Potential and limitations of phosphate retention media in water protection: A process-based review of laboratory and field-scale tests

Aleksandar Klimeski[1], Wim J. Chardon[2], Eila Turtola[1] and Risto Uusitalo[1]

[1]MTT Agrifood Research Finland, Soils and Environment, Jokioinen, Finland
[2]Alterra, Wageningen UR, Soil Science Centre, Wageningen, The Netherlands
e-mail: aleksandar.klimeski@mtt.fi

The application of phosphorus (P)-sorbing materials offers a possible solution for treating municipal wastewater and agricultural runoff. In this paper we discuss P retention and release mechanisms, and review studies on the P retention of different materials and their use as reactive media in filter beds. The main mechanisms for P retention are sorption on metal (mostly Fe or Al) hydroxide surfaces and, in alkaline conditions, the formation of Ca-P precipitates. The retention of P is strongly affected by the chemical composition of a material, its particle size and pH-related effects on sorption and precipitation both during testing and in practical operation. Laboratory tests are sensitive to solution chemistry (pH, alkalinity, ionic strength and composition, P concentration) and affected by material-to-solution ratio, contact time and agitation. Moreover, due to deviations from realistic field conditions, laboratory tests may produce imprecise estimates of the retention capacity and retention kinetics. In particular, materials that contain soluble substances (e.g., CaO) that elevate the pH of the ambient solution to high levels may in batch tests suggest a high capacity for P retention, but will most probably show much lower retention in field settings. On the other hand, materials containing metal oxides also retain P via slow reactions, and their retention capacity may be underestimated in short equilibrations. Appropriate laboratory test procedures will depend on their intended applications and material properties. Long-term field-scale tests are few in number, but some of them have shown promising results. Field-scale tests have, however, highlighted the design of the filters as a critical factor in their efficiency.

Key words: phosphorus sorption materials, retention capacity, sorption, retention kinetics, filter beds, eutrophication, runoff, remediation

Background

Human-induced eutrophication resulting from excessive inputs of nitrogen (N) and phosphorus (P) is a challenging issue worldwide. Elevated nutrient concentrations stimulate the growth of bacteria, algae and aquatic macrophytes, leading to the degradation of bodies of water. In freshwater environments, biomass production is most often proportional to P concentration (Schindler 1977, Baird and Cann 2005). In coastal marine systems, because N may also limit biomass growth, the control of N loading should therefore be coupled with a reduction in P inputs (Howarth and Marino 2006).

The Baltic Sea, which is susceptible to nutrient enrichment due to slow renewal of water and long residence times for nutrients, provides an excellent example of a eutrophied body of water. Most of the P loading in the Baltic Sea in 2000 originated from point sources (56% of the total load), with municipalities being the major contributor. From the rest of the total P loading (44%), a majority (around 80%) originated from agricultural activities (HELCOM 2009). The transport of P to surface waters from agricultural soils is greatest where they have high P status, especially through surface runoff as particulate and dissolved P (Turtola and Yli-Halla 1999, Penn and Bryant 2006).

Despite extensive work to decrease nutrient loading in the Baltic Sea, fulfilling the goals of current legislation and international agreements (e.g., the EU Marine Strategy Framework Directive, Urban Wastewater Treatment Directive, Nitrates Directive and Water Framework Directive) without further reductions in the nutrient discharges seems impossible (HELCOM 2009). Thus, the suite of P remediation measures must therefore be expanded with new methods that employ P-sorbing materials.

According to their origin, P sorbents fall into three groups: natural materials, industrial by-products and manufactured materials (Cucarella and Renman 2009). Materials may be also classified according to their chemical composition as follows: metals (mostly Fe and Al) containing materials, materials containing soluble divalent earth metals (Ca, Mg), and mixtures of the two. Some studies have also tested other available materials, such as tree

AGRICULTURAL AND FOOD SCIENCE

A. Klimeski et al. (2012) 21: 206–223

bark (Ballantine and Tanner 2010), but we have excluded them from this review, because P removal in such materials is likely based on microbial growth on the media (and associated P uptake), which is strongly seasonal at higher latitudes.

Tests of the ability of different materials to retain P have mostly taken place in the laboratory as batch and flow-through experiments. Materials such as acidic mine drainage residuals, steel smelter residues and shellsand have also been tested in practice as reactive media by constructing permeable barriers to treat agricultural runoff or wastewater from households (e.g., Penn et al. 2007, Shilton et al. 2006, Søvik and Kløve 2005). In fact, since the 1960s, researchers worldwide have carried out research on P-sorbing materials (e.g., Yee 1966, Neufeld and Thodos 1969, Shiao and Akashi 1977). Several potential materials are available in the countries surrounding the Baltic Sea, however, because only a limited number of field studies have explored this topic thus far, few have used P retention materials to mitigate eutrophication in the Baltic Sea catchment area.

This review aims to promote research on P retention materials by conducting a comprehensive survey and compiling a summary of the physical and chemical parameters that influence retention of P in solid media. In our review, we emphasize the known mechanisms of P retention/release and, based on this knowledge, aim to show the limitations and advantages of different experimental designs. We hope that this will result in more mechanism-focused research efforts to identify materials with the potential for P retention. Our aim was not to compile a complete collection of all published articles on the topic; rather, for that purpose, we recommend the extensive reviews of Johansson Westholm (2006) and Vohla et al. (2011).

Phosphorus retention and release mechanisms

Physical properties that affect the P retention of solid media include the shape, size and porosity of particles or aggregates, all of which affect their reactive surface area and hydraulic conductivity. The materials' chemical composition and crystallographic properties, together with the pH of the solid-solution system, determine the materials' affinity for P. In general, the most efficient P-sorbing materials tend to be those that contain Fe or Al hydroxides, or easily soluble Ca or Mg compounds (e.g., Penn et al. 2007).

For Fe and Al hydroxides, the P retention mechanism is phosphate sorption involving ligand exchange reactions (Hsu 1964). As Figure 1 [adapted from Sigg and Stumm (1981) and Bache and Ireland (1980)] shows, the reaction is considered reversible. If some change in the Al/Fe oxide–water system (e.g. the elevation of the solution's P concentration) increases the mass of P adsorbed onto the solid phase, the opposite happens when the change occurs in the reverse direction. In practice, however, the release of adsorbed P may be minimal if phosphate replaces two hydroxyl groups with the subsequent formation of a bidentate complex (Brady and Weil 2008). The formation of bidentate complexes takes place at low P saturation of oxide surfaces, whereas at higher P saturation, monodentate complexes dominate.
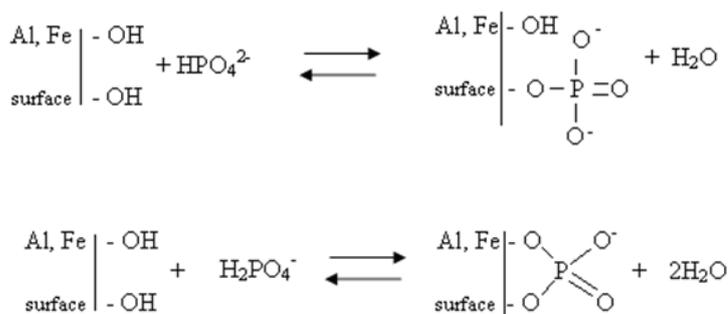
Fig. 1. The formation of monodentate (upper graph) and bidentate (lower graph) complexes on metal oxide surfaces.

AGRICULTURAL AND FOOD SCIENCE

A. Klimeski et al. (2012) 21: 206–223

The adsorption process extends over a wide pH range, and the adsorption maximum for anions of weak acids is usually highest at a pH equal to pKa (Sigg and Stumm 1981). Aside from highly acidic environments, pH influences the adsorption of P on metal oxides such that as pH rises, P adsorption decreases (e.g. Strauss et al. 1997) and the desorption of previously adsorbed P increases. This stems from an increase in the negative surface charge of Fe and Al hydroxides resulting from the deprotonation of hydroxyl groups and a simultaneous shift in the dominant phosphate species towards more negatively charged ones (e.g. $H_2PO_4^- \rightarrow HPO_4^{2-}$). Consequently, the increased negative charge of both reaction components causes electrostatic repulsion. At the same time, competition for ligand exchange sites by hydroxyl ions also increases, and these may outcompete some phosphate ions from the adsorption plane (Hingston et al. 1967).

In addition to pH, P adsorption on Fe/Al hydroxide surfaces is also affected by the ionic strength of the solution (see, e.g., Barrow et al. 1980, Yli-Halla and Hartikainen 1996, Antelo et al. 2005).[1] Even though ionic strength is known to affect P retention, its significance in the context of this paper remains largely unexplored. In laboratory tests, one should preferably match ionic strength to that of the intended field-scale application.

With materials rich in soluble Ca, removal of dissolved P largely occurs through the formation of Ca-phosphate precipitates. Therefore, an important indicator of the ability of a Ca-rich material to remove P is its content of water-extractable Ca (Moore and Miller 1994). Precipitation of Ca-phosphates is efficient at alkaline pH and, as Johansson and Gustafsson (2000) stated, a number of different precipitates, such as amorphous calcium phosphates ($Ca_4H(PO_4)_3$), octacalcium phosphate, and hydroxyapatite, may form. However, their study indicates that the formation of hydroxyapatite was the most likely mechanism for removing P when using CaO-rich materials such as blast furnace slag. The precipitation reaction for hydroxyapatite can be simply described as follows:

$$5Ca^{2+} + 3H_2PO_4^- + 7OH^- \leftrightarrow Ca_5(PO_4)_3(OH)_{(s)} + 6H_2O \qquad \text{(Yeoman et al. 1988)}$$

For fresh Ca-P precipitates, the reaction may be fully reversible, and a drop in the pH and Ca concentration of the solution may result in the dissolution of precipitated Ca-P associations (see Diaz et al. 1994, Ádám et al. 2007a). Consequently, if the Ca concentration or pH (or both) of the system decreases with time, one can regard fresh Ca-P precipitates as temporary P storage compounds.

