

Engineered addition of slag fines for the sequestration of phosphate and sulfide during mesophilic anaerobic digestion

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• Abstract

The potential for weathered steel slag fines ($D_{50} < 1.6$ mm) to sequester dissolved phosphorus and sulfur from fermenting biosolids was determined. Batch studies showed that sorption equilibrium between phosphates and sulfides was reached in less than 48 hr after adding basic oxygen furnace (BOF) slag grains to municipal digester sludge. When these same particles were added to pilot digesters (75 L) operating at a 30-day SRT, a classic dose-response was observed with respect to PO_4 and H_2S sequestration, and an inhibitory performance threshold emerged above 20 g BOF/L. Only a fraction of the BOF slag solids contributed to the digester TS mass, because a substantial portion dissolved into the supernatant, some of which contributed to alkalinity. After 160 days of continuous operation, approximately 63% of the total phosphate was sequestered from the supernatant and 78% of the hydrogen sulfide from the biogas, when a steady-state BOF slag dose of 10 g BOF/L was applied. At or below this level, BOF slag fines had no significant effect on mesophilic digester performance as judged by conventional operational metrics. This study demonstrated that upcycling BOF slag directly into the anaerobic digestion process could offer wastewater resource recovery facilities a novel nutrient management tool. © 2019 Water Environment Federation

• Practitioner points

- Basic Oxygen Furnace (BOF) Slag fines can be engineered as a cost-effective alternative to conventional phosphorus and sulfur control strategies.
- A rapid phosphate and sulfide removal from anaerobic digestates occurs within hours after BOF slag addition.
- 63% of phosphate and 78% of hydrogen sulfide were removed when digester sludge was dosed with 10 g BOF/L, without impacting digester performance.
- Only a fraction of the dosed BOF slag contributed to digester TS, likely due to partial dissolution into the digestate.
- BOF slag can potentially increase the nutrient content of biosolids, facilitate biogas recovery, and reduce odors.

• Key words

biosolids; resource recovery; sludge; wastewater treatment

INTRODUCTION

ANAEROBIC digestion is a classic treatment process that remains one of the most common ways of stabilizing biosolids concentrated by domestic wastewater treatment facilities and livestock feeding operations. There are thousands of anaerobic digesters continuously operating in North America (U.S. DA, U.S. EPA, & U.S. DOE,

2014). Anaerobic sludge digestion is widely practiced in both developed and developing countries and is centralized near metropolitan areas all over the world. Further, investments in digestion infrastructure targeting developing regions are projected to markedly increase over the next generation (Stanton, 1990); thus, the operational and economic challenges associated with engineering digester control is gaining increased attention.

Municipal and agricultural anaerobic digesters contain valuable macronutrients that must be carefully managed. Conventional digesters liberate and concentrate ammonia, phosphate, and sulfides, the fate of which has tremendous consequences for stable wastewater treatment and associated energy recovery. The specific partitioning and speciation of selected nutrients into digester gases and supernatants are pH sensitive; this partitioning continues to present significant process problems to the municipal and agricultural waste treatment sectors.

In addition to the increasing regulatory scrutiny for nitrogen and phosphorus discharges, ammonia and phosphate levels in digester liquors often combine to exceed the effective solubility product of struvite (MgNH_4PO_4 (s)), which causes widespread fouling in the piping networks responsible for mixing and heating these large fermentation tanks (Baker, Lee, & Li, 2006; Baur, Benisch, Clark, & Sprick, 2002; Snoeyink & Jenkins, 1980).

In North America, the operations and maintenance costs associated with digester struvite deposition (e.g., loss of effective pipe diameter and clogging of dewatering units) have been reported to average near \$100,000 USD annually, in average municipal wastewater treatment plants (Baur et al., 2002).

Of direct consequence to the phosphorus levels observed in modern anaerobic digesters, is the purposeful operation of wastewater treatment plants to enhance biological phosphorus removal (EBPR). An unintended consequence of EBPR operations can manifest in increased digester supernatant phosphate levels that favor conditions for struvite precipitation. The relatively higher phosphorus levels liberated in conventional digesters under EBPR scenarios can dictate needs for direct chemical addition(s) or side-stream treatment to manage orthophosphate (Buchanan et al., 2008).

Soluble phosphorus in digester supernatants is often controlled using di- or tri-valent metal salts (De-Bashan & Bashan, 2004; Morse, Brett, Guy, & Lester, 1998). The effectiveness of this approach depends on the available alkalinity, phosphate concentration, and the type and source of multivalent cation added (ferrous, ferric, aluminum, or calcium). While effective and predictable, the addition of metal salts can be relatively expensive as well as increase occupational health risks with respect to handling large quantities of these reagents (Morse et al., 1998). Further, the dewatered biosolids subject to this nutrient management scenario sequester, yield poor phosphorus bioavailability, which markedly reduces its reuse value for land application as fertilizers (De-Bashan & Bashan, 2004; Donnant & Salecker, 1999).

While sulfur does not generally pose the same operational challenges as nitrogen or phosphorus, it does partition

as hydrogen sulfide (H_2S) into the copious amounts of gases digesters typically produce (biogas). This ubiquitous form of sulfur presents odor and safety concerns and carries a substantial corrosion potential that compromises an otherwise valuable source of renewable natural gas (RNG).

The operational costs associated with H_2S , manifests where digester biogas is recovered for RNG that can augment conventional fuels for heat and power generation, or is otherwise used in converted vehicles. If poorly managed, the sulfides in biogas can lead to infrastructure deterioration and catastrophic failures of energy recovery equipment, estimates for which vary by facility size and digester operational parameters (Persson, Jönsson, & Wellinger, 2006).

