

# Laboratory Comparison of Four Iron-Based Filter Materials for Drainage Water Phosphate Treatment

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**ABSTRACT:** A laboratory investigation evaluated phosphate ( $\text{PO}_4^{3-}$ ) drainage water treatment capabilities of four iron-based filter materials. The iron-based filter materials tested were zero-valent iron (ZVI), porous iron composite (PIC), sulfur modified iron (SMI), and iron oxide/hydroxide (IOH). Only filter material retained on a 60-mesh sieve ( $>0.25$  mm) was used for evaluation. The laboratory investigation included saturated falling-head hydraulic conductivity tests, contaminant removal or desorption/dissolution batch tests, and low-to-high flow rate saturated solute transport column tests. Each of the four iron-based filter materials have sufficient water flow capacity as indicated by saturated hydraulic conductivity values that in most cases were greater than  $1 \times 10^{-2}$  cm/s. For the 1, 10, and 100 ppm  $\text{PO}_4^{3-}$ -P contaminant removal batch tests, each of the four iron-based filter materials removed at least 95% of the  $\text{PO}_4^{3-}$ -P originally present. However, for the 1000 ppm  $\text{PO}_4^{3-}$ -P contaminant removal batch tests, IOH by far exhibited the greatest removal effectiveness (99%  $\text{PO}_4^{3-}$ -P removal), followed by SMI (72%  $\text{PO}_4^{3-}$ -P removal), then ZVI (62%  $\text{PO}_4^{3-}$ -P removal), and finally PIC (15%  $\text{PO}_4^{3-}$ -P removal). The desorption/dissolution batch test results, especially with respect to SMI and IOH, indicate that once  $\text{PO}_4^{3-}$  is adsorbed/precipitated onto surfaces of iron-based filter material particles, this  $\text{PO}_4^{3-}$  becomes fixed and is then not readily desorbed/dissolved back into solution. The results from the column tests showed that regardless of low or high flow rate (contact time ranged from a few hours to a few minutes) and  $\text{PO}_4^{3-}$  concentration (1 ppm or 10 ppm  $\text{PO}_4^{3-}$ -P), PIC, SMI, and IOH reduced  $\text{PO}_4^{3-}$ -P concentrations to below detection limits, while ZVI removed at least 90% of the influent  $\text{PO}_4^{3-}$ -P. Consequently, these laboratory results indicate that the ZVI, PIC, SMI, and IOH filter materials all exhibit promise for phosphate drainage water treatment. *Water Environ. Res.*, **86**, 852 (2014).

**KEYWORDS:** phosphate, iron-based filter materials, drainage water, water treatment.

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## Introduction

Subsurface drainage, a common farm practice in cool, humid climates of Canada, parts of Europe, and the Midwest United States, is used to remove excess soil moisture by lowering shallow water table levels, thereby improving crop yields (Beauchamp, 1987; Pavelis, 1987; Smedema et al., 2004). A 1985 survey (Pavelis, 1987) showed that the states composing

the Midwest United States (Illinois, Indiana, Iowa, Ohio, Minnesota, Michigan, Missouri, and Wisconsin) had approximately 12.5 million ha containing subsurface drainage systems, the large majority of which was cropland. Although subsurface drainage systems, composed of buried drainage pipe networks, certainly provide substantial economic benefit, they also have adverse environmental consequences. Manure and inorganic fertilizer nutrients, such as phosphate, are often intercepted by the buried drainage pipes and then discharged directly to local waterways (Zucker and Brown, 1998). Phosphate released with drainage water can in turn contribute to the eutrophication of freshwater lakes, such as in the case of Lake Erie in the Midwest United States–Canada (Ohio Environmental Protection Agency, 2010) and for Grand Lake St. Marys in western Ohio (Hoorman et al., 2008). To mitigate the adverse environmental effects of phosphate resulting from agricultural subsurface drainage practices, various onsite water treatment options need to be considered, evaluated, and implemented.

Phosphate ( $\text{PO}_4^{3-}$ , also referred to as orthophosphate, dissolved phosphorus, soluble reactive phosphorus, etc.), as previously indicated, is commonly found in subsurface drainage water released from farm fields. The amount of  $\text{PO}_4^{3-}$  that is found in an agricultural drainage water depends on a number of factors, including type of fertilizer applied (manure or inorganic), amount of fertilizer applied, timing of fertilizer application relative to rainfall events, rainfall event intensity along with corresponding drainage water discharge rate, soil texture, type of crop, etc. (Algoazany et al., 2007; Beauchemin et al., 1998; Gentry et al., 2007; Lu, 2004). Kladienko et al. (1991) measured agricultural subsurface drainage phosphate-phosphorus ( $\text{PO}_4^{3-}$ -P) values in the range of 0.005 to 0.1 mg/L at an experimental field site in Indiana. At 27 farm sites in Quebec, Canada, Beauchemin et al. (1998) observed subsurface drainage water  $\text{PO}_4^{3-}$ -P values in the range of  $\sim 0$  to 0.6 mg/L. Laubel et al. (1999) monitored storm event  $\text{PO}_4^{3-}$ -P in the range of 0.04 to 0.39 mg/L at the subsurface drainage pipe network outlet for a small agricultural watershed in Denmark. A review of previous investigations indicate that subsurface drainage  $\text{PO}_4^{3-}$ -P values in agricultural settings are most often well below 0.25 mg/L, but values up to and even exceeding 1.0 mg/L have been reported (Kinley et al., 2007; Lu, 2004; Sims et al., 1998).

Agricultural subsurface drainage systems are best described as buried drainage pipe networks and are typically composed of drainage pipe laterals that feed into a main collector pipe that outlets into a ditch or small stream. Consequently, an in-line

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**Table 1—Iron-based filter material chemical<sup>a</sup> and physical properties.**

Filter material	pH	ORP <sup>b</sup> mV	Particle density g/cm <sup>3</sup>	Particle size distribution % by wt.			
				Coarse sand size 2.0–4.75 mm	Medium sand size 0.43–2.0 mm	Fine sand size 0.075–0.43 mm	Silt/Clay size <0.075 mm
ZVI	10.70	−481	7.03	0.06	67.50	32.42	0.02
PIC	10.30	−396	7.13	0.16	33.13	66.59	0.12
SMI	6.76	−647	5.93	0.05	34.98	64.93	0.04
IOH	7.50	51	3.62	0.14	96.65	3.20	0.01

<sup>a</sup> Values of pH and ORP were obtained from 1:2 by weight slurry mixtures of filter material to deionized water at ambient laboratory temperatures of 20 to 25 °C.

<sup>b</sup> ORP = oxidation/reduction potential.

filter treatment system located on the main collector pipe near the subsurface drainage system outlet could be a viable means for removing  $\text{PO}_4^{3-}$  from drainage waters before these waters are discharged into the environment. The type of porous, chemically reactive material that is incorporated into a filter system to remove  $\text{PO}_4^{3-}$  will be critical for effective water treatment, and in this regard, iron-based materials could be very promising.

Iron-based materials, such as elemental iron (i.e., zero-valent iron) and iron oxides/hydroxides, have been evaluated for  $\text{PO}_4^{3-}$  water treatment (McCobb et al., 2009; Robertson and Lombardo, 2011). There are three possible mechanisms by which zero-valent iron (ZVI) can remove  $\text{PO}_4^{3-}$ . Iron oxidation processes can lead to the generation of dissolved ferrous/ferric iron ( $\text{Fe}^{2+}/\text{Fe}^{3+}$ ) and the formation of iron oxide/hydroxide minerals or amorphous solids (Henderson and Demond, 2007; Huang and Zhang, 2005; Kamolpornwijit and Liang, 2006; Phillips et al., 2003; Stumm and Morgan, 1981; Takeno, 2005). Ferrous and ferric iron ( $\text{Fe}^{2+}/\text{Fe}^{3+}$ ) can combine with  $\text{PO}_4^{3-}$  to form low solubility iron-phosphate precipitates (Bohn et al., 1985; Stumm and Morgan, 1981). In addition, the iron oxide/hydroxide minerals or amorphous solids that can form via ZVI oxidation will have functional groups sites where  $\text{PO}_4^{3-}$  can become attached via ligand exchange (Bohn et al., 1985; Goldberg, 1985; McBride, 1994). Furthermore, these iron oxide/hydroxides (from ZVI oxidation), given low pH conditions, can exhibit a net positive surface charge (Sparks, 2003), which in turn promotes electrostatic adsorption of negatively charged  $\text{PO}_4^{3-}$  ions (Arai and Sparks, 2007).