Key parameters obtained in laboratory tests

In the design of P-retaining filter beds, important estimates assessed in the laboratory are the capacity of a material to retain P and the kinetics of P retention. The capacity estimate is obviously linked to the amount of P the filter can retain, and thus to the effective lifespan of the P retention filters. Reaction kinetics relates to the effects of contact time on P retention. For applications that aim to remediate large water volumes in short contact periods, fast reaction kinetics are clearly desirable. However, slow reactions that involve solid-state diffusion of surface-adsorbed P in the structure of a retention medium (e.g. Fe oxides) may play a major role with regard to the total retention capacity (see Makris et al. 2005, Chardon et al. 2012). In the first phase of material characterisation, laboratory experiments often serve to estimate retention capacity and retention kinetics. Laboratory tests are commonly performed either in a closed system as batch experiments or in an open system as flow-through columns.

---

[1]The effect of the ionic strength of a solution is linked to changes in the electrical double layer surrounding a charged metal oxide surface. Because oxide surfaces are protonated below the pH of the Point of Zero Charge (PZC) of the mineral and deprotonated above the pH of the PZC, they may have either positive (at low pH) or negative (at higher pH) surface potential (charge). This electric potential is balanced by the accumulation of opposite-charged ions (counterions) near the oxide surfaces. At low ionic strength, relatively few counterions are present in the immediate proximity of the surface where the attracting force field is at its strongest, and the attracting force depletes the counterions in the bulk solution. If the surface charge remains equal, but the ionic strength is high, more charge-balancing counterions appear in the proximity of the surface and the attracting force decays more rapidly as we move away from the surface (i.e., the double layer becomes compressed). For phosphate interacting with a positively charged surface, low ionic strength results in efficient adsorption on the metal oxides, because phosphate acts as a counterion. The situation, however, is the reverse for a negatively charged surface balanced by positively charged cations, because high ionic strength with a compressed double layer allows anions in the bulk solution to swarm closer to the surface and enter the adsorption plane (e.g., Antelo et al., 2005). As Barrow et al. (1980) discussed, the PZC is not an absolute constant value, but the adsorbed ions affect it. Barrow et al. (1980) reported that a goethite sample in its pristine state had its PZC at pH 8, but the PZC dropped to pH 4 after adsorbing P. In conditions of runoff or wastewater treatment (usually neutral pH levels), metal oxides may initially carry a positive surface charge, but the charge will gradually turn negative as the P saturation of the surface increases.

AGRICULTURAL AND FOOD SCIENCE

A. Klimeski et al. (2012) 21: 206–223

Batch retention tests

Batch experiments are easy to conduct, quick to accomplish and provide the first estimates of the P retention properties of a material. In a typical batch experiment, a fixed amount of a material comes into contact with P solutions, and the P isotherm method serves to estimate maximum retention.

From the large number of published laboratory studies on P retention by different materials, we list in Table 1 those that had P sorption capacities exceeding 3 mg g^{-1}. Even after applying selection criteria for P retention, the sorption capacities of the materials listed vary widely from 3.5 mg g^{-1} for utelite, a lightweight calcinated shale product, to 114 mg g^{-1} for red mud, a metal-containing waste product of Al oxide refining. All the studies except Makris et al. (2005) involved shaking, which we discuss later in this paper. However, because the test procedures vary, the results compiled in Table 1 are not readily, if at all, comparable (see also Johansson Westholm 2006). We do not discuss in-depth the details of the laboratory tests, because the reviews of Cucarella and Renman (2009) and Vohla et al. (2011) recently addressed them. Rather, we point out some factors worth considering when planning laboratory work on potential P-sorbing materials, and focus on the theory of P retention mechanisms. As a start, we claim that the applicability in real world settings of an estimate of maximum P retention obtained in batch tests differs for adsorption and precipitation reactions.

Materials that exhibit P adsorption on metal oxides

For adsorption on a solid surface, such as metal hydroxide, maximum P retention is achieved when all sorption sites become occupied. Then, the single-layer P saturation of metal oxide surfaces at a given pH is proportional to the number of sites available for P sorption and to the P mass introduced into the system. If the concentrations of P added to the system are not unrealistically high, adsorption isotherms should provide a reasonable estimate of the magnitude of P retention in a field application. For materials that retain P on metal oxides, P isotherms may underestimate rather than overestimate their maximum retention capacity (see Sawhney and Hill 1975), because a typical isotherm study accounts only for the fast reactions.

Researchers have recognized water treatment residuals (WTRs) as potential P sorbents (Makris et al. 2005, Leader et al. 2008). Various Fe, Al and Ca-WTRs form in tap water production when Fe or Al salts or lime are added to remove mineral and organic matter and to precipitate P. In this section, we discuss Fe and Al-WTRs for which metal oxides control P retention. They are typically used as soil amendments at sites that have low inherent P retention capacity, but receive frequent high P inputs as animal manure (e.g., loafing areas or feedlots) (Penn and Bryant 2006). Due to their high content of amorphous Fe and Al hydroxides and typically acidic reaction (e.g., Makris et al. 2005), P retention is efficient. In a study by Makris et al. (2005), for example, sorption capacities for seven different Al- and Fe-WTRs ranged from 7.5 to 10 mg g^{-1}, with 10 mg g^{-1} retention obtained at the highest P input level, and at which point sorption curves had not yet leveled off. The study further suggested higher P retention and faster retention kinetics for Al-WTRs than for Fe-WTRs, with P retention efficiency of 70–100% for Al-WTRs in ten days' equilibration time and without reaching a plateau in P sorption curves. In 10 days, none of the three Fe-WTRs removed as much P as the Al-WTRs, although one of the Fe-WTRs achieved 92% sorption efficiency in 80 days' equilibration time. Makris et al. (2005) conducted their equilibrations without shaking in order to avoid particle breakage, so the result is not entirely comparable with the other data in Table 1, although it does provide a good example of the effect of equilibration time on P retention capacity. The authors also emphasised that not only chemical composition, but physical properties such as the surface area and porosity of the materials are also major factors that affect the capacity and kinetics of P retention. The finer the porous structure, the longer the equilibration time needed to obtain a realistic picture of a material's capacity to retain P.

The total elemental composition of a material offers one possibility for assessing which P retention mechanism to expect. For metal oxides, however, the degree of crystallinity has a major effect on their P sorption properties, and total metal concentration cannot serve as the sole criterion. The least crystalline metal oxides (i.e. amorphous, short-range order oxyhydroxides) have the highest affinity for P (e.g., van der Zee and van Riemsdijk 1988, Gallimore et al. 1999). Conversely, by-products that have been heated to high temperatures may contain abundant total concentrations of Fe or Al, but many such metal oxides have an ordered crystalline form and thus a relatively low adsorption affinity (see Strauss et al. 1997). Heating may also affect the surface area of a material, as discussed by Li et al. (2006), who found that heating red mud first increased P retention as a result of dehydration, which made the material more porous. Heat treatments exceeding 700 °C, however, sintered the red mud, resulting in a smaller reactive surface and P retention capacity. Treatment with acid also influenced P retention; after acidifying red mud, Li et al. (2006) measured an increase in surface area and a rise in P retention.

AGRICULTURAL AND FOOD SCIENCE

A. Klimeski et al. (2012) 21: 206–223

Hartikainen and Hartikainen (2008) studied mine tailings rich in phlogopite (referred to as biotite). In their experiment with fresh material, the pH of the equilibrium solutions ranged between 6 and 7, and they found low P sorption (0.0045 mg g^{-1}). However, they also treated the material with acid to solubilise Al and Fe and thus induce the formation of hydroxides with a higher P sorption capacity. After acidification, or acidification and partial neutralization, sorption capacities increased to 10.9 and 15.4 mg g^{-1}, respectively, after seven days of reaction time. Experiments with acid-treated biotite, with low pH values (3–5) in the equilibrium solutions, revealed that adsorption on metal oxides (including those on the edge of a mineral structure) is the only plausible mechanism for P retention.

Materials that promote Ca- or Mg-phosphate formation as the main P retention mechanism

For Ca and Mg compounds that are water soluble and elevate pH, precipitation as Ca- or Mg-phosphates occurs in P-spiked solutions when the solubility product of the mineral is exceeded. If excess amounts of P are in solution (e.g., when isotherm studies use high P concentrations), more P can precipitate and, as the Ca or Mg concentration in solution decreases upon precipitation, more Ca or Mg compounds will dissolve. This continues as long as soluble compounds and enough dissolved P are present in the system to exceed the solubility product of the precipitates. In field applications, however, the P concentration rarely approaches the highest concentrations used in isotherm tests. In an open system (field application) flowing water will remove part of the Ca^{2+} or Mg^{2+} that dissolve, and the yield of the precipitates is then no longer proportional to the mass of soluble Ca- or Mg-compounds initially present.

