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Investigations of Electric Arc Furnace Slag Filters: Phosphorus Treatment Performance, Removal Mechanisms and Material Reuse

Simon Bird
University of Vermont

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INVESTIGATIONS OF ELECTRIC ARC FURNACE SLAG FILTERS: PHOSPHORUS TREATMENT PERFORMANCE, REMOVAL MECHANISMS AND MATERIAL REUSE

A Thesis Presented

by

Simon C. Bird

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of

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Thesis Examination Committee:

Aleksandra Drizo **Advisor**

Dr. Aleksandra Drizo, Ph. D

Dr. Donald Ross, Ph. D

Dr. Gregory Druschel, Ph. D

Chairperson

Dr. Breck Bowden, Ph. D.

Frances Carr **Vice President for Research and Dean of Graduate Studies**

Frances E. Carr, Ph. D

Date: September 24th, 2008

ABSTRACT

Around the world, the eutrophication of freshwater lakes and streams by the excess loading of phosphorus (P) has become one of the most important water quality issues. In Vermont, P pollution from urban and agricultural non-point sources has led to severe blooms of toxic cyanobacteria in Lake Champlain, and the degradation of the lake's value as a drinking water source and its recreation potential. Electric arc furnace (EAF) steel slag has been identified as an effective material for use as a filter media for the removal of P from both point and non-point sources of pollution. In order to further assess the feasibility of this technology for use in Vermont, several investigations were carried out starting in the winter of 2006. Three objectives for research were identified: 1) to construct 2 EAF steel slag filters in-series at the Constructed Wetlands Research Center (CWRC) and investigate their efficiency in P, TSS and metals reduction from dairy waste water in a cold climate; 2) investigate the potential for reuse of P saturated EAF steel slag as a soil amendment and plant fertilizer by testing bioavailability of sorbed P and quantities of P released to surface runoff; 3) To elucidate the principal mechanisms responsible for the removal of P in EAF slag filters when used for the treatment of dairy effluent.

The results indicated that 2 EAF steel slag filters constructed in-series are an effective method to increase the treatment efficiency and longevity of a filter system. Additionally, parameters for the concentrations of total suspended solids (TSS) and biological oxygen demand (BOD) were developed, both important factors for design of filter systems. In greenhouse trials, *Medicago sativa* plants achieved greater above ground biomass growth with P fertilization by triple super phosphate (TSP) than EAF steel slag at the shorter growth period (5 weeks). However, by the end of the longer growth period (10 weeks) except at the highest amendment rate, the plants treated with EAF steel slag had a higher growth rate than the TSP, suggesting that EAF steel slag is an effective slow release P source. Using a rain simulator, the amount of P lost to surface runoff from both a saturated and a semi-saturated EAF steel slag was found to be negligible, and except for total P in the saturated slag, to be below 1 mg L^{-1}. Voltammetric analysis and geochemical modeling were used to identify possible mechanisms for the removal of P from waste effluent. The Ca mineral hydroxyapaptite and the Fe(II) mineral vivianite were both shown to be likely mechanisms given the chemical conditions in EAF steel slag filters.

This research represents the first investigation of cold weather performance of EAF steel slag filters for the treatment of dairy parlor and milk house waste effluent. Additionally, it was also the first research on the bioavailability of P sorbed to EAF steel slag, and of the possibility of its reuse as a soil amendment, and of the mechanisms involved in P removal from dairy waste effluent.

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1.1. Introduction

1.1.1. Phosphorus Pollution

Phosphorus (P) pollution into freshwater lakes has become an increasing problem throughout the world (Smith, 2003). In the United States, the leading cause of impairment of water bodies has been found to be excess nutrient loading (U.S. EPA, 1996; USGS, 1999). Phosphorus is the major limiting nutrient in freshwater ecosystems, (U.S. EPA, 1996; USGS, 1999; LCBP, 2006). Excess P in freshwater systems results in a proliferation of primary producers, mainly various Cyanobacteria species formerly classified as blue-green algae, a situation which is called eutrophication, leading to both ecological and sociological degradation of freshwater systems (U.S. EPA, 1998; USGS, 1999). The massive blooms of Cyanobacteria can clog water intake pipes, and can limit lake activities, such as swimming, boating and fishing, and some species secrete chemicals that are toxic to animals including humans, resulting in beach closures. In addition, the decay of the blooms cause foul odors and tastes, further diminishing the recreational appeal of the lake, and decreases the dissolved oxygen (DO) levels in the water, resulting in fish kills and reduced biodiversity (U.S. EPA, 1998; USGS, 1999; Khan and Ansari, 2005).

1.1.2. Economic Impact of Lake Champlain

Lake Champlain is a large freshwater lake in the Northeast of the United States. The lake is mostly utilized for recreational activities, but over 180,000 people in Vermont and

New York depend on the lake for drinking water, with almost 25% of Vermont's population receiving drinking water from the lake (LCBP, 2003; Watzin *et al.*, 2005). In 1990, it was estimated tourism related activities contributed $2.2 billion to the Lake Champlain basin economy, of which 70% of that ($1.5 billion) was spent in Vermont, while by comparison $2.8 billion is attributed to manufacturing activities (ANR, 1997). The Lake Champlain Basin program estimated that tourist spending in the basin had risen to $3.8 billion by 1998-99, with 71% ($2.7 billion) being spent within Vermont (LCBP, 2003). In the years 1998-99 tourists spent $1.5 billion in Vermont lake-shore towns, $228 million of which on direct lake activities, such as boating, swimming, fishing and camping, and area residents spent an additional $118 million on lake activities (LCBP, 2003). These values are based on direct expenditures by tourists and residents, and do not reflect all of the economic value that the lake brings to the area which may be estimated through analysis of lake-basin property values in the lake basin and travel-cost studies (Holmes & Associates and Artuso, 1996).

One difficulty facing efforts to limit nutrient loading to Lake Champlain is that the watershed is very large, encompassing 8,234 sq. miles, including 18 rivers which empty into the lake. Additionally, the watershed crosses an international border between the US and Canada, and is a spread over patchwork of different governments including several different counties in 2 different states (Vermont and New York) and 1 Canadian province (Quebec) (LCBP, 2003). While Lake Champlain is clearly important economically to the surrounding Vermont and New York communities, there are other equally important reasons to preserve it. The lake provides much in unquantifiable benefits, such as the wealth of the biology, and beauty of its landscape which should not be ignored or given lesser importance (LCBP, 1996).

1.1.3. Lake Water Quality Issues

For over two decades Cyanobacteria blooms have been documented in the lake, and have resulted in numerous beach closings. In 1993 30% of the P inputs to the lake were attributed to municipal wastewater, by 2006 this had fallen to 10%, showing great improvements in wastewater treatment (LCBP, 2006). This was the result of large investments in sewage treatment by federal, state, municipal and private organizations since the 1970's (LCBP, 1996). Point sources are relatively easy to target and control and were therefore targeted first, now however, 90% of P inputs are attributed to non-point sources such as urban stormwater and agricultural runoff, which are more difficult to locate and treat, making further reductions in P inputs to the lake a much more laborious task (LCBP, 2006).

In the summer of 1999, three dogs deaths were attributed to their ingestion of Cyanobacteria from the lake that were caused by nutrient enrichment (Rosen *et al.*, 2001). Despite the vast attention and money spent on reducing P loading into Lake Champlain, little effect has been seen in Lake P levels. Since extensive monitoring began in 1990 most sampling points have shown either an increase in P concentration or no detectable trend could be detected in the data; only three points have met reduction targets (LCBP, 2006). Overall, from 1991 to 2003-04 not only was the lake Champlain P concentration not reduced, but there was a 50% increase in total P inputs (Page, 2006). Watzin *et al.* (2005) created a computer model of P inputs into Missisquoi, a shallow bay in the northern area of Lake Champlain with historically high P levels, to analyze the effects of different non-point pollution management scenarios. The scenarios simulated a 0%, 25% and 75% reduction in P inputs and projected lake P concentration over the next 20 years to be +15%, 0% and -33% respectively. The authors reported that the first two simulations saw increases in P levels were the result of resuspension of P of from lake sediments. This study shows that drastic reductions in P loading from non-point sources can have an affect on lake levels of P, however large decreases in P need to be made to maintain reductions in lake P concentrations (Watzin *et al.*, 2005).

1.1.4. Sources of Phosphorus Pollution

1.1.4.1. Point and Non-Point Pollution Sources

Diffuse pollution or non-point source (NPS) pollution differs from point source (PS) pollution, because in PS the pollution source is identifiable and discrete and thus controllable. Whereas the NPS pollution is the cumulative effect of many disperse sources, often inadvertently, such as houses, farms, and businesses. This makes identifying the sources, transport mechanisms, and quantifying the amount of pollution and its effects difficult. This limits the implementation of appropriate and effective solutions (Sims and Pierzynski, 2005). Because of this difficulty, NPS pollution has been typically not regulated by law, therefore governmental agencies and environmental groups have attempted to implement change through incentives and education (Carpenter *et al.*, 1998).

With the passage of the Clean Water Act in 1972, over $500 billion dollars has been spent to reduce PS of P, mainly by improvements to municipal wastewater treatment plants and industrial plants (USGS, 1999). Because of these upgrades P releases from water treatment facilities into Lake Champlain fell from 126 mt/yr in 1991 to 44 mt/yr in 2000, and most from PS of pollution in Vermont (Medalie and Smeltzer, 2004). Despite the drastic reduction in PS P pollution into Lake Champlain between 1990-2000 the actual concentration of P in the lake has steadily increased (Medalie and Smeltzer, 2004). Because the new technologies used for treatment all required large capital outlays limiting their use to larger municipalities and industries; therefore many untreated nutrient sources remain (U.S. EPA, 1998). This has left mainly NPS such as agricultural runoff and urban stormwater runoff as the primary contributors of P to freshwater lakes including Lake Champlain, where it contributes 80-100% of the P load (U.S. EPA, 1996; Carpenter *et al.*, 1998; USGS, 1999; Medalie and Smeltzer, 2004). The USGS estimated that non-point sources were responsible for 75% of P found in 20 study streams, with point sources accounting for the remainder. In a recent analysis, Troy *et al.* (2007) identified that although developed land comprises a small portion of the landuse in the Champlain Valley, it accounts for about 53% of the NPS pollution to the lake. Basin wide, agricultural lands contributed approximately 39% of the NPS load to lake Champlain. Although this can vary greatly between subwatersheds of the lake, and agriculture can be the largest source of P, such as Missisquoi Bay where it accounts for about 68% of the load (Troy *et al.,* 2007).

1.1.4.2. Trends in Agricultural in the US

Approximately 21% of Vermont's land area is farmland; therefore farms have potential for large effects on water quality in the state (USDA, 2002). Over the last two decades, dairy farming in Vermont and the US as a whole has declined, both in the number of farms and overall number of milking cows. However, the amount of milk produced has remained relatively stable because of a shift in techniques and an increase in average herd size on remaining farms (USDA, 2002; Weber, 2006; National Dairy Environmental Stewardship Council, 2007).

1.1.4.3. Agricultural Manure Disposal

With the changes in US agricultural systems during the 20th century, manure has changed from being viewed as a resource for building soils, to a nuisance waste product. The 1990's census data shows that there was a 50% increase in herd size, while the number of dairy farms fell by 40% (Sharpley *et al.*, 1998b) This was largely the result of the concentration of animal feeding and cropping operations in particular regions of the country, resulting in a one way flow of nutrients from centers of feed growth to those of livestock production (NRC, 1993; Sims, 1997; Sharpley *et al.*, 1998b). The result is the volume of manure and nutrients on livestock operations often exceeds the area of available cropland (Sharpley *et al.*, 2003; Sims and Kleinman, 2005). Averaged across all of the useable agricultural land in the US, there is an annual surplus of 30 lb./acre P (NRC, 1993).

Agriculture has evolved from being a sink of excess P: crop production requiring more P than soil levels provided, to a system that is a source of P: soil P levels in excess of crops needs, which leads to P losses to surface and ground waters (Sharpley *et al.*, 2001; Sharpley *et al.*, 2003). To dispose of this waste product, farmers apply all manures and other wastewaters to the limited fields they have, leading to large accumulations of P in the soils and P loading in surface waters through runoff (Sims and Kleinman, 2005). The rise in land prices because of development pressures has made it increasingly difficult for farmers to have enough land-base to safely spread their manure (National Dairy Environmental Stewardship Council, 2007). In studies of poultry litter the continued annual application of manure leads to increase soil P levels and thus higher P loss to runoff. However, any limits placed on the land application of litter would have severe repercussions on the farmers, both operationally and economically (Sims, 1997). Therefore on many farm fields soil P levels have reached very high levels, which drastically increases the risks of P being lost to runoff (Sharpley *et al.*, 2003).

1.1.4.4. Agricultural Sources of Phosphorus

Agricultural lands account for the largest of contribution of all land-use types of P to Lake Champlain (LCBP, 2003). Pollution from farms can include PS: such as discharges from manure storage pits, tile drains from fields or settling tanks, and contamination during broadcast applications (Sharpley and Withers, 1994; Sharpley *et al.*, 2003) and NPS: runoff from feed lots and fields (NRC, 1993; ANR, 1997; U.S. EPA, 2000). One of the biggest contributors of P from Vermont farms is the result of the considerable discrepancy between the large amount of nutrients imported onto the farms and the much smaller quantities that are exported in the farm products (Carpenter *et al.*, 1998; Sharpley *et al.*, 2001). This leads to excessive concentration of nutrients in the soils of farms, which increases the risks of P loss to runoff from fields (NRC, 1993; Carpenter *et al.*, 1998; Sharpley *et al.*, 2001).

1.1.4.5. Urban Sources of Phosphorus

In the Lake Champlain basin, urban land cover constitutes 6% of the area, yet is responsible for 37% of the total load of P to Lake Champlain (LCBP, 2003). As in agricultural environments, in urban settings the land-use surrounding streams has great influence on the in stream water quality, such as high levels of paved non-pervious areas and storm drains that bring wastewaters directly to streams (Sonoda and Yeakley, 2007). Urban sources of NPS pollution include construction sites, runoff from lawns and pet waste and stormwater runoff from developed areas (Carpenter *et al.*, 1998). In urban settings, P pollution is often intensified by the absence of natural systems, such as vegetation in riparian areas, which would aid in reducing excess P from runoff (Sonoda and Yeakley, 2007). Many advances have been made in removing P from PS and NPS pollution sources in the Lake Champlain basin since the 1970's, however the increase in development, continually expanding the amount of urban land area, has mostly negated these gains (LCBP, 2003). In Vermont, a permitting process called Act 250 regulates stormwater discharges from commercial, industrial, large residential and many road developments, limiting the impacts of new urban expansion. However, smaller developments, such as residential homes, are not required to go through the process, and can have large cumulative effects (ANR and DEC, 2002).

1.1.5. Vermont Farming Economy

Dairy farming is a historic, and economically important industry in Vermont (VT Dairy Task Force, 2005). It is not only important to the state of Vermont in direct economic terms, but also the image of the state, which adds significant value through attracting tourist visits and raising the standard of life for residents (LCBP, 2003). Vermont topography produces unique conditions for dairy farming; because of the state's mountainous terrain Vermont farmers have significantly less arable land (Meeks, 1991). In addition, the topography results in many streams and rivers, which are often within meters of farm production areas, such as milking parlors, milk houses, fertilizer and pesticide handling areas and manure storage facilities, thus increasing the risks of contamination of water resources (Karpiscak *et al.*, 2001; Jayarao, 2002).

Despite dairy farming's incredible value, the number of farms in Vermont has been steadily declining over the last decade as a result of continually low milk prices, and high expenses for feed and fuel (USDA, 2002; VT Dairy Task Force, 2005). The costs of any new environmentally-based manure management procedures will fall directly on the farmers, including those for new infrastructure, and time to perform and document the new procedures (Sharpley *et al.*, 1998a). Farmers do not have the ability to pass any of these added costs onto consumers since they have little control over the prices of their commodities (Karlen *et al.*, 1998; Sharpley *et al.*, 1998a). In addition, farmers generally have little of the specific technical knowledge needed to design and run programs to manage solid waste, and affordable technical assistance is rarely available (Nowak *et al.*, 1997).

Therefore, proposed methods to control nutrient releases from agricultural areas must be low cost, low energy and low maintenance, in order to fit within the tight economic and time constraints the farming industry is under (Sharpley *et al.*, 1998a).

1.2. Agricultural Regulations

1.2.1. Confined Animal Farming Operations (CAFO) Regulations

Dairy farming is a very large and important industry in the United States; in 1997 there were 116,874 dairy operations, producing approximately 1.8×10^9 tones of manure annually (Karpiscak *et al.*, 2001). In 1972 with the establishment of the Clean Water Act, the Environmental Protection Agency (EPA) created the National Pollutant Discharge Elimination System (NPDES) to regulate the point source discharges of pollutants into the nations water body's (U.S. EPA, 2006). The Clean Water Act specifically lists confined animal feeding operations (CAFO) as a point source, including in this definition any discharge of pollutants from land spread manure, a definition that was upheld by the U.S. Courts in the Water Keeper *et al.* vs. EPA decision (U.S. EPA, 2006). As the effects of nutrient loading on surface waters has become apparent, the United States Department of Agriculture (USDA) and EPA have focused increasing attention onto agricultural operations, and in March 1999 released the Unified National Strategy for Animal Feeding Operations. This states that all animal feeding operations (AFO) owners and operators must establish a site-specific Comprehensive Nutrient Management Plan (CNMP) (U.S. EPA, 2003a). In 2002 the EPA proposed a new regulation, the Effluent Limitations Guidelines and Standards (ELG) for feedlots (beef, dairy, swine, and poultry), which aimed to set an allowable limit for discharges of manure, wastewater and other process waters under the existing NPDES CAFO permit process (U.S. EPA, 2003a). Requirements from the ELG will be placed into a CAFOs NPDES permit to set standards for the volumes of discharge allowed for specific pollutants under the permit (U.S. EPA, 2003b).

1.3. Methods for Phosphorus removal

1.3.1. Best Management Practices

1.3.1.1. Non-Point Pollution Treatment.

In agriculture, a set of methods has been defined to tackle a host of issues from farm financial stability and tilling methods to waste management; these have became collectively known as Best Management Practices (BMP). In 1991 report on non-point water pollution the state of Maine defined a BMP as:

> "*A method or practice which, when installed or used, is consistent with efficient, practical, technically and environmentally sound animal or crop production*

> *practices. BMPs are those practices best suited to preventing, reducing, or correcting agriculture-related problems."* (Coxe and Hedrich, 2007).

Coxe and Hedrich (2007) have importantly noted that in this definition the word "best" does not infer the method that offers the greatest environmental protection, but one that in a cost/benefit analysis will ensure an improved protection of environmental resources and farm viability. Whereas others advocate that BMPs should provide the highest reduction in nutrient losses to surface or ground waters available (Sims and Kleinman, 2005). For example, the state of Vermont defines a BMP as:

> *"Best management practices are site specific on-farm remedies implemented either voluntarily or as required in order to address water quality problems and in order to achieve compliance with state water quality standards."*(AAM, 1996).

SERA-17, a working group of government and university-based scientists on P pollution has created a list of 32 BMPs. For agriculture these encompass a diverse set of practices from farm management change, such as changing tillage practices or cropping techniques, to farm landscape modifications like planting buffer strips of dense vegetation around fields and terracing (Sera-17, 2007).

BMPs have evolved over time and will continue to adapt as practices, technology and needs of both farmers and the surrounding communities shift (Coxe and Hedrich, 2007). As stated in the definitions above, BMPs aim to affect the management and/or infrastructure of the farm in manner that both improves water quality, by limiting the discharge of pollutants, and is economically viable. However, they are not designed to address the large P imbalances on farms created by the large discrepancy between P inputs through fertilizer and imported feed, and outputs in animal products, which greatly limits their long-term effectiveness (Sims and Kleinman, 2005; Ghebremichael *et al.*, 2007).

In the State of Vermont, the Clean and Clear program was created to promote the use of BMPs as a P loss reduction strategy, and to maintain a database of BMPs on their website for use in Vermont agriculture (ANR, 2007). The sources of pollution and volume of pollution can vary greatly between farms, and even within farms; therefore, a site-specific plan must be crafted for each farm to ensure that the correct BMPs are employed for maximum water protection (Sims and Kleinman, 2005).

In 1995, the state of Vermont legislature adopted the Accepted Agricultural Practices (AAP) rules, which are controls focused on using improved farming techniques to reduce NPS pollution from farms instead of requiring the building of structures and/or buying equipment (AAM, 2006). The major defining factor of AAPs is that the law governing them requires that the techniques/practices be “feasible” and “cost-effective” without any governmental financial assistance. Whereas, BMPs are focused on correcting farm waste discharges and often involve the construction of structures, such as manure storage facilities (AAM, 2006). A commonly recommended BMP for diffuse non-point source field runoff treatment and a required AAP in Vermont is a 10 foot wide vegetated buffer strip on all fields adjacent to surface waters of the state (AAM, 2006).

1.3.1.2. Vegetated Buffer Strips

Vegetated buffer strips (VBS) work by using a strip of dense vegetation to both anchor soil in place and slow runoff, causing larger sediments containing bound P to settle (Green and Haney, 2005; Dorioz *et al.*, 2006; Hay *et al.*, 2006). In a review of current research Dorioz *et al.* (2006) found VBS to be very efficient at the removal of particulate bound P, with reported removal rates between 50-97%. However, they found that the removal ability for dissolved P forms to be much more variable and less effective with reported rates from -83 to 95 %, with the majority between 20 to 30%.

The mechanisms for removing dissolved forms of P are very different from that of particulate-P, and are mostly achieved by contact with soil particles, which can be limited with surface runoff. The wide variation in removal rates is therefore due to different hydrological conditions and soil types. The negative rates demonstrate the propensity of P to remobilize into overlying surface water (Dorioz *et al.*, 2006). Research has shown that VBS are less effective with concentrated runoff, which can occur during large runoff events such as rainfall and irrigation, because of several site specific factors, such as slope and runoff volumes (Dorioz *et al.*, 2006; Hay *et al.*, 2006). In a study of two existing VBS treating dairy farm wastewater, both were found to have preferential flow patterns, despite the presence of a level lip spreader, meant to evenly distribute the flow. The researchers used a chloride tracer to identify the preferential flow path and found elevated DRP concentrations along this flow path. Although due to the unusually large length of these two VBS (33m and 40m long) most P was still being removed before discharge from the VBS (Kim *et al.*, 2006). This demonstrates the amount of maintenance that VBS require so as to reduce the occurrence of preferential flow patterns and maintaining their P removal efficiency.

Penn and Byrant (2006) tried to maximize the efficiency of grass VBS with the application of alum, gypsum and fly-ash to the soils. It was found that while there were reductions in both DRP and total phosphorus (TP) in runoff, especially with the alum treatments, over time the DRP concentrations in runoff from amended soils increased over that of soils that had not received any amendments. The authors concluded that this is a result of the very high initial soil P concentrations which quickly saturated the P sorption capabilities of the added substances, leading to them leaching P into runoff. In addition, the most effective treatment, alum, resulted in the death of all grasses in one of the studied plots, due to either soil acidification or Al toxicity (Penn and Bryant, 2006).

1.3.1.3. Dietary Phosphorus Reduction

The large surpluses of P on farms are the result of the discrepancy between the amount that enters in animal feed, and the P that is exported within agricultural products. It has been estimated that up to 50% of the imported P will remain on the farm, usually accumulating in the soils of the fields from the application of animal wastes (Sims and Kleinman, 2005). It has been found that dairy farmers often intentionally increase P in feed to 20-25% above recommended levels, in a belief that excess dietary P may increase milk production, but at the least will do no harm (National Dairy Environmental Stewardship Council, 2007). Most feed types contain enough P to meet recommended dietary levels, however farmers still add supplemental mineral P. Therefore by eliminating these supplements from the feed rations much of the excess dietary P can be eliminated (Powell and Satter, 2005; National Dairy Environmental Stewardship Council, 2007). A field trial was performed to compare DRP losses to runoff from the manures from dairy cows fed two different diets, a high (0.49 % P) and a low (0.31 % P) P diet. When equal amounts of manure were spread, the runoff from the high P diet contained 10 times more P than the low. Where the manure was spread keeping the amount of P spread equal (36 lbs. acre), the high P diet resulted in 4 times more DRP in the runoff (Ebeling *et al.*, 2002). Reducing the amount of dietary P from 0.45 % to the recommended level of 0.38 % represents a 15-20% reduction in the amount fed to dairy cows, and resulted in a 20-25% reduction in manure levels of P (Powell and Satter, 2005). Aside from the environmental advantages, reducing supplemental dietary P also has economical benefits for dairy farmers; it is estimated that reductions have saved American farmers saved $30-35 million dollars annually (Powell and Satter, 2005).