Iron oxides/hydroxides (IOH) have been specifically developed and manufactured for water treatment (Dennis, 2007). Similar to ZVI, there are three possible mechanisms by which IOH can remove  $\text{PO}_4^{3-}$ . Dissolution of IOH can release ferrous/ferric iron ( $\text{Fe}^{2+}/\text{Fe}^{3+}$ ) ions (Robertson and Lombardo, 2011), which can combine with  $\text{PO}_4^{3-}$  to form low solubility iron-phosphate precipitates (Bohn et al., 1985; Stumm and Morgan, 1981). Also, IOH particle surfaces have functional groups sites where  $\text{PO}_4^{3-}$  can become attached via ligand exchange (Bohn et al., 1985; Goldberg, 1985; McBride, 1994). Moreover, IOH materials, given low pH conditions, can exhibit a net positive surface charge that causes electrostatic adsorption of negatively charged  $\text{PO}_4^{3-}$  ions (Arai and Sparks, 2007; Sparks, 2003). Two recently developed iron-based materials, porous iron composite (PIC) and sulfur-modified iron (SMI), may also have filter treatment potential for drainage waters contaminated with  $\text{PO}_4^{3-}$ . The  $\text{PO}_4^{3-}$  removal mechanisms for PIC and SMI have

not yet been identified, but are likely similar to the  $\text{PO}_4^{3-}$  removal mechanisms for ZVI and IOH.

To date, there has been very little direct comparison of capabilities for drainage water  $\text{PO}_4^{3-}$  filter treatment between ZVI and IOH, and especially ZVI or IOH versus PIC or SMI. Consequently, for the purpose of providing a preliminary comparison of ZVI, PIC, SMI, and IOH in regard to  $\text{PO}_4^{3-}$  filter treatment potential, a laboratory investigation was carried out with hydraulic conductivity tests, batch tests, and solute transport column tests. For these laboratory tests, to better evaluate drainage water  $\text{PO}_4^{3-}$  filter treatment performance, actual agricultural drainage water was used, both unspiked and spiked with  $\text{PO}_4^{3-}$ . The stated research objective was, therefore, to conduct a preliminary laboratory comparison of ZVI, porous iron composite, SMI, and IOH filter materials with respect to hydraulic flow efficiency and drainage water treatment of  $\text{PO}_4^{3-}$ .

## Materials and Methods

**Iron-Based Filter Materials.** Four iron-based filter materials were evaluated in this investigation. The first material, ZVI, obtained from Connelly-GPM, Inc. (Chicago, Illinois; product name CC-1190), is best described as a ground iron aggregate composed of shavings from cast iron borings. The second material, PIC, obtained from North American Höganäs, Inc. (Hollsopple, Pennsylvania; product name Cleanit LC), is manufactured with high-purity elemental iron powder to which functional additives are mixed. The mixture was then processed through powder metallurgical technologies to achieve an iron composite media with high internal porosity (specific surface =  $\sim 10.0 \text{ m}^2/\text{g}$ ), where functional groups are evenly distributed in either free or partially alloyed forms. The third material, SMI, was obtained from SMI\_PS, Inc. (Lincoln, California), and can be described as a hydrogen-reduced, high-surface-area iron powder that has been additionally modified through chemical reaction with pure sulfur to produce sulfur/iron compound surface coatings on the iron particles. The fourth material, IOH, is manufactured by LANXESS AG (Leverkusen, Germany; product name Bayoxide E33), and can be described as a synthetic, high-surface-area ( $\sim 150 \text{ m}^2/\text{g}$ ) goethite (chemical formula:  $\alpha\text{-FeOOH}$ ). To improve hydraulic flow efficiency (i.e., increase hydraulic conductivity), fine-grained particles passing through a 60-mesh sieve (particle size  $< 0.25 \text{ mm}$ ) were removed from the ZVI, PIC, SMI, and IOH filter materials that were tested in this investigation.

Properties of the ZVI, PIC, SMI, and IOH filter materials are provided in Table 1. The pH and oxidation/reduction potential

(ORP) were measured on slurry mixtures of filter material–deionized water (1:2 w/w). All pH values were determined using an Oakton (Vernon Hills, Illinois) pHTestr 10 BNC. Oxidation/reduction potential was measured with a YSI Inc. (Yellow Springs, Ohio), EcoSense pH100 Meter and a YSI Inc., 115-1 ORP Probe. Table 1 shows that, with respect to pH, the ZVI and PIC slurries were strongly alkaline (>10), while the SMI and IOH slurries were near neutral (6 to 8). The ZVI, PIC, and SMI had ORP values less than -390 mV, indicating that ZVI, PIC, and SMI would likely produce very low redox conditions within a filter treatment system environment. The low ORP values for the water slurries with ZVI, PIC, and SMI were expected because Eh-pH diagrams for iron/water systems indicate that elemental iron is stable only under very low Eh (low ORP) conditions (Takeno, 2005). Oxidation of elemental iron with release of dissolved ferrous iron ( $\text{Fe}^{2+}$ ) also only occurs with low Eh (Stumm and Morgan, 1981; Takeno, 2005).

Iron-based filter material particle density values were determined using American Society for Testing and Materials procedures (Wray, 1986), which employ the Archimedes principle. (The particle density of an iron-based filter material is easily calculated once the weight of an iron-based filter material amount is measured along with its displaced water volume.) The laboratory-measured particle density of IOH was  $3.62 \text{ g/cm}^3$ , which was much lower than the particle density values of  $7.03$ ,  $7.13$ , and  $5.93 \text{ g/cm}^3$  that were obtained, respectively, for ZVI, PIC, and SMI. The cast iron shavings or scrap metal used as feedstock for producing ZVI, PIC, and SMI are composed predominantly of iron, although small but significant quantities of other constituents (such as carbon, silicon, manganese, etc.) are also present. Furthermore, PIC and SMI particle surfaces have attached functional groups or sulfur compounds containing not only iron but other constituents as well. Consequently, it could be expected that the particle density of ZVI ( $7.03 \text{ g/cm}^3$ ), PIC ( $7.13 \text{ g/cm}^3$ ), and SMI ( $5.93 \text{ g/cm}^3$ ) differed from that of elemental iron ( $7.87 \text{ g/cm}^3$ ). Table 1 particle size data, based on mechanical sieving methods (Wray, 1986) and a particle size classification from Perloff and Baron (1976), shows that the 60-mesh sieved ZVI and IOH materials were predominantly composed of medium sand sized particles, while the 60-mesh sieved PIC and SMI materials were predominantly comprised of fine sand sized particles.

**Test Solutions.** Saturated hydraulic conductivity tests were carried out with a 0.01-mole/L calcium sulfate ( $\text{CaSO}_4$ ) solution, unspiked drainage water obtained from the Ohio State University–Waterman Agricultural and Natural Resources Laboratory (ANRL) in Columbus, Ohio, and unspiked drainage water from the Defiance Agricultural Research Association (DARA) field site in Defiance, Ohio. Based on material retained by a 0.7- $\mu\text{m}$  filter, the 0.01-mole/L calcium sulfate solution had 0.0 mg/L total suspended solids (TSS), the Waterman ANRL drainage water had 0.0 mg/L TSS, and the DARA drainage water had 128.3 mg/L TSS.

