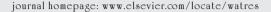


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Phosphorus removal by an 'active' slag filter-a decade of full scale experience

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ABSTRACT

Active filters, which facilitate phosphorus (P) removal via precipitation and/or adsorption, offer a promising 'appropriate technology' for upgrading small wastewater treatment systems. Research on active filters for P removal using steel slag material has been conducted in laboratories across the world, however, field experiments have been limited and long-term data is practically non-existent. This paper presents a decade of experience on P removal by active slag filters at a full-scale treatment plant. During 1993–1994 the filter removed 77% of the total phosphorus (TP), and over the first 5 years of the filter's operation it reduced the mean effluent TP concentration to 2.3 mgl⁻¹. However during the sixth year of operation P removal was significantly reduced. Over the 11 years of monitoring, 22.4 tonnes of TP was removed by the filter, 19.7 tonnes of this in the first 5-year period. It was determined that the slag material maintained its maximum removal potential until reaching a P-retention ratio of 1.23 kg TP per tonne of slag. This paper provides the first long-term field data for slag filters, and shows that they can provide P removal for a half a decade before filter replacement/rejuvenation is required.

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1. Introduction

Throughout the world, small communities and agriculture rely heavily on the use of waste stabilisation ponds and/or wetland wastewater treatment systems. While upgrading to remove nutrients is the focus of intense research activity for other wastewater treatment technologies, such as activated sludge, pond and wetland systems are poorly studied in this regard. The reality facing tens of thousands of small communities and farms is that in the future, discharge permits will be conditional on achieving high levels of nutrient removal (Geary and Moore, 1999; Shilton et al., 2005). Phosphorous (P), in particular, is a major concern as

both ponds and wetlands cannot consistently remove it to satisfactory standards. While technologies such as chemical dosing and/or activated sludge (configured for enhanced biological P removal) can be 'added-on' after a pond or wetland to achieve P removal, these technologies are simply not affordable or 'appropriate' for most pond and wetland applications. For example, it has been noted that the cost of chemical addition and the problems associated with the chemical build up in pond sediments makes this technology unfavourable as a long term, sustainable solution (Crites and Reed, 2002). Ideally, an appropriate solution would mimic the key attributes of ponds and wetlands in being relatively simple and inexpensive to operate, requiring no electrical or

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mechanical equipment, while still being robust and effective in treatment performance.

Subsurface flow wetlands and rock filters for polishing pond effluent are well-established technologies that can provide high-quality effluents in terms of BOD and solids. However, as the need for P removal has intensified, various studies have investigated using different types of filter media as a means of upgrading for higher P-removal efficiency. The term 'active filter' has been coined for such applications where, in addition to the physical straining, the filter media has other physico-chemical properties that facilitate P removal.

To date research on the active filter concept has predominantly focused on wetland systems (Mitchell, 1978; Roser et al., 1987; Bavor et al., 1989; Davies and Hart, 1990; Green and Upton, 1994; Mann, 1997; Johansson, 1999; Drizo et al., 1999, 2002; Arias et al., 2001, 2003; Del Bubba et al., 2003; Forbes et al., 2004). Recently, but to a lesser extent, the idea of using active filters to upgrade waste stabilisation pond effluent has been explored (Strang and Wareham, 2002; Shilton et al., 2005).

Research has been undertaken to assess various media for a range of properties including: hydraulic conductivity; porosity; granulometry; specific surface area and Fe, Al or Ca content (Zhu et al., 1997; Mann, 1997; Drizo et al., 1999, 2002; Johansson, 1999; Del Bubba et al., 2003). In particular, such work has pointed to adsorption and/or precipitation via complexation with Fe, Al, or Ca and Mg ions as potentially being the main mechanisms contributing to P removal for the various materials (Richardson, 1985; Steiner and Freeman, 1989; Mann, 1997; Johansson, 1999; Drizo et al., 2002). Studies of the physicochemical properties of 57 different potential filter media found that electric arc furnace (EAF) slag had the highest P-retention capacity (Forget et al., 2001; Drizo et al., 2002).