Laboratory batch isotherms commonly overestimate the performance of field-scale applications, particularly for precipitation-controlled P retention (see Arias et al. 2003, Søvik and Kløve 2005, Ádám et al. 2007a). The lower the P concentration entering a buffer that relies on P removal by precipitation, the larger the discrepancy is likely to be between maximum P retention, estimated with the laboratory isotherm technique, and field-scale performance. The greater efficiency of Ca-phosphate precipitation at high P concentrations and low water volumes makes Ca-phosphate precipitate-forming materials more suitable for the treatment of wastewater (high P concentration, more easily controlled water volumes) than of agricultural runoff. Since efficient Ca-phosphate precipitation requires basic pH and high alkalinity (pH buffering), an application that relies on Ca-phosphate precipitation may pose risks for adverse effects downstream (e.g. solubilisation of organic matter) if the volume of treated water is large. Such large-scale buffers may require more engineering-controlled systems which adjust pH to acceptable levels after P removal.

Table 1 shows that materials with a pH over 9 are more likely to contain CaO or Ca(OH)$_2$. The list includes many slag materials that may come from coal burning, or steel mill processes where limestone or dolomite are added to remove impurities in the iron ore. The slag of high temperature processes typically contains significant amounts of CaO and maintains a high pH (above 10) in water solutions (e.g. Ziemkiewicz 1998, Johansson and Gustafsson 2000). Due to their low cost, interesting chemical properties and high availability, different types of slag materials have been tested for their P retention characteristics. Kostura et al. (2005), for example, studied crystalline and amorphous steel slag samples with low metal oxide content ground to different sizes. The authors found that particle size and surface area were related to the material's active CaO content, which in turn directly affected the pH of the equilibrium solutions. Solution pH appeared to relate linearly with the P retention capacity of the slag samples, with an order of magnitude difference in estimated maximum P retention (from about 3 to 16 mg g^{-1}) as the pH rose from 7.3 to 9.1. Such a clear dependency indicates that the precipitation of Ca-phosphates is the main mechanism for P retention, and also suggests that if pH in field applications cannot be maintained at high levels (i.e., if the volume of the solution is great), the P retention capacity will be considerably less than the maximum potential determined in batch test conditions.

A G R I C U L T U R A L   A N D   F O O D   S C I E N C E

A. Klimeski et al. (2012) 21: 206–223

Table 1. Maximum P retention capacities and other parameters for different materials according to batch experiments.

Material	Source	Composition	Max. P retention (mg P g^{-1})	Particle diam. (mm)	pH	Material-to-solution ratio	Contact time	Initial P conc. (mg l^{-1})	Estimation method	Reference
Ca and Mg rich materials										
Red mud	By-product of aluminium works (Shandong Aluminum Corp., China)	46% CaO, 1.1% MgO, 12.8% Fe$_2$O$_3$, 6.9% Al$_2$O$_3$, 19.1% SiO$_2$	113.9	< 0.149	11.7	1:200	4 h	0.31-3000	Langmuir isotherm	Li et al. (2006)
Red mud + gypsum	By-product of aluminum works	Red mud + 5% gypsum	5	< 2	8.5	1:5	25 h	0-800	Langmuir isotherm	Cheung et al. (1994)
Utelite	Utelite Corp., Utah, USA	46.5% Ca, 9.3% Mg, 3.3% Fe, 14.7% Al	3.5	< 2	10.1	1:25	24 h	0-320	Langmuir isotherm	Zhu et al. (1997)
Blast furnace slag	By-product of ironworks (Australian Steel Mills Ltd., Australia)	38-43% CaO, 5-8% MgO, < 1.3% FeO, 13-16% Al$_2$O$_3$, 32-37% SiO$_2$	44.2	n.a	n.a	1:10	48 h	10-1000	Langmuir isotherm	Sakadevan and Bavor (1998)
Amorphous slag	By-product of steel works (ISPAT-NH Ostrava, Czech Republic)	32.1% CaO, 15.6% MgO, 7.2% Al$_2$O$_3$, 40.4% SiO$_2$	6.5	0-0.1	n.a	1:200	150 h	50-500	Langmuir isotherm	Kostura et al. (2005)
Crystalline slag	By-product of steel works (ISPAT-NH Ostrava, Czech Republic)	38%CaO, 13.7% MgO, 6.5% Al$_2$O$_3$, 38.6% SiO$_2$	18.9	0-0.1	n.a	1:200	150 h	50-500	Langmuir isotherm	Kostura et al. (2005)
Shellsand	Natural material produced by shells, snails (Norway)	32.8% Ca, 1.4% Mg, 0.05% Fe, 0.03% Al	9.6	3-7	8.8	1:30	24 h	0-480	Peak of the sorption isotherm	Adam, et al. (2007a)

AGRICULTURAL AND FOOD SCIENCE

A. Klimeski et al. (2012) 21: 206–223

Table 1, continued.

Material	Source	Composition	Max. P retention (mg P g^{-1})	Particle diam. (mm)	pH	Material-to-solution ratio	Contact time	Initial P conc. (mg l^{-1})	Estimation method	Reference
Al- and Fe-rich materials										
Untreated biotite	Beneficiation process of apatite ore (Kemira biotite, *Finland*)	0.003% Al, 0.02% Fe	4.5	> 0.2	9.6	1:50	7 days	0-5	Peak of the sorption isotherm	Hartikainen and Hartikainen (2008)
Acid-treated biotite	(as before)	1.3% Al, 0.4% Fe	10.9	> 0.2	3.2	1:100	7 days	0-500	Peak of the sorption isotherm	Hartikainen and Hartikainen (2008)
Partly neutralised biotite	(as before)	1.1% Al, 0.4% Fe	15.4	> 0.2	4.6	1:100	7 days	0-600	Peak of the sorption isotherm	Hartikainen and Hartikainen (2008)
Al-WTR	WTP, Melbourne, FL, *USA*		10	< 2	5.7	1:10	10 days	250-1000	Single point sorption	Makris et al. (2005)
Fe-WTR	WTP, Tampa, FL, *USA*		9.2	< 2	6.3	1:10	10 days	250-1000	Single point sorption	Makris et al. (2005)
Fly ash	By-product of coal combustion process (Shandong Aluminum Corporation, *China*)	2.7% CaO, 1.5% MgO, 7.3% Fe$_2$O$_3$, 25.4% Al$_2$O$_3$, 56.4% SiO$_2$	63.2	< 0.149	9.4	1:200	4 h	0.31-3100	Langmuir isotherm	Li et al. (2006)
Furnace slag	By-product of combusted coal	Similar composition to fly ash	8.9	0-5	12.3	1:20	24 h	10-1000	Langmuir isotherm	Xu et al. (2006)

A G R I C U L T U R A L   A N D   F O O D   S C I E N C E

A. Klimeski et al. (2012) 21: 206–223

Penn and McGrath (2011) obtained two estimates of the P retention capacity of a coarse-grained fraction of electric arc furnace slag in the laboratory. One estimate based on a batch isotherm technique (i.e., calculated Langmuir sorption maximum; 2 g of slag, 1:15 material-to-solution, 0–100 mg P l^{-1}, 16 h shaking). The other estimate was based on flow-through tests and the extrapolation of discrete (momentary) P removal measurements up to the point when the material no longer retained P (2 g of slag mixed with 5 g of sand, 0.5–15 mg P l^{-1}, 0.5–8 min contact time). They then compared these estimates to the P retention capacity measured on a pond-scale pilot structure containing about 450 kg of slag. For the material in its unmodified state (pH 10.9, 26% total Ca and 250 µg g^{-1} water-soluble Ca), the authors measured 59 µg g^{-1} cumulative P retention in the pond system, which was relatively close to the estimate obtained from their flow-through tests (88 µg g^{-1}), but considerably lower than the estimate from the batch isotherm technique (329 µg g^{-1}). After the material became P saturated, Penn and McGrath (2011) rejuvenated it by immersing it in aluminium sulphate solution, which lowered the material's pH to 7.1, consumed alkalinity and provided an Al hydroxide coating on the slag. The rejuvenated slag could retain another 54 µg P g^{-1}, which was of the same order of magnitude as the estimates from the laboratory tests (62 and 82 µg g^{-1} for flow-through and batch isotherm tests, respectively). Thus, the batch technique grossly overestimated the retention capacity of the presumably Ca-phosphate-controlled system (unmodified slag), whereas both laboratory test methods yielded similar estimates for the metal oxide-controlled system (rejuvenated slag).

Other types of materials that have been widely studied for P retention are the Ca-containing light-weight aggregates, such as utelite and Filtralite-P, and natural Ca-rich deposits, such as shellsand. A solid correlation typically exists between the apparent P retention capacity and the soluble Ca content of these materials (Zhu et al. 1997, Ádám et al. 2007b, Vohla et al., 2011). Retention capacities, however, are usually lower than for slag or red mud (see Table 1). Modified or manufactured materials have been suggested for the treatment of wastewater, as their price is higher than that of industrial by-products.