1.3.1.4. Field Manure Incorporation

It has been found that if manure is incorporated into fields using either tilling or manure injection into the subsurface the risks of loss of DRP to runoff is reduced (Sharpley *et al.*, 2001). The majority of P lost from agricultural fields usually occurs one or two large storms, therefore planning of manure application to avoid these times of year could reduce losses (Sharpley *et al.*, 2001). However, this is often not possible because it requires large storage capabilities for the manure, and many farmers contract out the spreading of manure, which limits the flexibility in scheduling of applications (Sharpley *et al.*, 2001). In the state of Vermont, it is an AAP for large and medium farms to incorporate manure into fields within 48h of application on fields susceptible to overland flow, unless the field is under conservation tillage management, to reduce the possibility of DRP losses to runoff (AAM, 2006).

Conservation tillage is a BMP which reduces DRP losses to runoff by leaving crop residue on the surface and limiting tilling activity to reduce the soils susceptibility to erosion (Lemunyon and Gross, 2005). The use of conservation tillage is successful at allowing P concentrated at the soil surface to move deeper into the soil profile, and has been found to reduce erosion losses by 30 to 90% (Lemunyon and Gross, 2005). However, this limits the farmer’s ability to apply manure or fertilizer to fields, which is the main disposal method for most farmers. Additionally, the P concentrated at the soil surface can be susceptible to loss during large storms (Lemunyon and Gross, 2005). Cover crops are also used to reduce the loss of soil and soil bound P to erosion; the plants also take soluble P up into their biomass, which can then be recycled into the soil for the next crop with tillage (Lemunyon, 2005).

1.3.2. Point Pollution Sources

1.3.2.1. Farm Storage of Manure

There are many potential point sources (PS) of pollution on farms, the state of Vermont has developed AAPs regulating the management of barnyards and manure storage areas to limit the risk of discharge of manure or other wastes to streams (AAM, 1996). One important AAP banned the spreading of manure on fields between December 15th and April 1st when the ground is generally frozen, and P from field applied manure could easily be transported into surface waters (AAM, 1996). The Vermont winter spreading ban necessitates storage facilities or other approved waste management strategies (including but not limited to; bedded packs, compost, appropriate field stacking) to hold farm waste generated during the winter months. A consequence of farms investing in liquid manure storage structures is the concentration of the farms waste in one location; which can create a significant risk for potential PS pollution if leaks or structural failures occur (Sharpley and Withers, 1994).

Along with Vermont's AAPs and BMPs, the National Resource Conservation Service (NRCS) has developed a list of state specific conservation Practices that provide a framework for farmers to follow to reduce the risks of discharging various pollutants into state surface waters. Many of the topics cover potential PS on farms, including diverting clean stormwater from roofs and barnyards so it does not get contaminated by manure in farm production areas, installation and maintenance of settling pits and manure storage (NRCS, 2008). However, one BMP directed at the PS of dairy milkhouse waste, the installation of VBS, was found to be inadequate in managing the large loads of P found in this waste stream (Jokela *et al.*, 2004).

1.3.3. Alternative Phosphorus Removal Technologies

1.3.3.1. Composting

The EPA (2006) reviewed deep stacking and composting as an alternative technology but determined them “not technically feasible” for CAFOs due to limited technical data on the reliability of fecal coliform reduction and limited applicability. The EPA (2006) listed windrow composting as a non-available technology due to weather dependency, high costs, large land requirements, and risk for runoff.

1.3.3.2. Redistribution of Manure

Researchers have looked at the overlying cause of the P problem (i.e. that some regions face soil P gluts from excess manure spreading, while others have low soil P levels from consistent crop production) and have attempted to send the manure back to the centers of crop production. Several projects have attempted to redistribute manure from areas of high concentration to areas of need, but the economics of transporting large quantities of heavy manure have always severely limited these attempts (Sharpley *et al.*, 2001). Manure was found to be rarely transported more than 10 miles from its point of origin, since it is a very bulky, low-test fertilizer because of its high water content (Sharpley *et al.*, 2001).

1.3.3.3. Aerobic Digestion

The EPA in the Revised National Pollutant Discharge Elimination System (NPDE) Permit Regulation and Effluent Limitation Guidelines for Concentrated Animal Feeding Operations (CAFO) in Response to Water Keepers Decision explored many technologies' feasibility for use on farms in the United States and the extent to which they are being used. Anaerobic digestion is a farm waste treatment system that has received significant attention over the last few years in Vermont. The EPA (2006) found that while this process has many benefits, such as stabilization of the manure, control of methane emissions, reduction of up to 99% of fecal coliform, and production of electricity, it also has many shortcomings. These include the continued need for liquid impoundments for processed wastewater, treated wastewater and stormwater. In addition, fecal coliform was found to re-grow during effluent storage and there was actually no reduction in P, it was simply concentrated into the digested solid products, which would then be land applied. The EPA rejected recommending this technology for all CAFOs for these reasons, and because of a high failure rate and large capital cost associated with the technology (U.S. EPA, 2006; National Dairy Environmental Stewardship Council, 2007).

1.3.3.4. Fluidized Bed Incinerators

Another technology that has been proposed is a fluidized bed incinerator, which is an incinerator that uses a bed of hot sand or other granular material to transfer heat from the source to the waste material (U.S. EPA, 2008). The EPA also rejected fluidized bed incinerators as not "technologically feasible" (U.S. EPA, 2006). They found this technology to have high costs and as a result to be a little used option by US farmers.

1.3.3.5. Chemical Disinfection

Chemical disinfection includes 4 different treatment methods: chemical addition, heat, mechanical and radiation. The chemical addition methods, including chlorination and ozone addition, were found to be not feasible since to be effective, a primary and/or biological treatment would be first required to reduce the total suspended solids (TSS) to below 30-50 mg/L before chemical treatment could occur. These methods also require a highly skilled operator, and very high start up and operational costs. In addition, in chlorination there is a risk of forming chloroform, a known animal carcinogen. The heating method includes lime addition, where high temperature (70°C) and high pH (>12) are maintained for more than 11.5 to 22 hours to kill pathogens. This method was rejected based on large start up and operational costs, scalability of technology, sludge production and large ammonia flushes.

1.3.3.6. Constructed Wetlands

Many investigations over the last 20 years have identified constructed wetlands (CW) as a viable alternative technology for the treatment of wastewater from municipal, industrial, urban-runoff and agricultural sources (Hammer, 1989; Moshiri, 1993; Kadlec and Knight, 1996; DuBowy and Reaves, 1998; Vymazal *et al.*, 1998; Kadlec *et al.*, 2000; Longhurts *et al.*, 2000; Hunt and Poach, 2001). Constructed wetlands have been shown to be extremely efficient in the reduction of biochemical oxygen demand (BOD) (90-98%) and TSS (85-95 %). The removal of total nitrogen (TN) and TP however, has been shown to be less effective (50-90% and 40-90%, respectively) showing a need for improved methods (Hammer, 1989; Moshiri, 1993; Kadlec and Knight, 1996; DuBowy and Reaves, 1998; Vymazal *et al.*, 1998; Kadlec *et al.*, 2000; Longhurts *et al.*, 2000; Hunt and Poach, 2001).

Constructed wetlands are cost effective for the treatment of wastewater (\$180-\$405/m^2 or \$180-270/cow), with costs dependent on the strength of the waste effluent and the topography of the site (McCarthy *et al.*, 1997; Henneck *et al.*, 2001). Energy use is minimal in most systems and maintenance requirements are minimal in comparison to other treatment systems (Kadlec, 1995). Constructed wetlands have been effectively used to treat NPS runoff from urban and agricultural sources (Carleton *et al.*, 2001). In a cold climate such as Vermont, subsurface-flow (SSF) CWs are more appropriate than surface flow (SF) systems for wastewater management for agricultural applications since they are better able to function at lower temperatures (Hill *et al.*, 2000).

Phosphorus is removed from the wastewater effluent through physical, biological and chemical mechanisms, including precipitation, sorption and biological immobilization (Reed *et al.*, 1995; Reddy *et al.*, 2001). Kadlec *et al.* (2000) and Rustige *et al.* (2003) have observed that while there has been considerable research on P removal by SF, the research on SSF wetlands remains comparably minimal. Rustige *et al.* (2003) compiled performance data from 62 sand-based CW in Germany, Austria and Switzerland comparing P retention efficiencies of horizontal and vertical flow systems. This study allows for the comparison of different systems and analysis of the SSF sytems potential for P removal; it also demonstrated how in horizontal flow systems the efficiency of P removal is dependant the loading rate. In vertical flow systems the same relationship was not seen; the authors were also unable to establish a model predicting P removal by SSF wetlands (Rustige *et al.*, 2003).

In surface-flow (SF) constructed wetlands emergent plants and their litter play a vital role in the elimination of pollutants from wastewater by providing the main physical structure in the water column. They provide shading, moderate water flow causing sedimentation, provide oxic habitat, stabilize sediments, build peat deposits, change flow paths and provide habitat for biota (Hammer, 1992; Guardo and Tomasello, 1995; Tanner, 2001). Through phytoremediation, not only do plants remove nutrients from the system, but they also absorb and accumulate metals (Brix, 1994). In SSF systems, the influent flows through a soil media, which provides the physical structure needed for biotic habitat and flow regulation, leaving plants to play a much more indirect role (Tanner, 2001). In SSF systems, the P removal mechanisms are generally either plant uptake, absorption by soil, or precipitation, with plant uptake considered to be a minor contributor, especially at higher loading rates (Kim and Geary, 2001). In a field study using a gravel wetland system, with unplanted cells and cells planted with either *Typha orientalis* or *Schoenoplectus validus* it was found that the plants made no significant contribution to P removal (Mann and Bavor, 1993). In contrast Drizo *et al*. (2008b) found vegetation in a SSF CW system installed in a cold climate to play a much more vital role (Drizo *et al.*, 2008b). They found that over three growing seasons two different wetland cells planted with *Schoenoplectus fluviatilis* (river bulrush) removed 10 and 17.7% of the total added DRP. This may seem negligible, except that it constitutes 50.3 and 36.5% of the total retained DRP by the wetland, showing that the plants were a major mechanism responsible for the removal of DRP (Drizo *et al.*, 2008b).

Research has shown that the substrate of a CW provides the greatest amount of P removal, therefore the choice of material is very important (Drizo *et al.*, 1999; Johansson, 1999b). In CW soils, the adsorption of P is controlled largely by the redox potential, pH and the presence of Ca, Al and Fe minerals in the media (Richardson and Craft, 1993). Typically, as wetland systems mature, the removal efficiency for P declines (Reed *et al.*, 1995; Kadlec and Knight, 1996). Mann and Bavor (1993) performed a two year field study using river gravel and found that the best P removal rates were obtained in the first year of operation, with releases of P from the system common by the second year. Kadlec and Knight (1996) have found that because of these physical restrictions, P removal from wastewater with CWs is a land intensive technology, making it inherently inefficient in comparison to conventional technologies. A solution that has been proposed to extend the functional life of wetland systems is to add a filtration unit outside of the wetland (Johansson and Gustafsson, 2000; Drizo *et al.*, 2002). This unit would contain a substance that strongly adsorbs P from the wastewater, and would be easily exchangeable when a state of saturation is reached.

1.4. Phosphorus Removal Filters

1.4.1. History and Design Considerations

An option that is gaining increasing attention worldwide is that of a P filter containing material with a high P sorption capacity designed for easy replacement of the material when its P retention capabilities begin to decline (Drizo *et al.*, 1999; Drizo *et al.*, 2002; Bourke *et al.*, 2005; Drizo *et al.*, 2006; Westholm, 2006; Weber *et al.*, 2007). A P filter could be easily integrated into a larger wastewater treatment system such as a CW, or could be a utilized individually as a complete stand-alone system, when nutrient reduction is the main goal (Drizo *et al.*, 2006; Weber *et al.*, 2007).

Sorption and precipitation are the principal P removal mechanisms in the filters, and so the selection of a substrate is the most important design parameter, affecting both the longevity and cost-efficiency of the system (Richardson, 1985; Richardson and Craft, 1993; Drizo *et al.*, 1999). The material should be rich in calcium, iron and aluminum, and have appropriate physical properties including particle size, porosity and the hydraulic conductivity, which influence contact time between the wastewater and the substrate as well as decreasing its potential for clogging (Drizo *et al.*, 1999; Johansson, 1999a).

When considering filter design one has to take into account the fact that the principal P removal mechanisms, adsorption and precipitation, are finite processes and that once the filter material becomes saturated with P it will have to be either washed or replaced (Faulkner and Richardson, 1989; Mann, 1997; Drizo *et al.*, 2006). Additionally, the volume, type and homogeneity of the effluents that are being treated can also have large effects on a system's removal efficiency. Phosphorus concentrations in rural, municipal and agricultural effluents (including those from dairy wastes, feedlot runoff, slaughterhouses, and pig farms) are extremely variable, ranging from 15 to 2000 mg P L^{-1}. Moreover, the biological and chemical composition and the volume of wastewater from these sources can also vary to a large extent depending on several variables. These include the size of the community or industry (in a case of rural or municipal effluent treatment), and farm type and size (e.g. dairy cows, chickens or hogs, farm practices and number of animals) (Geary and Moore, 1999; Longhurts *et al.*, 2000).

1.4.1.1. Materials Tested

Several different natural and anthropogenic materials have been examined for their P sorbing abilities including opoka, limestone, blast furnace slag (BF)(Johansson, 1999a;b; Johansson and Gustafsson, 2000; Westholm, 2006), iron meltor slag (IM) (Bourke *et al.*, 2005; Shilton *et al.*, 2006), shale (Drizo *et al.*, 1997), lightweight expanded clay aggregates, burnt oil shale (Drizo *et al.*, 1999) and electric arc furnace (EAF) slag (Drizo *et al.*, 2002; Dorioz *et al.*, 2006; Weber *et al.*, 2007). In all studies, slag, a recyclable co-product from the steel production industry, has been shown to have the most efficient P removal properties (Mann, 1997; Sakadevan and Bavor, 1998; Johansson, 1999b; Johansson and Gustafsson, 2000; Drizo *et al.*, 2002; Bourke *et al.*, 2005; Drizo *et al.*, 2006; Westholm, 2006). Additionally, the anthropogenic substances, such as the expanded clay aggregates, often require large inputs of energy to manufacture, which then brings into question their environmental sustainability, unlike steel slag which is a waste product (Westholm, 2006).

1.4.1.2. Previous Studies on Steel Slag for Phosphorus Removal

The three slag types whose P removal capacities have been investigated most thoroughly are BF, IM and EAF (Drizo *et al.*, 2006; Westholm, 2006; Drizo *et al.*, 2008a). These types each have a very different production methods which results in unique physico-chemical and mineralogical properties (Schmitt, 1997; Bourke *et al.*, 2005). Blast furnace steel slag originates from large integrated steel mills where iron ore is melted using blast furnaces. Iron melter slag is derived from a unique process where iron sand undergoes a direct reduction process in a small, integrated mill in Glenbrook, South Auckland, New Zealand (Bourke *et al.*, 2005). EAF slag is produced by a process where scrap steel is melted in “mini-mills” (Schmitt, 1997).

1.4.1.3. Blast Furnace (BF) Slag

EAF and BF slag differ mainly in the type of furnace that is used for their production. In the production of BF slag, in an integrated mill the iron ore is first reduced to molten steel and then mixed in an oxygen furnace with scrap metal. The extra steps and higher iron ore content required in this process result in a finer quality steel, but also a higher cost steel, making EAF slag a much more economically viable option.

Blast furnace slag has undergone the most extensive investigation of the three slag types, with the first research in Japan over two decades ago (Yamada *et al.*, 1986), it has been researched in many different countries from across the world (Mann and Bavor, 1993; Mann, 1997; Baker *et al.*, 1998; Johansson, 1999a;b; Drizo *et al.*, 2002). These studies have all found BF slag to have very efficient P removal (90-99%) using synthetic P solutions in controlled laboratory studies with various concentrations of P.

1.4.1.4. Iron Melter Slag

Iron melter slag has been extensively tested in field-scale trials in New Zealand (Bourke *et al.*, 2005; Shilton *et al.*, 2006; Pratt *et al.*, 2007a). New Zealand has pioneered the use of slag filter technology, with a filter which has been in continuous operation for over a decade (Shilton *et al.*, 2006). Bourke *et al.* (2005) described the production of IM steel process which uses a unique New Zealand geologic formation that formed as the result of volcanic activity 2.5 million years ago, which deposited in the ocean a large amount of an iron-bearing material called titanomagnetite. This was then ground and transported by the action of the ocean to the west coast of New Zealand's North Island and deposited along the coast in "iron sand" dunes up to 90 meters high. The sands are located at the surface, so no material needs to be removed to access them, and no special equipment excavating is required, which results a relatively low-cost iron product. Magnetic fields are used to separate the iron bearing material, and then it is further sorted and separated. Coal and limestone are added to the iron sands and a direct reduction method then converts the materials to iron in a multi-hearth furnace. An electric melter is then used to produce the steel and steel slag. This process produces a very distinctive slag both chemically and geologically, which gives it many unique performance qualities. It mainly differs in the very low amounts of Ca, and higher Fe, Al and Ti in comparison to EAF and BF slags (Bourke *et al.*, 2005).

New Zealand currently has ten municipal or private P removal filters utilizing IM slag for the treatment of municipal storm water runoff, and agricultural wastewater (Bourke, personal communication 2008). Pratt *et al.* (2007a) recently investigated the mechanisms involved in P removal in filters using IM slag.

1.4.1.5. Electric Arc Furnace (EAF) Steel Slag

Forget (2001) and Drizo *et al.* (2002, 2006) were the first researchers to investigate P removal efficiency by EAF slag produced in Contrecoeur, Quebec. EAF slag has been found to have high P removal efficiency (> 95%) in laboratory based vertical columns fed with synthetic P solutions using various P concentrations (20-400 mg P/L) and in field based vertical columns fed with real diary waste effluent (81% and 79% removal) (Drizo *et al.*, 2006; Weber *et al.*, 2006; Drizo *et al.*, 2008a).

Electric arc furnace slag is the coproduct of the EAF method of steel production, which involves combining recycled steel scrap, lime, coke and MgO (Schmitt, 1997; Australasian Slag Association Inc., 2004). The EAF furnace process utilizes intense heat produced by carbon electrodes to melt steel scrap, iron ore and other additives into molten steel. The EAF process is a much lower cost method than other production techniques because of the energy efficiency of the process and a smaller initial capital investment required for startup. As a result, use of this method has been expanding in North America over the last two decades, and was expected to account for 50% of steel production by 2005 (Schmitt, 1997). The high amount of scrap steel involved in EAF steel production also allows the mills to be located near urban centers. During production, the molten impurities are drawn off, and air cooled, with the base constituents quickly solidifying into oxides (Australasian Slag Association Inc., 2004). This solid slag can then be crushed to any desired grain size and the residual metallic material in the slag is drawn out and recycled back into the process (Australasian Slag Association Inc., 2004). Because of the use of scrap metal, this process results in a slag product with a different composition compared to other steel production methods (Schmitt, 1997).

The Australian Slag association tested samples of EAF slag from Australia and New Zealand and rated them as environmentally inert substances. Low level emissions of chromium, lead, nickel and molybdenum were detected, but these were below the maximum values allowed (Australasian Slag Association Inc., 2006). EAF slag is therefore highly suited to be used as a P removal filter material; since it is derived from a waste material, is comprised mainly of recycled material, and does not leach out any environmentally harmful substances.

1.4.2. Phosphorus Removal Mechanisms Via Steel Slag

To design the most effective and efficient P filters the mechanisms that control P removal must be fully understood. However, very few studies to date have focused on P removal mechanisms (Drizo *et al.*, 2002; Shilton *et al.*, 2006; Westholm, 2006; Pratt *et al.*, 2007b).

1.4.2.1. Phosphorus Removal in Blast Furnace Slag

Despite the otherwise surfeit of investigations on BF slag, there has not been any published field studies and only one investigation of the mechanisms responsible for P removal (Johansson and Gustafsson, 2000; Westholm, 2006). Several published papers have compared two different forms of BF slag, a crystalline form caused by slow cooling of the steel slag and an amorphous form that is created by being quickly cooled with water (Johansson, 1999a;b; Johansson and Gustafsson, 2000). The two types have very different surfaces, the crystalline type is porous, and the amorphous type more solid because the faster cooling process does not allow for crystallization (Johansson, 1999a). Conflicting studies have shown each to be more efficient at P removal. A suggested explanation is that in batch studies with synthetic solutions and longer retention times (24h) the water is able to penetrate the pores of the crystalline BF slag, creating more surface area for removal. With shorter retention times the P solution does not mix into the pores as well, and the amorphous BF slag surface is more advantageous (Johansson, 1999a).

It has been shown that in BF slag the P removal is happening at alkaline conditions (pH > 9) with large amounts of Ca present in solution. With BF slag precipitation reactions, mainly the formation of hydroxyapatite (HAP) ($Ca_5(PO_4)_3OH$), have been found to be the dominant mechanism for P removal (Johansson, 1999b; Johansson and Gustafsson, 2000). Johansson and Gustafsson (2000) used the equilibrium model MINTEQA2/PRODEFA2 to calculate the species of Ca and P expected in solutions containing BF slag. They concluded that a decrease in Ca in solution demonstrates that precipitation rather than adsorption is the driving mechanism in P removal. The graphs of ion activity calculated by the model also gave insight into the precipitate that might form based on solubility lines, clearly showing that all Ca-P phases except HAP were unlikely to form (Johansson and Gustafsson, 2000). However, all Ca sources are not created equal. In a column study, BF slag was found to remove significantly more P than limestone and opoka, although all three substances contain very high amounts of Ca (Johansson, 1999b). This results from the Ca in limestone and opoka being mainly in the form of $CaCO_3$, which is much less reactive than other forms, such as CaO, the prevalent form in steel slag (Johansson, 1999b).

1.4.2.2. Phosphorus Removal in Iron Melter Slag

Pratt *et al.* (2007a;b) described P removal in filters using IM steel slag. They investigated the P removal mechanisms in both spent (material from a filter that has been in constant operation for 11 years) and fresh IM slag in New Zealand. Using several methods, including scanning electron microscopy (SEM), electron dispersive spectrometry (EDS), X-ray diffraction (XRD) and chemical fractionation analytical techniques, they identified the three most prevalent mechanisms for the removal of P as:

1. Adsorption: amorphous Fe oxides/oxyhydroxides in the porous matrix and surface of IM slag.
2. Precipitation: Stable precipitates can form from Fe or Ca on the surface of the IM slag.
3. Organic sequestration: An organic rich resin forms on the surface of the slag, likely comprised of degradation resistant humic materials.

Ca has been shown to be very important in the removal of P with EAF and BF slag filter systems, whereas in IM slag filters Fe oxides have been identified as the dominant removal mechanism (Pratt *et al.*, 2007a; Pratt *et al.*, 2007b). Additionally, they stated that Ca oxides are unlikely to substantially influence the P removal as in IM slag Ca is present as relatively insoluble, non-P adsorbing silicates (Pratt *et al.*, 2007a). One important property of IM slag is that does not induce high pH in wastewater as EAF and BF slag do, which favors Ca-P precipitation (Johansson, 1999a; Drizo *et al.*, 2002; Pratt *et al.*, 2007a).

In another study, Pratt *et al.* (2007b) found the removal of P to be strongly regulated by both pH and Eh; the greatest removal ability was found to be near neutral pH (6.7) and redox conditions at oxidizing Eh (+300 mV) levels. At low pH (4), especially when reducing conditions (-400 mV) are created, the Fe oxides in the IM liberated P into solution. Fe oxides have a high inorganic P retention ability and the various oxide species dissociate at different Eh levels (Olila and Reddy, 1997; Johnson and Loeppert, 2006). Phosphoric acid is trivalent with four different forms; at low pH there is a low concentration of multivalent ions, which results in less adsorption to Fe oxides (Pratt *et al.*, 2007b). Additionally, Pratt *et al.* (2007b) found that at high pH (9.1) P is liberated from IM slag into solution, because hydroxide ions in solution can out-compete P for Fe oxide binding sites. The increasingly negatively charged surface of the Fe oxide is also less able to adsorb the P form which is most abundant at high pH, PO_4^{3-}. This research has demonstrated that IM slag is most efficient with wastewater that has a near neutral pH and has oxidizing redox conditions. This is an important design consideration because high organic content and BOD of wastewater generally results in reducing conditions (Pratt *et al.*, 2007b).

Pratt *et al.* (2007a) used semiquantitative energy dispersive spectrometry (EDS) in a analysis of exhausted IM slag from a wastewater treatment facility in Waiuku, New Zealand, and found large amounts of amorphous Fe oxide/oxyhydroxide with little associated P. This represents a drastic reduction in efficiency for the IM slag filters, since the Fe oxide/oxyhydroxides should be the primary P removal mechanism. It is thought that this was caused by the formation of an organic P resin layer on the surface of the slag, inhibiting of the adsorption of P onto the slag surface (Pratt *et al.*, 2007a). In contrast to what has been reported by Pratt *et al.* (2007a), chemical fractionation analyses by Drizo *et al.* (2008a) have shown Ca and Al to be responsible for more P removal than Fe oxides/hydroxides in IM slag. The authors found the presence of HAP ($Ca_5(PO_4)_3(OH,$

F, Cl)) in fresh IM slag samples after a three week resting period (Drizo *et al.*, 2008a). The differences found may be the result of a different extraction method used by Drizo *et al.* (2008a) ($NaHCO_3$ for Fe and NaOH for Al fractions) than by Pratt *et al.* (2007a) (citrate-dihtonite for both Fe & Al fractions) for the extraction of P bound to of Fe and Al fractions. However, in IM slag, there is significantly higher Al content than Fe, with Drizo *et al.* (2008a) finding an almost ten fold difference, and Pratt *et al.* (2007a) finding four fold higher Al levels than Fe in both fresh and exhausted iron steel slag porous matrix.