With respect to digester biogas, conventional H_2S removal techniques can be divided into two groups: chemical or biological. Common chemical removal technologies include digestate pretreatment or selective gas stripping in separate stand-alone column systems (Rasi, Lantela, & Rintala, 2011). A widespread pretreatment approach involves direct ferric chloride solution dosing that has been reported to significantly reduce H_2S concentrations; however, like similar metal salt dosing for phosphorus control, this approach carries significant operating costs and occupational health risks (Dezham, Rosenblum, & Jenkins, 1988). Other common chemically based sulfur management approaches include the following: sulfide sorption on activated carbons that are impregnated with caustic agents; catalytic oxidation with selective metaloxides; sorption on iron (oxy) hydroxide particles ($\text{Fe}(\text{O})_x\text{OH}_y$); and, scrubbing with sodium hydroxide mists, which can immobilize H_2S as sodium sulfide salts (Persson & Wellinger, 2009). Biological H_2S removal is commonly referred to as “desulfurization”, which employs sulfur-oxidizing biofilms. These microbial communities are enriched on solid-phase media enclosed in separate unit processes that are engineered to mediate sulfide oxidation into elemental sulfur, with oxygen inputs (Persson & Wellinger, 2009).

Despite advances in managing the phosphate and sulfide liberated by anaerobic digesters, conventional chemical addition practices are not in accordance with modern sustainability perspectives. In response to the modern challenges of selective nutrient management, we report a novel approach for simultaneous phosphorus and sulfur control by systematically introducing small doses of conditioned BOF slag sand to pilot-scale anaerobic digesters. Here, we demonstrate a beneficial reuse scenario that upcycles BOF slag for engineered nutrient sequestration, which is otherwise commonly used as low-value construction aggregate.

Steel production remains one of the fastest-growing industries worldwide (Huaiwei & Xin, 2011). In the United States alone, steel production generates 10–15 million tons of slags every year (Yildirim & Prezzi, 2011). Depending on the production mode, there are many different types of slag each with different physical chemistry and associated cementitious and mechanical properties; most slags are used as a low-cost geotechnical fill or aggregate in asphalt and concrete (Shi, 2004; Yildirim & Prezzi, 2011). Slags originating from basic oxygen furnaces have chemical and mineralogical properties that are

uniquely suited for resource recovery in wastewater applications. BOF slags are mostly composed of calcium, iron, and aluminum oxides and silicates, including both amorphous and crystalline phases; they also carry significant alkalinity (Grubb, Wazne, & Jagupilla, 2010; Grubb, Wazne, & Malasavage, 2010; Yildirim & Prezzi, 2011). Some slags have affinity for aqueous phosphate, which has been reported in several batches, column, and filter studies. The sequestration of phosphate by different steel slag types has been ascribed to two main mechanisms: (a) dissolution of calcium hydroxide, which in-turn precipitates as calcium phosphates; and, (b) phosphate sorption onto metal oxide or oxyhydroxide surfaces that are dominated by iron (Han et al., 2016; Shilton et al., 2006).

Certain steel slag minerals have a relatively high affinity for reduced sulfur which has been demonstrated through batch and flow-through column tests (Kim et al., 2012; Montes-Morán et al., 2012; Sarperi, Surbrenat, Kerihuel, & Chazarenc, 2014). Slag interactions with sulfides appear to be markedly different than their interactions with phosphates. The following mechanisms have been proposed to describe aqueous sulfide interactions with slag minerals: (a) Alkalinity driven acid dissociation of H_2S to HS^- and S^{2-} and consequent immobilization as metal sulfides; and, (b) The oxidation of H_2S to elemental sulfur, by surface-catalyzed redox reactions, mediated predominantly by iron (Fe) and manganese (Mn) (Kim et al., 2012; Montes-Morán et al., 2012).

While phosphorus and sulfur interactions with steel slags introduced to (abiotic) aqueous environments have been previously investigated, there are no studies on the potential effects of directly adding slag particles to active digesters. Thus, this

work evaluated the specific removal capacity that pre-conditioned BOF slag has on soluble phosphate and sulfide in mesophilic digester supernatant while concomitantly monitoring digester performance and stability.

MATERIALS AND METHODS

Anaerobic systems

Four pilot-scale digesters were contained in sealed polycarbonate vessels that were seeded with 75 L of actively digesting sludge collected from (and operated at) the 75th Street Wastewater Resource Recovery Facility (WRRF) in Boulder, Colorado. This is a nitrifying activated sludge plant, incorporating mesophilic anaerobic digestion that treats 10 million gallons of wastewater per day ($37,854 \text{ m}^3/\text{day}$). The four pilot digesters were continuously mixed using peristaltic pumps (Masterflex™ 7540-52; ColeParmer, USA) that forced sludge through inert silicon tubing (Masterflex™ I/P 73 tubing; ColeParmer) to continuously recirculate the digester contents. Temperature in each digester was controlled by electric resistance heating bands (BriskHeat, USA) that covered approximately 40% of the tanks external surface (below sludge line); they maintained the digesting sludge at $32 \pm 2^\circ\text{C}$. The digesters were fed to 7.5 L of thickened sludge (no polymer) to maintain a 30-day solids retention time (SRT). The sludge was introduced through a capped chimney inlet. Headspace gas occupied 25 L above 75 L of digesting sludge that was wasted through a valve centered under the conical bottom of the polypropylene containment. A schematic of the pilot 100 L digesters is shown in Figure 1.

