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# Phosphorus Removal Mechanisms in Active Slag Filters Treating Waste Stabilization Pond Effluent

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Phosphorus (P) removal mechanisms from waste stabilization pond effluent by a melter slag filter were investigated. The studied filter had treated pond effluent for a decade, but lost its P removal efficiency after 5 years. The P distribution in the slag was examined by scanning electron microscopy (SEM), electron dispersive spectrometry (EDS), X-ray fluorescence (XRF), X-ray diffraction (XRD), and chemical fractionation. The results showed the slag to be covered by a film comprising metal oxides/oxyhydroxides, organic resin, and Fe-phosphate precipitates. The slag porous matrix beneath this film hosted lower P concentrations and consisted of metal oxides/oxyhydroxides and calcium-magnesium silicates. The study revealed the following mechanisms for P removal from effluent by the melter slag: (1) P adsorption onto metal oxides/oxyhydroxides which are ubiquitous throughout the porous slag matrix and its surface film; (2) P precipitation, mainly as Fe-phosphates (determined by SEM/EDS) on the surface film, derived from the release of metal ions into the solution phase; and (3) P sequestration by an amorphous organic resin that comprises a substantial proportion of the surface film, which was deduced by SEM/EDS and XRF. Results of chemical extractions performed on the slag demonstrated that 1 M HCl, which has been used to determine Ca-associated P in previous studies, is an unreliable Ca–P marker. By contrast, the citrate–dithionite reagent was shown to be a good indicator of Fe/Al-associated P and revealed that adsorption onto metal oxides/oxyhydroxides, in the porous matrix as well as its surface film, is the most significant P removal mechanism achieved by the slag filter.

## Introduction

Many communities are faced with the problem of removing phosphorus (P) from wastewater. Active filters are gaining popularity as an effective treatment method for P removal. Several materials, including limestone, zeolites, and bauxite, have been assessed for their capacity to sequester P (1). Slag,

a byproduct of the steel industry, has become increasingly recognized for its capability in this regard (2).

There are many varieties of slag, exhibiting varying chemistry owing to the different slag production processes. For example, electric arc furnace (EAF) slag is produced when iron ore and steel scrap are melted in an electric arc furnace with lime (3); EAF slags are typically rich in Fe and Ca (3). Blast furnace (BF) slag is the byproduct of limestone, coke, and iron ore fused at temperatures above 1500 °C (4); BF slag contains high Si and Ca concentrations (5).

Melter slag is a Ti/Al-rich variety common in New Zealand, and is produced when iron sand is converted to melter iron (6). Several studies have demonstrated that melter slag removes contaminants from stormwater and wastewater (2, 6–8). For example, melter slag filters at Waiuku near Auckland, New Zealand, removed 77% of P from wastewater stabilization pond effluent for 5 years, before their P removal efficiency diminished (2). Melter slag filters are also being trialed in farm effluent treatment ponds in New Zealand with documented P removal efficiencies between 54 and 84% (7). However, the causes of P removal variations and performance decline with time remain unclear, because the major P removal mechanisms by the slag have not been established. Indeed, P removal mechanisms by other slag filter types, such as EAF slag and BF slag which have been used to treat effluent (3, 4, 9–12), are also poorly understood.

A number of researchers have interpreted adsorption onto metal oxides/oxyhydroxides on the surface of slag to be a significant P removal mechanism (4, 9–11, 13). Often, the presence of Al and Fe on slag is inferred to represent oxide and oxyhydroxide minerals of these metals, which are renowned for their strong adsorptive capacities (14, 15). However, elemental analyses alone may not accurately verify the occurrence of oxides/oxyhydroxides because the Al and Fe content of slag may be associated with nonoxide minerals, such as silicates. Consequently, studies purporting P adsorption by oxides/oxyhydroxides need to employ additional analytical techniques, such as chemical extractions (3, 4) rather than simply reporting elemental Al, Fe, and total P data to indicate P adsorption.