Drizo *et al.* (2008a) suggested that the differences in the reported mineralogical composition of spent and fresh IM slag samples in their study from Pratt et al. (2007b) may have been the result of several factors including: differences in P loading during the studies, different sampling locations for spent slag in the Waiuku filter bed, variations in production of fresh slag material, and weathering that occurred due to different lengths of storage in at the steel mill. Additionally, Drizo *et al.* (2008a) performed mineralogical analyses on the entire slag sample, whereas Pratt *et al.* (2007b) separated the surface coating of the slag from the porous matrix and conducted the analyses separately. This shows the multitude of factors, aside from material type, that can affect the mechanisms responsible for P removal in steel slag. These include the origin of the wastewater, the hydraulic loading rates (Drizo *et al.*, 2006), and the amount of weathering of the slag (time the material spent exposed to the atmosphere in stock piles prior to being used in a filter) (Pratt *et al.*, 2007a).

Iron melter steel slag has been shown to have a much smaller capacity for P retention then EAF slag. Drizo *et al.* (2008a) compared the removal efficiencies of IM slag and two EAF slags from different steel mills, one from Quebec, CA and another from Glenbrook steel mill, NZ. The Quebec EAF slag has been shown to retain a significantly higher amount of P than IM slag and even than the New Zealand EAF slag. In a 128 day column study using a synthetic P solution, the Quebec EAF slag had a P removal efficiency of 74.1% (0.85 g P kg^{-1} slag added and 0.63 g P kg^{-1} slag retained) and the IM slag had only 53.7% P removal efficiency (1.08 g P kg^{-1} slag added and 0.58 g P kg^{-1} slag retained), an almost 1.5 times lower efficiency than the EAF slag (Drizo *et al.*, 2008a).

1.4.2.3. Phosphorus Removal in Electric Arc Furnace Slag

There are several published studies investigating the use of EAF slag for P removal from synthetic P solutions and real dairy effluent; however, little research is available investigating the actual mechanisms responsible for the removal of P by EAF slag (Drizo *et al.*, 2002; Drizo *et al.*, 2006; Weber, 2006; Weber *et al.*, 2007). Table 1-1 shows that EAF slag is primarily comprised of Fe and Ca oxides (35% and 30% respectively), both of which play very important roles in the P cycle in soils (Drizo *et al.*, 2008a). In a column study using a synthetic P solution and a short HRT (8.3h), adsorption to the EAF slag surface was found to be the predominate P removal process, removing a total of 1.4 mg P g^{-1} EAF slag out of a total of 75.2 mg g^{-1} EAF slag added (Drizo *et al.*, 2002). Drizo *et al.,* (2002) sealed the columns to limit the CO_2 inputs into the system, which might promote the formation of $CaCO_3$, and utilized XRD to investigate formation of HAP. Despite the pH of the system being within a range that would promote the formation of HAP (9.5 – 10.5), a white deposit on the slag surface that would indicate its formation was not seen (Drizo *et al.*, 2002). In a later column study also using a synthetic P solution but with a longer HRT (12h), precipitation was found to increase the P removal efficiency of the filter to 2.4 mg P g^{-1} EAF slag, a 42% increase in removal over earlier studies, for a total removal of 80% of added P (Drizo *et al.*, 2006). The longer HRT allowed for precipitation processes to occur, with XRD analysis confirming that Ca-P species such as HAP were the primary mechanism that caused the increase in P removal (Drizo *et al.*, 2006).

Table 1-1: Chemical composition of the EAF steel slag produced in Contrecoeur, Quebec

Oxides (%)	EAF steel slag[1]
CaO	30.4
SiO_2	13.7
Fe_2O_3	34.7
Al_2O_3	4.67
MgO	13.1
MnO	1.30
TiO_2	0.68
K_2O	<0.01
Na_2O	<0.01
S	*
P_2O_5	0.32
V_2O_5	*
Cr_2O_3	0.32
Total	99.2

[1] Source: Drizo *et al.* (2008a)
***constituents not specified**

1.4.3. Parameters that affect Filters Performance

1.4.3.1. Hydraulic Residence Time

The HRT of an EAF slag filter is one of the most important variables controlling its efficiency of P removal (Johansson, 1999a; Drizo *et al.*, 2006; Weber *et al.*, 2006). In a column study using real dairy effluent, the HRT of the wastewater was used to increase the lifetime efficiency of the filter. After 104 days of operation at 12h HRT, the DRP removal efficiency was found to have dropped from 91 to 78%, the HRT was then increased to 24h, a HRT that has been found to be the most effective in EAF slag (Forget, 2001; Drizo *et al.*, 2006; Weber *et al.*, 2007). With the increase in HRT from 12 to 24h, it was found that high DRP was maintained, about 72% removal efficiency (Weber *et al.*, 2007). Vallet (2000) investigated EAF slag P reduction efficiency from a synthetic effluent at short HRT, ranging from 0.72 to 9.6h. He found that EAF steel slag columns fed at higher HRT (4.9 and 9.6h) had eight-ten fold longer lifespans compared to columns operating at 0.72 and 0.114 h HRT (Valet, 2000). Understanding the behavior and P reduction efficiency of EAF slag filters at short HRT is essential for the determination of their longevity and feasibility for use in diffuse pollution treatment (Drizo *et al.*, 2008a).

1.4.3.2. Series Filter Design

It has been proposed by several researchers that a multiple cell design, made up of several filters linked in series is more beneficial than a single large filter (Drizo *et al.*, 2002). This design can be used to reduce the effects of clogging and short circuiting that are often found in filters (Drizo *et al.*, 2002). A series design of EAF slag filters could also be used to increase the longevity of the filter unit by more efficiently taking advantage of the observed ability to rejuvenate P removal efficiency (Drizo *et al.*, 2002). Drizo *et al.* (2002) and Drizo and Picard (2006) proposed that a multiple stage EAF filter unit would allow for the ability to manipulate the effluent flow between stages, providing for drying and wetting cycles to maximize the P removal ability of the entire unit (Drizo and Picard, 2006).

1.4.3.3. Filter Longevity

P retention capacity of a filter, which is defined as the maximum amount of P per mass or volume of filter media that can be removed, is a crucial variable as it allows for the estimation of a filter's life span (Drizo *et al.*, 1999; Drizo *et al.*, 2002; Shilton *et al.*, 2006). The majority of research on the total load removal capabilities of both EAF and BF slag has been performed in controlled lab environments with synthetic solutions. Drizo *et al.* (2002; 2006) has proposed that for full-scale systems treating real effluents that these P removal values should be reduced by 50% because of the presence of organic matter and suspended solids, which carry large loads of total phosphorus (TP) bound to organic matter in the waste stream.

Generally in field studies of EAF and BF slag filters the limiting factor for the life of a filter has not been when the maximum amount of P possible has been removed, but when the filters clog (Weber, 2006; Weber *et al.*, 2007).

1.4.4. Rejuvenation of Phosphorus Retention Capacity

More than three decades ago it was discovered that some soils have an ability to rejuvenate P sorption sites after P saturation has already been achieved, if they are drained and rested before wetting again with a P solution (Sawhney and Hill, 1975). Drizo *et al.* (2002) was the first to test this property in P filters with a column study of EAF slag using a synthetic P solution, finding that it demonstrated properties of rejuvenation after P saturation. After the EAF slag had became saturated with P, it was dried and rested for 4 weeks. The filter was then restarted, and was found to have regained 74% of its prior ability to adsorb P. In field trials utilizing real dairy waste effluent a similar trend has been observed (Drizo *et al.*, 2008a).

Drizo *et al.* (2008a) recently revisited the phenomenon of rejuvenation to identify whether it would occur in EAF slag when fed with “real-world” dairy effluent. They also assessed the effects of when the resting period is initiated and duration on the rejuvenation process in EAF slag and investigated whether rejuvenation occurs in other types of steel slag material. Additionally, the effects of material particle size on P retention and rejuvenation in two different steel slag material types was also investigated. The study identified that by initiating a draining and resting period, the EAF slag is able to regain a percentage of its original P retention capacity through rejuvenation, resulting in greater overall treatment efficiency and prolonging the life span of the filters. In addition, draining and resting the filter before it had reached P saturation resulted in a significantly higher ($p < 0.01$) overall DRP removal efficiency, when compared to the draining and resting after the filter had reached P saturation (Drizo *et al.*, 2008a).

The same study found that P rejuvenation does not occur in IM slag material from New Zealand, which is an extremely important finding for the engineering and design of P filters using IM slag (Drizo *et al.*, 2008a). Since 2002, 15 large-scale IM slag systems have been constructed in New Zealand for the treatment of dairy pond effluents, some of which were designed to "exploit" the rejuvenation process, which had not been previously tested in this material. Consequently, some of these systems have reached P saturation much quicker than predicted by the designers (Bourke *et al.*, 2005); Bourke, personal communication 2008). Drizo *et al.* (2008a) also reported further evidence showing great variation the in performance between different slags, differences in the materials' P adsorptive capacities and, when applicable, the rejuvenation potential of the different slags. Because of these differences, the properties of slags produced from each individual steel mill should be determined prior to their commercial use (Drizo *et al.*, 2008a).

To date, the mechanisms responsible for the rejuvenation of the P adsorption capacity in EAF slag are not understood. Drizo *et al.* (2002) suggested that the rejuvenation of EAF slag filters P removal ability may be initiated by elevated pH levels, causing Ca, Fe and other minerals and ions to diffuse out of the solid and come into supersaturation with the EAF slag. These minerals would then bind into the EAF slags porous surfaces, creating new sites for P adsorption, precipitation and crystallization reactions to occur. Rejuvenation of EAF slag is an important attribute of this material, which needs to be considered in the design and management of P removal systems in order to maximize the lifespan and the cost efficiency of the filters (Drizo *et al.*, 2008a).

1.4.5. Field Studies

1.4.5.1. Phosphorus Removal Efficiency Over Time

Despite the number of studies that have been published showing the P removal abilities of IM, BF and EAF slags, most are lab-based column or batch studies, using synthetic P effluent (Johansson, 1999a; Drizo *et al.*, 2002; Drizo *et al.*, 2006; Hedström and Rastas, 2006). The lack of field based studies utilizing real waste effluent streams has limited the development of full scale slag system (Drizo *et al.*, 2002; Westholm, 2006). Hedström and Rastas (2006) found that BF slag systems using real wastewater effluent had significantly lower P removal abilities than comparable systems using synthetic P solutions. This may be the result of competing ions in solution or the presence of microorganisms that form bio-films on the slag surface, limiting the contact of the slag with solution (Drizo *et al.*, 2006; Hedström and Rastas, 2006). However, in two recent column studies using real waste effluent from a dairy farm, EAF slag was found to have retained higher amounts of P than was estimated in lab studies with synthetic solutions (Drizo *et al.*, 2002; Weber *et al.*, 2007; Drizo *et al.*, 2008a). This contradicts most all published literature about P filter performance using real waste effluents, and shows how with EAF slag filters the P retention can be maximized with proper management techniques, such as limiting TSS and OM additions with pretreatment (Weber *et al.*, 2007; Drizo *et al.*, 2008a).

1.4.5.2. Clogging of Systems

A design limitation that has become apparent in field studies is premature clogging of systems by solids (Hedström and Rastas, 2006; Weber *et al.*, 2007). Weber *et al.* (2007) compared the efficiency of EAF slag filters where treating dairy effluent with or without pretreatment by CWS. The filters without pretreatment received 1.3 fold higher DRP than the filters with pretreatment, during the same period, and still maintained a high amount of P removal, averaging 81% (1.9g P/kg added, 1.5g P/kg retained) (Weber *et al.*, 2007). The two filters without pretreatment however clogged at 155 and 169 days, running for a total of 180 days, whereas the filters with pretreatment ran successfully for 259 days. The clogging was linked to much higher TSS (7 fold higher) and organic matter (BOD) (3.5 fold higher) loading in the untreated effluent (Weber *et al.*, 2007).

To avoid clogging of P filters, efficient pretreatment must be used to reduce TSS concentrations in wastewater (Hedström and Rastas, 2006; Weber *et al.*, 2007). Additionally, a tradeoff has to occur with the efficiency of the filter, to reduce the risk of clogging, larger slag particles should be used. This has a negative affect on the P removal efficiency because the larger particle size results in a smaller overall slag surface area and increased hydraulic conductivity shortening slag-wastewater contact time, both vital variables for P removal (Johansson, 1999a). In a small column study comparing the P removal efficiency of two different EAF slag sizes (5-10mm & 10-20mm), the smaller size slag particles achieved higher P removal efficiency (74.1%) as expected, compared with the efficiency (62.5%) achieved in the larger size particles (Drizo *et al.*, 2008a). There have also been reports of cementing in BF slag filters, where the slag particles are bound together in a very strong and resistant structure; it is thought that this is the result of hydratisation of the crystalline slag surface (Johansson, 1999a).

1.5. Phosphorus Recovery from Filters

1.5.1. Phosphorus Stripping (or Recovery) from EAF Slag

The historical source of P for fertilizers has been from the mining of phosphate-bearing rocks located in Florida, Africa and Asia. This is a limited resource, and therefore in some cases less efficiently accessed, and contaminated sources of P are starting to be utilized (Isherwood, 2000). This shows the need to be able to recycle P from agricultural sources back into the environment, without as much of a time and travel distance restriction that exists with manure. Many different methods have been proposed to recover P, however most result in a P enriched complex that is not reusable as a fertilizer, since other, often toxic, waste products are removed in conjunction or it is a non-biologically available form (de-Bashan and Bashan, 2004). An ideal situation for P utilization is when the nutrient is bound to the substrate in a form that is largely bioavailable to plants, allowing P to be recycled as a fertilizer.

1.5.2. Potential of Steel Slag Re-use as a Fertilizer

The potential of re-using industrial by-products such as BF steel slag as a fertilizer was first discussed almost 100 years ago (New York Times, 1918). White (1928) was the first scientist to publish a preliminary report on the agricultural value of BF slag with research at Pennsylvania State College's School of Agriculture and Experimental Station. The researchers stated that BF slag contains silicates of calcium and magnesium and that it could be utilized as a replacement for lime as an agricultural source of calcium. In field trials, 13 of the 14 crops investigated showed greater yields with a 20-mesh size agricultural slag than with limestone, however granulated BF slag did not show greater yields than limestone (White, 1928). Additionally, White (1928) proposed that other mineral constituents of the BF slag might also promote increased plant growth. In 1998 the National Slag association published a report detailing extensive testing of 45 different EAF slag producers from across the US and Canada. They performed a detailed risk assessment of the materials for possible environmental and human health risks that might be caused from all possible uses of EAF slag from agricultural amendment to road fill. The results showed that the metals in the slag do not readily leach to the environment, and pose no risk to terrestrial or aquatic plants and animals (Wintenborn and Green, 1998). More recently Reclime®, a product from BF steel slag, has been approved in 14 states for agricultural use as a soil amendment (Recmix, 2007). Over the last 11 years Reclime® has been applied to over 100,000 acres in the US, and in field trials has shown increased yields over other limestone soil amendment products (Recmix, 2007).

The above studies have only discussed the use of virgin BF slag and the beneficial affects of its natural constituents. However after use as a P filter, steel slag would also have a large amount of P sorbed to the material, increasing its value as a fertilizer. The potential of steel slag as a P fertilizer has been investigated only in few studies, and has shown a large discrepancy in results. In all plant yield studies done, BF slag has been shown to be a very good source of P for plants, especially in comparison to burned opoka, another commonly studied substrate for P removal filters (Hylander *et al.*, 1999; Hylander and Simán, 2001; Hylander *et al.*, 2006). However in the several studies that used chemical extraction techniques to look at plant available P in different medias, BF slag often has shown little of the adsorbed P to be readily soluble in comparison to burned opoka (Johansson and Hylander, 1998; Johansson and Gustafsson, 2000).

Johansson and Hylander (1998) used chemical extractions to investigate 10 different materials that have been the focus of prior P retention studies, including 3 different types of crystalline BF slag, 2 types of amorphous BF slag, a natural opoka (a calcium rich mineral), a burned opoka, and lime, examining the plant availability of the sorbed P. Burned opoka and the 5 BF slag types had the greatest P removal rates (68-99.6%). Burned opoka and the coarser crystalline slag type both had high amounts of plant available P (15-40%) with lime showing the greatest percentage (40-60%). The high percentage of P recovered from the lime is explained by the fact that it has the lowest levels of Al, and high levels of Ca, so the P was more readily bound into Ca-P complexes which are more bioavailable than Al-P compounds (Johansson and Hylander, 1998). Johansson and Hylander (1998) hypothesized that the coarser crystalline slag had greater bioavailability than the other types of slag because that slag type was significantly newer than the others, over 1 year, therefore its sorption sites were fresher. Johansson and

Gustafsson (2000) used the MINTEQA2/PRODEFA2 model to determine that HAP is the dominate precipitate in BF slag filters, and stated that due to the low solubility of HAP, P saturated BF slag would not make a suitable fertilizer source.

However, in several pot studies using barley plants to test the suitability of BF slag as a fertilizer, it has been shown to be a better fertilizer source than the other tested materials. Blast furnace slag was seen to have a much higher yield response than burned opoka in all of these, and no incidence of Mn deficit as was seen in BF slag in other treatments (Hylander *et al.*, 1999; Hylander and Simán, 2001; Hylander *et al.*, 2006). The extraction method used by many studies was found to have drastically overestimated the actual plant availability of P in the materials tested (Hylander and Simán, 2001). Hylander and Siman (2001) concluded that P saturated BF slag might show such good results in the pot trials because the sorbed P solublizes at a rate commensurate with plant needs, and could be applied to agricultural fields as a slow release P source.

To be a sustainable solution for wastewater P treatment, the full life cycle of the EAF slag material must be taken into account, including the disposal after it becomes saturated with P (Weber *et al.*, 2007). To date, there is no published research investigating the application of EAF slag in field trials to analyze the availability of adsorbed P.

1.6. Research Hypothesis and Objectives

Prior to this research, there has been only one published study investigating the potential of EAF slag filters for dairy effluent treatment, described in section 4.6. Although in this study EAF slag filters achieved high P removal efficiency, they were housed in a specially designed research facility which was heated during the cold winter months.

Therefore, the major goal of this research is to further investigate the viability of EAF slag filters as a nutrient management practice in Vermont and other cold climate states without supplementing the temperature. Also, to assess its potential to be transferred to the agricultural sectors at regional and national scales.

The hypotheses of this research are that:

1) EAF slag filters will be efficient in reducing P during cold and sub-freezing temperatures.
2) That a series design utilizing an alternate feeding and resting will result in higher P removal efficiency and an extended life span of the filters.
3) Phosphorus saturated EAF slag material can be re-used as a soil amendment or slow release P fertilizer for plants.
4) P adsorption by Fe oxides and precipitation with Ca represent the principal P removal mechanisms in EAF slag.

The objectives of this research were:

1) To construct two filters in series (2 replicates each) at the Constructed Wetlands Research Center (CWRC) and investigate their efficiency in P, TSS and metals reduction during cold and sub-freezing temperatures.
2) To investigate P-saturated EAF slag potential as a soil amendment and plant fertilizer.
3) To assess P desorption to surface runoff from P saturated slag.
4) To elucidate principal P removal mechanisms within EAF slag filters when used for dairy effluent treatment.

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Chapter 2: EAF Steel Slag Filters for Phosphorus Removal from Milk Parlor Effluent in Cold Climates: the Effects of Solids Loading, Alternate Feeding Regimes and In-Series Design

Simon Bird
Department of Plant and Soil Science, University of Vermont, Hills Agricultural Building, 105 Carrigan Drive, Burlington, VT 05405

Abstract

Electric arc furnace (EAF) steel slag filters were investigated for their efficiency for the reduction of phosphorus (P) from wastewater on a dairy farm in Vermont. The primary objective for this study was to test the filters performance in P removal from high strength wastewater associated with the milking operations on a Vermont dairy farm at subzero temperatures. Other research objectives were to: i) examine the effects of total suspended solids (TSS) daily mass loading rates on the clogging, treatment performance and life span of P removal filters ii) investigate the use of alternating the feeding and resting periods of EAF steel slag to maximize the rejuvenation of TSS, dissolved reactive phosphorus (DRP) and total phosphorus (TP) removal efficiencies and increase the life span of the filter system.

Two replicate EAF steel slag filter systems comprised of two filters each (0.242 m^3 volume each) connected in series, were built and put in operation in the winter of 2006. During the first feeding period, the filters were fed at the hydraulic retention time (HRT) of 123 cm d^{-1}, and a TSS daily mass loading rates (LR) of 0.93 ± 0.08 g $kg^{-1}d^{-1}$ and DRP daily mass LR of 0.013 ± 0.001 g $kg^{-1}d^{-1}$. The first filter in-series achieved an average DRP removal efficiency of 42.94%; with the second filter in-series reducing the DRP by additional 66.14%, resulting in an overall DRP removal efficiency for the series of 76.11%. After only 52 days the filters became clogged with biofilm due to the high TSS LR, and the filters were drained and left to rest for a period of 12 weeks.

In the 2nd feeding period the filters were fed at the same HRT, however the TSS daily mass LR was reduced to 0.244 ± 0.0001 g $kg^{-1}d^{-1}$ and the DRP daily mass LR to 0.010 ± 0.001 g $kg^{-1}d^{-1}$. The first filter in-series had an average DRP removal efficiency of 39.68 %; the second filter in series 37.89 % resulting in total efficiency of 55.98 %. This represents a 16.43, 56.95 and 73.56 % increase in TSS, DRP and TP removal efficiencies, respectively, by the first filter in-series over the 1st period, and the life span of the system was extended by 3.25 fold (from 52 to 169 d). These results suggest that addition of a filter unit in-series design increased overall system's efficiency by 36%. Based on this research, we recommend alternate feeding and resting cycles and in-series design to be integrated in the design of EAF steel slag filter systems for highly concentrated agricultural effluents in cold climates.

Keywords

Phosphorus removal, concentrated waste influent, steel slag filters, cold climate, total suspended solids (TSS), dissolved reactive phosphorus (DRP)

Introduction

Over the past decade the eutrophication of surface waters caused by excess phosphorus (P) pollution from agricultural operations has become one of the major water quality issues worldwide (U.S. EPA, 2000; Ribaudo, 2003). An increase in water pollution associated with agricultural non-point source runoff has resulted in a more concerted national effort to enforce water quality regulations throughout the United States (USA) (Wise, 1998; U.S. EPA, 2001; Ribaudo, 2003). Lake Champlain is a large lake in the northeast of the USA that has become severely impacted by excess P loading, a large part of which is the result of agricultural runoff (LCBP, 2006). In 2003 the US EPA revised the national Concentrated Animal Feeding Operations (CAFOs) rules to define which farms are required to obtain a National Pollutant Discharge Elimination System (NPDES) Permit (U.S. EPA, 2003;2006). The result of these revisions was the determination that all medium and large CAFOs are required to obtain a NPDES permit if they have any discharge of agricultural wastewater to any waters of the state (U.S. EPA, 2006). An agricultural producer can only be exempted from needing a federal NPDES permit by demonstrating that there are no discharges of agricultural wastewaters from production areas to waters of the state, and that the farm is operating under a state approved nutrient management plan (NMP) (U.S. EPA, 2006). However, many farms will have difficulty preventing these discharges of high P effluent from their production areas. Alternative wastewater management systems are needed to provide relatively economical solutions to treat these wastewaters and prevent the discharge of P to surface waters. In Vermont, the Total Maximum Daily Load (TMDL) has been established to reduce agricultural P loading of surface to acceptable levels (ANR and DEC, 1997;2002). This regulation additionally requires all CAFOs to implement waste storage or treatment systems to prevent discharges from production areas and ensure that the farm is in compliance with state and federal regulations (AAM, 2006; U.S. EPA, 2006).

These newly revised federal CAFO and Vermont state water quality rules will severely impact Vermont's agricultural producers, who, as a result of the state's mountainous topography and wet climate, have much less arable land available for animal waste disposal in comparison to other USA agricultural communities (Meeks, 1991). The financial burden that a family farm may have to bear to implement these waste management practices may strain the already tight economics of farming in Vermont, resulting in increased loses of farms. These regulations create difficult goals for many farms in Vermont, which do not currently have access to solutions that are affordable and that will bring them into compliance with state and federal water quality regulations.