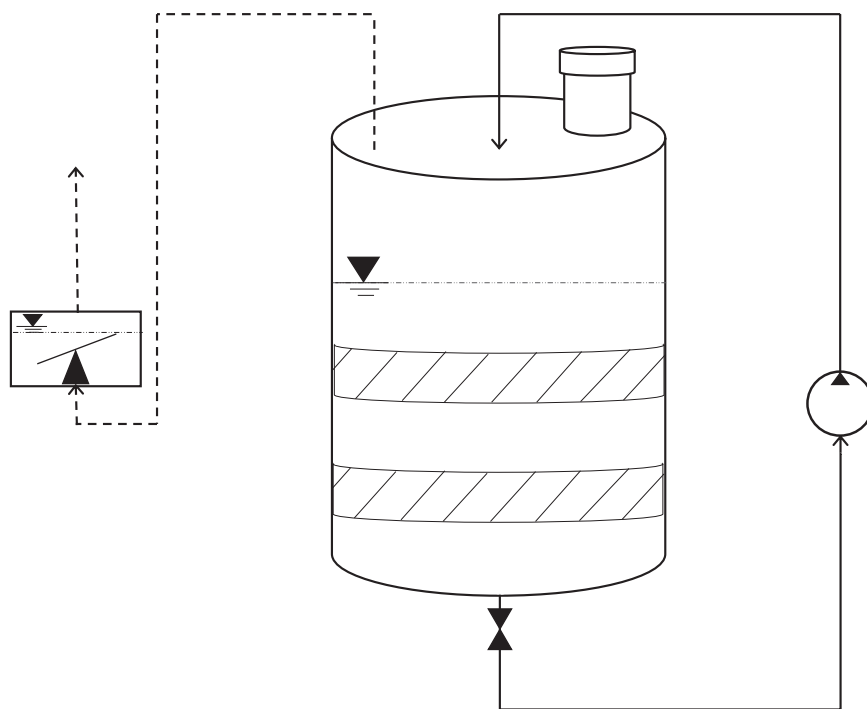


Figure 1. Schematic representation of the 100 L pilot digesters used in this study; 75 L contained actively digesting sludge. Solid arrow represents sludge recirculating flow direction. Dashed lines represent gas effluent from the digester, directed to a wet tip meter to quantify biogas flow. Digesters were heated with two electric resistance heating bands.

Slag characterization

Basic oxygen furnace (BOF) slag was obtained from the Indiana Harbor Steel Mill complex in East Chicago, Indiana, USA. The grain size <1.6 mm mesh size was weighed immediately prior to digester addition. Chemical and mineral composition was obtained by acid digestion, ICP-MS analysis, and powdered XRD analysis. Its major oxide chemistry is presented in Table 1.

As judged by widely accepted leaching potential tests (EPA Method 1311, 1992), the BOF slag used in this study has relatively low potential to release mobile heavy metals in mildly acidic environments (Proctor et al., 2000). Similar observations of BOF steel slags have been reported (Grubb, Wazne, & Jagupilla, 2010; Proctor et al., 2000; Shen & Forssberg, 2003).

Dose-response study

The ability of the BOF slag to sequester phosphates and sulfide from anaerobic digester sludge was investigated through the following dose-response scenario. Batch studies of digesting sludge were first used to determine the kinetic thresholds for BOF to equilibrate with sludge nutrients, in the sieved grain size range used. A timed series of batch tests were executed at different liquid:solid ratios (200:1 ≤ loading ratio ≤ 10:1) to observe the phosphate and sulfide residuals in digesting sludge following BOF slag additions. Batches containing 250 ml of BOF-dosed sludge were continuously mixed at 150 rpm and 30°C for 48 hr. Aliquots were taken at different intervals and analyzed for dissolved phosphates and sulfides. The contact time required for slag particles to equilibrate with dissolved phosphate and sulfide was significantly lower than the operational SRT chosen (30 days). Four pilot digesters were operated under identical conditions to isolate slag dose as the process variable. The following BOF slag dosing rates in the pilot digesters during steady-state operations were used: approximately 1 g BOF/L (Digester 1), 10 g BOF/L (Digester 2), and 50 g BOF-S/L (Digester 3). A fourth digester, with no slag, was used as a control for the duration of the pilot study.

BOF slag was introduced concurrently with raw sludge at the aforementioned doses, for more than a month, after which the systems were considered as acclimated, and steady-state was assumed. Digester performance was assessed at regular time intervals (every 3rd day) by analyzing representative samples of digester sludge and biogas immediately prior to feeding. Including the acclimation period, all pilot digesters operated continuously for more than 160 days. Because of obviously poor digester performance during acclimation, the BOF slag dosing rate to Digester 3 was lowered to from 50 to 20 g BOF/L and the digester stabilized soon thereafter. Following 96 days of operation, the BOF slag dosing rates fed to Digesters 1 and 2 were switched (1 g BOF/L ↔ 10 g BOF/L) in order to confirm that a dose-response effect observed could be replicated

in a sensitive range. Digester performance and nutrient sequestration potential were assessed by the following analyzes: pH, alkalinity, volatile fatty acids, total solids, volatile solids, biogas production, biogas primary composition, soluble phosphate, and sulfide gas concentration.

pH, alkalinity, and volatile fatty acids

Sludge samples from each of the four digesters were immediately analyzed using a SympHony SP70P pH meter, which was calibrated prior to each observation (VWR). Alkalinity and volatile fatty acid (VFA) content was estimated by modifications to the classic method developed by DiLallo and Albertson (1961). Briefly, digester sludge samples (50 ml) were centrifuged at 2500 g for 10 min. Next, the supernatants were recovered, and total alkalinity was obtained by titration to pH 4 with standardized hydrochloric acid (HCl). Next, the pH was lowered between 3.3 and 3.5 and boiled for 5 min to strip CO₂; the same samples were then cooled to room temperature and were backtitrated with a standardized NaOH solution to pH 7. The VFA concentration was obtained using the volume of NaOH added using a correction factor for different VFA levels (DiLallo & Albertson, 1961).