The emergence of steel slag media as one of the preferred media for 'active filters' has lead to a number of batch/ column experiments to assess the slag's P-removal capacity (Yamada et al., 1986; Mann, 1997; Johansson, 1999; Forget et al., 2001; Gruneberg and Kern, 2001; Shilton et al., 2005), but published data from full-scale applications of slag filters has been very limited for wetlands and is non-existent for pond applications.

While there is some potential for engineers in the ponds area to draw from previous work published on wetland treatment systems there is a potential risk in this as the wetland and pond environments have several different characteristics. For example, pond effluent contains high concentrations of algae, which can significantly elevate of the pH of the pond water due to their consumption of carbon dioxide. In spite of the limited research, the pressure to upgrade pond systems for P removal is so pressing that slag filters are already being installed in some full-scale applications (Bourke et al., 2005).

In the early 1990s, filters were constructed for 'polishing' pond effluent from a community near a steel mill in New Zealand. Because it was cheaply available these filters were constructed from steel slag. Back at that time it was never intended that these filters should provide P removal, but they did. This paper presents over a decade of field data of P

removal by steel slag filters treating effluent from a full-scale pond system. This represents the most long-term data ever reported for any type of active filter application.

2. The Waiuku Wastewater Treatment Plant

The Waiuku Wastewater Treatment Plant, located in Waiuku township near Auckland, New Zealand, was established in 1971 to treat wastewater from a population of nearly 6000. The plant consists of a primary facultative pond (surface area 6.5 ha) receiving the raw wastewater, and a second stage maturation pond (surface area 1.3 ha). In 1993, the plant was upgraded by the addition of filter beds filled with steel slag.

A 'melter' slag was used for the filter media. This media is a waste product from a nearby steel mill, New Zealand Steel (Glenbrook), and was selected based on its low cost, source close to the site, high porosity and high surface area to volume ratio. The slag has a bulk density of 1.37 g/cm³, a bulk porosity of 45% and had a grain size of '20/10' meaning the nominal top size was 20 mm and the nominal bottom size was 10 mm. The chemical composition of the slag is shown in Table 1.

There are 10 slag filters in parallel at the treatment plant. Each filter is $29.6\times97.4\,\mathrm{m}$ and in total cover $28,830\,\mathrm{m}^2$. The filter depth is $0.5\,\mathrm{m}$, although at average flow the water depth in the filters is only $0.45\,\mathrm{m}$. The flow is distributed at one end through perforated pipes at the filters surface and then flows through the $29.6\,\mathrm{m}$ width of the filter to be collected by a buried pipe at the other end of the bed. The filters treat an average daily flow of $2000\,\mathrm{m}^3\,\mathrm{day}^{-1}$, with a range of $1500-4500\,\mathrm{m}^3\,\mathrm{day}^{-1}$ in summer and winter. Taking into account the porosity and the 'wetted' active depth, at average daily flow the hydraulic retention time (HRT) of the effluent in the beds is approximately 3 days.

The treatment plant effluent has been monitored fortnightly for a range of parameters including total phosphorus (TP) since September 1993. The influent to the filters was also monitored for an entire year when the filters were established (1993–1994) and then again recently (2002–2003). Samples were taken between 1000 and 1130 h on the same weekday from the sampling points indicated in Fig. 1. All methods were in accordance with APHA 'Standard Methods' 18th Edition 1992.

3. Results

Figure 2 shows the effluent monitoring of TP leaving the filters over an 11-year period. The trendline represents a 4-week moving average. During the first 5 years (1993–1998) of operation the slag filters provided good P removal producing an average TP effluent concentration of $2.3\,\mathrm{mg}\,\mathrm{l}^{-1}$ over this time. However, from late 1998 this effectiveness was lost. The data also shows a seasonal fluctuation.

