



Mitigation of pollution from abandoned metal mines

Part 2: Review of resource recovery options from the passive
remediation of metal-rich mine waters

SC090024/R2

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Miranda Kavanagh

Director of Evidence

Executive summary

This report reviews the resource recovery options from passive remediation systems treating metal-rich waters released from abandoned mines, to produce material resources or non-hazardous wastes. Ground source heat and micro-hydroelectric potential of mine waters is also explored in this report.

It appears metals accumulate in passive remediation substrates over decadal time scales to levels which will often exceed limits for safe disposal to land but will often be below typical grade cut-off values for economic recovery. Studies have shown that metals are heterogeneously distributed in such treatment systems with higher concentrations in near-surface substrates closest to mine water inlets. This finding implies that substrate reuse or decontamination should be spatially targeted.

In addition, in aerobic and anaerobic treatment wetlands, metals are heterogeneously distributed between oxidised or reduced mineral phases and organic bound metal complexes. These phases may have different stabilities under recovery or disposal conditions. Chemical and biological leaching (either for recovery or decontamination) technologies are the most cost effective options for metal removal from low grade treatment substrates. A wide variety of lixiviants such as acids, chlorides, ferric iron and ammonia, are likely to be effective in the removal of heavy metals from oxidised and sulfidic Zn, Cu, Pb and Cd-rich materials. The choice of lixiviant will, however, depend on substrate and target metal chemistries. For instance, the high alkalinity of many treatment substrates may consume acidic lixiviants. For very low grade materials bioleaching is the most cost-effective approach. In these systems, acidic or ferric iron concentrations generated from microbial activities induce dissolution of oxidised or sulfidic minerals. The recovery of metals from pregnant leach solutions can be achieved by precipitation or selective solvent extraction. Decontaminated substrates may be amenable to disposal to agricultural land although the benefits of such practices are presently unknown. Hazardous metal-rich substrates might be subjected to stabilisation or solidification technologies followed by reuse in construction.

Ground source heat recovery from mine waters has been tested in the UK. With careful management of system pressures and by minimising exposure to atmospheric conditions, mine water-based heating and cooling schemes can function reliably and with minimal maintenance requirements. Although, as far as the authors are aware, mine water discharges in the UK have not been used in micro-hydroelectric schemes, discharges from abandoned metal mines are often found in upland regions and, given a suitable head and water flow rate, there may be potential to develop such schemes.

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1. Introduction

1.1 Overview of non-coal metal mine wastes and sludge disposal

Regardless of differences in design and operation, all passive remediation systems for the mitigation of metal pollution from abandoned mines share a number of common features. Firstly, because metals, unlike organic pollutants, cannot be eliminated or transformed by degradation, treatment systems are all designed to accumulate and retain metals as precipitated or complexed metal minerals. Secondly, retention mostly occurs on or within a receiving matrix or substrate (Mays and Edwards 2001). Thirdly, the remediation system has a finite lifespan after which the remediation matrix will be considered exhausted or saturated. At this point the substrate must be replaced and disposed of with minimal environmental impact as laid down by legislation for the disposal of hazardous or non-hazardous wastes (e.g. Landfill regulations 2002). On this basis the long-term stabilities of substrate materials need to be evaluated to determine whether special treatments are necessary for disposal (Swash and Monhemius 2005). Removal and disposal of residual wastes from a site are, therefore, a major cost element for determining the long-term maintenance requirements of the treatment systems and their associated disposal sites. A particular concern for substrates from non-coal metal mine wastes in the UK is that they are likely to be richer in heavy metals (such as Cd, Pb, Zn and Cu) than those obtained from coal wastes.

As a consequence of lifespan and disposal issues engendered by metal accumulation, passive remediation systems cannot be considered entirely passive and indeed their designs often include energy-consuming processes such as fluid pumping, scheduled inputs of substrate and the continuous monitoring of performance, all of which require resources and additional maintenance costs. The purpose of this review is to explore technologies and strategies to make passive remediation systems more financially and environmentally sustainable in the long term. This objective could be partially achieved through the implementation of technologies for the production of non-hazardous wastes which can be disposed of cheaply and cleanly. However, exhausted substrates and indeed the remediation infrastructures themselves are potential sources of energy and mineral resources. Recovery of these resources might be used to offset remediation running costs. In the ensuing sections of this report, different aspects of resource recovery from passive remediation systems are considered with a particular focus on metal recovery and the decontamination of mine water remediation systems.

Objectives:

1. To identify methods to remove metals (such as Cd, Pb, Zn Cu) to facilitate disposal of exhausted substrate as non-hazardous wastes by landfill or non-landfill routes (such as agricultural land, construction industry).
2. To identify, where possible, cost-effective and environmentally sustainable methods to recover these metals for commercial use .
3. To minimise capital investment for such recovery approaches by integrating them with current recovery infrastructures.
4. To identify other resource recovery options from metal mine treatment systems.

This is the second part (Part 2) of a two-part review collated as part of this project. The first part (Part 1: *Review of passive treatment technologies for metal mine drainage remediation*) considers potential options for passive treatment of metal mine water discharges across England and Wales. Although the two reviews have been compiled

separately, the extended Executive Summary (a separate document) draws conclusions from both, and relates these conclusions to each other. This is not least because the type of passive treatment system selected will crucially influence the potential for resource recovery, particularly with respect to metal recovery from spent treatment substrates.

1.2 Characteristics of wastes/resources from passive systems treating non-coal metal mine wastes

Exhausted substrates represent both the greatest potential cost (in terms of disposal) and the mostly likely source of commercial value from passive remediation systems. Depending on the treatment system, these wastes may comprise two or more components, namely metal mineral precipitates, a complex organic matrix, and/or inorganic materials such as limestones and clays. Aerobic or anaerobic/composting wetlands, for instance, comprise all three components while systems which use inorganic absorptive materials, such as hydrous ferric oxides (ochre pellets), manganese oxides or zeolites, will lack a significant organic component (see Part 1). In addition, wetland systems may harbour vegetation included for aesthetics and the renewal of carbon supplies to sustain microbial activity in such systems. This vegetation accumulates substantial quantities of metals, however, in terms of metal removal and retention the contribution to wetland performance is low (Manios *et al.* 2003), a conclusion in line with many other studies (such as Mays and Edwards 2001). On this basis, metal recovery from vegetation per se will not be considered in this review.

1.2.1. Metal composition of treatment substrates

Four key questions with regards to disposal and metal recycling are:

1. To what levels do metals accumulate in treatment systems and where?
2. Over what time period does this accumulation occur?
3. In what mineral form are the metals precipitated?
4. At what point might the treatment substrate be considered exhausted?

These questions are important not only with regard to the timing, cost and risk of waste disposal but also with regard to the suitability of exhausted substrates as analogues of low-grade materials currently exploited in metal recovery industries (see below). Unfortunately, although treatment systems such as wetlands have been used for decades and documented in extensive detail (Sheoran and Sheoran 2006), relatively few papers have reported on the fate of metal contaminants removed from wastewaters in the long-term (O'Sullivan *et al.* 2004). Nevertheless the data presented in Table 1 provides an insight into the range of metal accumulation rates and absolute values (<10 to <10,000 mg kg⁻¹ (<0.001-<1% w/w)) obtained in substrates from treatment systems with different influent pH values, metal loadings and removal mechanisms. These data indicate that levels of metal accumulation vary by many orders of magnitude and are principally controlled by metal loading rates and the time frames for accumulation. For instance, Zn and Pb retention in a constructed wetland remediating neutral waste waters from an operational lead-zinc mine (Tara Mines) in Ireland (O'Sullivan *et al.* 2004) was found to be cumulative over a five-year period at which point values within the sediments were found to be in the range of >10 up to <1000 mg kg⁻¹. These values can be compared directly with the grades of materials

currently exploited in commercial metal recovery and in waste disposal and decontamination activities (see below).

Table 1: Metal accumulation in the treatment of metalliferous waste waters

Treatment system	Accumulation period	pH	Zn mg ^l ⁻¹	Zn mgkg ⁻¹	Cu mg ^l ⁻¹	Cu mgkg ⁻¹	Pb mg ^l ⁻¹	Pb mgkg ⁻¹	Cd mg ^l ⁻¹	Cd mgkg ⁻¹	Locale	reference
Wetland	Decades	high	14.47	9,536	n.a.	n.a.	11.49	7,101	0.05	53	China	Yang <i>et al.</i> 2006
Wetland	Years	neutral - low	n.a.	n.a.	35-50	46.8-277	n.a.	n.a.	n.a.	n.a.	Canada	Sobolewski 1996
Wetland	Years	neutral	0.01-1.76	850	n.a.	n.a.	0.002-0.3	3,315	n.a.	n.a.	Eire	O'Sullivan <i>et al.</i> 2004
Compost	Months	neutral	80	1,232	80	1,157	n.a.	n.a.	n.a.	n.a.	UK	Manios <i>et al.</i> 2003
Adsorption (HFO)	Months	neutral	1.5	430-2,070 ^a	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	UK	Mayes <i>et al.</i> 2009
DAS ^b	Months	low	315	856-2,131 ^c	1.5	248-3,196 ^c	0.15	20-70 ^c	0.38	9.0	UK	Rötting <i>et al.</i> 2008
PRB ^d	Months	low	20	600-2,500	20	0-3,700	n.a.	n.a.	2	0-400	Spain	Gibert <i>et al.</i> 2003
GCLs ^e	Months	low	8-28	139-1,606	3-14	85-375	n.a.	n.a.	2.5-41	35-516	Canada	Lange <i>et al.</i> 2010
Wetland	Years	neutral	0.018	600 ^f	0.025	796 ^f	0.001	≈40 ^f	n.d.	≈1.5	USA	Knox <i>et al.</i> 2006
Wetland (IMP)	Years	neutral	n.d.	1.3-5.7	n.d.	0.93-1.33	<0.0002	1.6-2.5	n.d.	n.d.	USA	Mays and Edwards 2001
Wetland (WC)	Years	neutral	0.03	2.2-2.9	n.d.	1.65-1.66	<0.0002	1.4-3.2	0.02	n.d.	USA	Mays and Edwards 2001
Wetland (natural)	Years	low	n.d.	1.6-4.2	n.d.	1.05-1.21	<0.0002	1.6-4.2	n.d.	n.d.	USA	Mays and Edwards 2001
Wetland	Years	low	>80	100-9,900	0.4	10-160	n.d.	n.d.	0.1	10-70	UK	Swash and Monhemius 2005

n.a. = not applicable, n.d. = not detected, ^avalues of Zn as high as 3,270 mg kg⁻¹ were obtained in carbonate precipitates on the wall of the treatment tank, ^bdispersed alkaline substrate, ^ctop 30 cm of sediment, ^d sulphate reducing permeable reactive barrier with compost/limestone/iron, ^egeosynthetic clay liners testing a range of synthetic mine wastes, ^fwithin surface floc layer.