Other studies have suggested precipitation to be a key P removal process from effluent by slag (11, 12, 16). Baker et al. (16) conducted a study examining the effectiveness of blast oxygen furnace (BOF) slag in capturing P from synthetic effluent. Based on pH data and chemical modeling, the authors concluded precipitation to be the main P removal mechanism achieved by the slag. Additionally, Drizo et al. (11) found P precipitates (as determined by X-ray diffraction) on the surface of EAF slag in contact with synthetic effluent solution for 24 h. However, it should be noted that synthetic effluent does not contain all components occurring in pond effluent which affect P removal (e.g., bacteria, humic substances, organic colloids, competing anions). Indeed, results presented by Shilton et al. (17) showed significant differences in performance between synthetic P solution and real pond effluent.

These few studies presented above represent preliminary investigations into P removal mechanisms by slag. To date, there has been no comprehensive research to account for the various possible P removal mechanisms by slag filters. Drizo et al. (3), point out that the exact mechanisms of P retention by slag “remain uncertain and should be investigated in future studies”. Hence, the aim of this study is to examine P removal mechanisms from effluent by melter slag which had been used in a field-scale filter. Specifically, the study employs a combination of (1) elemental analysis, (2)

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**TABLE 1. Elemental Concentrations in Melter Slag Material as Determined by XRF. Note the Percentages for Each Material do not Add to 100% Because not all Element Contents are Shown (e.g., Si, Na, K, O)**

slag material	sample type	elemental concentration (expressed in wt % of sample material)									
		P	S	Al	Fe	Ca	Mn	Ti	Mg	C <sub>org</sub>	C <sub>carb</sub>
fresh	porous matrix	0.01	0.10	12.02	2.63	10.12	0.83	19.46	8.86	0.09	<0.01
exhausted	porous matrix	0.04	0.05	9.45	1.05	11.96	0.87	20.16	8.25	0.3	<0.01
fresh	surface	0.01	0.11	9.68	2.76	10.83	0.95	21.42	7.98	0.19	<0.01
exhausted	surface	3.37	0.36	3.63	17.24	5.79	1.27	6.85	3.19	8.3	<0.01

scanning microscopy observations, (3) mineralogical analysis by X-ray diffraction, and (4) chemical extractions, to elucidate P removal processes by the slag. An understanding of the relative significance of these mechanisms will aid design and enable progress in enhancing the longevity of slag filters.

## Materials and Methods

**Sample Collection.** Melter slag was obtained from stockpiles at the SteelServ Steel Mill, approximately 50 km south of Auckland, New Zealand. Additionally, exhausted slag was collected from filter beds which had been treating pond effluent for over a decade at the Waiuku Wastewater Treatment Plant, adjacent to the steel mill. There are ten beds at the site. Each bed is approximately 100 m long, 20 m wide, and 0.45 m deep, treating an average daily flow of 2000 m<sup>3</sup>day<sup>-1</sup>, corresponding to a hydraulic retention time of approximately 3 days for the effluent (2). The beds' P removal efficiencies ceased after approximately 5 years (2).

Slag was taken from five locations (four corners and center) on each filter bed. At each location a 0.3 m wide core of slag from the entire depth profile, down to 0.45 m, was exhumed. The exhausted slag from all sampling points was mixed thoroughly on a plastic sheet, to obtain a heterogeneous sample.

**Sample Preparation.** Slag from the steel mill is herein referred to as "fresh" material, as opposed to the "exhausted" slag from the Waiuku filter beds. However, even the fresh slag had undergone some weathering during its exposure to the atmosphere on storage piles. Weathering was indicated by red Fe-rusting on the fresh slag surfaces. Apul et al. (18) note that steel slag weathers immediately upon cooling, owing to a temperature decrease, oxidic conditions, and the presence of atmospheric moisture.

The fresh and exhausted slag was dried at 30 °C for 1 week. Both fresh and exhausted material were observed to be covered by a fine powder, which was separated from the slag by agitating 1 kg of the respective materials in a 75 µm aperture brass sieve for 10 min; after which time, no further powder was observed in the sieve-catch. After removing this surface film, the porous matrix of the fresh and exhausted slag materials were crushed to <75 µm in a mortar and pestle. Overall, 4 bulk samples were obtained for analysis: (1) fresh slag porous matrix; (2) fresh slag surface coating; (3) exhausted slag porous matrix; and (4) exhausted slag surface coating.