Since many potential sorbents contain both metal oxides and soluble earth alkali metals, they likely remove P through both Ca-phosphate precipitation and adsorption mechanisms. One example of such a material is red mud with high alkalinity and Ca content, but also Fe and Al. Due to the variable chemical composition of red mud, studies have reported widely variable estimates of P retention. Cheung et al. (1994), for example, amended red mud with gypsum and calculated a P sorption capacity of 5 mg g^{-1}. Li et al. (2006), however, reported a much higher estimate of P sorption capacity for (untreated) red mud (114 mg g^{-1}). Since CaO was the main component of the red mud that Li et al. (2006) studied, one would expect the efficiency of P removal to improve at elevated pH values as a result of Ca-P precipitate formation. However, the authors reported that the peak in P sorption by red mud was recorded at pH 7 (in the pH range 1-11), suggesting that other minerals, such as hematite and maghemite, in the material strongly influenced P sorption. Another example is Ca-Fe oxide granules produced by mixing $Fe_2(SO_4)_3$ and CaO, described by Uusitalo et al. (2012). The authors hypothesised that the Ca-Fe oxide granules initially retained P mainly as Ca-phosphates, but because the content of soluble Ca in the system decreased as a result of continued leaching of the material, Fe hydroxides became the principal P retention component. Thus, the mechanisms are not exclusive and their contribution to P retention may change with the changes in material properties over time.

Flow-through sorption studies

Unlike batch tests, a flow through set-up is an open system with no accumulation of dissolved species in the reaction vessel. For this reason, flow-through tests may provide a more realistic picture of what happens in field-scale applications. One drawback, however, is that this test set-up is time-consuming and requires analyses of a large number of percolate samples. Table 2 lists a selection of published flow-through experiments, the number of which is smaller than the number of studies that have employed batch tests.

Parameters that may substantially influence the outcome of flow-through tests include particle size, chemical composition of the material, initial P concentration, and contact time, which is related to the flow rate. A high P concentration in the feed solution may shorten the time needed to obtain P saturation, but then the solution composition may not match that in field conditions. Because P retention by the sorption mechanism is an equilibrium reaction, more P is retained when using high P concentrations in the feed solution. The concentrations used in flow-through tests are seldom as excessive as those used in batch tests and typically fall in the range found in wastewater. The time needed to achieve P saturation in flow-through tests may vary considerably depending on the amount of the material, its physical and chemical properties and percolation rate applied. A small amount of material (e.g., mixing it with inert filler material) or an increase in the percolation rate are the principal options for shortening the time needed to complete the test. Mixing the material with, for example, quartz sand may be a preferred option, because high flow rates may lead to non-homogeneous flow distribution in the material.

AGRICULTURAL AND FOOD SCIENCE

A. Klimeski et al. (2012) 21: 206–223

Table 2: Materials and parameters used in flow-through column experiments.

Material	Source	Partic. diameter (mm)	Test period (days)	P concentr. (mg l⁻¹)	P retention (mg g⁻¹)	Loading rate (l d⁻¹ g⁻¹)	P removal efficiency (%)	Volume of material (cm³)	Reference
Iron oxide tailings	Mineral processing industry, *Canada*	0.069	44	20		0.00075	90 (mass removal)	127	Zeng et al. (2003)
Filtralite P	Saint-Gobain Weber, *Norway*	0.5-4	229	4.9	0.473	0.00048	91 (conc. removal)	18800	Ádám et al. (2007b)
Shellsand	Natural material produced from shells, snails and alga, *Norway*	3-7	303	10	0.497	0.00027	92 (conc. removal)	18300	Ádám et al. (2007b)
Iron sludge	Vessem water treatment plant, *The Netherlands*	< 2	238	3.95	16.1	0.05-0.5	10-30 (at the end of the test)		Chardon et al. (2011)
Iron-coated sand	Someren, water treatment plant, *The Netherlands*	< 2	238	3.95		0.0039	90 (at the end of the test)		Chardon et al. (2011)
Electric arc furnace slag	Ispat Sidbec, Tracy, *Canada*	2.5-10	278	350-400	2.35	0.00074			Drizo et al. (2002)
Fly ash	Yatagan area, *Turkey*	0.063-0.125	3	140			80 (conc. removal)		Ugurlu and Salman (1998)
Granular ferric hydroxide	Commercially available product, *United Kingdom*	0.15-0.3		4.1		0.56	5 (at the end of the test)	0.2	Streat et al. (2008)
Ca-Fe oxide granules; fresh and pre-leached	Sachtleben Pigments Oy, *Finland*	2-5	30-60	50	6.8	0.025	40 (mass removal)	4	Uusitalo et al.. (2012)
Acid mine drainage sludge	Friendship Hill, PA, *USA*		160	0.1	7	1.2	60 (conc. removal)		Sibrell et al. (2009)
Electric arc furnace slag	Steel mill Ft. Smith, AR, *USA*	6.35–11	0.2	0.5-15	1.3	0.29-4.6		1.1	Penn and McGrath (2011)

AGRICULTURAL AND FOOD SCIENCE

A. Klimeski et al. (2012) 21: 206–223

Ádám et al. (2007b) conducted laboratory experiments with flow-through columns (height 1.5 m, inner diameter 14 cm) using Filtralite-P and shellsand as P-sorbing materials. For the former experiment, Ádám et al. (2007b) used secondary wastewater (average P concentration: 4.9 mg l^{-1}), whereas for the latter they used a synthetic P solution (10 mg l^{-1}) prepared with KH_2PO_4 in distilled water. The experiments with Filtralite-P and shellsand columns lasted for 229 and 303 d, with loading rates of about 5.0 and 4.5 l d^{-1}, respectively. Both materials retained almost equal amounts of P (about 0.5 mg g^{-1}); at the end of the experiment, the overall P removal efficiencies for the Filtralite-P and shellsand columns were 91% and 92%, respectively. Different ions and organic compounds present in the wastewater did not interfere with the ability of Filtralite-P to remove P. The P retention capacities for the shell-sand and Filtralite-P were considerably lower than those obtained with the batch tests (9.6 mg g^{-1} and 2.5 mg g^{-1}, respectively), where the initial P concentration was 480 mg l^{-1}.

Ugurlu and Salman (1998) performed a study with Ca-rich fly ash in which they conducted a flow-through test using a column 65 cm high with an inner diameter of 5 cm. The amount of fly ash in the column was 32 g, and the column was loaded with P solution (about 140 mg l^{-1}) for 72 h. The P removal efficiency was initially 95%, but decreased to 80% at the end of the test. Because the material was rich in CaO, the authors stated that the main mechanism responsible for P retention was precipitation as Ca-phosphates. Further evidence in support of this proposed mechanism was that the retention occurred at alkaline pH, and the dissolution of Ca from the material occurred during the experiment.

Drizo et al. (2002) investigated the P removal efficiency of electric arc furnace slag by packing the material in a column (height 15 cm, internal diameter 10.3 cm) with a pore volume of 0.6 l. A phosphate solution of 350–400 mg P l^{-1} was passed through the column at a percolation rate of 1.73 l d^{-1}, corresponding to a contact time of 8.3 h. The slag became P saturated after 124 d, after 360 pore volumes had passed through; at that point, they measured a P retention of 1.35 mg g^{-1}. An interesting phenomenon occurred after draining the material and letting it rest for a period of four weeks. The retention capacity of the filter renewed, enabling it to retain additional P and increasing its retention potential to 2.35 mg g^{-1}. According to the authors, the regeneration of P retention was due to the diffusion of Ca, Fe and minerals towards the particle surfaces, which created new sites for adsorption and precipitation. The P sorption capacity of the material estimated in batch tests with an initial P concentration of 320 mg l^{-1} was 3.9 mg g^{-1} (more than a third higher). The authors suggested that the P retention capacity of a material can be more realistically estimated in column studies. They also estimated that in constructed wetland systems, even when taking into account clogging by organic matter and suspended solids as well as interference by other compounds, the lifespan of the slag would be 17–50 years.

Chardon et al. (2012) studied the P-sorbing characteristics of iron sludge and iron-coated sand, by-products from groundwater treatment, using 10-cm-high columns with an internal diameter of 4.6 cm. One column was filled with iron-coated sand (20% Fe content) and three columns were filled with iron sludge (with 33% Fe content) mixed with quartz sand (1%, 5% and 10% of iron sludge; the Fe content of the mixture added to the columns ranged from 0.33 to 3.3%) to increase its hydraulic conductivity. Percolation was performed with a P solution of 3.95 mg l^{-1} concentration at a rate of 1 l d^{-1}, corresponding to a pore volume-related retention time of 1 h; the experiment lasted for 238 d. The iron-coated sand with the high Fe content retained P efficiently, and at the end of the test, the effluent concentration was only 10% of the influent concentration. The iron sludge columns, on the other hand, showed a rise in effluent P concentration from the early phases of the experiment, but cumulative retention at saturation was nevertheless as high as 14–18 mg g^{-1} of iron sludge. According to the study, the P retention efficiency of the materials was clearly related to the amount of Fe, and the P/Fe molar ratio in the most P-saturated part of the columns ranged from 0.10 to 0.12, corresponding to that found in batch equilibrations in 120 mg l^{-1} P solutions. Chardon et al. (2012) concluded that, due to the hydraulic properties of the materials, iron sludge would be more suitable as a soil amendment for highly P-saturated soils, but that iron-coated sand has potential in landscape P barriers or backfill material around field drains.

