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The design and optimisation of active mine water treatment plants

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Abstract

This paper provides a 'state of the art' overview of active mine water treatment. The paper discusses the process and reagent selection options commonly available to the designer of an active mine water treatment plant. Comparisons are made between each of these options, based on technical and financial criteria.

The various different treatment technologies available are reviewed and comparisons made between conventional precipitation (using hydroxides, sulphides and carbonates), high density sludge processes and super-saturation precipitation.

The selection of reagents (quick lime, slaked lime, sodium hydroxide, sodium carbonate, magnesium hydroxide, and proprietary chemicals) is considered and a comparison made on the basis of reagent cost, ease of use, final effluent quality and sludge settling criteria. The choice of oxidising agent (air, pure oxygen, peroxide, etc.) for conversion of ferrous to ferric iron is also considered.

Whole life costs comparisons (capital, operational and decommissioning) are made between conventional hydroxide precipitation and the high density sludge process, based on the actual treatment requirements for four different mine waters.

Key words: active treatment, high-density sludge, iron, manganese, mine water, precipitation, sulphide

INTRODUCTION

The selection of the most appropriate method for treating mine water is normally made on the basis of a combination of technical and economic considerations. The final decision is normally based on the maturity and robustness of the treatment process in combination with the whole life cost (capital, operational and de-commissioning costs). For most mine water projects, where the metal load (flow × concentration) is relatively low, passive treatment is both technically feasible and economically preferable, due to the relatively low operating costs. However, depending on the regulatory requirements, the decommissioning costs associated with passive treatment can be significant, and need to be fully recognised during a whole life cost appraisal. Active treatment is generally only adopted for those waters that are difficult to treat passively, or where other considerations, such as land availability, prevent the use of passive treatment.

A number of different technologies are available for the active treatment of mine waters. Selection of the most appropriate process for a particular project is paramount in ensuring that treatment objectives are met in a robust and cost effective manner, such that any long-term liabilities/risk regarding sludge stability and sludge disposal can be fully recognised and managed.

This paper considers the precipitation of metals (principally iron and manganese) from net acid waters (that is waters where the sum of the proton and mineral acidity exceeds the pH buffer capacity provided by the inherent alkalinity of the waters). The active treatment of such waters requires the addition of reagents to neutralise the acidity and form an insoluble metal

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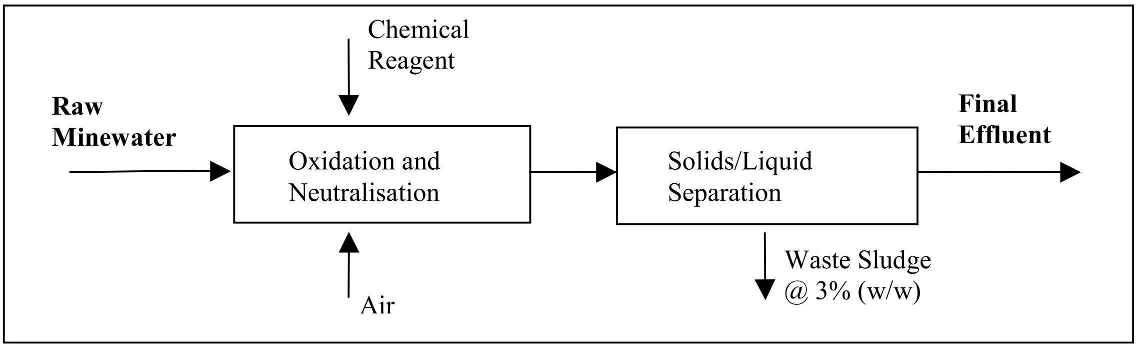

Figure 1. Conventional precipitation plant

precipitate. The removal of iron from net alkaline waters is normally undertaken by oxidisation only, through the precipitation of ferric hydroxide with little or no reagent addition.

PRECIPITATION PROCESSES

Most mine water treatment processes remove metals by rendering them insoluble, using either a commonly available chemical (e.g. calcium hydroxide) or by making use of the chemicals contained within the mine water (e.g. sulphate) to achieve metals removal. In addition there are a number of proprietary reagents available, but these are generally not widely used, due to their relatively high unit costs, concerns about sole source availability or lack of acceptance by the technical community.