In some studies attempts have been made to determine both the distribution of metals within the treatment substrate and/or their speciation. A key finding with respect to resource recovery is that metal accumulation is often localised within treatment systems, with higher accumulations typically found in surface layers and in zones near to influent inlets (see Gibert *et al.* 2003, Knox *et al.* 2006, Rötting *et al.* 2008, Sobolewski 1996, Jindal and Samorkhom 2005). For instance, in the study of Knox *et al.* (2006) metals accumulated in a vegetated surface flow wetland in the top organic rich layers of the sediment, that is the surface floc and organic layers. Likewise, in a laboratory study of metal removal using a dispersed alkaline substrate, metals were found to accumulate principally in the top 30 cm of a field-scale remediation tank (Rötting *et al.* 2008). Sobolewski (1996) found that the highest Cu values (5-10 times above background) were found in sediments sampled close to the inlets of two wetland systems. Likewise, O'Sullivan *et al.* (2004) generally found that metals accumulated in surface sediments near to point sources of metal-laden inflows. The authors concluded that since most contaminants were retained in the upper layer, potential harvesting of the accumulated metals may not be to the detriment of the established treatment ecosystem. Therefore, should these systems reach their metal removal capacity, there would be scope to renew their potential by removing and replacing the upper substrate layer. This conclusion may also be an important issue with respect to routine resource recovery from such systems. On this basis a critical component of resource recovery from passive treatment technologies will be an accurate estimate of the metal distributions at the field scale, derived using statistically valid sampling programmes.

Treatment type and hence the predominant abiotic and biotic metal removal mechanism is known to play an important role in dictating the form in which the metals are precipitated and retained in treatment systems; this is of course an important consideration with respect to the application of metal recovery technologies because metals bound to organic particles are only mobile after decomposition or weathering. In contrast, precipitated minerals will be more easily dissolved and mobilised by changes in pH (Mulligan *et al.* 2001b). On this basis, removal efficiencies are likely influenced by both mineral form and the chemistry/composition of the host substrate. For treatments which use inorganic absorptive materials, metals precipitate in a relatively homogeneous manner. For instance, the sorption of dissolved metals onto geosynthetic clays (Lange *et al.* 2010) and natural zeolites (Wingenfelder *et al.* 2005) occurs in the form of hydroxides or oxyhydroxides. Likewise, in a caustic magnesia barrier, zinc and lead were mainly precipitated as hydroxides and copper was precipitated as a hydroxysulphate (Cortina *et al.* 2003). In an aluminium-rich heavy metal-laden mine water treated with a calcite dispersed alkaline substrate comprising calcite sand mixed with woodchips, precipitation of Zn, Cu and Pb was also most likely associated with precipitated aluminium hydroxysulphate (Rötting *et al.* 2008).

In contrast to inorganic substrates, studies indicate that wetland treatment systems are highly heterogeneous and, as a general rule, comprise a number of minerals or metal complexes, the formation and distribution of which depend on stable gradients of reduction potential, pH and biological activity (Sheoran and Sheoran 2006). Typically the mineral forms are oxyhydroxides, carbonates and sulphides, the latter generated in wetlands with subsurface reducing conditions and active sulphide producing sulphate reducing bacteria (SRB). In treatment systems designed to retain metals as sulphides many studies have shown that significant proportions of metals are retained in the organic matter present in the treatment systems. For instance, in a peat-based wetland treating high and low strength copper-contaminated mine drainage (Sobolewski 1996), although a proportion of the Cu (based on sequential extraction) was retained as sulphide the bulk was present as organically bound Cu and precipitated oxyhydroxides (the precipitation of oxyhydroxides is not that surprising given that even highly reducing wetland systems will have a relatively oxygenated surface layer). A similar fate for retained metals was found for compost/limestone/iron substrates specifically engineered to promote metal removal from mine wastes through sulphide generation (Gibert *et al.* 2003).

Likewise, in a wetland with a substrate rich in organic matter (peat) treating mine drainage water (Eger 1994), it was concluded that heavy metals were retained mainly due to cation exchange reactions with the peat's colloidal surface. However, in the presence of sulphide and, given sufficient time and consistently low redox potentials, it is thought these organically bound metals are eventually transformed to sulphides (O'Sullivan *et al.* 2004). It is thought that the relatively rapid adsorption of dissolved metals onto organic sites in an organic-rich substrate is most likely in the early stages of wetland operation, with sulphide precipitation (especially Cu and Zn) becoming the dominant removal mechanism later (Machemer and Wildeman 1992). Even in aerobic wetland systems which have an underlying organic substrate, some metals will presumably be transformed to sulphides. Based on the findings from the relatively few studies which have examined the fate of metals in mine treatment systems, it can be concluded that while a relatively homogenous mineral precipitate (e.g. oxyhydroxides or carbonates) is produced in treatments which use inorganic absorptive materials, for wetland treatment systems and particularly anaerobic wetland systems a heterogeneous metal mineralogy will be the norm. This variation in mineral form within treatments is likely to have consequences with respect to the designation of these materials for disposal and with respect to the application of recovery technologies.

The final question to be addressed in this section is, at what point might a substrate be considered exhausted and require replacement? This aspect of passive systems treating coal or non-coal metal mine wastes is not well researched, where the focus has largely centred on removal efficiencies. Nevertheless, it has been suggested that constructed wetlands have a finite and short lifespan with respect to metal retention (Horne, 2000). More specifically, lifetime estimates of years to decades have been proposed from a survey of 83 systems spanning different metal removal technologies (Ziemkiewicz 2003). This decadal timeframe was supported in another review of treatment wetlands (Sheoran and Sheoran 2006); however, it was concluded that the physical accumulation of sediment material may necessitate periodic dredging for solids simply to allow for the addition of organic matter and the maintenance of hydraulic flow. In a treatment wetland in the USA, metal sludge was found to accumulate at a rate of about 1.25 to 1.5 inches (3 to 4 cm) per year (Stark, 1992). For this system, it was suggested that dikes that provided 0.9 meters of freeboard should provide sufficient volume for 25 to 50 years of treatment. A 16-year-old constructed wetland (Yang *et al.* 2006, see Table 1) was capable of maintaining high stability for the removal of metals during this time period. Obviously, reduction in metal removal efficiency may be a strong indicator that a substrate has reached capacity and thus continuous monitoring of passive remediation systems will be an essential component of their long-term management. At the point at which substantial dissolved metal breakthrough occurs, the removal of substrate followed by recovery or decontamination will be required.

2. Review of potential technologies for metal recovery and their application for a variety of passive treatment systems

The industrial-scale recovery of metals such as copper and lead has a history stretching back thousands of years and consequently, these industries have had an enormous impact on the development of human societies. Because of their high inherent value, metals have always been extensively recycled and the current relative contribution of recycling to total global production has been estimated at ~60% for lead and ~15% for zinc (Dutrizac and Chen 1998). Although metal recycling is often carried out for economic reasons, increasingly recycling is done because of environmental considerations. The preceding section examined the nature of the metal-laden substrates likely to be derived from passive remediation treatments. These substrates can either be regarded as mineral resources or, as contaminated wastes which require metal recovery or decontamination for reuse. However, an extensive survey of metal mine waste treatment systems has not identified any experimental, pilot or full-scale application of recovery or decontamination technologies applied to exhausted substrates from such systems. What follows therefore is a survey of metal recovery and removal technologies which have been successfully applied to low-grade ores and metal-bearing materials generated from industrial and domestic waste streams. The incorporation of metal mine passive remediation waste streams into such existing recovery infrastructures seems the most likely option for cost-effective resource recovery or disposal. However, these infrastructures may not be available in the UK in which case they will either have to be developed specifically for the treatment of such wastes or alternative disposal options considered.

2.1 Metal recovery

Two key questions with regard metal recovery from metalliferous resources are

1. Are the resources of sufficient grade to make metal recovery economic?
2. Which current or future technologies are most appropriate for the types and grades of metal resource produced by mine water treatment systems?

