

Use of Iron Oxides Produced From the Treatment of Coal Mine Drainage as Adsorbents to Remove Phosphorus from Secondary Wastewater Effluent

Final Report for OSM PA (AMD-04) Phosphorus Grant

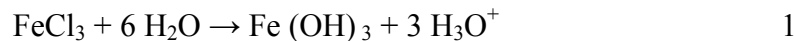
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Abstract:

The use of AMD produced iron oxides, ferric chlorides produced from AMD iron oxides, and AMD discharge water were investigated as phosphate sequestering agents in municipal wastewater treatment. All of these materials are capable of sequestering phosphates in secondary effluent. Eight different iron oxide solids were investigated as part of this study. The solids were found to be relatively pure, greater than 80% iron oxide, in a semi crystalline Goethite type structure. The phosphate adsorption capacity for AMD iron oxides is around 7 mg P/gram of solid for dried iron oxides and increases to around 12 mg P/gram of solid never dried iron oxides. These values are about 13 to 23 times lower than the phosphate adsorption capacity of freshly precipitated iron oxides prepared from ferric chloride, 160 mg P/gram iron oxide. Six different iron oxides were converted to ferric chlorides and investigated as sequestering agents for municipal wastewater treatment. All of the samples have adsorption capacities greater than, or equal to commercial ferric chloride. Elemental analysis of the AMD iron oxide solids reveals that the materials are free of heavy metal contaminants, and leaching studies have confirmed that AMD ferric chlorides do not increase the concentration of metals in effluent water. AMD discharge water from four discharges in Westmoreland County was examined as sequestering agents for phosphates. Ferrous iron in the discharge water readily oxidizes in the effluent water, and is converted to iron oxides which have phosphate adsorption capacities greater than, or equal to commercial ferric chloride.

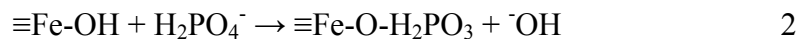
Introduction:

Metallic oxides, such as iron oxide, are extensively used in the wastewater treatment industry to remove phosphorus from the effluent stream (1-3). Ferric chloride, FeCl_3 , is typically added during treatment and readily hydrolyses to form an amorphous ferrihydrite, $\text{Fe}(\text{OH})_3$, through the chemical reaction given below.



Freshly precipitated ferrihydrite has a large surface area and sequesters phosphorus through a complex mechanism that includes both sorption and precipitation.

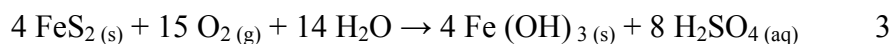
The sorption of phosphates to metallic oxides has been extensively investigated and sorption models have been proposed (1-6). Sorption takes place on the surface of the particle through the following reaction (2-4).



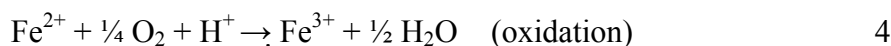
In buffered deionized water, a Langmuir isotherm can be used to describe the binding process (5, 6). Both the surface area and surface charge of the particles strongly influence the binding process. Freshly precipitated ferrihydrite has a surface area of 200-300 m²/g and has a large capacity to bind phosphates, while crystalline or semi-crystalline iron oxides, such as goethite and hematite, have surface areas at least 10 times lower, and their binding abilities are greatly diminished (2,3). Kang and co-workers (2) have shown that the binding constant for ferrihydrite, goethite, and hematite are similar if corrected for surface area. This suggests that the binding sites of all iron oxides do not differ significantly and that the phosphate binding takes place through a common mechanism, irrespective of crystallinity or crystal structure. The sorption of ions to the surface of metallic oxides is a function of the surface charge, and the surface charge is a function of pH (5) and the ionic strength of the solution. Anions, such as a phosphate, can display a strong pH dependent binding to the surface of iron oxides (2, 3, 5). In buffered deionized water, the sorption of phosphate to ferrihydrite can decrease by as much as 50% with one change in pH unit.

The eastern coal mining region is plagued with a number of environmental scars from past mining practices including Abandon Mine Drainage (AMD). Pennsylvania's four major river basins are affected by drainage coming from thousands of abandoned coal mines that have contaminated more than 3,000 miles of streams (7). The AMD pollutants enter into the streams degrading water quality and benthic substrates that causes adverse impacts to the aquatic ecology and the designated uses (e.g., recreation and potable water).

AMD formation is a function of the geology and hydrology of the mine site and the mining technology employed. It occurs as a consequence of a series of complex geo-chemical and microbial reactions that take place when oxygenated water comes into contact with pyrite (FeS₂) contained in the coal, refuse, or the overburden associated with a mine operation (8). The resulting AMD varies considerably and can be highly acidic (pH as low as 2.5), or nearly neutral (pH slightly above 6), and contain dissolved metals such as iron, manganese, and aluminum. The concentration and composition of the metal ions is strongly influenced by the pH of the AMD. A number of chemical reactions that take place during pyrite weathering, oxidation of ferrous iron, and hydrolysis, lead to the formation of an iron oxide precipitate. These reactions may be summarized in the overall reaction given by equation 3, below:



In water, iron (Fe) undergoes oxidation and hydrolysis reactions. Oxidation is the process of decreasing acidity whereas hydrolysis increases acidity. The reactions for Fe are as follows:



Alkalinity and acidity do not mutually exclude each other. Thus, when water contains both alkalinity and mineral acidity, a comparison can be made to determine whether the water is net alkaline (alkalinity is greater than acidity) or net acidic (acidity is greater than alkalinity) (9). The "hot" acidity measurement can be used for this determination with a measurement value less than

0 mg/l representing net acidic and a value greater than 0 mg/l representing net alkaline. An alternative is to subtract the stoichiometric acidity of the metals from the alkalinity with a value less than 0 mg/l representing net acidic and a value greater than 0 mg/l representing net alkaline. Net alkaline water has sufficient alkalinity to neutralize the mineral acidity that results from the oxidation and hydrolysis of the metal ions. In aerobic environments, oxidation and hydrolysis reactions lead to a decrease in the concentration of iron and the formation of iron oxide precipitates. There are a number of successful AMD treatment options, one is constructed wetlands (9), that take advantage of the oxidation and hydrolysis chemistry of iron in order to restore impacted waters. One of the byproducts of AMD treatment is iron oxide solids, ferrihydrite, which can be produced with few contaminants. To date, there are few industrial applications for iron oxides produced from AMD.

In our laboratory we have started to investigate the use of AMD produced iron oxides as adsorbents for contaminants such as phosphates. Ochiana and Echard (10) studied the binding of phosphates to AMD produced iron oxides in buffered deionized water. They found that sorption exhibits Langmuir isotherm behavior and is strongly pH dependent, which is consistent with sorption studies with synthetic iron oxides. However, AMD produced iron oxides are aged and exhibit binding that is about 15 times lower than freshly precipitated iron oxides. This lower sorption ability was somewhat expected. Lijklema (6) has shown that aging synthetic iron oxides for 24 hours decreases their binding ability by more than 50%. Freshly precipitated ferrihydrite is amorphous and can be pictured as lightly crosslinked polymers (fractal) with a very high surface area. Aging allows the iron oxide to further condense, crosslink, and recrystallize, which decreases the surface area and increases the particle size. Extended aging may further increase the crystallinity of the iron oxide which further reduces the surface area (11). Kairies and coworkers (24) have studied the physical properties of iron hydroxide precipitates from passively treated mine drainage produced from the bituminous coal region of Pennsylvania and Maryland. Using x-ray diffraction, they have shown that AMD produced iron hydroxide precipitates are Goethite and not amorphous ferrihydrite. The binding constants obtained by Ochiana and Echard (10) strongly suggest that the AMD iron oxide samples used in their study are not amorphous, and are most probably Goethite or another crystalline form of iron oxide.

Our initial studies did show that AMD produced iron oxides are capable of removing phosphates from buffered deionized water. This report details our phosphate sorption studies using effluent water from two Unity Township Municipal Authority (UTMA) treatment systems, and a sequencing batch reactor bench to study using anoxic liquor from the UTMA 14 Mile Run facility.

Experimental:

The secondary effluent water used in this study was obtained from UTMA facilities located in Pleasant Unity, Pennsylvania, and their 14 Mile Run facility located in Unity Township, adjacent to Saint Vincent College. The effluent water was vacuum filtered with the aid of Whatman #1 filter paper to remove suspended solids, and the Pleasant Unity effluent was spiked with disodium phosphate (J. T. Baker) so that the ortho-phosphate concentration was between 10-20 mg/l phosphate, or 3-6 mg/l phosphorus. This phosphate addition was needed for

the Pleasant Unity facility because the effluent contains minimal phosphate due to required phosphorous removal to meet NPDES effluent limits. Effluent water from the 14 Mile Run facility used in this study contains 3-6 mg/l of phosphorus since the treatment system does not have a phosphorus limit. The effluent water was stored in acid washed brown glass bottles, and was characterized using methods outlined in Standard Methods (12). The results are presented in Table 1.

Parameter	Mean Concentration (mg/l)	± 90% Confidence Limit
pH	6.6	0.1
NH ₄ ⁺	<0.05	
NO ₃ ⁻	9	1
Ca ⁺²	34	3
Mg ⁺²	5	2
Alkalinity	60	6
BOD	<3	
DO	5.2	0.4
TSS	3	1

Table 1. Water quality for unfiltered secondary effluent from UTMA.

AMD iron oxides were collected from seven treatment systems around Western Pennsylvania and stored in sealed plastic containers. The seven sites were chosen because they were produced from AMD sources with different water chemistries, using different treatment systems. Data for these sites is given in Table 2. All of the various samples were stored at approximately 70% moisture content to prevent them from drying out, and these samples are referred to in this study as aged iron oxides. No attempt was made to purify the iron oxides. Dried iron oxide samples were prepared by drying the 70% moisture samples at a constant temperature for at least 24 hours. The dried samples were ground in a mortar and pestle and stored in glass vials.

Sample	Discharge Name	County	Type of Discharge	Type of Treatment
HB-110	Howe Bridge	Clarion	Net acidic	Passive Wetland
SVC-M-110	Saint Vincent Mesocosm	Westmoreland	Net alkaline	Passive Wetland
BC-110	Brandy Camp	Elk	Net acidic	Active-lime
BV-110	Blue Valley	Elk	Net alkaline	Active-permanganate
HR-110	Hays Run	Elk	Net alkaline	Passive Wetland
SVC-3-110	Saint Vincent Wetland 3	Westmoreland	Net alkaline	Passive Wetland
AIS-110	Saxman Run	Westmoreland	Net alkaline	AIS-semi active
Phillips	Phillips Discharge	Fayette	Net alkaline	AIS-semi active

Table 2. Table of sites where aged AMD iron oxide samples were collected.

