Physicochemical composition of wastes and co-located environmental designations at legacy mine sites in south west England and Wales: Implications for their resource potential

R. A. Crane,[1], D. E. Sinnett[2], P J Cleall[1] and D. J. Sapsford[1]*

[1] School of Engineering, Cardiff University, Queen's Building, The Parade, Cardiff, CF24 3AA. United Kingdom

[2] Centre for Sustainable Planning and Environments, University of the West of England, Coldharbour Lane, Bristol BS16 1QY

* Corresponding author: cranera@cadiff.ac.uk

Highlights (85 characters max)

- Physicochemical composition of key UK metalliferous mine waste is determined
- Cu, Zn, As, Pb, Ag and Sn recorded in appreciable concentrations
- Waste has significant economic value but unlikely a sole driver for site rehabilitation
- Many mine sites are protected for their environmental and cultural resources
- Remediation strategies must consider cultural, geological and ecological designations

Abstract

This work examines the potential for resource recovery from metalliferous mine wastes in south west England and Wales. It does this through an assessment of the physicochemical composition of several key metalliferous legacy mine waste piles and an analysis of their co-location with key cultural, geological and ecological designations. Solid samples were taken from 14 different sites and analysed for metal content, mineralogy, paste pH, particle size distribution, total organic carbon and total inorganic carbon. The majority of sites contain relatively high concentrations (in some cases up to several % by mass) of metals and metalloids, including Cu, Zn, As, Pb, Ag and Sn, many of which exceed guideline concentrations. However, the economic value of metals in the waste could be used to offset rehabilitation costs. Spatial analysis of all metalliferous mine sites in south west England and Wales found that around 70% are co-located with at least one cultural, geological and ecological designation. All 14 sites investigated are co-located with designations related to their mining activities, either due to their historical significance (e.g. mining infrastructure), rare species assemblages (e.g. lichens and bryophytes) or geological characteristics (e.g. mineralisation). This demonstrates the need to consider the cultural and environmental impacts of rehabilitation and resources recovery on such sites. Further work is required to identify non-invasive remediation and resource recovery methodologies to allow sites to be rehabilitated at minimal cost and disturbance.

1 Introduction

There are few locations world-wide where historic metal mining is more evident than in mainland Britain. Extensive mining of major ores for metals including copper, lead, tin and zinc at locations such as the Devon Great Consols in south west Devon and Parys Mountain in north west Wales fuelled profound societal and industrial change world-wide (particularly during the Industrial Revolution) but as a consequence created a significant legacy of waste. Most mine sites in the UK were in peak operation in the 18th and 19th centuries and, as a result, mine sites were not subject to restoration practices which have been required in more recent years. In England and Wales alone, it has been estimated that there are over 8,000 disused metal mines located predominately in 12 ore producing regions (Jarvis, 2007; Palumbo-Roe, 2010). Rather than simply rehabilitating such sites one option is to also recover any economically valuable metals that are present. Mine wastes and tailings are an obvious target for metals recovery as there are often significant quantities of such material in relatively easily accessible locations (i.e. above ground). To date, however, there is a paucity of studies that have characterised mine waste sites in terms of their metal content and extractability. This study is the first effort to present these data for prominent legacy mine sites in England and Wales.

Legacy mines also provide environmental or landscape 'resources'. This study examines the resource potential of these legacy mine wastes in the context of site rehabilitation. Further to the potential recovery of economically valuable metals, there are often other drivers. For example, site remediation may: enable the land to be developed; enhance the conservation of industrial heritage and the related tourism features; and/or decrease the release of pollutants from the site into the surrounding environment. Similarly, there are also often a range of existing services that the mine sites provide which must be considered when implementing site remediation, including: cultural, scientific and educational features (such as historic industrial ruins); and rare fauna and flora. Thus it is important to appreciate the multifaceted value, both positive and negative, depending on perspective, that these sites currently have and would have if remediated. Within this a cost benefit approach must be applied to accurately assess to what extent the economic gain (that can be made through metal extraction) can offset the economic cost of such an intervention. This study thus considers multifaceted characterisation of value and resource through various lenses and the authors use the word "resource" in a wide sense (e.g. Freeman, 2014) to cover both tangible resource of, for example, the metal/ore as well as functional and intangible resource stemming from the ecological, sociocultural and landscape value of the mine sites.

In this work key geological, ecological and cultural designations (herein grouped under the umbrella of "environmental designations") of case study legacy mine sites are presented as a means of assessing the potential positive and negative consequences of the remediation of these sites. The specific aims of this paper are therefore to: (i) present data from the physicochemical characterisation of mine wastes from 9 major sites in the south west of England and 5 major sites from Wales; (ii) delineate the co-located environmental designations of the case study sites with respect to environmental and ecological services, human health and environmental pollution; (iii) appraise broader considerations of value and resource relevant to metal mine sites; and (iv) consider potential decision making tools to determine appropriate methodologies for optimising resource value. Very few studies currently exist which have applied this holistic approach to mine waste characterisation and to our knowledge this is the first time that the co-location of UK mine waste with geological, ecological and cultural designations has been examined.

2. Key drivers/deterrents for the reclamation of legacy mine waste

2.1. Environmental pollution

A large number of historic metal mine sites world-wide are responsible for the release of metals and metalloids into surface and groundwater (Hudson-Edwards, 2011; Plumlee, 2011). For example, a preliminary national assessment in 2009 revealed that as much as 6 of surface water bodies in England and Wales are currently adversely affected by pollution from historic metalliferous mines (Mayes et al., 2009). In the UK ore extraction ceased at the majority of mine sites in the first half of the twentieth century or earlier, and as such ownership and/or legal liabilities for clean-up are often either unclear or orphaned (Palumbo-Roe, 2010). This is also the case in many of the ore fields of North America (e.g. the USA and Canada have approximately 35,000 and 10,000 legacy metal mine sites respectively), Asia (e.g. Japan has approximately 5,500 legacy metal mines) and Europe (e.g. Sweden has approximately 1,000 legacy metal mines) (Mayes et al., 2009). The financial cost of remediating and rehabilitating these mine wastes is significant. For example, in 2012 a series of joint reports commissioned by the Department for Environment, Food and Rural Affairs (DEFRA) and the Welsh Government in collaboration with the Environment Agency estimated that the total cost to remediate all of the water related environmental problems associated with abandoned non-coal mines in the UK would be approximately £370 million, excluding operating costs, and take upwards of ten years (Jarvis, 2012a; Jarvis, 2012b). Moreover, the pollutant discharge from such sites often continues for many decades through to centuries, before water quality recovers to the pre-mining baseline. For example, despite ceasing major operations in the late 18th century Parys Mountain in north Wales remains a major contributor of Cu and Zn to the Irish Sea, discharging an estimated 24 and 10 tonnes of each element respectively each year (Mullinger, 2003).

2.2 Ecological resource

The unique (and often extreme) physicochemical conditions and lack of disturbance has resulted in the development of a rich ecological resource on many different metalliferous mine wastes world-wide (Bradshaw, 2000). For example, legacy mine sites often contain numerous species of rare metal-tolerant plants and lichens (Rodwell et al., 2007), grasslands, wildflowers, orchids and important invertebrates, birds and mammals (e.g. the lesser horseshoe bat) (Barnatt & Penny, 2004). In the UK this has resulted in specific recognition and protection for some mine waste sites. Examples include: the designation of Sites of Special Scientific Interest (SSSI) status for rare metal-tolerant plants, and lichens, and two priority habitats: Calaminarian grasslands (BRIG, 2008) and Open Mosaic Habitats on Previously Developed Land (OMH) (BRIG, 2010).

2.3. Geological and mineralogical resource

The amount of metal produced at major UK mine sites has generally been relatively well recorded over the peak production years (i.e. during the Industrial Revolution), however, definitive figures for the quantity and type of waste produced are often lacking, with estimates typically calculated from predictions on the mineral to waste ratios, which are often highly variable, even for the same commodity (Palumbo-Roe, 2010). To date a number of studies have attempted to quantify the mass, distribution and composition of mine waste located at specific sites across the UK, however, no conclusive inventory is yet to be created due to the large number of mine waste sites and the inherent complexity of differentiating between the mine waste and the natural ground surface. As such a first estimate (e.g. to within an order of magnitude) for the mass and composition of mining waste present at many major legacy metal mine sites in the UK has not yet been conducted with their associated economic value therefore unknown.

Historic ore beneficiation processes were typically less efficient than today and as such it is likely that appreciable concentrations of economically valuable metals were discarded as waste and are currently stored at legacy metal mine sites in the UK and world-wide. Furthermore, the material has often already undergone size reduction during historic ore beneficiation and is often stored as unconsolidated material in relatively accessible locations (in piles above ground). Mine waste (in particular mine tailings waste) is also often of a relatively homogenous physical and chemical composition compared to other waste streams such as municipal solid waste. These extraction and processing activities have often resulted in the occurrence of rare and unusual geological, mineralogical or physiographical features deemed worthy of protection. Many mine wastes in the UK are therefore designated, for example, as Sites of Special Scientific Interest (SSSIs) because of these characteristics. Similarly, where relics demonstrate technological advancement of the mining industry they may also be designated as Scheduled Monuments.

2.4. Sociocultural resource

The cultural heritage of many mine sites is considerable and the waste piles themselves are an intrinsically valuable component of this heritage landscape, i.e. in addition to remnant buildings and processing equipment (Howard et al., 2015). As such many landscape-scale historic mining districts have been granted official conservation status, for example the Cornwall and West Devon Mining Landscape World Heritage Sites as well as the numerous individual Scheduled Monuments and Listed Buildings that are associated with a rich legacy of mining. Physical features such as hushing scars; prospection pits and mine shafts; roads, tramways and leats linking the mines and settlements as well as the spoil tips themselves are regarded as valuable heritage (e.g. Schlee, 2007). The ecological and cultural significance of mine wastes, coupled with their setting within the mine site and the wider landscape, provide a range of benefits to local people and visitors, with the former mine sites often being important economically with respect to industrial heritage tourism (e.g. Jones, 2001). These benefits can be framed as ecosystem or, perhaps more helpfully in this context, landscape services (Swanwick, 2009). For example, prior to its World Heritage Site status being granted it was estimated that the mining attractions in Devon and Cornwall benefitted from nearly 1 million visitors each year, with around 2.5 million visitors to the region citing the mining heritage as an important consideration in their visit. This generates significant revenue to the local economy at an estimated £120 million per year (Atlantic Consultants, 2003). Economic growth associated with mining heritage tourism has also been highlighted as a realistic development option in many economically marginal areas of Wales and there is active promotion led by the European Union for the maintenance of mining heritage e.g. the commercial Mining Heritage Network (Jones, 2001; Edwards, 1996).