With respect to the first question, a key consideration for the economics of metal recovery is the 'grade cut-off' of a mineral resource which can be defined as the minimum grade (percentage metal content) below which recovery is uneconomic. The grade cut-off is determined from a wide range of parameters (such as metal prices, ore deposit size, location relative to infrastructure, cost of power and available recovery technologies). On the basis of these very variable parameters, the cut-off grade for a particular resource must be determined periodically and on a case-by-case basis. For instance, with respect to metal-laden substrates from passive mine treatment systems in the UK, factors such as their small scale, the remoteness of dispersed mine treatment systems and the fact that the UK no longer possesses any suitable heavy metal recovery infrastructures will have a major bearing on the economics of recovery.

On the other hand it should be considered that these metal resources will not incur costs associated with the excavation and physical processing of primary materials.

Although cut-off values are highly specific to the ore and mine setting, a survey of typical cut-off grades (percentage w/w) for a range of heavy metals indicates that copper is economic at grades $>0.5\%$ or $>5000 \text{ mg kg}^{-1}$ (Davenport *et al.* 2002), however, economic grades of Zn and Pb are $>1\%$ or $>10,000 \text{ mg kg}^{-1}$. Below these values metal laden materials are characterised as wastes. Clearly, from the survey of metal values which have accumulated in mine treatment systems (Table 1), none had reached these target values during the stated accumulation periods. However, this survey represents a relatively restricted set of studies and technologies are potentially available which can concentrate these sub-marginal materials (see below).

In addition to metal ores, which are natural materials containing economically valuable minerals, metals can be extracted from industrial and domestic wastes when present in sufficient amounts. The concept of recovery-reuse-recycling of metal-containing waste can make these wastes a good secondary source of metals (Agrawal *et al.* 2009). For instance during 2009, about 54% (117,000 tonnes) of the slab zinc produced in the US was recovered from secondary material such as electric arc furnace (EAF) dust and galvanising residues (USGS 2010). However, these residues typically comprise high levels of Zn (10-20% wt%) and are easily incorporated into recovery processes. In contrast, a lot of metals are discarded as a component of municipal solid wastes (MSW). In many countries (such as Taiwan and Japan) these wastes are largely disposed of by incineration and metals become concentrated in the residual ashes. The compositions of Cu, Zn and Pb in Taiwan fly ash and bottom ash has been assessed, respectively, at 1.29%, 2.21% and 0.58% (w/w) (Kuo *et al.* 2007). These values are above typical mining grade cut-off values and it has been estimated that the amount of Cr, Cu, Fe, Cd, Al, Zn and Pb that could be recovered in Taiwan from incineration residues might reach, respectively, 2.69×10^2 , 1.46×10^4 , 4.91×10^4 , 6.92×10^1 , 5.10×10^4 , 1.85×10^4 and 4.66×10^3 tonnes/year. Furthermore, ashes such as these have been directed (at a field scale) into metal-smelting processes (Zeltner and Lichtensteiger 2002), although as yet recovery from this material does not appear to be globally widespread. The incineration of MSW which produces a dry metal-enriched byproduct can be considered as akin to a pyrometallurgical approach used in the refining of primary ores. Metal-laden wastes from passive remediation systems may be amenable to such treatments. For instance, a typical treatment wetland substrate will comprise a substantial organic component and in excess of 10 % water. On this basis a combination of dewatering, roasting/incineration followed by hydrometallurgical extraction or bioleaching might be considered.

2.2 Metal decontamination and disposal or non-metal based reuse of substrates

On balance, it seems unlikely that metals will accumulate in all mine water treatment systems to levels suitable for economic recovery. However, based on the form, volume and levels of metal accumulation, exhausted substrates (despite their immobilised loadings) may be considered as hazardous wastes which pose a toxicological risk to receiving environments. Specifically, the content, chemical behaviour and significance of the heavy metals in such waste materials can be defined in terms of different aspects of environmental legislation with respect to disposal, material reuse and protection of the environment. However, as stated above, at present very little consideration has been given to the disposal of exhausted substrates derived from mine water treatments systems. Nevertheless, these materials have in some instances (i.e. residues from Wheal Jane constructed wetlands) been considered as hazardous wastes with respect to landfill disposal (Swash and Monhemius 2004). A critical

component of these assessments were solubility tests to assess the short- and long-term behaviours of metals in landfill and included EPA Toxicity Characteristic Leaching Procedure (TCLP) tests (USEPA, 1986). The TCLP test is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid and multiphase wastes and determine whether a waste meets the definition of a hazardous waste with respect to landfill disposal. Critically, these land disposal regulations require that 'hazardous wastes are treated until the heavy metals do not leach at Universal Treatment Standard (UTS) levels from the solid waste at levels above the maximum allowable concentrations prior to placement in a surface impoundment, waste pile, landfill or other land disposal unit' (Code of Federal Regulation 40 CFR 260). Landfill regulations (2002) within the UK operate along similar lines and require a batch-leaching test (BS EN 12457) of materials for disposal. These tests report on the amounts leached from a given mass and the results designate such materials into one of three categories (Table 2).

Table 2: Limit values (mg kg⁻¹) for compliance leaching test using BS EN 12457/3 at cumulative L/S^a 10 l kg^{-1b,c}

Metal	Inert waste landfill	Stable non-reactive hazardous waste in non-hazardous landfill	Hazardous waste landfill
Zn	4	50	200
Cu	2	50	100
Pb	0.5	10	50
Cd	0.04	1	5
Cr	0.5	10	70

^aLiquid / Solid

^bEnvironment Agency, *Guidance on sampling and testing of wastes to meet landfill acceptance procedures*, Version 4.3a (December 2003).

^cThe leaching limit values were derived by the Technical Adaptation Committee by risk modelling based on the technical requirements for the protection of soil and groundwater for the different classes of landfill imposed by Annex I of the Landfill Directive.

Of critical importance is the variety of passive remediation treatment systems used to remove and immobilise metals from mine waste. As discussed above, the substrates are likely to encompass a wide range of organic and mineral associations which will have a profound effect on the outcome of leachability tests and hence the cost of landfill disposal or the requirement for remedial treatment. For instance, aerobic residues (ochres) produced in the Wheal Jane wetland treatment system were found to be acidic in nature and for disposal to a landfill, would require mixing/blending with lime to prevent generation of acidic leachates. In addition they would require dewatering, densification and solidification as a prerequisite for landfilling to minimise any subsequent settling/subsidence of the landfill site. In the Wheal Jane study, consideration was given to the disposal of substrates from different passive treatment technologies applied at the same location. For instance, if aerobic ochres and anaerobic organic-rich materials were mixed, it was concluded this would encourage the creation of anoxic conditions, leading to the breakdown of the iron oxyhydroxide and release of heavy metals. On this basis it was recommended that residues which contain a high percentage of organic matter should be disposed of separately, incorporated into bricks, dried and burnt to recover metals (Zn, Pb, Cu and Cd).

With respect to reuse rather than disposal of exhausted substrates from mine treatment systems very little discussion has been generated in the literature and no specific research has been carried out on the potential benefits or pitfalls of uses such as soil amendment or soil manufacture, or the use of these materials in civil construction, land reclamation or capping. Clearly research is required with a focus on the impact on soil health and productivity and the long-term stability of waste materials in agricultural

settings or stabilised construction materials. Nevertheless, direct parallels for these materials can be drawn with the reuse of other potentially hazardous materials such as sewage sludges/composts derived from waste digestion, ashes derived from the incineration of municipal solid wastes (MSW) and dredged contaminated river and harbour sediments. Depending on the compositional variations discussed above, MSW sludges and composts are potentially analogous to organic-rich treatment wetland sediments, while metal-contaminated sediments may be analogous to low organic carbon treatment wetlands. Incineration products are potentially analogous to inorganic-based metal-retaining substrates such as ochres, clays and zeolites.

The most important pollutants in sewage sludges have been identified as the heavy metals such as Hg, Cu, Ni, Pb, Zn, As, Cd, Se, Mo, Co, Cr and Ag (Andrews *et al.* 1998). At present, a large proportion of sewage sludge produced annually in the UK is recycled to agricultural and silvicultural (forestry) land and the UK government sees this as the best practicable environmental option for disposal. The remainder of sewage sludge goes to landfill and incineration, which are both seen as increasingly less sustainable and cost-effective options. The principal benefit of land disposal is as a fertilizer or soil conditioner and it remains to be determined whether organic-rich wetland substrates might be beneficial as such. Research will need to establish potential nutrient contents such as N, P, C, K and S compositions in such materials. However, regardless of these potential benefits metal contamination is a concern with respect to the maximum allowable concentrations of metal pollutants in order to maintain soil quality in the long term. Whether a potential pollutant metal has a negative impact on the environment depends on its concentration in a particular soil. An exceeded concentration will mark a threshold from where the soil will pass from a sink into a potential source of 'risk compounds' to a receptor. This threshold depends upon soil and site-specific properties such as pH, cation exchange capacity (CEC) and cation distribution and must be based on experimental and field experience derived from eco-toxicological effects over defined pathways. Nevertheless, certain regulatory limits (Table 3) can be compared to total values found within mine treatment substrates.

Table 3: Metal limits (mg kg⁻¹) for waste materials and soils from various legislative sources

Metal	PAS:100 (limits for composts) ^a	PAS:110 for AD digestate ^a	Dutch guidelines for contamination in soils ^c	SGV- residential ^d	SGV- industrial ^d
Zn	400	400	140 (720)	n.a.	n.a.
Cu	200	200	36 (190)	n.a.	n.a.
Pb	200	200	85 (530)	450	750
Cd	1.5	1.5	0.8 (12)	10	230
Cr	100	100	100 (380)	130	n.a.
Ni	50	50	35 (210)	50	n.a.

