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Up-scaling of oxidation and accretion reactors: engineering and economic considerations

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Abstract

Discharging mine waters can be treated actively, passively or by a combination of both treatment methods. The main aims of this research are to illustrate the design procedure for sizing an ochre accretion treatment scheme, and compare the costs of such a treatment with the costs of aerobic wetlands.

The research presented below shows that surface catalysed oxidation of iron may be an alternative option to the installation of wetlands. However, this option depends on the value of the land available and on a mine water discharge that is alkaline with low iron loadings. It is argued that this technology is most suitable for the polishing of discharge and not the gross treatment for a discharge with significant iron loadings.

However, it is important to consider that ochre accretion can be rapid and subsequent ochre accumulation may inhibit the effectiveness of the distribution system, reducing the effectiveness of this technology. Therefore, in designing a treatment system it may be prudent to consider a larger size reactor which would reduce the clogging effect of ochre accretion and allow for the reduction in reactor performance due to uneven discharge application over the surface media.

Key words: adsorption, mine water, reactors, remediation, oxidation

INTRODUCTION

Mine water discharges typically exhibit a range of iron and sulphur concentrations. The principal cause of the iron concentrations is the mineral pyrite which is present in strata worked for the extraction of coal. The oxidation of pyrite is an acid generating process (Eq. 1).

$$FeS_2 + \frac{7}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad \text{(Eq. 1)}$$

Discharging mine waters can be treated actively or passively. Active treatment involves continuous input into the treatment system and generally involves the addition of chemicals and/or electricity for pumping to reduce the contaminant loadings. For iron removal lime dosing is often used to raise the pH and thus increase the rate of Fe(II) oxidation and subsequent precipitation as iron oxyhydroxide. Aeration will also assist O_2 transfer for the oxidation of Fe(II) to Fe(III) and its subsequent precipitation of ochre. Passive treatment with wetland requires no ongoing input of energy or chemicals but often requires large areas of land to remove the iron concentration to below a suitable level**.** When sufficient land is available then mine waters have been successfully treated using such passive systems. Younger (2000) suggests that there are six types of passive treatment systems consisting of: (1) aerobic surface flow wetlands; (2) anaerobic compost wetlands with significant surface flow; (3) mixed compost limestone systems SAPS (**S**uccessive **A**lkalinity **P**roducing **S**ystems); (4) subsurface reactive barriers; (5) closed-system limestone dissolution systems; and (6) roughing

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filters. Younger (2000) illustrates the large areas of land required by suggesting that for a flow of 1536 L min^{-1} from a mine water discharge with an initial inflow of 58171 g d^{-1} of Fe (26.3 mg L^{-1}), 5800 m^2 of aerobic wetland is required to achieve compliance with regulatory emission standards.

The sixth method of passive mine water treatment discussed by Younger (2000) – roughing filters – was successfully used by Best and Aikman (1983) in the early 1980s. This technology is the subject of this study and involves surface oxidation and precipitation of iron, a process we term ochre accretion. This system consisted of a simple treatment method where emerging mine water was allowed to discharge evenly over a cascade of steps and into a brushwood filter allowing ochre accretion and reducing 82% of the dissolved iron (Best and Aikman 1983). Ochre accretion occurs due to the adsorption of aqueous Fe(II) species present in a mine water discharge, onto an ochre surface, with subsequent rapid catalytic oxidation of adsorbed Fe(II) by dissolved O_2 and surface precipitation as a sparingly soluble Fe(III) mineral phase. The reaction is irreversible under oxic conditions and allows the transformation of adsorbed Fe(II) to freshly formed iron oxyhydroxide (Burke and Banwart 2002).

The choice of treatment technology is dependent on the influent chemistry, the land available to develop the treatment facility and the available resources. Often discharges that have high iron loadings have to be treated actively or large areas of land are required for wetland development. Mine water discharges that have low iron concentrations i.e. < than 5 mg L^{-1} can be treated effectively with a reduced wetland or if insufficient land is available, then reactors for ochre accretion can be used.

The main aims of this research are to illustrate the design procedure for sizing an ochre accretion treatment scheme, and compare the costs of such a treatment with aerobic wetlands. The specific objectives are to:

1. Apply existing design curves in order to select appropriate reactor sizes based on iron loadings.
2. To assess the costs of the full-scale treatment using these reactors.
3. Compare this treatment with wetlands.