It is much more difficult to assign a monetary value to many of the other services provided by such sites which include recreation for local populations, cultural and spiritual enrichment, education and research (Bloodworth et al., 2009; Barnatt & Penny, 2004; Swanwick, 2009). For example, local communities also often place an emotional value on mining landscapes (Ballesteros, 2007). Many legacy mine sites also have educational and academic value and are often the subject of a diverse range of lower and higher education and research in subjects from earth sciences, archaeology and engineering to social sciences and economic history. The cultural value of the sites is reflected by the wide number and type of stakeholders including archaeological and local history groups. However, the rural location of many mine wastes means that in addition to ecological and cultural resources arising from past mining activity there is likely to also be additional designations that may be adversely impacted on by pollution from the waste. Therefore it is crucial that the multifaceted nature of such sites and the landscapes in which they are located is understood.

3. Methodology

3.1 Site selection

In England and Wales there are estimated to be over 3,000 legacy non-ferrous metal mines (Jarvis, 2007) concentrated in three main ore producing regions: Cornwall and west Devon; Northumbria and north Humber; and Wales. The focus of this study is on the districts of Cornwall and west Devon and Wales because they both contain significant quantities of metalliferous legacy waste (Figure 1), are representative of Cu/Sn and Pb/Zn mining areas, have a high density of UK Mine Waste Directive sites (Palumbo-Roe, 2010) and a range of cultural and environmental designations.

Cassiterite (SnO_2), chalcopyrite (Cu,FeS_2) and later arsenopyrite (Fe,AsS) bearing ore were principally extracted in Cornwall and west Devon and processed for Sn, Cu and As respectively. Chalcopyrite and galena (PbS) bearing ore was principally extracted in Wales and processed for Cu and Pb respectively. In many cases galena also contained relatively high Ag content, especially at Cwm Ystwyth, which was also extracted. Large quantities of sphalerite (Zn,FeS) was also mined, however, Zn was only occasionally removed and much remains in mine waste. The sites investigated which are located in south west England were: Alfred Consols (ALF), Caradon (CAR), Consols (CON), Devon Great Consols (DGC), Levant (LEV), Nangiles (NAN), Prince of Wales (PWM), Poldice (POL) and Wheal Maid (WHM). The sites investigated which are located in Wales were: Esgair Mwyn (EGM), Frongoch (FRG), Grogwynion (GRG), Parys Mountain (PYM) and Wemyss (WEM). Sites were selected which contain considerable mine waste volumes and are also located across different mining districts (as determined by different geographical and mineralogical constraints) of the region. Within south west England this was the Tamar valley and Tavistock (PWM, DGC), Caradon (CAR), Gwennap Kennal Vale and Perran Foundry (CON, NAN, POL, WHM), Port of Hayle (ALF) and St Just (LEV) mining districts. Within Wales this was the Central Wales (EGM, FRG, GRG, WEM) and Anglesey (PYM) mining districts.

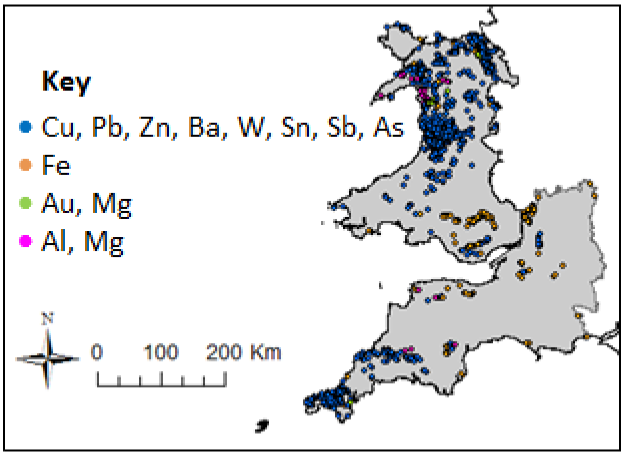

Figure 1. Location of metalliferous mines in south west England and Wales. Produced using BRITPITS database; Licence No. 2014/098BP ED British Geological Survey NERC. Boundary data from UK Data Service. URL: http://census.edina.ac.uk.

3.2 Sample collection procedure

Mine waste samples were collected from each site following the methodology of ASTM D6009-12 (ASTM, 2012) which provides an appropriate method for the sampling of unconsolidated, aggregated waste piles. Many sites contained notable waste pile(s) of which the largest was typically targeted for characterisation (see Supplementary Data for sampling locations). Samples were collected using a stainless steel trowel at equal distances around the base of each mine waste pile at a depth of 0.2m. The sample depth of 0.2m was selected because it was determined as likely to represent a suitable compromise between sampling beneath the surface weathered zone whilst also exerting minimal aesthetic damage on the waste piles. Moreover, visual inspections in the field revealed the material, in almost all occasions, to be relatively homogenous with depth, i.e. no surface weathered zone could be identified.

At most sites the mine waste is considered to be mine tailings (based on literature records and the relatively fine particle size observed). Each sample had a volume of approximately 5 L with a mass typically between 6 and 8 kg, depending on bulk density. Once collected the samples were dried at 105°C for 24 hrs. The number of samples taken from each site was dictated by the pile volume, ranging from 3 samples taken for LEV to 21 samples taken from WHM (see Supplementary Data).

3.3 Sample and site characterisation procedures

Composite samples were created for each site by riffling each sample 6 times and then mixing (using a mixing pad) each final aliquot together thoroughly. Each composite sample was then riffled to yield an appropriate mass for each analysis technique. Particle size distribution (PSD) measurements were performed via dry sieving and sedimentation (BS, 2009) using 400 g from each composite. Uncompacted aggregate bulk density measurements were performed following BS 812: 1995 (BS, 1995). A cylinder of 1876 mL in volume was used and a tamping rod of 16 mm in diameter. Paste pH measurements were performed via ASTM D4972 – 13 (ASTM, 2013), using a 1:1 solid liquid ratio, i.e. 40 g from each composite and 40 mL of Milli-Q water (resistivity > 18.2 MΩ cm). Samples were prepared for X-ray diffraction (XRD), inductively coupled plasma optical emission spectroscopy (ICP-OES), total organic carbon (TOC) analysis and total inorganic carbon (TIC) analysis by crushing (to particle size <75 µm), using a Labtech Essa LM1-P puck mill crusher at 935 RPM for 120 seconds, a 200 g subsample of each composite sample. Each crushed sample was then prepared for XRD analysis by packing approximately 2 g of the material into an aluminium XRD stub. Analysis was performed using a Phillips Xpert Pro diffractometer with a CuKα radiation source (λ = 1.5406A; generator voltage of 40 keV; tube current of 30 mA). Spectra were acquired between 2θ angles of 5–90°, with a step size of 0.02° and a 2 s dwell time. Each crushed composite sample was prepared for ICP-OES analysis via a 4 acid digest (EPA, 1996). Firstly, 0.01 g was placed in a PTFE lined microwave digest cell and 3 mL of analytical grade 45.71% hydrofluoric acid (HF) was then added and left for 12 hrs. 6 mL of aqua regia solution (1:1 ratio of analytical grade 32% hydrochloric acid (HCl) and 70% nitric acid (HNO_3)) was then added and the container was then placed in a microwave digest oven (Anton Paar Multiwave 3000) and heated at 200°C (1400 watts) for 30 minutes (after a 10 minute up ramp time period) and then allowed to cool for 15 minutes. The resultant solution was then neutralised using 18 mL of analytical grade 4% Boric acid (H_3BO_3) at 150°C (900 watts) for 20 minutes (after a 5 minute up ramp time period) and then allowed to cool for 15 minutes. ICP-OES analysis was performed using a Perkin Elmer Optima 2100 DV ICP-OES. Total carbon (TC) measurements were performed using a Leco SC-144DR sulphur/carbon analyser. Samples of 0.35 g mass were loaded into the instrument and heated at 1350°C in a pure O_2 (>99.9%) atmosphere. The concentration of CO_2 released by each sample was then measured using an infrared detection cell at a constant flow rate. Total inorganic carbon (TIC) measurements were performed using a Shimadzu SSM-5000A using 99.9% O2 at 500 mL/min and catalytically aided combustion oxidation performed at 900°C. Total organic carbon (TOC) was calculated by subtracting each TIC measurement from each samples corresponding TC measurement.

3.4 Hydrometallurgical extraction experiments

Hydrometallurgical extraction experiments were conducted using a 1:10 solid-liquid ratio; 40 g of each composite sample and 400 mL of a 1M H_2SO_4 solution. Samples were sealed in 500 mL glass jars and constantly agitated at 200 RPM using a Stuart SSL1 orbital shaker table. Liquid samples for ICP-OES analysis were extracted from each batch system after 24 hrs and filtered using a 0.45 μm PTFE filter.

3.5 Spatial analysis of mine locations, ecological and cultural designations

In addition to the analytical characterisation of the waste materials spatial analysis was undertaken to: i) understand the scale of past mining activity in the south west of England and Wales; and ii) examine the co-location of mine sites with areas protected for their geological, ecological or cultural benefits. The British Geological Survey BRITPITS database was used along with spatial data for the main geological, ecological and cultural designations (as detailed in Table 1) held by Natural England, Historic England and Natural Resources Wales. These designations were selected as they meet at least one of the following criteria: they are 'specified' ecological receptors under Part 2A of the Environmental Protection Act (1990) (DEFRA, 2012), they are known or suspected to be co-located with past mining activity and there are spatial data available for them.