Uusitalo et al. (2012) also investigated Ca-Fe oxide granules, made by mixing $Fe_2(SO_4)_3$, CaO and water. This initially alkaline (pH about 9.5) product consisted mainly of gypsum ($CaSO_4 \times 2H_2O$, by about 70%) with an Fe content of about 10%. Experiments were conducted with both fresh and leached material to investigate how the removal of soluble species (such as Ca^{2+} and OH^-) affects P retention by the granules. To prepare the leached material, the granules were kept in water for a period of six weeks, which resulted in a mass loss of about 60%. A vacuum extractor with sample columns served to perform the P retention experiment. The extractor enabled a 50-ml pulse of P solution (concentration 50 mg l^{-1}) to be passed through a column in a period of 30 min. During the experiment, about 40 and 90 solution pulses (for fresh and leached granules, respectively) were fed through a 6-g mass of the material. Both fresh and leached granules removed about 40% of the applied P mass, showing

AGRICULTURAL AND FOOD SCIENCE

A. Klimeski et al. (2012) 21: 206–223

cumulative P retentions of 6.8 and 15 mg g^{-1}, respectively. The apparently higher P retention by the pre-leached granules was due to preserved reactive Fe oxides, whereas most of the gypsum originally present dissolved during the pre-leaching step. When correcting the retention capacity of the leached granules to their fresh-weight equivalents, it seemed that leaching had no substantial effect on P retention, and the leached granules retained 5.6 mg P g^{-1} of their original weight. The authors considered the granules a promising material for field testing at sites characterised by high P concentrations in water.

Zeng et al. (2004) used flow-through settings to investigate the P retention efficiency of iron oxide tailing material with a P retention capacity of 7 mg g^{-1} in batch test conditions (at pH 6.7). The material was mixed with sawdust in proportions of 0%, 25%, 50% and 100% iron tailings by volume, and packed in columns 25 cm high with an internal diameter of 2.45 cm. A synthetic P solution (of KH_2PO_4) with a concentration of 20–22 mg P l^{-1} and pig slurry with a P concentration of 40–50 mg l^{-1} served as feed solutions. During the experiments, both solutions were pumped at a rate of 0.115 l d^{-1} for up to 44 d. The sawdust had no P retention capacity, but the P concentrations in the other columns decreased to a few mg l^{-1} over the duration of the study. No estimates of P retention capacity in the column test set-up were available.

To study the competitive sorption of arsenate and phosphate to ferric hydroxide, Streat et al. (2008) conducted a mini-column experiment. Ferric hydroxide prepared with a freeze/thaw technique was placed in a column (height 0.8 cm, inner diameter 0.56 cm) with a bed volume of 0.2 ml. The As and P concentrations in the influent were 10 mg l^{-1} and 4.1 mg l^{-1}, respectively, and the loading rate was 0.113 l d^{-1}. After about 2000 pore volumes, the removal efficiency for As and P were 30% and 10%, respectively. This pure ferric hydroxide could be regenerated by using 0.1 M NaOH, which enabled the release of 94-95% of the previously retained P and As. Similarly, Sibrell et al. (2009) used acid mine drainage sludge (rich in Fe hydroxide) in flow-through columns (internal diameter 2.5 cm, height 50 cm) and also performed regeneration tests with NaOH. The flow rate was 120 l d^{-1}, whereas the feed solution concentration was about 0.1 mg P l^{-1}. The material removed about 60% of the incoming P even after 40 000 bed volumes. The material was then stripped with 0.1 M NaOH, which enabled the material to release 76% of the previously retained P. Furthermore, the authors added $CaCl_2$ solution (Ca:P = 2:1, expressed as a molar ratio) to the NaOH solutions in order to precipitate the phosphate and achieved almost complete removal of P at a Ca:P molar ratio of 1.6:1. This process enables the completion of a cycle so that the retained P can be transformed into a P fertilizer.

Desorption and dissolution tests

In landscape P filters, ambient conditions vary, and hardly any available P sinks would just take up P and never release it after approaching P saturation. For Ca-phosphate precipitates, changes in pH and solution Ca and P concentrations may dissolve the precipitates. For metal oxides, P sorption or desorption may occur depending on changes in the ambient P concentration, the degree of P saturation, pH and ionic strength. For Fe-containing materials, an additional factor that may affect sorption/desorption reactions is the redox state of the system. Because Fe^{3+} is redox-sensitive, a shortage of other electron acceptors, such as dissolved oxygen or nitrate, may reduce it to Fe^{2+}. Low-redox conditions may lead to the consequent dissolution of P associated with Fe. Even though Fe^{2+} re-oxidises and precipitates when again in contact with air, P retention by Fe-containing materials may still remain vulnerable to variable redox potential (Pratt et al. 2007). Desorption and dissolution tests serve to estimate the ability of a material to hold previously retained P. Desorption tests are usually conducted in pure water or in P-free electrolyte solutions, whereas more aggressive solvents (e.g., ammonium oxalate buffer) or reducing agents (e.g., sodium dithionite) may be used in dissolution tests.

Chardon et al. (2012) percolated P-free solution through an iron sludge column after reaching P saturation and found that 37% of the previously retained P was released into the solution. The retention-release curve was strongly hysteretic, thus suggesting that most of the release occurred at full P-saturation of Fe oxides, but then rapidly decreased such that small amounts of P was released after the gradient of the original P retention curve begun to decrease (at a P content of about 30–40 mg g^{-1} Fe).

Uusitalo et al. (2012) reported 25% and 80% reductions in the total content of P and Ca, respectively, after immersing P-saturated Ca-Fe oxide granules in an oligotrophic lake for 16 days. The P/Fe ratio was then about 0.12 [i.e. close to that reported by Chardon et al. (2012) for their P-saturated iron sludge sample]. Uusitalo et al. 2012 also measured a similar rate of P release (around 20%) to that in lake immersion when they extracted P-saturated Ca-Fe oxide granules sequentially with water, a mixture of anion and cation exchange resins, and dithionite solution (at a pH of 6.9 and reaching a redox potential < −300 mV).

AGRICULTURAL AND FOOD SCIENCE

A. Klimeski et al. (2012) 21: 206–223

Pratt et al. (2007) conducted tests with steel slag saturated with P and observed that at pH 6.7 under oxidising conditions, only negligible (< 1%) amounts of Fe and P were released into the solution. However, a release of 25% of total Fe and 95% of total P was recorded at a redox potential of –400 mV and a pH of 4.9.

Leader et al. (2008) studied the desorption of P from a Fe-WTR in a batch test with 0.01 M KCl solution and found that only about 1% of the previously retained P (0.95 mg g^{-1}) was desorbed from the material. In line with this result, Makris et al. (2005) observed that only a small percentage of the previously retained P was extracted from Al- and Fe-WTRs in 5 mM oxalate solution. The amount of extracted P from Al-WTR was minimal (0.2%), but higher values were obtained (1.3-8.3%) for the Fe-WTR.

Desorption/dissolution mechanisms should be taken into account when estimating a material's P retention capacity in field applications, especially when agricultural runoff is concerned. As a result of seasonal patterns, the concentrations of dissolved elements in runoff may vary widely (e.g., snowmelt or storms *vs*. base-flow conditions), and P release can result from the dissolution of Ca-P precipitates (with a decrease in ambient pH, Ca and P concentrations) or desorption from metal hydroxides (in low-P solutions, at low ionic strength, or as a result of pH elevation).

P removal in wastewater filter beds

Phosphorus-sorbing materials have been applied as reactive media in filter beds for wastewater treatment in meso- (single household) and large-scale applications. The P sorption capacity of a material usually proves to be lower in larger-scale applications than in laboratory tests. Studies of filter bed efficiencies in larger set-ups appear in Table 3.

As the scale increases, obstacles to P removal are often connected to hydraulic conductivity and high flows. Precipitates, suspended solids and organic material may clog the filter. The incoming flow also tends to form preferential pathways in the material, resulting in a short residence time, limited contact of P with the filtering material and, consequently, lower-than-expected P removal efficiency of the system.

Meso-scale applications

Søvik and Kløve (2005) tested a shellsand filter fed with wastewater from a single household. The filter consisted of a pre-filter and a main filter with an area of 0.9 m^2 and a volume of about 0.7 m^3. The system was loaded with 30.9 m^3 of wastewater by alternately changing the rate from 0.5 to 3 l h^{-1}. In the first test period (see Table 3), the mean influent total P concentration was 7.7 mg l^{-1}, whereas in the second period, it varied between 4 and 6 mg l^{-1}. The filter became P saturated at the end of the test, after removing 190 g P with a retention capacity of 0.29 mg g^{-1} shellsand. Laboratory batch experiments (using initial P concentrations of up to 1500 mg l^{-1}) suggested maximum retentions of 0.8 mg g^{-1} and 8 mg g^{-1} with material-to-solution ratios of 1:1 and 1:15, respectively. Thus, a clear discrepancy was evident between the laboratory batch tests and the practical-scale application.

Penn et al. (2012) studied the performance of a P removal filter containing electric arc furnace slag sieved to about 6–11 mm in a 320 ha watershed consisting of residential, golf course and undeveloped areas. The volume of the slag material was about 1.5 m^3, and the performance of the structure was monitored for five months. The flow-weighted runoff P concentration was about 0.5 mg l^{-1}, with an average flow and retention time of 29.8 l min^{-1} and 18.9 min, respectively. During the 5-months period, the structure retained 25% of the P input (which was almost entirely as dissolved P). The cumulative P input affected retention such that the retention efficiency declined over time, as did the flow rate (i.e. contact time of water inside the structure) such that as the flow increased, retention efficiency decreased. According to the calculations of Penn et al. (2012), the amount of P delivered to the structure corresponded to 102.8 µg P g^{-1} of slag, and the P mass removed by the structure was 26 µg g^{-1}. The authors had predicted P removal of up to 79 µg g^{-1} of this size fraction using a model they developed from laboratory flow-through studies (with retention time and P concentration as input variables). After the 5-months period, the model obviously overestimated P removal of the slag material. The authors argued that the discrepancy stemmed from the different chemical characteristics of the slag used in the field and the slag sample from the same steel mill they had studied in the laboratory (e.g., the pH of the slag used in the field was clearly lower than the pH of the slag tested in the laboratory). The coarse size of the slag also clearly affected P retention though its influence on the reactive surface area, but Penn et al. (2012) made the trade-off in favour of high permeability in order to allow conducting peak flows (carrying the majority of the P mass) through the slag.

