Methodological Aspects of Using Blast Furnace Slag for Wastewater Phosphorus Removal

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Abstract: Blast furnace (BF) slag is a by-product of steel plants. The objective of this study was to evaluate experimental methods to determine the phosphorus sorption capacity of BF slag. The handling of BF slag, before usage and clogging were also considered, as well as estimating the phosphorus retention capacity. Agitation and pilot-scale experiments were performed using both wastewater and phosphate solutions. This investigation showed that sorption capacities derived by wastewater experiments were considerably lower compared to those by phosphate solutions. Fresh BF slag briefly exposed to rainfall had a higher phosphorus sorption than weathered BF slag, indicating the importance of handling the slag carefully before usage. The risk for leakage of sulfuric compounds is considerable, especially during the initial operation phase of BF slag filters. Locations of BF slag filter beds for wastewater treatment must be carefully chosen from an environmental point of view.

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CE Database subject headings: Phosphorus; Sorption; Clogging; Wastewater management; Filters.

Background

Small on-site wastewater treatment systems for residential buildings in Sweden contribute significantly to the anthropogenic discharge of phosphorus, approximately 20% of the gross discharge (SEPA 2003). Discharge from municipal wastewater treatment plants is only approximately 15% (SEPA 2003), though as much as 85% (SCB 2004) of the Swedish population are connected to wastewater treatment plants. Small wastewater treatment systems may be upgraded by phosphorus sorbing reactive filter materials to improve their phosphorus retention. Suggested reactive filter materials for this purpose are, e.g., limestone (Johansson 1999; Hill et al. 2000), opoka (Johansson and Gustafsson 2000), wollastonite (Brooks et al. 2000; Hill et al. 2000), shell sand (Roseth 2000), light expanded clay aggregates (Leca) (Zhu et al. 2003), fly ash (Mann and Bavor 1993; Johansson 1999), and blast furnace (BF) slag (Yamada et al. 1986; Sunahara et al. 1987).

The sorption capacity of the filter material is an important parameter for the longevity of wastewater treatment applications. During the last decade, phosphorus sorption of BF slag has been studied intensively (Lee et al. 1997; Sakadevan and Bavor 1998; Johansson 1999; Johansson and Gustafsson 2000; Grüneberg and Kern 2001; Agyei et al. 2002; Khelifi et al. 2002; Cameron et al.

2003; Oguz 2004; Hylander et al. 2005; Korkusuz et al. 2005). The obtained sorption capacity of these studies varied to a great extent. The variation cannot be explained only by the difference between the materials, e.g., crystalline and amorphous BF slag, but by the differences in the experimental methods, such as agitation versus filter experiments, influent solution, phosphorus content of influent, contact time, grain size of filter material. A higher reaction temperature caused higher phosphorus retention according to Yamada et al. (1986) and Agyei et al. (2002). An increased influent phosphorus concentration resulted in an increased phosphorus sorption when conducting agitation experiments (Sunahara et al. 1987; Agyei et al. 2002). A higher concentration of salt in the solution seemed to decrease the phosphate sorption on the BF slag. Yamada et al. (1986) investigated the effect of NaCl content on phosphorus retention, showing that a higher NaCl concentration decreased the phosphorus sorption.

For practical wastewater treatment applications, phosphorus sorption capacities of filter materials are not solely relevant but environmental and other practical aspects, such as possible leaching of hazardous compounds and clogging of filter. So far, leaching of hazardous compounds from BF slag filter in wastewater treatment applications has not achieved attention. However, the leaching has been considered in the use of by-products as construction material (Tossavainen 2005).