Total soluble phosphate

Supernatants were filtered through a 0.45 μm hydrophilic polycarbonate membrane (HTTP) (MilliporeSigma, USA). The obtained filtrates were diluted in ultrapure deionized water, and phosphate was analyzed by the ascorbic acid reduction method using a TNT 845 Hach kit (Hach Company, USA).

Total and volatile solids

The solids content of the sludge in the respective digesters were determined by the following standard methods: Total solids (TS) were obtained by gravimetric measurements before and after oven-drying known volumes of sludge at 105°C for 8 hr (APHA, 1999). Volatile suspended solids (VSS) were obtained by gravimetric measurements before and after drying/igniting the obtained residues in a muffle furnace at 550°C for 2 hr (APHA, 1999).

Biogas production

For each digester, biogas production was measured by directing the headspace gas into a calibrated, liquid gas trap designed for this purpose (wet tip gas meter; Nashville, TN). This meter includes an internal magnetic-actuator that totalizes incremental volumes of biogas passing through its chambers. The meters were calibrated biweekly as recommended by the manufacturer.

Biogas composition

The biogas composition from the headspace of each pilot digester was regularly monitored for its CH₄ and CO₂ content,

Table 1. Major oxide composition (wt%) of dry granulated basic oxygen furnace slag used in this study

SiO ₂	Al ₂ O ₃	CAO	SO ₄	Fe ₂ O ₃	K ₂ O	Na ₂ O	MGO	MNO	P ₂ O ₅	FREE CAO	
										GRAIN	POWDER
14.7%	6.6%	31.7%	0.4%	25.8%	–	0.1%	10.8%	2.5%	0.7%	0.4%	1.5%

using an Eagle 2 portable gas detector (RKI instruments, USA); H₂S concentration was measured using two different methods; for H₂S concentrations <500 ppm_v, a GasAlert Micro5 IR portable gas detector (BW Technologies, USA) was used. For H₂S concentrations >500 ppm_v, CH29101 Dräger tubes were used (Dräger, Germany). The gas concentrations were corrected for altitude and reported as normalized to standard conditions.

RESULTS

Kinetics determination in batch tests

A timed series of batch tests were executed at different liquid:solid ratios (200:1 ≤ loading ratio ≤ 10:1) to observe the phosphate and sulfide residuals in digesting sludge following BOF slag additions. The results showed that the kinetics of interactions between the BOF slag particles and the soluble phosphates or sulfides is relatively rapid in this context. Soluble phosphates and sulfides equilibrated with the added BOF slag in 48 hr or less, across a broad dose range (Figure 2). These results suggest that slag dosed in a continuous flow scenario would be at equilibration with these nutrients during the SRT ranges through which mesophilic digesters are commonly operated (i.e. weeks).

Pilot-scale performance

Soluble phosphate. The soluble phosphate concentration in response to direct BOF slag addition is shown along with the associated removal efficiency in Figure 3. Analysis of the total soluble phosphate in the digester supernatant revealed a nonlinear dose-response to BOF slag addition. The trend in the average residual phosphate concentration with BOF slag dose followed the following series: Control > 1 g BOF/L > 10 g BOF/L > 20 g BOF/L > 50 g BOF/L. As shown in Figure 4, after 30 days of steady-state operations, the BOF slag fed to Digester 3 was lowered from 50 to 20 g BOF/L; thereafter, the soluble phosphate concentration increased as a consequence. After 66 days of steady-state operation the BOF

slag doses respectively fed to Digesters 1 and 2 were switched: Digester 1, previously fed a steady-state slag dose of 1 g BOF/L, received 10 g BOF/L; and vice-versa for Digester 2. Within one SRT, the phosphate removal associated with the dosing schedule reflected its previous pattern, with the higher slag dose corresponding decreased soluble phosphate level.

Hydrogen sulfide gas. The influence of BOF slag dose on the mass fraction of hydrogen sulfide in digester biogas is summarized along with the associated removal efficiency in Figure 5. Biogas analysis revealed a nonlinear dose-response to BOF slag addition with respect to sulfide sequestration. The ordered average H₂S biogas concentration observed, in response to BOF dose, trended as follows: Control > 1 g BOF/L > 10 g BOF/L > 20 g BOF/L > 50 g BOF/L. As shown in Figure 6, after 30 days of steady-state operations, the BOF slag fed to Digester 3 was lowered from 50 to 20 g BOF/L; thereafter, the biogas hydrogen sulfide concentration increased more than twofold. After switching slag doses fed to Digesters 1 and 2, the sulfide removal associated with the dosing schedule reflected its previous pattern, with the higher BOF slag dose corresponding significantly decreased H₂S concentration.

pH, alkalinity, and volatile fatty acids. The average pH level in all digesters is summarized in Figure 7. With exception to the digester receiving the highest slag dose (50 g BOF/L), the pH remained circumneutral for the other dosing rates (7.20 < pH < 7.41); increased variance was also evident at the highest BOF slag dose. When the dosage was lowered to 20 g BOF/L, the sludge's pH approached the circumneutral values observed in the other digesters. The alkalinity and volatile fatty acid (VFA) content of digesting sludge is shown in Figure 8, along with the associated alkalinity:VFA ratio for each digester. Alkalinity significantly increased with increasing BOF slag dose, from 4,585 mg CaCO₃/L (Control) to 5,877 mg CaCO₃/L (50 g BOF/L). There was no significant difference in VFA levels in digesters receiving slag doses of 10 g BOF/L or lower, including the (control)