Conventional precipitation

The best available technique for the treatment of mine waters with a high metal loading is currently considered to be chemical precipitation. Although a number of different reagents are readily available (Table 1), precipitation is most frequently achieved by alkali addition. Typically treatment is undertaken in two stages (Figure 1), with the metals rendered insoluble by the addition of a reagent in the reaction vessel, followed by solids/liquid separation in a clarifier. However, the optimum pH required for minimum metal solubility varies with the metal species and type of precipitation process (the solubility curves for metal hydroxides are shown in Figure 2). A process designer is therefore faced with either adopting multi-stage treatment, with each metal removed at its optimum pH, or by compromising on a single pH, which enables the effluent concentrations of all the target metals to be achieved. For example, the optimum pH for manganese removal is >10, but at this pH aluminium is soluble. It is not therefore possible for a conventional precipitation process operating at a single pH to simultaneously achieve low aluminium and manganese concentrations. For most mine waters a satisfactory effluent quality can be achieved by operating at a single pH, and therefore multistage removal is not frequently used.

Precipitation reagent

Table 1 provides a summary of the unit cost and theoretical dose rate for the more commonly used precipitation reagents. Pulverised fuel ash and cement kiln dusts are also currently being considered as reagent options, although the presence of potential contaminants, together with the large associated volumes of inserts, make them less attractive, despite their relatively low

Table 1. Commonly used precipitation reagents, theoretical doses and costs

Reagent		Unit cost (£/tonne)	Theoretical		Actual		
			Dose kg per kg Fe	Cost per kg Fe (£)	Efficiency %	Dose kg per kg Fe	Cost per kg Fe (£)
Calcium oxide	CaO	100	1.00	0.10	65	1.54	0.15
Calcium hydroxide	$Ca(OH)_2$	100	1.33	0.13	65	2.05	0.21
Magnesia	MgO	220	0.72	0.16	80	0.9	0.20
Magnesium hydroxide	$Mg(OH)_2$	250	1.04	0.26	80	1.3	0.33
Sodium hydroxide	NaOH	330	1.43	0.47	95	1.50	0.50
Sodium carbonate	Na_2CO_3	195	1.89	0.37	95	2.00	0.39

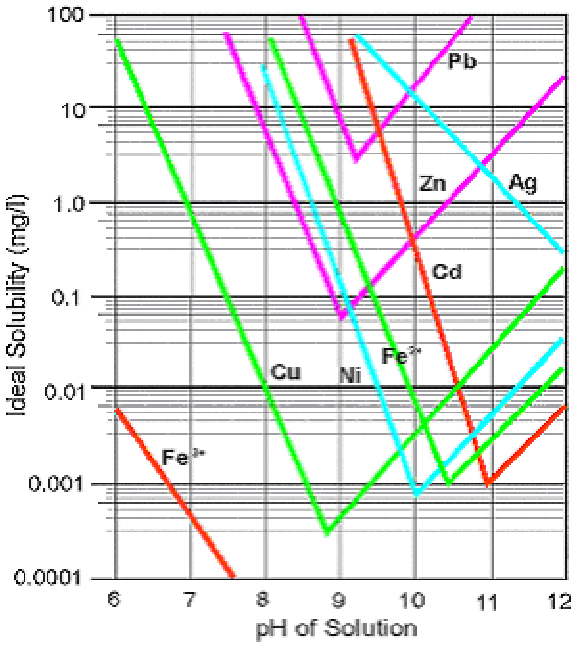

Figure 2. Solubility of metal hydroxides

cost. The actual reagent consumption is normally greater than that predicted stoichiometrically, due to the rate of the reaction, size of the reaction vessel and other plant-specific factors. Typical reagent efficiencies and the resulting dose rate/unit cost are quoted in Table 1. In selecting the most appropriate reagent for a particular application it is necessary to consider the whole-life cost, taking into account the capital cost of the reagent handling equipment, the total actual reagent consumption and the cost of handling the material.

Table 1 indicates that, based solely on reagent cost, calcium oxide (CaO) is theoretically the cheapest reagent, followed by hydrated lime ($Ca(OH)_2$). Both can be added directly to the mine water; however, to provide better process control it is normal practice to make up a dilute slurry containing between 5 and 10% by weight hydrated lime. Calcium oxide powder (quick lime) is prepared by mixing with water in a slaker to form a hydrated lime slurry. Calcium hydroxide (hydrated lime) can be delivered to site either as a powder or pre-prepared slurry form. Powdered lime (calcium oxide or calcium hydroxide) is generally the most cost effective option for the treatment of mine waters with a large metal load, whereas pre-prepared slurry may be more economic for low-demand applications.