AMD water was obtained directly from the discharge, placed in acid washed plastic containers, and stored at 4° C until used. These water samples were stored for less than 3 hours before using. The AMD samples were analyzed for alkalinity, acidity, and metals, using methods outlined in Standard Methods (12). All phosphate adsorption studies were performed in acid washed glassware, and were equilibrated for a minimum of 12 hours. Water samples were removed from the equilibrated samples by the aid of a syringe and filtered through a Whatman 0.45 µm polypropylene filter. Phosphate analysis was performed using Hach method 8114 and a DR-890 colorimeter (13).

All metals were analyzed using a Varian Vista-MPX ICP or a Varian SpectrAA Flame AA, calibrated with metals standards purchased from Fisher Scientific,. Detection and quantification limits were determined for each of the elements analyzed. The quantification and detection limits were calculated as 3 times and 5 times the noise range, respectively. These values are summarized in Table 3.

	Al	As	Ca	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	Pb	Se	Zn
	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)
Quant limit	0.1	0.8	0.08	0.3	0.7	0.1	0.03	0.3	0.03	0.08	0.3	1.7	0.5	0.5
Detect limit	0.07	0.5	0.05	0.02	0.4	0.06	0.02	0.2	0.02	0.05	0.2	1	0.3	0.3

Table 3. Quantification and Detection limits for metals analyzed in this study. All concentrations are expressed in mg/l.

SBR studies were conducted over a 4 to 5 day period. At the start of a trial, a plastic 500 ml acid washed Nalgene bottle was filled with anoxic liquor from UTMA 14 Mile Run facility, and spiked with the appropriate additive. The bottle was capped and stirred for 5 hours. At the end of the 5 hour period the liquor was placed in a 1000 ml beaker and aerated using aquarium stones and a laboratory air compressor for about 18 hours. Next, solids were allowed to settle for about 45 minutes. After settling, 300 ml of the clear effluent was decanted from the solids, the solids were placed back in the plastic bottle, and 300 ml of raw water from the UTMA facility was added along with the appropriate additive. This process was then repeated for four additional days.

Results and Discussion:

Analysis of AMD Iron Oxides: The AMD Iron Oxide solids were characterized using both chemical and physical analysis and the results of the chemical analysis for six different solid samples are given in Table 4. Except for the Brandy Camp sample, all of the samples are between 50% to 62% iron. If the iron oxide samples are predominantly Goethite (α -FeOOH) as Keiries (24) has shown, then the composition of iron oxide in the samples varies between 80 to 99% iron oxide for the dried samples. Brandy Camp is the one exception. The Brandy Camp solid is produced via a hydrated lime active treatment of the discharge that also includes aeration, flocculation and clarification. As a result of the hydrated lime addition, the solid contains significant amounts of Ca, and Mg that co-precipitates with the iron oxide. As a result, the Brandy Camp sample is only 32% FeOOH.

Sample	Al (w %)	Ca (w %)	Fe (w %)	Mg (w %)	Mn (w %)	As (mg/Kg)	Cu (mg/Kg)	Ni (Mg/Kg)	Pb (mg/Kg)	Zn (mg/Kg)
Howe Bridge	0.04	<0.01	55	<0.01	1.6	<50	ND	<80	21	300
Brandy Camp	2.9	24	20	2.0	1.4	ND	9.1	600	<20	570
Blue Valley	0.34	1.4	62	0.7	0.2	69	9.5	<80	<20	590
Hayes Run	4.3	0.7	55	0.03	0.49	110	<6	ND	<20	230
Saint Vincent-3	0.32	0.5	56	0.03	0.06	<50	<6	ND	<20	200
Saxman AIS	0.37	0.4	50	0.02	0.11	110	<6	<80	<20	1060
Phillips AIS	0.35	1.4	54	0.04	0.03	<50	ND	ND	<20	123

Table 4. The Chemical composition of AMD iron oxide solids dried to 110 degrees. The designation ND in the table means Not Detected. Data for HB-110 obtained from Kairies et al. (24).

Analysis of trace metals in the samples revealed that the samples are relatively free of heavy metals. All of the samples were analyzed for Cd, Co, Cr, and Se, and the concentration for all of these metals were below the detection limit. Except for the Brandy Camp sample, the concentration of Cu and Ni were very low. Zinc is another metal found in significant quantities in the iron oxide solids, with concentrations ranging from 123 to 1060 mg/kg. Zinc has been shown to selectively adsorb to the surface of iron oxides (5,23), and Kairies (23) has noted that the concentration of zinc in the iron oxide samples they have analyzed are typically 2 to 3 orders of magnitude greater than the concentration in the mine water.

The mineralogy of the AMD produced iron oxides was investigated by x-ray diffraction analysis, and the results are given in Table 5.

Sample Name	Major crystalline phase	Minor Crystalline phase(s)
Howe Bridge	Goethite (FeOOH)	Lepidocrocite (FeOOH)
Brandy Camp	Calcite (CaCO ₃)	
Blue Valley	Goethite (FeOOH)	Hematite (Fe ₂ O ₃)
Hayes Run	Goethite (FeOOH)	Hematite (Fe ₂ O ₃)
Saint Vincent-3	Goethite (FeOOH)	Hematite (Fe ₂ O ₃)
Saxman AIS	Goethite (FeOOH)	Hematite (Fe ₂ O ₃)
Phillips AIS	Goethite (FeOOH)	

Table 5. Major crystalline phases observed by x-ray diffraction analysis for AMD produced iron oxides. All samples were dried to 110°C.

Except for the Brandy Camp sample, all of the iron oxide solids contain the crystalline phase Goethite. The Blue Valley, Hayes Run, SVC, and AIS iron oxide solids all have lower intensity diffraction peaks which indicate that these samples have small crystallites and a significant amount of amorphous ferrihydrite [Fe(OH)₃]. Both the Phillips and Howe Bridge

iron oxide sample have much sharper, and more intense diffraction peaks (about 4 times the intensity of the other samples). This strongly suggests that these samples have larger crystallites, and a higher percentage of crystalline iron oxide. Kairies (23) performed x-ray diffraction analysis on their iron oxide samples, and found that they were predominantly Goethite. They obtained iron oxide samples from the Howe Bridge discharge and noted that their samples were predominantly Goethite with minor amounts of Quartz and Lepidocrocite. The findings of this study are very consistent with the work of Kairies and coworkers.

The unusual sample in this study was once again Brandy Camp. The Brandy Camp iron oxide has an x-ray diffraction pattern with very sharp intense peaks that can be assigned to Calcite. Goethite peaks are not discernable in the background noise. The lack of Goethite peaks may suggest that the iron oxide phase of this sample is amorphous, or that it is not observable because the sample is about 32% iron oxide and 60% CaCO_3 , and the intense peaks of Calcite cause a dynamic range problem making it difficult to observe the low intensity peaks of Goethite. Kairies and coworkers (23) found that the highest crystalline iron oxides are found close the inlet to a constructed wetland, and the percent crystallinity of the iron oxide decreases the further away from the inlet the sample is collected. They have suggested that the iron oxides that precipitate fast are highly crystalline, while the iron oxides that precipitate slowly from waters that contain high concentrations of metals such as calcium, aluminum, and manganese are poorly crystalline because the adsorbed metals interfere with the crystallization of iron oxide. It is possible that the Brandy Camp sample is indeed amorphous, and the high concentration of calcium in the water along with the high pH in which the iron was precipitated prohibited the crystallization of the iron oxide phase.

Both the Phillips and the Saxman Run AIS iron oxide samples were produced from alkaline discharges with similar water chemistries using an Activated Iron Solids (AIS) process (14-16), but the Saxman Run AIS sample has a lower crystallinity. In the AIS process, influent water is mixed with iron oxide solids so that the total iron concentration is around 1000 mg/l. The influent is aerated to strip off dissolved CO_2 and to increase the pH of the water to 6.5 to 7.0. It is believed that the ferrous iron in solution binds to the surface of the iron oxide where it is oxidized to ferric iron. This heterogeneous oxidation is about 1000 faster than homogeneous oxidation. While the two solids were produced in similar reactors operating under similar conditions, they have very different percent crystallinities. The x-ray pattern for the Phillips sample has diffraction peaks about 4 times more intense than the Saxman Run AIS sample. A Phillips sample collected and processed without substantial aging did not show the intense peaks indicating there was less crystallinity than the aged Phillips sample. One of the differences in their treatments is that the initial iron concentration of the Phillips discharge is about twice that of the Saxman Run, and the Phillips iron oxide was flocculated with the help of an anionic acylamide polymer. The differences in crystallinity of the aged AIS samples may be caused by 1) the higher iron oxidation and precipitation rates of the Phillips discharge, 2) an affect of the polymer on crystallization of the Phillips AIS, and/or 3) the higher zinc contamination in the Saxman Run AIS sample (approximately 10 times greater than the Phillips AIS).

Another measure of the amorphous nature of an iron oxide is the percentage of the sample that can be extracted with an ammonium oxalate buffer (11, 22). The extraction results for Hayes Run, Blue Valley, SVC, and Brandy Camp samples are given in Table 6.

Percent Extractable Iron Oxide			
Sample	50° C Drying Temperature	513° C Drying Temperature	600° C Drying Temperature
Hayes Run	100	12	15
Blue Valley	99	26	11
Saint Vincent-3	71	8	11
Brandy Camp	13	0	0

Table 6. A comparison of the impact of drying temperature on the percent extractable iron oxide for two AMD produced iron oxides.

The Hayes Run, Blue Valley, and SVC iron oxide samples that were dried at 50° C appear to be highly amorphous, with 71% to 100% of the sample extracted with ammonium oxalate buffer. In contrast, iron oxide samples that are dried at higher temperatures, 500-900° C, appear to be crystalline with only a small fraction of the sample extractable. The Brandy Camp sample which is 60% calcium carbonate displayed poor extractability even when dried to only 50°. The poor extractability of the Brandy Camp sample is expected because of the high percentage of calcium carbonate in the sample. The calcium carbonate inhibits the extraction of the amorphous iron oxide by increasing the pH of the oxalate solution. Sorensen and co-workers (22) investigated the oxalate extractability of their iron oxide samples. They found that after heating iron oxides to 600°, less than 2% of the iron oxide could be extracted. They also noted that impurities such as calcium, silica, and transition metal ions decreased the crystallinity of iron oxide samples, and increased the oxalate extractable fraction. It is plausible that impurity ions such as Ca, Mg, and Mn which are found in AMD may help to prevent complete crystallization of our iron oxides that were heated to high temperatures.