Table 1 Ecological and cultural designations included in the study

Designation	Summary and protection
Geological and ecological	
Local Nature Reserve (LNR)	Designated because of their nature conservation and/or geological interest by local authorities under the National Parks and Access to the Countryside Act (1949) and the Natural Environment and Rural Communities Act (2006).
National Nature Reserve (NNR)	Sites of biological and geological interest with a strong research and educational remit, most are publicly accessible. They are designated under the National Parks and Access to the Countryside Act (1949) but also receive protection under the Wildlife and Countryside Act (1981).
Site of Special Scientific Interest (SSSI)	Sites of biological and geological interest in the UK designated under the Wildlife and Countryside Act (1981). They range in size from less than a hectare to over 30,000 ha. SSSIs often overlap with other designations including LNRs, NNRs, SACs and SPAs.
Special Area of Conservation (SAC)	Designated for their internationally significant habitats and species under the 1992 Habitats and Species Directive and the Conservation of Habitats and Species Regulations (2010). Together with SPAs they are also known as Natura 2000 sites, all terrestrial SACs and SPAs are also SSSIs.
Special Protection Area (SPA)	Designated to protect threatened or endangered internationally significant bird species under the 1979 Birds Directive and the Conservation of Habitats and Species Regulations (2010).
Ancient Woodland (AW)	Defined as woodland that has been present since 1600AD. They take hundreds of years to develop and are irreplaceable yet are not protected

	by specific legislation. They are however protected under the planning policy in both England and Wales.
Priority Habitats (PH)	Priority habitats are published through the Natural Environment and Rural Communities Act (2006). They are not specifically protected but local planning policies should provide opportunities for their preservation and enhancement.
Open Mosaic Habitat on Previously Developed Land (OMH)	A relatively new priority habitat in acknowledgement of the ecological significance of many previously developed (brownfield) sites. An inventory of potential OMH sites has recently been published.
Cultural	
Area of Outstanding Natural Beauty (AONB)	Designated solely for their landscape qualities under the National Parks and Access to the Countryside Act (1949).
National Park (NP)	Also designated under the National Parks and Access to the Countryside Act (1949) they have an explicit purpose to promote education and recreation as well as conservation of landscape, wildlife and cultural heritage.
Scheduled Monument (SM)	Designated under the Ancient Monuments and Archaeological Areas Act (1979) for their archaeological character.
World Heritage Site (WHS)	Designated by the United Nations Educational, Scientific and Cultural Organisation (UNESCO) for their natural or cultural features of international significance.
Landscape of Historic Interest (LHI)	A non-statutory recognition of the special or outstanding historic character of landscapes in Wales. There is an expectation that they are considered as part of the planning process (CADW, 2007).

The BRITPITS database details all known mine locations in Great Britain as point data categorised by the commodity (e.g. coal, Cu, Pb, gravel), type of mine (e.g. underground, open pit), status (e.g. active, ceased) geological age (e.g Carboniferous, Permian), lithostrat (e.g. Alluvium, West Maria Lode) as well as address and operator information. Co-ordinates are for the working or entrance to the mine (tolerance of 5 m) (Cameron, 2012), not the location of the waste, but the assumption was made that all non-active mine sites have waste materials in their immediate vicinity. There are around 170,000 entries in the complete database, of which 4670 are non-active metalliferous mines in England, with 717 in the south west region and 3350 in Wales which are the focus of this study.

The analysis was carried out in ArcMap 10.1. First, the BRITPITS data were limited to those mine sites with the metalliferous commodities (Sb, As, Cu, Ba, Au, Fe, Pb, Mn, Ag, Sn, Sr and Zn), those that were mine locations (as opposed to associated infrastructure such as rail depots and wharfs) and those that were non-active (ceased, inactive, dormant, historic; there were only two active metalliferous mines in the areas of interest). Where multiple commodities were mined BRITPITS contains duplicate records, one per commodity, so these records were merged.

Next, the spatial joining function in ArcMap was used to identify which mine sites are co-located with the geological, ecological and cultural designations (Table 1). Additional designations were also considered but no mine sites were co-located with these in the SW of England or Wales; these were Parks and Gardens, Battlefields and Nature Improvement Areas so these will not be discussed further. The split between geological and ecological, and cultural designations is arbitrary in some cases. Some designations have a clear basis in nature conservation (e.g. LNRs, SACs) or heritage (e.g. SMs, WHSs) whereas others are more nuanced. The decision was taken for cultural designations to include those where landscape and/or recreation as opposed to wildlife conservation is a primary objective (e.g. AONBs, National Parks) (Gaston et al., 2006).

Finally, this analysis was refined using the case study mine sites. The estimates of the spatial extent of the sampled spoil tips, drawn from aerial imagery, were used to gain further insight into the co-location with the designations. Polygons were drawn around an aerial view of the waste pile which has been sampled (see Supplementary Data for individual sampling locations) using the contrasting colour between the waste pile and the surrounding vegetation along with field observations as a guide. The specific designations at the site level were then examined more closely to identify those that are dependent (versus independent) on the mine waste as a way of exploring the opportunities and constraints for resource recovery. In addition, the case study sites were compared spatially to those on the inventory of Mine Waste Directive sites (Environment Agency, 2014). These are known or are suspected to be causing a risk to water quality and/or human health and therefore likely to require remediation.

To estimate the volume of waste in the case study locations polygons were used in conjunction with digital surface models produced using Light Detection and Radar (LiDAR). The data were at 1 m resolution with the exception of DGC and NYM where only a 2 m resolution was available. ArcMap was used to estimate the elevation of the land surface surrounding the waste material. This was estimated using at least ten points around the boundary of the polygon and the average elevation calculated. The polygon volume tool was then used to calculate the volume of waste above this elevation. This is a conservative estimate as the topography of sites was variable with many of the wastes being located on a slope. In addition, the presence of vegetation at some waste piles likely led to inaccurate readings due to it both shrouding the edge of the waste pile and also enabling greater elevations than the land surface to be recorded in the LiDAR data. Figures 2 and 3 display location of case study mine sites in south west England and Wales respectively and their co-location with statutory designations.

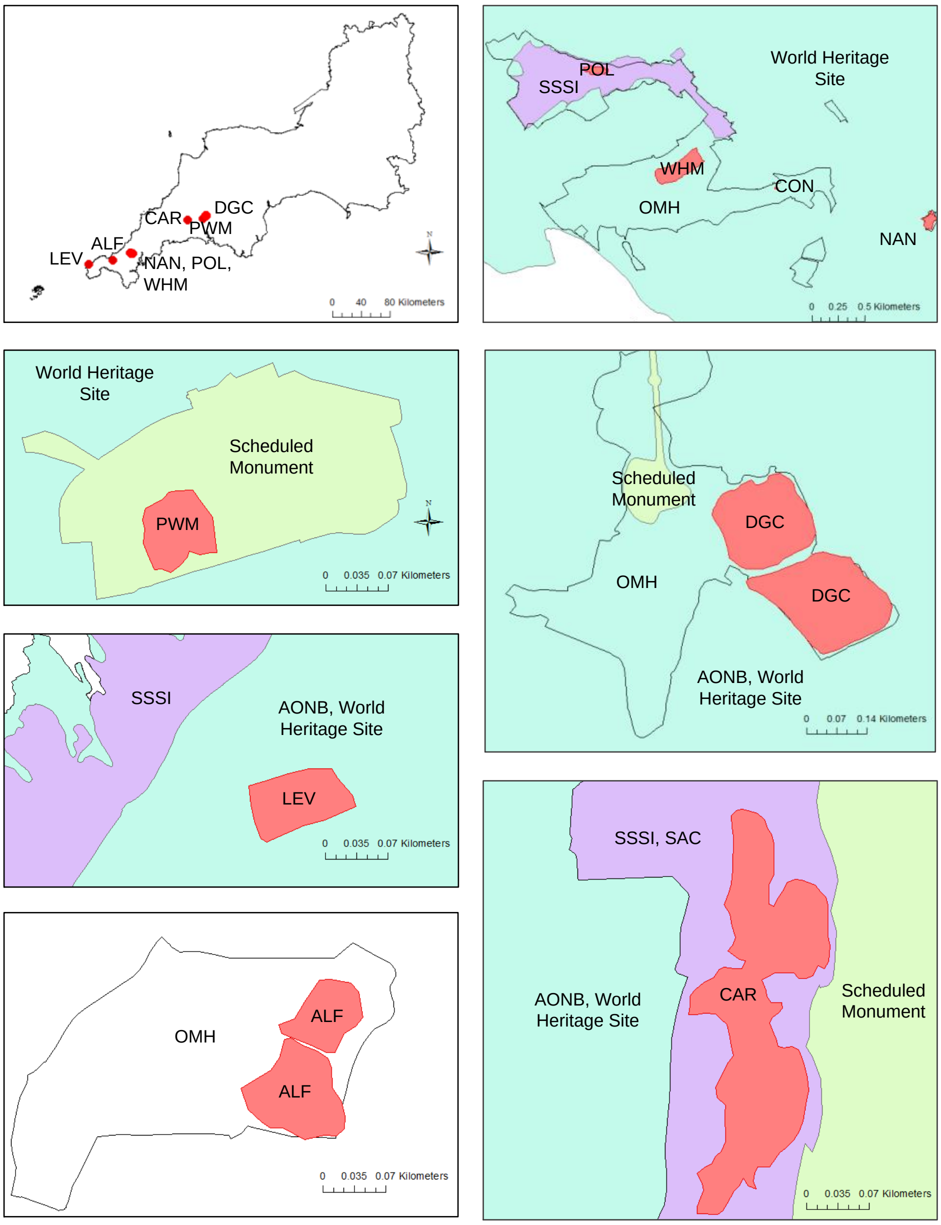

Figure 2. Location of case study mine sites in south west England and their co-location with statutory designations. Produced using BRITPITS database; Licence No. 2014/098BP ED British Geological Survey NERC. All rights reserved. AONB, SAC, SSSI © Natural England copyright. Contains Ordnance Survey data © Crown copyright and database right [2016]. SM, WHS © Historic England 2016. Contains Ordnance Survey data © Crown copyright and database right 2016. Boundary data from UK Data Service http://census.edina.ac.uk.