Spiked Waterman ANRL drainage water was used for the contaminant removal batch tests, the first stage of the desorption/dissolution batch tests, and the saturated solute transport column tests. Waterman ANRL drainage water was spiked with various concentrations of  $\text{PO}_4^{3-}\text{-P}$  by dissolving specific amounts of monobasic potassium phosphate ( $\text{KH}_2\text{PO}_4$ ). Unspiked Waterman ANRL drainage water had an average soluble phosphorus concentration of 0.095 ppm (standard

deviation = 0.029 ppm). With respect to other dissolved anions and cations commonly found in agricultural waters, laboratory analysis done by the Ohio State University (OSU)–Service Testing and Research Laboratory (STAR) in Wooster, Ohio, determined that the unspiked Waterman ANRL drainage water contained ~56 ppm calcium ( $\text{Ca}^{2+}$ ), ~23 ppm chloride ( $\text{Cl}^-$ ), ~18 ppm magnesium ( $\text{Mg}^{2+}$ ), ~6 ppm nitrate (as  $\text{NO}_3^-\text{-N}$ ), 1 ppm potassium ( $\text{K}^+$ ), and 13 ppm sulfate (as  $\text{SO}_4^{2-}\text{-S}$ ). The OSU–STAR laboratory also confirmed that the soluble phosphorus originally present in the Waterman ANRL drainage water is predominantly in the form of  $\text{PO}_4^{3-}\text{-P}$ . The contaminant removal batch tests were conducted using Waterman ANRL drainage water spiked with 1, 10, 100, and 1000 ppm  $\text{PO}_4^{3-}\text{-P}$ . Waterman ANRL drainage water spiked with 100 ppm  $\text{PO}_4^{3-}\text{-P}$  was used for the first stage of the desorption/dissolution batch tests. The saturated solute transport column tests were carried out with Waterman ANRL drainage water spiked with 1 or 10 ppm  $\text{PO}_4^{3-}\text{-P}$ . The spiked  $\text{PO}_4^{3-}\text{-P}$  concentrations (1, 10, 100, or 1000 ppm) in the drainage water used for the batch and column tests would be considered high to extraordinarily high compared to  $\text{PO}_4^{3-}\text{-P}$  concentrations normally found in agricultural drainage waters (Kinley et al., 2007; Lu, 2004; Sims et al., 1998), and these high to extraordinarily high  $\text{PO}_4^{3-}\text{-P}$  concentrations were chosen to more rigorously test ZVI, PIC, SMI, and IOH for drainage water  $\text{PO}_4^{3-}$  removal. Ultrapure deionized water was used for the second stage of the desorption/dissolution batch tests, while the third stage of these batch tests used a 0.01-mole/L potassium sulfate ( $\text{K}_2\text{SO}_4$ ) solution.

The 0.01-mole/L  $\text{CaSO}_4$  solution, the DARA drainage water, the Waterman ANRL drainage water spiked with 1 ppm  $\text{PO}_4^{3-}\text{-P}$ , the Waterman ANRL drainage water spiked with 10 ppm  $\text{PO}_4^{3-}\text{-P}$ , and the Waterman ANRL drainage water spiked with 100 ppm  $\text{PO}_4^{3-}\text{-P}$  all had near neutral pH values (6 to 8). The Waterman ANRL drainage water spiked with 1000 ppm  $\text{PO}_4^{3-}\text{-P}$ , the ultrapure deionized water, and the 0.01-mole/L  $\text{K}_2\text{SO}_4$  solution had respective pH values of 5.88, 5.83, and 5.72, which would be considered acidic (4 to 6). The unspiked Waterman ANRL drainage water had a pH of 8.25, which would be considered alkaline (8 to 10). All test solutions used in this study had ORP values that ranged between 100 and 200 mV.

**Saturated Falling-Head Hydraulic Conductivity Tests.** Saturated hydraulic conductivity governs the rate at which water flows through a filter material under saturated conditions. To be hydraulically practical, a filter material must have a sufficiently high saturated hydraulic conductivity, at least equal to and preferably much greater than  $1.0 \times 10^{-3} \text{ cm/s}$ , which is a stormwater sand filter design criteria (Barr Engineering Company, 2001; Blick, et al., 2004; Claytor and Schueler, 1996). Standard falling-head hydraulic conductivity tests (Freeze and Cherry, 1979; Todd, 1980) were used for hydraulic conductivity measurement.

The saturated falling-head hydraulic conductivity tests were carried out on 60-mesh sieved ZVI, PIC, SMI, and IOH filter material columns packed within permeameters. Hydraulic conductivity measurements were obtained from two separately packed columns for each individual filter material. The ZVI, PIC, and SMI materials were soaked with distilled water and allowed to drain and equilibrate for 24 hours prior to being packed within the permeameters. This was done to release as much hydrogen gas as possible generated by the interaction of elemental iron with water (Kamolpornwijit and Liang, 2006).

By releasing this hydrogen gas from the ZVI, PIC, and SMI materials before they were packed into the permeameters, there was hopefully less chance of hydrogen gas bubbles forming, which would block pores and reduce hydraulic conductivity. Unsoaked, dry IOH material was packed into the permeameters because interaction between IOH and water was not expected to produce hydrogen gas.

The packed filter material columns within the permeameters were 152 mm in length, 41 mm in diameter, and were first saturated with the 0.01-mole/L  $\text{CaSO}_4$  solution before the initial hydraulic conductivity measurement. Dry bulk density averaged  $2.47 \text{ g/cm}^3$  for the two ZVI columns,  $1.27 \text{ g/cm}^3$  for the two PIC columns,  $2.26 \text{ g/cm}^3$  for the two SMI columns, and  $0.51 \text{ g/cm}^3$  for the two IOH columns. Laboratory temperatures during testing ranged from 20 to 25 °C. Hydraulic conductivity measurements for each column (again, two packed columns for each filter material) were obtained over a period of 8 to 12 days, first using the  $\text{CaSO}_4$  solution, then the unspiked Waterman ANRL drainage water, and finally, the DARA drainage water.

**Phosphorus Analysis Methods for Batch and Column Tests.** Concentrations of soluble phosphorus (soluble-P) within batch test supernatant and column test effluent were measured using inductively coupled plasma (ICP) methods. These ICP methods have commonly been used to measure metal concentrations in water samples (APHA et al., 1998); however, ICP methods have now also gained acceptance for phosphorus analysis of soils and agricultural waters (Matula, 2011; Self-Davis et al., 2000). In this study, soluble-P was measured using a Perkin-Elmer (Waltham, Massachusetts) Optima 3300 DV ICP-OES (inductively coupled plasma optical emission spectrometer) or a Thermo Finnigan Element 2 (San Jose, California) ICP-SFMS (inductively coupled plasma sector field mass spectrometer). The phosphorus detection limit for the ICP-OES ranged from 0.01 to 0.08 ppm. The phosphorus detection limit for the ICP-SFMS was 0.009 ppm. The ICP-SFMS was used in place of the ICP-OES to obtain more accurate results when low concentrations of soluble-P were expected. It is important to note that in this study the drainage water used in the batch and column tests was spiked with high levels of  $\text{PO}_4^{3-}\text{-P}$ ; therefore, the batch test supernatant or column test effluent soluble-P measurements essentially represent  $\text{PO}_4^{3-}\text{-P}$  values.

**Contaminant Removal Batch Tests.** Contaminant removal batch tests were carried out with ZVI, PIC, SMI, and IOH at ambient laboratory temperatures ranging from 20 to 25 °C. Control batch tests with no filter material (NFM) were also carried out to quantify  $\text{PO}_4^{3-}$  amounts adsorbed by the experimental apparatus. These contaminant removal batch tests provided a preliminary assessment of the  $\text{PO}_4^{3-}$  removal capabilities and, in turn, decided that further testing of ZVI, PIC, SMI, or IOH was warranted. Each of the filter materials (and NFM) was tested against Waterman ANRL drainage water spiked with 1, 10, 100, and 1000 ppm  $\text{PO}_4^{3-}\text{-P}$ . The repeatability of results for  $\text{PO}_4^{3-}$  removal was confirmed by conducting a set of three batch test replicates for each combination of filter material (or NFM) and Waterman ANRL drainage water spiked with 1, 10, 100, or 1000 ppm  $\text{PO}_4^{3-}\text{-P}$ . One batch test within each three replicate set was chosen for pH and ORP measurement using methods previously described.