^aPublicly Available Specification (PAS) British Standards Institution 2005; ^bPublicly Available Specification (PAS) British Standards Institution 2010; ^cValues which require action in parenthesis; ^dCLEA soil guideline value (SGV) for industrial areas (Environment Agency, 2002). Values for Cd derived from SGV for cadmium in Science Report SC050021/Cadmium SGV, 2009; n.a. = data not available as of June 2010.

A comparison of values in Tables 1 and 3 indicate that metal accumulations within a range of treatment systems do exceed regulatory limits. In this sense, they may be considered as not suitable in this untreated form for addition to land.

As with organic rich sludges, the landfill disposal of metal-contaminated dredged sediments is becoming ever more prohibitive. For these materials, the benefits of disposal to agricultural or forestry land are less obvious with much lower organic

carbon and nutrient contents; however, clearly the same PAS100 or equivalent limits for such disposal routes exist. An alternative fate for these materials is their stabilisation and solidification by various processes. This approach provides some degree of beneficial reuse, since stabilised sediment may be used for land development applications (such as filling excavated sites or capping of industrial "brownfield" sites). Other uses are for shoreline stabilisation, manufacture of aggregates and construction (Siham *et al.* 2008). The use of dredged material in road construction is one of the main factors considered by French harbour managers given that road construction companies consume large amounts of natural aggregates and mineral resources are being depleted (Siham *et al.* 2008). Stabilised contaminated sediments are used for a number of end uses including road, railway construction and made grounds (Eggen *et al.* 2008). With respect to the metal-laden mine water treatment substrates from Wheal Jane, options such as solidification using cement or conversion to bricks have been considered as final disposal/recycling options (Swash and Monhemius 2004). It should be borne in mind that many mine water passive remediation technologies, by their nature, produce metal-laden substrates which are inherently stable and as such could be directly used without further processing for reuse in construction. This assumption would have to be tested.

2.3 Metal removal technologies and their applications

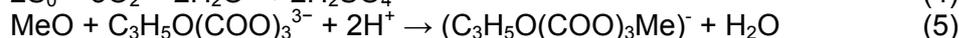
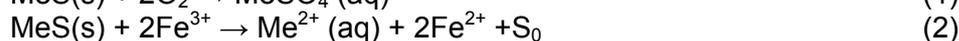
Applications of metal removal technologies are varied and are largely dictated by the economic considerations and regulatory constraints discussed above. For instance, such technologies may be aimed at the economic recovery of metals from high-grade primary ores, or the recovery of metals from lower grade primary and secondary materials. Alternatively, technologies may be applied for the decontamination of metals from wastes deemed hazardous. To some extent the choice of technology depends on these objectives, however, the generalised behaviour of metals in geochemical settings means that regardless of purpose, similar metal removal approaches can be applied to a wide range of source materials.

Metal removal approaches can be divided into physical-chemical methods (such as pyrometallurgy and hydrometallurgy) or biologically mediated extractive approaches (bioleaching). Pyrometallurgy encompasses any extraction technology which uses high temperature regimens where the heat is generated, at least initially, by the burning of fossil fuels such as coke, oil and gas or from the use of electric furnaces. Pyrometallurgical techniques (such as smelting and roasting) are mostly applied to high-grade primary ores. For the recovery of high-grade Cu, Zn and Pb sulphide ores, physical separation by techniques such as floatation is followed by roasting to eliminate sulphur, followed by smelting of the resultant 'calcine' in a reducing environment. These approaches are unlikely to be relevant for the recovery or removal of metals from metal mine waste treatment systems; however, incineration or drying may be beneficial for concentrating low-grade materials by removing organic matter and moisture content.

Hydrometallurgy (chemical leaching) is the extraction of metals from ores and secondary materials by the use of aqueous solutions. This approach is especially relevant for the recovery of metals from low-grade materials whereby dispersed metals are selectively dissolved into solution. Obviously the success of such a process requires that the metal is selectively soluble in a suitable lixiviant (which itself can be recycled after use) and there is a means by which the metals can be selectively removed from solution by chemical or electrolytic means. A very wide range of lixiviants have been developed and used for both metal recovery and decontamination operations. Often pyrometallurgical and hydrometallurgical processes are linked to

electrowinning, a process by which a relatively pure metal is precipitated on an electrode directly from a molten or aqueous solution. Metals can be further purified by electrorefining whereby the crude metal forms an electrode in the presence of a suitable electrolyte. The success of hydrometallurgical extraction processes are linked to a ready supply of water and energy.

Bioleaching or biomining is the process by which metals are dissolved from ores as a result of the metabolic and catabolic activities of microbial communities. Given the relevance of such processes to the recovery or removal of metals from both primary and secondary metal laden materials, a brief explanation of the general principles is provided here. Bioleaching occurs either directly by the bacterially mediated oxidation of metal sulphides (Equation 1), or indirectly where metal oxidation and dissolution occurs as a result of reactions with Fe^{3+} under acidic conditions (Equation 2). Here the reaction is propagated and sustained by the general oxidative activities of iron and sulphur oxidising bacteria (Equations 3 and 4). Alternatively, dissolution of metals from non-sulphide ores can be achieved by their acid dissolution or complexation with organic acids (such as citric acid, Equation 5) excreted by heterotrophic bacteria and fungi. Both these approaches may be applicable to metal-laden waste substrates depending on the extent to which they are comprised of sulphide and iron mineral sources and/or organic compounds. Iron, sulfur and carbon waste materials can be added to the system to stimulate the desired process.



where Me = metal

Generally, the capital costs of bioleaching are less than those of conventional chemical and pyrometallurgical methods. This is because bioleaching is a relatively simple technology that does not require careful continuous control and monitoring (Mishra *et al.* 2005). The costs of different applications broadly increase with the level of sophistication, where dump leaching is less expensive than stirred reactors. Furthermore, no heat or pressurisation is required so maintenance costs are low compared to conventional technologies such as pressure oxidation and roasting. Operated correctly, therefore, heap bioleaching offers economic recovery of resources that would be too marginal for other process routes (Peterson and Dixon 2007). Furthermore, since acid solutions are generated in situ by microorganisms, there are fewer environmental problems such as those associated with hydrometallurgical leaching processes or the gaseous emissions generated by pyrometallurgy.

Biooxidation is a variation of bioleaching which uses the microbiological oxidation of minerals which contain unreactive metal compounds of interest. As a result, metals remain in the solid residues in a more concentrated form. This approach is probably not relevant to the extraction of heavy metals which have relatively reactive chemistries. In contrast, bioreduction may be an important approach for metal recovery which uses the activities of iron and sulphate reducing to precipitate dissolved metals from solutions as a result of decreases in reduction potential and the presence of sulphide. Specific applications of the processes described in this section are described in the following sections.

2.3.1 Economic recovery and decontamination technologies

The development of extractive metallurgical techniques for application to primary and secondary materials has, for obvious reasons, largely been driven by the mining industry. With declining inventories of high-grade ores (which are most amenable to pyrometallurgical extraction) there has been a move towards using hydrometallurgical and even bioleaching approaches to ever lower grade ores, and the use of secondary materials. In some instances, economic recovery approaches have even been considered for contaminated soils and sediments. With respect to heavy metals such as Cu, Zn and Pb a wide variety of lixiviant solutions are available and widely used. For instance, the hydrometallurgical treatment of copper ores and concentrates is highly developed and accounts for approximately 20% of the world's primary copper production. In a general sense, acidic leaching is very effective for dump treatment of low-grade heavy metal sulphide ore materials (Abraitis *et al.* 2004). For instance, sulfuric acid and combinations of nitric and sulfuric acid added to Ni-Cu mine tailings are capable of effective leaching at ambient temperatures and atmospheric pressure (Xie *et al.* 2005). However, ferric chloride, ferric sulphate, ammonia and cyanide can all mobilise Cu from low-grade ores (Altundoğan and Tümen 1997).

Ammoniacal leaching is also practiced for recovery of metals such as nickel and zinc sulphide ores. This alkaline lixiviant is a particularly attractive proposition when ore bodies are associated with large amounts of acid-consuming constituents such as calcite and magnesia (Sengupta *et al.* 2009) and, accordingly, the presence of acid-consuming constituents (limestone) in mine remediation substrates may have particular implications for leaching treatments. Zinc oxide ore is an important source of zinc metal second only to zinc sulphide ores (Espiriari *et al.* 2006). Zinc oxide ores can also be treated by acidic leaching processes, however, zinc is dissolved at low pH only following the dissolution of many other metals, so acidic leaching processes are often uneconomic unless coupled to a selective extractant such as di-2-ethylhexyl phosphoric acid (D2EHPA) (Wen-qing *et al.* 2007). In addition, zinc in the form of Zn oxides and ferrites can be leached from Electric Arc Furnace (EAF) dusts (which are very high grade wastes from steel manufacture) with ammonium chloride-alkali chloride solutions or $\text{FeCl}_3\text{-HCl}$ (Dutrizac and Chen 1998). Sodium hydroxide has also been found to be an effective lixiviant for Zn and Cd with the additional benefit that iron is not co-dissolved (Dutra *et al.* 2006). For Pb ores and their secondary materials, mixtures of acidic ferric and sodium chlorides are suitable leach solutions (Lin *et al.* 2001). The use of high concentrations of chloride salt solutions at low pH conditions combines the acid-leaching action and the formation of metal chloro-complexes to extract lead (Dermont *et al.* 2008); however these leaching approaches do not appear to be widely used for lead recovery.