Magnesium hydroxide ($Mg(OH)_2$) is typically more expensive than lime, but less expensive than caustic soda. Compared to conventional lime precipitation it forms a denser sludge, but due to the slower reaction kinetics it requires a 50% larger reaction vessel. Magnesium hydroxide has the advantage of neutralising effluents without precipitating sulphate. It is therefore used in conventional processes to avoid sulphate precipitation and where sludge disposal costs need to be reduced by the formation of a lower mass of caustic soda. It tends to be used for treatment of mine water sources with relatively low metal loads. In these circumstances the relatively high reagent cost is offset by the simplicity of application. Because caustic soda is normally used as a fully dissolved liquid solution, it can be easily dosed in a system using a simple dosing pump and therefore requires little maintenance. It also reacts very quickly with the mine water, requiring a small reaction vessel. Due to the speed of the reaction, the resulting precipitate is, however, very fine and tends to be difficult to settle. The use of caustic soda is advantageous in mine waters containing high sulphate concentrations (>2000 mg/L) as, unlike lime, treatment can be achieved without the co-precipitation of gypsum.

Carbonate reagents such as sodium or calcium carbonate are only capable of raising the pH to about 8.5 (compared with about ten for hydroxide). Carbonate reagents are not therefore suitable for the precipitation of metals requiring a high pH. Calcium carbonate is very slow to react and only appropriate for mine waters with a pH below 6, making this reagent largely unsuitable for use in active treatment plants. Sodium carbonate can be used for the precipitation of ferric iron, but in comparison with other reagents tends to be expensive.

Iron precipitation

In most conventional active mine water treatment plants, iron is removed by oxidation from the ferrous to the ferric state, followed by precipitation from solution as a metal hydroxide. The primary benefits of iron oxidation are that ferric iron is insoluble at a relatively low pH (whereas the optimum pH for ferrous removal is 10.5), ferric hydroxide sludge tends to be more stable than ferrous sludge, and the iron oxidation process tends to encourage the co-precipitation of other metals at moderate pH.

Iron oxidation is most commonly achieved using oxygen derived from the introduction of air into the reaction tanks through a sparge pipe. The rate of iron oxidation is dependent on the prevailing pH and the rate of oxygen transfer into the liquid. The rate of oxidation decreases by a factor of 100 for every unit drop in pH, and without bacteriological assistance virtually ceases below pH 4. The rate of oxygen transfer into the water is affected by the bubble size, with only about 5% of the available oxygen transferred from the coarse bubbles produced by a sparge pipe. The rate can be increased by up to 400% by using a high-energy turbine mixer to break up the bubbles.

Hydrogen peroxide, chlorine, potassium permanganate and ozone can all be used as alternative oxidising reagents. The principal advantage of these alternatives is the speed of reaction and the ease of application. Their application can eliminate the need for a large reaction tank, and hence reduce the capital cost. In comparison with conventional aeration, however, the reagent costs are significant and these reagents only tend to be used for applications with low metal loads.

Manganese precipitation

The removal of manganese is one of the more challenging aspects for both the passive and active treatment of mine water, as a relatively high pH environment is required to precipitate manganese as $Mn(OH)_2$ or MnOOH, thereby achieving low metal concentrations. A pH of 10.6 is necessary to minimise the residual manganese concentration in mine water treated in a conventional hydroxide precipitation plant. Manganese can be precipitated at a lower pH, using other reagents such as carbonate or a mixture of hydroxide/carbonates through a two-stage precipitation process involving reactor tanks maintained at different conditions of redox and pH. For example, manganese concentrations of less that 0.35 mg /L are achieved by the Wheal Jane Minewater Treatment Plant whilst operating at an average pH of 9.3.

Precipitation of other metals

Other metals, such as zinc, copper and cadmium can be removed by straight hydroxide precipitation, but can require high pHs and careful control to achieve minimal residual solubility. Experience with the precipitation of industrial effluents has shown that these metals can be effectively removed by co-precipitation with iron. Co-precipitation is achieved by oxidising ferrous iron (either present in the mine water or added as ferrous chloride) to ferric at a pH of between 8 and 9, resulting in the removal of most metals, irrespective of their individual optimum pH conditions.