Surface area measurements were performed on the Hayes Run (237 m²/g), Saxman AIS (308 m²/g), Phillip AIS (315 m²/g), and SVC wetland (211 m²/g). While there is variation in the samples surface areas, all of the value fall in the range measured by Kang et al (200-300 m²/g)(2). We have studied our AMD produced iron oxides using light microscopy and found that the solids are not uniform in size. There are a number of small particles that are 4-5 µm in size, as well as larger aggregates of particles.

Adsorption of Phosphates to Dry AMD Iron Oxides: Adsorption studies were conducted on AMD iron oxides collected from seven different discharges throughout Pennsylvania (see Table 2). Iron oxide samples were dried at 110° C and were allowed to equilibrate for a minimum of 12 hours in the spiked effluent water. The effluent water was then filtered and analyzed for phosphate concentration. A typical plot of equilibrium phosphate concentration versus iron oxide concentration is given in Figure 1.

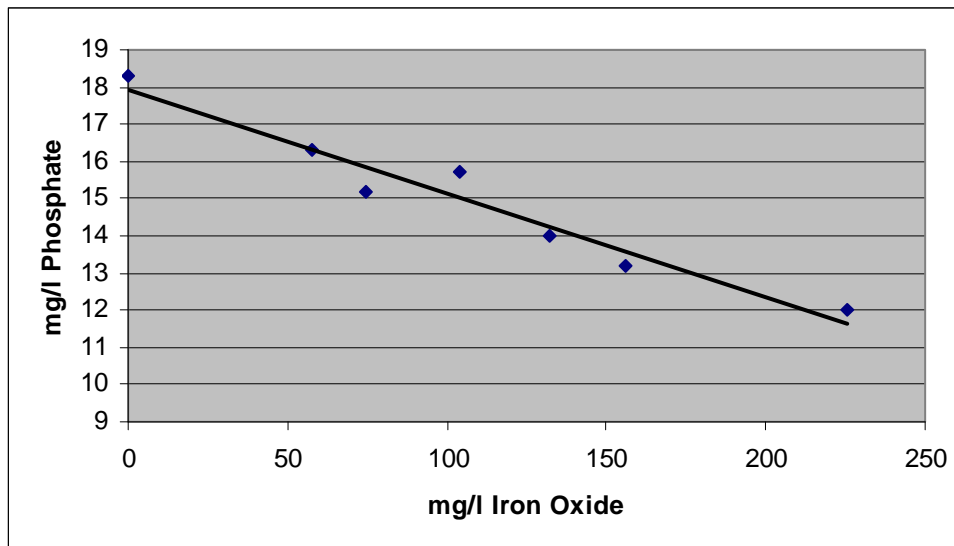


Figure 1. Plot of equilibrium phosphate concentration versus iron oxide concentration for Howe Bridge iron oxide sample dried to 110° C and equilibrated with effluent water.

Figure 1 clearly shows that AMD produced iron oxides are capable of removing phosphate from effluent water. The slope of the plot is a measure of the adsorption capacity of the iron oxide. As the slope becomes steeper, the iron oxide becomes more effective at sequestering phosphate, especially at lower iron oxide concentrations. Langmuir isotherm plots for the binding of phosphate to AMD iron oxides in effluent water are not linear. The nonlinear Langmuir plots suggest that the binding of phosphate to the surface of iron oxide in effluent water is more complex than simple monolayer adsorption. Kang and co-workers (2) determined the adsorption of phosphate to synthetic iron oxides in effluent water could be modeled using a Freundlich isotherm, as exhibited in equation 6.

$$Q = K C^n$$

6

In equation 6, Q is the amount of phosphorus adsorbed at equilibrium per gram of iron oxide, C is the equilibrium solution phase concentration of phosphorus, K and n are empirically derived parameters. A Freundlich isotherm plot for the Howe Bridge sample is given in Figure 2.

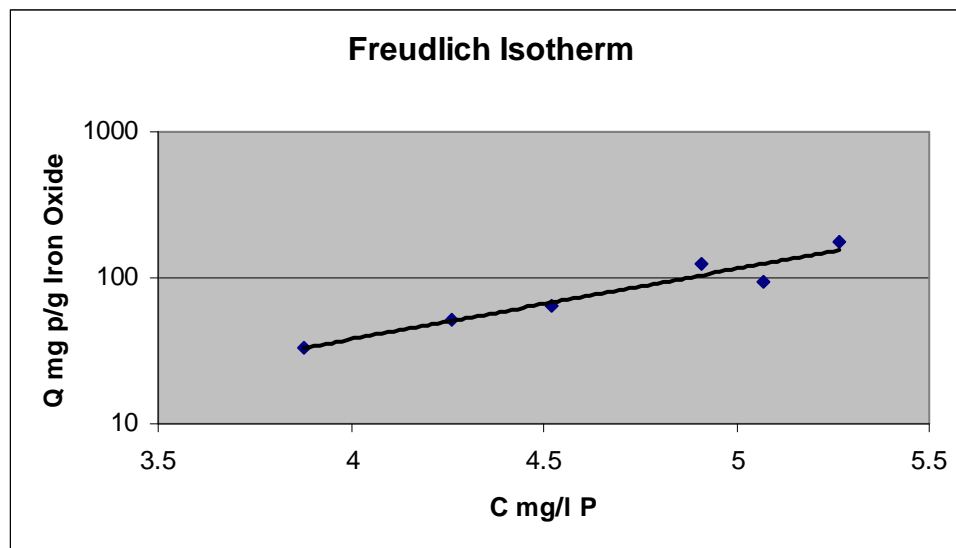


Figure 2. Freundlich isotherm plot for Howe Bridge iron oxide sample dried to 110° C and equilibrated with effluent water.

The isotherm plot is linear with a K value of 0.0343 (mg/l P/g iron oxide)/(mg/l P), and an n value of 5.05. Table 7 summarizes both the phosphate versus iron oxide plots and the Freundlich isotherm parameters for a series of both AMD iron oxides and synthetic iron oxide samples.

Sample	Solution pH	Plot of Phosphate Concentration vs. Iron Oxide Concentration		Freundlich Isotherm Parameters		
		-Slope (mg phos.)/(mg iron oxide)	R ²	K (mg/l P/g iron oxide)/(mg/l P)	n	R ²
AMD produced iron oxides dried to 110° C.						
HB-110	7.39	0.0279	0.950	0.0343	5.05	0.924
SVC-M-110	7.44	0.0317	0.956	0.0101	5.60	0.905
BC-110	7.84	0.0357	0.900	2.03	2.24	0.982
BV-110	7.62	0.0271	0.953	0.088	4.71	0.989
HR-110	6.77	0.0478	0.983	6.46	1.53	0.941
SVC-3-110	7.64	0.0149	0.874	0.005	6.72	0.906
AIS-110	7.56	0.0388	0.962	0.127	5.10	0.846

Table 7. Summary of slopes and regression coefficients for plots of phosphate concentration versus iron oxide concentration, Freundlich isotherm parameters, and regression coefficients for a series of dried AMD produced iron oxides and synthetic iron oxides. All studies were conducted in spiked in effluent water.

Comparing the slopes for the phosphate versus iron oxide plots for the first seven AMD iron oxide samples it can be seen that all the values are relatively close with an average -slope of 0.032 (mg phosphate)/(mg iron oxide). This suggests that all of the AMD iron oxide samples used in this study have similar sorption characteristics for phosphate.

From the slopes of the plots of phosphate concentration versus iron concentration, a phosphate adsorption capacity can be calculated and these results are given in Table 8. The mean phosphate adsorption capacities on the left hand side of the table are for AMD iron oxide samples, while the data on the right hand side of the table are some comparison values. The mean phosphate adsorption capacities measured in this study are similar to the values determined by Parfitt et al. (4) for Goethite and Hematite. This is expected since x-ray diffraction data has revealed that our samples contain Goethite. Again, if the values on the left hand side of the table are compared with the phosphate adsorption capacities for iron oxide tailings and Fe/Cr hydroxide solids, it is apparent that iron oxides produced from AMD have phosphate binding capacities very similar to these other materials. Zeng (25) has shown that in column studies, iron oxide tailings with a phosphate adsorption capacity of 8 mg P/g solid can significantly reduce phosphate concentrations from swine manure effluent. This work suggests that iron oxide tailings have a potential use in reducing phosphate levels in waste streams. Although it was not a focus of this study, AMD iron oxides have a similar adsorption capacity and are expected to perform just as well in column flow through studies.

Sample	Mean Capacity (mg P/g)	Source	Sample	Mean Capacity (mg P/g)	Source
Howe Bridge	6.9	This Study	Amorphous iron oxide	155	This Study
SVC-M	10.3	This Study	Lepidocrocite	16.7	Parfitt et al. (4)
Brandy Camp	3.0	This Study	Goethite	6.7	Parfitt et al. (4)
Blue Valley	8.2	This Study	Hematite	5.3	Parfitt et al. (4)
Hayes Run	6.5	This Study	Fe/Cr hydroxide	6.5	Namasivayam et al. (26)
SVC-3	5.2	This Study	Iron oxide tailings	8	Zeng et al. (25)
Saxman AIS	6.9	This Study			
Phillips AIS	4.9	This Study			

Table 8. Mean Sorption Capacities (mg P/g) for a series of AMD produced iron oxide samples, on the left, compared with a series of iron oxide samples from other sources, on the right.

All of the AMD produced iron oxides were dried to 110° C, and while most of the iron oxide solids are produced from net alkaline discharges, the Howe Bridge discharge is net acidic (see Table 2). It can be seen that the phosphate adsorption capacity of the Howe Bridge sample, is 6.9 mg P/g solid, and is not significantly different from the iron oxides produced from alkaline mine drainage (SVC, Hayes Run, Blue Valley, Saxman AIS). The water chemistry of the AMD discharge does not appear to have a large impact on the phosphate sequestering properties of the iron oxide. As mentioned above, the Brandy Camp sample is not very pure. About 60% of the sample is composed of calcite, and if the adsorption capacity of the Brandy Camp sample is corrected for the calcite content then the phosphate adsorption capacity is 9.4 mg P/g iron oxide. This value is slightly larger than most of the adsorptive capacities measured in this study, and may reflect that the iron oxide phase is more amorphous, or impurities in the iron oxide such as calcite may also sequester phosphate. This is not surprising because phosphate is known to

adsorb to a number of surfaces including metallic oxides (1, 5), silica (17), calcite (18), clays (19, 20), and fly ash (21).