Most experiments done to investigate the phosphorus retention capacity of BF slag are laboratory tests (agitation and column tests) using artificial phosphorus solutions (Yamada et al. 1986; Mann and Bavor 1993; Lee et al. 1997; Johansson 1998; Sakadevan and Bavor 1998; Agyei et al. 2002; Khelifi et al. 2002). However, research findings from experiments with artificial phosphorus solutions (particularly agitation experiments) cannot be extrapolated to wastewater applications due to, e.g., hydraulic differences and competing ions. The findings may only result in a comparison between the efficiency of different materials. Additional studies of BF slag being loaded with wastewater are of interest to evaluate its suitability as a filter medium for wastewater treatment. Further, environmental and practical aspects of using BF slag should be elucidated. Assessing different

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	Table 1.	BF	Slag	Materials	Used	in	the	Different	Experimen	its
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Term of BF slag	Grain size (mm)	Storage of BF slag at steel plant	Treatment before experiment	Experiment
Fresh	0.5-2	Outdoors about one year	_	Agitation
Weathered	0.5-2	Outdoors a couple of years		Agitation
Weathered ⁺⁺	1–5.6	Outdoors a couple of years	Rinsed and washed $(L/S=16)$	Agitation
Weathered ⁺	1–5.6	Outdoors a couple of years	Rinsed	Pilot scale

experimental approaches is also of interest to better understand how laboratory experimental results should be interpreted to the following design of full-scale systems.

Objectives and Scope

The objective of this study was to evaluate different experimental methods to determine the phosphorus sorption capacity of BF slag. Further, practical aspects, such as clogging, handling of BF slag prior to usage and effluent quality, of utilizing BF slag in wastewater treatment applications were evaluated. Moreover, the phosphorus sorption capacities of blast furnace slag in contact with artificial phosphate solution and municipal wastewater were determined. Environmental aspects of using blast furnace slag in wastewater treatment applications were discussed.

Agitation experiments and a pilot-scale study with horizontal flow were performed in this investigation. Both municipal wastewater and artificial phosphorus solutions were used in these experiments. Crystalline blast furnace slag of different ages was collected at the SSAB steel plant in Luleå, Sweden.

Materials and Methods

Materials

Blast Furnace Slag

The BF slag used in the experiments originated from the SSAB steel plant in Luleå, northern Sweden. Two particle sizes of crystalline BF slag, 0.5-2 and 1-5.6 mm, were used in the experiments. Further, two types of 0.5-2 mm BF slag were used: One which had been outdoors in a pile for about one year (fresh), the other (weathered) for a couple of years. During storage time, the material was exposed to various weather conditions (rain, snowfall, etc.). This situation may have caused leaching of important elements for phosphorus sorption. The weathered BF slag material was rinsed once with tap water in a hydraulic conductivity test prior to some of the experiments (weathered⁺). Part of this BF slag was further washed with tap water at a liquid/solid ratio (L/S, [volume/volume]) of 16 (weathered⁺⁺) prior to the experiment to remove dust and any excess of easily soluble calcium compounds. Information about the materials investigated in the experiments is compiled in Table 1. Crystalline (ungranulated) BF slag material consists of ternary compounds, the most

common being melilite, a series of solid solutions from akermanite (2CaO·MgO·2SiO₂), merwinite (3CaO·MgO·2SiO₂), and anorthite (CaO·Al₂O₃·2SiO₂) to gehlenite (2CaO·Al₂O₃·SiO₂) (Lindgren 1992; Tossavainen and Forssberg 2000). The content of major elements in the investigated BF slag was 30–33% CaO, 33–36% SiO₂, 15–19% MgO, 11–13% Al₂O₃, 2–3% TiO₂, 1–2% S, 0.3–0.5% MnO, 0.281% Fe₂O₃, and <0.012% P₂O₅. The content of minor elements and the physical properties of the BF slag used in this study are given in Tables 2 and 3, respectively.