It can be determined from the mean concentrations given in Table 2 that the filters reduced the TP by 77% in 1993 but by 2003 the average effluent TP concentration was actually slightly higher than the influent concentration. Table 2 also presents average concentrations for nitrogen and solids in

| Table 1 - Comparison of New Zealand steel melter slag and other blast furnace slag chemical composition, % by w | reight |
|---|--------|
| (Kvatch et al., 2005 in Bourke et al., 2005) | |

| Constituent | Chemical | New Zealand | Blast furnace ASA data (after weathering) ^a | National Slag Association ^b | |
|-----------------|---|-------------|--|--|---------|
| | formula steel (Glenbrook) melter slag | (Glenbrook) | | Mean | Range |
| Calcium oxide | (Cao) | 15.9 | 41 | 39 | 34–43 |
| Silicon dioxide | (SiO ₂) | 12.4 | 35 | 36 | 27-38 |
| Iron oxide | (Fe ₂ O ₃) | 2.61 | 0.7 | 0.5 | 0.2-1.6 |
| Aluminium oxide | (Al ₂ O ₃) | 18.3 | 14 | 10 | 7–12 |
| Magnesium oxide | (MgO) | 13.4 | 6.5 | 12 | 7–15 |
| Manganese oxide | (MnO) | 1.15 | 0.45 | 0.4 | 0.2-0.8 |
| Titanium oxide | (TiO_2) | 35.3 | 1 | * | * |
| Potassium oxide | (K ₂ O) | * | 0.3 | * | * |
| Vanadium oxide | (V ₂ O ₅) | 0.22 | < 0.05 | * | * |
| Sulphur | S | 0.10 | 0.6 | 1.4 | 1.0–1.9 |

^{*} Constituents not specified

^b US National Slag Association (1985)

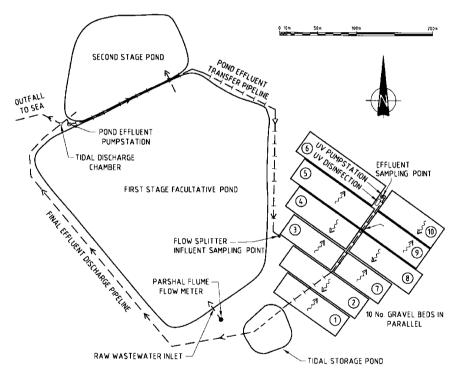


Fig. 1 - The Waiuku Wastewater Treatment Plant.

these two periods. Since these other parameters are reasonably consistent then it seems that the loss of TP removal efficiency is not simply because of some unexpected change in the wastewater characteristics over this time.

By simple mass balance (using an average influent TP of $8.4\,\mathrm{mg}\,\mathrm{l}^{-1}$) it can be determined that for the first 5 and full 11-year periods, respectively, the mass load of TP applied to the filters was 27.6 and 60.7 tonnes, while the outputs from the filters were 7.9 and 38.3 tonnes. This means that of the 22.4 tonnes of TP that was removed by the filters during the

full 11-year period, 19.7 tonnes was retained during the first 5 years.

Figure 3 shows the cumulative P addition to the filters plotted against the P retained (both expressed as ratios to the total weight, 17,770 tonnes, of the 'wetted' slag). The dotted lines labelled 1–11 mark the number of years of cumulative P addition

This analysis shows a clear linear trend for just over 5 years up to approximately 1.7 kg TP tonne⁻¹ slag of 'P added', which corresponds to a P-retained ratio of 1.23 kg TP tonne⁻¹ slag.

^a Australasian Slag Association (2002)

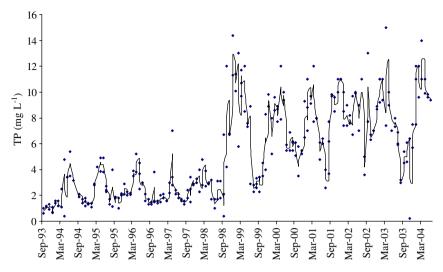


Fig. 2 - Total Phosphorus (TP) levels from slag filters effluent in Waiuku Treatment Plant.