The iron oxide samples with the poorest adsorption capacities are the samples obtained from Saint Vincent Wetland #3 (5.2 mg P/g solid) and Phillips AIS (4.9 mg P/g solid). The SVC sample was obtained near the inflow pipe at the bottom of Wetland cell one. The material was fairly loose (runny) and needed to be vacuum filtered to increase the solid concentration to 30% before drying. Additionally, the sample was greenish-brown in color and did not turn orange until it was exposed to air for a few hours. The green color indicates that the sample was in a reducing environment, and at least the surface of the iron oxide was reduced to Fe(II). Elemental analysis of the sample revealed that the sample is 89% iron oxide with no unusual contaminants. Mineralogy suggests that the sample is semi-crystalline Goethite, and the surface area of the sample ($211 \text{ m}^2/\text{gm}$) is similar to the Hayes Run sample ($237 \text{ m}^2/\text{gm}$). At this point it is unclear how, or why this sample behaves differently. During air drying the sample is fully oxidized back to Fe (III). While the adsorption capacity of the SVC sample may be difficult to explain, the lower adsorption capacity of the Phillips discharge solid is most likely a result of the higher crystallinity of the sample. Kang and coworkers (2) have clearly shown that iron oxide samples with a higher crystalline composition have a lower surface area and a decreased sorption capacity.

It should be noted that except for the impure Brandy Camp sample, the sorption capacities of all of the AMD iron oxide samples are quite similar especially considering that these are native materials, and no attempt has been made to purify them, or control their oxidation and precipitation chemistries. Given the range of samples used in this study, and their similarities in phosphate adsorption, it is probably reasonable to assume that any iron oxide solid produced from coal mine drainage should have an adsorption capacity for phosphate of between 5 to 10 mg P/g solid. Our work also suggests that discharge chemistry, and type of AMD treatment does not greatly impact phosphate sorption on the AMD iron oxides. AMD produced iron oxide samples all have similar phosphate adsorption capacities, and these adsorption capacities are very similar to other iron oxide waste materials such as mine tailings (25) and Fe/Cr oxides (26). Zeng and coworkers (25) have shown that iron oxide mine tailings with a phosphate adsorption capacity of 8 mg P/g solid show promise as phosphate sequestering agents. Iron oxide mine tailings have effectively sequestered phosphate from swine manure waste in column flow studies. AMD iron oxides with phosphate adsorption capacities of between 5 to 10 mg P/g solid are expected to perform just as well as mine tailings. While these materials may show promise at removing phosphate from waste streams, their phosphate adsorption capacities are about 23 times lower than amorphous iron oxide produced from the precipitation of ferric chloride. In order for AMD iron oxides to have real potential in municipal wastewater treatment applications, the materials should have phosphate adsorption capacities approaching that of iron oxides produced from ferric chloride. We have studied a number of measures that may improve phosphate sorption.

Impact of Solution pH On Phosphate Adsorption: Changes in equilibrium pH can impact the surface charge of an iron oxide particle and greatly affect its surface binding characteristics. A number of investigators have reported that phosphate adsorption on the surface of iron oxides decreases with an increase in pH in solutions in buffered deionized water (2, 3, 5). In contrast, Kang (2) has reported that pH has little impact on the phosphate adsorption to synthetic iron oxides in secondary effluent water. Zeng (25) has reported that there was a modest increase in phosphate adsorption capacity for iron oxide tailings as the pH decreased from 10 to 6, and then a more noticeable increase in adsorption capacity as the pH is decreased below 6. While Namasivayam (26) reported that the sorption of phosphate to Fe/Cr hydroxide increased slightly with a decrease in pH.

The impact of pH on phosphate adsorption was investigated for the Saxman Run AIS sample that was dried to 110°C, and the results are given in Figure 4. Increasing the pH from 6 to 8 increases the adsorption capacity by about 2 mg P/g solid. Apparently, AMD iron oxides are not strongly affected by pH in secondary effluent water, consistent with the findings of Kang, and Namasivayam. Kang (4) has proposed that in secondary effluent water, phosphate is sequestered on the surface of the iron oxide through both surface adsorption and precipitation. This surface precipitation of phosphate is mediated by the presence of calcium and magnesium ions in the secondary effluent. At higher pH values, the precipitation mechanism becomes a more dominant route to phosphate removal. This surface precipitation of phosphate in secondary effluent water may explain why Langmuir isotherm plots for secondary effluent are not linear.

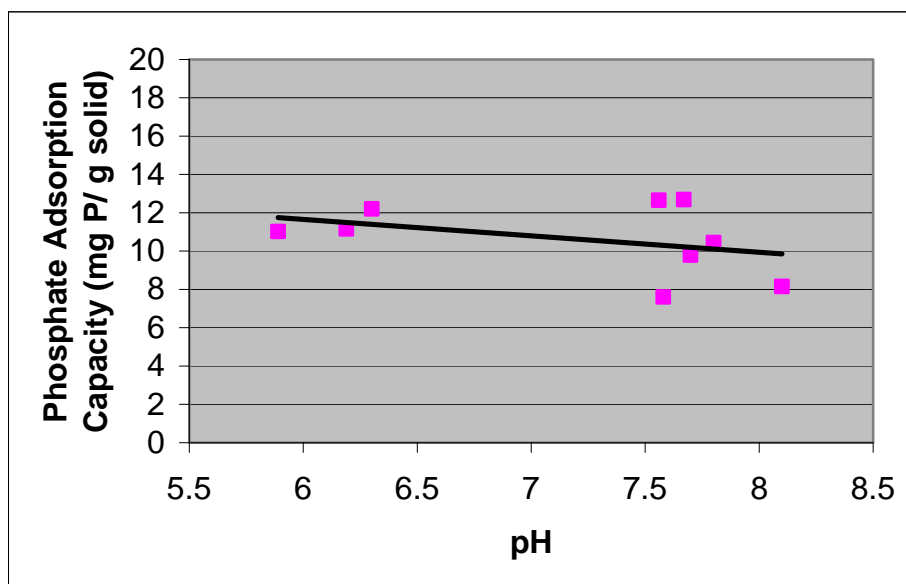


Figure 4. A plot of Phosphate adsorption capacity versus pH for AIS iron oxide dried at 110° C. All phosphate binding studies were conducted in secondary effluent water.

Impact of Sample Drying On Phosphate Adsorption: In this study, and in the work of Ochiana and Echard (10), it is evident that aged and dried AMD iron oxides have phosphate adsorption affinities that are much lower than the adsorption affinities of freshly precipitated iron oxides. It is well known that drying iron oxides can increase their crystallinity and reduce their

surface area (11, 22, 23). Sorensen and co-workers (22) used a series of diffraction techniques to study the effects of heating on crystalline transformations of amorphous iron oxide. They have shown that heating an amorphous iron oxide to just 50°C causes it to adopt a local quasi-goethite structure. Heating an iron oxide to 600°C or above transforms the iron oxide to hematite. As the sample is heated above 600°C there is a continued loss in surface area because the iron oxide particles fuse together. Therefore, it is important to study the impact of drying on the phosphate adsorption characteristics of AMD iron oxides. Figure 3 shows the impact of drying on the phosphate adsorption affinity of two different AMD produced iron oxides.

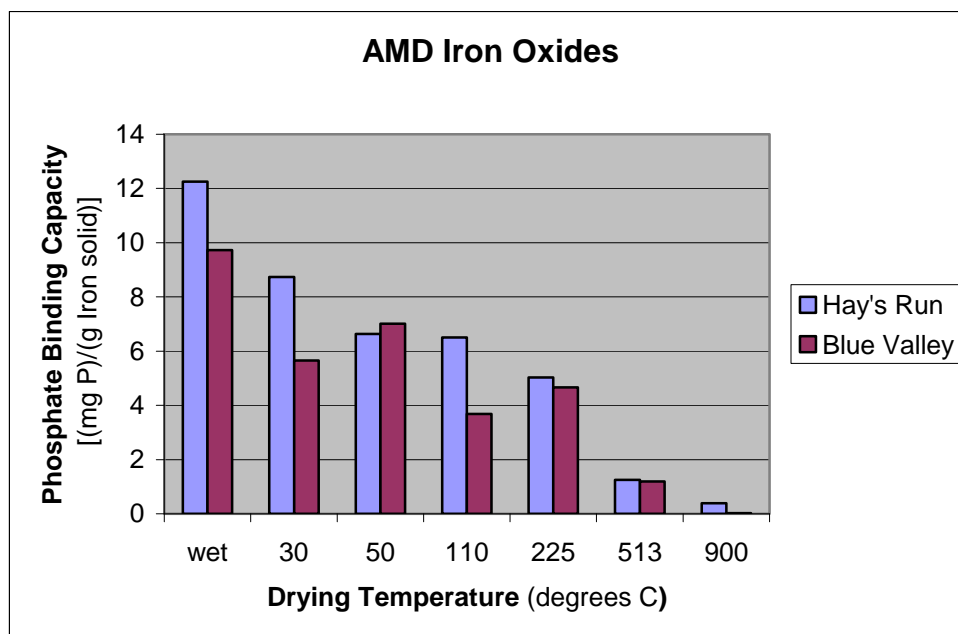


Figure 3. Plot of Phosphate Binding Capacity versus the Drying Temperature for Hayes Run and Blue Valley AMD produced iron oxides. All phosphate adsorption affinities were measured in spiked effluent water. It should be noted that the x axis is not linear.

In Figure 3, both iron oxide samples display a decrease in equilibrium phosphate adsorption capacity as the drying temperature is increased. It should be noted that the wet samples were not freshly precipitated, but were obtained from the treatment systems at about 30% solid and stored in a sealed container until used, about 3 months. While this storage may not be important for passive treatment iron oxide solids, due to lengthy aging in the treatment system (day to months), this aging could affect the phosphate sorption characteristics of active and semi-active treatment solids (e.g., AIS treatment) where the iron oxide solids have short aging times (less than 2 hours). The Hayes Run iron oxide sample showed a 53% decrease in adsorption affinity when dried to 110°C, while the Blue Valley sample showed a 38% decrease in adsorption affinity when dried to 110°C. When both samples are heated to 600°C, the binding affinity of the solids decreases by more than 90%. Converting AMD iron oxides to hematite drastically reduces the phosphate binding capacity, and this reduction in binding capacity is consistent with the work of Kang (2) who has shown that synthetic iron oxides experience a similar decrease in phosphate binding upon conversion to hematite. While dried iron oxide would be considerable cheaper to

transport, wet (30% solids) never dried iron oxides appear to have about twice the adsorption capacity. The next question that was addressed was, what impact does ageing have on phosphate sequestering, or does a freshly precipitated AMD iron oxide have an enhanced phosphate adsorption capacity?