As discussed above a key issue with hydrometallurgical approaches is that they are ill suited to very low grade materials such as would be the case for the levels of metal which accumulate in passive mine treatment systems. Many of the applications of chemical leaching described above use ore and secondary materials which contain >10% w/w (100,000 mg kg⁻¹) metal loadings. An alternative approach is bioleaching. Heap bioleaching has become a reasonably well established technology for the extraction of low-grade secondary Cu sulphides and the oxidation of refractory gold ores (Petersen and Dixon 2007). This approach allows large volumes of material to be treated in situ. Essentially, this process requires biooxidation to be carried out on crushed ore stacked on pads with an air-ventilation system at the base to supply oxygen to the microbial population inoculated onto the rock (Figure 1). Acidic leachates are recycled by irrigation to the top of the heap. Heat builds up in the heap as a result of chemical and biological activities which facilitates faster processing. A number of different operational processes have been developed, such as the HydroZinc™ process by Teck Cominco Metals Ltd described by Petersen and Dixon (2007) which involves heap bioleaching of a zinc sulphide ore (≈15%) followed by neutralisation,

solvent extraction and Zn electrowinning. In addition, bioleaching has been used to recover considerably lower concentrations of Zn ($\approx 1\%$) present in steel wastes using the iron oxidising bacterium *Acidithiobacillus ferrooxidans* (Bayat *et al.* 2009). Mulligan *et al.* (2004) investigated the feasibility and economics of microbially recovered metals from mixed metal oxide low-grade ores. These ores comprised Cu ($7,245 \text{ mg kg}^{-1}$) and Zn (201 mg kg^{-1}) in the presence of iron and were leached in the presence of the fungal species *Aspergillus niger* fed with agricultural wastes such as potato peels pre-soaked in sulphuric acid for 24 hours. Under these conditions *A. niger* produced organic acids and 68% of the copper and 46% of the zinc was dissolved from the ore material compared to only 15% recovery of these metals without its presence.

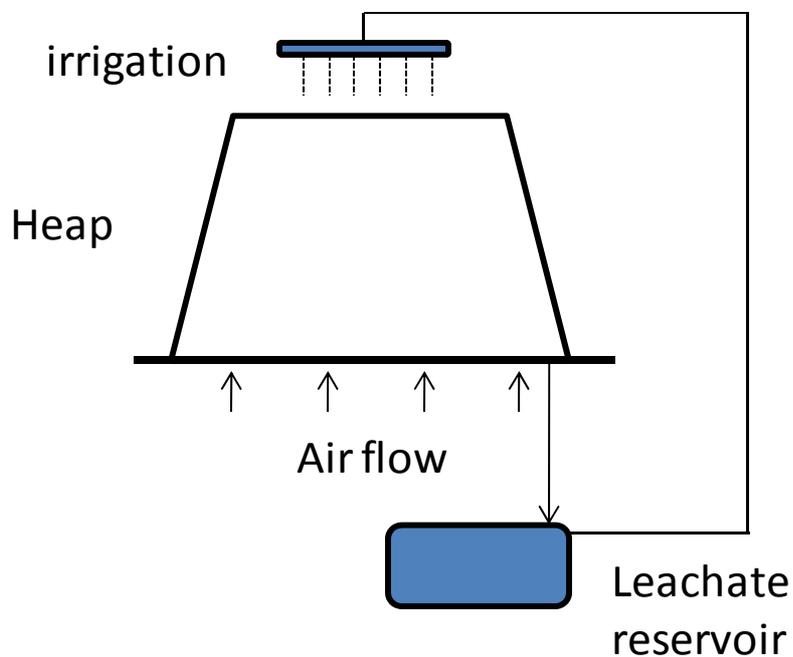


Figure 1: Schematic of biological heap leach procedure

The key to the success of industrial extraction procedures has been the development of solvent extraction reagents which can selectively recover a given metal. Once the metals in an ore are leached into an aqueous solution using the techniques described above, a desired component is selectively transferred to a water-immiscible solvent to achieve metal concentration and separation. The metal is then recovered by electro-reduction. An important issue for successful commercial use of such reagents is their cost and recyclability. Even though most flow-sheets ensure that reagents are recycled there is always some loss and this can translate to high capital costs in plants (Tasker *et al.* 2007). Other options for metal removal are precipitation and adsorption approaches. For instance, precipitation can be achieved by raising pH with sodium hydroxide by addition of sodium sulphide. Metals can also be removed from solution by cation exchange reactions.

In some instances, for very low-grade wastes the primary purpose of metal removal is decontamination of these hazardous materials (Dermont *et al.* 2008); however, it would

be desirable if this decontamination could be coupled to metal reuse and sale. With this in mind, the feasibility of remediation of copper contamination in soil ($1,730 \text{ mg kg}^{-1}$) by soil washing was investigated with a view to metal reuse (Di Palma and Medici 2002). This process involved soil washing with EDTA (ethylenediaminetetraacetic acid) followed by the acid disruption of the EDTA-metal complex followed by ferric sulphate treatment to form a copper sulphate solution. A copper hydroxide precipitate was eventually recovered by the addition of sodium and calcium hydroxide solutions and the EDTA solution reused for another extraction cycle. The relatively low Cu recoveries (60%) in this study were attributed to the presence of humic substances.

In a general sense, decontamination technologies such as soil and sediment washing represent a permanent solution to contamination compared to the non-permanent outcomes of solidification and stabilisation described below. Many soil-washing processes are based, firstly, on particle size separation and this physical approach is typically applied before chemical extraction. However, physical separation techniques are mostly applicable to particulate forms of metals. On this basis, it remains to be determined whether this technology would be effective for the diffuse metal distributions likely in passive remediation treatment substrates, especially in substrates with heterogeneous organo- and mineral metal forms. With respect to chemical extraction different options have been investigated for decontamination, including inorganic acid leaching (such as H_2SO_4 , HCl , and HNO_3), organic acid leaching (citric acid, acetic acid), bioleaching, chelating agents such as EDTA, surfactants and biosurfactants (Meunier *et al.* 2009). Chelating agents need to be recycled to be economic. A study of contaminated soil in Salt Lake City (Hong *et al.* 2002) which contained Zn ($1,410 \text{ mg kg}^{-1}$) Pb ($12,000 \text{ mg kg}^{-1}$) and Cu (675 mg kg^{-1}) showed that the chelator diethylenetriaminepentaacetate (DTPA) was capable of extracting 100, 74, and 55% of the Pb, Zn, and Cu, respectively, and could be recovered by the use of cationic and anionic precipitants under alkaline pH conditions. In addition DTPA was relatively biostable. Many methods have also been developed to remove heavy metals from leachates including precipitation, co-precipitation, electrodeposition, electrocoagulation, cementation, membrane separation, solvent extraction, ion exchange, adsorption and biosorption (Meunier *et al.* 2009).

Far fewer remediation techniques are available for contaminated sediments because of the wide range of contaminants present and the muddy properties of sludge sediments which make them more difficult to treat than open-structured soils (Seidel *et al.* 2004). On this basis there exists significant demand for further development (Mulligan *et al.* 2001a). For the decontamination, pre-treatment is usually required to remove debris and critically to dewater the dredged sediments. A typical treatment path which might be applicable to passive treatment substrates is as follows: freshly dredged sludge is divided into a less polluted coarse fraction and a strongly polluted, organic-rich fine fraction to reduce the quantity of sediment which has to be treated by leaching (Löser *et al.* 2007). In a second step, the fine fraction is planted with aquatic plants converting the sludge into a soil-like material sufficiently permeable for leaching. Chemical leaching can be achieved by continuously circulating a liquid containing the leaching agent. For instance, a soil washing and leaching process was tested for removing lead from soils (Lin *et al.* 2001). In this study a soil-washing circuit, including size and gravity separations, was employed to remove metallic lead particles and leaching was applied to remove fine metallic lead species. The leaching experiments with a ferric and sodium chloride solution indicated that under the pH of 2 and at an Eh of 1,300 mV, the metallic lead species could be dissolved in the leaching solution within 60 minutes. Two critical features of this study of interest for the treatment of mine substrates is that this system was designed for portability and included a metal recycling component, where Pb was recovered in a concentrate amenable for smelting.

In addition to soils and sediments, chemical leaching is also applied to industrial and domestic sludge wastes which contain accumulations of heavy metals (Bayat and Sari

2010). As with soils, acidic leaching can be used when the metals are present in significant amounts; however, large volumes of acid are required to adjust pH and a large amount of alkali is then required to neutralise the waste. In a review of metal removal from metal-contaminated sludge destined for land application (Babel and del Mundo Dacera 2006), chemical extraction, bioleaching, electroreclamation and supercritical fluid extraction (SFE) techniques were assessed. SFE is a liquid extraction process employing compressed fluids which are usually liquids or gases under supercritical conditions and can be employed instead of normal solvents; electroreclamation is based on electrokinetic phenomena that occur when the soils or sludges are electrically charged (with direct current) by means of one or several electrode arrays. Metal ions migrate to the anodes. All of these evaluated techniques were found to be effective but each had advantages and disadvantages. It was concluded that bioleaching was probably superior in terms of recovery cost and environmental damage; however, it may be limited in its environmental application. Both electroreclamation and supercritical fluid extraction (SFE) were successful but were considered to be still in the early stages of development.