Phosphate Solutions and Wastewater Used in the Experiments

The phosphate solutions (0–20 mg PO_4-P/L) used in the agitation experiments consisted of Na_2HPO_4 mixed with distilled waster. The range of phosphorus concentrations was selected with respect to the properties of typical municipal wastewater (Metcalf and Eddy 1991; Kadlec and Knight 1996). Municipal wastewater, mechanically and biologically treated in a wastewater treatment plant, was used in the agitation experiments when fresh and weathered BF slag was evaluated. Prior to the experiments, the wastewater was filtered through a 0.45 µm filter. The phosphorus concentration after filtration was 0.75 mg tot-P/L. A part of the wastewater used in these experiments was spiked with Na_2HPO_4 to a phosphorus concentration of approximately 4.2 mg tot-P/L.

The municipal wastewater used in the pilot-scale experiments passed through the step screen and was collected in the following grit chamber. The wastewater was collected once a week and was stored at +4°C, except for the amount of influent needed daily in the pilot-scale experiment. The influent total P and PO₄-P concentrations into the BF slag filter were 1.0–5.3 and 0.5–4.3 mg/L. The BOD₇ and suspended solids (SS) concentrations were 26–28 and 5–25 mg/L, respectively.

Agitation Experiments

Fresh, weathered, and weathered⁺⁺ BF slags were used in this experiment. Duplicate 1 g samples of BF slag materials were brought into contact with 75 mL of phosphate solutions (5, 10, 15, and 20 mg PO₄–P/L). The fresh and weathered BF slags were brought into contact with wastewater or Na₂HPO₄ spiked wastewater. Initial pH was adjusted to 7.0 with HCl in all solutions. The flasks were shaken at 200 rpm in room temperature (approximately 20°C) for 20 h. After the agitation, the suspensions were filtered (0.45 μ m) and pH was measured. All of the

 Table 2. Chemical Composition of BF Slag Used in Experiments, Minor Elements (mg/g)

Cr	As	Ва	Be	Co	Cu	La	Мо	Nb	Ni	Pb	Sc	Sn	Sr	Zn	Zr	V	W	Y
33	<3	550	5	<1	<1	37	<5	<5	<1	<10	27	<5	360	2	14	170	<5	40

Note: Analyses delivered by SSAB

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Table 3. Physical Properties of BF Slag Used in Experiments

Physical parameter	Fine BF slag	Coarse BF slag
Grain size (mm)	0.5-2	1-5.6
Density (kg/m ³)	1,245	1,158
Porosity (%)	55	54
Hydraulic conductivity (m/day)	1,990	4,260

Note: The parameters were determined a week before the start of the experiments.

supernatant solutions were analyzed regarding total phosphorus, whereas those solutions which reacted to fresh and weathered BF slags were also analyzed with respect to Ca.

Pilot-Scale Experiment

Experimental Setup

A box lined with plastic was filled with weathered⁺ 1-5.6 mm BF slag to a height of 5 cm and covered with plastic to avoid evaporation. Drainage compartments comprised of washed gravel were placed at both ends of the box (see Fig. 1). Wastewater was pumped to a settling tank to separate suspended solids of the wastewater and conveyed through a rotating wastewater distributor and distributed on the gravel. The wastewater was then percolated through the filter bed with a horizontal flow during hydraulically saturated conditions. The experiment was conducted at room temperature (about 21° C). Operational data of the experiment can be seen in Table 4.

Sampling

The effluent was collected in a container stored at room temperature and emptied biweekly. Water samples were taken after the settling tank and in the effluent container, see Fig. 1. Tot-P and PO_4-P were sampled biweekly and samples for SO_4-S and SS analyses were taken weekly during the investigation. Temperature, pH, and volume of the percolated wastewater were measured during sampling.