Table 2 – Annual means for total phosphorus, ammonium, suspended solids, and total inorganic nitrogen for the performance periods of 1993–1994 and 2002–2003

| Annual mean (mgl^{-1}) | 1993- | 1993–1994 | | 2002–2003 | |
|--|--------------|---------------|--------------|---------------|--|
| | Influent | Effluent | Influent | Effluent | |
| Total phosphorus (TP) | 8.2 (7.6) | 1.9 (1.2) | 8.6 (0.6) | 8.9 (1.7) | |
| Ammonium (NH ₄ ⁺ -N) | | 11.4 (4.8) | | 10.9 (6.8) | |
| Total inorganic nitrogen (TIN) | | 10.4 (6.4) | | 11.0 (6.5) | |
| Suspended solids (SS) | | 15.9 (9.7) | | 11.8 (2.6) | |

The number in parentheses is the standard deviation and the number of samples analysed in each case was 24.

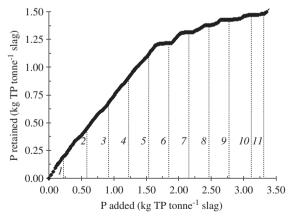


Fig. 3 – The relationship between added and retained P (kg TP tonne⁻¹ slag) during 1993–2004.

Beyond this point the rate of P retention decreases and even ceases for short periods, although, overall during this latter 6-year period some further, but limited, P retention is still obtained.

4. Discussion

Shilton et al. (2005) used exactly the same slag material in a field-based, column experiment treating domestic pond effluent in a different region of New Zealand and over a 6-month period found the filter achieved an average PO₄ removal efficiency of 72%. Their result obtained in the field compares very closely with the 77% TP removal efficiency obtained over the initial 5-year period by the Waiuku filters. To put these results in a broad context, ponds alone are only capable of reliability achieving around 35% P removal. However, if an active filter can be added to remove a further 77%, then this increases the P-removal capacity of the overall treatment system to a respectable 85%.

Being able to predict the longevity of the filters P-removal capacity is important for assessing the financial feasibility of active filter technology. The P-retention ratio of 1.23 kg TP tonne⁻¹ slag derived in the previous section is therefore an important key design parameter as it links filter size (and cost) to mass P removal (efficiency over time). For other filter materials a reliable laboratory-based method is needed for predicting longevity of filters (Drizo et al., 2002). While there

has been some important progress in this regard, to date, there are still some anomalies in the literature particularly when relying on batch experiments. For example, data from a 'field' active filter for P removal using a calcite material showed a tenfold lower P retention then previously estimated from laboratory batch experiments (Arias et al., 2003; Brix et al., 2001). Of the previous literature published on active filter longevity, perhaps the most relevant to the New Zealand melter slag material is the work on electric arc furnace (EAF) slag produced in Quebec, Canada (Drizo et al., 2002; Forget et al., 2001; Lospied, 2003). At a HRT of 24h, the Canadian EAF yielded a saturation value of 3.65 kg P tonne⁻¹ slag. However, for estimating the life expectancy of a full-scale system, the researchers recommended that the ratio obtained from the laboratory experiments using synthetic solution should be reduced to an estimated value of 1.18 kg TP tonne⁻¹ slag due to the absence of organic matter, solids and other impurities that are present in a real effluent (Drizo et al., 2002). Although, the slag materials studied in Canada and New Zealand are produced by different steel making processes and do have somewhat differing chemical compositions, it was interesting to observe that both slag materials showed similar Psaturation potential (1.18 kg TP tonne⁻¹ slag for the Canadian EAF slag as compared to 1.23 kg TP tonne⁻¹ slag for the New Zealand melter slag material).