One of the most common methods to reduce discharges of P from farms in Vermont is the use of best management practices (BMP) (Pierson *et al.*, 2001; Jokela *et al.*, 2004; Sharpley *et al.*, 2006). Jokela *et al.* (2004) demonstrated that if all available BMPs and Accepted Agricultural Practices (AAPs) were implemented on all the farms in the

Vermont and Southeastern Québec (Canada) portion of the Lake Champlain watershed, P loads to surface waters would still exceed the twenty year target set by the U.S. EPA (LCBP, 2003; Jokela *et al.*, 2004). Therefore, there is a great need to find new alternative methods that are capable of efficiently reducing P from both point and non-point pollution sources of wastewater.

The first field test of electric arc furnace (EAF) steel slag filters was conducted at the University of Vermont (UVM) Constructed Wetlands Research Center (CWRC), showing them to be an efficient method to reduce P from a dairy farm effluent both as an upgrade unit to an existing constructed wetland (CW) and as a 'stand alone' independent filter system (Weber *et al.*, 2007). Weber *et al*. (2007) reported average dissolved reactive phosphorus (DRP) removal efficiency of 75% for an EAF steel slag filter used as an upgrade to an existing constructed wetland and 72% for a stand-alone filter. However, the filters were located indoors in the UVM Phosphorus Research Facility, with a controlled environment that was heated during winter months to room temperature (20^{o} C), and therefore not representative of on-farm conditions that an EAF steel slag filter would encounter in Vermont.

To assess the viability of EAF steel slag filters application on dairy farms in Vermont and other cold climate areas, the primary objective in this study was to evaluate the performance of EAF steel slag filters for the removal of P from a high-strength milk parlor wastewater at subzero temperatures. Other objectives were to: i) investigate the effects of TSS daily mass loading rates on the premature clogging of P filters, P removal performance and life span of filter system, ii) test the effects of alternating feeding and resting periods on EAF steel slag filters TSS, DRP and TP removal efficiencies and the filter systems life span.

Methods

Description of Research Site and Wastewater Effluent

This experiment was conducted at the UVM CWRC, which was constructed to treat wastewater from the UVM Paul Miller Dairy farm. The filters were constructed to treat the wastewater effluents from both the milk parlor and milk house. Milk parlor effluent consists of milking equipment and other associated equipment wash water, rejected milk and animal waste. The milk house wastewater contains wash water and detergents associated with cleaning of the milk storage equipment. At the UVM dairy farm these effluents combined amount to 0.07 – 0.130 m^3 d^{-1} on average (Munoz, 2006). Munoz (2006) recently provided a list of the medications, chemicals and detergents that on average may be present in the milking operation wastewater. Wastewater from the milking operations is first stored in an underground 3.8 m^3 (1000 gallon) settling tank located outside the dairy parlor facility, where it undergoes anaerobic digestion. The settling tank effluent is then gravity fed through an underground pipe (0.20 m diameter) to an 11.4 m^3 (3,000 gallon) underground holding tank (Munoz *et al.*, 2006).

EAF steel slag filters construction

The construction of EAF steel slag filters at the UVM CWRC took place in November 2005 (Bird and Drizo, 2006). Two 1.2 m x 2.4 m x 1.2 m enclosures (Quazite®, Strongewell, Lenoir City, TN) were buried in the ground next to the 11.35 m^3 underground holding tank. Two 0.242 m^3 (55 gallon) polypropylene drums (US Plastics, Lima, OH) were placed in each enclosure, making two replicates of two filters each connected in series (F1 & F2 and F1' & F2'). The area around the filters was filled in with gravel to provide support for the barrels and insulation, with additional foam insulation placed around the outside of the enclosures and on the undersides of the enclosures lids. Each filter had a baffle installed in the middle, extending from the top of the column to 0.15 m from the bottom, creating the designed flow path (Figure 2-1). The influent for the filters was pulled directly from the CWRC milk house waste holding tank using a pump (Zoeller Z80 pump) controlled by a timer (Fisher Scientific).

The filters were filled with EAF steel slag (Multiserve, Quebec, Canada). Drizo *et al.* (2008) recently provided a description of the chemical composition of this material. Based on the previous research conducted at the UVM-CWRC (Weber *et al.*, 2007; Drizo *et al.*, 2008) two different particle sizes of EAF steel slag material were employed: 5-10 mm and 10-20 mm, with the larger size used at the inlets to reduce the incidence of clogging. Slag particles were weighed and added to the filters in layers approximately 0.05 m height. Each layer was leveled and compacted, and the remaining space in the filter height recorded (Drizo *et al.*, 2006; Weber *et al.*, 2007). The average weight of the 5-10 mm EAF slag aggregates in each of the four filters was 340.6 kg, while the average weight of the 10-20 mm slag material aggregates was 74.13 kg, representing 81.9 and 18.1% of total filter weight, respectively. The theoretical pore volume of each filter was first estimated using known values from previous filter experiments. In January 2006, the filters were filled with fresh water and the exact pore volume of each filter was recorded. The average filter pore volume was 87.1 L, which was very close to the estimated theoretical volume (85.9 L). To achieve the desired hydraulic retention time (HRT) of 18 h and to reduce the risk of freezing, each filter received 131 L of milk parlor wastewater per day spread over 6 separate pump cycles (Zoeller Z80 pump) lasting 28 minutes (flow rate of 1.553 L min^{-1}) and controlled by a timer (Fisher Scientific). The filters had a cross sectional area of 0.106 m^{2}, resulting in a hydraulic loading rate (daily flow to the filters divided by the cross sectional surface area of the filter) of 123 cm day^{-1}.

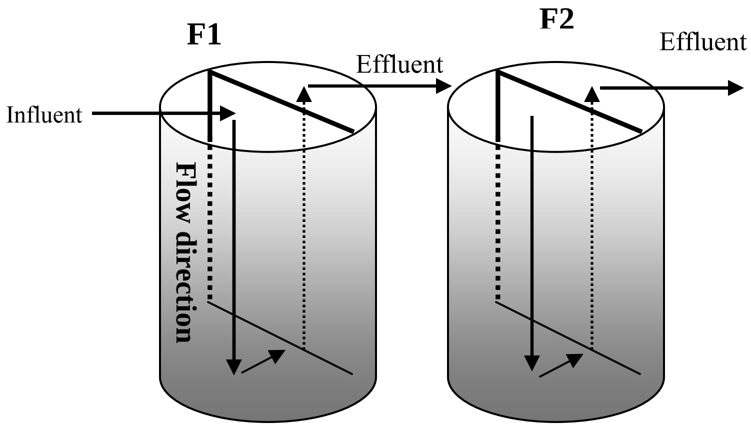

Figure 2-1: Phosphorus filters design. In order to facilitate sampling, and maintain the same flow path baffles that were installed in each filter in series. The first half of each filter was fed from the top to the bottom, while the second half was fed from the bottom to the top of a filter.

The filters were first put into operation in the winter of 2006, and therefore were frequently exposed to sub-zero temperatures (January 20th until March 13th 2006). During this first feeding period, to reduce the risk of freezing, 6 separate pump cycles lasting 30 minutes (flow rate of approximately 1.5 L min^{-1}) were used for the feeding. At the end of the first 52 days feeding period, the EAF steel slag material was excavated from the first filters in series (F1 and F1') to a depth of approximately 0.3 m, placed on a plastic tarp and rinsed thoroughly with fresh water. The material was then placed back in the barrels, and left to rest for approximately 3 months (88 days).

In June 2006, a second pump was installed in the holding tank to feed each set of filters independently and ensure better control of flow rates. During this second feeding cycle, the feeding regime was simplified to 2 daily pump cycles of 44 mins at approximately 3 L min^{-1}. To decrease the TSS loading, a metal screen (5 x 5 mm mesh) was built and placed in the CWRC milk house waste holding tank in order to separate larger solids from the pump intakes. A synthetic material (geotextile) was placed at the pump intakes and a cheesecloth filter was placed around the inlet pipes for the first filters (F1 & F1') to further reduce solid particles in the filters influent.

The second feeding cycle was carried out during summer and fall warmer weather (6/9 – 10/4/2006) and lasted 117 days. Overall, filters were exposed to 2 feeding cycles (52 d and 117 d) with an 88 d resting period in between.

Water samples were taken from the holding tank and each filters influent and effluent once a week and analyzed for total suspended solids (TSS), dissolved reactive phosphorus (DRP) and pH. Samples for total phosphorus (TP) determination were taken once every three weeks on average. TSS concentrations were determined gravimetrically by weighing samples before and after drying at 55˚C for 2-3 days (APHA, 1998). DRP concentrations were determined using the molybdate - reactive P method (APHA, 1998). TP was determined by a standard microwave assisted digestion method using 10 mL of sample and 10 mL of concentrated HNO_3, which was then microwaved (APHA, 1998). The sample was then diluted to 100 mL with 0.01 HNO_3 and the sample was analyzed by ICP-AES (Perkin Elmer 3000 DV). The pH was recorded for all samples using a standard pH probe (Hanna instruments, HI 223, Microprocessor pH meter).

The entire set of data was analyzed using the MIXED procedure of the SAS System for Windows. Because the filter data are spatially correlated and the days are not equally spaced, a spatial covariance structure for both spatially and temporally correlated data points was used (Littell *et al.*, 2006).

Results

TSS, DRP and TP removal efficiencies during the 1st Feeding Cycle (1/20 – 3/13/2006)

The average influent TSS, DRP and TP concentrations to the first filter (F1) was 3395.03 ± 2.67 mg L^{-1}, 42.46 ± 12.75 mg L^{-1} and 54.77 ± 9.5 mg L^{-1}, respectively. The filters were fed at an average TSS DRP and TP daily loading rates (LR) of 1.08 ± 0.004, 0.013 ± 0.001 and 0.02 ± 0.001 g kg^{-1} EAF slag d^{-1} respectively (Table 2-1).

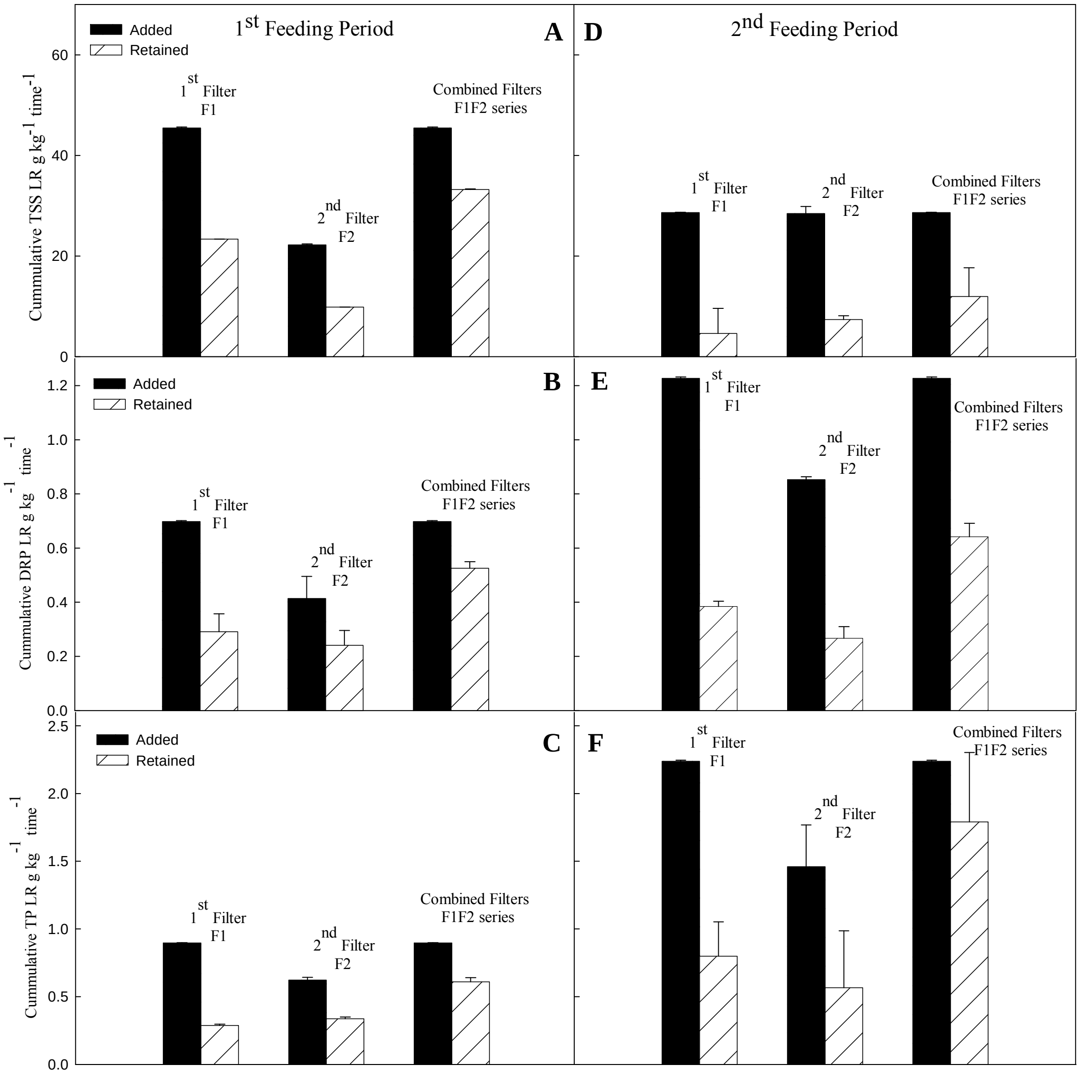

Figure 2-2: Cumulative total suspended solids (TSS)(A, D), dissolved reactive phosphorus (DRP)(B, E) and total phosphorus (TP)(C, F) loading rates to the filters during the first 52 d feeding cycle (A, B,C) and during the 2nd 117 d feeding cycle (D, E, F).

The cumulative amount of TSS fed to the first filter in series (F1) during the first feeding cycle was 45.44 ± 0.18 g TSS kg^{-1} EAF slag (18.7 kg total)(Figure 2-2A). Filter F1 retained 23.34 ± 0.004 g TSS kg-1 EAF slag (9.60 kg total) resulting in a TSS removal efficiency of 51.34% (Figure 2-2A). The second filter in series (F2) retained an additional 9.84 ± 0.004 g TSS kg-1 EAF slag (3.98 kg total), resulting in an overall TSS removal efficiency by the filter series of 72.45 ± 2.34 % (Figure 2-2A). Although the use of in-series design improved TSS removal efficiency by 21.3%, the filters became clogged and inoperable after only 52 days.

During the first feeding period filter F1 received 0.7 ± 0.003 g DRP kg^{-1} EAF slag (0.287 kg total) and of that it retained 0.29 ± 0.066 g DRP kg^{-1} EAF slag (0.119 kg total) (Figure 2-2B), for a cumulative DRP removal efficiency of 42.94 ± 2.6% (Figure 2-3A). The second filter in series (F2) received 0.41 ± 0.08 g DRP kg^{-1} EAF slag (0.167 kg total) and retained 0.24 ± 0.06 g DRP kg^{-1} EAF slag (0.098 kg total) (Figure 2-2B)resulting in a cumulative DRP removal efficiency of 66.14 ± 2.3% (Figure 2-3A).

The F1F2 filter series received 0.70 ± 0.003 g DRP kg^{-1} EAF slag (0.287 kg) and retained 0.53 ± 0.03 g DRP kg^{-1} EAF slag (0.217 kg) (Figure 2-2B)resulting in a cumulative DRP removal efficiency of 76.1 ± 3.5% (Figure 2-3A). The filters in-series increased the system's DRP removal efficiency by 43.5% when compared to the single filter unit's performance (Figure 2-3A, Table 2-1).

The amount of total phosphorus (TP) added to filter F1 during the first feeding cycle was 0.896 ± 0.003 g TP kg^{-1} EAF slag (0.368 kg total) with the filter retaining 0.287 ± 0.01 g TP kg^{-1} (0.118 kg total), for a TP removal efficiency of 43.17 ± 5.59% (Figure 2-2C).

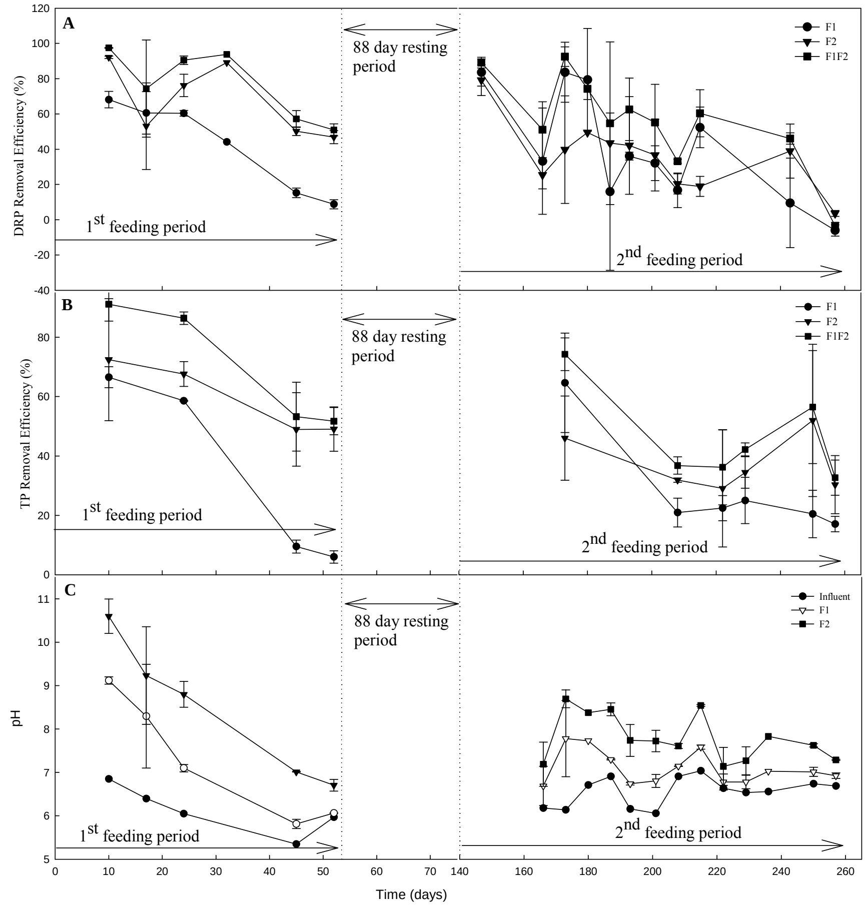

Figure 2-3: DRP and TP removal efficiencies (A and B) and pH (C) over the entire 257 days of investigation. The 1st feeding period lasted 52 days and the second for 117 days with an 88 day resting period between.

The second filter in series (F2) received 0.623 ± 0.02 g TP kg^{-1} EAF slag (0.253 kg total) and retained 0.336 ± 0.013 g TP kg^{-1} (0.137 kg total), resulting in a TP removal efficiency of 57.18 ± 6.47 %. In total the F1F2 filter series received 0.88 ± 0.001 g TP kg^{-1} EAF slag (0.368 kg) and retained 0.61 ± 0.03 g TP kg^{-1} (0.255 kg) resulting in a cumulative TP removal efficiency of 74.38 ± 2.3 % (Figure 2-2C). As with DRP, the use of series design for the EAF steel slag filters increased TP removal efficiency by 23% (Figure 2-3B).

The pH of the influent remained fairly consistent throughout the investigation, ranging from 5.13 to 6.85 (average 5.96 ± 0.64) (Figure 2-3A). Filter F1's effluent pH values ranged from 5.13 to 9.18 (average 7.02 ± 1.4) and the second filter in series (F2) effluent pH values were slightly higher and ranged from 5.47 to 10.88 (average 8.2 ± 1.75) (Figure 2-3A). The effluent pH values followed a similar trend in both the first and second filters in series, being higher during the first 20 days of investigation after which stabilizing gradually at lower values (7 and 7.3, respectively) (Figure 2-3A).

TSS, DRP and TP removal efficiencies during the 2nd Feeding Period (6/9 – 10/10/2006)

The second feeding cycle of the filters commenced after a resting period of 88 days, and lasted for 117 days. Although the filters were fed at the same HLR (123 cm d^{-1}) as during the first feeding cycle, the placement of a screen inside of the holding tank reduced the influent TSS concentration to filter F1 by 86.87 % (from an average 3,395.03 to 910.09 mg TSS L^{-1}). Additionally, the installation of a geotextile material around the pumps inlet and a cheesecloth filter on the filters inlet pipes reduced TSS concentration by a further 5.38 % (from 915.09 to 865.86 mg TSS L^{-1}). As a result, the first filter in series (F1) received 37 % lower amount of TSS (28.59 ± 0.11 g kg^{-1} EAF slag) (Figure 2-2D) when compared to the previous feeding cycle (Figure 2-2A), and had a much lower retention (4.59 ± 4.96 g TSS kg^{-1} EAF slag). When viewed in series, the same trend was seen as before, with a 37.77 % the filters TSS removal efficiency was seen (Figure 2-2D). Overall, the first filter in series (F1) received a total of 73.95 ± 0.11 g TSS kg^{-1} EAF slag

(31.97 kg TSS) during the entire period of investigation (both feeding period 1 and 2), and retained 27.93 ± 4.96 g TSS kg^{-1} EAF slag (14.9 kg TSS) resulting in a TSS removal efficiency of 62.23 % (Figure 2-3A). The second filter in series (F2) retained an additional 17.19 ± 0.77 g TSS kg-1 EAF slag (11.33 kg TSS) (both feeding cycle 1 and 2) for a total removal by the F1F2 filter series of 45.12 ± 0.49 g TSS kg^{-1} EAF slag (25.52 kg TSS) with a TSS removal efficiency of 61.01 % (Table 2-1).

During the second feeding cycle the first filter in series (F1) received an additional 1.23 ± 0.005 g DRP kg^{-1} EAF slag (0.504 kg DRP) and retained 0.385 ± 0.02 g DRP kg^{-1} EAF slag (0.158 kg DRP) resulting in an average DRP removal efficiency of 39.7 ± 0.44% (Figure 2-2D). The second filter in series (F2) was fed 0.852 ± 0.012 g DRP kg^{-1} EAF slag (0. 346 kg total) and retained 0.27 ± 0.04 g DRP kg^{-1} EAF slag (0.109 kg total) for an average DRP removal efficiency of 37.89 ± 5.33% (Figure 2-2D). When viewed as a single unit the filter series F1F2 received 1.23 ± 0.005 g DRP kg^{-1} EAF slag (0.504 kg) and retained 0.64 ± 0.05 g DRP kg^{-1} EAF slag (0.267 kg) resulting in an average DRP removal efficiency of 55.97 ± 7.6 % (Figure 2-2E) during the second feeding cycle. As in the first feeding cycle, using a series design with the EAF steel slag filters increased the systems DRP removal efficiency by 29.12 % in comparison to the use of a single filter (Figure 2-2E, Table 2-1). During the entire 169 days of operation the F1F2 filter series received a total of 1.93 ± 0.008 g DRP kg^{-1} EAF slag (0.791 kg) and retained 1.18 ± 0.09 g DRP kg^{-1} EAF slag (0.489 kg) resulting in a DRP removal efficiency of 62.73 ± 5.65

%. The use of the series filter design improved the DRP removal efficiency by 35.09 % (Table 2-1).

The amount of TP added to filter F1 during the second feeding cycle was 2.24 ± 0.009 g TP kg^{-1} EAF slag (0.920 kg total), with the filters retaining 0.799 ± 0.253 g TP kg^{-1} (0.329 kg total), resulting in a cumulative TP removal efficiency of 11.32 ± 8.33 % (Figure 2-2F). Filter F2 received 1.46 ± 0.309 g TP kg^{-1} EAF slag (0.591 kg total) of which they retained 0.566 ± 0.42 g TP kg^{-1} (0.227 kg total), for a cumulative TP removal efficiency of 33.74 ± 22.27 %. In total, during the second feeding cycle the F1F2 filter series received 2.37 ± 0.009 g TP kg^{-1} EAF slag (0.920 kg) and retained 1.79 ± 0.512 g TP kg^{-1} (0.556 kg) resulting in a cumulative TP removal efficiency of 41.76 ± 13.07 % (Figure 2-2F). As was seen with DRP, the use of series design improved TP removal efficiency by nearly 72.89 % (Figure 2-3).

During the second feeding cycle the pH of the influent ranged from 6.06 to 7.04 (average 6.57 ± 0.30). The pH of the effluent of the first filter in series (F1) ranged from 6.37 to 7.73 (average 7.02 ± 1.4) and the second filter in series (F2) effluent pH values were slightly higher, ranging from 6.83 to 8.84 (average 7.71 ± 0.56). This followed the same trend as exhibited during the first feeding period (Figure 2-3).

This linear mixed models analysis showed no statistically significant difference between filters F1 (the first filter in-series) and F2 (the second filter in-series), even though F1 retained 23% more DRP per kg of materials than did F2. The interaction between filter and feeding period also was not statistically significant, indicating that any difference between filters was similar in each period. However, there was a statistically significant difference ($p<0.05$) between feeding periods in DRP removal. Both terms involving day of experiment were statistically significant (day within period, $p=0.04$ and day by filter within period, $p=0.01$), as expected, since the DRP removal performance changes from day to day. A simplified model analyzing total DRP removal was also run using the MIXED procedure. This removes any day effect from the model and compares the total DRP removal performance between filters and between feeding periods. This analysis found a statistically significant difference between filters in their total DRP removal performance ($p<0.05$). No significant difference was found between periods, nor was the filter by period interaction significant.