**Experimental.** Chemical extractions were performed on the four bulk samples, in order to identify important P host sites. The P bound to Fe and Al oxides/oxyhydroxides was determined by the citrate–dithionite extraction technique described by Rayment and Higginson (19). Citrate–dithionite dissolves the total Fe and Al oxides/oxyhydroxide pool in a sample (20), thereby releasing any associated P.

The organic-bound P fraction was determined using the oxidizing agent H<sub>2</sub>O<sub>2</sub>. According to Tessier et al. (14), organic matter degrades in oxidizing conditions, releasing bound elements into solution. Powdered slag samples (0.1 g of each) were placed in beakers, to which 2 mL of 30% H<sub>2</sub>O<sub>2</sub> was added. The beakers were shaken continuously for 4 h and 18 mL of deionized water was added to each, bringing the solutions to 20 mL.

The Ca-associated P content of the samples was measured using a 1 M HCl extraction (21); where 0.1 g of powdered slag was placed in a beaker containing 5 mL of 1 M HCl, which was shaken for 16 h. The 5 mL solution was diluted with 15 mL of deionized water producing a total volume of 20 mL. The proportions of P extracted by each of these reagents were related back to the total P content of the slag materials, which was determined by X-ray fluorescence spectroscopy (XRF).

All solutions were immediately filtered through 0.45 µm Millipore paper to prevent P readsorption onto the leached powders. The clear extracts were retained for analysis.

**Analysis.** Powders of the four bulk slag samples were analyzed by XRF for their total P, S, Fe, Mn, Ti, Al, Ca, and Mg contents at the SteelServ Laboratory, Glenbrook. The samples were examined for total carbon by measurement of CO<sub>2</sub> gas in a nondispersive infrared (NDIR) gas analyzer following combustion in a Leco furnace at 950 °C. Inorganic carbon (C<sub>carb</sub>) was determined by measurement of CO<sub>2</sub> gas in a NDIR gas analyzer following digestion of the sample in HNO<sub>3</sub> and heating to 250 °C in the Leco furnace. Organic carbon (C<sub>org</sub>) levels in these samples were determined by subtracting C<sub>carb</sub> from total carbon concentrations. Carbon analysis was conducted by Veritec Pty Ltd at Rotorua (Veritec).

Total P in the chemical extracts was measured by ICP optical emission spectrometry (OES) at Veritec. P levels were below the laboratory detection limit (0.01 mg/L) in all blank samples, with the exception of the citrate–dithionite blank (P = 0.64 mg/L). In this instance, the blank P concentration was subtracted from the slag extract sample P levels.

The mineralogy of the four bulk samples was determined using X-ray diffraction (XRD) with a Co Kα; Siemens D5000 X-ray diffractometer and accompanying peak identification software. Scanning electron microscope (SEM) observations and semiquantitative energy dispersive spectrometry (EDS) electron microprobe analyses were conducted on the powders using a Jeol JSM 6500 F with a Moran Scientific V8.5 Multi Channel Analyzer.

## Results and Discussion

**Chemistry and Mineralogy of the Fresh Slag.** Elemental analysis by XRF revealed high Al, Ca, Ti, Fe, and Mg concentrations within the porous matrix of the fresh slag and its surface coating (Table 1). However, the P, C<sub>carb</sub>, and C<sub>org</sub> concentrations in these fresh materials are relatively low (<0.05 wt %, Table 1).

SEM/EDS showed an abundance of amorphous oxide minerals in the fresh slag (Figure S1). The noncrystalline nature of these phases precluded a precise assessment of their mineralogy. These phases are termed "oxides/oxyhydroxides" herein, because the alteration of oxides and silicates to hydrous oxides within the fresh slag, during its period of resting on the stockpiles, cannot be discounted. In addition to these amorphous phases, XRD revealed that the fresh slag porous matrix and surface coating contain crystalline oxides and calc-silicates (Table 2).