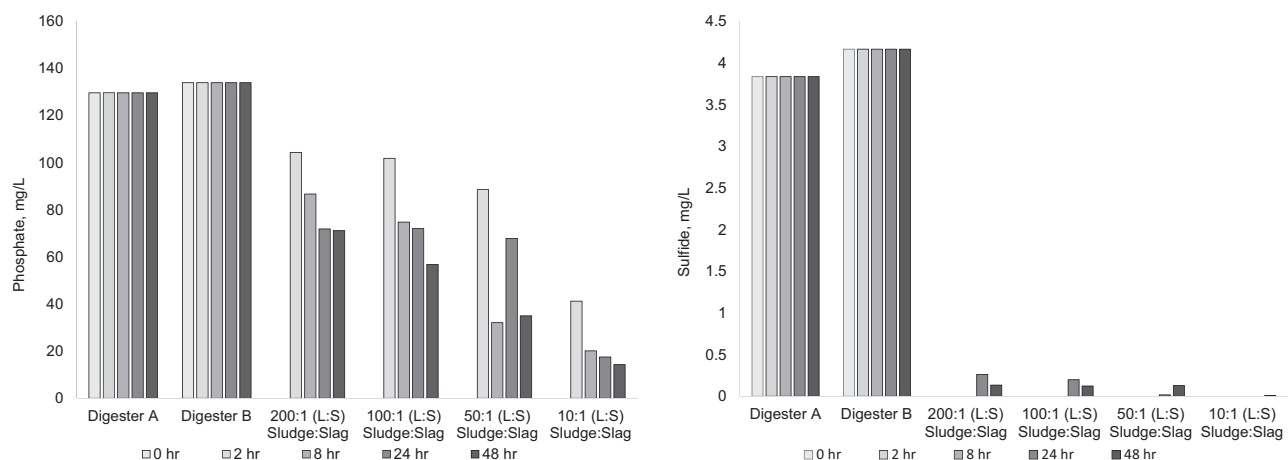


Figure 2. Nutrient concentration after selected time periods in batch observations of BOF slag additions to digesting sludge at different sludge:BOF slag mass ratios: (Left) Soluble phosphate residual; (Right) total sulfide species residual.

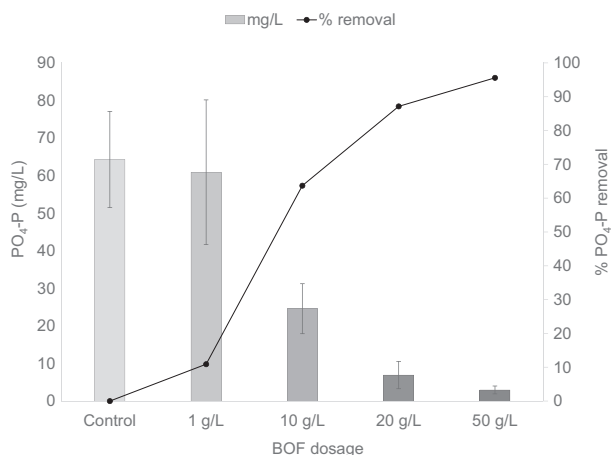


Figure 3. (Left axis) Average soluble PO₄-P concentration in the supernatants of 75 L pilot digesters in response to different BOF slag doses during 160 days of continuous operation. (Right axis) Average soluble phosphate reduction in response to BOF slag addition, with respect to a control digester operated under otherwise identical conditions without BOF slag; soluble phosphate was measured every 3 days. Bar height represents average concentration; error bars represent standard deviation.

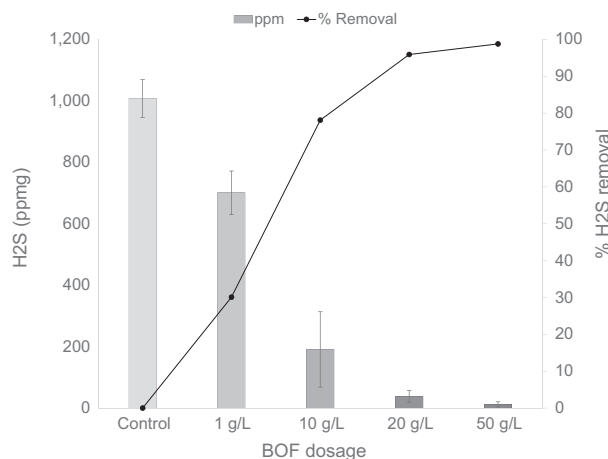


Figure 5. (Left axis) Average hydrogen sulfide concentration in the headspace of 75 L pilot digesters in response to different BOF slag doses during 160 days of continuous operation. (Right axis) Average hydrogen sulfide reduction in response to BOF slag addition, with respect to a control digester operated under otherwise identical conditions without introducing BOF slag; hydrogen sulfide was measured every 3 days.

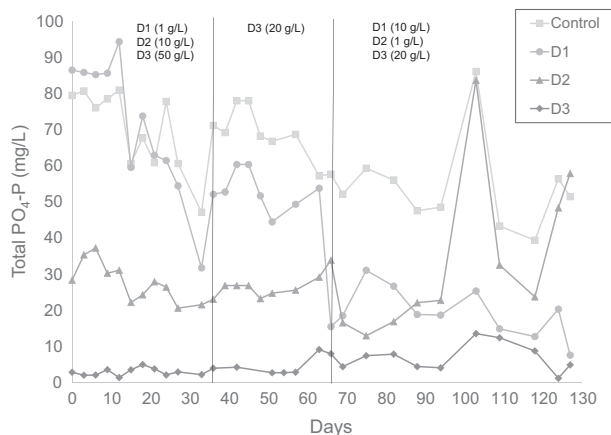


Figure 4. Total soluble phosphate concentration in digesters feed different BOF slag doses. Digesters were maintained at 30-day SRT, and time scale begins after more than 30 days of acclimation. Vertical lines represent dates where dosing scenarios changed. After 36 days of steady-state operations, Digester 3 slag dose was reduced from 50 g to 20 g BOF/L; after 69 days of steady-state operations, the slag doses respectively fed to Digester 1 (1 g BOF/L) and Digester 2 (10 g BOF/L) feeds were switched.

digester (442 mg CaCO₃/L). VFA levels markedly increased in response to slag doses above 10 g BOF/L. Under mesophilic conditions, the ratio of VFA to alkalinity in actively digesting sludge can be indicative of pending fermentation failures; a VFA: alkalinity ratio of 0.3 is widely accepted as a threshold for operational interventions (Fannin, 1987; Wheatley, 1990). This threshold was exceeded in the digester receiving the highest slag dose, but given the propagated variance error, no trends in VFA:ALK response at or lower than 20 g BOF/L were evident.