Analyses of Water Samples

pH was measured with a WTW pH 330 meter. Digestion of total phosphorus samples was done according to the Swedish standard SS 02 81 27. Phosphate and total phosphorus were analyzed with a continuous auto-analyzer (TRAACS 800, Bran+Lubbe) based on molybdenum blue method. The suspended solids, SS, were analyzed according to the standard SS-EN 872. The sulfate concentrations were analyzed with Hach, DR-EL2 which uses a turbidimetric method. Barium ions react with sulfate ions producing milky barium sulfate precipitation. The amount of turbidity is



Fig. 1. Experimental setup of the pilot-scale study

Table 4. Operation Parameters of the Pilot-Scale Experiment

Parameter	Value	Unit
Hydraulic retention time in settling tank ^a	1.6	day
Range of hydraulic retention time in settling tank	1.5-3.9	day
Hydraulic retention time in BF filter ^a	3.8	day
Range of hydraulic retention time in BF filter	3.4-9.2	day
Duration of experiment	96	day
Average of flow ^a	3.0	L/day
Range of flow	1.3-3.4	L/day
Mass of 1-5.6 mm BF slag	10.3	kg

^aTime weighted average.

proportional to the amount of sulfate present, and the turbidity can be measured spectrophotometrically. The calcium concentrations were determined by Hach method 8204 which is based on titration with EDTA.

Calculations

The sorbed amounts of phosphate and total phosphorus in the agitation experiments were determined by the product of P concentration difference before and after agitation, and volume. In the pilot experiment, the phosphate and total phosphorus sorption were determined as the product of P concentration difference in the influent and the effluent, and volume. Phosphorus retention maximum was determined from Langmuir equation (Metcalf and Eddy 1991)

$$R_L = \frac{abC_e}{1 + bC_e} \tag{1}$$

where C_c =concentration of P in the solution after sorption (mg P/L); R_L =amount of P sorbed per unit weight of the material (mg/kg); a=P sorption maximum (mg/kg); and b=constant related to the binding strength of P on the material (L/mg P).

Phosphorus Extraction Estimations of BF Slag from Pilot-Scale Experiments

When the loading period of the pilot-scale experiments was finished, the phosphorus content of the BF slag materials was estimated by a phosphorus extraction method. Slag samples were taken at two different positions, i.e., 10 cm from the inlet and 10 cm from the outlet. These two samples were taken from the surface down to the bottom and divided into three layers of about 1.5 cm thick: Called "surface," "middle," and "bottom."

The phosphorus content of the BF slag filter materials was analyzed as follows: 25 mL 0.04 M H_2SO_4 was added to each 1 g BF slag sample and boiled in an autoclave at a temperature of 120 °C for 30 min with 0.25 g peroxide sulfate ($K_2S_2O_8$). The leachate was then analyzed with respect to total phosphorus with a continuous auto-analyzer (TRAACS 800 Bran+Lubbe) based on molybdenum blue method. Before analysis, the total phosphorus samples were digested according to the Swedish standard 02 81 27.

Results and Discussion

Influence of Experimental Methods on Phosphorus Sorption

When trying to determine the phosphorus sorption capacity of the BF slag, the obtained results depend on the chosen experimental

		Phosphorus sorption capacity (mg tot-P/kg BF slag)					
Water quality	Initial phosphorus concentration	Fresh BF slag (0.5–2 mm)	Weathered BF slag (0.5-2 mm)	Weathered ⁺⁺ BF slag (1–5.6 mm)			
Phosphate solution	20 mg tot-P/PL	1493±11	638±53	239±46			
Phosphate solution	10 mg tot-P/L	821 ± 0.1	563 ± 64	185 ± 15			
Phosphate solution	5 mg tot-P/L	380 ± 0.5	321±12	118±7			
Filtered wastewater, P-spiked	4.2 mg tot-P/L	176 ± 5.3	105 ± 0.0				
Filtered wastewater	0.75 mg tot-P/L	38±0.0	25±1				

Note: The phosphorus sorption values are based on an average of duplicate samples and the standard deviations are given.

method. The phosphorus sorption of BF slag increased with a higher initial phosphate concentration, see Table 5. At an initial phosphorus concentration of 20 mg/L, 1,493 mg tot-P/kg fresh BF slag was sorbed. The corresponding value for the initial phosphorus concentration of 10 mg/L was 821 mg tot-P/kg.