Due to the restriction of the available space at the University Dairy farm, it was not possible to install and investigate performance of a single large filter unit against two smaller filter units in series. Therefore, we were unable to perform a statistical comparison of the affect of series construction versus a single filter on the DRP removal efficiency. The mean DRP removal rate of both filters was significantly different from zero ($p < 0.001$), indicating that both filters in-series had a statistically significant effect on DRP removal efficiency.

Table 2-1: EAF steel slag filters life span, average hydraulic loading rates (q), TSS and DRP mass loading rates and DRP removal efficiencies.

Filters life span (days)	q (cm d^{-1})	TSS LR (g kg^{-1} d^{-1})	DRP LR (g kg^{-1} d^{-1})	DRP Removal Efficiency (%)	
Before resting		**F1**	**F1**	**F1**	**F1F2**
52^{a1}	123	1.08 ± 0.004	0.013 ± 0.001	42.94 ± 2.60 %	76.11 ± 3.48 %
After resting					
169^{b1}	123	0.24 ± 0.001	0.010 ± 0.003	39.7 ± 0.44 %	55.98 ± 7.59 %
Total					
175^{ab1}	123	0.53 ± 0.06	0.012 ± 0.003	42.80 ± 0.75%	69.70 ± 1.48 %
180^{c2}	43.2	0.285 ± 0.04	0.011 ± 0.002	72.00 ± 0.26	
Over 260^{d2}	43.2	0.024 ± 0.01	0.008 ± 0.001	75.00 ± 0.21	

[a] Filters fed by milk parlor wastewater without any pre-treatment; [b] filters fed by milking operations wastewater, with a screen and synthetic material added as a pre-treatment; [c] filters fed by mixed barnyard runoff and milking operations wastewater, not receiving any pre-treatment; [d] filters fed by mixed barnyard runoff and milking operations wastewater, having constructed wetland as a pre-treatment; [1] filters designed as two units connected in series; [2] filters designed as single units.

The initiation of a resting period combined with the installation of the filters for TSS removal extended the life span of the system by 3.25 fold (from 52 to 169 d). Moreover, exposing the filters to a prolonged resting period enabled the rejuvenation of the EAF steel slag filters P retention capacities, which occurred in all filters (Figures 2-2 and 2-3). At the end of the first feeding cycle, the DRP and TP removal efficiencies of the first filter in series (F1) had decreased to only 8.79 ± 2.62 % and 6.0 ± 2.07%, respectively. At the beginning of the second feeding cycle, the same filter (F1) DRP and TP removal efficiencies had increased to 83.54 ± 7.7 % and 75.0 ± 24.67 %, respectively, an approximately 10 fold increase over the values prior to the resting period. The resting period also resulted in an increase in removal efficiency of the filter series (F1F2). The

DRP and TP removal efficiencies increased 1.8 fold after the resting period, from 50.96 ± 3.37to 89.09 ± 3.04% (DRP) and 51.73 ± 4.56 to 89.43 ± 8.1% (TP), respectively (Figure 2-3).

Discussion

The effects of solids and DRP daily mass loading rates on DRP and TP removal efficiency

TSS mass loading rates: The first feeding cycle was carried out during the winter of 2006 (January until mid March) represented a test of the EAF steel slag filters P removal efficiency under the worst case scenario: sub-zero temperatures, extremely high effluent strength (organic matter ~6000 g BOD5 m^{-3}, total suspended solids ~ 3400 g TSS m^{-3}). As a comparison, the U.S. EPA (2006) reported that to achieve P removal, a wastewater treatment systems influent TSS concentration should not exceed 100 g m^{-3}. Apart from being fed at an over 30 fold higher TSS concentration, the HLR employed in this study (123 cm d^{-1} HLR) were 22.4 fold higher then the recommend rates for similar on-site treatment systems in North America (Knight *et al.*, 2000). Given this extreme feeding regime, it is not surprising that the filters became clogged after only 52 days of operation (Figure 2-3).

The clogging of a filters substrate material caused by development of biofilm has been identified as one of the biggest operational problems in similar on-site wastewater treatment systems, such as constructed wetlands and rock and sand filters (Platzer and Mauch, 1997; Ádám *et al.*, 2006; Langergraber *et al.*, 2007). Langergraber *et al.* (2007)

stated that developing operational methods for the treatment of high HLRs in constructed wetlands without clogging of the systems represents one of the most important unsolved problems in this area of research.

To investigate the effects of TSS and DRP daily mass loading rates, alternate feeding and resting regimes and in series design on the removal efficiencies of DRP and TP, data from the present study was compared to results reported by Weber *et al*. (2007). Weber *et al.* (2007) investigated EAF steel slag filters treatment performance of dairy effluent combined with stormwater, and with and without the use of a constructed wetland pre-treatment unit. Consequently, the TSS loading rates reported for the waste effluent with constructed wetland pretreatment were 11.9 fold lower than without the pretreatment (0.024 and 0.285 g TSS g kg^{-1} d^{-1} respectively, Table 2-1). In that study, the filters fed at the higher TSS loading rates became clogged after 180 days in operation while filters fed at a lower rate (0.024 g TSS g kg^{-1} d^{-1}) were in operation for 270 days before their efficiency dropped to below 60%, and went on to have a total life span of 499 days before they became fully saturated with P (Drizo *et al*., 2008). Similarly the filters in this study, which were fed a 3.3 fold higher TSS loading rate (1.08 ± 0.004 g TSS g kg^{-1} d^{-1}), had a 3.4 fold shorter life span (52 days) in comparison to the filters fed without wetland pre-treatment as described by Weber *et al*. (2007) (Table 2-1).

Further comparison of the TSS influent mass loading rates with the filters life span in each study revealed that EAF steel slag filters will become clogged with biofilm when they have been fed approximately 50 g TSS kg^{-1} EAF steel slag (Table 2-1). Therefore to achieve a minimum filter lifespan of 1 year, the TSS loading rates to EAF steel slag filters should not exceed 0.020 g TSS g kg^{-1} d^{-1} or 50 g TSS m^{-3} d^{-1}, which is in accordance with the value recommended for similar on-site systems (Knight *et al.*, 2000).

DRP mass loading rates: A comparison of the DRP daily mass loading rates between the present study and that of Weber *et al.* (2007) shows that unlike the TSS loading rates, they were very similar (Table 2-1). This suggests therefore, that the TSS loading rate, not the DRP loading rate is the predominant parameter affecting their DRP treatment efficiency. The filter F1, which was fed at 3.3 fold higher TSS loading rate, achieved a DRP removal efficiency of 37.77 %, being 1.9 fold lower then the DRP efficiency of 72.00 ± 0.26 % achieved by filters fed at the lower TSS loading rates (Table 2-1). Similarly, Weber *et al.* (2007) reported that there was not a significant difference in the DRP loading rates and removal efficiencies between the filters fed with wastewater that had been pretreated by a constructed wetland treated (75.00 ± 0.21 %) versus untreated effluent (72.00 ± 0.26%)(Table 2-1). However, the filters fed with pre-treated effluent (at the lower TSS loading rates) had a 2.2 fold longer life span then the filters fed without a constructed wetland pre-treatment (Weber *et al.*, 2007; Drizo *et al.*, 2008).

The effects of in-series design and the use of alternating feeding and resting periods

Drizo *et al.* (2008) recently showed EAF steel slag material has the ability to rejuvenate its P removal efficiency. They also found that the implementation of a resting period when their DRP removal efficiency decreases below the design objective results in the largest increase in DRP removal efficiency and significantly prolongs the filters operational life span. However the effect of altering the feeding and resting periods on filters TSS removal efficiency has not been previously investigated.

The results from this study show that after resting period of over 12 weeks the first filter in series (F1) retained an additional 4.59 ± 4.96 g TSS kg^{-1}, which is much lower than the amount retained during the first feeding cycle (23.34± 0.004 g TSS kg^{-1})(Figure 2-2A&D). Similarly, the quantities of TSS retained by the filter series during the second feeding cycle were much lower than in the first feeding period (11.94 and 33.18 g TSS kg^{-1} respectively) (Figure 2-2). Therefore with TSS, the incorporation of a resting period in the design of EAF steel slag filters does not have any effect on their treatment efficiency and system longevity. The increase in treatment efficiency and longevity of the filters observed during the second feeding cycle can also be attributed to two other operational factors. The first is that the TSS daily mass loading rates were 4.5 fold lower (0.24 ± 0.0001 g kg^{-1} d^{-1}) when compared to the first feeding period (1.08 ± 0.004 g kg^{-1} d^{-1}) due to the TSS filters that had been installed and the effect of washing the EAF steel slag between feeding cycles.

During the resting period, because the filters were clogged, the EAF steel slag material had to be removed from the filters. The formation of biofilm had caused the slag material to solidify, therefore the large clumps had to be broken up and the material was then washed with tap water to remove some of the solids. It has been shown that DRP and TP sorbed to the EAF steel slag material does not readily desorb to surface runoff, therefore this action would not have significantly affected the P sorption capacity of the slag material in this study (see chapter 3). The material was then returned to the respective filters, and left to rest.

The resting period increased the first filter in series (F1) DRP capacity by 56.9 %, which is higher than the 28% increase that was observed after a 12 week resting period in EAF steel slag filters also fed by a dairy effluent until reaching their P saturation point (Drizo *et al.*, 2008). The resting period had an even greater effect on filters TP retention capacity, which increased 73.6 % (from 0.29 ± 0.01 g TP kg^{-1} at the end of the first feeding cycle to 1.09 ± 0.24 g TP kg^{-1} after the second feeding cycle).

Overall, the incorporation of a second filter unit into in-series design increased DRP and TP removal efficiencies by 43.58 and 41.96 %, respectively, in the first feeding period and by 29.12 and 72.89 in the second feeding period, contributing significantly to the filters treatment performances (Figures 2-2 and 2-3). This has been expected given that it has been well established that multiple and hybrid CW systems have less problems with preferential flows and thus generally exhibit better performances in pollutant reduction when compared to that of single cell units (Vymazal, 2007). One of the prime advantages of a multi-stage filter system over a similarly sized single filter is that with time as clogging occurs in the filter system and biofilm develops over the slag particles, the first filter in-series can be drained and left to rest (in a case of EAF steel slag material) or removed (if other materials are used). The remaining filter unit or units, which will have had significantly less TSS loading, can then become the primary P treatment filters. Therefore the life span of a filter system could be prolonged by draining and resting individual treatment cells while the system as a whole continues to operate. Contrary, if the system consists just of one larger single cell, once the inlet zone of the filter becomes clogged with solid material, the entire system would have to be switched off while the filter material is replaced. Additionally, in this research we demonstrated that in real on-farm applications of EAF steel slag filters, with basic solid separation techniques the TSS loads can be dramatically reduced. As stated above, with the use of a metal screen around the pumps feeding the filters and a geotextile material placed around the pumps intake, the mass loading of TSS in the 2nd period was reduced by 3.7 fold in comparison to the 1st period. However, during the 2nd period, the TSS concentration in the influent was actually 2 fold higher (6968.99 mg L^{-1}) than in the 1st period, and the solid separation techniques employed was able to reduce this by 87.6 %.

EAF steel slag filters treatment efficiency under sub-zero temperatures

During much of the first feeding cycle the EAF steel slag filters were operated under sub-zero temperatures. Many steps were made to reduce the incidence of freezing in the filter system, and the few times that freezing did occur it was mostly in the connecting piping between filters, which were more exposed. Some freezing did occur in the actual filters themselves, however this was the result of the clogging causing shortcutting of the flow path, creating areas of stagnant flow vulnerable to the effects of freezing. The observed removal efficiency of the EAF steel slag system (40.72 % for the first filter, F1 and 62.73 % for the in-series system, F1F2) is impressive considering that P retention capacity of EAF steel slag filters is decreased at such low temperatures (Stumm and Morgan, 1996; chapter 4). This demonstrates that with simple design modifications to provide insulation and protection from cold, an EAF steel slag filter system can function effectively in northern climates.

EAF steel slag filters effects on pH

The results from this research provide further evidence that when fed at the HRT of 24 h or less, EAF steel slag filters effluent pH is within the range of US water quality regulations (U.S. EPA, 2002). Moreover, the results also showed that both DRP and TP removal efficiencies are positively correlated to filter's effluent pH values, which is consistent with the previous findings as presented in chapter 4 and Drizo *et al.* (2008).

Conclusions

The results from this study showed that TSS daily mass loading rates represent the most limiting factor to the EAF steel slag filters treatment efficiency and longevity. TSS daily loading should not exceed 0.020 g kg^{-1} EAF steel slag day-1 (50 g TSS m^{-2} filter day^{-1}) in order to prevent clogging and ensure long term functioning of the filter system.

Implementation of a resting period in a filters design increases the total DRP and TP retention capacities through rejuvenation of the EAF steel slag material, resulting in higher pollutant treatment performances, and a significantly increased system life span. The EAF steel slag filter systems P treatment performances were further enhanced by incorporation of an in-series design of multiple treatment units. The filters still showed impressive DRP removal rates when subjected to sub-zero temperatures, showing that they are an appropriate treatment technology for areas in cold climates.

Based on this research, we recommend that alternate feeding and resting cycles and the use of multiple filter units arranged in series should be integrated into the design of EAF steel slag filters used for the treatment of highly concentrated agricultural effluents in cold climates.

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Chapter 3: Investigations on Phosphorus Recovery and Reuse as Soil Amendment from Electric Arc Furnace Slag Filters

Simon C. Bird
University of Vermont; Department of Plant and Soil Science; 105 Carrigan drive;
Burlington, Vermont 05405

Abstract

Electric arc furnace (EAF) steel slag has been identified as an effective filter material for the removal of P from both point and non-point sources. In order to ensure the sustainability of this technology the reuse of P saturated EAF steel slag as a soil amendment for agriculture, forestry and mine reclamation should be explored. Therefore to determine the feasibility of land applying P saturated EAF steel slag three criteria were investigated: 1) seed germination and plant growth in saturated and untreated EAF steel slag material; 2) saturated EAF steel slag materials potential as a P fertilizer or soil amendment; 3) P desorption and metals leachate from saturated EAF steel slag material to surface runoff. *Festuca rubra* and *Medicago sativa* both germinated and showed good establishment in P saturated and untreated EAF steel slag. At the first harvest period (5 weeks) Medicago sativa plants achieved higher above ground biomass growth in triple super phosphate fertilizer (TSP) than in EAF steel slag. However, by the second harvest (10 weeks) the plants with EAF steel slag additions showed significantly higher growth than at the first (5 week) harvest, suggesting that EAF steel slag to be an effective slow release P source. A rain simulator was used to assess the desorption of DRP, TP and metals from a saturated and semi-saturated EAF steel slag. The results revealed that the total amounts of DRP and TP released to surface runoff from sorbed EAF steel slag were negligible when compared to the total quantities of P retained by this material. Overall the results of this study demonstrated that EAF steel slag would make a potentially useful soil amendment for the slow release of bioavailable P with minimal risk for loss of P to surface runoff.

Introduction

While being considered one of the major causes of water pollution and eutrophication (U.S. EPA, 2000; Sharpley *et al*., 2003), phosphorus (P) is also an irreplaceable and essential component of human, animal and plant life (Fielding, 2001). In freshwater environments it represents the resource limiting factor for the proliferation of life, with its sole source originating in phosphate-bearing rocks (Driver *et al*., 1999; Watzin *et al*., 2005). Due to the fact that these P reserves are non-renewable, over the past 15 years there has been a significant research effort in P recycling and recovery, particularly within the wastewater treatment industry (Valsami-Jones, 2001). However, little is known about P recovery and recycling potential from materials used in low-cost alternative technologies for wastewater treatment such as constructed wetlands and filter systems (Johansson and Hylander, 1998; Hylander and Simán, 2001).

Steel slag filter technology has emerged during the past decade as a promising solution for P reduction from municipal (Bourke *et al*., 2005; Shilton *et al*., 2006), domestic (Baker *et al*., 1998; Johansson, 1999) and agricultural effluents rising from both point and non point pollution sources (Bourke *et al*., 2005; Weber *et al.,* 2007; Drizo *et al*., 2008). However, the efficiency of slag filters decreases over time, with the material becoming saturated with P after 2-10 years of use, depending on the material source and filter design (Hylander and Simán, 2001; Bourke *et al*., 2005; Drizo *et al*., 2006; Drizo *et al*., 2008).

The issues of water pollution and manure management are all interrelated, and new treatment methods must use an integrated approach to efficiently remove P from wastewater and retaining onto a substrate in a plant available form, creating a new valuable product that can be then utilized as a P source (Greaves *et al*., 1999; Hylander and Simán, 2006). To the best of our knowledge there has not been any previous research on the potential re-use of sorbed P from iron melter (IM) slag or electric arc furnace

(EAF) steel slag filters. The potential of blast furnace (BF) steel slag material as a fertilizer was first described almost 100 years ago (New York Times, 1918; White, 1928), while the first research on plant availability of sorbed P from steel slag columns fed with a synthetic P solution was conducted one decade ago (Johansson and Hylander, 1998). Following this study, Hylander and Siman (2001) investigated plant availability of P sorbed to several different soils, opoka and BF slag materials. These studies are important as they represent the first investigations on the plant availability and potential re-use of P from exhausted slag filters. However, these studies were all conducted on the BF slag material treated only with a synthetic P solution. In practical field applications, steel slag material taken from P saturated filters having treated real dairy or municipal waste water will be covered with bio-film and Ca-P deposits, which may limit P availability to plants. Before EAF steel slag can be field applied as a source of P, the actual mass of bioavailable P must be experimentally determined, so that applications can be tailored to plant needs. It should be remembered however that the use of EAF steel slag to remove P from wastewater and the use of the sorbed P as a fertilizer source must be one component of a holistic approach, not a singular solution.

Therefore, the objectives of this paper were: 1) to investigate seed germination, plant growth and development in P-saturated EAF steel slag material which was fed by a high strength milk parlor effluent; 2) to determine saturated EAF steel slag material potential as a fertilizer or soil amendment; 3) to investigate P desorption and metals leachate from saturated EAF steel slag material.

Materials and Methods

Materials: The EAF steel slag material used in all three experiments was obtained from Heckett MutliServ, Contrecoeur, Quebec Canada. The properties and composition of this material have been previously described (Drizo *et al*., 2006; Weber *et al*., 2007; Drizo *et al*., 2008).

Experimental set up: The two EAF steel slag filters (0.242 m^3 volume each) established to treat effluent from a dairy farms milk parlor (total suspended solids (TSS) ~ 6000 mg L^{-1}; organic matter (BOD^5) ~ 3,000 mg L^{-1}) at the University of Vermont Constructed Wetlands Research Center (UVM CWRC) were in operation for 251 days before becoming clogged with bio-film and their P removal efficiency declined to 50% or less.

Experiment I: Preliminary study of seed germination, plant growth and development in phosphorus saturated EAF steel slag material

Plant species selected for this study were red fescue (*Festuca rubra* L.) and alfalfa (*Medicago sativa* L.). They were chosen because both are common species in Vermont, with alfalfa being a common agricultural field crop. In addition, both species have a tolerance to higher pH (7-8) soil conditions (USDA 2005).

The experiment was carried out at the University of Vermont Green House facility. Five different media treatments were investigated including: 1) 100% used P saturated EAF

(SEAF) steel slag, taken from the filters after 251 days of operation, containing 1.52 g DRP kg^{-1} from a previous experiment as described in Weber et al., (2007); 2) a mixture containing 50% SEAF slag and 50% soilless mix (metro mix 360, Griffin Nursery, Latham, NY.) (SSEAF); 3) a 100 % fresh untreated EAF (UEAF) steel slag; 4) a mixture containing 50 % fresh UEAF slag and 50 % soilless mix (SUEAF) and 5) a 100 % soilless mix as a control (soil). The pots were then planted, with 6 pots of each treatment type getting 25 red fescue seeds each and the other 6 pots getting 25 alfalfa seeds (Oliver Seeds, Milton Vt.) each. The pots were then placed in the greenhouse employing a randomized complete block design (Kuehl, 2000). After 60 days of growth the above-ground biomass was harvested from each pot. Fresh plant material was weighed and then oven dried at 100˚C overnight, to determine the dry matter (DM) mass.

Experiment II: Investigations of plant bioavailable Phosphorus and Saturated EAF steel slag potential as a soil amendment.

The source of saturated EAF steel slag were filters that received milk parlor effluent for 169 days containing 0.675 g DRP kg^{-1}, from a previous experiment as described in chapter 2. *Medicago sativa* (alfalfa) was selected for this study because it is well known as the most cultivated forage legume, covering approximately 32 millions of hectares worldwide (Michaud *et al*., 1988). In order to assess plant available P in EAF steel slag we investigated the effects of three different parameters (fertilizer type, P application rates and duration of growth period) on above ground plant biomass development.

The two P sources used in this experiment were: saturated EAF steel slag and a standard commercial phosphate fertilizer (Triple super phosphate, Espoma, Millville, NJ) (TSP), which served as a reference. Four different P application levels were tested, based on the State of Vermont recommendations for soil P fertilization: a low (20 lbs/acre furrow slice (5.5 g P m^{-3}) two medium (40 & 60 lbs./ acre f.s.(11 & 16.5 g P m^{-3})) and a high (120 lbs./ acre f.s. (33 g P m^{-3})) (Jokela et al., 2004). These application rates are representative of *Medicago sativa* (alfalfa) response to soil P conditions from stressed to abundant. The masses of EAF steel slag added to each pot to achieve these application rates were 36.66 g, 72.44 g, 109.8 g and 219.5 g respectively, and the masses of TSP fertilizer added were 0.034 g, 0.068 g, 0.101 g, and 0.203 g respectively. To meet plant nutrition needs, nitrogen (Ammonium sulfate, Espoma, Millville, NJ) was added at 12.25 g N m^{-3} and magnesium and potassium (Green Mountain Fertilizer, Milton, VT) at a rate of 76.75 g K m^{-3} and 33 g Mg m^{-3} was added to all treatments (Boswich, 2007). A nutrient depleted washed sand growing media (Jolly Gardner, Poland Spring, ME) with 0.00047 g P kg^{-1} was used to ensure that the only source for all plant nutrients was the added fertilizer or EAF slag.

Experimental Design: A randomized design was used for this experiment at the University of Vermont Green House facility. The treatments included: 1) washed sand with the TSP (WSF), 2) washed sand with EAF slag (WSS), and 3) washed sand with no added P (WSN). Eight replicates of each treatment were made, except for the WSN treatment, for which only 4 replicates were made resulting in a total of 68 pots. The pots were randomly placed in the greenhouse, and were re-randomized twice weekly. Watering was done daily to maintain moisture (15% by weight) in each pot. A 15 % by weight moisture level was determined empirically as the maximum volume of water that could be added to the individual pots without causing flow out of their drainage holes, thus preventing potential P loss from the soil. Each day 5 pots were selected at random, each pot was weighed, and the mass of water to be added was calculated by subtracting the observed weight from the known weight of the pot when at 15% soil moisture content. The amount of water to be added to each of the 5 pots was then averaged and the result was added to all pots. Twice a week all 68 pots were weighed individually and water was added until 15% moisture content was achieved. Plants above-ground biomass from each treatment was harvested after 5 weeks and 10 weeks of growth. At the time of the second harvest (10 weeks), flowering was observed in several pots, indicating that the plants had been able to reach maturity.

Statistical analysis: Several statistical analyses were performed in order to determine differences in above-ground biomass achieved by the different substrates at 5 and 10 weeks growing period. Normality of the samples was checked by visually examining plots of the residuals and ranks, and homogeneity of variance (HOV) with scatter plots. A log transformation was found to be the most effective at correcting normality and HOV. ANOVA was then used for comparisons (SAS, 2001).

Experiment III: Phosphorus desorption from saturated EAF steel slag

Experimental Set-up: This experiment was performed at the UVM Horticulture Research Center. Three treatments were used to test desorption of P and metals from EAF steel slag. These included: 1) EAF steel slag with no other amendments; 2) soil without any amendments and 3) a mixture of half EAF steel slag and half soil by volume to simulate EAF steel slag under saturated field conditions. Additionally, two different EAF slag samples were tested, a semi saturated EAF steel slag (EAFA) that contained 0.675 g DRP kg^{-1} EAF slag (as described in chapter 2) and saturated EAF steel slag (EAFB) that contained 3.18 g DRP kg^{-1} (Drizo *et al*., 2008) . Two replicates were made for each treatment for a total of 12 experimental units. The soil used was taken from a field under continuous corn management at the UVM Horticulture farm, which received minimal manure spreading, thus having a medium available soil P levels (0.0048 g P kg^{-1}).

The rain simulation study was carried out according to the National Research Project for Simulated Rainfall-Surface Runoff Studies protocol (Sera-17, 2002; Hanrahan, 2004). The protocol was modified by closing the soil pans drainage holes in the bottom to control macropore loss and to ensure complete saturation of the substrate and surface runoff. The pans were fabricated of stainless steel, and the dimensions were 1 m long x 0.2 m wide and 0.075 m deep, the substrate material was packed to a height of 0.05 m, the height of the outlet at the front of the pan.