A number of researchers have assumed the total Al, Fe, Mg, and Ti content on slag exists as oxides/oxyhydroxides (2, 3, 5, 11, 12, 22). However, none of these investigations

TABLE 2. XRD Results for Slag Samples

slag material	major peaks identified			mineral
	2-theta angle	D-spacing	intensity	
fresh porous matrix	38.97	2.683	100	merwinite: $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$
	(1) 43.1, (2) 52.51	(1) 2.437, (2) 2.023	(1) 91, (2) 88	spinel: $\text{MgAl}_2\text{O}_4$
	29.92	3.467	60	wollastonite: $\text{CaSiO}_3$
fresh surface coating	52.58	2.021	100	native Fe
	(1) 38.94, (2) 39.14	(1) 2.685, (2) 2.672	(1) 69, (2) 65	merwinite: $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$
	(1) 56.12, (2) 29.88	(1) 1.903, (2) 3.472	(1) 64, (2) 52	kennedyite: $\text{Fe}_2\text{MgTi}_3\text{O}_{10}$
	(1) 41.6, (2) 47.7	(1) 2.521, (2) 2.214	(1) 63, (2) 50	geikeilite: $\text{MgTiO}_3$
exhausted porous matrix	39.01	2.681	100	merwinite: $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$
	56.23	1.899	80	reinhardbraunsite: $\text{Ca}_5(\text{SiO}_4)_2(\text{OH})_2$
	35.02	2.975	64	fassaite: $\text{CaMgAlTiSi}_2\text{O}_6$
	35.81	2.911	52	epidote: $\text{Ca}_2\text{Fe}_3\text{SiO}_4(\text{OH})$
exhausted surface coating	(1) 52.33, (2) 52.44	(1) 2.03, (2) 2.026	(1) 100, (2) 88	native Fe
	41.65	2.518	78	ferrospinel: $\text{MgFe}_2\text{O}_4$
	(1) 38.94, (2) 39.13	(1) 2.685, (2) 2.673	(1) 71, (2) 63	merwinite: $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$
	34.86	2.988	65	fassaite: $\text{CaMgAlTiSi}_2\text{O}_6$

conclusively assessed slag's mineralogy. In the present study, SEM/EDS and XRD confirmed that Al, Fe, Mg, and Ti are predominantly present as oxides/oxyhydroxides in the fresh slag material (Figure S1). The verification of the presence of oxides/oxyhydroxides on the slag investigated in this study is an important step in assessing P removal mechanisms, because these minerals adsorb inorganic ions, such as  $\text{PO}_4^{3-}$ , from solution (15). In this regard, this work demonstrates that the fresh melter slag has the potential to remove P from effluent; by physical adsorption, chemisorption, or ion exchange with the Fe oxides/oxyhydroxides.

The Ca concentrations (ca. 10–11 wt %) in the porous matrix and surface coating of the fresh slag (Table 1) are reflective of the presence of calc-silicates, including wollastonite, within these materials (Table 2). Wollastonite has a high adsorption capacity for P (23), but was not observed within the fresh slag porous matrix through SEM/EDS.

The  $C_{\text{carb}}$  results in Table 1 signify a relatively low level of carbonate minerals in the fresh slag, which is further evidenced by the lack of carbonate phases detected by SEM/EDS and XRD. Hence, the Ca content of melter slag is present as relatively insoluble, non-P adsorbing silicates and thus Ca is unlikely to substantially influence P removal from effluent.

This finding is in contrast to results of previous investigations which have proposed that Ca has a significant role in P removal from effluent (5, 11, 13). These studies suggested that  $\text{Ca}^{2+}$  released by slag into solution, forms stable phosphate precipitates, such as hydroxyapatite  $[\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6]$ . However, SEM/EDS observations in this investigation suggested only minor development of Ca/P crystallization on the exhausted slag, as discussed in further detail in the following section. It should be noted that the aforementioned studies (5, 11, 13) have focused on BF and EAF slags, which have higher Ca contents than melter slag. Additionally, BF and EAF slags induce high pH effluent levels (11, 13). By contrast, melter slag does not generate highly alkaline pH in pond effluent (pH 6.7 to 7.4, ref 6). The varying properties of different slag materials merits examination of P removal mechanisms on a slag-by-slag basis. Hence, it would be useful to apply the techniques (SEM, XRD, XRF) adopted in this study, to other slag filter types.