In each filter material contaminant removal batch test, 5 g of filter material (60-mesh sieved) and 40 g of spiked Waterman

ANRL drainage water were combined in a 50-mL polypropylene centrifuge tube (BD Biosciences, Bedford, Massachusetts). The filter material and batch test solution were thoroughly mixed by placing the centrifuge tube on a laboratory rotator (Mini LabRoller Rotator, Labnet International, Inc., Woodbridge, New Jersey) operated at 20 rpm. Each contaminant removal batch test was then stopped after 24 hours of mixing. Procedures for the control batch tests were the same, with only spiked Waterman ANRL drainage water (40 g), but no added filter material. Once pH and ORP values were obtained for one batch test within each three replicate set, all batch test centrifuge tubes containing filter material (or NFM) and solution were then centrifuged (Beckman Model TJ-6 Centrifuge, Beckman Coulter, Inc., Fullerton, California) at 2500 rpm (800 g) for 15 minutes to separate the filter material from the solution. The supernatant solution was then decanted into a second 50-mL polypropylene centrifuge. Supernatant concentrations of soluble-P (essentially,  $\text{PO}_4^{3-}\text{-P}$ ) were measured using the ICP methods previously described.

**Desorption/Dissolution Batch Tests.** The desorption/dissolution batch tests were carried out for the purpose of determining if the  $\text{PO}_4^{3-}$  that adsorbed or precipitated onto ZVI, PIC, SMI, or IOH particle surfaces could be readily desorbed or dissolved back into solution via washing with water or an electrolyte solution. Each desorption/dissolution batch test was carried out in three stages at ambient laboratory temperatures ranging from 20 to 25 °C. The repeatability of results for the phosphate desorption/dissolution batch tests was confirmed by conducting two replicate batch tests for each filter material (or NFM).

For the first stage of each phosphate desorption/dissolution batch test, 5 g (dry weight) of filter material (60-mesh sieved) and 40 g of Waterman ANRL drainage water spiked with 100 ppm  $\text{PO}_4^{3-}\text{-P}$  were combined in a 50-mL centrifuge tube. The filter material and the spiked drainage water were thoroughly mixed with a laboratory rotator operated at 20 rpm. The first stage of each dissolution/desorption batch test was then stopped after 24 hours. Procedures for the control batch tests were the same, but with NFM. All batch test centrifuge tubes containing filter material (or NFM) and solution were then centrifuged at 2500 rpm (800 g) for 15 minutes to separate any filter material from the solution. The Stage 1 supernatant solution was then decanted into a clean 50-mL polypropylene centrifuge tube.

For the second stage of each desorption/dissolution batch test, once the Stage 1 supernatant had been removed, 40 g of ultrapure deionized water only was added to the original centrifuge tubes, which had either 5 g of filter material or were empty (NFM—control tests). As with the first stage, the centrifuge tubes with filter material (or NFM) and the added ultrapure deionized water were placed on a laboratory rotator and mixed for 24 hours, then centrifuged for 15 minutes, followed by decanting of the Stage 2 supernatant into a clean 50-mL centrifuge tube.

For the third stage of each desorption/dissolution batch test, once the Stage 2 supernatant had been removed, 40 g of 0.01-mole/L  $\text{K}_2\text{SO}_4$  solution were added to the original centrifuge tubes, which again had either 5 g of iron-based filter material or were empty (NFM—control tests). As with the first and second stages, the centrifuge tubes with filter material (or NFM) and  $\text{K}_2\text{SO}_4$  solution were placed on a laboratory rotator and mixed for 24 hours, then centrifuged for 15 minutes, followed by



**Table 2—Characteristics of low-to-high flow rate saturated solute transport column tests.**

Filter material	Packed dry bulk density g/cm <sup>3</sup>	Column pore volume cm <sup>3</sup>	Total effluent amount L	Total effluent amount pore volumes	Combined low flow rate steps average contact time and (Avg. flux) minutes (mL/cm <sup>2</sup> •h)	1st high flow rate step average contact time and (Avg. flux) minutes (mL/cm <sup>2</sup> •h)	2nd high flow rate step average contact time and (Avg. flux) minutes (mL/cm <sup>2</sup> •h)	3rd high flow rate step average contact time and (Avg. flux) minutes (mL/cm <sup>2</sup> •h)
Control <sup>a</sup>	NA	NA	21.07	NA	NA (2.48)	NA (139.41)	NA (249.59)	NA (249.71)
ZVI	2.82	180.10	19.02	105.58	243.00 (2.22)	10.79 (50.02)	2.75 (196.22)	2.90 (186.27)
PIC	1.22	249.22	20.09	80.62	305.95 (2.44)	8.28 (90.13)	3.22 (231.79)	2.69 (277.48)
SMI	2.15	191.64	20.12	104.97	231.73 (2.48)	7.26 (79.09)	3.34 (172.09)	3.01 (190.96)
IOH	0.51	258.32	20.51	79.39	320.44 (2.41)	9.84 (78.64)	4.00 (193.30)	3.65 (211.76)

<sup>a</sup> Control column tests were conducted with no filter material (NFM) present.

NA = not applicable.

decanting of the Stage 3 supernatant into a clean 50-mL centrifuge tube. Soluble-P measurements were obtained for the supernatant solutions from the first, second, and third stages of these desorption/dissolution batch tests with ICP methods previously described.

**Low-to-High Flow Rate Saturated Solute Transport Column Tests.** By allowing control of solution flux, and in turn, the filter material to solution contact time, saturated solute transport column tests can help better evaluate the likely PO<sub>4</sub><sup>3-</sup> removal behavior of 60-mesh sieved ZVI, PIC, SMI, or IOH filter materials within an actual filter treatment system. For these column tests, continuously operated variable-flow-rate peristaltic pumps (Model 3384 and Model 3386, Control Company, Friendswood, Texas) delivered influent PO<sub>4</sub><sup>3-</sup> spiked Waterman ANRL drainage water to the bottom inlet of a vertically oriented Teflon permeameter containing a packed filter material (or empty—NFM) column. Ambient laboratory temperatures during testing ranged from 20 to 25 °C. As with the hydraulic conductivity tests, and based on the same reasoning, the ZVI, PIC, and SMI materials, but not IOH, were soaked with distilled water and allowed to drain and equilibrate for 24 hours prior to being packed within the permeameters. Filter material columns contained within the Teflon permeameters had a diameter of 51 mm and a length of 150 mm. Plastic laboratory tubing was used to deliver solution between the influent supply container, peristaltic pump, permeameter, and effluent sample container.