In order to address this question, 20 liters of water from cell 1 of the number-3 SVC wetland were filtered to collect the suspended iron oxide particles that had not yet precipitated from solution. An equilibrium sorption study was conducted on these iron oxide particles within an hour of collecting the sample. The equilibrium study revealed that the adsorption capacity of the freshly produced AMD solid was about 10 mg P/g solid, where the gram of solid refers to the dry weight. A second study was conducted where 20 liters of mine drainage from the SVC discharge was placed in a large circular glass tank. The mine drainage was constantly stirred with a mechanical mixer to keep the iron oxide solid in suspension, and to provide oxygen to the system to oxidize the ferrous iron. The tank was stirred for 12 hours, and then the solids were collected by filtration, and immediately used in a sorption study. The equilibrium study revealed that the adsorption capacity of the freshly produced AMD solid was once again 10 mg P/g solid, where the gram of solid refers to the dry weight. The binding capacity doubled again from the 110° dried sample but the increase in binding capacity was not significantly different from the aged material. Apparently, ageing or storing the iron oxide in the wet state (30% solids) has little impact on the adsorption capacity. Kairies and coworkers (24) have shown that fast precipitation of iron oxide from AMD at circum-neutral pH values produced an iron oxide in which the major fraction is Goethite. Apparently, amorphous hydrous iron oxide exists in the colloidal state, and as the iron oxide particles become large enough to begin to precipitate, their mineralogy changes to Goethite. Once the material becomes semi-crystalline Goethite, the binding capacity is greatly diminished, and this transition to Goethite appears to take place before the particle settles from solution. This is also likely to be the condition of iron oxide solids produced active and semi-active treatment processes (e.g., AIS Treatment).

Impact of Acid washing On Phosphate Adsorption: Work by Dzombak, Schwertmann, Xiaoguang, Ford, and Kairies (5,11,17,23,24) has shown that iron oxide surfaces are capable of binding a variety of cations and anions. Since there are a limited number of adsorption sites on the surface of an iron oxide, and other ions such as sulfate, may compete for these binding sites with phosphate. If these binding sites are occupied, then phosphate may be excluded for binding to the surface of the iron oxide particle. Washing the surface with acid (HCl), and a large quantity of deionized water can desorb ions from the surface of the oxide, which may increase the phosphate adsorption capacity. In the laboratory, dried samples of AMD iron oxides from SVC, Saxman Run AIS, Hayes Run, and Blue Valley were each slurred with 0.1 M HCl for about one half hour and then filtered. The filtered solid was washed with several liters of deionized water to remove any contaminating ions. The samples were then dried to 110° for 12 hours. The dried samples were then used in equilibrium adsorption studies, and the adsorptive capacity of the acid washed solid was compared with that of the native iron oxide solid. Within the limits of experimental error, there was no difference in the adsorption capacity between the acid washed iron oxide and the unwashed sample. This suggests that it is not necessary to wash the solids, and if the acid washing does remove adsorbed ions, they either do not impact phosphate adsorption, or the gain in adsorption capacity due to a clean surface is offset by the loss of amorphous iron oxide during acid washing.

Conversion of the AMD Iron Oxides to Ferric Chlorides: AMD iron oxide solids produced from alkaline mine drainage are at least 80% pure iron oxide, and are relatively free of heavy metal contaminants. Another way to improve the phosphate adsorption capacity of these solids is to dissolve the solid materials in a stoichiometric amount of HCl, and then reprecipitate the iron oxide in the effluent. Six of the AMD iron oxide samples were dissolved in HCl to form a ferric chloride solution, the concentration of iron in the solutions was analyzed by Flame AA, and then known amounts of the ferric chloride solution were added to effluent water. Phosphate adsorption capacities for these ferric chlorides were determined and the results of the study are given in Table 9.

Sample	Adsorption Capacity (mg P/g)
Howe Bridge-FeCl ₃	190
Brandy Camp FeCl ₃	240
Saint Vincent FeCl ₃	180
Blue Valley FeCl ₃	250
Hayes Run FeCl ₃	200
Saxman AIS FeCl ₃	180
Commercial FeCl ₃	160

Table 9. Mean adsorption capacities for AMD produced ferric chlorides. All adsorption capacities were measured in effluent water.

The adsorption capacities for the AMD produced ferric chlorides are compared with the adsorption capacity of commercial ferric chloride. Commercially available Ferric Chloride has an adsorption capacity of 160 mg P/g iron oxide. Inspection of the data in Table 9 reveals that iron oxides produced from laboratory synthesized ferric chlorides all have phosphate adsorption capacities at least as large as commercial ferric chloride, and in most instances larger than commercial ferric chloride. For instance, ferric chloride synthesized from Brandy Camp iron oxide has an adsorptive capacity of 240 mg P/g iron oxide. This value is 1.5 times larger than adsorptive capacity of commercial iron oxide. The larger than expected adsorption capacity for the iron oxide produced from Brandy Camp ferric chloride can be attributed to the sorption of phosphate to oxides, hydroxides, and carbonates of Al, Ca, Mg, and Mn that co precipitate with the iron oxide in the Brandy Camp active system. Thus the impurities in the AMD iron oxides contribute to the high adsorption capacity (1,5,18). Since all of the AMD iron oxides contain some impurities, all of the AMD ferric chlorides are expected to have elevated adsorption capacities relative to commercially available ferric chloride. The Blue Valley ferric chloride has a phosphate adsorption capacity higher than expected, given that the sample has the highest purity of iron oxide. It is unclear why the adsorption capacity value is so high and not closer to 160 mg P/g iron oxide.

The AMD iron oxide solids have phosphate adsorption capacities that are 13 to 23 times lower (depending on drying) than iron oxides produced from commercial ferric chloride, and this lower adsorption capacity may limit their usefulness in some phosphate sequestering applications such as municipal wastewater treatment. On the other hand, ferric chlorides synthesized from

AMD iron oxides show great promise as phosphate sequestering agents because they have phosphate adsorption capacities up to 1.5 times higher than commercial ferric chloride. While high adsorption capacities are very desirable, AMD iron oxides such as the Brandy Camp solid may not be the most desirable feed stock for ferric chloride production because of its high calcite composition. If one takes a closer look at the adsorption capacity of the Brandy Camp ferric chloride, it can be seen that the adsorption capacity is 1.5 times higher than commercial ferric chloride based on per gram of iron oxide. Since approximately 60% of the Brandy Camp sample is calcium carbonate, and that 60% of the sample accounts for one third of the adsorption capacity. The iron oxide in the sample accounts for the other two thirds of the binding capacity. Apparently, precipitating calcium chloride has a lower adsorption capacity for phosphate than iron oxide. Secondly, on a per gram basis, it takes almost as much HCl to dissolve one gram of calcium carbonate as it does to dissolve one gram of iron oxide. Therefore, about 60% of the HCl is being used in the Brandy Camp sample to dissolve calcium carbonate which produces a phosphate sequestering agent that is less effective than iron oxide. Finally, it is well known that solutions that contain high levels of dissolved calcium are prone to scale and corrosion. Ferric chloride solutions with high concentrations of calcium such as the Brandy Camp sample, may create additional maintenance issues in wastewater treatment facilities. It should be noted that all of the other AMD iron oxide solids have low calcium and magnesium contents, and have a much higher percentage of iron (50 to 62%). These materials are expected to be ideal feedstock for ferric chloride production.

Addition of AMD Directly to Effluent Water: The purpose of this study was to determine if it is feasible to utilize iron oxides from AMD in some fashion, to sequester phosphates from waste streams such as municipal wastewater. One of the major costs involved in utilizing iron oxides from AMD is the transportation costs associated with collecting the material, and then transporting the materials to where they will be used. In western Pennsylvania it is not unusual for wastewater treatment plants to be located on receiving streams that are impacted by AMD, and in some instances there is an AMD discharge adjacent to the treatment plant. For example, the Latrobe Sewage Treatment Authority, the Greater Greensburg Sewage Treatment Authority, and UTMA's 14 Mile Run Facility are all within 20 miles of Saint Vincent College, all discharge into AMD impacted streams, and all have AMD in close proximity to the treatment facility. In addition, a series of community groups are exploring the possibility of bringing municipal sewage to Crabtree, Pennsylvania, and treating a major discharge in an adjacent facility. Although it is not popular from a regulatory standpoint, the best way to incorporate AMD iron oxide into wastewater treatment may be to add AMD directly into the municipal wastewater stream. This could be done a number of ways including adding mine drainage directly to the front end of a wastewater treatment system. Addition of alkaline mine drainage could potentially improve denitrification by buffering the redox potential of the anoxic zone, adding additional alkalinity to the treatment system, reducing phosphate levels, and improving the settling of solids. On the other hand, AMD could be preaerated and then combined with the wastewater effluent in a detention pond, followed by polishing in a wetland system. The biota in the detention pond and wetland system could significantly reduce all or the effluent nutrients, and virtually eliminate residual organics from the wastewater treatment system. In addition, a system such as this would provide a valuable wetland habitat.

Since combining AMD with municipal wastewater has many benefits, and could prove to be the most cost effective way of sequestering phosphates, an adsorption study was performed on four AMD discharges within Westmoreland County. The water chemistry for the four discharges is detailed in Table 10 along with the phosphate adsorption capacity of the discharges expressed in mg phosphorus per gram of iron oxide.

Three of the four discharges have pH values near 6, are net alkaline, and iron is the major contaminate in the water. The West Derry discharge is net acidic, the pH of the water is below 3, and there are significant amounts of iron, manganese, and aluminum.

Discharge	pH	Discharge Chemistry in mg/l				Adsorption capacity mg P/g iron oxide
		Alkalinity	Fe	Mn	Al	
Saint Vincent	6.4	210	79	3.6	0.35	150
Saxman Run	5.9	120	31	3.0	<0.1	160
Crabtree	6.2	140	73	2.9	2.6	215
West Derry	2.8	0	77	12	68	700

Table 10. AMD Discharge water chemistry and phosphate adsorption capacities for the discharges.