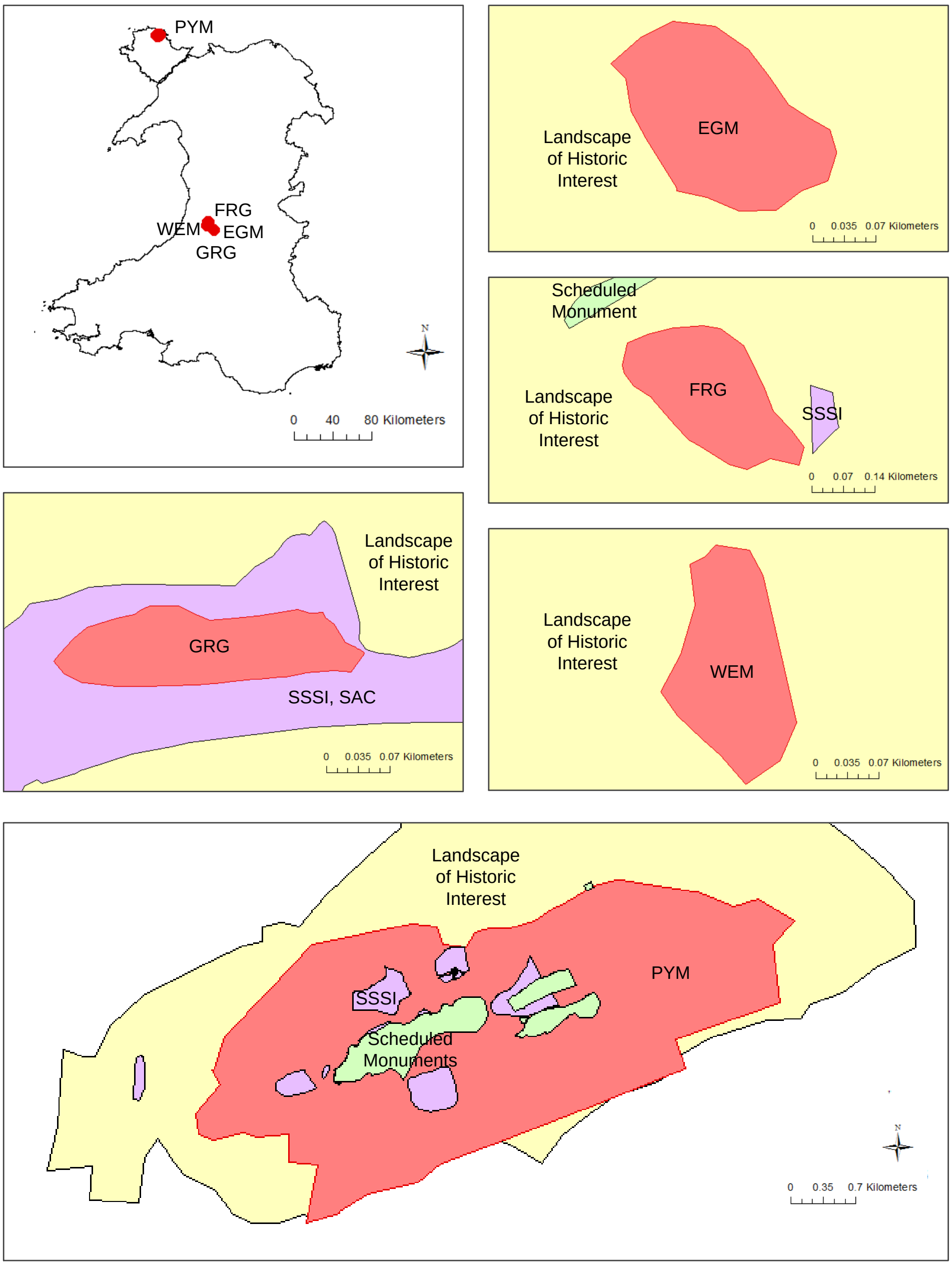

Figure 3. Location of case study mine sites Wales and their co-location with statutory designations and Landscapes of Historic Interest. Produced using BRITPITS database; Licence No. 2014/098BP ED British Geological Survey NERC. All rights reserved. SAC, SSSI, LHI, SM © Natural Resources Wales copyright. Contains Ordnance Survey data © Crown copyright and database right [2016]. Boundary data from UK Data Service http://census.edina.ac.uk.

4 Results and Discussion

4.1 Physicochemical characterisation of mine wastes

Table 2 displays location, estimated volume, bulk density, total mass, paste pH and TOC data for mine waste taken from SW England and Wales respectively. The paste pH for all sites is recorded to be <7 and so cationic metal species are expected to be relatively mobile in the environment. TIC was recorded as 0.00% for all composite samples (except the EGM site where it was recorded as 0.04 wt.%) which indicates that the mine waste all have significantly low carbonate alkalinity. The XRD patterns of the composite samples all indicate quartz (α-SiO_2) as the major crystalline component present with minor muscovite ($H_2KAl_3(SiO_4)_3$) and potassium feldspar ($K_5Na_5AlSi_3O_8$) recorded for some samples (Appendix A). The original ore minerals arsenopyrite and chalcopyrite were not detected for any of the mine waste samples from SW England, and no Pb-bearing minerals, e.g. galena (PbS), were detected for the mine tailing samples from Wales. Particle size as a function of cumulative mass passing for all sites is shown in Appendix B. It can be noted that the PSD is relatively variable between sites, with a variation in 0.57-24.81 wt.% recorded for the silt and clay size fractions (particle size range <0.063 mm), upper and lower values for CAR and FRN respectively; a variation in 19.9-78.8 wt.% recorded for the sand size fractions (particle size range 0.063-2 mm), upper and lower values for LEV and DGC respectively; and a variation of 3.6-79.1 wt.% recorded for the gravel size fraction (particle size range 2-64 mm), upper and lower values for PWM and LEV respectively.

As noted above, when estimating the volume of waste in each pile the average elevation from the area immediately surrounding the waste was used as a baseline, which has resulted in these estimates being conservative because much of the surrounding material is unlikely to be at the original elevation and the typography of some sites was extremely variable. For example, the volume of mine waste at DGC and GRG have been determined in other studies to be 274,250 (Mighanetara, 2008) and 50,311 (Excal, 1999) respectively compared to 198,923 and 9510 m^3 here.

Table 2. Location, volume, bulk density, total mass, paste pH, TOC and TIC data for mine waste. The location data refers to the location where the first sample was taken from. * No LiDAR data; † mine waste is located in a valley floor so not possible to estimate volume using LiDAR.

Site name	Location (latitude)	Location (longitude)	Estimated volume using LiDAR (m^3)	Bulk density (g/cm^3)	Estimated mass (tonne)	Paste pH	TOC (wt.%)	TIC (wt.%)
South west England								
ALF	50°11′01.72″N	05°23′00.62″W	20516	1.44	29543	3.62	0.42	0.00
CAR	50°30′12.88″N	04°26′59.43″W	29286	1.26	36900	4.22	0.22	0.00
CON	50°14′12.46″N	05°09′00.03″W	32	1.04	33	3.73	0.53	0.00
DGC	50°32′16.75″N	04°13′17.32″W	198923	1.30	258600	3.33	0.16	0.00
LEV	50°09′10.80″N	05°40′58.47″W	1408	0.92	1295	3.78	0.68	0.00
NAN	50°14′04.73″N	05°08′13.07″W	15277	1.23	18791	2.68	0.28	0.00
POL	50°14′36.08″N	05°09′58.90″W	8941	1.06	9477	4.92	0.15	0.00
PWM	50°30′45.42″N	04°15′24.76″W	1799	1.39	2501	3.35	0.04	0.00
WHM	50°14′15.32″N	05°09′34.15″W	Unknown†	1.28	n/a	2.39	0.20	0.00
Wales								
EGM	52°18'26.58"N	03°49'39.58"W	Unknown*	1.49	n/a	5.56	0.38	0.04
FRG	52°21'7.05"N	03°52'38.90"W	16802	1.54	25875	3.28	0.16	0.00
GRG	52°19'53.76"N	03°53'18.01"W	9510	1.46	13885	6.36	0.25	0.00
PYM	53°23′14.37″N	04°20′59.73″W	Unknown†	1.03	n/a	2.89	1.35	0.00
WEM	52°20'59.13"N	03°53'12.75"W	34560	1.35	46656	3.89	0.33	0.00

Table 3 displays metal concentration data for composite samples from each site. An indication is also provided of where values exceed various guideline concentrations developed to trigger risk assessments to protect human and ecological health. In general relatively high concentrations of As, Cu, Pb and Zn were determined for the sites located in SW England. For example, As concentrations were recorded as being greater than 0.1% for all sites (with the exception of ALF and NAN) with a maximum of 1.92% recorded for DGC. Relatively high concentrations of Cu and Sn were also recorded, with a maximum of 1.76 and 0.078% for CON and PWM respectively. Relatively high concentrations of Cu, Pb and Zn were recorded for samples taken from sites located in Wales. Particularly high concentrations of Pb were recorded for all sites, with a maximum of 4.67 wt.% recorded for FRG. Relatively high concentrations of Zn were also recorded with a maximum of 0.62 wt.% recorded for FRN. Moreover, a number of these metals and metalloids are determined to be exceeding guideline concentrations (some substantially) used to trigger risk assessments to protect human and ecological health. As was recorded to exceed human health guidelines for all sites sampled in SW England and PYM in Wales, whereas Pb was recorded to exceed both human and ecological health guidelines for all Welsh mine sites, and also CON, NAN and WHM for ecological risk. Cr, Cu, Zn and Cd were recorded as exceeding ecological guidelines for almost all sites, and Ni for a number of sites. As such it can be concluded that all sites comprise significant human health and ecological risks associated with toxic metal and metalloid concentrations.

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 Cu is economic at grades approximately >0.5%, Zn and Pb at >1% (Environment Agency, 2012) and Ag at >0.02% (Smith, et al., 1982). A number of sites have yielded metal concentrations above this threshold, namely: CON (Cu = 1.76%), LEV (Cu = 0.52%), PYM (Cu = 0.92%), EGM (Pb = 2.36%), FRN (4.67%) and GRG (1.30%). Metal concentrations (wt.%) for individual samples (which were used to create the composites) are displayed in the Supplementary Data. It can be noted that in general a relatively high variance was recorded between each sample, with a relative standard deviation (RSD) greater than 100% commonly recorded. This indicates that each mine waste pile is relatively heterogeneous. It can also be noted that there is a relatively close fit between the average of these data and the results for the composite sample, with a variance of <10% typically recorded for each metal. This demonstrates that the composite samples are a relatively good representation of the individual samples.

Table 3. Notable metal and metalloid concentration data for composite samples from all sites where green cells indicate concentrations above screening levels for ecological risk[1]; orange indicate those above guideline levels for human health risk[2,3] and red indicate those above both.