Sakadevan and Bavor (1998) obtained a maximum phosphorus sorption capacity of about 40,000 mg P/kg BF slag at an initial phosphate concentration of approximately 10,000 mg P/L. These results show a theoretical sorption capacity of the BF slag, but because the common phosphorus concentration of municipal wastewater is much lower, such high capacities would not be practically attained for this kind of wastewater.

Table 5 shows the phosphorus sorption capacities of BF slag acquired from different agitation experiments with an initial phosphorus concentration of about 5 mg/L. The highest phosphorus sorption was obtained for fresh BF slag shaken with an artificial phosphate solution, 380 mg tot-P/kg BF slag. The corresponding value for fresh BF slag shaken with filtered and phosphate-spiked wastewater with a phosphorus concentration almost equal to 5 mg tot-P/L (4.2 mg tot-P/L) was 176 mg tot-P/kg BF slag. Similar results were received for the weathered BF slag.

One explanation for the big difference between the results obtained with phosphate solutions and wastewater may be due to the presence of competing ions in the wastewater such as chloride (Yamada et al. 1986), sulfate and negatively charged, dissolved organic substances (Ramakrishna and Viraraghavan 1997). Another explanation could be microorganisms that may form a biofilm on the BF slag particles covering the sorption sites while degrading organic matter in the wastewater. When using artificial phosphorus solutions, the phosphorus constituent is orthophosphate, i.e., the ion that reacts most efficiently with calcium. Wastewater not only contains orthophosphate, but also, e.g., organic phosphorus compounds and polyphosphates (Snoeyink and Jenkins 1980; Sedlak 1991). These are not as reactive as dissolved inorganic orthophosphates (Droste 1997). pH has an effect on the phosphorus sorption as well. Calcium phosphate precipitation is facilitated by high pH (Jenkins et al. 1971; Agyei et al. 2002). In this study, pH of the solutions after reaction were 10.5 (fresh BF slag) and 9.8 (weathered BF slag) for the phosphate solutions. Corresponding values for the wastewater were 8.7 (fresh BF slag) and 8.5 (weathered BF slag) due to the buffering capacity of wastewater.

Therefore, phosphorus sorption capacities acquired from experiments using artificial phosphorus solutions are overestimated when transferred to wastewater, as illustrated in Fig. 2 where the phosphorus reductions obtained for fresh and weathered slag in agitation experiments are shown. The phosphorus reduction for, e.g., fresh BF slag was almost 100% for the initial phosphorus solution of 5 mg tot-P/L. Corresponding phosphorus reduction for a wastewater solution with an initial concentration of 4.2 mg tot-P/L was 56%. Similar results were acquired for the weathered BF slag.

However, the advantage of using artificial phosphate solutions allow for the possibility to repeat parts or whole experimental setups as the solution can be replicated. Wastewater quality is continually changing, making comparing results of different setups more difficult as the results are inconsistent.

For practical wastewater applications, results from wastewater experiments are more relevant. So far, few studies estimating the phosphorus sorption capacity of BF slag with wastewater have been performed. Grüneberg and Kern (2001) as well as Cameron et al. (2003) stated that they would continue with their filter experiments until they had reached complete phosphorus saturation of the slag. Other similar studies have not been found.

Agitation experiments are easily and rapidly accomplished and their use is suitable when different materials are to be evaluated and compared (as the investigation of fresh and weathered slag in this study). However, the acquired absolute values for the phosphorus sorption capacities from such experiments cannot be extrapolated to practical filter applications. When BF slag is shaken with solutions, the direct contact between the grains and solution differs compared to when a solution is filtered through the slag. Further, the sorption results of agitation sorption experiments are dependent on the numerical value of the ratio between the solid and dissolved phases. A more comprehensive discussion of these aspects was presented by Drizo et al. (2002). Further, agitation of BF slag may cause a destruction of the material which increases the sorption sites and thus the sorption capacity can be overestimated.