The phosphate adsorption capacities of the alkaline AMD discharges are very similar to the ferric chlorides produced from AMD iron oxides, and the adsorption capacity from commercial ferric chloride, 160 mg P/g iron oxide. This is not surprising since the only ion in a significant concentration in mine drainage that could compete with phosphate adsorption is sulfate. Both Parfitt and Namasivayam have investigated the competitive binding of anions to iron oxide (4) and Fe/Cr hydroxide (26). Sulfate has been shown to have a much lower binding affinity to metal oxides as compared to phosphate. This suggests that high levels of sulfate found in AMD should not impact the binding of phosphates.

Water from the West Derry discharge was found to have an extremely high phosphate binding capacity due to its high concentration of other metals such as manganese and aluminum. Iron oxide is not unique in its ability to sequester phosphates. A number of metallic oxides and hydroxides are capable of sequestering phosphates (1,5,25,26). While the West Derry mine drainage appears to be the ideal phosphate sequestering agent, it requires over 700 mg/l of alkalinity to neutralize the discharge water. West Derry mine drainage has a phosphate adsorption capacity equivalent to 177 mg/l of ferric chloride, and a ferric chloride solution with that concentration of iron requires about 500 mg/l of alkalinity to neutralize. While alkaline discharges will provide a wastewater treatment plant with alkalinity, acidic discharges like West Derry will increase the amount of alkalinity a treatment must provide to maintain a stable pH.

Sequencing Batch Reactor Bench-scale Studies: All of the previous studies were conducted with effluent water from one of UTMA treatment facilities. Phosphate adsorption studies performed in effluent water are relatively easy to perform, and are quite reproducible. These

studies have provided an efficient way to survey adsorption capacities of AMD iron oxide solids, ferric chlorides produced from AMD solids, and AMD itself. However, it is unclear whether the biota in the sewage treatment plant impacts the efficiency of phosphate sorption. In particular, Stabnikov, and Ivanov (3,27) have shown that iron oxides and red clay are reduced to ferrous ions during anaerobic digestion of activated sludge. They have shown that ferrous iron binds and precipitates phosphates, and the addition of iron oxide solids to the anaerobic digester significantly reduces the phosphate levels in the entire facility. It might be expected that the addition of solid iron oxide to the anaerobic zone of a wastewater treatment system may redissolve iron oxide solids through redox process, which would lead to a significant decrease in phosphate levels. If a significant amount of iron oxide reduction does occur, then the adsorption coefficient of the iron would increase dramatically from about 7 mg P/g iron oxide to 160 mg P/g iron oxide. On the other hand, it might be envisioned that the biological floc might completely cover the surface of the iron oxide particles, and dramatically reduce the adsorption coefficient of the solid iron oxide.

In order to better study the biological impact of wastewater treatment on iron oxide reduction and phosphate removal, a SBR study was conducted over a 5-day period. At the start of a 5-day trial a plastic 500 ml acid washed bottle was filled with anoxic liquor from UTMA 14 Mile Run facility, and spiked with the appropriate additive. The bottle was capped and stirred for 5 hours. At the end of the 5 hour period the liquor was placed in a 1000 ml beaker and aerated for about 18 hours. Next, solids were allowed to settle for about 45 minutes. About 300 ml of the clear effluent was decanted from the solids, the solids were placed back in the plastic bottle, and 300 ml of raw water from the UTMA facility was added along with the appropriate additive. This process was then repeated for four additional days.

The purpose of the SBR study was to mimic in the laboratory the operation of the UTMA treatment system. Table 11 compares a number of operational parameters of the laboratory SBR system with the UTMA facility.

Effluent	SBR	UTMA
Parameter	Ave (mg/l)	Ave (mg/l)
BOD	5±1	5.2±0.4
Redox anoxic zone	-150±60	
Redox aeration	253±5	
DO anoxic	0.0	0.4±.5
DO aeration	6±1	6.4±2
TSS	11±1	3±1
Nitrate	17±1	9±1

Table 11. A comparison of the operational parameters for the laboratory SBR system with the UTMA facility.

The SBR system used in this study performs similarly to the UTMA facility, with a couple minor differences. Both systems are capable of reducing the BOD to 5 mg/l. Both systems have an anoxic treatment where DO drops to a low level followed by an aeration zone where the DO is maintained at about 5 mg/l. The first major difference between the two systems is that Total Suspended Solids, TSS, in the effluent of the SBR is about 4 times higher and the UTMA facility. With the SBR system, 300 ml of effluent is decanted off of the solids. In the process of pouring off the effluent, it is difficult not to upset the sludge blanket at the bottom of the beaker and resuspend some of the solids. A more efficient design is needed to separate the solids from the clear effluent. Secondly, our SBR system appears to have a lower denitrification ability compared to the UTMA facility. Our nitrate levels are about twice as high as UTMA's. One major difference between the SBR and the UTMA operation is that in the SBR the liquor is anoxic for 5 hours and then aerated. At the UTMA facility the raw water mixes with solids in the anoxic zone and after about 5 hours travels in the aeration zone. At the end of the aeration zone there is a return line where about 30% of the flow goes back to the anoxic zone. Therefore, a significant fraction of the liquor in UTMA's treatment system passes back through the anoxic zone to help denitrification.

The SBR process was used to determine the phosphate adsorption coefficient for two of the AMD solids and the results are given in Table 12.

Sample	Phosphate Adsorption Capacity (mg P/g solid)					
	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Average
Hayes run	3.5	5.4	5.4	6.1	5.5	5.6
Saxman AIS	2.7	4.1	4.0	5.0	4.5	4.4

Table 12. Phosphate adsorption capacities for two AMD iron oxide samples determined with the aid of the SBR system.

For all of the SBR trials performed in this study, the system was not at steady state for the first cycle, and the adsorption coefficients were consistently low. It is quite possible that transporting the anoxic liquor that was used in the SBR from the sewage treatment plant shocked the bacteria and impacted the results. After the first cycle was complete, the adsorption values do not change appreciably from cycles 2 through 5 and these values were averaged together and are displayed in the final column of Table 12. It should be noted that there is a great deal of scatter in the adsorption capacities obtained from the SBR data as compared to the effluent water studies. The main reason for scatter in the data comes from the SBR operation. It was difficult to measure and pour solutions such as the raw water and the anoxic liquor while insuring that each container receives the correct volume of material with a consistent concentration of suspended solids.

If the adsorption capacity data obtained from the effluent water study for the Hayes Run sample, 6.5 mg P/g solid, is compared with the average adsorption capacity obtained from the SBR process, 5.6 mg P/g solid, it is evident that the SBR process is about 14 % smaller. In a similar fashion, the adsorption capacity obtained from effluent water study for the Saxman AIS sample 5.2 mg P/g solid, is about 15 % larger than the average adsorption coefficient obtained

from the SBR study. It does not appear as if the anoxic zone in the SBR causes significant reduction of the solid iron oxide to a dissolved iron. If this were the case, the adsorption capacities in the SBR tests should be much higher and close to the adsorption capacity of the AMD discharge samples shown in Table 10. In order to determine if iron oxide reduction to ferrous ions was taking place under anoxic conditions, a second SBR trial was performed where 1,10-phenanthroline was added to the anoxic liquor along with the appropriate amount of iron oxide solid. After about an hour of anoxic incubation the sample began to turn a pale red color. The red color of the ferrous ion complex of 1,10-phenanthroline increased in concentration to 0.1 to 0.2 mg/l of Fe^{+2} after four hours of incubation. After 24 hours of incubation the concentration of Fe^{+2} increased to between 0.4 to 0.6 mg/l. Clearly iron reducing bacteria are present in the sewage plant biota, and are capable of reducing AMD iron oxides. However, the reduction process is slow, and not greatly affected by the amount of iron oxide added to the anoxic liquor. For example, if anoxic liquor is incubated with 25 mg/l of iron oxides, the rate of accumulation of ferrous ions appears to be the same as a sample that is incubated with 250 mg/l of iron oxide. Both Stabnikov (3) and Ivanov (27) have shown that the reduction of iron oxide in an anaerobic digester is a slow process, and takes several days to reach steady state. It is not surprising that 4 to 6 hours of anoxic treatment is not a long enough time for significant reduction of the iron oxide. Iron reduction by bacteria in the anoxic zone of a wastewater treatment system appears to be too slow to greatly impact the phosphate removal process.

The ferric chlorides produced from AMD iron oxides were used as a phosphate sequestering agent in the SBR process. The mean absorption capacity for each of the ferric chlorides were calculated and compared to the absorption capacity determined in effluent water, Table 13.

Ferric Chloride	Absorption Capacity (mg P/g iron oxide)	
	Effluent water	SBR System
Sample		
Howe Bridge	190	150
Brandy Camp	240	150
Blue Valley	250	190
Hayes Run	200	150
Saxman AIS	180	150
Commercial	160	210

Table 13. A comparison of phosphate adsorption capacities for ferric chlorides produced from AMD iron oxides.

Except for the commercial ferric chloride, all of the AMD ferric chlorides exhibited adsorption capacities in the SBR system that were smaller than those in effluent water and close to the value of 160 mg P/g iron oxide for freshly precipitated amorphous iron oxide. It appears that the calcium salts in the Brandy Camp sample were also effective in sequestering a significant amount of phosphate in effluent water, but were much less effective in sequestering phosphate in the SBR system. In general, the lower phosphate adsorption capacities obtained in the SBR

studies suggest that the bacteria may decrease the available iron oxide surface area on to which phosphate can bind.

Heavy Metal Leaching: Both AMD iron oxide solids and ferric chlorides derived from AMD iron oxides have potential as a phosphate sequestering agents. Their application in treating industrial and municipal wastewaters is not just a function of their phosphate adsorption capacity. These products must not harm the wastewater stream by adding metals to the effluent. Heavy metals have the potential to severely degrade a wastewater stream, and if leaching of these metals did occur from AMD iron oxide material, the material would not be suitable as a sequestering agent. In addition to heavy metals, calcium, magnesium and aluminum all have the potential to increase scale on piping and other equipment that is in contact with the wastewater. Therefore, it is important that AMD iron oxides do not significantly increase the hardness of the wastewater. In order to determine whether the AMD iron oxide materials pose a leaching risk a series of studies were conducted. In the leaching study the effluent water was analyzed for the following metals: Al, As, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Se, and Zn.

In the first leaching study effluent water was combined with AMD iron oxide to form slurry that was 500 mg/l iron oxide solid. The sample was capped, and stirred for 12 hours. A portion of the sample was filtered through a 0.45 micron filter and analyzed for dissolved metals. The results of this study are given in Table 14 along with the untreated effluent which was used as a control.