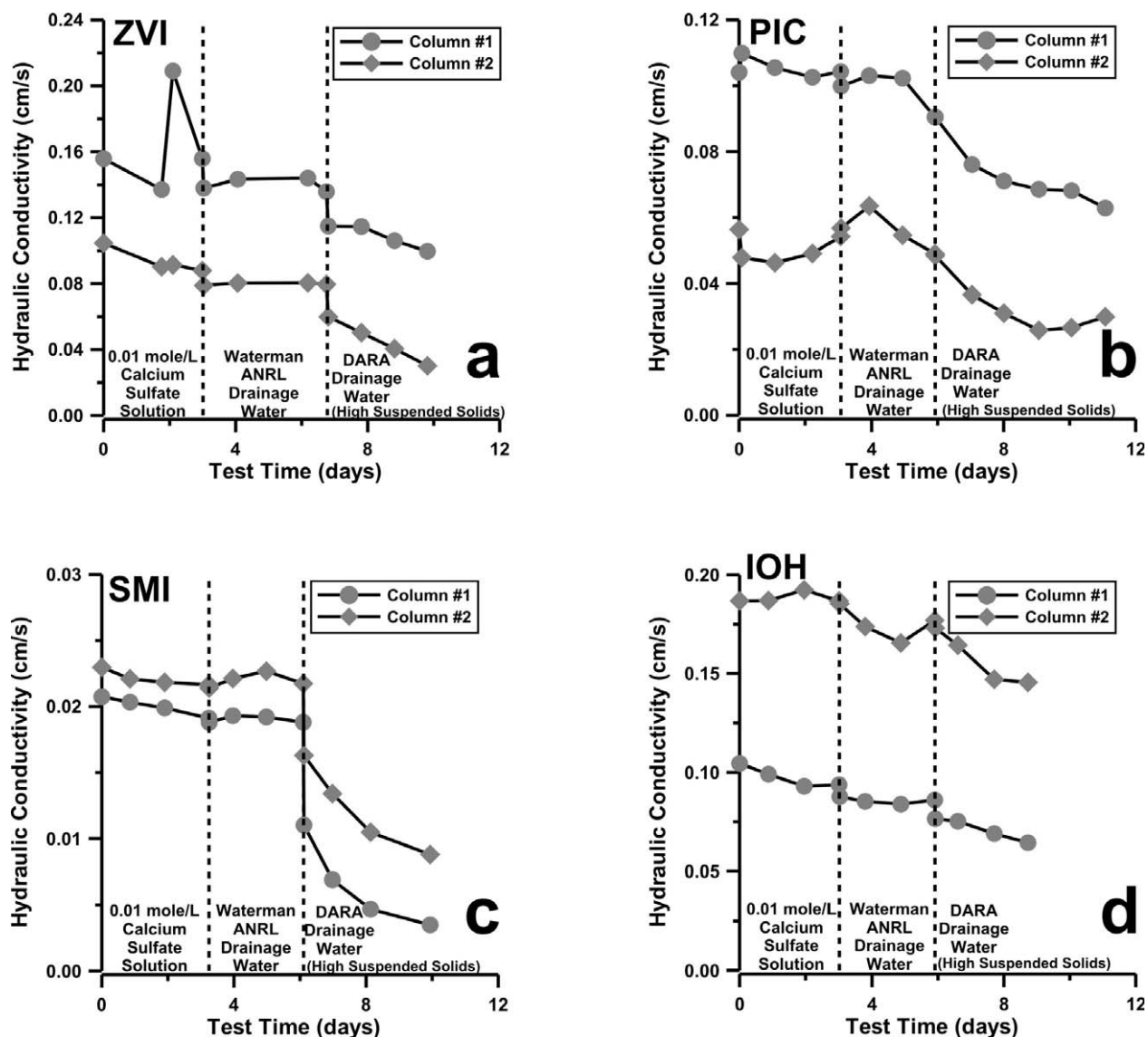
Effluent exiting the permeameter was collected over time in glass containers or polypropylene centrifuge tubes. During a column test, one out of two effluent samples (every other sample) was collected in a 1.9-L glass jar. The time period it took to collect the effluent sample in the glass jar and the total amount of effluent in the glass jar were then used to calculate column flow rates. Every other effluent sample (one out of two) not collected in a glass jar was instead collected in a 50-mL polypropylene centrifuge tube. The effluent in the centrifuge tube was measured for pH, and then the centrifuge tube containing the sample was centrifuged at 2500 rpm (800 g) for 15 minutes to separate out any filter material that might be present in the effluent sample. The supernatant effluent sample was next decanted into a second 50-mL polypropylene centrifuge tube for later analysis of soluble phosphorous (essentially, PO<sub>4</sub><sup>3-</sup>-P) using the ICP methods previously described. In addition, column flow rates were also calculated for effluent samples collected with centrifuge tubes.

Information in Table 2 on the five saturated solute transport column tests includes type of filter material (or NFM), filter material dry bulk density, column pore volume, total effluent amount (in liters and pore volumes), average solution to filter material contact time, and flux. A control column test with no filter material present was carried out to quantify PO<sub>4</sub><sup>3-</sup> removal resulting from experimental apparatus and procedures. Column test operation and effluent sample handling techniques for the control column test were the same as those for the filter material column tests. The influent Waterman ANRL drainage water used in each column test was spiked first with 1 ppm PO<sub>4</sub><sup>3-</sup>-P and then 10 ppm PO<sub>4</sub><sup>3-</sup>-P. All column tests were carried out with high-flow rate steps interspersed with low-flow steps. By conducting the filter material column tests with both low and high flow rates, insight was gained on the water filter treatment contact time needed for effective removal of PO<sub>4</sub><sup>3-</sup>. Column test duration was approximately 2 weeks, and for the ZVI, PIC, SMI, and IOH tests, the total amount of PO<sub>4</sub><sup>3-</sup> spiked Waterman ANRL drainage water flushed through the columns ranged from around 80 to 105 pore volumes.

## Results and Discussion

**Saturated Falling-Head Hydraulic Conductivity Test Results.** The 60-mesh sieved ZVI, PIC, SMI, and IOH hydraulic conductivity measurements are presented in Figure 1. The hydraulic conductivity values obtained first with the 0.01-mole/L CaSO<sub>4</sub> solution averaged 0.129 cm/s for the two ZVI columns, 0.078 cm/s for the two PIC columns, 0.021 cm/s for the two SMI columns, and 0.143 cm/s for the two IOH columns. The hydraulic conductivity values obtained next with the unspiked Waterman ANRL drainage water averaged 0.110 cm/s for ZVI, 0.078 cm/s for PIC, 0.021 cm/s for SMI, and 0.131 cm/s for IOH. The final hydraulic conductivity values obtained with the DARA drainage water averaged 0.077 cm/s for ZVI, 0.049 cm/s for PIC, 0.009 cm/s for SMI, and 0.114 cm/s for IOH. All saturated hydraulic conductivity measurements for the four iron-based filter materials were far greater than the 1.0 × 10<sup>-3</sup> cm/s hydraulic conductivity criterion used for stormwater sand filters (Barr Engineering Company, 2001; Blick, et al., 2004; Claytor and Schueler, 1996). Based strictly on hydraulic conductivity considerations, IOH was best, followed by ZVI, then PIC, and finally, SMI.

Hydraulic conductivity tends to have a strong, positive correlation with average particle size (Freeze and Cherry,



**Figure 1—Saturated falling-head hydraulic conductivity test results: (a) ZVI, (b) PIC, (c) SMI, and (d) IOH. Note: The hydraulic conductivity scale is different on all four graphs. The relatively small differences in measured hydraulic conductivity when comparing column 1 to column 2 for a particular filter material may be due in part to packing irregularities between columns.**

1979). Of the four iron-based filter materials tested, the lowest hydraulic conductivity values were exhibited by PIC and SMI, and these results are probably due in large part to PIC and SMI having a much greater amount of fine sand sized particles (>60%, Table 1) compared to ZVI or IOH, which were composed mostly of medium sand sized particles. The highest average hydraulic conductivity was obtained with IOH, which had by far the greatest amount of medium sand sized particles (>95%, Table 1).

The DARA drainage water contained significant amounts of suspended solids that were not present in the 0.01-mole/L  $\text{CaSO}_4$  solution or the Waterman ANRL drainage water (see “Materials and Methods—Test Solutions” earlier in this document). Suspended solids can clog pore constrictions as a result, accounting for the lower hydraulic conductivity values found for each particular filter material with the DARA drainage

water as compared to the  $\text{CaSO}_4$  solution or the Waterman ANRL drainage water (see Figure 1). In a relative sense, the DARA drainage water hydraulic conductivity reduction was fairly small with IOH, as opposed to ZVI, PIC, and SMI, where the relative DARA drainage water hydraulic conductivity reductions were much greater. Consequently, with atypical drainage waters containing significant amounts of suspended solids, hydraulic conductivity reduction may be a concern with ZVI, PIC, and SMI.