Filter experiments loaded with wastewater can result in phosphorus sorption capacity of the investigated filter medium but information about other aspects is received as well. The retention of phosphorus containing particles and dissolved organic phos-



Fig. 2. Phosphorus reduction rates related to quality of BF slag and phosphorus solutions used in agitation experiments

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Fig. 3. Phosphorus sorption capacities related to handling of BF slag before utilization and phosphate concentrations at equilibrium, reaction time 20 h

phorus can be investigated. Furthermore, operation problems, such as clogging can be studied. Such filter experiments thus improve forecasting filter results of full-scale applications for treating wastewater.

Practical Aspects of Using BF Slag as a Phosphorus Sorbent

Clogging

Clogging appears in filter beds from the settling of wastewater particles at the entrance of the filter. Microorganisms may degrade organic matter in the wastewater, thereby forming a biofilm on the BF slag particles. This may cause clogging when the filter has been in operation for some time (Stark 2004). The magnitude of clogging in wastewater filter beds depends on numerous factors, such as the grain size of the filter material, hydraulic load, filter's degree of water saturation, pH in the filter, influent concentrations of suspended solids, and organic matter.

In the pilot-scale experiment, the grain size of the filter was 1-5.6 mm while the retention time in the settling tank and the filtration rate were 38 h and 0.3 m/day, as respectively. No clogging problems occurred. The hydraulic head loss during the operational period of the 3 month long pilot-scale study was estimated at 1-2%.

However, in the completed pilot-scale experiment, the influent load of SS, 7-23 mg SS/L, was low compared to concentrations obtained after conventional septic tanks. The effluent SS concentration of a Swedish septic tank for municipal wastewater was estimated at 50-100 mg SS/L (SEPA 1991). Therefore, the risk of clogging is larger in a practical wastewater filter application compared to the results acquired in the present pilot-scale study. For this reason, when constructing full-scale systems, it is important to have an efficient wastewater pretreatment before the BF filter.

Handling of BF Slag before Application

The handing of BF slag before being used in a filter bed application may affect the phosphorus sorption capacity of the slag. In performed agitation experiments, fresh, weathered, and weathered⁺⁺ BF slag of a coarser grain size were investigated when reacting with artificial phosphorus solutions. The results of the experiments showed fresh BF slag to have the highest phosphate sorption whereas the weathered⁺⁺ BF slag had the lowest. At an initial phosphorus concentration of 20 mg/L, 1,493 mg tot-P/kg fresh BF slag was sorbed. The corresponding



Fig. 4. Final calcium concentration and pH in agitation experiment where fresh and weathered BF slag reacted with phosphate solutions of different concentrations

value for weathered⁺⁺ BF slag was 239 mg tot-P/kg, see Fig. 3. These results indicated changing BF slag properties when being exposed to precipitation such as rain and snow. The fresh and weathered BF slag samples investigated in this experiment were collected in uncovered slag heaps stored outdoors, but for different durations. The fresh BF slag had been stored for about one year and the weathered slag for a couple of years. The slag being stored outside for a shorter period had higher phosphorus sorption capacity.

The amount of dissolved calcium in the solution is vital for phosphorus sorption in BF slag. Fig. 4 shows the final calcium concentration and pH after the agitation experiment with fresh and weathered slag. The final calcium concentration and pH in the solutions with fresh BF slag were higher than weathered, even though more phosphate was retained by the fresh BF slag. This verifies the hypothesis that BF slag is depleted of calcium when being exposed to rainfall or melting of snow.

If BF slag is planned to be used for phosphorus removal, proper storage before usage is critical, i.e., it may be good to cover the slag and try to use it in a wastewater treatment application as soon as possible after being produced.

Sorption Capacity of BF Slag

To compare results of phosphorus sorption capacity experiments is problematic since the prerequisites often differ between studies. A study performed by Drizo et al. (1999) had similar prerequisites as the present study with the exception of initial phosphorus concentrations (2.5-40 mg/L). A comparison between these studies showed that the Langmuir sorption maximum for fresh BF slag was higher than for all the other filter materials (see Table 6). Thus, the agitation experiments of this study indicated that fresh BF slag has a potential of being an efficient phosphorus sorbent.