	Li	Na	Mg	Al	K	Ca	Ti	Cr[1,2]	Mn	Fe	Ni[1,3]	Cu[1]	Zn[1]	As[1,2]	Ag	Cd[1,2]	Sn	Pb[1,2]
South west England																		
ALF (wt.%)	0.0233	0.2297	1.4343	5.5579	1.2753	0.1888	0.3367	0.0209	0.2353	10.5592	0.0041	0.1540	0.0426	0.0935	<DL	0.0013	0.0019	0.0120
CAR (wt.%)	0.0132	0.5295	0.3014	6.2791	4.1266	0.8129	0.1141	0.013	0.0474	3.3928	<DL	0.2345	0.0078	0.1219	<DL	0.0002	<DL	0.0023
CON (wt.%)	0.0157	0.3451	0.593	5.1893	0.7046	0.1272	0.2100	0.0108	0.1411	13.6919	0.0016	1.7572	0.0916	0.8293	0.0023	0.0019	0.0238	0.0587
DGC (wt.%)	0.0135	0.4312	0.5295	4.6035	0.8871	1.1426	0.2207	0.0315	0.0610	9.9893	0.0019	0.1833	0.0101	1.9176	<DL	0.0012	0.0290	0.0067
LEV (wt.%)	0.0152	0.3721	1.7030	6.6606	1.9049	0.4451	0.5196	0.0128	0.1433	15.2487	0.0042	0.5168	0.0646	0.2543	<DL	0.0018	0.0216	0.0099
NAN (wt.%)	0.0249	0.3660	0.4250	7.8022	2.2552	0.0806	0.3049	0.0147	0.0354	3.5632	0.0003	0.0126	0.0170	0.0405	<DL	0.0002	0.0039	0.0466
POL (wt.%)	0.0243	0.4456	0.2455	7.2796	3.9765	2.8003	0.1231	0.0105	0.0549	2.7428	0.0004	0.0549	0.0131	0.1059	<DL	0.0001	0.0084	<DL
PWM (wt.%)	0.0119	0.5053	0.5990	6.2204	1.1573	0.0897	0.3126	0.0141	0.0628	6.9515	0.0019	0.0937	0.0254	1.5872	<DL	0.0008	0.0782	0.0120
WHM (wt.%)	0.0098	0.6279	0.6080	5.9665	0.6063	0.0949	0.2704	0.0116	0.0396	11.4857	0.0020	0.0446	0.0680	0.1823	<DL	0.0014	0.0300	0.0386
Wales																		
EGM (wt.%)	0.0138	0.7943	0.9825	7.8934	2.3115	0.4153	0.4998	0.0098	0.0986	4.6388	0.0035	0.2406	0.2103	<DL	<DL	0.0007	<DL	2.3602
FRN (wt.%)	0.0124	0.494	0.3235	2.8913	0.8196	0.1054	0.1758	0.0081	0.017	2.4758	0.0010	0.0337	0.6155	<DL	0.006	0.0016	<DL	4.6662
GRG (wt.%)	0.0145	0.9206	1.0651	8.9666	2.4768	0.5315	0.5331	0.0114	0.1329	4.9254	0.0049	0.0210	0.1948	<DL	<DL	0.0007	<DL	1.3009
PYM (wt.%)	0.0013	0.5467	0.1661	2.7089	1.3942	0.134	0.1600	0.0225	0.0544	27.3302	0.0091	0.9191	0.1494	0.1369	0.0034	0.0052	0.0569	0.9124
WEM (wt.%)	0.0151	0.635	0.5845	6.2005	1.6870	0.0975	0.3769	0.0141	0.0416	3.3651	0.0019	0.0059	0.1797	<DL	<DL	0.0006	<DL	0.6984

[1] Proposed Soil Screening Values under the framework for Ecological Risk Assessment (Environment Agency, 2008); [2] Category 4 Screening Values for public open space where there is considered to be a 'negligible tracking back of soil' (Defra, 2014); [3] Soil Guideline Value for Commercial land use (Environment Agency, 2009a; Environment Agency, 2009b; Environment Agency, 2009c; Environment Agency, 2009d; Environment Agency, 2009e). Data on screen levels for ecological risk of As was not available.

4.2 Mine waste resource value and hydrometallurgical extraction efficacy

Key elements of economic value at each site (Cu, Zn, Ag, Sn and Pb) are shown in Table 4. This allows a first estimate of the total economic value for each key element at each site. It should be acknowledged, however, that this value could not be recovered in practice because of the limitations of mineral processing and the constraints imposed by the physicochemical properties of the material. Conversely when estimating the volume of waste in each pile the average elevation from the area immediately surrounding the waste was used as a baseline, which has resulted in these estimates being conservative because much of the surrounding material is unlikely to be at the original elevation and the typography of some sites was extremely variable. In addition as explained in Section 3.5 the single largest waste pile was sampled at each site. In many cases additional (but often minor) waste piles were observed at each site. These piles have not been accounted for both in terms of sample collection (see Supplementary Data for details) and total waste volume estimation using LiDAR. Moreover, the accurate sampling of large mine wastes piles is an intrinsically difficult exercise because the number of samples collected are limited by the resources and time available for any characterisation programme and the amount collected is never enough to fully characterise the waste pile (unless the entire waste pile is sampled and characterised). Also due to operational constraints relatively few samples were taken from each site (see Supplementary Data for details) and it is therefore almost certain that such samples do not entirely represent the overall mine waste pile. The results displayed in Table 4 should therefore be considered not as definitive but rather likely only to be accurate to the nearest order of magnitude.

As an indicator of the ease of extraction using conventional hydrometallurgical processes the recovery of metals in 1 M H_2SO_4 is also included (Table 5). The greatest Cu value is calculated for the DGC mine (£1,657,600) where reasonably high value of Sn (£887,000) is also recorded.

Relatively high value per tonne of Cu is also calculated for PYM (£32.15/tonne). Zn is not recorded in appreciable value (>£50,000) for any of the mine sites in the south west of England; however, relatively high value is estimated for a number of sites in Wales, including FRG (£1,989,000) and WEM (£104,700). Relatively low Ag value is recorded for all sites in the south west of England and a number of sites in Wales; however, relatively highly value is estimated for FRG (£552,400) and PYM (£11.99/tonne). Relatively low Pb value is estimated for all sites in the south west of England, whereas relatively high value is estimated for all sites in Wales, with maximum of £1,521,300 calculated for FRG. It can therefore be stated that the deportment of value resides with Cu>Sn>Zn>Pb>Ag for the English study sites, whereas it is Pb>Ag>Zn>Cu>Sn for the Welsh study sites. When comparing these data to ore deposits (where economically valuable metals are typically present in much greater concentrations and total mass) it is unlikely that the mine wastes studied would be considered as suitable targets for resource recovery of the metals alone. However, the study has shown that the metal resource is present in quantities which are potentially sufficient to offset the costs of site remediation and rehabilitation. Furthermore the hydrometallurgical extraction data (Table 5) demonstrates 1M H_2SO_4 as able to solubilise Cu, Zn, As and Pb with reasonably high efficacy (often >20%). In contrast Ag and Sn were determined as poorly soluble, with <5% dissolution recorded for all mine wastes. Results therefore demonstrate that strong acids (such as H_2SO_4) could be successfully utilised (even at relatively low concentrations) for the significant removal of acid soluble metals such as Cu, Zn, As and Pb from UK mine wastes. Following subsequent recovery (e.g. via electrowinning) the value of such metals could then be utilised to offset a proportion of the remediation costs.

Table 4. Key elements of economic value at each site displayed in terms of value per tonne and total value per site. Value per tonne was calculated by multiplying current metal price (21/03/2016) of each metal by their concentration in the mine water composite samples. Metals prices used were: Cu = £3498/tonne, Zn = £1249/tonne, Ag = £354,000/tonne, Sn = £11840/tonne and Pb = £1260/tonne. Total value per site was calculated by multiplying value per tonne by estimated total waste mass (from Table 2) and rounded to the nearest £100.

	Cu	Zn	Ag	Sn	Pb
South west England					
ALF (£/tonne)	5.39	0.53	0.00	0.23	0.15
ALF (£$_{tot}$)	159,200	15,700	0	6,800	4,500
CAR (£/tonne)	8.20	0.10	0.00	0.00	0.03
CAR (£$_{tot}$)	28,700	100	n/a	n/a	0
CON (£/tonne)	61.47	1.14	8.29	2.82	0.74
CON (£$_{tot}$)	2,000	0	300	100	0
DGC (£/tonne)	6.41	0.13	0.00	3.43	0.08
DGC (£$_{tot}$)	1,657,600	33,600	0	887,000	20,700
LEV (£/tonne)	18.08	0.81	0.00	2.56	0.12
LEV (£$_{tot}$)	23,400	1,000	0	3,300	200
NAN (£/tonne)	0.44	0.21	0.00	0.46	0.59
NAN (£$_{tot}$)	8,300	4,000	0	8,600	11,000
POL (£/tonne)	1.92	0.16	0.00	0.00	0.00
POL (£$_{tot}$)	18,200	1,600	0	0	0
PWM (£/tonne)	3.28	0.32	0.00	9.26	0.15
PWM (£$_{tot}$)	8,200	800	0	23,200	400
WHM (£/tonne)	1.56	0.85	0.00	3.55	0.49
WHM (£$_{tot}$)	Unknown	Unknown	Unknown	Unknown	Unknown
Wales					
EGM (£/tonne)	8.42	2.63	0.00	0.00	29.74
EGM (£$_{tot}$)	Unknown	Unknown	Unknown	Unknown	Unknown
FRG (£/tonne)	1.18	7.69	21.35	0.00	58.79

FRG (£$_{tot}$)	30,500	198,900	552,400	0	1,521,300
GRG (£/tonne)	0.73	2.43	0.00	0.00	16.39
GRG (£$_{tot}$)	10,200	33,800	0	0	227,600
PYM (£/tonne)	32.15	1.87	11.99	6.74	11.50
PYM (£$_{tot}$)	Unknown	Unknown	Unknown	Unknown	Unknown
WEM (£/tonne)	0.21	2.24	0.00	0.00	8.80
WEM (£$_{tot}$)	9,600	104,700	0	0	410,600

Table 5. Percentage recovery of key elements in 1 M H_2SO_4 (200 RPM agitation speed, 1:10 solid-liquid ratio and 24 hrs reaction time).

Site	Cu	Zn	As	Ag	Sn	Pb
South west England						
ALF	21.41	22.30	49.30	n/a	0.00	14.48
CAR	29.79	32.35	71.09	n/a	n/a	42.74
CON	28.33	6.14	60.04	0.31	0.00	3.45
DGC	29.53	18.18	59.70	n/a	0.00	29.85
LEV	77.95	41.81	68.35	n/a	0.00	23.89
NAN	10.83	10.34	49.63	n/a	0.00	5.69
POL	95.27	63.34	106.82	n/a	0.00	n/a
PWM	14.24	7.79	9.05	n/a	3.21	24.41
WHM	21.86	18.70	59.81	n/a	0.00	6.30
Wales						
EGM	11.39	58.19	n/a	n/a	n/a	0.09
FRG	43.37	7.93	n/a	0.06	n/a	0.05
GRG	22.45	34.82	n/a	n/a	n/a	0.19
PYM	65.63	14.10	10.46	0.34	0.00	0.26
WEM	29.76	5.26	0.00	0.00	0.00	0.35

4.3 Extent of mine sites in the south west of England and Wales and their association with geological, ecological and cultural designations

This section focusses on the key considerations which are likely to impact the feasibility of mine waste remediation and/or resource recovery processes. This considers the geological, ecological or cultural designations that are co-located in areas of mining and how they may act as constraints and opportunities for such interventions. This begins with an overview of the scale of this co-location in the south west of England and Wales followed by a more in-depth examination of the specific reasons for designation in the case study locations.