**Chemistry and Mineralogy of the Exhausted Slag.** Table 1 reveals that P is approximately 4× more concentrated in the exhausted slag porous matrix than in the fresh matrix, indicating that the exhausted slag sequestered P from the effluent (Table 1). The  $C_{\text{org}}$  levels of the exhausted slag porous matrix are 3× higher than those of the fresh slag materials (Table 1), a consequence of filter's long-term contact with organic-rich pond effluent. The lower proportions of S and

Fe in the exhausted slag porous matrix relative to the fresh slag matrix, is probably a result of dilution caused by the concentration increase of the other elements (e.g., P and  $C_{\text{org}}$ ).

The mineralogy of the exhausted slag porous matrix is similar to that of the fresh slag porous matrix, consisting mainly of amorphous Al, Fe, and Ti oxides/oxyhydroxides. Calc-silicates were also detected in the exhausted slag porous matrix by XRD (Table 2).

In comparison to the exhausted slag porous matrix, its surface coating is exceptionally rich in P (Table 1). Additionally, this surface coating hosts notably higher S, Fe, Mn, and  $C_{\text{org}}$  levels than the other slag materials (Table 1), suggesting that these elements were sourced from the effluent. In contrast, Al, Ca, Ti, and Mg concentrations in the exhausted slag coating are much lower than their respective levels in the other slag materials (Table 1), again likely due to relative dilution by the accumulated elements, notably Fe, P, and  $C_{\text{org}}$ .

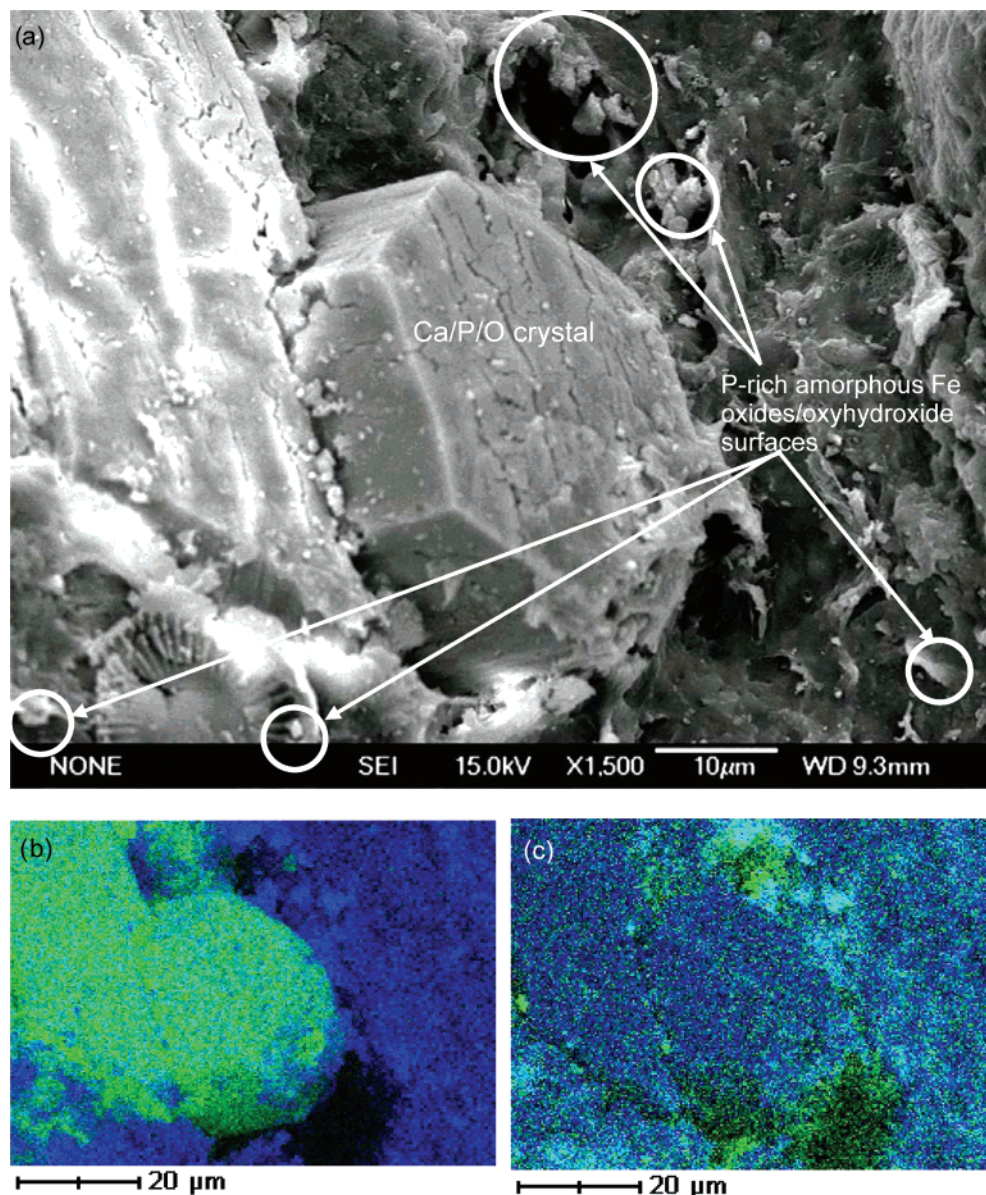
The elemental data in Table 1 suggests that the P removed from the effluent by the slag filters is predominantly sequestered by its surface coating/film, which was readily removed from the exhausted slag porous matrix by agitation after drying. SEM/EDS showed that this surface coating consists of (1) amorphous Fe-oxide/oxyhydroxides (Figure 1), native Fe, and crystalline Fe-oxides (Table 2); (2) Fe/P/O and Ca/P/O precipitates (likely strengite, Figure S2, and hydroxyapatite, Figure 1, respectively); (3) fibers of an amorphous organic resin (Figure 2); and (4) Ca/S/O rich phases, which, based on EDS chemistry and crystal geometry, are most probably gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). EDS mapping of the exhausted slag coating material revealed that P is associated with (1) amorphous Fe oxides/oxyhydroxides (Figure 1); (2) amorphous organic resin (Figure 2); (3) Fe/P/O precipitates (Figure S2), and to a lesser extent, Ca/P/O precipitates (Figure 1); and (4) Ca/S/O precipitates.