The Waiuku data showed a clear decrease in efficiency after the first 5-year period. Loss of significant P-removal efficiency after a period of time is to be expected if precipitation and/or absorption mechanisms are predominantly responsible for the P removal (Johansson, 1999; Drizo et al., 1999; Drizo et al., 2002; Arias et al., 2001). Through the 11 years of data seasonal fluctuation in effluent P concentration is seen and this may be due to temperature effects on the physico-chemical removal mechanisms. Alternatively, it could be due to spring growth of the ponds algal population resulting in elevated pH of the pond water and thus improved precipitation within the filter. As mentioned previously, elevated pH occurs in wastewater stabilisation ponds during periods of strong algal growth as the algae removes CO₂ faster than it is replaced. Shilton et al. (2005) also identified that higher temperatures and the presence of algae improved slag filter performance in laboratory studies. Clearly rigorous studies into the mechanisms of P removal in active filters is still needed to fully understand these systems and optimise their design and such work is currently underway at Massey University, New Zealand and the University of Vermont in the USA.

5. Conclusions and recommendations

- During 1993–1994, the Waiuku filters removed 77% of the TP and during the first 5 years of the filters operation they proved effective at reducing the mean effluent TP concentration down to 2.3 mgl⁻¹.
- Over the 11 years of monitoring, 22.4 tonnes of TP was removed by the filter, 19.7 tonnes of this was removed in the first 5-year period.
- The filters performed well for this initial 5-year period after which their performance markedly declined, this lost of maximum removal efficiency corresponded to the filters

- reaching a P-retention ratio of 1.23 kg TP tonne⁻¹ of slag material
- Active filters are simple, effective and robust making them ideal as an 'appropriate technology' for upgrading P removal after pond systems.
- Future research is recommended in terms of refining a methodology for predicting filter longevity and for improving the design and understanding of the filter removal mechanisms.

This paper provides the first long-term field data for slag filters, and in this application shows that they can provide good quality P removal for a half a decade before filter replacement or rejuvenation is required.

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REFERENCES

- Arias, C.A., Del Bubba, M., Brix, H., 2001. Phosphorus removal by sands for use as media in subsurface flow constructed reed beds. Water Res. 35 (5), 1159–1168.
- Arias, C.A., Brix, H., Johansen, N.H., 2003. Phosphorus removal from municipal wastewater in an experimental two-stage vertical flow constructed wetland system equipped with calcite filter. Water Sci. Technol. 48 (5), 51–58.
- Australasian Slag Association, 2002. A Guide to the Use of Slag in Roads Revision 2. Australian Slag Association Inc., Wollongong, NSW 2500, Australia.
- Bavor, H.J., Roser, D.J., Fisher, P.J., Smalls, I.C., 1989. Performance of solid-matrix wetland systems, viewed as fixed-film bioreactors. In: Cooper, P.E., Findlater, B.C. (Eds.), Constructed Wetlands in Water Pollution Control. Pergamon Press, Oxford, pp. 646–656.
- Bourke, W., Bilby, S., Hamilton, D., McDowell, R., 2005. Recent water improvement initiatives using melter slag filter materials. EnviroNZ05 Conference, Auckland, New Zealand, 28–30 September, 2005.
- Brix, H., Arias, C.A., Del Bubba, M., 2001. Media selection for sustainable phosphorus removal in subsurface flow constructed wetlands. Water Sci. Technol. 44 (11–12), 47–54.
- Crites, R.W., Reed, S.C., 2002. Land Treatment Systems for Municipal and Industrial Wastes.
- Davies, T.H., Hart, B.T., 1990. Reed bed treatment of wastewaters in a pilot-scale facility. In: Cooper, P.E., Findlater, B.C. (Eds.), Constructed Wetlands in Water Pollution Control. Pergamon Press, Oxford, pp. 517–520.
- Del Bubba, M., Arias, C.A., Brix, H., 2003. Phosphorus adsorption maximum of sands for use as media in subsurface flow constructed reed beds as measured by the Langmuir isotherm. Water Res. 37, 3390–3400.
- Drizo, A., Frost, C.A., Grace, J., Smith, K.A., 1999. Physicochemical screening of phosphate-removing substrates for