**Contaminant Removal Batch Test Results.** Results for the contaminant removal batch tests are provided in Table 3. For the 1, 10, and 100 ppm  $\text{PO}_4^{3-}\text{-P}$  spiked drainage water contaminant removal batch tests, the pH for the ZVI and PIC tests were alkaline to strongly alkaline (measurements were greater than 9), while much lower, near neutral to alkaline pH (measurements between 7 and 9) were obtained for the control, SMI, and IOH

**Table 3—Results for contaminant removal batch tests.**

Initial solution	Filter material	pH	ORP <sup>a</sup> mV	Average soluble phosphorous concentration at test completion <sup>b</sup> ppm	Coefficient of variation for soluble-P concentration at test completion <sup>b</sup> ppm
Drainage water <sup>c</sup> spiked with 1 ppm PO <sub>4</sub> <sup>3-</sup> -P	Control <sup>d</sup>	7.87	77	1.06	0.064
	ZVI	9.16	-308	ND <sup>e</sup>	NA <sup>f</sup>
	PIC	10.07	-802	ND <sup>e</sup>	NA <sup>f</sup>
	SMI	8.47	-532	ND <sup>e</sup>	NA <sup>f</sup>
	IOH	8.22	-13	ND <sup>e</sup>	NA <sup>f</sup>
Drainage water <sup>c</sup> spiked with 10 ppm PO <sub>4</sub> <sup>3-</sup> -P	Control <sup>d</sup>	7.87	118	9.20	0.009
	ZVI	9.17	-658	ND <sup>e</sup>	NA <sup>f</sup>
	PIC	10.01	-650	ND <sup>e</sup>	NA <sup>f</sup>
	SMI	8.55	-536	ND <sup>e</sup>	NA <sup>f</sup>
	IOH	7.71	55	ND <sup>e</sup>	NA <sup>f</sup>
Drainage water <sup>c</sup> spiked with 100 ppm PO <sub>4</sub> <sup>3-</sup> -P	Control <sup>d</sup>	7.16	144	93.91	0.006
	ZVI	9.38	-598	3.00	0.038
	PIC	9.88	-622	2.45	0.074
	SMI	8.66	-713	4.62	0.199
	IOH	7.68	78	0.42	0.043
Drainage water <sup>c</sup> spiked with 1000 ppm PO <sub>4</sub> <sup>3-</sup> -P	Control <sup>d</sup>	5.96	140	1000.48	0.014
	ZVI	7.74	-342	375.72	0.013
	PIC	6.37	-656	825.04	0.028
	SMI	9.00	-732	278.68	0.120
	IOH	7.86	-16	8.59	0.044

<sup>a</sup> ORP = oxidation/reduction potential.

<sup>b</sup> Based on three replicate batch tests.

<sup>c</sup> Drainage water obtained from the Ohio State University–Waterman Agricultural and Natural Resources Laboratory in Columbus, Ohio.

<sup>d</sup> Control batch tests were conducted with no filter material (NFM) present.

<sup>e</sup> ND = not detected.

<sup>f</sup> NA = not applicable.

tests. For the 1000 ppm PO<sub>4</sub><sup>3-</sup>-P spiked drainage water batch tests, control test pH was acidic (<6), the pH for the ZVI, PIC, and IOH tests were near neutral (6 to 8), and the SMI batch test pH was alkaline (measured value equaled 9). Batch test ORP values were between 77 and 144 mV for the control tests and ranged from -16 to 78 mV for IOH tests. All ORP values for the ZVI, PIC, and SMI contaminant removal batch tests were less than -300 mV, indicating the presence of very low redox conditions.

The coefficient of variation values listed in Table 3 are generally small, which indicates that the soluble phosphorus (essentially, PO<sub>4</sub><sup>3-</sup>-P) concentrations were quite consistent (similar) within any three replicate batch test set representing a particular combination of an iron-based filter material (or NFM) and one of the spiked drainage waters. Average soluble-P concentrations for the control tests indicate that contaminant removal batch test experimental procedures and equipment alone do not account for substantial PO<sub>4</sub><sup>3-</sup>-P loss. The 10 ppm PO<sub>4</sub><sup>3-</sup>-P spiked drainage water control batch tests exhibited the greatest average percent soluble-P reduction, which was a relatively modest loss of just 8%. For the 1, 10, and 100 ppm PO<sub>4</sub><sup>3-</sup>-P spiked drainage water contaminant removal batch tests, each of the four iron-based filter materials removed at least 95% of the soluble-P originally present. However, for the 1000 ppm PO<sub>4</sub><sup>3-</sup>-P contaminant removal batch tests, IOH by far exhibited the greatest removal effectiveness (99% soluble-P removal), followed by SMI (72% soluble-P removal), then ZVI (62% soluble-P removal), and finally PIC (17% soluble-P removal). Based on 1000 ppm PO<sub>4</sub><sup>3-</sup>-P contaminant removal batch test

results, 7.92 mg of soluble-P was removed per gram of IOH, 5.76 mg of soluble-P was removed per gram of SMI, 4.96 mg of soluble-P was removed per gram of ZVI, and 1.36 mg of soluble-P were removed per gram of PIC.

Table 3, as a whole, shows that ZVI, PIC, SMI, and IOH all have, to a greater or lesser extent, promise for treatment of drainage water PO<sub>4</sub><sup>3-</sup>. Consequently, these contaminant removal batch test results indicate that further laboratory investigation of ZVI, PIC, SMI, and IOH filter materials for PO<sub>4</sub><sup>3-</sup> treatment is certainly warranted. Furthermore, these contaminant removal batch tests also imply that ZVI, PIC, SMI, and IOH could possibly be used in large mixing reactors to treat PO<sub>4</sub><sup>3-</sup> present in industrial and municipal wastewaters before these waters are released into the environment.

**Desorption/Dissolution Batch Tests.** Results of the desorption/dissolution batch tests are shown in Table 4. The Stage 2 and Stage 3 percent desorbed/dissolved values represent the percent of soluble-P desorbed/dissolved during Stage 2 or Stage 3 relative to the total amount of the soluble-P that was originally removed during Stage 1. With one exception, the control (NFM) desorption/dissolution batch tests results indicate that experimental equipment and procedures do not account for substantial soluble-P removal during Stage 1 or substantial soluble-P desorption/dissolution during either Stage 2 or Stage 3. The exception was with Stage 3 for one of the two control tests in which the desorbed/dissolved soluble-P concentration of 1.55 ppm is unexpectedly high, and is probably just an outlier that is best explained by some form of cross-contamination.

**Table 4—Results for desorption/dissolution batch tests.**

Batch test	Stage 1 soluble P supernatant conc. (ppm)	Stage 2 soluble P supernatant conc. (ppm)	Stage 3 soluble P supernatant conc. (ppm)	Stage 1 percent soluble P removal (%)	Stage 2 percent soluble P desorption/dissolution (%)	Stage 3 percent soluble P desorption/dissolution (%)
Control 1	97.69	0.28	1.55	NA	NA	NA
Control 2	99.92	0.38	0.38	NA	NA	NA
ZVI 1	2.29	3.01	6.09	97.59	3.12	6.33
ZVI 2	2.29	3.05	6.62	97.58	3.16	6.88
PIC 1	0.87	1.83	5.62	99.03	1.94	5.93
PIC 2	0.89	1.88	6.46	99.02	1.98	6.83
SMI 1	0.06	0.05	0.03	99.93	0.05	0.02
SMI 2	0.07	0.07	0.03	99.93	0.07	0.02
IOH 1	0.06	0.06	0.03	99.93	0.07	0.02
IOH 2	0.06	0.07	0.02	99.93	0.07	0.01

NA = not applicable.

Stage 1 of the desorption/dissolution batch tests were carried out in the same manner as the 100 ppm  $\text{PO}_4^{3-}$ -P contaminant removal batch tests. The results from Stage 1 of the desorption/dissolution batch tests are fairly comparable to the results obtained by the 100 ppm  $\text{PO}_4^{3-}$ -P contaminant removal batch tests, with both showing that ZVI, PIC, SMI, and IOH removed almost all soluble-P originally present. Although the differences are typically small, marginally greater amounts of soluble-P were removed by ZVI, PIC, SMI, and IOH during Stage 1 of the desorption/dissolution batch tests as compared to the amounts of soluble-P removed during the 100 ppm  $\text{PO}_4^{3-}$ -P contaminant removal batch tests (see Tables 3 and 4).