AQUEOUS SPECIATION AND OXIDATION KINETICS OF FERROUS IRON

The auto-oxidation kinetics of Fe(II)(aq) species have been previously reviewed. This is also discussed by Burke and Banwart (2002) but is repeated below to allow the processes to be clearly presented. Oxidation of Fe(II) by molecular oxygen occurs with a simple one-step electron transfer in which the first step in the four-electron reduction of the dioxygen molecule determines the overall rate. Equation (2) shows the stoichiometry for the overall oxidation of Fe^{2+} ions by O_2.

$$O_2(aq) + 4Fe^{2+} + 6H_2O \leftrightarrow 4FeOOH(s) + 8H^+ \qquad \text{(Eq. 2)}$$

The overall rate of the 4 electron transfer is described by the following general second-order rate law for oxidation of ferrous iron, where the $\text{subscript}_{(i)}$ refers to an individual ferrous iron species, and the subscript $_{(T)}$ refers to the total concentration of ferrous iron.

$$-\frac{d[Fe(II)]_T}{dt} = -\Sigma k_i[Fe(II)]_i[O_2] \qquad \text{(Eq. 3)}$$

The second order rate constant for oxidation of Fe(II) adsorbed on mineral surfaces, by $O_2(aq)$, has been estimated by Wehrli (1990) to be of the same order of magnitude as that for the $Fe(OH)^+$ hydrolysis species. Subsequent to that study, Zhang *et al.* (1992) described the aqueous speciation of Fe(II) adsorbed on the surface of iron oxyhydroxide mineral as surface complexation equilibria. Together, these studies allow the pH dependence of iron oxidation kinetics, in the presence of sorbing mineral surfaces, to be defined in terms of the pH dependence of aqueous Fe(II) speciation, and the relative rate of oxidation of the various species.

For the pH range considered in the developed model, the following hydrolysis species (Wehrli 1990) and surface Fe(II) complexes (Zhang *et al.* 1992) are defined for the $Fe^{2+} – H_2O – FeOOH(s)$ system. The notation XFeOH refers to a single adsorption site on the uncharged mineral surface of FeOOH(s).

As described by Wehrli (1990), the main effect of hydrolysis and surface complexation is that oxidation of dissolved ferrous iron increases dramatically at cir-

$$Fe^{2+} + H_2O \leftrightarrow FeOH^+ + H^+ \qquad \log K^*_1 = -10.3 \quad (T = 25^oC, I = 0.1M) \qquad \text{(Eq. 4)}$$

$$Fe^{2+} + 2H_2O \leftrightarrow Fe(OH)_2(aq) + 2H^+ \qquad \log K^*_2 = -22.2 \quad (T = 25^oC, I = 0.1M) \qquad \text{(Eq. 5)}$$

$$Fe^{2+} + XFeOH \leftrightarrow XFeOFe(II)^+ + H^+ \qquad \log {}^sK^*_1 = -1.99 \quad (T = 25^oC, I = 0.1M) \qquad \text{(Eq. 6)}$$

$$Fe^{2+} + XFeOH + H_2O \leftrightarrow XFeOFe(II)OH + 2H^+ \qquad \log {}^sK^*_2 = -8.39 \quad (T = 25^oC, I = 0.1M) \qquad \text{(Eq. 7)}$$

cum-neutral and near-basic conditions, where these species dominate. This results from the significantly higher rate of electron-transfer when Fe(II) is covalently bound to electron-donating oxyions of the hydroxide ligand. This effect holds either for complexation by OH^- in solution (Eqs (4–5)) or, analogously, by oxyanions associated with the hydrated mineral surface (Eqs (6–7). Surface catalysed oxidation of Fe(II) is generally initiated in the presence of Fe(III) oxide surfaces above pH 5, where significant adsorption of Fe^{2+} occurs due to formation of the surface complex $XFeOFe^{2+}$. The presence of mineral oxide surfaces thus extends the pH range where rapid oxidation of Fe(II)(aq) occurs, well into the near-acid region.

The following stoichiometric reaction represents this irreversible (under oxic conditions) transformation of adsorbed Fe(II) to freshly formed Fe oxyhydroxide. A consequence of surface precipitation is conservation of adsorption sites, represented as XFeOH, which react further (Eqs 7–8) to adsorb Fe(II) species from solution, and catalyse their oxidation on the FeOOH(s) surface (Eq. 8).

$$4XFeOFe^{2+} + O_2 + 6H_2O \rightarrow 4FeOOH(s) + 4XFeOH + 4H^+ \qquad \text{(Eq. 8)}$$

This conservation of sites is attractive when considering possible application to treatment technology since reactive surface area would not decrease with accretion of reaction product, thus extending the lifetime of the catalytic surface. A consequence of surface precipitation is conservation of adsorption sites represented as XFeOH, which react further to adsorb Fe(II) species from solution and catalyse their oxidation on the $FeOOH_{(s)}$ surface.