The pans were placed in the simulator (fabricated by Brad Joern of Purdue University) with an approximately 2% grade, and all outlets and piping were constructed to limit contamination of the surface flow water by rainwater after it had left the soil pan. Well water (P concentration 0.044 mg L^{-1}) from the UVM Horticultural center was used to simulate rainwater. A TeeJet™ (1/2-HH-SS50WSQ) nozzle (Spraying Systems Co., Wheaton, IL) was placed 3.05 m above the surface of the pans resulting in an average water rate of 355 mL s^{-1}.

Experimental Design: The rain simulation treatments were chosen to represent three different field situations; 1) EAFA & EAFB slag in a 50-50 mixture by volume with soil, 2) EAFA and EAFB slag without soil media, and 3) soil with no slag from either source, with replication provided by making two identical pans for each treatment. One of the two pans from each treatment was randomly selected, and randomly placed within the rain simulator for the first run, which lasted 2 hours from the time of initial runoff. After the first run, the pans were removed from the simulator, and the second tray from the treatment was then randomly placed in the simulator and also run for 2 hours after initial runoff occurred. The experiment was then repeated the following day using the same method.

During each rain simulation experiment, runoff samples were collected after 5, 15, 30, 60, and 120 minutes after initial runoff began, resulting in 5 samples over a 2 h period. Composite samples were obtained by placing a container at the outlet of the treatment tray and at each sample interval removing it and replacing it with a new container to collect the next interval of runoff. A grab sample was then taken from the container, and stored until the end of the run when they were retuned to the lab, filtered and refrigerated.

Analysis: The pH was recorded for all samples using a standard pH probe (Hanna instruments, HI 223, Microprocessor pH meter). Dissolved reactive phosphorus (DRP) concentration was determined using the molybdate-reactive P method (APHA *et al*., 1998). Total P, Ca and metals content was determined using persulfate digestion method (APHA, 1989), and analyzed by ICP-AES (Perkin Elmer 3000 DV)

Statistical analysis was then performed using SAS analytical software (SAS Institute Inc., Cary N.C.). Normality of the samples was checked by visually examining plots of the residuals and ranks, and homogeneity of variance (HOV) with scatter plots, and a log transformation was used on the data. An analysis of covariance was used to investigate differences between the different treatments (SAS, 2001).

Results and Discussion

Experiment I: Preliminary study of seed germination, plant growth and development in saturated EAF steel slag material

Seed germination and plant growth occurred in all treatments with plants above-ground biomass growth in the 100% soil media being significantly higher ($p < 0.05$) when compared to the above-ground biomass achieved in the remaining three media (fresh or P

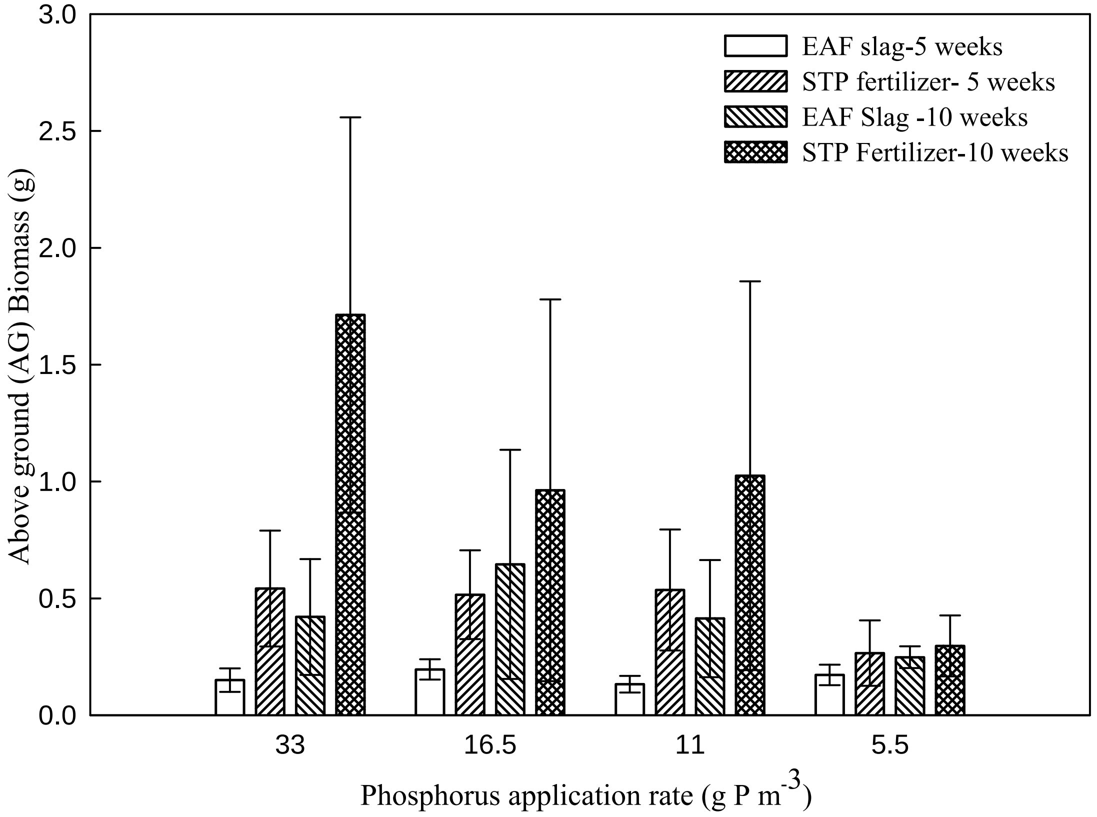

Figure 3-1: The total grams of above ground biomass produced by each treatment with either EAF steel slag or triple super phosphate (TSP) addition at 4 different levels of P application rates

saturated EAF steel slag or soil and slag mixture). The most important finding from this experiment was that seed germination and plant growth were achieved in the 100% EAF steel slag (both fresh and P saturated EAF steel slags) treatments. This result indicates that similarly to BF, EAF steel slag contains essential nutrients and minerals for plant growth and does not contain any plant inhibiting properties. In addition, for the first time it demonstrated the plants ability to germinate and grow in saturated EAF steel slag whose surfaces were completely covered with the organic biomass deposits that had accumulated during the 169 day feeding period with milk parlor and feedlot effluent.

Table 3-1: The average above-ground biomass of the alfalfa plants after EAF steel slag or triple super phosphate (TSP) addition after 5 weeks and 10 weeks growth. Numbers with different letters within rows denote significant differences.

	5 week harvest		10 week harvest	
g P/m^3	STP	EAF slag	STP	EAF slag
5.5	0.265^a	0.173^a	0.296^a	0.248^a
11	0.536^a	0.132^b	1.024^c	0.413^d
16.5	0.515^a	0.196^b	0.962^a	0.645^a
33	0.542^a	0.150^b	1.713^c	0.420^d

Experiment II: Investigations of plant bioavailable phosphorus and saturated EAF steel slag potential as a soil amendment.

Above-ground biomass was produced in all treatments, after both the 5 and 10 weeks growing periods, further indicating that P sorbed by the EAF steel slag is available to plants. The results showed that all three investigated parameters (P fertilizer type, P application rates and growth period before harvest) had a statistically significant ($p<0.01$) effect on above-ground biomass growth and development in the alfalfa plants. Apart from the lowest P addition (5.5 g P m^{-3}), all treatments that received TSP fertilizer additions had significantly higher above-ground biomass growth ($p < 0.001$) (Figure 3-1) at the 5 and 10-week growing period with the single exception of the 16.5 g P m^{-3} application rate at the 10 weeks growth period.

For both fertilizers, a significant difference in above-ground biomass was observed at both the medium (11 g P m^{-3} & 16.5 g P m^{-3}) and the high P application rates (33 g P m^{-3}) (Table 3-1). At both 5 and 10-weeks growth, the highest above-ground biomass was achieved at the highest application rate (33 g P m^{-3}). At the 10 week growth period, with the 16.5 g P m^{-3} application rate there was no longer a significant difference seen between the two fertilizer types, and at the 11 g P m^{-3} the difference has become almost insignificant (p=0.054) (Table 3-1). This indicates that by the 10-week harvest period, except at the highest P application rate, there was much higher growth in the EAF steel slag treatments than in the TSP treatments. None of the P was lost to runoff, because the moisture level of the pots was maintained so that no leaching occurred. Therefore plant available P had become limiting in the mid-rate TSP treatments, either because of plant uptake or that the P had been sorbed to soil minerals. That there was no significant difference in above-ground biomass between growth period or fertilizer type at the lowest P addition rate (Table 3-1) and the observed increased above-ground biomass response at higher P amendment rates (Figure 3-1) demonstrates both that the range of P applications used accurately represented conditions of stressed to abundant and that the of the sand media used was deficient P.

This result indicates that the EAF steel slag may require a longer period of time to solubilize and become available to plants, which is similar to previous findings by Hylander and Simán (2001). They compared barley plants growth with P additions from either saturated BF slag or commercial fertilizer and found that the P sorbed to BF slag solubilized at a rate commensurate to that of the barley plants requirements, postulating that the majority of the chemical fertilizer applied may have been sorbed to soil particles, thus being unavailable for plant uptake. However, it should be taken into consideration that in another study that investigated P bioavailability of saturated BF slag material, the same authors found that the addition of a chemical fertilizer produced a higher yield in plants than BF slag (Hylander *et al*., 2006).

Therefore, further investigations are necessary to elucidate bioavailability of EAF steel slag. One of the ways to improve P solubility could be the inoculation of EAF steel slag with phosphate-dissolving bacteria (Goldstein, 2007).

Experiment III: Phosphorus and metals release during simulated rain event

DRP and TP release from EAF steel slags:

Apart from EAFB steel slag and soil mixture (Figure 3-2b), the runoff DRP concentrations were the highest during the first 30 minutes of runoff, before decreasing gradually over time and stabilizing below 0.2 mg L^{-1} (EAFA and EAFB steel slag and EAFA steel slag and soil mixtures) and 0.1 mg L^{-1} (soil) for the remaining 90 minutes of investigation (Figure 3-2). DRP concentrations in the EAFB steel slag runoff were higher when compared to other treatments throughout the experiment, which can be attributed to the fact that EAFB slag contained 4.7 fold higher amount of DRP (3.18 g DRP kg^{-1}) and was saturated with DRP, compared to the semi-saturated EAFA steel slag (0.675 g DRP kg^{-1}), and also had 663 fold more sorbed DRP than the soil substrate (0.0048 g P kg^{-1}).

TP concentrations in the pure slag and slag and soil treatments runoff peaked later than with DRP (between 15-30 minutes) then decreased gradually over the remaining time,

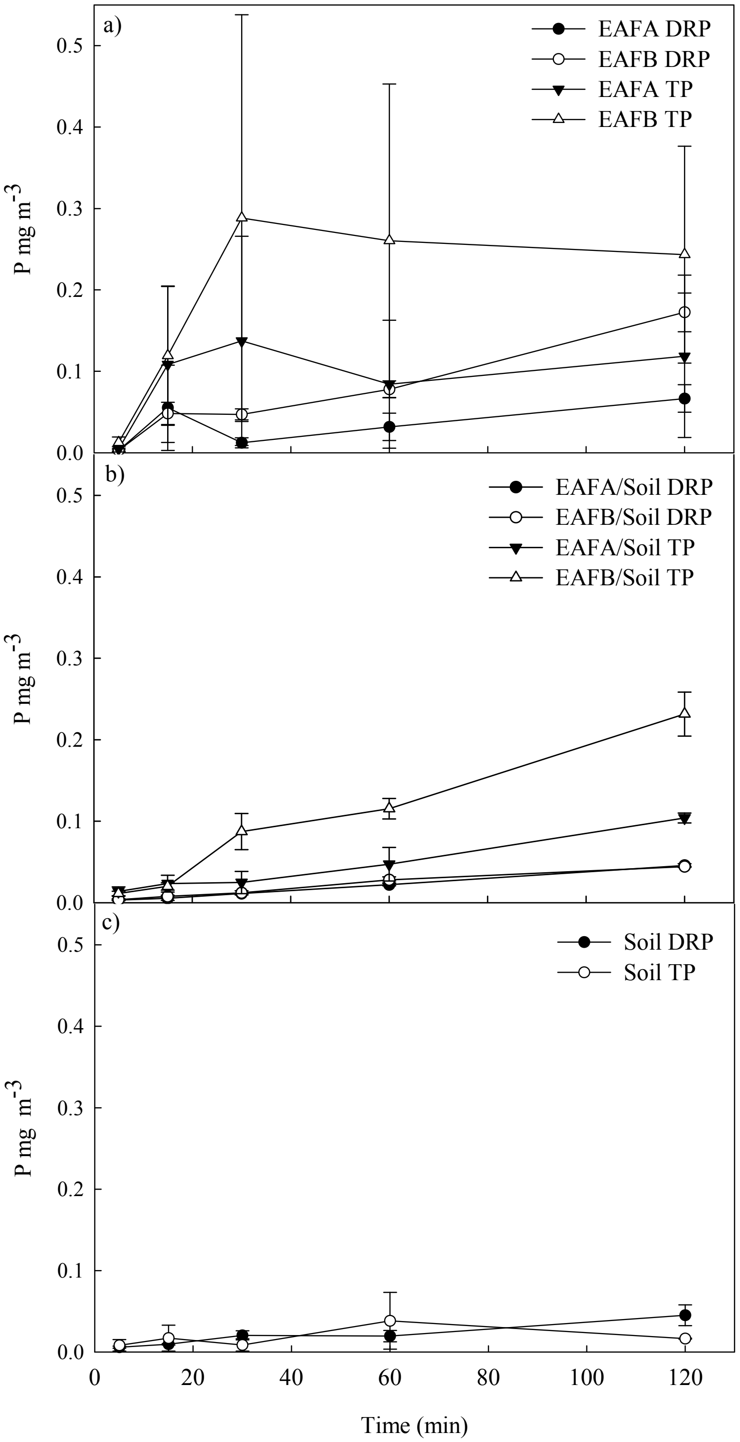

Figure 3-2: The mass loading (mg P m^{-3} substrate) of P desorbed to surface runoff over time (minutes) from the initiation of runoff from (a) the saturated and semi-saturated EAF steel slags, (b) the two EAF steel slag and soil mixtures and (c) the soil media alone.

following similar trend to DRP (Figure 3-2a and b). However, in the soil treatment the highest TP concentration occurred during the first 15 minutes, then decreased drastically with time without exhibiting any delayed peaks in concentration as observed in other treatments (Figure 3-2c).

To determine the point of time within the simulated rain event when the major DRP and TP mass release occurs, a percentage of a total DRP and TP lost in a runoff was calculated for each individual time period. These results showed that despite that the highest DRP and TP concentrations were found at the beginning of the experiment, the highest quantities of DRP and TP were released during the last 90 minutes of rain simulation. The most important finding was that the percentage of DRP released from both the soil treatment (84.6%) and EAFB and EAFA steel slag and soil mixtures (88.3 and 90.2 %, respectively) during this 90 time period was higher then DRP released from EAFB and EAFA steel slag (85.3 and 65.6%, respectively) treatments. In the case of TP, EAFB steel slag and soil (93.3%) and EAFB steel slag (82.9%) exhibited the highest release, followed by EAFA/soil and EAFA (82.6 and 71.6%, respectively), with soil treatment releasing the smallest quantity of TP (57.8%). The fact that the EAF steel slags showed slow desorbtion of TP to runoff in comparison to the soil treatment is consistent with the results from the previous experiment (II), further confirming that EAF steel slag has a slower rate of solublization of sorbed P in comparison to soil.

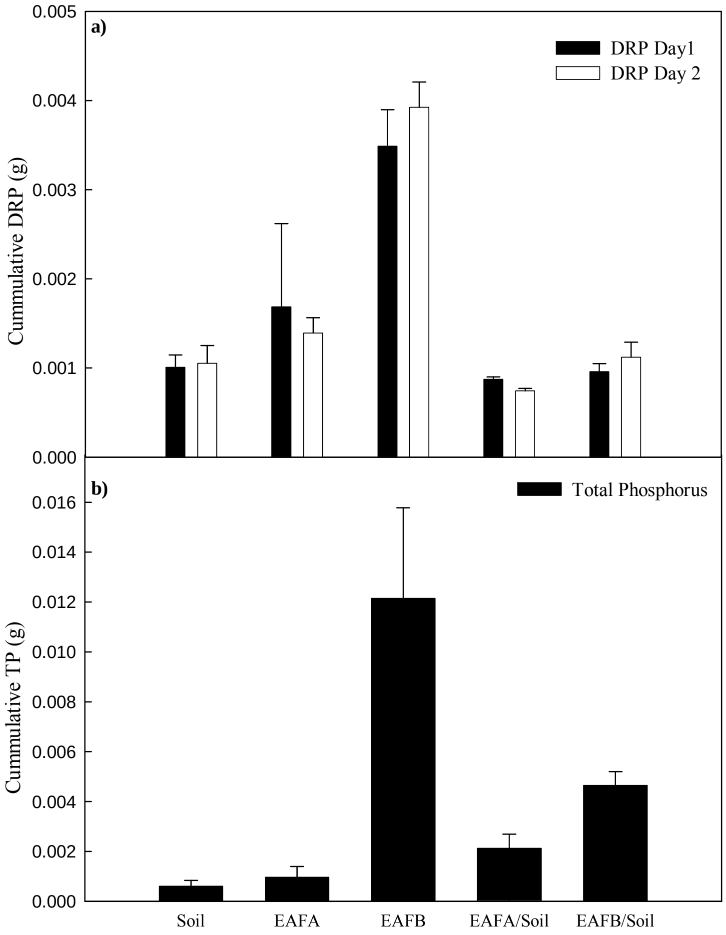

Figure 3-3: The amount (g) of dissolved reactive phosphorus desorbed to surface runoff over the course of the experiment on day 1 and 2 is shown (a), and the amount of TP lost to surface runoff on day 1 of the experiment (b).

The total cumulative amount of DRP and TP (g) lost to surface runoff was negligible (Figure 3-3, Table 3-2). Although EAFB steel slag released the highest amounts of DRP and TP (3.5 x 10^{-3} g and 12.1 x 10^{-3} g, respectively) being significantly higher compared to the quantities released by the other treatments (Figure 3-3) these represented only 3.25 x 10^{-3} % and 3.15 x 10^{-2} % of the total DRP and TP sorbed to this material. Similarly, the semi-saturated EAFA steel slag released a total of 1.69 x 10^{-3} g and 0.97 x 10^{-3} g of DRP and TP to runoff, representing 7.40 x 10^{-3} % and 8.89 x 10^{-2} % of the total DRP and TP sorbed to this material.

EAFB slag/soil mixture released 3.6 fold lower amount of DRP (0.96 x 10^{-3} g) and 2.6 fold lower amount of TP (4.7 x 10^{-3} g) when compared to EAFB steel slag alone. Similarly, EAFA slag and soil mixture released 1.9 fold and 2.2 fold lower amounts of DRP (0.87 x 10^{-3} g DRP) and TP (2.1 x 10^{-3} g) when compared to EAFA steel slag treatment. The soil treatment released higher amounts of DRP and TP (1.0 x 10^{-3} and 0.6 x 10^{-3} g) when compared to EAF steel slag and soil mixtures representing the highest percentage loss (1.42 % for DRP), of DRP it contained prior to experiment (Figure 3-3, Table 3-2). The rain simulation was run for two consecutive days to see whether a longer rain event would increase DRP desorption. The results from the two days demonstrated that of the amount of desorbed P remained stable, and did not increase with prolonged rain simulation (Table 3-2). The amount of DRP and TP added to each treatment in the rain was uniform across all treatments and found to be negligible, (3.6 x 10^{-4} g DRP and

Table 3-2: The total amount of dissolved reactive phosphorus (DRP) in the media, and total DRP lost in the runoff (g) by each treatment, and percentages of the total DRP desorbed to surface runoff on day 1 and day 2 of the experiment and total amount of metals lost to runoff from each treatment on day 1 of the experiment.

Treatment	DRP in media (g)	DRP Day 1 (g)	% lost Day 1	DRP Day 2 (g)	% lost Day 2	Ca (g)	Fe (g)	Zn (g)	Cu (g)
Soil	0.071	1.007E-3	1.42	1.05E-3	1.48	0.261	0.018	6.49E-04	4.03E-04
EAFA	22.78	1.69E-3	7.40E-03	1.39E-3	6.10E-03	0.460	0.001	6.43E-04	1.73E-03
EAFB	107.3	3.49E-3	3.25E-03	3.92E-3	3.66E-03	0.685	0.011	1.13E-03	2.66E-03
EAFA/Soil	11.43	0.87E-3	7.64E-03	0.74E-3	6.51E-03	0.276	0.015	5.22E-04	2.54E-04
EAFB/Soil	53.70	0.96E-3	1.78E-03	1.12E-3	2.09E-03	0.343	0.041	9.44E-04	8.42E-04

1.3×10^{-4} g TP total added to each treatment over the course of the experiment) and therefore not factored into the calculations.

One might expect that mixing EAF steel slag with soil would diminish pore volume of the material, thus slowing the movement of water through the mixture while increasing the contact time between the ‘rain’ and EAF steel slag causing higher P DRP desorption then from EAF steel slag alone. This scenario also simulated the conditions that would occur in a field application of EAF steel slag. However, when taking into consideration the higher amounts of P in the EAF steel slags when compared to soil the results showed that roughly the same percentage of the total amount of sorbed DRP in the EAF steel slag was lost to surface runoff from the steel slag alone and steel slag mixed with soil (Table 3-2).

The amount of DRP and TP desorbed to runoff during the experiment was negligible in comparison to the total sorbed quantities. This finding is very important for the EAF steel slag filters field applications as it demonstrates that the amount of desorbed DRP and TP was negligible (Table 3-2) and, perhaps more importantly, the DRP and TP concentrations in the runoff were below 1 mg L^{-1} (except for TP in saturated slag EAFB). In field applications, to meet regulatory requirements for P discharge, filter material will be replaced once its efficiency decreases below 50% (Drizo *et al*., 2008). From the standpoint of practical use this further demonstrates the viability of EAF steel slag as a P removal technology on dairy farms, since the material could very cheaply be disposed of on the farm using existing equipment and infrastructure. This technology eventually might allow for the transport of P back to the main regions of crop growth or industry need, unlike with manure bound P, which is rarely transported more than 10 miles (Sharpley *et al.*, 2001).

Fe, Ca, Cu and Zn release from EAF steel slag

The highest concentrations of Fe, Ca, Cu and Zn in the runoff were generally seen between 15 and 30 minutes after runoff began. However, several treatments showed lower secondary peaks at the 60 minute sampling period and also the metal concentrations remained at higher levels in the runoff during the experiment. This is very different than DRP and TP, which leveled out at low concentrations after a high initial peak. As with DRP and TP, EAFB had the highest releases of Ca, Cu and Zn of all the treatments. However the largest release of Fe was seen in the EAFB/Soil (0.041 g) treatment, being 2.2 fold higher than the soil treatment (0.018 g) and 3.6 fold higher than the EAFB (0.011 g) treatment (Table 3-2). The EAFA treatment lost the least amount of Fe (0.001 g), with the EAFA/soil treatment desorbing 10 fold higher amount of Fe (0.015 g) than the steel slag by itself. EAFB (0.685 g) released 2.6 fold more Ca than soil (0.260 g) and 1.5 fold more than EAFA (0.460 g) treatments. Both EAFA/soil (0.276 g) and EAFB/soil (0.343 g) treatments desorbed amounts of Ca similar to that of the soil treatment, which are also seen to be very close to half the amount of Ca released by each steel slag treatment by itself.

There was little difference seen in the desorption of Zn between the soil (6.49×10^{-4}) and EAFA (6.43×10^{-4} g) and EAFA/soil (5.22×10^{-4} g) treatments. EAFB steel slag and EAFB and soil mixture desorbed the most Zn 1.75 fold (1.13×10^{-3} g) and 1.5 fold (9.44×10^{-4} g) more Zn than either the EAFA or the soil treatments. The largest amount of Cu was from EAFB (2.66×10^{-3} g), with EAFA showing the second highest loss (1.73×10^{-3} g). The EAFB/soil treatment shows the third highest loss (8.42×10^{-4} g), however the soil treatment (4.03×10^{-4} g) lost more Cu than the EAFA/Soil (2.54×10^{-4} g). EAF steel slag filters have been shown to remove Cu from dairy waste effluents, and would therefore be expected to lose some of this to runoff. (Table 3-2)

Conclusions

The results from this research reveal several important facts about P-saturated and semi-saturated EAF steel slag filter material that are extremely important for these systems future field applications.