AGRICULTURAL AND FOOD SCIENCE

A. Klimeski et al. (2012) 21: 206–223

Table 3. Phosphorus removal efficiencies obtained in larger scale applications of P-sorbing materials.

Material	Source	Particle diameter (mm)	Test period	P concentration (mg l⁻¹)	P removal efficiency (%) or P retention	Volume (m³)	Reference
Wastewater treatment							
Shellsand	Natural, shells and snails, Norway	> 1 pre-filter, < 1 main filter	May 1999–Mar. 2000, Apr. 2001–Dec. 2001	7.7, 4-6	285 mg kg⁻¹ (P retention)	0.7	Søvik and Kløve (2005)
Slag	By-product from steel works, Australia	10–20	11 years (1993-2003)	Total P 8.2 in the 1st year (annual mean)	77% in the initial 5 years (mass removal)	12973	Shilton et al. (2006)
Granular Ochre	Oxidation and precipitation of Fe from mine water, United Kingdom		Nov. 2003-Mar. 2005, Leitholm	Total P 4-6	12% (concentration removal)	1.7	Dobbie et al. (2009)
Ochre pellets	Oxidation and precipitation of Fe from mine water, United Kingdom	6.4–9.5	May–Sept. 2005, Nov. 2005–Jan. 2006 at Leitholm, Jun. 2004–Feb. 2005 at Windlestone	Total P 4-6, Leitholm 0.4-4.8, Windlestone	May–Sept. 2005: 12%, Nov. 2005–Jan. 2006: 66%; Windlestone (initially 73%, 20% after 1000 h operation)	0.9	Dobbie et al. (2009)
Ditchwater treatment							
Acid mine drainage residual	Acid mine drainage treatment, USA		Jun. 2005–May 2006	Dissolved P 7-16	99% (mass removal)		Penn et al. (2007)
Electric arc furnace slag	Steel mill Ft. Smith, AR, USA	6.35–11	Jul. 2010–Dec. 2010	0.5	25% (mass removal)	1.5	Penn et al., (2012)
Steel smelter slag	SteelServ, South Auckland, New Zealand	2-5	Jul. 2006–Jun. 2007	Dissolved P 0.3	93% (mass removal)		McDowell (2007)
Burnt lime (CaO) and mixed lime (CaO, Ca(OH)₂ and CaCO₃)		< 3	Filter 1 (May 1997–Apr. 2002), Filter 2 (Feb. 1997–Jun. 2003), Filter 3 (Aug. 1999–Nov. 2001)	Dissolved P F1: 2.6 F2: 0.011 F3: 0.009	F1: 62% F2: 52% F3: 46% (mass removal)	F1: 15 F2: 450 F3: 337.5	Kirkkala et al. (2011)

AGRICULTURAL AND FOOD SCIENCE

A. Klimeski et al. (2012) 21: 206–223

Large-scale wastewater treatment

Dobbie et al. (2009) investigated P retention by ochre (hydrous iron oxide) filters at the Leitholm (south-east Scotland) and Windlestone (north-east England) wastewater treatment plants (the experiments were also described in Heal et al. 2004). At Leitholm, with settling as the primary treatment and biological filter as the secondary treatment, they studied a tertiary treatment step with granular ochre or ochre pellets (volume 2.1 m^3). The mean influent total P concentration measured in the experiments at Leitholm ranged from 4 to 6 mg l^{-1}, and the efficiency of the filter bed was around 12% for both forms of ochre. Total P removal efficiency decreased with higher incoming flows (the highest flow was 4 l s^{-1}). To achieve a longer residence time, they reduced the flow to 0.05 l s^{-1}, which consequently increased the removal efficiency to 66%. At Windlestone, the ochre pellets were used in horizontal and vertical flow tanks. Total P concentration in the influent varied from 0.4 to 4.8 mg l^{-1}. Under horizontal and vertical flow conditions, P removal efficiencies first ranged between 73% and 78%, respectively, but under vertical flow, the efficiency decreased to 20% after 1000 hours of operation. Placing gravel before the main filter that helped to remove organic material and suspended solids improved the performance of the filter. The experiments highlighted the importance of a sufficiently long residence time in the filter and demonstrated that other substances present in the system may affect the performance of the structures.

Shilton et al. (2006) monitored ten large steel slag filter beds (29.6 × 97.4 m, depth 0.5 m) in a wastewater treatment plant close to Auckland, New Zealand. Wastewater from a population of 6000 entered the filters after passing through a sedimentation pond. The treated flow was 1500-4500 m^3 day^{-1}, depending on the season. Effluent total P was measured for 11 years (1993–2003), whereas the influent total P concentration was measured in the first and last year of the test period. In the first year, the filters were efficient and removed 77% of total P, lowering the annual mean total P concentration from 8.2 mg l^{-1} to 2.3 mg l^{-1}. The effluent concentration also remained at this level during the first five years of operation. Beginning in the sixth year, the efficiency gradually decreased, and by the end of the test period, the filters had become saturated. The retention capacity of the filters for the initial five-year period was 1.2 mg g^{-1}. During the experiment, effluent P concentrations varied by season, with higher temperatures and algal growth in the sedimentation pond improving the performance. The authors postulated that this was due to CO_2 removal induced by the spring growth of the algal population, resulting in elevated pH values and more efficient precipitation of Ca-phosphates.

Agricultural runoff treatment

McDowell et al. (2007) investigated the use of altered steel smelter slag for treating agricultural runoff in the North Island of New Zealand. The study took place in the Mangakino stream that drains an area of 688 ha (mostly agricultural land). P socks (1 m long and 9 cm in diameter) were woven of geotextile with a 2-mm mesh size. Steel smelter slag was placed in the socks, which were then immersed in polyaluminium chloride solution (1% w/v) overnight in order to increase their P sorption capacity. The P socks were laid on the stream bed in a herringbone fashion. The mean flow rate during the test period was 19 l s^{-1}, the mean total P concentration was 0.057 mg l^{-1}, and the dissolved fraction contributed 33% of total P. The socks reduced dissolved and total P concentrations in the stream by 25% and 16%, respectively, and the amount of P retained by the slag was 2.6 mg g^{-1}. Even though the P socks retained significant amounts of P from the stream, the authors concluded that wide-scale use of this technique is limited due to the costs of labour and chemicals.

Penn et al. (2007) at the University of Maryland, USA, investigated agricultural ditch water treatment using a flow-through structure with a horizontal surface area of 2 m^2 and a depth of 0.3 m. The flow rate in the ditch was 5.7 l s^{-1}, and dissolved P concentrations varied from 7 to 16 mg l^{-1}, with dissolved forms comprising 75–95% of total P. As a P sorbent, the authors used about 230 kg acid mine drainage residual that allegedly had a high P sorption capacity (48 mg g^{-1}), fast sorption kinetics, high hydraulic conductivity, and posed low risk to the environment (low heavy metals concentration, near neutral pH). The filter was efficient throughout a period of one year, removing virtually all of the dissolved P from the water that passed through the barrier. High water flows in rainy periods created problems, however, so that only a portion of the flow passed through the filter. During an extreme storm, the structure treated only 9% of the flow. According to the authors, Fe/Al-rich materials remove P faster than Ca/Mg-based ones. However, they stressed that when using Fe-rich materials, it is important to enable free drainage during low water flow in order to prevent Fe^{3+} reduction to Fe^{2+} and subsequent dissolution. The filter soon became clogged (Penn et al. 2012).

AGRICULTURAL AND FOOD SCIENCE

A. Klimeski et al. (2012) 21: 206–223

Kirkkala et al. (2012) studied the efficiency of three buried filters of lime mixed with sand. In one of the filters, the sand was mixed with waste lime from a sugar refinery (i.e. a mixture of CaO, $Ca(OH)_2$ and $CaCO_3$). The filters were placed alongside ditches flowing into the Yläneenjoki river in southwestern Finland and were monitored for periods of 1.5 to 6.5 years. One of the filters was characterised by the downward movement of water, whereas in the two others, water entered from the bottom and exited via discharge pipes at the top of the filters. The volumes of the three filters varied between 15 and 450 m^3, and the mean outflow rates from 0.061 l s^{-1} (0.158 l s^{-1} after renovation) to 0.39 l s^{-1}. The mean total P (TP) and dissolved reactive P (DRP) concentrations in the incoming water to the (wastewater-influenced) smallest filter were 3 and 2.6 mg l^{-1}, respectively, whereas much lower influent concentrations (< 0.1 mg l^{-1} for TP and about 0.01 mg l^{-1} for DRP) were measured at the two other sites. The smallest filter that received the highest concentration was estimated to have retained 3.6 mg P g^{-1} during 4 years of operation, whereas the two other filters only retained 0.02–0.03 mg P g^{-1} during the 1.5- and 6-year periods of observation, thus revealing huge differences in retention efficiencies according to the inflow P concentration and site. However, the relative retention (mass removal) was surprisingly similar for all three filters: 60–82% for TP and 46–60% for DRP. Even though the filters used by Kirkkala et al. (2012) performed well during the monitoring periods, the authors discussed the possibility of P release after exhausting the lime. The two largest filters contained enough lime to maintain the pH of the effluent water throughout the study at about 10–12, which is a sufficiently high pH for efficient Ca-P precipitation. Other challenges included the forming of preferential flow paths. The two largest filters decreased the concentration of suspended solids (SS) by 67–94%, but such a high sediment removal rate may be problematic, as it likely hastens clogging of the filters and leads to by-pass flows. The high effluent pH was considered less problematic, however, because the effluent was mixed with large volumes of stream water after leaving the filter.