Baker et al. (16) used SEM/EDS to examine P distribution in a mixed media filter treating synthetic wastewater. They showed that P was closely associated with a thin Fe oxide coating on the filter grains; a similar relationship to the P and amorphous Fe oxide/oxyhydroxide distribution observed on the exhausted slag material in this study (Figure 1).

**P removal Mechanisms by the Melter Slag Filter.** The above findings point to several interrelated P removal mechanisms from the effluent by the melter slag, described as follows:

(1) Adsorption: Phosphate ions in effluent are removed from solution by adsorption onto amorphous Fe oxides/





**FIGURE 1.** (a) Ca/P/O-rich crystals on amorphous Fe oxides/oxyhydroxides on the exhausted slag surface coating, (b) the light green region defines Ca/P rich zones (i.e., the Ca/P/O crystals, likely hydroxyapatite based on shape and composition), (c) the light blue sections represent Fe/P/O rich phases, likely amorphous Fe oxides/oxyhydroxides (refer to online copy if clarification of colors is needed).

oxyhydroxides which dominate the porous matrix and surface coating of the slag.

(2) Precipitation: Stable Fe/P/O precipitates form on the surface coating of the slag, as do less common phosphates of other cations in the effluent, such as  $\text{Ca}^{2+}$ . These precipitates are restricted to localized regions within the slag material and were not detected by XRD.