Biogas production and primary composition. The biogas production rates of the pilot digesters are shown in Figure 9. When compared to the gas emanating from the control digester, there was no significant difference in the biogas volume generated by digesters receiving 10 g BOF/L or less; that rate averaged 4.7 ± 1 L/hr. However, gas production was compromised in the digester receiving the highest slag dose (50 g BOF/L). When the BOF slag fed to Digester 3 was lowered from 50 to 20 g BOF/L the gas production re-stabilized within the range of the other pilot digesters. A result analogous to biogas production was evident when comparing the methane (CH₄) and carbon dioxide content (CO₂) in the digesters headspace (Figure 10). The CH₄ and CO₂ content of gas emanating from the control digester was not significantly different from the biogas composition generated by the digesters receiving 20 g BOF/L or less: that composition averaged 63 ± 2% CH₄ and 34 ± 3% CO₂ by volume. However, in the headspace of the digester receiving the highest slag dose (50 g BOF/L), methane levels averaged below 50%. After 30 days of steady-state operations, the BOF slag fed to Digester 3 was lowered from 50 to 20 g BOF/L; thereafter, the methane content rebounded to the same range as the other pilot digesters.

Total and volatile solids. The total and volatile solids content of the sludge in the pilot digesters is summarized in Figure 11. Compared with the control digester, no significant differences in total solids (TS) content, or its volatile fraction (VSS) were observed in digesters receiving 10 g BOF/L or less; however, above this BOF dose level, increases in average solids content were significant, but did not appear to be proportional to slag mass additions. In digesters receiving at least 20 g BOF/L, the TS increased significantly in response to slag dose, where the variance in the VSS fraction increased markedly as well. Total solids in the digester receiving 20 g BOF/L averaged 26 g/L,

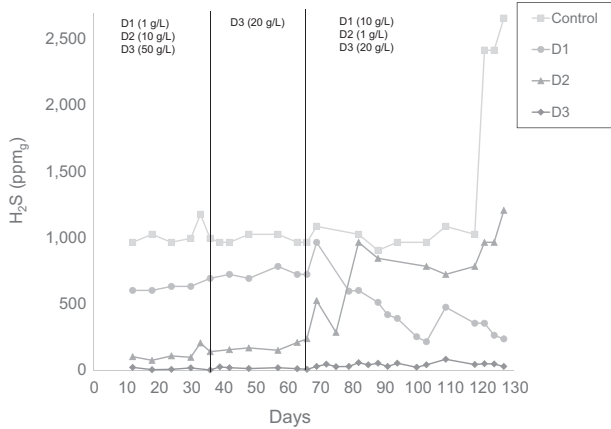


Figure 6. Hydrogen sulfide levels in the biogas generated by digesters feed different BOF slag doses. Digesters were maintained at 30-day SRT, and time scale begins after more than 30 days of acclimation. Vertical lines represent dates where dosing scenarios changed. After 36 days of steady-state operations, Digester 3 slag dose was reduced from 50 g to 20 g BOF/L; after 69 days of steady-state operations, the slag doses respectively fed to Digester 1 (1 g BOF/L) and Digester 2 (10 g BOF/L) feeds were switched.

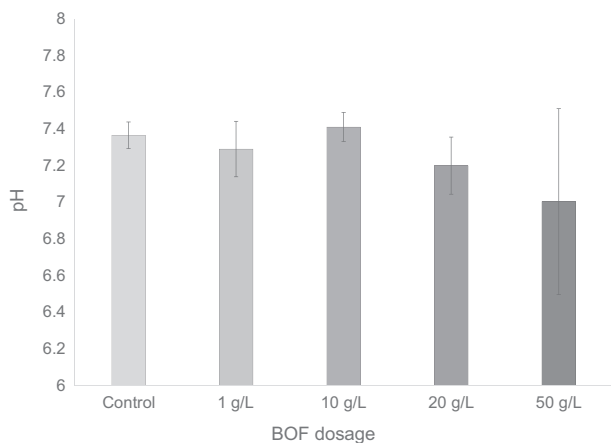


Figure 7. Average pH in digesting sludge contained in 75 L pilot digesters in response to different BOF slag doses during 160 days of continuous operation; pH was measured every 3 days.

with 66% volatile content, while TS in the digester receiving 50 g BOF/L averaged 35 g/L only 40% of which on average, was volatile.