Sample	Average concentration of metal (mg/l)			
	Ca	Mg	Mn	Cu
Effluent water	45	7.5	0.03	ND
Saxman AIS	43	7.9	ND	0.02
Hayes Run	42	8.2	0.01	ND
Brandy Camp	40	8.2	0.01	ND
Blue Valley	48	10.0	ND	ND
Saint Vincent-3	41	8.3	ND	ND

Table 14. Average concentration of metals found in effluent water and in effluent water spiked with 500 mg/l of iron solids. The metals As, Cd, Co, Cr, Fe, Ni, Pb, Se, and Zn were not detected in any of the samples.

Most of the metals that the samples were analyzed for (Al, As, Cd, Co, Cr, Ni, Pb, Se, and Zn) were not detected in either the untreated effluent or the samples. Copper was detected in the effluent water slurried with Saxman Run AIS solids. However the 0.02 mg/l copper concentration is not of concern because dilution in the wastewater stream would decrease the concentration well below concentrations needed to protect receiving streams. Manganese was detected in the untreated effluent water, 0.03 mg/l and in the effluent water slurried with the Hayes Run solid, 0.01 mg/l, and the Brandy Camp solid, 0.01 mg/l. Once again, the manganese concentration is well below levels to be a concern. It is interesting to note that manganese was not detected in effluent water slurried with Saxman Run AIS, Blue Valley, and Saint Vincent wetland solids. Apparently, these solids removed the trace amount of manganese from the effluent water. If the calcium and magnesium concentrations of the untreated effluent water are compared with the slurried effluent waters, it is evident that addition of the iron oxide solid to the

effluent water does not increase the concentrations of these metals. It is highly likely that in the effluent water with a neutral pH and nearly saturated with dissolved CO₂ is also near the calcium and magnesium saturation. Notice that the effluent water slurried with Brandy Camp solids slightly decreased in calcium concentration even though the Brandy Camp solids are 60% calcium carbonate. This suggests that the calcium carbonate in the Brandy Camp solids acts as nucleation sites for the precipitation of additional calcium carbonate from the effluent.

In the second leaching study, effluent water was spiked with 30 mg/l of ferric chloride produced from AMD iron oxides, the samples were stirred for 12 hours and then filtered through 0.45 micron filters. These samples were analyzed for the same metals as above, and the results are given in Table 15. For comparison purposes the table includes unspiked effluent water and effluent water spiked with 30 mg/l of technical grade FeCl₃.

Sample	Average concentration of metal (mg/l)			
	Ca	Mg	Mn	Fe
Unspiked Effluent water	45	7.5	0.03	ND
Saxman AIS	40	7.9	0.03	ND
Hayes Run	38	7.9	0.10	ND
Brandy Camp	47	8.8	0.04	ND
Blue Valley	38	7.9	0.05	0.2
Saint Vincent-3	50	11.0	0.15	0.2
Commercial Technical Grade FeCl ₃	37	8.0	0.04	0.3

Table 15. Average concentration of metals found in effluent water and in effluent water spiked with 30 mg/l of ferric chlorides. The metals As, Cd, Co, Cr, Cu, Ni, Pb, Se, and Zn were not detected in any of the samples.

Consistent with the previous leaching study, most of the metals that the samples were analyzed for were never detected, either in the effluent water, or in the spiked water samples. A small amount of iron 0.2 to 0.3 mg/l was detected in the Blue Valley, Saint Vincent, and commercial FeCl₃ spiked effluents. Dr. Carl Kirby from Bucknell University (28) has studied the filtration of AMD samples, and has shown that 0.45 micron filters are not always capable of removing fine colloidal particles iron oxides. In this leaching study, the spiked effluent water was filtered after 12 hour of stirring, and solid material was not allowed to settle before filtration. It is possible that a small amount of particulate iron in some of the samples was not removed by the filtration.

Manganese was detected in all of the samples, and 0.03 mg/l of the manganese is in the original untreated effluent water. Most of the AMD produced ferric chlorides increased the concentration of manganese above 0.03 mg/l with the Hayes Run ferric chloride (0.10 mg/l) and Saint Vincent ferric chloride (0.15 mg/l) increasing the manganese concentration to the greatest extent. The commercial grade ferric chloride solution also had measureable manganese. It should be noted that ferric chlorides produced from AMD iron oxides slightly elevate the concentration of manganese in the effluent water while solid iron oxides decrease the concentration of manganese. In oxygenated water with a neutral pH, the equilibrium concentration of oxidized

manganese is low. If an iron oxide with adsorbed manganese is added to the water, thermodynamics prevents the manganese from dissolving into solution. However, if a ferric chloride that is contaminated with manganese and is added to oxygenated water at neutral pH, the manganese must reprecipitate from solution. The reprecipitation of the metals such as manganese may be slow and kinetically controlled. The elevated concentration of manganese may reflect the fact that either a longer precipitation time or better filtration is required to remove this metal. In any case, manganese concentrations are below 0.2 mg/l pose no real concern. Inspection of the calcium and magnesium concentrations in Table 15 shows the same trend in concentration that was found in Table 14. The effluent water appears to be saturated with calcium and magnesium, and the addition of calcium and magnesium as part of the ferric chloride spiking solution does not elevate the concentration of these ions in the effluent water.

Our 12 hour leaching studies have shown that both the AMD iron oxide and the ferric chlorides produced from AMD iron oxides do not have the potential to contaminate effluent water with heavy metals. In fact, both of these additives do not significantly increase the concentration of any metal that was part of this study. We chose to add 500 mg/l of iron oxide solid and 30 mg/l of ferric chloride because these values represent large doses of the additives, and we wanted our study to reveal possible leaching problems.

In another study, the effluent from the SBR bench-scale study was analyzed for metals. Both the Saxman Run AIS and the Hayes Run AMD solids were used in SBR studies at concentrations ranging from 100 to 500 mg/l solids. For all of the samples analyzed the average calcium concentration was 49 ± 3 mg/l, the magnesium concentration was 10 ± 1 mg/l, and manganese and iron were detected in some of the samples. The manganese and iron concentrations were always below 0.2 mg/l.

In a similar study, SBR studies were performed on the following AMD ferric chlorides: Howe Bridge, Brandy Camp, Blue Valley, and Saxman AIS where ferric chloride was added over the concentration range of 3 to 18 mg/l. Metals analysis revealed that the effluent contained 40 ± 5 mg/l calcium, 9 ± 2 mg/l magnesium, and some of the samples contained copper, iron and manganese. Copper was found in 10 of the 15 samples analyzed, and the concentration never exceeded 0.02 mg/l. Iron was found in 2 samples and the concentration was below 0.2 mg/l. Manganese was found in 5 of the 15 samples and the concentration was below 0.2 mg/l. This data once again suggests that AMD iron oxide solids and ferric chlorides do not leach metals, and do not increase the hardness of the effluent water.

Feasibility and Cost Comparisons: In this project we explored three different methods of introducing iron from AMD into a wastewater stream in order to sequester phosphate. The first method involves direct addition of AMD iron oxides to the wastewater stream. These materials were found to be over 80% iron oxide in a semi-crystalline Goethite structure. These solids have a much lower affinity for phosphate as compared to iron oxides freshly prepared from ferric chloride. The second method involves addition of a ferric chloride produced from AMD iron oxides into the waste stream. After addition, the ferric chloride hydrolyzes to form an amorphous iron oxide with a high affinity for phosphate. The last method involves direct addition of mine drainage to the wastewater stream. In the last method, ferrous ions in the mine drainage are oxidized by air to ferric ions, which hydrolyze to form a colloidal iron oxide. This

iron oxide was shown to be as efficient in sequestering phosphate as iron oxides produced from ferric chlorides. All three methods have the potential to be used in phosphate removal under the right conditions, and the focus of this section is to explore some of the potential uses of AMD iron as a sequestering agent.

In the western part of Pennsylvania AMD is a major aquatic pollutant, many treatment systems are in operation to remove iron from mine drainage, and tons iron oxide solids are produced. In this study we surveyed 8 different materials and found them to typically be 50% to 62% iron or 80% to 96% iron oxide. The iron oxide is in a semi Goethite state and has a phosphate adsorption capacity in effluent water between 4.9 to 10.3 mg P/g of solid. Water chemistry and type of mine drainage treatment does not seem to greatly impact the phosphate adsorption capacity of the iron oxide as long as it was not produced by active lime treatment, Brandy Camp sample. Active lime treatment was found to greatly reduce the purity of the iron oxide, with the major impurity being calcite.

If AMD iron oxides were used in conventional municipal wastewater treatment. The material could be added to the treatment system in a dried form or as a slurry. Both methods of introduction would require a capital improvement to the treatment plant. In a 30 day trial at the UTMA (29) we found that it can be difficult to add iron oxide to a treatment system as a slurry. The iron oxide solids tend to settle quickly requiring substantial mixing to keep it in suspension and a high pumping flow rate to keep feed lines from clogging. If there is a power failure and mixing or pumping is stopped, the solids may be difficult to resuspend or may tend to cause clogging issues in feed lines. While it is possible to pump iron oxide slurry for long periods of time, there are likely to be fewer O&M issues with a dry feed hopper system as a way to add iron oxide to a treatment system. This may also lower handling costs due to the removal of water. It should be noted that based on analysis conducted in this study, drying the iron oxide solids will reduce the phosphate sorption capacity by approximately 30% require additional volumes of iron oxide to be fed into the treatment system.

The second issue to consider with the potential use of AMD iron oxides in wastewater treatment is the amount of material required to achieve the required phosphate removal. The adsorption capacity of the aged AMD iron oxides is significantly lower than the recently precipitated iron oxides produced from ferric chlorides. If an AMD iron oxide with a phosphate adsorption capacity of 7 mg P/g solid were used, and an operator wished to remove 2 mg/l of phosphorus, it would require almost 300 mg of AMD iron oxide solids per liter of effluent. This is a large amount of iron oxide, and can lead to increases in other O&M costs, such as increased solids production and accumulation of iron oxides within the treatment system in dead spots; poor mixing areas of the treatment system such as under diffuser heads and in the corners of the reactor. We have operated a SBR reactor at the Latrobe Sewage Treatment plant for 6 years in order to treat and produce the Saxman AIS iron oxide (15,16). Settling of iron oxides at the bottom of the reactor tank occurs, and it can form a dense solid that does not resuspend where there are dead spots in the aeration tank. This can be overcome with increased or improved mixing in the treatment system. Based on the required AMD iron oxide dose a one million gallon a day (MGD) treatment plant would require 1.25 tons per day of iron oxide to maintain the 300 mg/l dose concentration. It should be pointed out that a dose rate of 1.25 tons per day would also increase costs for solids removal, trucking, and disposal in a landfill. It is the conclusion of this

study that adding AMD iron oxides directly to a municipal wastewater treatment facility is not practical because of the high volume of AMD solids required in comparison to the much lower dose of ferric chloride required to achieve the same level of phosphate removal.