Conclusions

In general, high P retention is usually achieved with materials that have either: 1) basic pH and high Ca content (e.g. steel slags and red mud), or 2) high Fe or Al (e.g. water treatment residuals and Fe precipitates). In addition to the total elemental content of materials, their solubility and degree of crystallinity affect P sorption. The content of harmful elements, such as heavy metals, must be low enough not to result in pollution swapping, but currently (at least in Finland) no guideline concentrations regulate the heavy metal content in P filter applications. We recommend using the guideline concentrations for soil amendments as reasonable maximum levels for problematic elements in P filters.

As for laboratory tests of the ability of a material to retain P, standardised test protocols would be an ideal solution. In practice tests must nevertheless be modified on the material properties and the practical applications proposed. For example, some filter settings in full-scale operation will mandate short contact times, low or widely variable P concentrations and rapid wash-out of soluble elements, whereas another type of use may allow long contact times in high P concentrations and solutions that become nearly saturated in soluble compounds. Batch tests are often favoured for material characterisation because they require less time than flow-through column tests do. However, if flow-through tests more closely resemble field conditions, they should be used instead, despite the longer time and higher costs for analyses.

When extrapolating laboratory results to a field scale, some of the previously retained P will under certain conditions be released from the material. Such unfavorable conditions may include changes (either an increase or decrease) in pH, ionic strength, element concentrations, and redox potential. Taking into account the release of previously retained P improves estimates of material performance in field set-ups.

As P retention structures are scaled up, challenges to overcome include preferential flow, fluctuations in incoming flow (volume and chemistry), clogging due to suspended solids and possibly material alterations, as well as reduced retention capacity due to contamination by organic material or to competition by other elements. In field conditions, P appears in inorganic and organic forms, whereas laboratory experiments use mostly inorganic P, which may also influence results. Sufficient contact time between the filter material and the flow solution is likewise a crucial point in developing P filters. Several studies have shown that some materials are capable of removing P from household wastewater or agricultural runoff, but more studies are needed to optimize the design of filter beds intended for field conditions.

AGRICULTURAL AND FOOD SCIENCE

A. Klimeski et al. (2012) 21: 206–223

Figure 2 summarises the steps that we find useful in laboratory characterisation, and the route to further larger-scale applications of P-sorbing materials. The availability and price of the P sorbents and the recycling value of used material (not discussed in this review) are usually also taken as criteria in material selection. The recycling value takes into account as alternatives for disposal the possibility of regeneration and further use of the P obtained from the regenerated material or the potential to use the material as a soil amendment. For structures intended for broad use, price and reuse potential are naturally of the utmost importance. For treating flows coming from restricted hot-spots of P losses in catchments of sensitive watercourses, the main criterion may be the efficiency of a material to retain P.
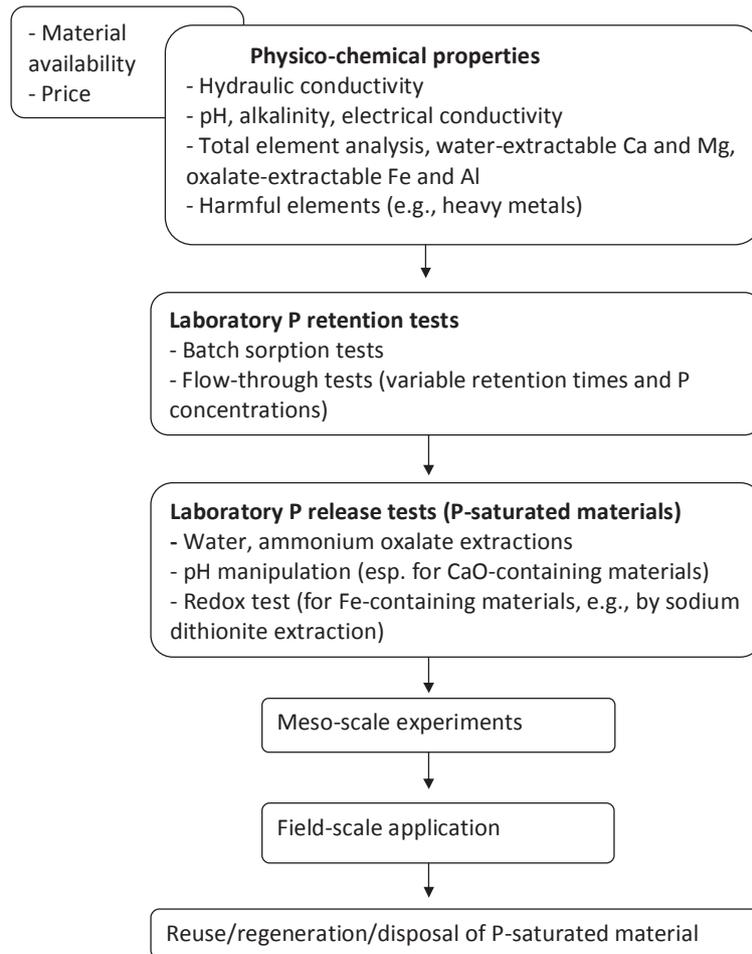
Fig. 2. Suggested test scheme for material characterisation in the laboratory and further test route to field-scale applications.

Acknowledgements

AGRICULTURAL AND FOOD SCIENCE

A. Klimeski et al. (2012) 21: 206–223

References

Ádám, K., Søvik, A.K., Krogstad, T. & Heistad, A. 2007a. Phosphorus removal by the filter materials light-weight aggregates and shellsand - A review of processes and experimental set-ups for improved design of filter systems for wastewater treatment. *Vatten* 63: 245–257.

Ádám, K., Krogstad, T., Vråle, L., Søvik, A.K., & Jenssen, P.D. 2007b. Phosphorus retention in the filter materials shellsand and Filtralite P® - Batch and column experiment with P solution and secondary wastewater. *Ecological Engineering* 29: 200–208.

Antelo J., Avena, M., Fiol, S., López, R. & Arce, F. 2005. Effects of pH and ionic strength on the adsorption of phosphate and arsenate at the goethite–water interface. *Journal of Colloid and Interface Science* 285: 476–486.

Arias, C.A., Brix, H. & Johansen, N.-H. 2003. Phosphorus removal from municipal wastewater in an experimental two-stage vertical flow constructed wetland system equipped with a calcite filter. *Water Science and Technology* 48 (5): 51–58.

Bache B.W. & Ireland, C. 1980. Desorption of phosphate from soils using anion exchange resins. *Journal of Soil Science* 31: 297–306.

Baird, C. & Cann, M. 2005. Environmental Chemistry. 3rd Edition. New York: W.H. Freeman and Company. p. 472–477.

Barrow, N.J., Bowden, J.W., Posner, A.M. & Quirk, J.P. 1980. Describing the effects of electrolyte on adsorption of phosphate by a variable charge surface. *Australian Journal of Soil Research* 18: 395–404.

Ballantine, D.J. & Tanner, C.C. 2010. Substrate and filter materials to enhance phosphorus removal in constructed wetlands treating diffuse farm runoff: a review. *New Zealand Journal of Agricultural Research* 53: 71–95.

Brady. N.C & Weil, R.R. 2008. The nature and properties of soils.14th Edition. New Jersey, Columbus, Ohio: Pearson Prentice Hall, Upper Saddle River,. p. 612–621.

Chardon, W.J., Groenenberg, J.E., Temminghoff, E.J.M., & Koopmans, G.F. 2012. Use of reactive materials to bind phosphorus. *Journal of Environmental Quality* 41: 636–646.

Cheung, K.C., Venkitachalam, T. H. & Scott, W. D. 1994. Selecting soil amendment materials for removal of phosphorus. *Water Science Technology* 30 (6): 247–256.

Cucarella, V. & Renman, G. 2009. Phosphorus sorption capacity of filter materials used for on-site wastewater treatment determined in batch experiments – a comparative study. *Journal of Environmental Quality* 38: 381–392.

Diaz, O.A., Reddy, K.R. & Moore, P.A., Jr. 1994. Solubility of inorganic phosphorus in stream water as influenced by pH and calcium concentration. *Water Research* 28: 1755–1763.

Dobbie, K.E., Heal, K.V., Aumônier, J., Smith, K.A., Johnston, A. & Younger, P.L. 2009. Evaluation of iron ochre from mine drainage treatment for removal of phosphorus from wastewater. *Chemosphere* 75: 795–800.

Drizo A., Comeau, Y., Forget, C. & Chapuis, R.P. 2002. Phosphorus saturation potential: A parameter for estimating the longevity of constructed wetland systems. *Environmental Science and Technology* 36: 4742–4648.