Filter Saturation versus Effluent Quality

During the pilot-scale investigation, phosphorus compounds were sorbed to the filter. The reduction rates of both total phosphorus and phosphate were initially about 100% and decreased to approximately 70% by the end of the experiment. The sorbed amount of phosphate in the BF filter was estimated to 58 mg PO_4 -P/kg. The corresponding value for total phosphorus was 75 mg P/kg. As the effluent concentrations of total phosphorus and phosphate were similar, most phosphorus containing particles were removed in the filter.

The effluent concentrations of phosphate and total phosphorus increased with time, but were below 0.5 mg/L during the first 50

Table 6. Langmuir Sorption Maxima for Different Filter Materials

Substrate	Sorption maximum (mg/kg)
Fresh BF slag ^a	1,600
Weathered BF slag ^a	680
Bauxite ^b	610
Shale ^b	650
Burnt oil shale ^b	580
Limestone ^b	680
Zeolite ^b	480
LECA ^b	420
Fly ash ^b	860

^aPresent study.

^bDrizo et al. (1999).

days (11.5 bed volumes passed), when the influent total phosphorus concentration varied between 1 and 3.5 mg/L (Fig. 5). At the end of the experiment, the effluent concentration slightly exceeded 1 mg/L, while the concentration in the influent was above 3 mg/L. Since the phosphate concentration in the influent was higher than in the effluent, the BF slag was not saturated with phosphate. Further, this uncompleted saturation of the filter was confirmed by the extraction analyses of the slag. From the samples taken at the inlet of the pilot filter, 16-18 mg tot-P/kg TS was extracted, whereas, analyses at the outlet approximately showed 6 mg tot-P/kg TS, see Table 7.

This pilot-scale experiment showed that the total sorption capacity of the BF slag cannot be utilized in the design of full-scale filters, if high effluent quality concerning phosphorus is to be attained. Therefore, phosphorus sorption values related to effluent quality achieved from filter experiments should be employed when designing a filter for wastewater treatment.

With the experimental setup of low influent phosphate concentrations and hydraulic retention time, it takes a long time to determine the phosphate sorption capacity of the filter material. If the phosphate sorption capacity is to be achieved faster, Drizo et al. (2002) recommended higher influent phosphorus concentration than concentrations in domestic wastewater. This results in overestimated phosphate sorption capacities, and thus overestimated filter longevities. Therefore, we suggest a higher hydraulic retention time rather than high influent phosphate concentrations which causes an underestimated phosphate sorption capacity.



Fig. 5. Influent and effluent concentrations of phosphate and total phosphorus during the operation of the pilot-scale experiment

Table 7. H₂SO₄ Extracted Phosphorus from the BF Slag at the End of the Pilot-Scale Experiment (96 days)

	Total phosphorus extracted (mg tot-P/kg BF slag)						
Sample location	Inlet	Outlet					
Surface	16	5.6					
Middle	16	6.3					
Bottom	18	5.6					

Environmental Aspects of Using Blast Furnace Slag in Wastewater Treatment Applications

The content of heavy metals is low in BF slag and soluble amounts of heavy metals from BF slag are smaller than rock materials, e.g., gabbro and granite (Tossavainen and Forssberg 2000). Vanadium is the only minor element that may leach out in larger amounts (Tossavainen and Forssberg 2000).