Firstly, Festuca rubra and Medicago sativa were able to germinate and grow in both untreated and P saturated EAF steel slag material, demonstrating that some of the sorbed P in EAF steel slag may be plant available and that the saturated steel slag does not have any plant inhibiting attributes. Secondly, the first in-depth investigation of the potential of P saturated EAF steel slag as a P source for plants in comparison to a commercial chemical P fertilizer was performed. The commercial fertilizer showed faster growth, but the Medicago sativa fertilized with EAF steel slag showed a positive growth effect over the course of the 10-week experiment. Therefore, although the TSP fertilizer demonstrated better efficiency for quick plant growth, the EAF steel slag showed definitive potential as an effective slow release P fertilizer. The slower desorption rate seen in EAF steel slag in comparison to other P sources is possibly more similar to general plant growth needs with less risk of P being lost to surface runoff.

Thirdly, using simulated rain events, we showed that the amount of DRP and TP lost to surface runoff from both saturated and semi-saturated slag to be below 1 mg L^{-1} with the sole exception being TP from the saturated slag which reached nearly 4 mg L^{-1}. Overall, the quantities of DRP and TP lost to runoff were negligible in comparison with the quantities retained, for both saturated and semi-saturated slag. Ca losses from both saturated and semi-saturated slags were also higher than the soil treatment but more Fe was released from the EAFB/soil and soil treatments than the slags. Ca and Fe mineral formation is assumed to be a primary mechanism for the removal of P, and this result indicates that the majority of desorbed P may be the result of dissolution of Ca minerals

Therefore these results demonstrate that EAF steel slag filter material could be used as a soil amendment in agriculture, horticulture, forestry or assist in the reestablishment of vegetation in the reclamation of land affected by acid mine waste. The P saturated EAF steel slag could be easily returned to the steel mill where it can be crushed to a finer consistency more suited for application. Moreover, we also showed that EAF steel slag filter material re-use in field applications would not pose any environmental risks with the desorption of dangerous concentrations of metals and minerals.

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Chapter 4: Investigations of the Phosphorous Retention Mechanisms in EAF Steel Slag Filters treating dairy farm effluent: Voltammetric Analysis and Geochemical Modeling

Simon Bird
Department of Plant and Soil Science, University of Vermont, Hills Agricultural Building, 105 Carrigan Drive, Burlington, VT 05405

Abstract

Electric arc furnace (EAF) steel slag filters have been shown to be an effective method for the removal of P from both point and non-point wastewaters. However, the mechanisms responsible for the retention of P in the EAF steel slag are poorly understood. Therefore, the objectives of this research were to: 1) to investigate the application of a novel voltammetric techniques for the analysis of the P chemistry in the EAF steel slag filters and 2) use geochemical modeling to identify possible P retention mechanisms in EAF steel slag filters treating dairy effluent.

Voltammetric sampling was found to be a highly effective tool for the in-situ sampling of redox species in EAF steel slag filters. The voltammetric analysis identified the EAF steel slag solution to be a reducing environment, with HS^- identified in all samples. Fe^{2+} was generally below the detection limits of the voltammetric analysis, indicating that it is precipitating out of the solution. PHREEQ geochemical modeling software was used to characterize the chemical solution in the EAF steel slag filters. Hydroxyapatite and vivianite were both found to be generally oversaturated in the solution, indicating that the precipitation of both of these minerals could be responsible for the removal of P from wastewater by EAF steel slag filters.

Introduction

High levels of dissolved reactive phosphorus (DRP) in runoff from agriculture and urban settings is a leading cause of the eutrophication of surface waters throughout the world (Sharpley *et al.*, 2001; Shilton *et al.*, 2006; Drizo *et al.*, 2008). For more than a decade, many different media types have been investigated in order to identify filter substrate materials with superior P removal efficiency. Materials investigated have generally had high levels of Ca or Fe, and have included light expanded clay aggregates (LECA) (Zhu *et al.*, 1997), limestone (Drizo *et al.*, 1999), shale (Drizo *et al.*, 1997; Drizo *et al.*, 1999), opoka (Johansson and Gustafsson, 2000), and wollastonite (Brooks *et al.*, 2000) with increasing attention on steel slags (Johansson, 1999b; Drizo *et al.*, 2002; Bourke *et al.*, 2005; Westholm, 2006; Weber *et al.*, 2007; Pratt *et al.*, 2007a; Drizo *et al.*, 2008).

Several different types of slag have been investigated for the removal of P from around the world, including blast furnace slag (BF) (Johansson, 1999a;b; Westholm, 2006), iron melter slag (IM) (Bourke *et al.*, 2005; Pratt *et al.*, 2007a; Pratt *et al.*, 2007b) and electric arc furnace slag (EAF) (Drizo *et al.*, 2002; Drizo *et al.*, 2008). Although all of these materials are the co-products of the production of steel, both with the raw products used and the manufacturing processes used, creating very chemically different slag materials (Bourke *et al.*, 2005). For example the blast furnace process, of which BF slag is a co-product, involves limestone, coke, and iron ore fused at temperatures above 1500°C, and has a high content of silicon (Si) and calcium (Ca) oxides (Johansson and Gustafsson, 2000). IM slag is produced in New Zealand and is a titanium (Ti) and aluminum (Al)-rich material (Pratt et al, 2007b). Whereas EAF is largely made from recycled steel scrap that is melted down, and is rich in Fe and Ca (Drizo *et al.*, 2006; Drizo *et al.*, 2008).

EAF slag has been gaining attention as a promising material for the removal of P from wastewater. However, the majority of research on EAF steel slag has been focused on the material's P removal efficiency and the phenomena of rejuvenation of P removal efficiency with only limited investigations on P removal mechanisms (Pratt *et al.*, 2007b; Drizo *et al.*, 2008).

Drizo *et al*., (2006; 2008) proposed that in EAF steel slag filters with a hydraulic retention time (HRT) of 24 h, P precipitation with Ca and the formation of stable minerals such as hydroxyapatite (HAP) represent the primary P removal mechanism. Investigations of BF slag have also identified CA-P precipitation and HAP formation as the dominant P removal mechanism (Johansson and Gustafsson, 2000). More recently Pratt *et al.,* (2007a:b) conducted detailed laboratory investigations of P removal mechanisms in IM slag by manipulating the pH and Eh of P saturated IM slag taken from an exhausted filter in New Zealand and measured the dissolution of Fe and P. They found that in IM slag, P absorption to Fe-oxides/oxyhydroxides was the primary mechanism for P removal, and that these were highly affected by both the pH and Eh of solution (Pratt *et al.*, 2007b).

Despite the oxidation state of P being unaffected by changes in redox conditions, these changes can significantly affect an EAF steel slag filter's P retention efficiency because of the strong effects of redox on Fe chemistry (Williams *et al.*, 1971; Ponnamperuma, 1972; Patrick and Kahlid, 1974). Oxic conditions in the filters favor the formation and stability of Fe-oxy/hydroxides that can adsorb P (Patrick and Kahlid, 1974; Pratt *et al.*, 2007b). Whereas conversely, reducing conditions will result in their reductive dissolution and release of the sorbed P, but also can lead to the formation of Fe (II) - P minerals such as vivianite (VIV) (Williams *et al.*, 1971; Ponnamperuma, 1972; Zanini *et al.*, 1998). Determination of redox conditions is usually achieved by analysis of a sample using a platinum (Pt) electrode, but this type of measurements has shown to be highly vulnerable due to atmospheric contamination and inhibition of proper measurement by other solution constituents such as organic matter (Grenthe *et al.*, 1992).

Solid-state voltammetric electrodes have been used extensively for *in-situ* analysis in marine and freshwater environments to measure redox dependant chemical species (Brendel and Luther, 1995; Sundby *et al.*, 2003). Voltammetric analysis using Au-amalgam electrodes allows for the simultaneous analysis of multiple major redox species (O_2, Mn^{2+}, Fe^{2+}, Fe^{3+}, and HS^-) across spatial and temporal gradients (Sundby *et al.*, 2003; Luther *et al.*, 2008). Voltammetric analysis can be done *in-situ* and in real time, without any atmospheric or other contaminating influence on the samples that may happen with sample removal and transport.

Understanding the mechanisms responsible for P removal in EAF steel slag filters is necessary to maximize their efficiency in reducing and preventing P pollution from agricultural effluents. Therefore, the major objectives of this research were: 1) to investigate the application of a novel voltammetric techniques for the analysis of the P chemistry in the EAF steel slag filters and 2) use geochemical modeling to identify possible P retention mechanisms in EAF steel slag filters treating dairy effluent.

Materials and Methods

Filter construction operation and sampling

Two EAF steel slag columns were constructed at the at the University of Vermont (UVM) Constructed Wetland Research Center (CWRC) located at the Paul Miller dairy farm, treating dairy wastewater that had already passed through a constructed wetland. They were located in a specially built Phosphorus Research Facility (PRF) that maintained temperature above 15º C. A more detailed description of the CWRC and the PRF can be found in Weber *et al.,* (2007) and Drizo *et al.,* (2008). Two columns were constructed of PVC pipe, and each had 20 cm diameter and 70 cm height. Each column contained approximately 33.7 kg of EAF slag, with a pore volume of 7.12 L. The columns were connected in series, and were fed twice daily using a peristaltic pump (Masterflex L/S, Cole-Parmer, IL, 2005) for 30 minutes, which resulted in a hydraulic residence time (HRT) of 12 h in each column, and a total HRT of 24 h for the filter series. At day 126, two additional daily feeding periods were added, decreasing the HRT to 6 h per filter, for a total of 12 h in the system. The columns were run for a total of 150 days, with a 14-day resting period between days 58 - 76. Weekly sampling was performed for DRP using the molybdate-reactive P method (APHA *et al.*, 1998), pH (Hanna instruments, HI 223, microprocessor pH meter), Eh (Fisher Scientific Accumet AP71 with accument Pt, Ag/AgCl combination ORP electrode) and Fe^{2+} and Fe total (Hach colorimeter). Two duplicate 14 mL samples were taken and filtered using 0.45 µm syringe filter, one sample was acidified using concentrated nitric acid, and both were refrigerated until the end of the experiment. The acidified sample was used to determine soluble anions (PO_4^{3-}, Cl, F^-, NO_2^-, NO_3^- and SO_4^{2-}) by ion chromatography (IC)(Dionex 2500 series system). The second sample was used to determine soluble metals (Ca, P, K, Mg, Na, Al, Fe, Mn, Cu, Zn, S, Ti, Pb, As) using inductively coupled plasma spectrophotometer (JY-Horiba ICP-OES).

Voltammetric Analyses

Voltammetric electrodes were used in-line during the use of the columns, to allow for *in-situ*, real time measurement of redox species in the filters. Electrodes were constructed after the techniques of Brendel and Luther (1995). Briefly, a gold wire was placed in a PEEK™ tube and filled with epoxy (West system, 105 epoxy resin and 206 hardener), the end of the tube was polished with diamond polish to remove any imperfections or scratches, and amalgamated with mercury. Pt counter and Ag/AgCl reference electrodes were also constructed after methods described in Luther *et al.* (2008). The probes were run using a DLK-60 potentiostat and multiplexer (AIS inc.). Three electrodes were placed in ports in the connecting piping of the columns, with one at the inlet of filter 1, the second between the outlet of filter 1 and the inlet of filter 2 and the final one at the outlet of filter 2. The Pt counter electrode and Ag/AgCl reference electrode were placed at the sampling location between the two columns to provide for optimal electrical connection to all three electrodes. Cyclic voltammetry was performed at each sampling point at 1000 mV/second between -0.1 and -1.8 V (vs. Ag/AgCl) with an initial potential of -0.1 V held for 2 seconds. Electrochemical measurements were made once a week and began when the pump started, with 10 cycles run on each individual electrode, in order to clean the electrode surface of containments and provide enough measurements for repetition in sampling. One electrode was run at a time, with the multiplexer sequentially switching between the three over 30 mins of the pump run, for a total of 8 complete runs of 10 cycles each for each probe. After analysis was completed, the electrodes were washed with DI water, and were run in stream water to strip off any residual metals from the surface. They were then stored in DI water until the next analysis. A composite voltammetric display of electrode scans shows visible evidence of excess noise at the influent of filter F1 and effluent of filter F2 sampling locations (Figure 4-2a and c), and a reduction in the ranges of current measured in comparison to the effluent of filter F1 (Figure 4-2b). The occurrence of such noise suggests that electrical interference was present in the system. While steps were taken to minimize noise by providing makeshift faraday cages for the voltammetry equipment, the electrical systems of the building and the pumps driving the system contributed significant noise to the analyses.

Geochemical modeling

The USGS geochemical modeling software PHREEQC was used in order to study the speciation and saturation index states in the solutions taken from three sampling points, inlet and outlet of filter 1 and the outlet of filter 2 (Parkhurst and Appelo, 1999). Inverse modeling was used to describe possible mass changes of minerals to explain the observed chemical differences between the inlet and outlet of the two filters.

Results & Discussion

Filters Phosphorus Removal Performance

The cumulative DRP retained and DRP removal efficiencies for filters F1 and F2 over the 150 days of investigation are presented in Figure 4-1a. During this period filter F1 received 0.99 g DRP kg^{-1} slag (30.6 g DRP total) and retained 0.30 g DRP kg^{-1} slag (9.19 g DRP total); filter F2 received 0.73 g DRP kg^{-1} slag (22.3 g DRP total) and retained 0.33 g P kg^{-1} slag (10.1 g DRP total) resulting in a cumulative removal of 0.63g DRP kg^{-1} slag (19.2 g DRP total) by the entire filter system (Figure 4-1a). The amount of DRP retained by filter F1 is over 3 fold lower when compared to the EAF steel slag filter investigated in an earlier study conducted by Weber *et al.,* (2007). In that study a single filter unit received 1.2 g DRP kg^{-1} slag and retained 1.02 g DRP kg^{-1} slag over a period of 111 days. In both experiments the filters were fed at the same HRT (12 h), therefore the observed difference in treatment performance is most likely attributed to the different DRP loading rates employed in these two studies. It is interesting to note that the filter described by Weber *et al.* (2007), which achieved a 85% DRP removal efficiency over the entire course of investigation was fed at a 1.6 fold higher DRP loading rate (0.085g DRP kg^{-1} slag day^{-1}) than the filter in the present study (0.052 g DRP kg^{-1} slag day^{-1}).

The concentration of DRP in the wastewater fed to F1F2 filter system ranged from 20.6 to 59.9 mg DRP L^{-1} (average 33.3 mg DRP L^{-1}). The effluent concentration of the system ranged from 1.2 to 34.3 mg DRP L^{-1} (average 11.5 mg L^{-1}). The DRP removal efficiency of filter F1 was much lower (averaging 60%) than reported in other studies on EAF steel

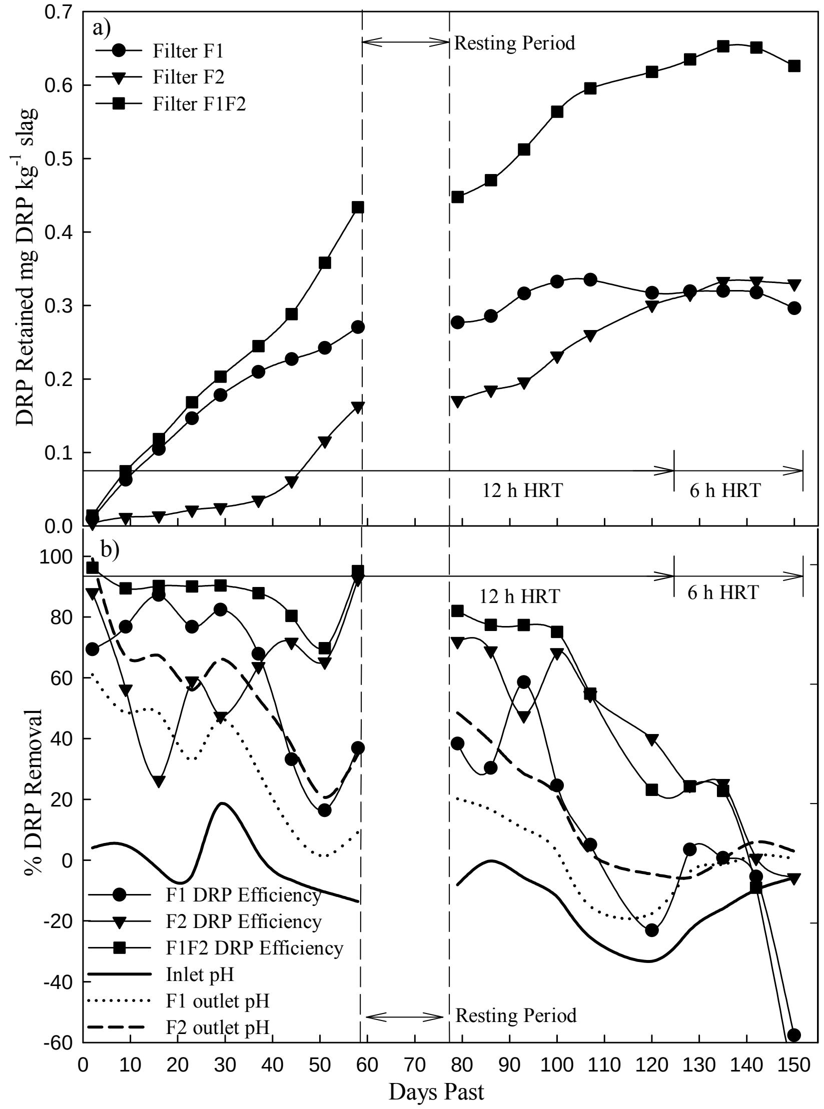

Figure 4-1: Cumulative DRP retained by EAF steel slag filters (a), DRP removal efficiency and pH (b).

slag for dairy effluent treatment (Weber *et al.*, 2007; Drizo *et al.*, 2008). Moreover, while other studies showed DRP removal efficiencies by EAF steel slag of over 90% during the first few weeks of operation (Weber *et al.*, 2007; Drizo *et al.*, 2008), in this study the average DRP removal efficiency for filter F1 achieved during the first 40 days of operation was 76% (Figure 4-1b). The effect of HRT on the DRP removal performance of EAF steel slag filters is clearly demonstrated by these results. The lower HRT (12 h) employed in this study decreased filter's DRP removal efficiency by 14% when compared to other studies that employed 24 h HRT (Weber *et al.*, 2007; Drizo *et al.*, 2008). DRP efficiency continued to decrease over the next 18 days, varying between 16-36%. Drizo *et al.,* (2002; 2008) has shown that drying the EAF steel slag filters and leaving them to rest for a period of 3-5 weeks allows for rejuvenation the material's P retention capacity, thus prolonging their life span. Therefore, on day 58 the filters were drained and left to rest for 18 days (day 58 to 76) to test whether a shorter resting period would have a similar rejuvenation effect on the filters P removal efficiency (Figure 4-1b). Apart from a brief increase in DRP removal efficiency observed on day 93 (60%) of the 2nd feeding period (day 76 to 126), the DRP removal efficiency remained mostly low (average 22%) falling to zero on day 120 (Figure 4-1b). This suggests that the 18 day resting period is not sufficient to allow for rejuvenation of P retention capacity.

To ensure that EAF steel slag filters were completely saturated with P, in the 3rd feeding period (days 126-150), P loading was increased 2 fold by decreasing HRT from 12 to 6 h and a concurrent decrease in DRP removal to below 0% was seen (Figure 4-1b).

Apart from the first 40 days of operation, the 2nd filter in series, F2, outperformed F1 in DRP reduction for the remaining period of investigation. The average DRP removal efficiencies achieved by this filter were 63%, 59% and 11% in the 1st, 2nd and 3rd periods of investigation, respectively (Figure 4-1b). Overall, the results showed that in series filter design (F1F2) achieved a higher rate of DRP removal efficiency and longer life span when compared to a single filter unit F1 (Figure 4-1a & b). These results confirm previous findings by the authors who showed that in series filters design results in a higher DRP removal efficiencies and longer life span of the system (Drizo and Bird, 2008).

Filter effects on pH

During the first feeding period (1-58 d) of the experiment, the pH of the dairy effluent fed to the filters ranged from 7.18 to 8 with an average of 7.5 (±0.25 SD) (Figure 4-1b). The pH of the filters' effluents was higher than the influent throughout the entire period of investigation (Figure 4-1b). Filter F1 effluent pH, ranged from 7.56 to 9.08 over the first 58 d, averaging 8.34 (±0.54 SD) in the first period; in the 2nd feeding period it ranged from 7.08 to 8.04, averaging 7.6 (±0.41 SD). A similar increase in effluent pH compared to the influent was also seen in Filter F2, with the pH ranging from 8.05 to 10.05

Table 4-1: The correlation matrix for filters F1 and F2 for each of the three time periods. Days 23-58 are the initial run, days 61-102 are after the resting period and days 110-132 are with the reduced HRT of 6 h. The data presented is the percent change between the inlet and outlet, and has been reformatted from the correlation matrix to columns so as to allow for the comparison of each time period.

		Filter 1			Filter 2		
		23-58 d	79-120 d	128-150 d	23-58 d	61-102 d	110-132 d
DRP	Ca	0.76	0.78	0.84	-0.44	0.56	0.98
	Fe	-0.31	0.45	-0.24	0.13	0.40	-0.37
	Fe^{2+}	0.70	0.41	-0.72	0.45	-0.04	0.88
	TFe	-0.02	0.87	-0.27	0.55	-0.88	-0.94
	TP	0.95	0.85	0.98	0.61	0.78	0.89
	PO_4^{3-}	0.70	0.87	0.97	-0.08	0.26	-0.03
	pH	-0.84	-0.28	-0.86	-0.75	-0.83	0.71
TP	Ca	0.90	0.63	0.76	-0.46	0.21	0.89
	Fe	-0.55	0.21	-0.07	0.29	-0.06	-0.51
	Fe^{2+}	0.70	0.33	-0.73	0.11	0.26	0.88
	TFe	-0.21	0.87	-0.08	0.13	-0.83	-0.99
	DRP	0.95	0.85	0.98	0.61	0.78	0.89
	PO_4^{3-}	0.55	0.95	1.00	-0.37	0.15	-0.01
	pH	-0.91	-0.57	-0.92	-0.58	-0.65	0.87
PO_4^{3-}	Ca	0.23	0.71	0.71	0.54	0.59	-0.20
	Fe	-0.01	0.07	-0.01	0.66	-0.40	0.84
	Fe^{2+}	0.54	0.19	-0.76	-0.68	-0.47	-0.45
	TFe	0.55	0.90	-0.01	0.77	-0.58	0.08
	DRP	0.70	0.87	0.97	-0.08	0.26	-0.03
	TP	0.55	0.95	1.00	-0.37	0.15	-0.01
	pH	-0.54	-0.33	-0.93	0.57	-0.39	-0.49

(averaging 8.95 ±0.59 SD), and 7.41 to 8.76 (averaging 8.09 ±0.53 SD) in the 1st and 2nd feeding period, respectively (Figure 4-1b). U.S. EPA regulations limit the pH in discharges to freshwater to the range of 6.5–9, which shows that on average F1 was well below this limit, and only went over it on the first sampling day (U.S. EPA, 2002). However, in F2 the average for the first feeding period is seen to be close to the higher limit of acceptable pH's, with the effluent pH often above the limit during the 30 d of investigation.

During the 3rd feeding period, the influent pH was slightly lower when compared to the 1st and 2nd periods, ranging from 6.94 to 7.38, averaging 7.18 (±0.19 SD). A 2 fold decrease in HRT resulted in lower pH values of filters effluents, ranging from 7.43 to 7.57 (average 7.51 ±0.06 SD) and from 7.38 to 7.68 (7.55 ±0.13 SD) in F1 and F2, respectively.

P Retention Mechanisms

Voltammetric data analysis

The chemical composition of the effluent solution as measured by voltammetric analysis remained mostly stable throughout the experiment with no differences seen over time or sampling location in the chemical species observed (Figure 4-2a-c). The most significant change seen over the course of the experiment was an increase in HS^- levels at the outlets of filter F1 and F2 immediately after the resting period (day 58 to 76) (Figure 4-2b & c).

The voltammetric measurements showed that the HS^- peak occurred between -0.8 to -1.2 V, which is more negative than found by Luther *et al.* (2008), who demonstrated that HS^- is indicated by peaks at approximately -0.6 V in marine environments. This discrepancy may be attributed to significant differences in solution composition and high HS^- concentrations, conditions typical of the dairy wastewater fed to the EAF steel slag filters, which are known to cause shifting of the peaks towards more negative values and decrease the measured current (Brendel and Luther, 1995; Luther *et al.*, 2008). Additionally the separation of working electrodes form counter electrodes in the inlet and outlet ports of the system caused a non-negligible junction potential which affected peak positions in the filter 1 inlet and filter 2 outlets (while this set-up was clearly not ideal, it was dictated by the available equipment to run the voltammetric analyses). Peak assignments were supported by sulfide addition experiments and colorimteric observations made in similar solutions to identify the principle sulfur species in this system (data not shown). An initial peak is also seen at approximately -0.2 V in the effluent of F1 between days 21 and 58, and the effluent of F2 after the resting period (days 76-150) (Figure 4-2b & c). Luther *et al.,* (2008) identified two chemical species that may show peaks in this range, O_2 (peak location approximately -0.33 V) and $S_2O_3^{2-}$ (peak location approximately -0.15 V). Significant O_2 in the system accounting for this peak is unlikely as there is no observed secondary H_2O_2 peak (Luther *et al.*, 2008), formed as a result of O_2 reduction at the Ag-amalgam surface, therefore this peak is most likely $S_2O_3^{2-}$, again supported by addition experiments and observations made in similar solutions (data not shown).