While it may not be practical to add AMD iron oxides directly to a typical wastewater treatment facility, Stabnikov, and Ivanov (3,27) has shown that addition of iron oxide materials to an anaerobic digester is an effective way to sequester phosphate and use a solid material. This study has shown that AMD iron oxides are reduced by the bacteria found in the UTMA facility. It may be possible to add much smaller doses of AMD iron oxide to an anaerobic digester, where the wastewater treatment facility has an anaerobic digester for sludge processing, and see a significant benefit to a treatment system. This is a promising area that deserves further study. In addition to potential use of AMD iron oxides in anaerobic digestion, AMD iron oxides have a potential use in columns and filters to remove ions such as phosphate. Zeng and coworkers (25) has shown that iron oxide tailings with a phosphate adsorption capacity of 8 mg P/g solid have performed well in column test where phosphates were removed from swine manure. AMD iron oxides have a similar binding capacity and can be expected to perform just as well. In addition, AMD iron oxides have been shown not to leach metals, and may be a candidate in water filtration systems as an absorbent for both cations and anions (1,5). While it may not be practical to use AMD iron oxides directly in a moderate size municipal wastewater treatment system, there appears to be other potential applications where they could be quite useful.

Ferric chloride is a popular additive which can sequester phosphates and aid in flocculation and solids settling (1). Ferric chloride is typically shipped to a treatment plant as 30% solution of ferric chloride. One of the desirable aspects of using AMD produced ferric chloride in wastewater treatment, is that many treatment facilities already have the infrastructure to dose ferric chloride, eliminating any new infrastructure costs and development of new dosing systems. Because it does not require any changes or modifications, addition of AMD ferric chloride would probably be the easiest method of utilizing AMD iron oxides in wastewater treatment. The biggest concern for a treatment facility would be the ability to obtain a consistent product that is cost competitive with their current supply of ferric chloride. This study has shown that ferric chlorides can be produced from almost any AMD iron oxide solid as long as it is not heavily contaminated with calcium carbonate from active lime treatment. In fact, the SBR study has shown that most of the AMD solids investigated, have an adsorption capacity of 150-160 mg P/g iron oxide, comparable to the 160 mg P/g iron oxide for commercial ferric chloride. It does not appear that it would be difficult to produce an AMD ferric chloride that would have an almost identical sorption ability to commercial ferric chloride. Production of AMD ferric chlorides for wastewater treatment maybe one of most promising economic reuses for AMD iron oxides. What is attractive about ferric chloride production is that iron oxides that are not suitable as pigments can be used to make ferric chlorides.

The final method of adding AMD iron to wastewater was the direct addition of AMD discharge water to wastewater. Results of this study strongly suggest that combining the waste streams has scientific and technical merit, and should be explored further. A number of issues would need to be overcome that include: 1) regulatory aspects that make it difficult to mix the two waste streams, 2) dilution of the municipal waste stream that may affect operating conditions of the wastewater treatment plant, 3) infrastructure costs needed to address the increase flows

that may affect clarification units; and 4) collection and conveyance of AMD to a wastewater location. This approach may be well suited to new installations where wastewater facilities can be located in close proximity to AMD discharges and there is also a required phosphate limit. In effluent water, ferrous ions found in AMD discharge water are readily oxidized, and the resulting iron oxide has an adsorption capacity very similar to ferric chloride. Other metals in solution such as manganese and aluminum also form precipitates, and are very effective in sequestering phosphate. The two leaching studies that were performed clearly show that AMD products do not leach metals into solution. In fact, there is no evidence that AMD would contaminate the effluent water stream, or negatively impact the operation of the wastewater facility.

In order to use AMD directly in municipal wastewater treatment it is necessary that there is a discharge located close to the treatment plant. The discharge must be captured and piped to the treatment facility. Once the discharge is captured and conveyed to the treatment plant, the only O&M cost associated with this treatment is the electrical cost associated with pumping the discharge if there is not suitable head. If the discharge is alkaline with an iron concentration of about 80 mg/l, and the treatment system wished to remove 2 mg/l of phosphorus, then it would require about 80 ml of AMD water per liter of wastewater to sequester the phosphate. This addition of AMD water would increase the flow through the treatment system by about 8%, which is feasible as long as the treatment system has excess hydraulic capacity. As an example, a one million gallon a day wastewater facility would require 80,000 gallons a day of AMD discharge water with an 80 mg/l iron concentration, or 55 gallons per minute of AMD flow. This mixed treatment approach can only be possible if there is a discharge close to the treatment plant, and if regulations permit this kind of mixed treatment. In southwest Pennsylvania, having an AMD source close to a treatment plant is not uncommon.

Another option worthy of exploring in utilizing AMD discharge water to remove nutrients from waste waters is to treat the wastewater in a conventional plant and treat the AMD discharge water in a separate facility (e.g., aeration system). The effluent leaving the wastewater treatment system is combined with the treated AMD water, and allowed to flow into a large detention pond and wetland system. The AMD iron oxides and biota in the wetland system will remove phosphates, nitrates and organic matter. By combining the flows after wastewater treatment some of the regulatory issues can potentially be avoided, and the AMD discharge volume is not a factor in the wastewater treatment system, so that all of the discharge water can be treated in an adequately designed aeration and passive treatment system. Combining effluent water and the aerated AMD discharge water may be one of the most cost effective ways of reducing nutrients in effluent water while treating an AMD discharge. This may be applicable to small communities with low wastewater flow and where there is not land constraints do not limit the size of the AMD treatment and tertiary treatment system (i.e., detention pond and wetland system)..

If AMD iron oxides are reused in some capacity in water treatment, there is a cost associated with harvesting the solids and transporting them for processing and further distribution. Dr. Robert Hedin estimates that the cost of removing solids from a constructed passive treatment system is about \$50 per ton. Dr. Jon Dietz estimates that the cost of dewatering solids costs associated with the AIS treatment process is \$28 per ton; it should be noted that this is a cost of treatment and not an additional recovery cost. Both Dr. Hedin and Dr.

Dietz estimate that the cost of drying 30% by weight solids to 50% weight solids is \$15 to \$20 dollars per ton. The cost to truck the solids to a central processing plant will vary depending on the location of the discharge in relation to the processing facility and we have estimated an average transportation cost of \$30 per ton. Therefore, it costs between \$75 to \$100 dollars per ton to obtain, dry, and transport an AMD iron oxides to a processing facility. If these materials are being used to produce a ferric chloride, there is an additional cost for HCl, capital cost for equipment to dissolve the iron oxides in HCl and then pump the ferric chloride or HCl. There is a transportation cost associated with distributing the HCl solution to the various water authorities. Finally, there are labor and administration costs to operate the facility, and these cost were not estimated as part of this project.

Conclusions:

This study has shown that AMD produced iron oxides, ferric chlorides produced from AMD iron oxides, and AMD discharge water are all capable of sequestering phosphates in municipal wastewater treatment. Eight different iron oxide solids were investigated as part of this study. The solids were found to be relatively pure, greater than 80% iron oxide, in a semi-crystalline Goethite type structure. Solids from the Brandy Camp discharge were the one exception, they were found to be heavily contaminated with calcite. The phosphate adsorption capacity for AMD iron oxides is around 7 mg P/g of solid for dried iron oxides and increases to around 12 mg P/g of solid never dried iron oxides. These values are about 13 to 23 times lower than the phosphate adsorption capacity of freshly precipitated iron oxides prepared from ferric chloride, 160 mg P/gram iron oxide. The low adsorption capacity of these materials lowers their potential use as phosphate sequestering agents in municipal wastewater treatment in comparison to ferric chloride currently used. It is estimated that it would require a concentration of 300 mg/l of solids to remove 2 mg/l of phosphorus which may increase O&M costs at the wastewater treatment system. While the AMD iron oxides may not be suitable as sequestering agent in municipal wastewater treatment, Zeng (25) has shown that materials similar to AMD iron oxides may have been found to be effective adsorbents in flow through columns to remove contaminants such as phosphates. Stabnikov and Ivanov (3,27) have also shown that iron oxides are reduced in anaerobic digestion and sequester phosphate when the supernatant is dosed into the wastewater treatment system. AMD iron oxides may have applications in large treatment systems that incorporate anaerobic digestion.

Six different iron oxides were converted to ferric chlorides and investigated as sequestering agent for municipal wastewater treatment. All of the samples have adsorption capacities greater than, or equal to commercial ferric chloride. Ions such as calcium, magnesium, and aluminum are found on AMD iron oxides, and are also present in AMD ferric chlorides. They increase the adsorption capacity of the ferric chloride relative to commercial ferric chloride because all of the adsorption capacities are based on just the concentration of iron alone. Elemental analysis of the AMD iron oxide solids reveals that the materials are free of heavy metal contaminants, and leaching studies have confirmed that AMD ferric chlorides do not increase the concentration of metals in effluent water. Finally, the results of this study strongly suggest that AMD produced ferric chlorides are excellent candidates as sequestering agents for phosphates in wastewater treatment. This may be one of the best commercial reuses of AMD solids.

AMD discharge water from four discharges in Westmoreland County were examined as sequestering agents for phosphates. Ferrous iron in the discharge water readily oxidizes in the effluent water, and is converted to iron oxides which have phosphate adsorption capacities greater than, or equal to commercial ferric chloride. This may be a cost effective way of using AMD iron to remove phosphates from a waste stream. We estimate that it would require 55 gpm of discharge water with an iron concentration of 80 mg/l to sequester 2 mg/l of phosphorus from a one million gallon a day (MGD) treatment facility and may be possible under the certain circumstances where the discharge is in close proximity to a wastewater treatment facility and there is adequate hydraulic capacity available in the facility.

There may also be approaches using AMD discharge water to sequester phosphates in tertiary treatment where the AMD discharge is combined with treated wastewater effluent in a large wetland system. This would require pre-aerating the AMD discharge to oxidize the iron prior to wetland system and may also require overcoming regulatory hurdles of combining wastewater flows.

Finally, if AMD solids are to be used in an industrial application such as ferric chloride production Dr. Hedin and Dr. Dietz estimate that it would cost between \$75 to \$100 a ton for iron oxides to be collected dewatered to 50% solids and transported to a processing facility in western Pennsylvania.

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