Table 4 indicates that very little of the soluble-P (essentially,  $\text{PO}_4^{3-}$ -P) originally adsorbed or precipitated onto ZVI, PIC, SMI, or IOH particle surfaces during Stage 1 were then desorbed/dissolved back into solution during the Stage 2 wash with ultrapure deionized water. This is especially true for SMI and IOH, where far less than 1% of the soluble-P originally adsorbed or precipitated onto SMI or IOH particle surfaces during Stage 1 was then desorbed or dissolved back into solution by the ultrapure deionized water wash. Furthermore, only 2 to 3% of the soluble-P originally adsorbed or precipitated onto ZVI or PIC particle surfaces during Stage 1 was then desorbed or dissolved back into solution by the ultrapure deionized water wash.

During Stage 3, a solution with a fairly high concentration of  $\text{K}_2\text{SO}_4$  electrolyte was used to potentially displace any  $\text{PO}_4^{3-}$  that might have been electrostatically attached to ZVI, PIC, SMI, and IOH particle surfaces. Iron oxides/hydroxides, like IOH, or those formed by oxidation of ZVI, PIC, or SMI, given low enough pH conditions, can exhibit a net positive surface charge that causes electrostatic adsorption of negatively charged  $\text{PO}_4^{3-}$  ions (Arai and Sparks, 2007; Sparks, 2003). The molar amount of sulfate ( $\text{SO}_4^{2-}$ ) added during Stage 3 was 3 times greater than molar amounts of  $\text{PO}_4^{3-}$  introduced during Stage 1, and as a result of chemical mass action considerations, it was expected that  $\text{SO}_4^{2-}$  could in turn displace significant amounts of any  $\text{PO}_4^{3-}$  that had been electrostatically adsorbed by the iron-based filter materials. Stage 3 results in Table 4 show almost no desorption/dissolution of soluble-P by either SMI or IOH. Approximately 6 to 7% of the soluble-P originally adsorbed or precipitated onto ZVI or PIC particle surfaces during Stage 1 was found to desorb or dissolve back into solution during the

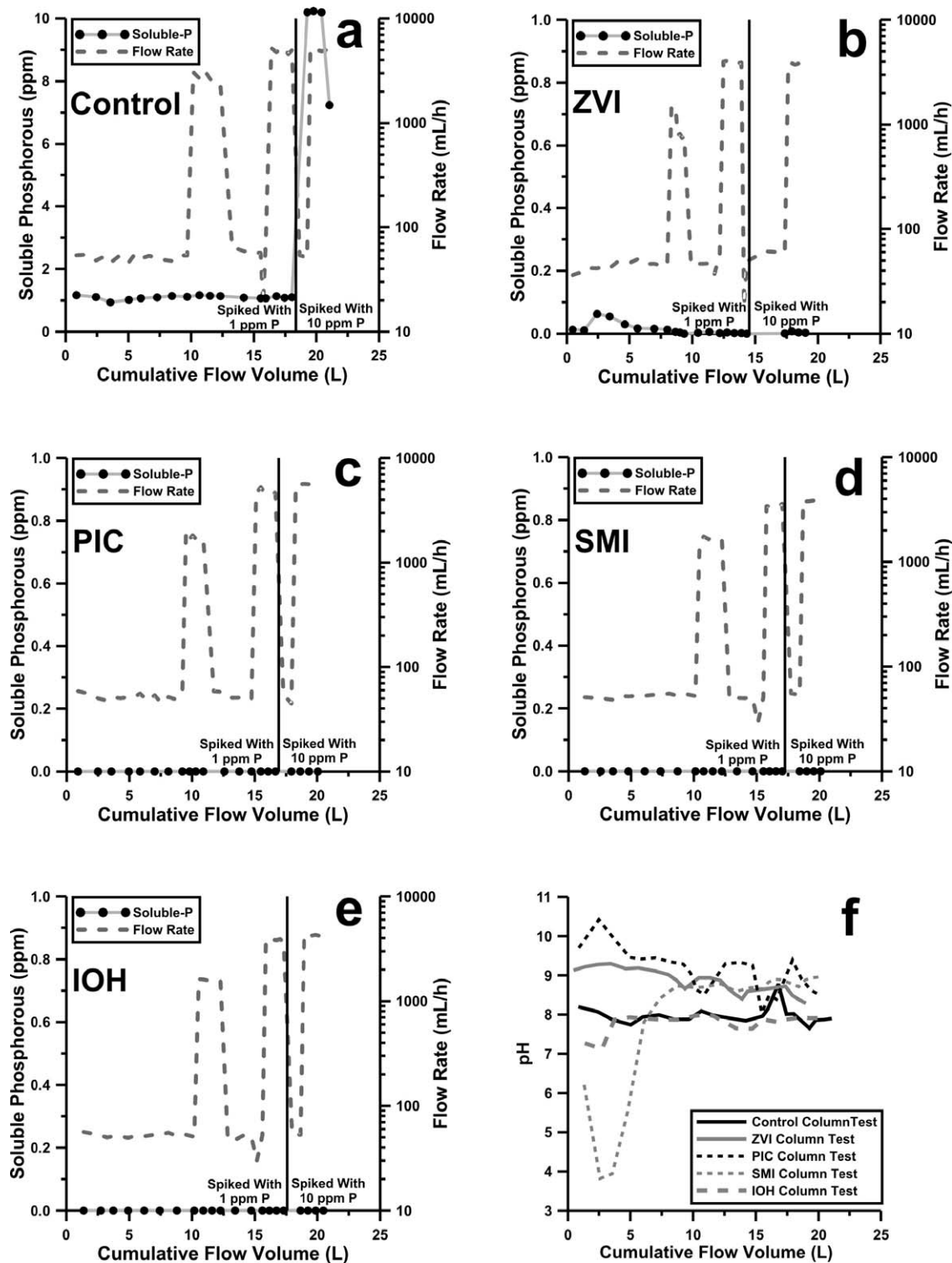
Stage 3  $\text{K}_2\text{SO}_4$  extraction wash. The Stage 3 ZVI and PIC results indicate that a proportionally small amount of  $\text{PO}_4^{3-}$  is adsorbed onto ZVI and PIC particle surfaces via relatively weak electrostatic interactions, and this  $\text{PO}_4^{3-}$  can be displaced, to some extent, using an electrolyte solution. On the whole, the desorption/dissolution batch test results (Table 4) show that once  $\text{PO}_4^{3-}$  is adsorbed or precipitated onto ZVI, PIC, SMI, or IOH particle surfaces, this  $\text{PO}_4^{3-}$  becomes strongly fixed and is not readily desorbed or dissolved back into solution.

**Low-to-High Flow Rate Saturated Solute Transport Column Test Results.** As previously mentioned, these column tests allow control of solution flux, and in turn, the filter material to solution contact time; therefore facilitating better assessment of the likely drainage water  $\text{PO}_4^{3-}$  treatment capabilities for ZVI, PIC, SMI, or IOH within an actual filter treatment system. Results for the five column tests are displayed in Figure 2. Effluent soluble-P and flow rate for each of the five column tests are shown in Figures 2a, 2b, 2c, 2d, and 2e. The effluent pH for all five column tests is displayed in Figure 2f.

At the beginning and throughout most of each column test, the influent Waterman ANRL drainage water was spiked with 1 ppm  $\text{PO}_4^{3-}$ -P. Toward the end of each saturated solute transport column test, the influent Waterman ANRL drainage water was spiked with 10 ppm  $\text{PO}_4^{3-}$ -P. Vertical solid black dividing lines in Figures 2a, 2b, 2c, 2d, and 2e depict the column test transition from 1 ppm  $\text{PO}_4^{3-}$ -P spiked drainage water to 10 ppm  $\text{PO}_4^{3-}$ -P spiked drainage water. Each column test began with an extended low flow rate step followed by the first high flow rate step, after which there was a shorter low flow rate step, and then a second high flow rates step (see Figures 2a, 2b, 2c, 2d, and 2e). The completion of the second high flow rate step coincided with the column test transition from 1 ppm  $\text{PO}_4^{3-}$ -P spiked drainage water to 10 ppm  $\text{PO}_4^{3-}$ -P spiked drainage water. This transition was followed by a short low flow rate step and then the third and final high flow rate step, which completed the column test (see Figures 2a, 2b, 2c, 2d, and 2e). In all five column tests, the low flow rate steps were fairly consistent with average values between 40 to 60 mL/h. The first high flow rate step in the five column tests averaged between 1000 to 2800 mL/h, the second high flow rate step averaged between 3400 to 5000 mL/h, and the third high flow rate step averaged between 3700 to 5600 mL/h.