Bioleaching has now been widely developed as a mechanism for soil, sediment and waste sludge decontamination. In a study of a sediment remediation process comprising an initial conditioning step followed by a bioleaching process (Seidel *et al.* 2004), the metals in a sediment containing Cd 9 mg kg⁻¹, Co 42 mg kg⁻¹, Cr 270 mg kg⁻¹, Cu 142 mg kg⁻¹, Pb 135 mg kg⁻¹, and Zn 1,958 mg kg⁻¹ were, to different extents, successfully removed. The 24-week conditioning step involved drainage and planting to produce a more permeable soil-like characteristic. Bioleaching was carried out in percolator reactors supplemented with 2% elemental sulphur (see Equation 4). Elemental sulphur augmentation is less expensive than other reduced sulphur substrates. When using the conditioned sediment, it was found that the oxidation of easily degradable organic matter by heterotrophic microbes increased the temperature up to 50°C in the early leaching phase and temporarily inhibited sulphur-oxidising bacteria. However, most of the metal contaminants were leached within 21 days with Zn, Cd, Mn, Co and Ni removed by 61-81%. Cu was reduced by 21% and Cr and Pb were nearly immobile. The authors concluded that this would be a cost effective approach for producing a substrate for beneficial use. In a comparative evaluation of microbial and chemical leaching processes for heavy metal removal from dewatered metal plating sludge (Bayat and Sari 2010), bioleaching was considered more efficient than ferric chloride or sulfuric acid leaching. The concentrations (mg kg⁻¹) of metals in the plating sludge were: Zn 22,900-22,980; Pb 828-850; Ni 601-729; Cu 625-691; Cd 325-341; Cr 210-212 with recoveries of 97% Zn, 96% Cu, 93% Ni, 84% Pb, 67% Cd and 34% Cr under generated pH conditions of 2. The authors suggested that bioleaching may be an alternative to conventional physicochemical treatments of dewatered metal plating sludges and for the removal and reuse of hazardous heavy metals waste products from the mining and metal-refining industries, sewage sludges, residues from power stations and waste incineration plants.

A different bioleaching strategy was adopted by Pathak *et al.* (2003) where optimum added ferrous sulphate concentration and sludge solids were determined. The experiments were performed with metal laden (Cu 472 mg kg⁻¹; Ni 294 mg kg⁻¹; Zn 1,310 mg kg⁻¹; Cr 332 mg kg⁻¹) anaerobically digested sewage sludge employing an inoculum of indigenous iron-oxidising microorganisms (see Equation 3) enriched from the sludge. Leaching efficiencies were significantly enhanced (Zn 69%; Cu 52%; Cr 46%; Ni 45%) in the presence of ferric sulphate and added inoculum. In a study of the leaching behaviour of heterotrophic microorganisms (see Equation 5) isolated from an alkaline slag dump (Willschera and Boseckerb 2003), it was found that leaching with heterotrophic microorganisms was more selective with respect to a particular metal than that obtained by chemical leaching with added organic acids (oxalic or citric). The recovery rates for each metal were: 38% manganese; 46% magnesium; 68% calcium; 27% zinc; 15% iron; 26% nickel; 40% cobalt and 8% lead from the slag. However, the

authors concluded that the low concentrations of metals in the slag precluded economic recovery.

2.3.2 Combined treatment and recovery mine water treatment systems

Some research into metal mine water remediation has developed approaches which are not passive. These applications require greater capital investment and running costs, however, they have the advantage of selective recovery of different heavy metals, such as copper and zinc, present in mine waters. Two such approaches are detailed here.

The first approach centres on an adsorption process for metal recovery using selective inorganic chemically active adsorbents (ICAA) developed for the recovery of oxidised Fe, Cu, Zn, Cd and Pb from acid mine drainage (Deorkar and Tavlarides 1998). Accordingly, an integrated adsorption process was set up with three independently operating fixed-bed adsorbers, comprised of ICAA(A), ICAA(C) and ICAA(D), selectively removing Fe, Cu, and Zn, Cd and Pb respectively, from the acidic stream. A fourth bed, comprised of ICAA(D), acted as an acid scavenger and increased the pH of the effluent to greater than 7. These materials retained a stable adsorption capacity for up to 20 cycles and then could be stripped by treatment with sulfuric acid.

An alternative approach incorporates three integrated treatments comprising, in line of water flow, an anaerobic sulphidogenic bioreactor, an aerobic iron-oxidising bioreactor with a final lime treatment (Johnson *et al.* 2004). In the first reactor sulphide produced by dissimilatory sulphate-reducing bacteria (SRB) fed on organic material is used to increase alkalinity in the acidic waste streams with the precipitation of Cu and Zn as insoluble sulphides, which may then be recovered and processed for extractive metallurgy. Iron is precipitated in the following reactor, with aluminium precipitated after lime treatment.

2.3.3. Stabilisation and solidification technologies

On larger scales of waste resource management, metal decontamination for reuse or safe disposal may not be feasible. This may be especially true of substrates which are complex in terms of contamination and substrate composition. Alternatively, wastes can be subjected to stabilisation or solidification. Stabilisation involves chemical reactions with the immobilisation of the metals by addition of immobilising agents (Lock and Janson 2003), many approaches of which are comparable to methods employed in the passive remediation of metal mine wastes. Solidification is the physical containment of waste by incorporation of solid substrates into inert manufactured materials (Souza and Shrihari 2007) or its transformation by vitrification (Li *et al.* 2003). These technologies are generally applicable to contaminated soil, sediments or solid wastes and seek to restrict the movement of contaminants (often by reducing the permeability of the substrate to fluid flow). In some instances, the aim is to increase the strength and bearing capacity of the manufactured material for reuse (Mulligan *et al.* 2001b).

Various metal immobilisation additives have been used or suggested (Gray *et al.* 2006, Eggen *et al.* 2008, Mulligan *et al.* 2001b, Lock and Janson 2003, Tournay *et al.* 2008) including: FeS (to precipitate immobile sulphides), activated carbon, bitumen, fly ash, alkaline aluminosilicates (such as beringite), manganese oxides, synthetic zeolites, lime, organic matter, red mud (an iron and aluminium rich residue of bauxite leaching). These additives can simply be mechanically mixed with the waste material before use or disposal. After this process, rigorous testing of the leachability of the material is required.

Mixing process can also be adopted for the solidification of waste materials by the addition of cements and pozzolans (silicate materials mixed with lime) (Mulligan *et al.* 2001b). This approach can be adopted for disposal purposes; however, cements in themselves have enormous potential for accommodating metal-rich waste materials and, importantly, these additions can often substitute for the use of cement feed stocks (Souza and Shrihari 2007). For instance, contaminated sediments have replaced a portion of the raw feedstock materials in conventional Portland cement manufacture (Rehmat *et al.* 1999, Dalton *et al.* 2004). This replacement is possible because these materials contain silica, alumina, calcium and iron oxides, all of which are important in Portland cement manufacture and all of which may be present in some passive remediation substrates. Currently, the cement industry is increasingly the focus of studies investigating the potential for beneficial reuse of waste materials and this may apply to reuse options for mine remediation materials. Of particular importance for these reuse options is the fact that cement manufacture requires high temperatures, so organic components of substrates are degraded to carbon dioxide and water, and inorganic contaminants (heavy metals) are locked into the cement. Wastes which have a wide range of organic and inorganic loadings can be incorporated into cement and include materials such as solids derived from sewage, municipal solid and industrial waste incinerator ashes (Souza and Shrihari 2007). Technologies are also available for the incorporation of such wastes into building aggregates and masonry bricks (Seager *et al.* 2007).

Vitrification of hazardous wastes has been applied mainly to radioactive wastes with the purpose of homogeneously stabilising metals in a vitrified glassy matrix (Li *et al.* 2003). This process generates a large reduction in volume which is beneficial for long-term storage or landfill. Stabilisation and volume reduction can be achieved in a single process step. For instance, in the Westinghouse plasma torch vitrification process, air is passed through the torch, superheating it to approximately 5,000°C. Dewatered sediment is injected into the plume of the torch, heating it extremely rapidly with the result that organic species are combusted and destroyed. The mineral phases in the sediment reach melting point and fuse into a homogenous glassy liquid. Fluxing agents such as lime and soda ash may be added to adjust the viscosity of the melt before quenching to maintain the vitreous characteristics, with heavy metals trapped in the glass matrix. This material is suitable for a wide variety of applications, ranging from low value products such as road aggregate and sandblasting grit, to high value products such as glass fibre or sintered architectural tiles.

3. Other resource options from passive treatment systems

3.1. Ground source heat potential for mine waters

Rocks, minerals and groundwater have a huge capacity to store heat. They have an approximately constant temperature which, at shallow depth, roughly corresponds to the average annual air temperature (Banks *et al.*, 2003). At greater depth, temperatures increase due to the geothermal gradient. Heat pump technology allows the extraction of some of this low-temperature heat from the environment, its upgrade to a higher temperature and use for space heating and cooling (Banks *et al.*, 2009). Heat pumps that extract heat energy from the geological environment (rocks, soil, sediment, groundwater) are typically referred to as ground source heat pumps. Their use was first proposed as early as 1912 in Switzerland but commercial use did not become widespread until the 1970s with their development largely confined to Sweden, USA, Austria, Switzerland and Germany (Banks *et al.*, 2003). Until recently, the technology was almost unknown in the UK but in the last decade it has grown in popularity.

There are two main types of ground source heat pump, open loop and closed loop. Open loop systems involve the use of groundwater, pumped from a borehole, or mine shaft, and circulated directly through the heat pump, which extracts heat from the water. Closed loop systems, on the other hand, do not require groundwater abstraction. They involve either the heat pump refrigerant, or a separate circulatory fluid, being pumped through a closed loop installed in the ground. The fluid is heated and, on return to the surface, is passed through a heat pump.