There are 717 non-active metalliferous mines in the south west of England (Appendix C) and 3350 non-active metalliferous mines in Wales (Appendix D. Number of non-active mines by commodity in each type of geological, ecological and cultural designation in Wales

Commodity	Total number of mines in each designation															
	Total	LNR	NNR	SSSI	SAC	SPA	AW	PH[1]	OMH	AONB	CP	NP	SM	WHS	LHI	More than 1 designation (%)
Barytes	3	0	2	2	0	0	0	3	0	0	0	0	0	0	2	2 (67%)
Barytes Lead	4	0	0	0	0	0	0	4	0	0	0	0	0	0	1	1 (25%)
Copper	213	2	13	58	41	3	16	212	0	6	4	120	10	0	117	195 (92%)
Gold	74	0	0	17	9	3	7	70	0	12	1	62	2	0	52	74 (100%)
Gold Copper	19	0	0	0	6	0	7	18	0	0	0	19	0	0	18	19 (100%)
Iron Ore	60	0	0	5	3	0	9	59	0	1	0	0	1	0	20	31 (52%)
Ironstone	178	5	0	10	8	5	10	177	22	2	4	19	0	9	75	100 (56%)
Lead	1847	0	5	425	269	29	160	1791	23	375	7	260	27	0	474	1199 (65%)
Lead Copper	5	0	0	0	0	0	3	5	0	0	0	0	0	0	0	3 (60%)
Lead Copper Zinc	1	0	0	0	0	0	0	1	0	0	0	0	0	0	1	1 (100%)
Lead Silver	55	0	0	31	20	0	0	54	4	37	0	0	0	0	1	37 (67%)
Lead Silver Copper	1	0	0	0	0	0	1	1	0	0	0	0	0	0	1	1 (100%)
Lead Zinc	1	0	0	1	0	0	0	1	0	1	0	0	0	0	0	1 (100%)
Manganese	113	0	0	31	21	17	1	112	0	27	0	71	1	0	56	112 (99%)
Vein Minerals	775	1	11	109	48	43	102	749	3	12	0	74	35	0	441	575 (74%)

Zinc	1	0	0	1	0	0	0	1	0	0	0	0	1	0	1	1 (100%)
Grand Total	3350	8	31	690	425	100	316	3258	56	473	16	625	77	9	1260	2352 (70%)

[1] Priority habitat data in Wales is presented as the area within a 1.6 km (1 mile) grid square so the location of the mine cannot be said to be accurately co-located with the habitats. SSSI=Site of Special Scientific Interest, AW=Ancient Woodland, PH=Priority Habitat PH, OMH=Open Mosaic Habitat on Previously Developed Land, SAC=Special Area of Conservation (European), SPA=Special Protection Area, AONB=Area of Outstanding Natural Beauty, NP=National Park, CP=Country Park, SM=Scheduled Monument, WHS=World Heritage Site, Landscape of Heritage Interest; Sources: mine data from BRITPITS Licence No. 2014/098BP ED British Geological Survey © NERC. All rights reserved. All other data © Natural Resources Wales copyright. Contains Ordnance Survey data © Crown copyright and database right 2016.D). These are predominantly located in Sn and Cu mining areas of Cornwall (n=456), the As and Cu areas of Devon (n=49), the Pb and Zn areas of North East and Central Wales (n=2470), the Cu, Zn, Pb and Fe areas of North West Wales (n=819), and the ironstone regions of South Wales (n=45) and Gloucestershire (n=102). The majority of mine sites in SW England (68%) and Wales (72%) are co-located with at least one designation.

There are mines located on many of the designated sites in both SW England and Wales. However, numbers are generally small for ecological or geological designations compared with the total number of designated sites in the region (Table 6). Despite this, in some cases the proportion of the area of such designations that are co-located with mines is much greater due to a few very large sites such as, for example, Exmoor Heath (10,000 ha), Plymouth Sounds (6,000 ha) and Dorset Heath (5,000 ha) SACs and Dorset Heathlands SPA (8,000 ha). Similarly, in Wales, despite only 8% of SSSIs being co-located with mines they account for 71% of the area of SSSIs, this is due to four very large sites of over 19,000 ha: Berwyn, Elenydd, Eryri and Migneint-Arenig-Dduallt (which are also SACs and/or SPAs). In Wales, there is a disparity between this effect for the SSSIs and European sites where a relatively modest proportion of area are co-located with mine sites due to the inclusion of far larger areas of coastal sites (e.g. Liverpool Bay, Cardigan Bay). It is not possible to discern from this overview whether the SSSI sites are designated for their geology or ecology or whether the

LNRs, NNRs, SSSIs, SACs and SPAs are designated due to species and habitats that are intrinsically linked to the mining activities or whether they are coincidental to it. In the examples highlighted here the designations are not specifically linked to the presence of mine wastes. This is important as resource recovery could have a positive or a negative impact depending on the reasons for designation and this will be discussed in Section 4.4.

Regarding priority habitats co-located with the mine waste it is possible in some circumstances to discern whether these are intrinsically linked to the presence of the mine waste. In SW England the largest number of mines are co-located with priority habitats other than OMH which are unlikely to be dependent on the characteristics of the mine waste and may even be negatively impacted by it. Although these habitats do not receive statutory protection local authorities are expected to consider their protection and enhancement in local planning policies. Resource recovery might therefore offer an opportunity for these habitats to be restored or enhanced if combined with remediation. Overall, 13 priority habitats are co-located with mine sites in SW England, but in terms of area this only accounts for 0.6% of priority habitats. The greatest number of mines were located on Deciduous Woodland (n=215), with less than 15 on the other 12 types. In Wales around 7% of priority habitats are co-located with mines. However, in Wales, with the exception of OMH, the priority habitat data is not represented as polygons but as 1.6 km grid squares indicating the presence of the habitat, each grid square then details the area covered by the habitat within this but the exact boundaries are not available. This means that mine sites appear to be co-located with several habitats and this has inflated the proportion of habitats co-located with mines. There were 3741 priority habitats co-located with almost all of the metalliferous mines in Wales (n=3258). As with SW England, the greatest number in Wales were on Broadleaved Woodland (n=2517). There were also substantial numbers co-located with Lowland Dry Acid Grassland (n=1608), Lowland Dry Heathland (n=1294) and Purple Moorgrass and Rush (n=1127). In both SW England and Wales a greater proportion of mine sites are co-located with OMH at 4% and 7%, respectively. This is not surprising given that this priority habitat is explicitly focussed on brownfield and previously developed sites, including mine wastes, and was in part based on an analysis of the BRITPITS data (Lush, et al., 2013). These sites are much more likely to be adversely affected by any resource recovery as they have developed over time due to the edaphic conditions on site so an alteration of these may change the species assemblages present.

A far greater number of mines are co-located with areas of cultural significance representing both the rural landscapes together with the mining history of SW England and Wales. It is often impossible to disentangle the role of mining in some of the cultural designations. For example although AONBs and National Parks are not necessarily recognised for their mining activity *per se*, they are representative of the landscape character and cultural history of an area (e.g. mining is specifically mentioned in Cornwall and Tamar Valley AONB; Cornwall and Tamar AONB, 2015). The cultural designations generally operate at the landscape scale hence the large proportion of area co-located with mines for AONBs, National Parks and the World Heritage Sites (Table 6) demonstrating the ubiquity of mining in the heritage in these areas. There are two World Heritage Sites associated specifically with the mining heritage: the Blaenavon Industrial Landscape, which is recognised for the coal and ironstone mining activity and associated industries in south Wales; this makes up the vast majority of area of WHS in Wales (other two are castles and an aqueduct) and the Cornwall and West Devon Mining Landscape in SW England. Similarly, many of the Welsh mines are in the landscapes of historic interest designated by Natural Resources Wales.

This spatial analysis demonstrates the significance of the mining legacy in SW England and Wales and its complex interaction with geological, ecological and cultural designations. It also illustrates that the decision as to whether to recover resources from former mine sites is likely to be dependent on a range of factors outside of the economic viability of such an endeavour and that these can only be determined at the site level.

Table 6. Total number and area of designations in the south west of England and Wales, those co-located with mine sites and the number of metalliferous mine sites in each designation

Designation	Total number (area/ha)	Number (area/ha) co-located with mine sites[1]	Percentage of sites (area) co-located with mine sites	Number of mines located within the boundary of the designated area
South west of England				
Geological or ecological				
LNR	185 (4242)	5 (327.5)	3% (8%)	11
NNR	51 (13,980)	1 (61.4)	2% (0.4%)	1
SSSI	975 (201,077)	22 (24,686)	2% (12%)	69
SAC	74 (319,298)	9 (27,409)	12% (9%)	44
SPA	16 (72,344)	1 (8186)	6% (11%)	3
AW	4287 (74,648)	17 (7716)	0.4% (10%)	68
PH[2]	26 (457,173)	14 (2733)	54% (0.6%))	173
OMH	1004 (7481)	39 (321.0)	4% (4%)	52
Cultural				
AONB	15 (9098)	7 (5197)	47% (57%)	203
NP	3 (167,844)[a]	2 (164,822)	67% (98%)	40
SM	7010 (15,060)	12 (206.9)	0.2% (1%)	23
WHS	4 (30,170)	1 (19,719)	25% (65%)	198
Wales				
Geological or ecological				
LNR	93 (6134)	6 (438.1)	6% (7%)	8
NNR	72 (25,504)	5 (2295)	7% (9%)	31
SSSI	1064 (183,435)	80 (129,934)	8% (71%)	690
SAC	99 (683,541)	22 (94,742)	20% (14%)	425
SPA	23 (681,395)	5 (75,467)	22% (11%)	100
AW	48,614 (94,941)	199 (2144)	0.4% (2%)	357
PH[4]	71,237 (480,495)	3741 (32,386)	5% (7%)	3258
OMH	1034 (6,561)	23 (451.5)	2% (7%)	53
Cultural				
AONB	5 (107,268)	3 (76,822)	60% (72%)	473
NP	3 (410,349)	3 (410,349)	100% (100%)	625
CP	37 (4267)	5 (1428)	14% (33%)	16
SM	4180 (6248)	32 (318.0)	1% (5%)	77
WHS	3 (3401)	1 (3290)	33% (97%)	9
LHI	58 (426,005)	30 (265,765)	52% (62%)	1260

[1] Caution should be used when using these figures as not all mines are represented in BRITPITS and the point locations are not necessary in the same location as mine wastes; [2] Refers to broad habitats as opposed to individual sites; [a] Includes a small portion of New Forest; [4]Priority habitat data in Wales is presented as the area within a 1.6 km (1 mile) grid square so the location of the mine cannot be said to be accurately co-located with the habitats. Sources: mine data from BRITPITS Licence No. 2014/098BP ED British Geological Survey © NERC. All rights reserved. Local Nature Reserve (LNR), National Nature Reserve (NNR), Site of Special Scientific Interest (SSSI), Special Area of Conservation (SAC), Special Protection Area (SPA), Ancient Woodland (AW), Priority Habitat (PH), Open Mosaic Habitat on Previously Developed Land (OMH), Area of Outstanding Natural Beauty (AONB) and National Park data for England © Natural England copyright. Contains Ordnance Survey data © Crown copyright and database right 2016. Scheduled Monument and World Heritage Site data for England © Historic England 2016. Contains Ordnance Survey data © Crown copyright and database right 2016. The Historic England GIS Data contained in this material was obtained on 29th June 2015. The most publicly available up to date Historic England GIS Data can be obtained from HistoricEngland.org.uk. All other data © Natural Resources Wales copyright. Contains Ordnance Survey data © Crown copyright and database right 2016.