- use in constructed wetland systems. Water Res. 33 (17), 3595–3602.
- Drizo, A., Forget, C., Chapuis, R.P., Comeau, Y., 2002. Phosphorus removal by EAF steel slag—a parameter for the estimation of the longevity of constructed wetland systems. Environ. Sci. Technol. 36, 4642–4648.
- Forbes, M.G., Dickson, K.R., Golden, T.D., Hudak, P., Doyle, R.D., 2004. Dissolved phosphorus retention of light-weight expanded shale and masonry sand used in subsurface flow treatment wetlands. Environ. Sci. Technol. 38, 892–898
- Forget, C., Drizo, A., Comeau, Y., Chapuis, C.P., 2001. Élimination du phosphore d'effluents de pisciculture par marais artificiels à substrat absorbant. Américana 2001 Conference, Montréal (Québec), Canada, 28–30 March, 2001.
- Geary, PM., Moore, JA., 1999. Suitability of a treatment wetland for dairy wastewaters. Water Sci. Technol. 40 (3), 179–186.
- Green, M.B., Upton, J., 1994. Constructed reed beds: a cost effective way to polish wastewater effluents for small communities. Water Environ. Res. 66 (3), 188–192.
- Gruneberg, B., Kern, J., 2001. Phosphorus retention capacity of iron-ore and blast furnace slag in subsurface flow constructed wetland. Water Sci. Technol. 44 (11–12), 69–75.
- Johansson, L., 1999. Blast furnace slag as phosphorus sorbents—column studies. Sci. Total Environ. 229, 89–97.
- Kvatch, I., Patrick, J., Herrington, P., 2005. Environmental Impact Assessment of Melter Slag Used in Road Construction. OPUS Consultants Central Laboratories Report 5-21078.00.
- Lospied, C., 2003. Évaluation des capacités et des conditions d'enlèvement du phosphore dissous par les scories d'aciéries. M.Sc. Thesis, Ecole Polytechnique, Montreal, Canada.

- Mann, R.A., 1997. Phosphorus adsorption and desorption characteristics of constructed wetland gravels and steelworks byproducts. Austr. J. Soil Res. 35, 375–384.
- Mitchell, D.S., 1978. The potential for wastewater treatment by aquatic plants in Australia. Water (Australia) 5 (3), 15–17.
- Richardson, C.J., 1985. Mechanisms controlling phosphorus retention capacity in freshwater wetlands. Science 228, 1424–1427.
- Roser, D.J., McKersie, S.A., Fisher, P.J., Breen, P.F., Bavor, H.J., 1987. Sewage treatment using aquatic plants and artificial wetlands. Water (Australia) 14 (3), 20–24.
- Shilton, A., Pratt, S., Drizo, A., Mahmood, B., Banker, S., Billings, L., Glenny, S., Luo, D., 2005. 'Active' filters for upgrading phosphorus removal from pond systems. Water Sci. Technol. 51 (12), 111–116.
- Steiner, G.R., Freeman, R.J., 1989. Configuration and substrate design consideration for constructed wetlands wastewater treatment. In: Hammer, D.A. (Ed.), Constructed Wetlands for Waste Water Treatment: Municipal, Industrial and Agricultural. Lewis Publishers, Boca Raton, Florida, pp. 499–508.
- Strang, T.J., Wareham, D.G., 2002. Phosphorus removal in a waste stabilization pond system with limestone rock filters. Conference Papers of the fifth IWA International Specialist Group Conference on Waste Stabilisation Ponds. Auckland, New Zealand.
- US National Slag Association, 1985. http://www.tfhrc.gov/hnr20/recycle/waste/.
- Yamada, H., Kayama, M., Saito, K., Hara, M., 1986. A fundamental research on phosphate removal by using slag. Water Res. 20, 547–557.
- Zhu, T., Jenssen, P.D., Maehlum, T., Krogstad, T., 1997. Phosphorus sorption and chemical characteristics of lightweight aggregates (LWA) potential filter media in treatment wetlands. Water Sci. Technol. 35 (5), 103–108.