As shown in Equations 6 and 7, Fe^{2+} adsorption is strongly influenced by pH. Stumm and Morgan (1996) report a narrow interval of one or two pH units where the extent of sorption rises from zero to almost 100%. This pH dependence is critical in the performance of ochre accretion as a treatment process. In the absence of surfaces to adsorb and catalyse the oxidation of Fe(II), the onset of rapid oxidation occurs only at neutral to alkaline pH. Surface-catalysed oxidation thus extends the pH range of rapid ochre formation well into the near acid region. However, according to the stoichiometry of Equation 2, each mole of Fe(II) will produce 2 charge equivalents of acidity upon oxidation to Fe(III) hydroxide mineral. Therefore, it is important to realise that hydrolysis and precipitation of metal ions consumes alkalinity due to release of protons, reducing the performance of this technology. Equation 11 defines alkalinity using this convention.

DESIGN PROCEDURE

Design curve application

Figure 1 demonstrates approximations for reactor dimensions from design curves which can be used to size reactors for ochre accretion for mine water treatment. Figure 1 shows iron concentration against the required velocity (hydraulic loading) through the reactor to remove the iron concentration below 2 mg L^{-1}, plotted as a function of influent iron concentration and alkalinity. Iron concentrations in Figure 1 range from 5 to 50 mg L^{-1} in increments of 5 and alkalinity from 100 to 600 mg L^{-1} in increments of 100 in the inflow. The design curves for sizing reactors for full-scale treatment are based on simulations using the calibrated reactor model discussed by Burke and Banwart (2002).

The design curves presented are based on a two metre high reactor. The hydraulic loading (m s^{-1}) (V) is equal to the discharge (m^3 s^{-1}) divided by the cross sectional area (m^2), and multiplied by the porosity (dimensionless). Therefore, the required reactor cross-sectional area can be calculated for any alkaline mine water discharge where iron and alkalinity are available. Figure 1 also shows the hydraulic loading required for the treatment of selected mine water discharges in the UK (Banks *et al.* 1997) and the required cross sectional reactor area needed for the treatment.

However, the model simulations do not account for any reduction in performance due to inefficient discharge application over the surface media or preferential pathways within the media. Therefore, this reduction in the effectiveness of this treatment must be taken into account in reactor design and a larger size reactor may be required. Field trials of this technology suggested that up to 85% of the filter media may be inactive if flow rates are not distributed evenly (Jarvis and Younger 2000)

Design and construction

Figure 1 suggests that for an inflow of around 8 L s^{-1} and an Fe influent of around 10 mg L^{-1} a reactor of around 5 m^2 in horizontal dimension would be required. However the calculations below are based on a 25 m^2 reactor due to the reasons given above.

Figure 2 shows a possible design for such a reactor. It is feasible to install such a structure below the actual

$$[Alk] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - 2[Fe^{2+}] - [H^+] \qquad \text{molar equivalents per litre} \qquad \text{(Eq. 9)}$$