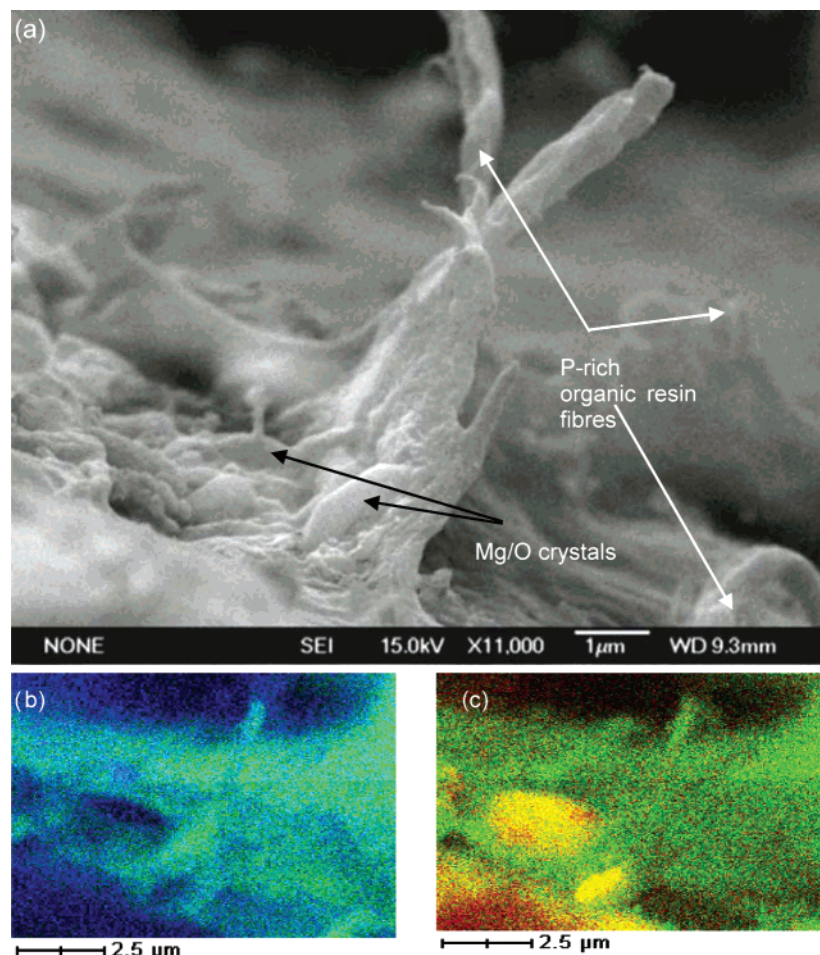
(3) Organic sequestration: Further P is sequestered by an organic-rich resin in the slag surface coating. This resin is likely composed of degradation-resistant humic materials, derived from the nutrient-rich effluent in the filter beds. Humic materials are renowned for their capacity to sequester inorganic ions from solution (24), and humus is a known adsorbent of phosphate (25). Organic capture of P is likely independent of the chemical and mineralogical components of the melter slag; hence, this removal mechanism could be triggered by other filter media with suitable surface and physical properties able to accommodate organic settling.

In addition to the above mechanisms, SEM/EDS provided evidence for P sorption onto Ca/S/O precipitates, most likely gypsum, on the slag surface coating. Gypsum has been noted

as a P sorbent in previous research (26, 27). However, in this study the distribution of Ca/S/O-rich crystals in the coating material was found to be sparse, and no Ca/S phases were detected by XRD.

**Quantifying the Significance of the Removal Mechanisms.** Citrate–dithionite, HCl and  $\text{H}_2\text{O}_2$  were applied to the exhausted slag to remove P associated with different host fractions (Table 3). The citrate–dithionite solution targets P associated with Fe and Al oxides/oxyhydroxides, the  $\text{H}_2\text{O}_2$  dissolves organic-bound P, while the 1 M HCl solution removes Ca-associated P.

The slag porous matrix and surface coating P content is readily liberated by the citrate–dithionite solution (Table 3). This indicates that adsorption onto the amorphous oxides/oxyhydroxides is the most significant P removal mechanism achieved by the slag filters. The citrate–dithionite reagent has been universally acknowledged as a reliable liberating reagent for Fe and Al by various researchers (15, 19–21). Moreover, the presence of P associated with amorphous Fe oxides/oxyhydroxides on the slag was evidenced by SEM/EDS.



**FIGURE 2.** (a) organic fibers coating Mg/O-rich crystals on the exhausted slag coating, (b) EDS map highlighting P-rich regions on the organic material (in aqua blue), (c) yellow regions are Mg/O-rich crystals, likely brucite based on hexagonal geometry and elemental composition given by EDS (refer to online copy if clarification of colors is needed).