Sludge characteristics

Although alkali precipitation is effective at removing dissolved metals from solution, the resultant precipitate is gelatinous and difficult to dewater. Settled sludge concentrations of between 2 and 5% solids are frequently achieved on separating the solids from the treated water using a conventional clarifier/thickener or lagoons. This sludge density can be increased to between 20 and 35% (w/w) through dewatering via a filter press. After pressing, the filter cake from a conventional neutralisation plant can contain between three to four tonnes of water for each tonne of metalliferous hydroxide, yielding a dry solids density of between 0.25 and 0.3 t/m^3. Consequently, the cost of sludge disposal can represent a significant proportion of the overall operating cost for mine water treatment. This cost can be deferred by using temporary on-site holding lagoons. However, the lagoons will eventually need desludging or converting into a permanent on-site storage, which will require a waste management licence for the facility, together with the associated long-term monitoring and aftercare requirements.

High-density sludge process

The performance of a hydroxide precipitation plant can be improved by the introduction of sludge recirculation to produce a high density sludge (Kostenbader and Bosman). This process encourages nucleation, with the metals precipitated on to the surface of previously created sludge particles that grow to about 2 to 3 microns in diameter (Figure 3, courtesy of Dr K. Williams Cardiff University). Solids concentrations of 15 to 25% (wt/wt) can be obtained from clarifier–thickener units operating at High Density Sludge (HDS) plants. This sludge can be further dewatered to about 50% in a drying bed and to between 50 and 80% solids in a centrifuge/filter press. Although a number of HDS process schemes have been developed, they all rely on the use of multistage neutralisation and the recirculation of a proportion of the sludge (Figure 4). HDS can be formed by mixing the recirculated sludge with either the lime prior to introducing the mine water, or with the mine water prior to adding the lime.

In addition to the reduction in sludge disposal costs, HDS settles at significantly greater velocities, and is more easily thickened than conventional hydroxide precipitates. The enhanced sludge settling characteris-

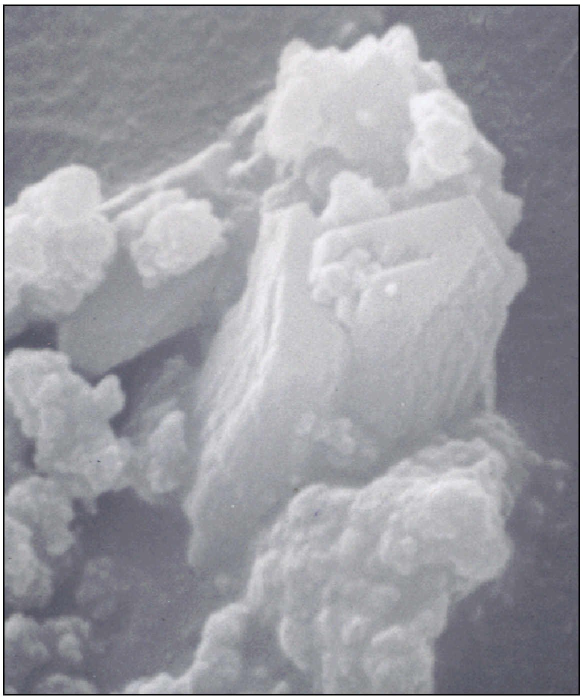

Figure 3. Micrograph of high-density sludge

tics allows solid–liquid separation to be undertaken in a smaller thickener/clarifier, resulting in a significant saving in capital cost. For example, at the Wheal Jane Minewater Treatment Plant in Cornwall, the use of a HDS process together with a lamella clarifier has allowed the footprint of the solids/liquid separation unit to be reduced to about 13% of that required by a conventional hydroxide precipitation plant. Recirculation of sludge can also be beneficially reduce lime utilisation. Depending on the plant configuration, the lime efficiency can be improved by up to 10% in comparison with a conventional precipitation plant. Although HDS plants are most commonly employed for treating mine waters containing high iron, the process is applicable to waters containing little iron, but high concentrations of zinc, copper or aluminium.