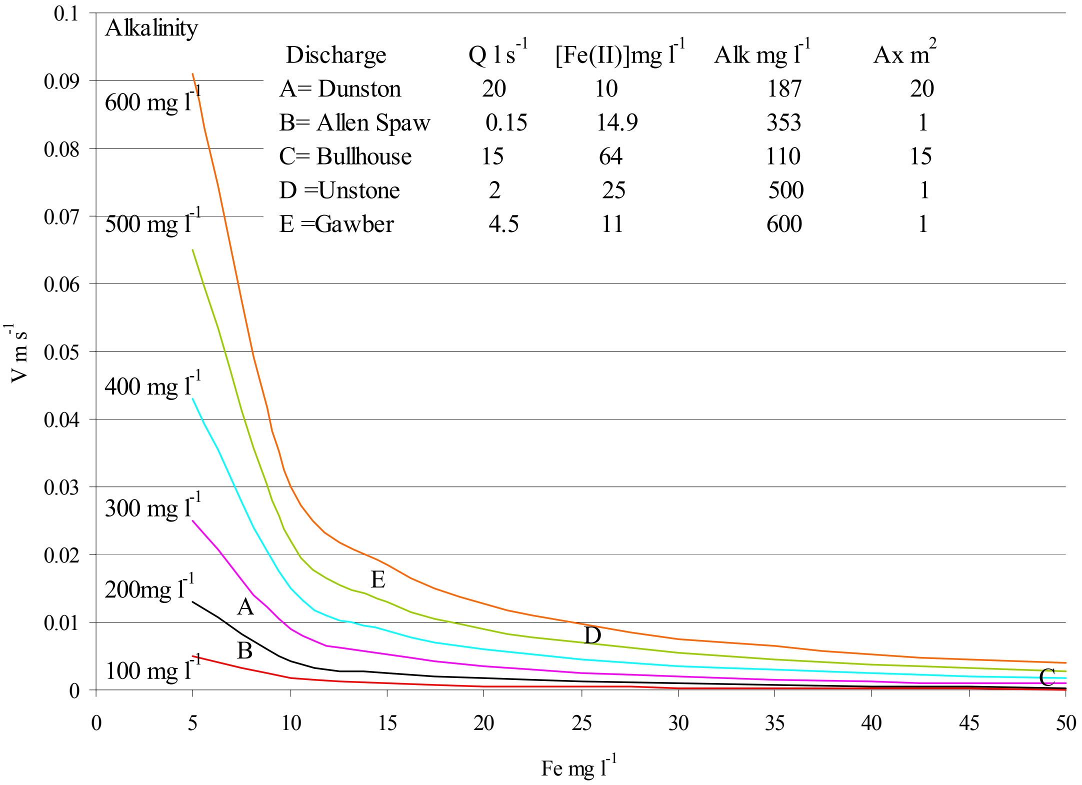


Figure 1. Design curves for reactor sizing

discharge therefore alleviating the requirement to pump and therefore substantially reducing the maintenance costs. However, many discharges that may benefit from this study are pumped and such costs already exist. A pre-cast concrete structure may be the most feasible due to the comparatively low construction costs, with a square or cylindrical shape the favoured option. Trickling filter media that are used in the water treatment industry may be the favoured material to install inside the reactor casing. The trickling filter media used in this study were of sufficient strength to withstand the weight of ochre accumulation within the reactor. The weight of the ochre accumulation on the reactor media must be considered when choosing suitable reactor media. Furthermore, cleaning of the trickling filter media may be time consuming and not cost effective. Cheaper alternative materials may be blast furnace slag or any suitable waste material, where surface area can be maximised. Due to routine maintenance it may be cost effective to install two reactors allowing the shutting down of one while the remaining reactor is left operational.

The rate of ochre accumulation in the reactor has to be considered due to any reduction in performance of the technology. Therefore, it is necessary to calculate the rate of ochre accumulation to allow the frequency of ochre removal in the reactor to minimise the reduction in reactor performance.

Using the influent flow rate and iron concentration given above (inflow of around 8 L s^{-1} and an Fe influent of around 10 mg L^{-1}) and a target effluent concentration of 2mg L^{-1}, the iron load can be calculated:

$$\text{Fe load removed (kg d}^{-1}) = (8 \times 60 \times (10^{-2}) \times 1.44) / 1000$$
$$= 5.53 \text{ kg d}^{-1}$$

If all the iron is assumed to be removed as $Fe(OH)_3$, then:

$$Fe(OH)_3 \text{ load removed (kg d}^{-1}) = 5.53 \times (107/56)$$
$$= 10.57 \text{ kg d}^{-1}$$

If the specific gravity of ochre is assumed to be 1.3, then this can be converted to a volume:

$$\text{Volume of ochre removed (L d}^{-1}) = 10.57/1.3 = 8.13 \text{ L d}^{-1}$$

However, the solids are likely to have a high water content. If the water content is assumed to be 90%, then the actual volume of sludge accumulating in the reactor is:

Actual volume of ochre sludge = 81.3 L d^{-1} (0.08 m^3 d^{-1})

If the initial porosity of the media is assumed to be 80%, then the total volume available for accumulation of solids is 6.8m^3 (2 × 4.25 × 0.8). If it also assumed that the reactor media will require cleaning when the porosity is reduced to 50%, then the operational volume available is 2.5 m^3. On this basis the reactor would require cleaning once every 32 days, possibly by acid washing with the costs of such cleaning shown in Table 1.