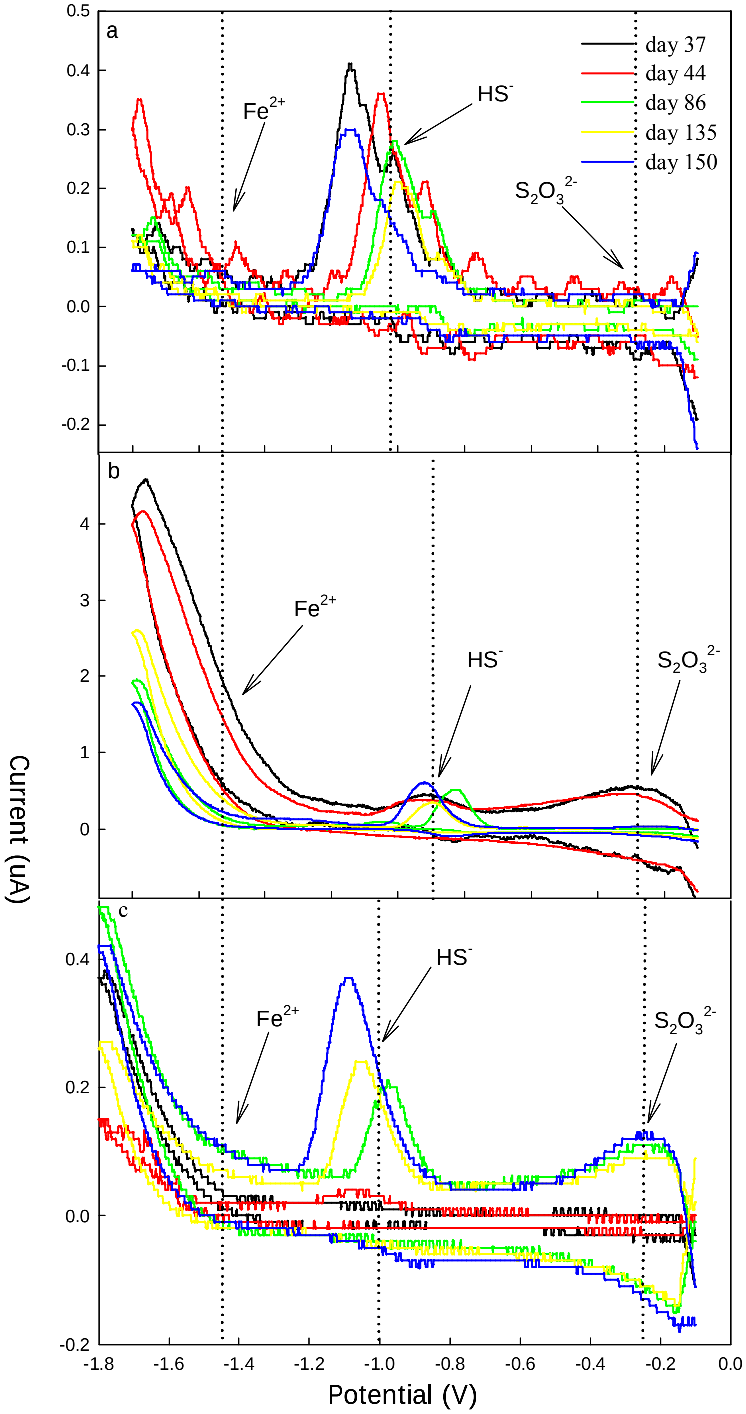

Figure 4-2: A composite voltammetric display of electrode scans measured on days 37, 44, 86, 135 and 150 at the 3 sampling points: the inlet to filter F1 (a); the outlet of F1/ the inlet to filter F2 (b) and the filter F2 outlet (c).

The voltammetric graphs also indicated below-detection levels of Fe^{2+} in solution at the outlets of the filters, which in accordance to Luther *et al.,* (2008) would be indicated by peaks between -1.4 to -1.5 V (Figure 4-2a-c). The low levels of Fe^{2+} were unexpected due to the fact that the EAF slag is largely comprised of Fe oxides (35% by mass), and the highly reducing environment of the solution which should cause dissolution of the Fe oxides on the EAF slag surface. This finding suggests that other mechanisms could be regulating the levels of dissolved Fe in solution.

Measurements of the redox potential were also preformed with a platinum (Pt) and Ag/AgCl combination electrode at the same sampling points (influent to filter F1 and filter F1 and F2 effluents), which showed a slightly oxic (Eh = 50-70 mV) solution. Whereas the voltammetric analysis produced strong evidence of a reducing solution, finding HS^- at all sampling locations, and none of the measured peaks were interpreted to indicate the presence of O_2 or H_2O_2 (peak location at approximately -1.23 V)(Figure 4-2a-c). We believe that the reducing environment as indicated by the voltammetric analysis is more accurate, and that the very high level of organics in the dairy effluent affected the Pt electrode, inhibiting the measurement. This first use of voltammetric sampling in steel slag filters was shown to be an effective and valuable tool for *in-situ* analysis of the solution chemistry of P removal filters.

Geochemical Modeling

Six different sampling dates (days 23, 44, 58, 79, 120 and 142) were selected to provide a full geochemical picture of the EAF steel slag filters, as their P removal efficiencies and

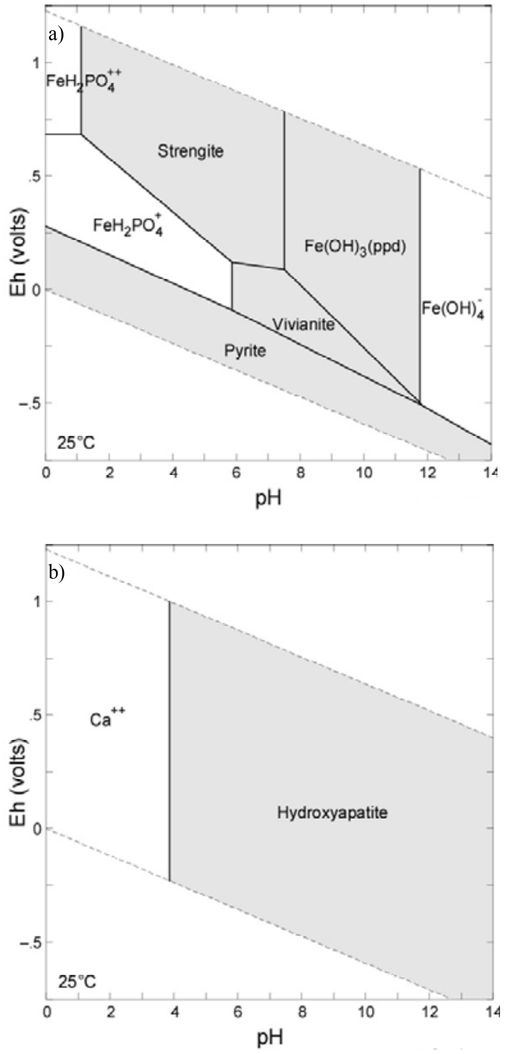

Figure 4-3: Solubility diagrams for Fe (a) and Ca (b) for the range of pH and Eh environments as modeled by Geochemist's Workbench 6.3

the solution chemistry changed over time. Additionally, for each sampling day that the model was run, two different scenarios were selected with the only difference being two different redox conditions tested. The first was the mildly oxic (50-80 mV) Eh to represent the values as measured by Pt electrode and the second was reducing Eh (-300 mV) to represent the results indicated by the voltammetric analysis.

Table 4-2: The saturation indices as computed by the PHREEQC geochemical modeling program. The indices were computed for two different Ehs for each sampling date, a mildly oxic Eh as measured by Pt electrode, and a reducing Eh as indicated by voltammetric sampling.

Days of operation	Sample location	Eh	Saturation indices			
			HAP	VIV	AlO(OH)	FeO(OH)
23	1	oxic	2.41	2.2	-0.67	-0.37
23	2	oxic	5.18	3.22	-1.62	2.42
23	3	oxic	3.5	-0.5	-2.25	2.81
23	1	reducing	2.42	2.18	-0.67	-6.64
23	2	reducing	5.18	3.67	-1.62	-3.59
23	3	reducing	3.5	3.41	-2.25	-2.13
44	1	oxic	2.06	1.7	-0.65	-0.88
44	2	oxic	4.77	3	-0.84	0.63
44	3	oxic	6.31	2.74	-1.56	2.43
44	1	reducing	2.06	1.62	-0.65	-6.86
44	2	reducing	4.77	2.96	-0.84	-5.42
44	3	reducing	6.31	3.35	-1.56	-3.36
58	1	oxic	1.18	1.68	0.36	-0.72
58	2	oxic	4.93	3.4	-0.96	1.21
58	3	oxic	6.06	2.04	-1.69	2.6
58	1	reducing	1.19	1.64	0.36	-7.33
58	2	reducing	4.94	3.4	-0.96	-5.38
58	3	reducing	6.06	3.21	-1.69	-3.6
61	1	oxic	0.59	1.4	-0.83	-0.66
61	2	oxic	4.29	2.75	-1.4	1.53
61	3	oxic	5.07	-0.15	-2.17	2.51
61	1	reducing	0.59	1.39	-0.83	-6.92
61	2	reducing	4.29	2.83	-1.4	-4.7
61	3	reducing	5.07	2.35	-2.17	-2.91
102	1	oxic	-0.88	0.65	-0.41	-1.87
102	2	oxic	1.83	1.57	-0.54	-1.19
102	3	oxic	3.15	2.4	-0.76	-0.11
102	1	reducing	-0.88	0.63	-0.41	-8.13
102	2	reducing	1.83	1.55	-0.54	-7.45
102	3	reducing	3.15	2.39	-0.76	-6.37
124	1	oxic	0.95	1.21	-0.76	-0.81
124	2	oxic	3.36	2.74	-0.96	0.21
124	3	oxic	4.29	2.6	-1.07	0.49
124	1	reducing	0.96	1.15	-0.76	-7.09
124	2	reducing	3.36	2.71	-0.96	-5.97
124	3	reducing	4.29	2.58	-1.07	-5.76

The PHREEQC models showed that P removal mechanisms in EAF steel slag filters are largely controlled by the precipitation of Fe and Ca P minerals. Hydroxyapatite (HAP) is a Ca mineral that has been previously shown to be important to the removal of P in EAF steel slag filters operating at 24 h HRT (Drizo *et al.*, 2006). The modeling demonstrated for the first time that Ca precipitation as HAP most likely plays an important role for P removal at shorter HRT (12 h)(Tables 4-2 and 4-3). Moreover, we have shown that Fe-P precipitation and formation in the form of the Fe(II) mineral vivianite ($Fe_3(PO_4)_2 \bullet 8H_2O$) may also have a significant role (Tables 4-2 and 4-3). The pH (6.68-10.05) and Eh (≤ 0) ranges indicated in our experiment correspond to the range of conditions necessary for

($Fe_3(PO_4)_2 \cdot 8H_2O$) (VIV) formation, where VIV is the most stable Fe^{2+} mineral (Figure 4-3a) (Nriagu and Dell, 1974). The range of conditions supporting the formation of HAP ($Ca_5(PO_4)_3OH$) is much larger, therefore this mineral could have been formed under the observed chemical conditions in the filters (Figure 4-3b)(Lindsay, 1979).

The model produces saturation indices where the greater the reported value, the more likely the mineral will precipitate out of solution, and the more negative values indicating that the mineral should be dissolving. The saturation indices produced by the models indicate that as the waste effluent moves through the filters HAP becomes increasingly supersaturated, the single exception being on day 23, when the outlet of filter 2 is seen to be less supersaturated then the outlet of filter 1. There was also one single observation at the inlet of filter 1 (day 102), when HAP was not supersaturated in solution (Table 4-2). HAP formation is not affected by the redox conditions in the filter; hence no difference was observed between the two models run. It is known that in solutions without the presence of Ca-P seeds a higher activation energy is required to promote the precipitation of HAP, making factors such as pH and Ca and P concentration important variables (Lazic, 1995). In a study of the P removal mechanisms in BF slag and opoka, Johansson and Gustafsson (2000) found that the critical point of supersaturation needed for the formation of HAP in unseeded solution was $10^{2.5}$ times the HAP solubility line. In this study the level of solution supersaturation exceeded the value proposed by Johansson and Gustafson (2000) by a further $10^{2.5}$ times. Additionally, the level of supersaturation with EAF steel slag was approximately 10^{2} times more saturated when compared to the BF slag as measured in their study (Johansson and Gustafsson, 2000). In that study, a synthetic phosphate solution was used, whereas our filters were fed at a higher loading rate with a high strength dairy wastewater that has high concentrations of P and Ca. Additionally, EAF steel slag has much higher levels of Ca-oxides than BF slag, which can dissolve maintaining high solution concentrations.

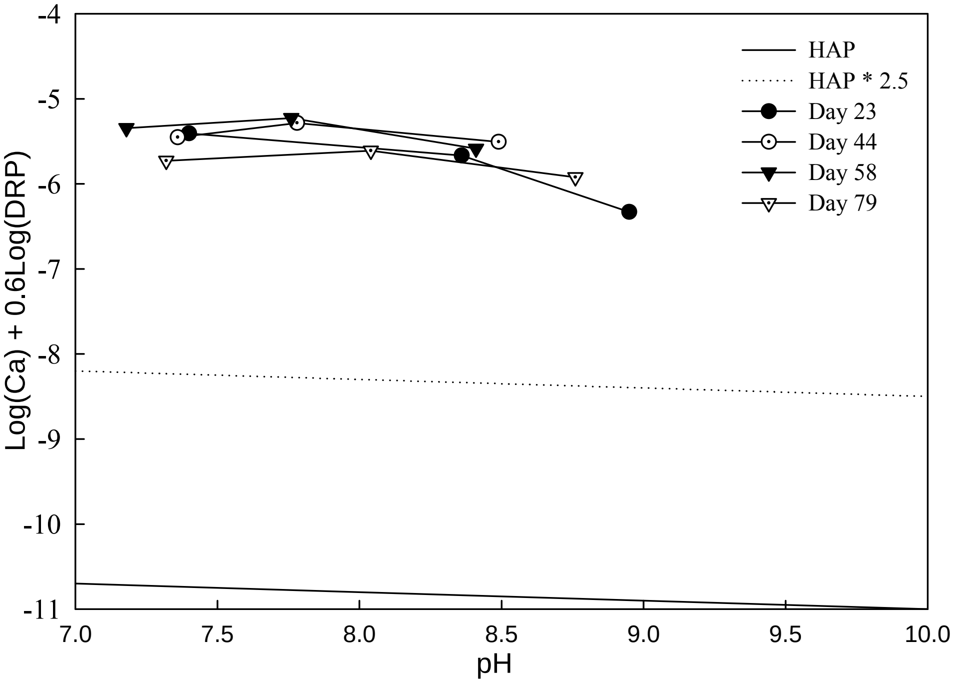

Figure 4-4: A plot of Log(Ca) + 0.6Log(DRP) vs. pH at the inlet of F1 and outlets of F2 on 4 different sampling locations. The solubility line of HAP as calculated based on Log K and a secondary line representing $10^{2.5}$ the line of solubility.

The saturation index of VIV showed much greater variability in the solution when compared to HAP. VIV is a mineral of Fe^{2+}, and is therefore highly affected by the redox state of the solution, quickly oxidizing to Fe^{3+} if the solution becomes less reducing. In all models supersaturation of VIV was much higher after passing through filter 1. The saturation index was either stable or lower after passing through filter 2, except on day 44 with the reducing Eh (Table 4-2). Despite this, very little difference is seen in the saturation index for VIV between the two models at the outlet of filter 1. However, at the outlet of filter 2 the differences between the two models become very dramatic, with much lower reported saturation indices in the mildly oxic models, and on two days (day 23 and 61) shown to be dissolving into solution.

Table 4-3: The results of the PHREEQC inverse modeling are shown for the 6 days that were analyzed. The highest and lowest values of HAP and VIV predicted by the models are shown for filter 1 and 2 and under both of the Eh scenarios, mildly oxic (50-70 mV) and reducing (-300). Also displayed for each day is the DRP removal efficiency of each filter. N/A signifies days for which the model was unable to compute the mass change.

Days of operation	Filter	Eh	% DRP Removal	HAP Phase Mole change		Viv Phase Mole Change	
				Low	High	Low	High
23	1	oxic	76.79	-4.33E-04	-4.62E-04	-3.93E-06	-7.43E-04
23	2	oxic	59.01	-2.67E-05	-7.85E-05	-6.92E-05	-7.43E-04
23	1	reducing	76.79	-4.11E-04	-4.62E-04	-2.68E-05	6.93E-04
23	2	reducing	59.01	-2.81E-05	-7.85E-05	-6.92E-05	-7.85E-05
44	1	oxic	33.21	-7.72E-05	-9.62E-05	-1.16E-04	-1.44E-04
44	2	oxic	71.75	-2.62E-04	-2.68E-04	-4.05E-04	-4.05E-04
44	1	reducing	33.21	-7.72E-05	-9.66E-05	-1.16E-04	-1.45E-04
44	2	reducing	71.75	-2.62E-04	-2.68E-04	-3.93E-04	-4.05E-04
58	1	oxic	36.90	-7.49E-05	-1.85E-04	-1.12E-04	-2.61E-04
58	2	oxic	92.51	-3.69E-04	-3.72E-04	-3.90E-06	-5.74E-04
58	1	reducing	36.90	-1.86E-04	-1.86E-04	-1.99E-04	2.79E-04
58	2	reducing	92.51	-3.71E-04	-3.71E-04	-5.57E-04	-5.57E-04
61	1	oxic	38.33	-1.41E-04	-1.41E-04	-1.65E-04	-2.11E-04
61	2	oxic	71.98	-3.76E-06	-1.41E-04	-2.05E-04	-2.10E-04
61	1	reducing	38.33	-9.20E-05	-1.41E-04	-1.75E-06	-2.11E-04
61	2	reducing	71.98	-3.76E-06	-1.41E-04	-2.05E-04	-2.05E-04
102	1	oxic	-23.06	N/A	N/A	N/A	N/A
102	2	oxic	40.05	N/A	N/A	N/A	N/A
102	1	reducing	-23.06	N/A	N/A	N/A	-6.56E-06
102	2	reducing	40.05	N/A	N/A	N/A	N/A
124	1	oxic	-5.43	N/A	N/A	N/A	N/A
124	2	oxic	0.67	-1.47E-06	-1.47E-06	-2.20E-06	-3.36E-06
124	1	reducing	-5.43	N/A	N/A	N/A	N/A
124	2	reducing	0.67	-1.26E-06	-1.47E-06	-3.11E-07	-2.20E-06

Pratt *et al.* (2007a;b), in studies of IM slag, identified amorphous Fe oxide/oxyhydroxides on the slag surface as the main P removal mechanism (Pratt *et al.*, 2007a; Pratt *et al.*, 2007b). This mechanism is unlikely to be responsible for the P removal in EAF steel slag filters due to the range of conditions seen. Fe oxide/oxyhydroxides are formations of the oxidized Fe^{3+} and under the measured pH and Eh in EAF steel slag would undergo reductive dissolution, releasing any sorbed P (Figure 4-3a & Table 4-2). This was also demonstrated by Pratt *et al.* (2007a) who manipulated solution Eh and pH and measured the dissolution of P from used IM slag in a laboratory study. The largest losses of P were found when the Eh was lowest (-400 mV), causing reduction of the Fe oxide/oxyhydroxides and release of the associated P (95% of total sorbed)(Pratt *et al.*, 2007a).

The geochemical modeling demonstrated that both HAP and VIV are generally supersaturated in the solution of EAF steel slag filters. On both days 120 and 142 an inverse model could not be created, most likely due to the constraints placed on the model dictating mineral precipitation out of solution (Table 4-2 and Figure 4-1). At this late stage in the filters lifespan, DRP removal is seen to be very poor, and therefore little mineral formation is expected, and mineral dissolution might be occurring. Since this study was to investigate only the formation of these minerals, the formation constraint was used. For most of the days run the inverse modeling showed a negative transfer of P, meaning that HAP and VIV were precipitating out of solution. The average moles of HAP and VIV as predicted by both the oxic and reduced models for days 23, 44, 58 and

79 were converted to mg L^{-1} and the amount of associated P was calculated. It is seen on each day that the models predicted higher removal rates than we observed with both DRP and soluble TP removal for each filter (Table 4-3). Additionally, the model found Al and Fe oxyhydroxides to be undersaturated under reduced conditions on all days, and at all 3 sampling locations, suggesting that these minerals would be dissolving into the solution (Table 4-2). These results suggest that HAP and VIV precipitation represent the main P removal mechanisms in EAF steel slag filters operating at 12 h HRT. The higher estimates of mineral precipitation seen in the models may be explained by overlap of competing models, where all of the predicted mineral formation would not be happening simultaneously, resulting in an over estimation. With the inverse modeling PHREEQC identifies all possible models involving the specified minerals which conform to the known solution compositional change. Most of the models found did not contain both VIV and HAP, however it is intended that all models found are to be viewed jointly to explain possible chemical scenarios (Parkhurst and Appelo, 1999).

A correlation matrix was used to analyze possible correlations in data at the 3 different time periods, first feeding period (day 23-58), a second feeding cycles after resting period (days 76-126) and after the reduction in HRT to 6 h (days 127-150). The percent change of DRP, PO_4^{3-} and TP was compared to the percent change in total soluble Ca, Fe (ICP) Fe^{2+}, TFe and pH for filters F1 and F2. In filter F1, there were strong correlations between the changes in Ca and all forms of P, with the exception of PO_4^{3-} at the first time period. With F2 the correlations were not as strong, with a negative correlation seen between DRP and TP at the early period, and PO_4^{3-} at the last period. In both filters, the correlations with Fe^{2+} and TFe were erratic, with no pattern seen. This may be further evidence that other constituents in the solution inhibited the colorimetric analysis. The three forms of P measured, TP, DRP and PO_4^{3-} by the filters F1 and F2 mostly show a negative correlation to the percent change of the pH in the filters, indicating that as the pH became higher, there was higher P removal efficiency (Table 4-1).

In a study of BF slag using the MINTEQA2 program to model the chemical environment, HAP formation was identified as the main mechanism for P removal (Johansson and Gustafsson, 2000). Whereas, in studies of IM slag, Fe oxides/oxyhydroxides have been shown to be the primary mechanism for P removal (Pratt *et al.*, 2007a; Pratt *et al.*, 2007b). However, both of these slags have significant compositional differences from EAF steel slag. EAF steel slag is 65% Ca and Fe oxides where BF slag is mainly Ca-oxides (34%) with little Fe content (0.4%) and IM slag has only a low concentration of Fe-oxides (5.9%) and Ca-oxides (9.7%) (Johansson and Gustafsson, 2000; Pratt *et al.*, 2007a; Drizo *et al.*, 2008). Therefore in EAF steel slag it is possible that both Fe and Ca mineral formation can be responsible for P removal, unlike in the other two slag types.

Conclusions

The DRP removal efficiency was approximately 3 times lower than in earlier studies of EAF steel slag with a 12 h HRT, with filter F1 removing a total of 0.3 g DRP kg^{-1} slag.

The use of series design increased P removal efficiency by 75%, from 45% to 79%, greatly expanding the life of the system in comparison to a single filter unit.

Voltammetry was shown to be a highly effective method for the *in-situ* analysis of EAF steel slag filters chemical composition and redox conditions. The voltammetric analysis revealed that the solution was highly reducing, with the presence of HS^- observed in all samples and no evidence of O_2 or H_2O_2 at any of the sampling points. A Pt Eh probe showed a mildly oxidizing redox environment, but this measurement may have been inhibited by the high amounts of organics and contamination associated with sampling and transportation. The voltammetry additionally showed that the solution chemistry remains mostly stable spatially, as it passed through the filter system, and temporally, over the length of a daily run and over the lifespan of the filter. Very low concentrations of Fe^{2+} were seen in solution considering the redox conditions and the undersaturated conditions for Fe oxyhydroxide formation from the EAF steel slag. This may indicate that an internal process is limiting the release of Fe^{2+} from the filters, such as precipitation of VIV.

The stability diagrams for HAP and VIV indicated that the formation of both minerals could be supported in the chemical conditions of the EAF steel slag filters solution. The PHREEQC geochemical software models predicted the formation of both HAP and VIV in the EAF filters on all days sampled. The estimated amounts of P removal by the models by precipitation of HAP and VIV exceeded the observed removal of DRP and soluble TP in both filters on the 3 days modeled. This demonstrates that HAP and VIV formation can explain all of the removal of P seen, and indicates that these minerals are capable of providing a mechanism for the removal of P.

This research demonstrates that the observed solution chemistry in EAF steel slag filters promotes the precipitation of HAP and VIV minerals in sufficient quantities to explain the observed mass loss of P from the solution. However, further research utilizing visual microscopy and scanning electron microscopy (SEM) to identify the presence of these minerals in P saturated EAF steel slag would be useful.

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