Sulphide precipitation

The sulphide precipitation process for metals removal relies on the generation of sulphide activity, either through reagent addition or by the biological reduction of sulphate to hydrogen sulphide in a specially engineered reactor. The sulphide produced reacts with the dissolved metals, which precipitate as insoluble sulphides. The principal advantages of the process are: the lower residual concentrations of dissolved metals achieved by sulphide precipitation; the reduction in sulphate concentrations in the effluent; and the precipitation of the metals as a dense, relatively easily dewatered sludge. However, the capital and operating costs associated with sulphide precipitation are far higher than the equivalent costs for either conventional or HDS precipitation. Therefore, applications tend to be limited – to the treatment of waters containing sufficiently high metal concentrations to allow the higher treatment costs to be partially off-set by commercial metal recovery on site. For example, at Budelco, Holland, an SRB process is used to recover zinc from contaminated groundwater (Scheeren 1993) and at Kennecott, Utah, the process is used to remove and recover copper from contaminated groundwater (van Lier 1999).

Other technologies/proprietary chemicals

A number of proprietary chemical processes are available for the treatment of mine water as summarised in Table 2.

PROCESS SELECTION

Although the selection of the most appropriate active mine water treatment process is dependent on the particular circumstances of each project, most active treat-

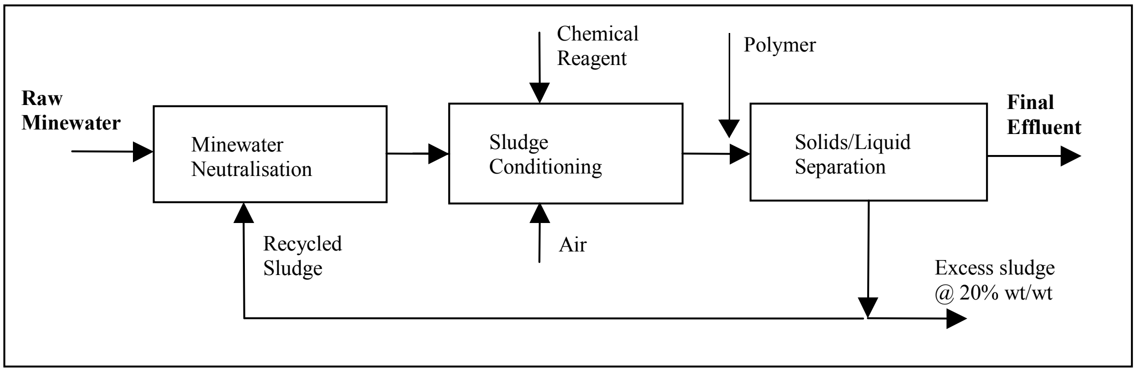

Figure 4. High-density sludge plant

Table 2. Other technologies/proprietary chemicals

Process/chemical	Description
Keeco KB1	Micro silica encapsulation technology.
Aquafix	Water power solid reagent dosing plant for use in remote locations without power.
Virotec Bauxsol	Modified 'Red Mud' residues from bauxite refineries, providing alkaline solids capable of neutralising acidity and removing metals from mine water.
Savmin	Hydroxide precipitation of metals, followed by precipitation of calcium sulphate using gypsum crystals as a catalyst and significant additions of acid and alkali reagents.
Ion exchange	An adsorption process that uses the reversible interchange of ions of the same charge between a solid ion-exchange medium and a solution, requiring reagents for resin regeneration as well as a conventional precipitation process.