4.4 Geological, ecological and cultural considerations at the case study sites: opportunities and constraints to resource recovery and reclamation

All of the case study sites have some form of recognition either for their potential or known geological, ecological or cultural resources (Table 7). These can provide an opportunity for resource recovery or a constraint against it. For example, if mine waste is negatively impacting on ecological or cultural receptors that are not dependent on the characteristics of the mine waste then this could provide a powerful argument for resource recovery, decontamination and/or recovery of land value resource. However, some mine wastes have rare geological or ecological features or are valued for their cultural heritage and these could act as a constraint to reclamation if the existence of these features were to be adversely affected by such activities.

Taking potential constraints first several of the sites are co-located with ecological designations that are directly related to the presence of mine wastes. In SW England CAR and POL are protected for their metallophytic bryophytes (liverworts and mosses) (Natural England, 1999a) as SSSIs. Bryophytes are adapted to Cu-rich substrates and include a number of internationally and nationally rare species, including one, *Cephaloziella integerrima*, which has only been recorded at two other sites since 1950 (Natural England, 1999b). CAR is also designated as a

SAC for its Calaminarian grasslands of the *Violetalia calaminariae* (JNCC, 2015), recognised as one of the best in the UK and, globally, is one of only two known sites of the Cornish path-moss *Ditrichum cornubicum*, which is protected under the Wildlife and Countryside Act (1981) (Natural England, 1999a).

In Wales too, GRG and PYM are co-located with SSSIs, also designated for their bryophyte communities (Natural Resources Wales, 2004; Carmarthenshire County Council, n.d.a,b; Countryside Council for Wales, 1995, 1999). In addition, GRG is co-located with a SAC for its unique assemblage of metallophyte lichens (Calaminarian grasslands of the *Violetalia calaminariae*), one of which, *Epigloea filifera* has not been reported anywhere else in Britain (Natural Resources Wales, 2004). The SSSI at PYM has over 125 lichen species and includes a *Lecidea* which is unique in Britain and possibly a new species (Countryside Council for Wales, 1995).

The designation at GRG is also both a SAC and SSSI for its alluvial shingle deposits which are associated with a mosaic of habitats including heathland communities not usually found in England or Wales. These support nationally scare species of beetle and otters the latter of which are protected under the Wildlife and Countryside Act (1981) and European Council Directive 92/43/EEC on the conservation of Natural Habitats and of Wild Fauna and Flora (Countryside Council for Wales, 1999; Natural Resources Wales, 2004).

The SSSIs at GRG and PYM, together with that at FRG are also designated for their geological characteristics. This includes mineralisations of the waste at FRG and PYM which are unique to Britain (Countryside Council for Wales, 1995; 1999). At GRG the fluvial geomorphology is characterised by an actively braiding river system which may be linked to the mining activity (Countryside Council for Wales, 1999).

In addition, six of the case study sites have been identified as potential OMH sites (ALF, CON, DGC, NAN, POL and WHM) although three of these, CON, POL and WHM, fall on the same OMH. The inclusion of OMH requires some caution as the initial inventory for these sites has been predominantly based on an analysis of previous land uses (e.g. BRITPITS and the National Land Use Database for Previously Developed Land) and aerial imagery. Therefore an ecological survey would need to be carried out to ascertain the presence of an OMH (Lush et al., 2013).

These designations have the potential to act as a significant constraint to resource recovery, specifically the management plan for one SSSI highlights that "care must be taken during preservation or derelict land operations to safeguard the specialised conditions the plants require" (Natural England, 1999b). This means that any activities that changed either the physical or chemical characteristics of the waste are likely to be met with opposition. Many of the species are dependent directly on the elevated metal concentrations in the spoils (Batty, 2005) or tolerant of them. The removal of the metals would reduce the toxicity of the spoils to other vegetation types which could then colonise the spoils potentially to the detriment of these rare species.

Turning to the historic environment designations, all of the case studies in SW England, except ALF, fall within the Cornwall and West Devon Mining Landscape World Heritage Site. This World Heritage Site was designated in 2006 in recognition of the "contribution the area made to the industrial revolution and formative changes in mining practices around the world" (UNESCO, 2006, p. 155). The designation also specifically recognises the significant ecological resources linked to this mining activity in the "distinctive plant communities of waste and spoil heaps and estuarine areas" (UNESCO, 2006, p. 155). In addition there are numerous listed buildings (not discussed here) and SMs that are individually protected for their contribution to the mining landscape. Two sites, DGC and PWM are co-located with SMs whilst CAR is adjacent to one. These are protected for various built features including transport infrastructure, mine shafts, pumping engine houses and processing infrastructure (Historic England, 2002a,b; Historic England, 2006). Interestingly the Prince of Wales Mine at Harrowbarrow Scheduled Monument specifically recognises the importance of the mine wastes as a record of the technologies in use at the time and as landmarks (Historic England, 2006).

None of the case study sites in Wales are in the Blaenavon Industrial Landscape World Heritage Site. However, all of them fall in one of three landscapes of historic interest (Table 7). All are recognised for their land management activities including agriculture and forestry but have a strong association with past mining (Dyfed Archaeology, n.d.a,b; Cadw, Welsh Assembly Government, Countryside Council for Wales, 2007). Although not receiving of a legal protection these landscapes are protected under planning policy from development that might have an adverse impact on their character (Welsh Government, 2016, para.6.5.25). In addition there are several SMs associated with mining activity on the FRG and PYM sites (RCAHMW, 2000, 2004, 2008) as well as many individual aspects of the mining infrastructure including the sublimation chambers and kilns at PYM (RCAHMW, 2007).

As already mentioned the mining landscapes have the potential to provide substantial economic benefits. Prior to its WHS designation the Devon and Cornwall mining landscape generated significant tourism industry and associated revenue to the local economy (Atlantic Consultants, 2003), given that designations can play an important role in tourists choice to visit an area (Reinus & Fredman, 2007; Selman, 2009) and the increase in heritage tourism in recent decades (Williams & Shaw, 2009) this is likely to have increased since the designation.

In terms of cultural designations not dependent on the mining activity none of the case study mines fell in the National Parks of SW England and Wales or AONBs in Wales despite the large land areas occupied by these designations. However, in SW England two case study sites are in AONBs: LEV and DGC. AONBs are designated in recognition of the area’s landscape character, historic and natural environments. So although they are not specifically dependent on the mining legacy both the Tamar Valley and Cornwall AONBs recognise the significance of the mining heritage within their wider landscape (Cornwall AONB, 2011; Tamar Valley AONB, 2014) but would also be protective of contamination impacting on the natural environment.

The value placed on heritage features is not straightforward. Whilst cultural aspects are valued by the public (Swanwick, 2009; Howley, 2011), landscapes perceived as ‘natural’ or ‘unspoilt’ are often preferred (Swanwick, 2009). The value of heritage features is subject to temporal changes, with features becoming increasingly important over time (English Heritage, 2008). Landscape quality is inherently subjective and different groups have different preferences (Swanwick, 2009). Although designations such as AONBs and National Parks in SW England and Wales explicitly recognise the contribution of the mining heritage to the overall landscape the individual features including wastes can also be perceived to have a detrimental impact on the quality of landscape (English Heritage, 2008). Conversely, inappropriate restoration can also do more harm than good from both a nature conservation and landscape perspective. The Cornwall AONB has been estimated to generate bring in 4.5 million visitors to Cornwall estimated to spend £1.5 billion (Cornwall AONB, 2011). Therefore any activities on mine sites need to balance the potential negative impacts on these designations. Resource recovery is likely to be dealt with under mineral planning, permission for which takes into account whether planned activities will have adverse effects on ecological systems, historic environments and human health (DCLG, 2012; Welsh Government, 2016). Therefore the co-location of many waste sites with designated areas that may be detrimentally affected by resource recovery is a significant constraint.

Turning to the potential opportunities for resource recovery to enhance or restore the ecological or cultural resources none of the case study mines in are co-located with sites protected for their geological or ecological characteristics not related to their mining legacy. However, DGC is adjacent to an ancient woodland; Clitters Wood. Several of the sites are co-located with or adjacent to priority habitats: ALF, WHM and NAN with Lowland Heathland, and WHM and PWM with Deciduous Woodland. In Wales all sites are co-located with at least three priority habitats (Table 6), but as already discussed these habitats overlap in the data. Ecological surveying and risk assessment would be necessary to determine whether priority habitats are affected by the mine sites. These habitats do not receive statutory protection *per se* but they are protected under planning policy (DCLG, 2012; Welsh Government, 2016). As Table 3 demonstrates all of the case study sites have wastes with concentrations, particularly Cd, Cu and Zn, that may pose a risk to specified ecological receptors (e.g. SSSIs, SPAs, SACs, AONBs, National Parks), and this is likely to be the case across many of the abandoned mine wastes in the UK. They may also be impacting on aquatic ecology through mine water discharges (Mayes, et al., 2009) or other designated terrestrial ecological receptors not co-located with the mine waste through the mobilisation of pollutants in water or food-chain transfer. The potential risk to ecological receptors is likely to add weight to the case for remediation and therefore act as an opportunity for resource recovery as a means of remediating the waste.

It is clear from this study that there is substantial variation between mine wastes in terms of their characteristics and the context in which they are situated. A multitude of different perspectives will need to be sought when considering their long term management and whether resource recovery is appropriate. This will need to balance the requirements of a range of stakeholders and disciplines including environmental scientists, heritage professionals, ecologists and representatives from the different management bodies and regulators associated with these designations (Selman, 2009). It should also be recognised that land managers, experts and the general public may have very different preferences in terms of the future of such sites and these views will also need to be considered (Bloodworth et al., 2009; English Heritage, 2008; Howard, et al., 2015; Selman, 2009; Swanwick, 2009). Human Ecology Mapping (HEM) approaches offer promising spatial data gathering and analytical tools that may enable the views of multiple stakeholders to be considered (McLain, 2013). These methods, particularly "sense of place" (see Williams, 1998) might be useful in examining the resources and values of metalliferous mine sites integrating a spatial dimension with the human-landscape connection. Ultimately, the decision to recover resources from mine wastes needs to balance the potential negative impacts on geological, ecological and cultural designations with any positive impacts on those not explicitly dependent on the mining heritage.