**TABLE 3. Proportions of P Removed by Various Reagents Applied to the Slag Materials**

sample type	percentage of total P extracted by various reagents		
	citrate–dithionite	HCl	hydrogen peroxide
exhausted slag	100%	100%	2.5%
porous matrix			
exhausted slag	100%	99.3%	3.5%
surface coating			
calcium phosphate	2%	88%	not measured
rock from Nauru			

To verify that the citrate–dithionite solution did not target Ca–P in the slag samples, a control test was performed where citrate–dithionite and 1 M HCl were added to Ca-rich rock phosphate from Nauru. The extraction procedures were identical to those given in the methods section. The results confirmed that the citrate–dithionite does not target Ca-precipitated P (Table 3), which is the main constituent of the rock phosphate. Still, it should be noted that the citrate–dithionite solution does not necessarily exclusively dissolve Fe and Al oxide/oxyhydroxide minerals. The solution may also dissociate other minerals hosting oxidized Fe (i.e.,  $\text{Fe}^{3+}$ ), such as Fe/P precipitates. However, a study by Willett and Cunningham (28) demonstrated that the reductive dissolution of Fe/P/O precipitates is not achieved as readily as the reductive dissolution of Fe oxides/hydroxides.

The results of the 1 M HCl extraction yielded much higher amounts of P (almost 100%, Table 3) than expected for the

slag which was observed to contain low amounts of soluble Ca carbonates and Ca phosphates, based on XRF, XRD, and SEM/EDS. This finding suggests that the 1 M HCl solution, used to target Ca–P in previous studies (3, 21), is nonselective in removing Ca–P. Olila and Reddy (15), examined P release from Fe-rich lake sediments, and found that 1 M HCl liberated high Fe concentrations. Furthermore, Willett and Cunningham (28) demonstrated that dissolution of Fe-phosphate and the release of P from Fe oxides and hydroxides occurs at low pH. Additionally, Hunger et al. (29) suggested that 1 M HCl can overestimate Ca–P fractions. The pH (<2) of the 1 M HCl solution certainly appears to render it unreliable in solely targeting Ca–P.

In contrast to the results of the citrate–dithionite and HCl extractions, very low amounts of P were liberated from the exhausted slag by  $\text{H}_2\text{O}_2$  (Table 3). This suggests that, although P capture by organic substances occurs within the matrix and surface coating of the exhausted slag, this process accounts for very little overall P removal by the slag filters.

**Implications for Slag Filter Longevity.** The fresh melter slag porous matrix and surface coating consist mainly of amorphous and crystalline oxides/oxyhydroxides; renowned adsorbents of phosphate. Furthermore, visual observation of slag grains revealed that they are vesicular, indicating extremely high surface area and adsorption potential. However, results of this study showed that the exhausted slag matrix's P content is low compared with the P content the surface coating material (Table 1). Additionally, EDS revealed that large areas of amorphous oxide/oxyhydroxide surfaces hosts very little adsorbed P in the exhausted slag



porous matrix. This may be explained by the presence of the organic resin in the slag's surface coating (Figure S3). It is proposed that this resin inhibits removal of further P by the porous matrix by blocking adsorption sites and preventing the release of metal cations from the slag to form P precipitates. This may have contributed to the declining P removal efficiency exhibited by the Waiuku filter (2). It is hypothesised that removal of this surface coating from the exhausted slag may lead to further P uptake, by exposing reactive adsorption sites.

Additionally, it should be noted that the adsorption efficiency of slag may not only be a function of effluent throughput, but might also depend on the weathering of the slag. Chemical alteration of the slag mineralogy potentially produces adsorptive secondary Fe oxide/oxyhydroxide phases. Results of this study clearly demonstrated a different composition of the fresh slag compared with the exhausted material, particularly on the surface coating. In this respect, further research into determining an index of chemical weathering for slag, using methods such as abrasion pH tests (30), should be considered.

Overall, the present study has shown that future slag filter design should consider that adsorption onto metal oxides/oxyhydroxides is the overwhelming P removal process achieved by the material. Hence, in terms of enhancing the longevity of melter slag filters, it is ideal to maximize the exposure of these oxide/oxyhydroxide adsorption sites to waste stabilization pond effluent.

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## Supporting Information Available

Scanning microscopy images of interest to the research paper. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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