Abandoned mines may be viewed as an attractive energy resource for several reasons (Banks *et al.*, 2003, 2004):

- Existing discharges from flooded mine workings may provide considerable quantities of water at a constant temperature.
- Mine systems consist of extensive areas of disused workings where flowing groundwater is in contact with rocks so can act as a heat exchanger.
- In deep mines there may be a substantial geothermal component to the temperature, as well as the solar component, adding to the efficiency of the system.

Several authors have investigated the idea of extracting heat from mine waters in open loop systems. Banks *et al.* (2003, 2004,) have demonstrated that the concept is feasible and give examples from the USA, Canada, Norway and Scotland where the technology has successfully been applied. Further feasibility studies in Canada and the USA have been described by Watzlaf and Ackman (2006) and Raymond and Therrien (2008) while Demollin-Schneiders *et al.* (2005) and Malolepszy *et al.* (2005) describe a pilot project to provide district heating and cooling from mine water in Heerlen in the Netherlands. In Poland, feasibility studies have reached a relatively advanced stage (Malolepszy *et al.* 2005), partly due to the high temperatures (>20°C) (Janson *et al.* 2009) observed in some of the deep mine waters pumped in the Upper Silesian Coal Basin. Similar studies have been carried out in Germany (Wieber and Pohl 2008) where flooded mine water is used in Freiberg for heating and cooling purposes in the 500-year old Castle Freudenstein (Kranz and Dillenardt 2010).

In the UK, the idea of using mine water in abandoned, flooded mine workings as a source of heat was first considered in the 1990s in Scotland with a successful pilot-scale scheme. This resulted in the development of two mine water heat pump schemes at housing association apartment complexes in Shettleston, Glasgow, and Lumphinnans, Fife, in 1999-2000 (Banks *et al.* 2009). The schemes use abstraction boreholes drilled to depths of 100 m (Shettleston) and 172 m (Lumphinnans) within flooded coal mine workings. The mine water (at a temperature of around 12-14°C) passes through a steel gauze filter to remove particulate matter before entering the heat pump, then the cooled mine water is reinjected to the ground via a shallower borehole. At both sites, the heat pumps produce hot water at a temperature of around 55°C and have a heat output of up to 65 kW.

The Coal Authority in the UK spends large amounts of money each year pumping mine water from old mines, treating it and running it to waste. However, many former colliery sites are now being redeveloped as commercial or residential sites which will have heating and cooling requirements. The possibility of using mine water as a source of heat for such new developments could allow the Coal Authority to recoup some of its operating expenditure (Banks *et al.* 2009). Prospects are enhanced by the fact that many pumped mine waters typically have elevated temperatures, particularly those from greater depths (such as Horden, County Durham, at 17.2°C (Banks *et al.* 2009)). The Coal Authority is actively investigating using such technologies at several of its sites, including at the Bates mine water treatment system in Blyth, Northumberland (Coal Authority, personal communication) where water pumped from the former Bates Colliery had an average temperature over the period 2003-2007 of 15.6°C. The area surrounding the treatment system is currently undergoing redevelopment with the potential for a high heating and cooling requirement.

One of the main reasons for the reluctance in the UK to use mine water in open loop ground source heat systems is the risk of iron and manganese oxyhydroxide (in particular) precipitation within the heat exchanger and pipework of the system, thus limiting the lifetime of the heat pump. The potential for precipitation is enhanced by an increase in pH caused by the degassing of carbon dioxide from the mine water, exposure to atmospheric oxygen leading to oxidation and subsequent precipitation reactions and a change in temperature which alters the solubility products and saturation indices and increases the rate of oxidation and precipitation of minerals. However, Banks *et al.* (2004, 2009) and Watzlaf and Ackmann (2006) suggest ways in which the potential for precipitation can be minimised, in particular maintaining an airtight system so that the pumped mine water is not exposed to atmospheric oxygen or to significant changes in pressure, since the change in temperature alone is not sufficient to result in considerable changes in saturation indices of potentially precipitating mineral phases (Banks *et al.* 2009). Indeed, experiences from the successful schemes at Shettleston and Lumphinnans in Scotland show that significant mineral precipitation has not been observed in the pipework, heat exchanger or recharge wells under normal operation. However, following vandalism at Lumphinnans, oxygen has been allowed to mix with the mine water and significant iron oxyhydroxide precipitation has occurred within the recharge well. Watzlaf and Ackmann (2006) also propose the use of an additional loop to isolate the mine water from the heat pump, including a heat exchanger to transfer the heat between the mine water and heat pump. Therefore, with careful management of system pressures and by minimising exposure to atmospheric conditions, mine water-based heating and cooling schemes can function reliably and with minimal maintenance requirements (Banks *et al.* 2009).

In terms of cost, although the initial capital cost of installing ground source heat systems may be high, operational costs are much lower than that of conventional heating and cooling options, as demonstrated by Watzlaf and Ackmann (2006) who calculated a potential 62% reduction in heating and cooling costs for the prospective use of mine water in the Pittsburgh coal seam in the USA for heating and cooling. In

addition, as suggested by Renz *et al.* (2009), the most cost-effective way of using mine water in ground source heat schemes is to use the heat of water already being pumped (or discharging by gravity) for dewatering or treatment purposes.

The studies described above focus mainly on the potential use of coal mine waters in open loop ground source heat schemes. Clearly, abandoned coal mine workings, due to their greater depth and therefore higher water temperatures, may be viewed as having greater potential for use as an energy resource, but abandoned metal mine workings, despite their shallower depth, may also offer potential for ground source heat. The technology is based around using the heat stored within the shallow subsurface which is derived mainly from solar heat warming up the near surface rocks and groundwater during summer. As the rocks have a large heat storage capacity, any seasonal variations are minimal and the temperature of the shallow subsurface therefore remains relatively constant throughout the year (generally warmer than air in winter and cooler than air in summer). The earth's surface is thus used as a huge solar energy collector.

The fundamental criterion for a potential ground source heat scheme is a constant and adequate (depending on space heating requirements) flux of water. Many discharges from abandoned metal mines therefore have great potential for use in such schemes as they have been flowing for a considerable period of time at relatively constant flow rates, many of which are in excess of 5 L/s (Hugh Potter, personal communication). The amount of heat (G) that can be extracted from a flow of water is given by:

$$G=Q\times\Delta T\times SC$$

where Q is flux of water (l/s), ΔT is temperature difference across heat pump (typically 5°C) and SC is specific heat capacity of water (4,180 J/l/°C). Therefore, for a discharge flowing at 1 l/s, the ground source heat available would be in the order of 21 kW. Together with an electrical energy input to the heat pump of 7 kW (in a typical heat pump, for every 1 kW of electrical energy consumed, around 3-4 kW of space heating are delivered), a total heating effect of 28 kW would be possible, sufficient to heat several houses.

In addition, the annual temperature variation of the discharge is an important consideration for a potential ground source heat scheme. Although the higher the temperature of discharge the greater the potential for use in a ground source heat system, lower temperature discharges may also be feasible since the temperature is upgraded within the heat pump to the necessary temperature for space heating. The required electrical input to the heat pump, however, would increase, thus reducing the efficiency of the system. The efficiency of a heat pump is measured by its coefficient of performance which is defined as the ratio of total heating effect to electrical input. In general, a coefficient of 3 to 4 is necessary for a heat pump to operate efficiently (Banks, 2008). Similar considerations would need to be made if the post-treatment discharge were to be used in a ground source heat scheme since the temperature of the water following treatment would be expected to be considerably lower than at pre-treatment.

In order to assess the potential of an abandoned metal mine water for use in open loop ground source heat schemes, clearly the most important criterion is an assessment of the potential groundwater yield, whether this is via a gravity-driven discharge or pumped from a shaft or borehole drilled into the abandoned workings. In the case of a gravity-driven discharge, a record of the variation in flow rate over a single year will be required to ascertain the average annual flow rate together with the maximum and minimum flow rates. If the water source is to be pumped from a shaft or borehole, a pumping test will be necessary to determine the potential groundwater yield. Knowledge of the depth to abandoned workings is also a requirement, along with a

record of the water temperature throughout the course of a year in either the discharge or flooded abandoned workings.

3.2 Micro-hydroelectric potential for mine waters

Hydropower is one of the oldest methods of harnessing renewable energy, with the first water wheels used for irrigation purposes some 2,000 years ago. Hydropower systems convert potential energy stored in water held at height to kinetic energy to turn a turbine to produce electricity. Systems vary in size from large-scale power plants to micro-hydro plants, which are generally considered to be schemes below 100 kW (Smith 1994; Nunes and Genta 1996).

Small-scale hydro is one of the most cost-effective and environmentally attractive energy technologies and has proved to be particularly suitable for rural electrification in less developed countries (Paish 2002). The technology tends to be extremely robust with systems requiring little maintenance. In contrast to large hydro, involving the building of dams and the flooding of large areas of land, micro-hydro typically consists of only a weir with little or no water stored.

The energy available in a body of water depends on the flow rate and the head and is given by:

$$P=HQge$$

where P is power (watts), H is head (metres), Q is flow rate (m^3/s), g is the acceleration due to gravity (m/s^2) and e is an efficiency factor. In the case of micro-hydro systems, efficiencies tend to be in the range 60 to 80% (Paish 2002). Useful power can therefore be obtained from even a small stream. For instance, a small turbine on a hill stream with a flow of 15 l/s and a head of 15 m will generate about 1 kW, enough to meet the basic demands of a house.