Gallimore, L.E., Basta, N.T., Storm, D.E., Payton, M.E., Huhnke, R.H., & Smolen, M.D. 1999. Water treatment residual to reduce nutrients in surface runoff from agricultural land. *Journal of Environmental Quality* 28: 1474–1478.

Hartikainen, S.H. & Hartikainen, H.H. 2008. Phosphorus retention by phogopite-rich mine tailings. *Applied Geochemistry* 23: 2716–2723.

Heal, K.V., Smith, K.A., Younger, P.L., McHaffie, H., & Batty, L.C. 2004. Removing phosphorus from sewage effluent and agricultural runoff using recovered ochre. In: Valsami-Jones, E. (ed.). *Phosphorus in Environmental Technologies: Principles and Applications*. London, UK: IWA Publishing. p. 321–335.

HELCOM 2009 Eutrophication in the Baltic Sea – An integrated thematic assessment of the effects of nutrient enrichment and eutrophication in the Baltic Sea region: Executive Summary. *Baltic Sea Environment Proceedings*. No. 115A. Cited 12 December 2011. Available on the internet: http://meeting.helcom.fi/c/document_library/get_file?p_l_id=79889&folderId=377779&name=DLFE-36817.pdf

Hingston, F.J., Atkinson, R.J., Posner, A.M. & Quirk, J.P. 1967. Specific adsorption of anions. *Nature* 215: 1459–1461.

Howarth, R.W. & Marino, R. 2006. Nitrogen as the limiting nutrient for eutrophication in coastal marine ecosystems: Evolving views over three decades. *Limnology and Oceanography* 51: 364–376.

Hsu, P. H. 1964. Adsorption of phosphate by aluminum and iron in soil. *Soil Science Society Proceedings* 28: 474–478.

Johansson, L. & Gustafsson, J. P. 2000. Phosphate removal using blast furnace slags and opoka-mechanisms. *Water Research* 34: 259–265.

Johansson Westholm, L. 2006. Substrates for phosphorus removal – Potential benefits for on-site wastewater treatment? *Water Research* 40: 23–36.

Kirkkala, T, Ventelä, A.-M., & Tarvainen, M. 2012. Long-term field-scale experiment on using lime filters in an agricultural catchment. *Journal of Environmental Quality* 41 (2): 410–419.

Kostura, B., Kulveitova, H., & Lesko, J. 2005. Blast furnace slags as sorbents of phosphate from water solutions. *Water Research* 39: 1795–1802.

Leader, J.W., Dunne, E.J., & Reddy, K.R. 2008. Phosphorus sorbing materials: Dynamics and physicochemical characteristics. *Journal of Environmental Quality* 37: 174–181.

Li, Y., Liu, C., Luan, Z., Peng, X., Zhu, C., Chen, Z., Zhang, Z., Fan, J. & Jia, Z. 2006. Phosphate removal from aqueous solutions using raw and activated red mud and fly ash. *Journal of Hazardous Materials B* 137: 374–383.

Makris, C. K., Harris, W. G., O'Connor, G.A., Obreza, T.A. & Elliott, H.A. 2005. Physicochemical properties related to long-term phos-

AGRICULTURAL AND FOOD SCIENCE

A. Klimeski et al. (2012) 21: 206–223

phorus retention by drinking-water treatment residuals. *Environmental Science and Technology* 39: 4280–4289.

McDowell, R.W., Hawke, M., & McIntosh, J.J. 2007. Assessment of a technique to remove phosphorus from streamflow. *New Zealand Journal of Agricultural Research* 50: 503–510.

Moore, P.A. Jr., & Miller, D.M. 1994. Decreasing phosphorus solubility in poultry litter with aluminum, calcium and iron amendments. *Journal of Environmental Quality* 23: 325–330.

Neufeld, R.D. & Thodos, G. 1969. Removal of orthophosphates from aqueous solutions with activated alumina. *Environmental Science and Technology* 3: 661–667.

Penn, C.J. & R. Bryant, B. 2006. Application of phosphorus sorbing materials to streamside cattle loafing areas. *Journal of Soil and Water Conservation* 61: 303–310.

Penn, C.J., Bryant, R.B., Kleinman, P.J.A. & Allen, A.L. 2007. Removing dissolved phosphorus from drainage ditch water with phosphorus sorbing materials. *Journal of Soil and Water Conservation* 62: 269–276.

Penn, C.J. & McGrath, J. M. 2011. Predicting phosphorus sorption onto steel slag using a flow-through approach with application to a pilot scale system. *Journal of Water Resource and Protection* 3: 235–244.

Penn, C.J., McGrath, J. M., Rounds, E., Fox G. & Heeren, D. 2012. Trapping phosphorus in runoff with a phosphorus removal structure. *Journal of Environmental Quality* 41: 672–679.

Pratt, C., Shilton, A., Pratt, S., Haverkamp, R.G., & Elmetri, I. 2007. Effects of redox potential and pH changes on phosphorus retention by melter slag filters treating wastewater. *Environmental Science and Technology* 41: 6585–6590.

Sakadevan, K. & Bavor, H.J. 1998. Phosphate adsorption characteristics of soils, slags and zeolite to be used as substrates in constructed wetland systems. *Water Research* 32 (2): 393–399.

Sawhney, B.L. & Hill, D.E. 1975. Phosphate sorption characteristics of soils treated with domestic waste water. *Journal of Environmental Quality* 4: 342–346.

Sibrell, P.L., Montgomerry, G. A., Ritenour, K. L. & Tucker, T.W. 2009. Removal of phosphorus from agricultural wastewaters using adsorption media prepared from acid mine drainage sludge. *Water Research* 43: 2240–2250.

Sigg, L. & Stumm, W. 1981. The interaction of anions and weak acids with the hydrous goethite (α- FeOOH) surface. *Colloids and Surfaces* 2: 101–117.

Schindler, D.W. 1977. Evolution of phosphorus limitation in lakes. *Science* 195: 260–262.

Shiao S. J. & Akashi, K. 1977. Phosphate removal from aqueous solution from activated red mud. *Journal of the Water Pollution Control Federation* 49: 280–285.

Shilton, A. N., Elmetri, I., Drizo, A., Pratt, S., Haverkamp, R.G. & Bilby, S.C. 2006. Phosphorus removal by an 'active' slag filter–a decade of full scale experience. *Water Research* 40: 113–118.

Søvik, A.K. & Kløve, B. 2005. Phosphorus retention processes in shell sand filter systems treating municipal wastewater. *Ecological Engineering* 25: 168–182.

Strauss, R., Brümmer, G.W. & Barrow, N.J. 1997. Effects of crystallinity of goethite: II. Rates of sorption and desorption of phosphate. *European Journal of Soil Science* 48: 101–114.

Streat, M., Hellgardt, K. & Newton, N.L.R. 2008. Hydrous ferric oxide as an adsorbent in water treatment Part 3: Batch and mini-column adsorption of arsenic, phosphorus, fluorine and cadmium ions. *Process Safety and Environmental Protection* 86: 21–30.

Turtola, E. & Yli-Halla, M. 1999. Fate of phosphorus applied in slurry and mineral fertilizer: accumulation in soil and release into surface runoff water. *Nutrient Cycling in Agroecosystems* 55: 165–174.

Ugurlu, A. & Salman, B. 1998. Phosphorus removal by fly ash. *Environment International* 24: 911–918.

Uusitalo, R., Ekholm, P., Lehtoranta, J., Klimeski, A., Konstari, O., Lehtonen, R. & Turtola, E. 2012. Ca-Fe oxide granules as potential phosphate barrier material for critical source areas: a laboratory study on P retention and release. *Agricultural and Food science in Finland* 21: 224-236*.*

Van der Zee, S.E.A.T.M. & van Riemsdijk, W.H. 1988. Model for long-term phosphate reaction kinetics in soil. *Journal of Environmental Quality* 17: 35–41.

Vohla, C., Kõiv, M., Bavor, H.J., Chazarenc, F., & Mander, Ü. 2011. Filter materials for phosphorus removal from wastewater treatment wetlands – A review. *Ecological Engineering* 37: 70–89.

Xu, D., Xu, J., Wu, J. & Muhammad, A. 2006. Studies on the phosphorus sorption capacity of substrates used in constructed wetland systems. *Chemosphere* 63: 344–352.

Yee, W.C. 1966. Selective removal of mixed phosphates by activated alumina. *Journal of the American Water Works Association* 58: 239–247.

Yeoman, S., Stephenson, T., Lester, J.N., & Perry, R. 1988. The removal of phosphorus during wastewater treatment: A review. *Environmental Pollution* 49: 183–233.

Yli-Halla, M. & Hartikainen, H. 1996. Release of soil phosphorus during runoff as affected by ionic strength and temperature. *Agricultural and Food science in Finland* 5: 193–202.

Zeng, L., Li, X. & Liu, J. 2004. Adsorptive removal of phosphate from aqueous solutions using iron oxide tailings. *Water Research* 38: 1318–1326.

Zhu, T., Jenssen, P.D., Mæhlum, T. & Krogstad, T. 1997. Phosphorus sorption and chemical characteristics of lightweight aggregates (LWA) – Potential filter media in treatment wetlands. *Water Science and Technology* 35 (5): 103–108.

Ziemkiewicz, P. 1998. Steel slag: applications for acid mine drainage control. *Proceedings of the 1998 Conference on Hazardous Waste Research*, p. 44–62. Held in Snowbird, Utah, USA, May 18-21, 1998.