BF slag consists of 1–2% reduced sulfuric compounds which can be oxidized and leached out (Kanschat 1996). During the oxidation, protons are formed and possibly resulting in a pH decrease (Kanschat 1996). However, BF slag contains alkaline oxides such as calcium-aluminum-silicates. During the weathering of the silicates, protons are consumed and hydrocarbonates are produced. Thus, a decrease in pH caused by an oxidation of sulfuric compounds is counteracted by the pH-buffering properties of alkaline oxides in the BF slag (Lindgren 1998). During the first month, the pH was 8–9 in the effluent of pilot-scale experiment. Thereafter, the pH decreased to 7–8. The effluent pH was higher than the influent pH during the whole experiment. The decrease in the effluent pH could not be correlated by oxidization of sulfuric compounds.

In the present pilot-scale experiment, the release of sulfuric compounds was considerable. When the filter had operated for five days, the effluent SO_4 -S concentration was 1235 mg/L. After two weeks, the SO_4 -S concentration was stabilized to 80-150 mg/L. These SO_4 -S concentrations exceed the SO_4 -S limit for Swedish drinking water which is 33 mg/L. The influent SO_4 -S concentration varied between 2.2 and 6.8 mg/L during the experiment.

Due to the oxidation and subsequent leakage of sulfuric compounds, using BF slag in road constructions located close to water resources for drinking water purposes is not recommended (Kanschat 1996). If BF slag is to be used as a component in a wastewater treatment system, there is a risk of polluting ground-water with sulfuric compounds. Therefore, it is of importance to locate a BF filter away from drinking water resources to guarantee the drinking water quality, especially when used as a component in an on-site sanitation system.

Sulfuric odors were observed from the open pilot-scale box during the whole experiment. This indicates that the full-scale BF slag filter should be covered in order to avoid sulfuric odors.

Conclusions

This investigation emphasized the varying phosphorus sorption of BF slag as a result of which experimental method has been used for the estimations. Experimental setups with wastewater resulted in a considerably lower phosphorus sorption compared to phosphate solutions, at equal phosphate concentrations.

Results from agitation experiments showed that Langmuir adsorption maximum for fresh BF slag was higher than some other suggested phosphorus sorbents, e.g., Leca, limestone, and fly ash. In the pilot-scale experiment, 58 mg PO_4 –P/kg was sorbed to the weathered BF slag while the effluent exceeded 1 mg/L. However, the BF slag was not saturated with respect to phosphorus. This pilot-scale experiment showed that the total sorption capacity of the BF slag cannot be utilized in the design of full-scale filters, if high effluent quality concerning phosphorus is to be attained. Therefore, phosphorus sorption values related to effluent quality achieved from filter experiments should be employed when designing a filter for wastewater treatment.

The risk of a clogging BF filter was considered in this investigation. Clogging was avoided in the pilot-scale experiment by using a grain size of 1-5.6 mm, an infiltration rate of 0.3 m/day, and an influent particle concentration of 7-23 mg SS/L. This load of suspended solids was low compared to the effluent concentration from conventional Swedish septic tanks. Therefore, it is important to have an efficient wastewater pretreatment before the BF filter in a full-scale system.

The results of this study indicated that the properties of the BF slag change when exposed to precipitation, such as rainfall. Fresh BF slag had the highest phosphate sorption compared to weathered (69%) and weathered⁺⁺ BF slag (23%) at an initial phosphate concentration of 10 mg tot-P/L.

During the initial operation phase, leaching of sulfuric compounds was extensive in the pilot-scale experiment. This leakage can be a considerable environmental problem, when BF slag is used in a wastewater treatment application, especially if the effluent is released close to drinking water resources. High content of sulfuric compounds causes taste and odors in drinking water. Further, the sulfuric compounds caused odors during this study.

In the pilot-scale experiment, acid pH in the effluent was not observed. However, there might be a risk for a lowered effluent pH from the long-loaded wastewater filters as the buffering agent of BF slag, calcium, is leached.

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Notation

The following symbols are used in this paper:

- a = P sorption maximum (mg/kg);
- b = constant related to binding strength of P on material(L/mg P);
- C_e = concentration of P in the solution after sorption (mg/kg); and
- R_L = amount of P sorbed per unit weight of material (mg/kg).

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