DISCUSSION

The kinetics of phosphate and sulfide interactions (apparent immobilization) with BOF slag particles added to anaerobic digester sludge appeared to be relatively fast compared with common solids retention times. As judged by widely accepted phosphorus analyses, a clear dose-response behavior was observed when sieved BOF slag particles were added to pilot mesophilic digesters operating at a 30-day SRT. With respect to otherwise identical digester operations not

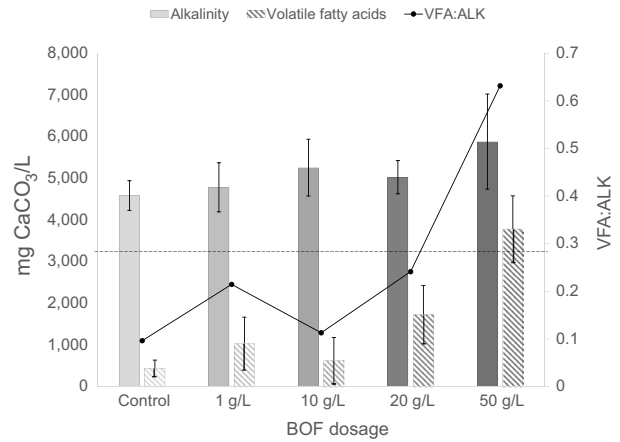


Figure 8. (Left axis) Average alkalinity and volatile fatty acids (VFA) concentration expressed as calcium carbonate mass equivalents in digesting sludge contained in 75 L pilot digesters in response to different BOF slag doses during 160 days of continuous operation. (Right axis) Averaged ratio of VFA to alkalinity in response to BOF slag additions; alkalinity and VFA were measured every 3 days. Bar height represents average concentration; error bars represent SD. The dotted line corresponds to the VFA: alkalinity threshold indicative of pending fermentation failures in mesophilic anaerobic digesters.

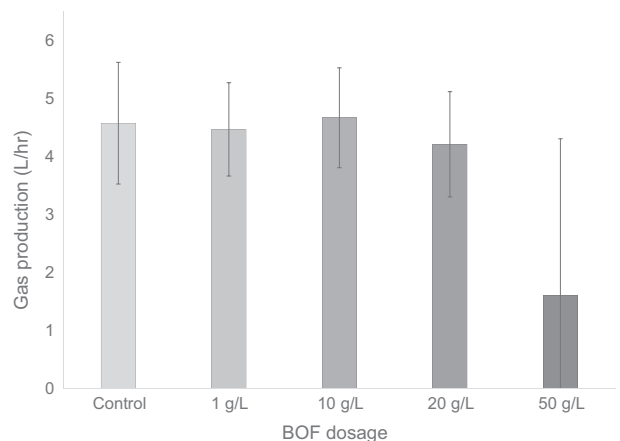


Figure 9. Average biogas production emanating from 75 L pilot digesters in response to different BOF slag doses during 160 days of continuous operation; gas production was continuously measured.

including slag, a steady-state dose of 10 g BOF/L resulted in a 66% reduction in the soluble supernatant phosphate levels. Similar phosphorus reduction levels have been reported by addition approximately 200 mg Al/L (as Aluminum from Alum) and 300 mg Fe/L (as Iron from ferric chloride (Baker et al., 2006)). While a phosphate immobilization mechanism in digester sludge has yet to be identified, candidates likely include partitioning to the iron and calcium containing minerals in BOF slag, which have relatively high specific surface area (Piatak, Parsons, & Seal, 2015; Shi, 2004; Yildirim & Prezzi, 2011). Phosphate immobilization has been comprehensively described as applicable to aqueous environments

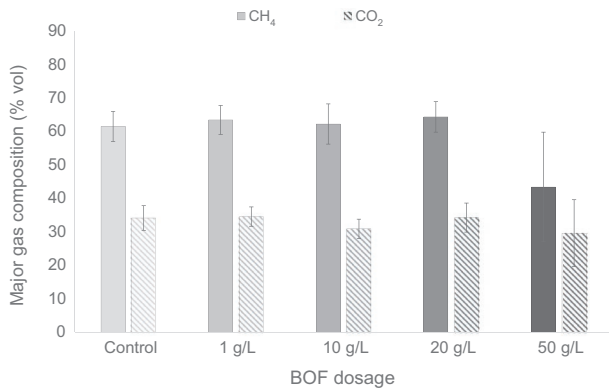


Figure 10. Average methane and carbon dioxide content of biogas emanating from 75 L pilot digesters in response to different BOF slag doses during 160 days of continuous operation; gas composition was measured every 3 days.

(Bowden, Jarvis, Younger, & Johnson, 2009; Johansson, 1999; Johansson & Gustafsson, 2000; Richardson, 1985; Shilton et al., 2006). In digesting sludge, dissolved phosphate may interact with different mineral surfaces and precipitate in or around the BOF slag particles as ferric, ferrous, and calcium phosphates. This mechanism is supported by the observations of Bowden and coworkers (Bowden et al., 2009), who performed continuous flow experiments that challenged columns packed with BOF slag grains with solutions containing phosphate in the range between 1 and 50 mg/L. These researchers reported up to 62% soluble phosphorus removal, the majority of which they ascribed to immobilization on different minerals. X-ray diffraction, SEM, and EDX analysis suggested that metal oxide surfaces were a major phosphate immobilization mechanism when $\text{pH} < 7.5$; but, that calcium phosphate precipitation was the dominant immobilization mechanism when $\text{pH} > 8$. These authors also acknowledge that BOF slag contains significant amounts of magnesium-rich particles, which may interact with dissolved phosphate and ammonia to increase struvite formation potential. Other studies have reported a broad range of specific phosphate immobilization on steel slag grains, up to 5 mg P/g slag (Xue, Hou, & Zhu, 2009), but the conditions of these studies were not well defined in terms of their translational potential to anaerobic digester environments.