The column influent 1 ppm  $\text{PO}_4^{3-}$ -P spiked drainage water had a pH of 7.76, and the column influent 10 ppm  $\text{PO}_4^{3-}$ -P spiked





**Figure 2**—Low-to-high flow rate saturated solute transport column test results: (a) Control test soluble-P and flow rate, (b) ZVI test soluble-P and flow rate, (c) PIC test soluble-P and flow rate, (d) SMI test soluble-P and flow rate, (e) IOH test soluble-P and flow rate, and (f) effluent pH. *Note:* The soluble-P scale in “a” is different than the soluble-P scale in “b”, “c”, “d”, and “e”.

drainage water had a pH of 7.43. Effluent pH in each of the five column tests did not seem to be influenced by the transition from 1 ppm  $\text{PO}_4^{3-}$ -P spiked drainage water to 10 ppm  $\text{PO}_4^{3-}$ -P spiked drainage water or from changes between low and high flow rates

(compare effluent pH in Figure 2f with 1 ppm  $\text{PO}_4^{3-}$ -P to 10 ppm  $\text{PO}_4^{3-}$ -P transition points and flow rates in Figures 2a, 2b, 2c, 2d, and 2e). The control column test effluent had an average pH value of 7.98, which, when compared to influent pH

values of 7.76 and 7.43, indicates that column test equipment and procedures did not greatly affect pH. Average effluent pH values for the ZVI and PIC column tests were 8.84 and 9.12, respectively. Effluent pH was acidic (<6) near the beginning of the SMI column test, but by the end of the SMI test, effluent pH had risen and leveled off to a value of close to 9. The average effluent pH for the IOH column test was 7.81, which was similar to influent spiked drainage water pH values and the effluent pH for the control column test. Consequently, IOH does not seem to greatly affect column test effluent pH; however, ZVI, PIC, and SMI cause a substantial increase in column test effluent pH to alkaline levels (>8). The high column test effluent pH values for ZVI, PIC, and SMI may reflect a chemical reaction between iron and water, such as  $\text{Fe}^0 + 2\text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + \text{H}_2 + 2\text{OH}^-$  which produces ferrous iron, hydrogen gas, and hydroxyl anions (Kamolpornwijit and Liang, 2006). The production of hydroxyl anions would cause significant pH increase, as was found with the ZVI, PIC, and SMI column test effluents. These column test effluent pH results imply that additional drainage water treatment may be required with filter systems containing ZVI, PIC, and SMI, if the release of alkaline waters into the environment is a potential problem.

Effluent soluble-P concentrations for the control column test (Figure 2a) clearly shows that there was almost no  $\text{PO}_4^{3-}$ -P loss resulting from equipment and procedures. The effluent soluble-P concentrations for the ZVI column test were all below 0.1 ppm (Figure 2b). The effluent soluble-P concentrations for the PIC, SMI, and IOH, as depicted in Figures 2c, 2d, and 2e, were in all cases below detection limits (<0.009 ppm). Consequently, regardless of influent  $\text{PO}_4^{3-}$ -P concentrations and flow rate, ZVI, PIC, SMI, and IOH were found to remove almost all  $\text{PO}_4^{3-}$ . The column test results, therefore, provide additional support for the potential use of ZVI, PIC, SMI, or IOH within filter treatment systems used to remove drainage water  $\text{PO}_4^{3-}$ .

Perhaps most remarkable, with regard to the saturated solute transport column test results, is that even with a very high influent  $\text{PO}_4^{3-}$ -P concentration of 10 ppm and high flow rates in which the filter material to solution contact time was only 2.5 to 4.0 minutes, ZVI, PIC, SMI, and IOH were still able to remove almost all  $\text{PO}_4^{3-}$ . This particular column test result is an indication of not just extremely effective  $\text{PO}_4^{3-}$  removal, but also a relatively fast chemical reaction rate where less than 4 minutes of contact time is needed for ZVI, PIC, SMI, and IOH to remove  $\text{PO}_4^{3-}$  from agricultural subsurface drainage waters. Furthermore, the desorption/dissolution batch test and saturated solute transport column test results, when taken together, signify that chemical reactions between the iron-based filter materials and  $\text{PO}_4^{3-}$  are rapid and not generally reversible, thereby implying that the dominant  $\text{PO}_4^{3-}$  removal mechanism is likely some form of ligand exchange, or maybe, precipitation of low solubility iron-phosphate compounds, but not electrostatic adsorption (McBride, 1994; Stumm and Morgan, 1981).

The cost-effectiveness of using iron-based filter materials to treat phosphate in agricultural drainage water will depend on a number of factors. The price per unit weight or per unit volume for the iron-based material used in the filter treatment system will certainly be one important factor. (These materials presently range in price from \$1/kg to \$20/kg.) With widespread water treatment use, the price of these iron-based materials could decrease substantially in the future. Iron-based filter material factors just as important as price are the phosphate treatment

capacity and the contact time needed for drainage water phosphate removal. Treatment capacity and contact time will determine the amount of iron-based material needed for the phosphate filter treatment system. The less iron-based material needed, the more cost-effective the phosphate filter treatment system. Additional contaminant removal batch tests and long duration, variable flow rate saturated solute transport column tests will have to be carried out to determine the phosphate treatment capacity and treatment contact time of each iron-based filter material evaluated in this study. Final factors to take into account regarding cost-effectiveness of the iron-based filter materials is whether these materials can be regenerated or recycled. By flushing with caustic soda, spent IOH filter material can be regenerated and then reused several times for phosphate drainage water treatment (based on prior manufacturer experience using IOH for arsenic removal). Spent ZVI, PIC, and SMI will have monetary value as scrap iron that can be recycled for manufacturing purposes.

### Summary, Conclusions, and Future Research

A preliminary laboratory evaluation regarding the use of iron-based filter materials for removing  $\text{PO}_4^{3-}$  in agricultural drainage waters was carried out with saturated falling-head hydraulic conductivity tests, contaminant removal batch tests, desorption/dissolution batch tests, and low-to-high flow rate saturated solute transport column tests. Four iron-based filter materials were tested: zero valent iron (ZVI), porous iron composite (PIC), sulfur modified iron (SMI), and a synthetic goethite iron oxide/hydroxide (IOH). The greatest saturated hydraulic conductivity values were obtained with IOH, but ZVI, PIC, and SMI all had high enough hydraulic conductivities to allow water flow rates probably sufficient for filter treatment. Results from the 1000 ppm  $\text{PO}_4^{3-}$ -P contaminant removal batch tests indicate that IOH had the largest  $\text{PO}_4^{3-}$  removal capacity, followed by SMI, with ZVI next, and then PIC. The desorption/dissolution batch tests showed that in general, especially for IOH and SMI, once  $\text{PO}_4^{3-}$  is adsorbed or precipitated onto particle surfaces of the iron-based filter materials, this  $\text{PO}_4^{3-}$  becomes strongly fixed and is not readily desorbed or dissolved back into solution. Effluent soluble-P measurements for the saturated solute transport column tests indicate that the ZVI, PIC, SMI, and IOH filter materials are all capable of rapid and effective removal of drainage water  $\text{PO}_4^{3-}$ . Although all four iron-based filter materials showed promise, the overall laboratory findings imply that IOH may have a slight edge with respect to agricultural drainage water  $\text{PO}_4^{3-}$  treatment. More laboratory testing of ZVI, PIC, SMI, and IOH is needed to determine the minimum contact time for  $\text{PO}_4^{3-}$  removal (via higher flow rate column tests) and mechanisms for  $\text{PO}_4^{3-}$  removal (via rigorous adsorption isotherm tests). These laboratory studies should then be followed by field scale filter treatment studies.

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