Water distribution system

This treatment technology relies on effective distribution of the discharge over the filter media. Preferential pathways would have to be reduced to a minimum within the reactor to allow full use of the surface area available and to prevent clogging within the reactor. Where influent oxygen levels are low (<2 mg L^{-1}), maximising the surface distribution of the influent may be necessary to increase the dissolved oxygen concentration. Any mechanical distribution methods (e.g. spinning/travelling arms), may not be cost effective and therefore distribution via slotted fixed pipes or open channels is likely to be the favoured option. Drain outlets would have to be placed strategically to allow the system to drain freely and quickly, reducing any ponding within the system which would dramatically reduce the effectiveness of the treatment process.

COSTING AND COMPARISON WITH WETLANDS

Costing of reactor installation

Many mine water discharges are not treated because they can be prohibitively expensive. Therefore, when considering treating a mine water discharge it is necessary to consider the environmental impact of the discharge and the cost of treatment. This then allows a decision to made if it is more cost and environmentally effective to treat a more polluting discharge. This allows more mine water discharges that have a more extreme influence on the environment to be treated. The approximated costs of installing and operating such a system discussed above are shown in Table 1. No estimate of land purchase cost is included here but it is considered in the following section.

Mine water discharges that exhibit differing characteristics to the one discussed above and used in the calculations below, would have a significant effect on the cost of reactor installation and maintenance. Mine water discharges with high dissolved iron concentrations would have to be treated by larger reactors, therefore attracting a significant increase in costs. It is expected that a doubling of the dissolved iron concentration and discharge rate would result in a corresponding increase in reactor size. Where a discharge becomes acidic then ochre accretion may become uneconomic and an alternative treatment technology may be required, e.g. wetlands.

Table 1. Approximate capital and maintenance costs for a 25 m^2, 2 m deep system

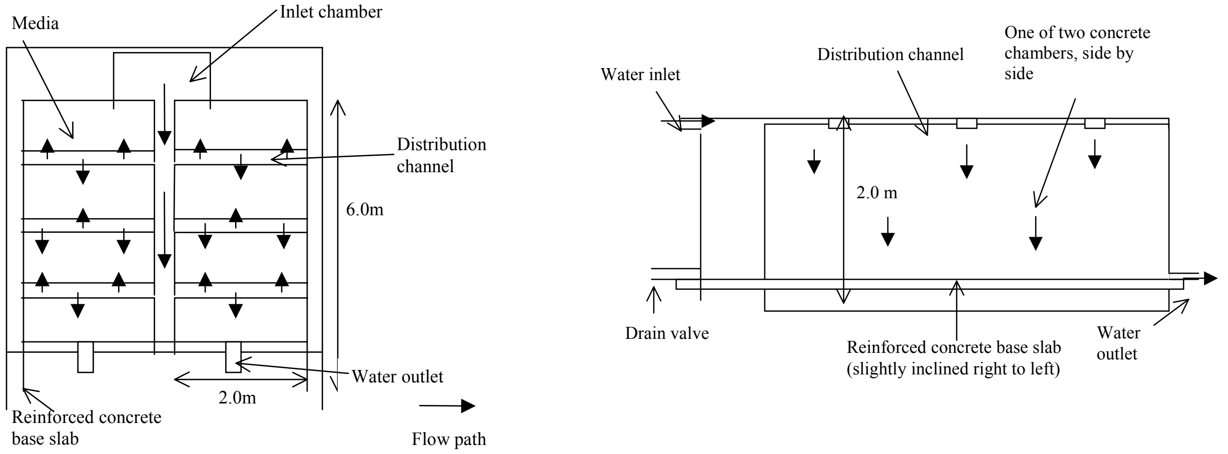
Item	Cost (£)
CAPITAL	
Excavation[1]	2,000
Reinforced concrete base slab	3,500
Pre-cast concrete walls	10,000
Inlet chamber	2,000
Steelwork	7,500
Access road[2]	4,000
Inlet distribution system	1,000
35% contingency[3]	10,500
Total	**40,500**
MAINTENANCE (annual)	
Inlet/outlet pipe and channel cleaning	5,000
Media cleaning[4]	2,000
Total	**7,000**

Notes:
1. At a cost of £2/m^3, including pipework
2. Assumes a 3m wide Type I hardcore track (0.3 m thick on terram liner), approximately 200 m long, at a cost of £6–7/m.
3. Contingency is high due to uncertainties in exact construction materials and site conditions.
4. Assumes *in situ* cleaning; no consideration of media disposal.