A significant dose-response was also observed with respect to the sulfur content of biogas, where a 10 g BOF/L steady-state dosing scenario, prevented 78% of the hydrogen sulfide from reaching the digester headspace (vs. control). It is important to note that a concurrent nutrient reduction effect—both phosphorus and sulfur—was realized from the same BOF slag dose. The reduction in the gaseous concentration of H_2S may be attributed to the sorption of aqueous sulfide species on the surfaces of different mineral phases, reducing the sulfide available to partition in the headspace. The H_2S removal potential observed here, can be compared with the direct dosing of 10 mg/L of reagent grade ferric chloride into anaerobic digesters (Dezham et al., 1988). Different mechanisms have been previously proposed for aqueous

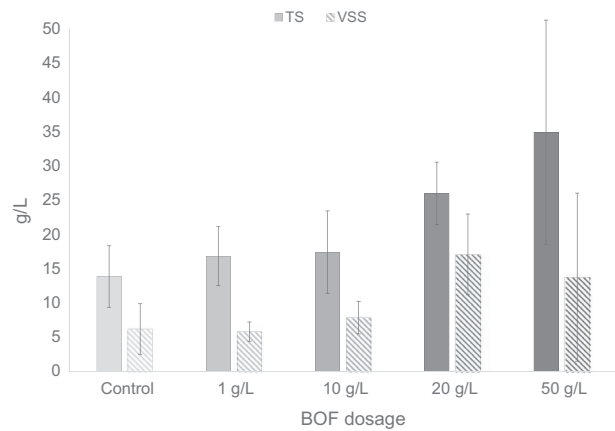


Figure 11. Average solids content of sludge contained in 75 L pilot digesters in response to different BOF slag doses during 160 days of continuous operation; solids content was measured every 3 days.

sulfide immobilization of sulfide on BOF slag solids; this most notably includes surface complexation with Fe and Mn containing mineral phases (Asaoka et al., 2013; Hayashi et al., 2014; Kim et al., 2012). The immobilization potential of sulfide on slags have been reported as high as 38 mg S/g slag (Kim et al., 2012); however, the conditions of these studies were also poorly defined in terms of their translational potential to anaerobic digester environments.

While anaerobic digestion can offer an important control point for sulfur and phosphorus management during wastewater treatment, process alterations cannot compromise fermentation performance or solids reduction. In this context, this study also evaluated slag addition effect on digester pH, alkalinity, volatile fatty acids, total and volatile solids, as well as gas production rates. Stable and customary mesophilic digester performance, regardless of slag amendment included the following characteristics: (a) circumneutral pH; (b) VFA:alkalinity < 0.3 ; (c) 30 L gas produced/kg VSS reduction; and (d) $\text{CH}_4 > 60\%$ gas content. These common digester performance metrics were met by the digesters including 10 or less g BOF/L in their sludge feed. Beyond this augmentation level, one or more of these digester performance thresholds were not sustained—or—the variance became so great, process stability was obviously compromised.

The dose-response patterns observed here suggests that the added BOF slag immobilized soluble phosphate to the degree that it may have become a limiting nutrient to the digesting biomass at the higher applied doses (< 10 g BOF/L). With respect to methanogenic activity, higher slag doses compromised digester performance; this may be attributed to a classic nutrient-limited situation, an inhibitory effect, or both. This is consistent with reports that suggest acute phosphorus limitations can impact methane formation during anaerobic degradation (Britz, Noeth, & Lategan, 1988; Fedorak & Hrudey, 1986; Hussain, Kumar, & Mehrotra, 2015; Parkin & Owen, 1986). BOF slags may also release inhibitory compounds above the thresholds tolerated by the microbial communities responsible

for fermentation—at any step in the process. Elements that are abundant in BOF slag minerals, including calcium, iron, and aluminum have been reported to inhibit methanogenic activity (Chen, Cheng, & Creamer, 2008; Van Bodegom, Scholten, & Stams, 2004).

The BOF slag solids added to the digesters in this study included a conditioning step that segregated maximum grain size below a characteristic length of 1.6 mm. Slag amendment with this grain size distribution “cut off” had a measurable effect on increasing the TS levels in the digesters at or above a 10 g BOF/L dose. It is important to note that this mass dose regimen was based on the dry weight of sieved BOF slag grains and the net digester sludge volume.

Since some of the dry BOF slag solids dissolve in digester supernatant after addition (i.e., liquid phase), any net TS gain is not proportional to the slag dose. While typical solids measurements were observed to assess classic digester performance response, the effects of BOF slag dosing on solids separation potential was beyond the scope of this study. This investigation was limited to assessing selected nutrient sequestration effects; the influence of BOF slag additions on the rheological properties of digesting sludge and associated dewatering characteristics are important considerations for future studies. This was a pilot study focusing on the dose-response window BOF slag fines may frame for the sequestration of phosphate and sulfide from digesting sludge. As with any conventional digester amendment, full-scale implementation of such a nutrient management approach suggests site-specific attention to concomitant effect such fines may have on subsequent solids handling practices.

CONCLUSIONS

We report the first systematic assessment of the effects of BOF slag particles on the concomitant immobilization of dissolved phosphate and sulfide in digesting sludge. When added directly to pilot anaerobic digesters under conditions typical of anaerobic digester environments, a classic dose-response behavior was observed with respect to P and S sequestration, and a clear inhibitory performance threshold was reached. Only a fraction of the BOF slag solids added contributed to the digester TS mass, because a substantial portion dissolved into the supernatant; much of this dissolution contributed to calcium-associated alkalinity. The surfaces of intact BOF slag solids that do not dissolve appear to sequester both phosphates and sulfide in a practically irreversible manner, which has no apparent impact on mesophilic digester performance below a certain dose threshold. It is important to note that this was a pilot-scale demonstration; the BOF slag mass added was weathered and received minimal pretreatment. These results suggest that further value engineering to optimize BOF slag fines for anaerobic digester applications can yield cost-effective benefits with a high probability of success for managing phosphate and sulfide loads in anaerobic digesters. This study demonstrated a new sustainable approach to upcycling BOF slag into a novel nutrient management tool; this approach may also enable or

otherwise complement other beneficial reuse paths that include profitable nutrient recovery and agricultural applications.

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