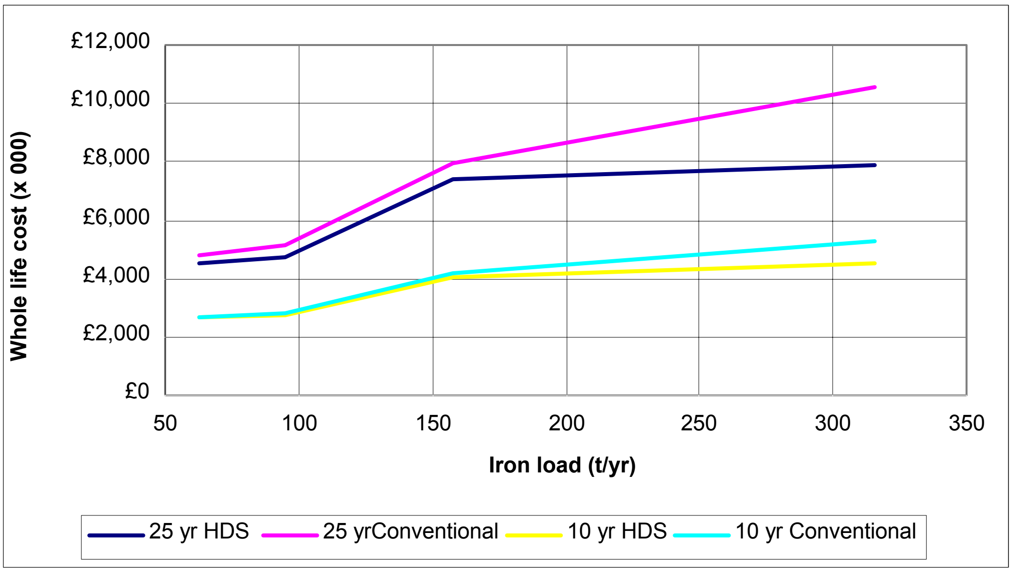

Figure 5. Comparison of 10 year and 25 year whole life costs for active treatment plants

ment plants use hydroxide reagents to precipitate dissolved metals either conventionally or in HDS form. The most common oxidising agent is air (oxygen), although, hydrogen peroxide can be economically advantageous where the reagent demand is low.

PROCESS OPTIMISATION

The optimisation of an active treatment plant must be undertaken systematically due to the interdependence of the precipitation and solid-separation processes. Key process variables are the operating pH, aeration rate, sludge recirculation ratio and flocculant dose rate, and these combined parameters influence both final effluent quality and the settling behaviour of the resultant sludge. Providing effluent quality is not compromised, a decrease in the operating pH will not only save lime, but could result in less sludge by minimising the volume of gypsum precipitated. Optimising the aeration rate is an effective way of reducing the power demand, and may result in less sludge generation and reduced reagent consumption by minimising carbonate formation. Optimisation of the sludge recirculation rate will also help to reduce reagent consumption (by maximising the contact between unreacted reagent and mine water) and may also reduce carbonate production. Once the other variables have been optimised, the polymer type and dose rate indicated by jar tests at bench or pilot scale can be further optimised through controlled plant scale trials. By changing the polymer type and optimising the dose added to the Wheal Jane Minewater Treatment Plant, polymer consumption has been reduced from 3 to 1.6 mg /L.

CASE STUDIES

The following four hypothetical case studies have been used to estimate the whole life costs associated with conventional and HDS treatment. The flows and metal concentrations assumed for these case studies are typical of mine water treated by small to medium sized active treatment plants. The developed costs are based on actual performance data from large and medium sized plants. For each case it has been assumed that:

- The plant uses slaked lime as the precipitation reagent and that the sludge is dewatered using a centrifuge prior to disposal at a landfill site. The HDS plant has been assumed to produce a final sludge product containing 50% solids, whilst the conventional plant has been assumed to produce 33% solids. A unit sludge cost of £37 per wet tonne has been assumed, inclusive of transport costs.
- A lime efficiency of 60% has been assumed for the conventional treatment plant and 70% for the HDS plant.
- Less flocculant is consumed by the HDS plant, due to the enhanced settling properties of the sludge.
- Land purchase and the cost of mine water pumping to the plant have been excluded.

The whole life cost of the plants has been estimated for both ten and 25 years. The results are summarised in Figure 5. This reveals that although the whole life cost of the HDS plant is always less than the cost of conventional treatment, the cost difference is marginal for metal loads of less than 150 t/yr. Above this load, HDS offers a significant cost saving. At lower metal loads, however it can be argued that HDS offers the more environmentally sustainable option, due to lower lime consumption, reduced sludge volumes and lower haulage.

SUMMARY AND CONCLUSIONS

The selection of the most appropriate form of active treatment for any mine water must be made on a project specific basis. However, for the treatment of most net acid waters the use of lime is the most cost effective reagent for all but the smallest applications. Where a full active treatment plant is necessary (reaction vessels, clarifiers and mechanical sludge dewatering units) the installation of an HDS plant will result in the lowest whole life cost for installations removing more that 150 t/yr of metal. For loadings less than 150 t/yr, savings achieved through the installation of an HDS plant are marginal.

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