A thorough literature search has revealed little in the way of case studies of micro-hydro schemes for mine water discharges, although the wide range of possible flow rates and heads used in such schemes is apparent. Fast-flowing streams in upland areas tend to have the most suitable characteristics for a micro hydro-scheme, principally due to the high flow rates and high head available. Montanari (2003), for example, studied a plant situated in the Emilian Appennine mountain range in Italy which used a flow rate of $1.83 \text{ m}^3/\text{s}$. Karlis and Papadopoulos (2000) carried out a feasibility study of a typical small hydroelectric plant in Greece which had an available head of 160 m. They predicted an annual electrical energy production of 6.5 million kWh.

Village-scale hydroelectric programmes exist in many developing countries throughout the world as they provide a cheap and reliable source of power from a renewable, indigenous source. They tend to be very small scale (Smith 1994) but can provide electricity to remote villages. Most village hydroelectric schemes are designed to provide their rated output with less than the minimum available flow, so that they can operate at full output all year. The dry season flow must therefore be accurately determined, preferably over a number of years.

Clearly a potential problem for the use of mine water discharges in micro-hydro schemes is the precipitation of iron and manganese oxyhydroxide (in particular) within the turbine but a possible solution, as described by Paish (2002), could be to pass the water through a settling tank, before descending to the turbine, in which water would be slowed down sufficiently for suspended particles to settle out. Alternatively, the outflow from a treatment system could be harnessed if a large enough head could be provided. In terms of environmental permissions, the Environment Agency is currently undertaking a review of small-scale hydropower and how it issues the necessary

permits but at present it may be necessary to gain an abstraction licence, an impoundment licence and a flood defence consent, depending on the individual scheme, before a system can be developed. Important factors to consider when designing a scheme are the maintenance of sufficient water flow in the river reach to sustain the ecology and the maintenance of a safe passage for fish.

Despite these limitations, mine water discharges, particularly those from abandoned metal mines which tend to be in upland regions, clearly have potential for use in micro-hydro schemes. The suitability of a site will depend on the available head and water flow rate, which should be monitored on a daily basis over a period of at least one year to determine an average annual flow rate on which a potential scheme could be designed. Even where discharges have insufficient available head and/or flow rate to generate enough power for the demands of a house or full-scale remediation plant, it may have potential to generate adequate power for small-scale equipment at remediation sites. On the other hand, if the amount of power generated is greater than that required, there is the option to sell any excess electricity to the National Grid. Additional hydrological parameters which are required for Environment Agency licensing include a flow duration curve, mean flow and baseflow index, in order to ascertain any potential impacts the scheme may have on the watercourse. The ecological impacts of such schemes also need to be determined.

4. Links to technology suppliers and recovery and decontamination industries

The principal aim of this review has been the identification and appraisal of a wide range of options for resource recovery and decontamination of metal-rich substrates derived from mine treatment systems. This information, in conjunction with lab- and pilot-scale metal removal experiments and substrate stability tests, may be used by passive remediation funders and managers to inform their choice of post-treatment reuse or clean-up strategies. However, the implementation of such technologies at field scales will inevitably require the involvement of remediation and recovery technology providers and the formation of stakeholder partnerships comprising the substrate producer, the remediation or recovery technology provider and the end users or receivers of processed materials (Seager *et al.* 2007). The implementation of recovery or decontamination technologies will also often require the involvement of a regulator.

The following section describes a variety of organisations which represent industrial technology providers, recycling and decontamination industries and resource users within the UK and internationally. Depending on the chosen treatment option, technology providers are most likely to be drawn from the mining, waste management/recycling industries or from the environmental engineering and consultancy sectors. Each of these sectors is represented by a number of umbrella organisations, each of which provides listings and up-to-date information on specific contractors, consultants and technology providers from their given sector. Critically many of these organisations have been set up to facilitate collaborative partnerships. Organisations or information resources of particular relevance to metal-contaminated substrates derived from passive mine remediation systems include:

1. Mining Industry Research Organisation (MIRO, www.miro.co.uk) supports collaborative technological development throughout the minerals industry. With a head office in the UK, MIRO has experience in mining and mineral extraction, mineral processing, environmental technologies, waste management, new materials and land reclamation. The organisation aims to highlight industrially relevant science and technology and links to important industry projects such as the Mineral Industry Sustainable Technology Programme (MIST) and the Sustainable Land-Won and Marine Dredged Aggregate Minerals Programme.
2. European Association of Mining Industries (Euromines, www.euromines.org) promotes research into new deposits, mining and ore dressing, mining exploration, extraction, environmental health.
3. Mineral Products Association Cement (MPA cement, www.cementindustry.co.uk) has a sustainability agenda for minimising UK wastes by processing selected material and byproducts from other industries.
4. British Metal Recycling Association (BMRA, www.recyclemetals.org) represents the £5 billion UK metal recycling sector with over 300 members involved in processing steel, aluminium, copper and most other ferrous and non-ferrous metals. However, the focus of the BMRA seems principally directed to scrap metal recovery rather the mineral recovery.
5. MineralsUK (<http://bgs.ac.uk/mineralsuk/home>) is the British Geological Survey's (BGS) Centre for Sustainable Mineral Development. Run by the BGS

Economic Minerals Programme, the Centre is a global leader in the compilation, provision and analysis of mineral statistics and the major UK national provider of spatial and statistical minerals information. It also carries out research in metallogenesis, land-use impacts of mineral extraction and geomaterials.

6. Construction Industry Research & Information Association (CIRIA, www.ciria.org.uk) is a member-based research and information organisation dedicated to improvements in the construction industry.
7. Waste Resource Action Programme (WRAP, www.wrap.org.uk) works in England, Scotland, Wales and Northern Ireland to prevent waste, promote recycling and develop markets for valuable products. WRAP works directly with all sectors of the recycling industry including waste management contractors, materials recovery facility (MRF) operators, re-processors and manufacturers that use recycled content in the manufacturing process. In addition WRAP provides guidance and access to funds for waste recycling projects.
8. Environmental Remediation Directory (www.remediation.co.uk) provides listings of remediation services, contractors, consultants and technology providers in the remediation industry.
9. Environmental Data Services (ENDS directory, www.endsdirectory.com) provides information on UK environmental consultancies and is designed to 'enable clients to quickly review the characteristics of, and make comparisons between, different companies'.
10. Contaminated Land: Applications in Real Environments (CL:AIRE, www.claire.co.uk) has a remit to stimulate the regeneration of contaminated land in the UK and takes an active role in development of a research strategy to address the practical problems in contaminated land remediation in the UK.
11. The Environmental Industries Commission (www.eic-uk.co.uk). Through its innovative sector working groups, the EIC actively promotes a supportive legislative and fiscal framework that emphasises cost-effective policies, coherent standards and practical solutions. The EIC facilitates the exchange of information and experience on R&D, market opportunities, funding and training.
12. Soil and Groundwater Technology Association (www.sagta.org.uk) shares know-how and experience of the technical aspects of assessing and dealing with contaminated land, with one focus being the stimulation and acceleration of the development of cost-effective technologies and methodologies.

5. Conclusions and recommendations

This review sought to address key considerations with respect to resource recovery from passive mine water treatment systems. The principle conclusions are:

1. A limited number of studies of passive remediation systems have shown that metals accumulate in substrates to levels ranging from <10 to $<10,000$ mg kg⁻¹ (<0.001 - $<1\%$ w/w). Even these higher levels are lower than typical mineral grade cut-off values considered for economic recovery in mine operations.
2. In passive treatment systems, however, metal accumulation levels depend on influent metal loading rates where accumulation occurs over decadal timescales.
3. Furthermore, metals are heterogeneously distributed in such systems with higher concentrations in the substrate surface layers nearest mine water inlets. Recovery technologies should, therefore, be spatially targeted.
4. Metal speciation in both aerobic and anaerobic treatment wetlands is heterogeneous with metals precipitated as oxidised and reduced mineral phases as well as organic bound metals complexes. This heterogeneity may have a profound effect on the outcome of leachability tests (stability in landfill) and hence the cost of disposal or the requirement for remedial treatment.
5. After metal accumulation within passive treatment systems metal concentrations may exceed the PAS100 limits for use as composts. In this sense, these untreated substrates may be considered as not suitable for addition to land.
6. However, chemical leaching (via a variety of lixiviates) and cheaper bioleaching approaches are likely to remove metals from passive treatment substrates.
7. Alternatively, metal-laden passive remediation substrates may be subjected to stabilisation or solidification technologies for reuse as construction cements or backfilling materials or for stable disposal.
8. The use of mine water discharges in ground source heat and micro-hydroelectricity schemes has potential within the UK.

The principal recommendations for future research in this area are:

1. Detailed characterisations of metal accumulation rates and their spatial distributions and particle sizes within pilot- and field-scale non-coal mine remediation systems.
2. Derive estimates of UK-wide bulk quantities of metal-rich materials produced from passive non-coal mine remediation systems. Calculation of grade cut-off values for such materials.
3. Pilot-scale physical, chemical and biological leach experiments to determine metal recovery/decontamination efficiencies from conditioned non-coal mine remediation substrates.
4. Application of pilot-scale recovery processes of metals from pregnant leach solutions.

5. Leachability tests (TCLP) to determine the hazardous or non-hazardous nature of remediated and un-remediated materials.
6. Assessment of the effect of low metal substrate disposal on nutrient levels, soil health and plant productivity in addition to long-term stabilities of waste materials in agricultural settings or stabilised construction materials.
7. Assessment of the suitability of treatment substrate for cement feedstocks.

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