Comparison with aerobic wetland costs

The costs envisaged with this type of treatment technology must be compared with alternative passive treatment technologies, particularly wetlands. To compare the design costs with the required wetland costs for the above criteria it is necessary to use the US Bureau of Mines formula which gives a required area of 700 m^2. The estimated costs for such a wetland are given in Table 2.

Table 2 shows that the capital and maintenance costs for an aerobic wetland are below half of those for the new oxidation and accretion system. However, the cost of land is not included into the above calculations and therefore where land is expensive wetlands may become uneconomical. Therefore, there must be some point where wetlands become prohibitively expensive due to the larger area of land needed. A sensitivity analysis was carried out using a simple discounted cash flow analysis for the two options (Figure 3), which



(A) Plan view

(B) Cross-section

Figure 2. Schematic diagram of system configuration

Table 2. Typical estimates of cost for a 700 m^2 aerobic wetland treatment system

Item	Cost (£)
CAPITAL	
Excavation[1]	2,000
Liner	3,000
Topsoil[2]	2,500
Planting[3]	2,500
Inlet/outlet structures	3,000
Access road[4]	4,000
15% contingency	2,850
Total	**19,850**
MAINTENANCE (annual)	
Regular maintenance	3,000

Notes:
1. As Table 1
2. Calculated at £10/m^3
3. Based on approximate price of 4 plants/m^2 at £0.80/plant
4. As Table 6.1

indicates that for the particular mine water discharge considered above the cross-over in costs occurs when land prices approach £188k/ha.

CONCLUSIONS

The research presented above shows that surface catalysed oxidation of iron may be an alternative option to the installation of wetlands. However, this option is dependent on the land available being extremely costly and a mine water discharge that is alkaline with low iron loadings. It is suggested that this technology is most suitable for the polishing of discharges and not the gross treatment for a acidic discharge or with significant iron loadings where wetlands may be the preferred option. However, it is important to consider that ochre accretion can be rapid and subsequent ochre accumulation may inhibit the effectiveness of the distribution system, reducing the effectiveness of this technology. Initial calculations of the rate of accumulation of ochre within the reactor discussed above suggest that such a system may require cleaning frequently. Therefore, in designing a treatment system it may be best to consider a larger size reactor than given in the dimensions in Figure 1. This would reduce the clogging effect of ochre accretion and allow for the reduction in reactor performance due to uneven discharge application over the surface media.

As a final comment it is important to stress that the work has been carried out as research and development. The work was not intended to create precise design values for the exact reactor dimensions required at a given mine water discharge. As is standard for implementation of effluent treatment process technology, the installation of pilot-scale reactors at the discharge to be treated is indispensable to assess site-specific performance and gain valuable operational data.

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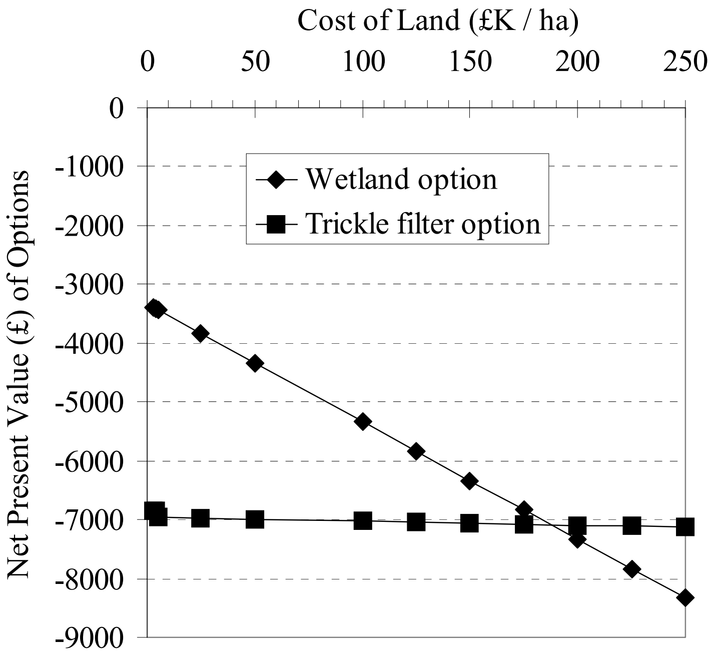

Figure 3. Cost comparison of reactors with conventional wetland treatment for various land prices

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