td>
<td>153.217</td>
<td>2.429</td>
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</tr>
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<td></td>
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<td></td>
<td>152.463</td>
<td>1.853</td>
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<table>
<thead>
<tr>
<th>Ag flake acc 2</th>
<th>concentration ppm</th>
<th>Ag flake rej 2</th>
<th>Concentration ppm</th>
<th>Ag flake ww-2</th>
<th>concentration</th>
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<tbody>
<tr>
<td>1.839 g fiber/ink</td>
<td>80.364</td>
<td>1.347 g fiber/ink</td>
<td>197.835</td>
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<td>100 ml</td>
<td>79.781</td>
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<table>
<thead>
<tr>
<th>Ag flake acc 2</th>
<th>concentration ppm</th>
<th>Ag flake rej 3</th>
<th>Concentration ppm</th>
<th>Ag flake ww-3</th>
<th>concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.2 g fiber/ink/water</td>
<td>355.895</td>
<td>13.2 g fiber/ink/water</td>
<td>607.891</td>
<td>100 ml</td>
<td>5.92</td>
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<tr>
<td>50 ml</td>
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<tr>
<td></td>
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<td>st. dev.</td>
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<td>total average</td>
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<td>total average</td>
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Silver nanoparticle AAS readings

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<th>Ag nano rej 1</th>
<th>Concentration ppm</th>
<th>Ag nano ww-1</th>
<th>Concentration ppm</th>
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</thead>
<tbody>
<tr>
<td>1.119 g fiber/ink</td>
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<td>0.359 g fiber/ink</td>
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<tr>
<td>100 mL</td>
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<table>
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<th>Ag nano rej 2</th>
<th>Concentration ppm</th>
<th>Ag nano ww-2</th>
<th>Concentration ppm</th>
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<td>1 g fiber/ink</td>
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<td>100 mL</td>
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Nickel AAS readings

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<th>Ni Rejects</th>
<th>Concentration ppm</th>
<th>Ni-ww 1</th>
<th>Concentration ppm</th>
</tr>
</thead>
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<tr>
<td>1.84 g fiber/ink</td>
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<td>10.9 g fiber/ink/water</td>
<td>511.988</td>
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</tr>
<tr>
<td>100 ml</td>
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<td>100 ml</td>
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<th>Ni-ww 2</th>
<th>Concentration ppm</th>
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