There are a number of limitations to the spatial analysis. First, the sampling campaign found that the mine locations in BRITPITS are not always in the same place as the waste. This means that there are uncertainties over the co-location of the sites. This is particularly important for smaller sites such as SSSIs and OMHs. Therefore the large scale analysis presented here is probably a conservative estimate of the designations linked to mining activity and, as already highlighted, detailed analysis of the specific sites in question needs to be undertaken. Some ecological and cultural designations have not been included in this study as no national level datasets are available. Similarly, the impact of mine wastes on water quality and any downstream ecological receptors was also not examined here. These, again, illustrate the need for site analysis and the involvement of a range of stakeholders including those from the local area (Mayes, et al., 2009; Howard, et al., 2015; Selman, 2009).

Table 7 Ecological and cultural designations co-located with the case study mine wastes in the south west of England and Wales

	Potential opportunities				Potential constraints	
Case study	Reduce risks to water quality and/or human health	Resource recovery (£[a])	Geological and ecological designations	Cultural designations	Geological and ecological designations	Cultural designations
South west of England						
ALF		186,200	Lowland heathland PH.		OMH.	
CAR	West Caradon MWD site potential water pollution.	28,800			Phoenix United Mine and Crow’s Nest SAC; Crow’s Nest SSSI; PH due to SSSI but no main habitat type.	Caradon Mining District in the Cornwall and West Devon Mining Landscape (CWDML) WHS; adjacent to South Caradon 19th century copper mine SM.
CON		2,457			OMH.	Gwennap Mining District in the CWDML WHS.
DGC	MWD site potential water pollution.	2,598,900	Adjacent to Clitters Wood AW.	Tamar Valley AONB.	OMH.	Early 20th Century arsenic works at Devon Great Consols Mine SM; Tamar Valley Mining District in the CWDML WHS.
LEV		27,900		Cornwall AONB.		St. Just Mining District in the CWDML WHS.
NAN		31,900	Adjacent to Lowland heathland PH.		OMH.	Caradon Mining District in the CWDML WHS.
POL		19,800			OMH; West Cornwall Bryophytes SSSI.	Gwennap Mining District in the CWDML WHS.
PWM	MWD site potential water pollution.	32,600	Adjacent to Deciduous woodland PH.		OMH.	Prince of Wales Mine at Harrowbarrow SM; Tamar Valley Mining District in the CWDML WHS.

WHM	MWD site potential human and health risk water pollution.	Unknown	Lowland heathland PH.		OMH.	Gwennap Mining District in the CWDML WHS.
Wales						
EGM	MWD site potential water pollution.	Unknown	Blanket Bog (BB); Lowland Dry Acid Grassland (LDAG); Lowland Dry Heathland (LDH); Lowland Wet Heathland (LWH); Purple Moorgrass and Rush Pastures (PMRP)			Upland Ceredigion LHI
FRG	MWD site potential water pollution.	2,303,100	LDAG; LDH; PMRP		Adjacent to Mwyngloddfa Frongoch SSSI	Adjacent to Frongoch Lead Mine SM; Upper Ceredigion LHI
GRG		271,600	Arable Land; BB; Broadleaved Woodland (BW); Coastal and Floodplain Grazing Marsh (CFGM); LDAG; LDH; PMRP		Grogywnion SAC, Gro Ystwyth SSSI	Upper Ceredigion LHI
PYM	MWD site potential water pollution.	Unknown	BW; Fen (basin, valley and floodplain mire); Fen (swamp); LDAG; LDH; LWH; PMRP		Mynydd Parys SSSI	Parys Mountain Windmill Engine House, Precipitation Pits and Great Opencast SM, Mona Mine and Sublimation Chambers, Mynydd Parys SM, Amlwch and Parys Mountain LHI.

WEM	MWD site potential water pollution.	524,900	BB, BW; CFGM; LDAG; LDH; PMRP			Upland Ceredigion LHI.

[a] Estimated total value of Cu, Zn, Ag, Sn and Pb at each site; Sources: mine data from BRITPITS Licence No. 2014/098BP ED British Geological Survey © NERC. All rights reserved. Mine Waste Directive (MWD) inventory data © Environment Agency copyright. Contains Ordnance Survey data © Crown copyright and database right 2016; Local Nature Reserve (LNR), National Nature Reserve (NNR), Site of Special Scientific Interest (SSSI), Special Area of Conservation (SAC), Special Protection Area (SPA), Ancient Woodland (AW), Priority Habitat (PH), Open Mosaic Habitat on Previously Developed Land (OMH), Area of Outstanding Natural Beauty (AONB) and National Park data for England © Natural England copyright. Contains Ordnance Survey data © Crown copyright and database right 2016. Scheduled Monument and World Heritage Site data for England © Historic England 2016. Contains Ordnance Survey data © Crown copyright and database right 2016. The Historic England GIS Data contained in this material was obtained on 29th June 2015. The most publicly available up to date Historic England GIS Data can be obtained from HistoricEngland.org.uk; All other data © Natural Resources Wales copyright. Contains Ordnance Survey data © Crown copyright and database right 2016.

5. Decision making tools and technology options for intervention

5.1. Decision making tools for optimising resource value

As discussed above legacy metalliferous mining waste sites have multifaceted value and resource associated with them. This results in the selection of the strategy for optimising resource value being a non-trivial problem and requires the consideration of a number of competing criteria to allow identification of appropriate approaches. In similar multi-criteria problems various decision support frameworks have been developed, many being based on Multi Criteria Decision Analysis (Wang, 2014), it is proposed that such an approached can be adopted here.

In many environmental problems the criteria considered are classified within a sustainability assessment framework under three areas or pillars, namely: economic, environmental and social issues (Pettit et al., 2011). However, for the problem considered here it is necessary to also consider the technical aspects of resource recovery from wastes. In the proposed approach three MCDA methods are adopted: simple ranking method, Analytic Hierarchy Process (AHP) and Compromise Programming, this allows either the individual use of one or the sequential use of all to allow sensitivity analysis to be undertaken (Pettit et al., 2011). Typical criteria that can be used are listed in Table 8. The particular criteria considered and their method of assessment will depend on the nature of the particular site or inventory of sites considered. However, it can be seen that many of the environmental and social criteria can be directly related to the various ecological and cultural designations listed in Table 1, for example cultural receptor criteria can be linked to, for example, AONB, NP and LHI data and ecological receptor criteria to, for example, SAC, PH and SSSI data.

Table 8. Examples of decision criteria

Environmental	**Economic**	**Social**	**Technical**
Ecological receptors	Capital Cost	Public acceptance	Feasibility
Human receptors	Operating Costs	Cultural receptors	Infrastructure
Emissions to Water	Value of resource	Amenity use	Safety
Emissions to air	Land values	Health impacts	
Impacts on unique fauna/flora habitats	Reduced financial liability / risk	Nuisance	
Impact on landscape		Employment	

It is suggested that this methodology will be applied for two main purposes. This first of these is site specific and will aid comparison between different options and scenarios. For example, the choice between various ex-situ and in-situ remediation technologies can be made and compared against a ‘do-nothing’ scenario. The second purpose is to allow inventory appraisal where a number of sites at a regional or national inventory scale can be ranked for potential resource recovery and also enable classification of an anthropogenic deposit as a reserve or resource.

5.2. Technology options for resource recovery from metal mine wastes

It has been demonstrated that many historic UK metal mine sites comprise environmental/landscape resources in their existing state. However, in light of stricter future legislation associated with the European Union Water Framework Directive it is likely that intervention (namely for pollution control) will need to be implemented in the future at many sites. Given the multifaceted resource value of metal mine sites, these interventions need to be sensitive to the existing resource (as indicated by the site designations presented) and/or enhance the resource value of the sites, for example by protecting or enhancing industrial heritage. Thus the cost-benefit analyses might include the reduced cost of remediation when including metal resource recovery and the additional benefits might include preservation, protection and enhancement of industrial heritage with the possible tourist revenue generation that may arise. The methodology proposed by (Conesa, et al., 2008), which strives to protect the cultural heritage components of metal mine sites whilst rehabilitating the site from an environmental perspective, is suggested as a useful approach, and it could be extended to include metal resource recovery.

If the resource comprises the mine site in its current form then remediation for pollution mitigation would have to be done either through established *in situ* techniques for preventing or reducing infiltration, reducing leachability and waste stabilisation or containment, *ex situ* techniques could only be applied where the impact was minimal and the site could be rehabilitated to a condition satisfying the appropriate stakeholders.

Where the metals present are one of the resources to be recovered from the site then an important processing decision is whether the mine wastes can be excavated. If this is an option for the site then a wide range of standard processing routes are available for separation, comminution, concentration and/or recovery metals from excavated materials. For example, gravity separation methods might in some cases be applied to separate metal-bearing minerals from gangue minerals which can be returned to site. Metals can then be recovered from the metal-bearing concentrate using established hydrometallurgical, biohydrometallurgical or pyrometallurgical approaches.

If physical separation is not an option e.g. for cost reasons or because of mineralogy and metal deportment is not favourable, then the hydrometallurgical and/or biohydrometallurgical techniques of heap (or dump) leaching may be of particular utility for the removal of metals from mine wastes and tailings. These techniques are routinely used in the mining industry for recovery of metals (e.g. Cu, Au) from low grade ores. Material is placed on to an impermeable liner system and a lixiviant is recirculated though the pile, metals are recovered from the metal-rich “pregnant” liquor. Where material is fine (e.g. tailings) then the material can be agglomerated prior to heap leaching to improve subsequent recovery. Similar methods such as soil flushing have been adopted for decontamination of soils and sediments (Leštan, 2008; Seidel, 1998) - these parallel methods are essentially only different in their aim: metals recovery or decontamination and thus are applicable within the context discussed here.

In situ approaches for metal recovery could be attractive given the constraints for mine site reclamation discussed above, and in this context could under certain conditions be considered as a more “passive” remediation option (see Cundy, 2013). Phytoremediation (or phytomining depending on context) is an established *in situ* technology, however the process is very low intensity and intervention is still required for periodic harvesting, processing of the biomass for metal recovery also requires significant further processing. *In situ* heap/dump leaching and metals recovery is a promising option but requires that the material to be flushed overlies an impermeable stratum or engineered barrier. A pump and treat system can then be applied to ensure capture of the effluent downstream in collection boreholes/trenches without resulting in secondary pollution. A compromise may be to capture and recover metals already being released from sites in mine drainage. Low intensity metal capture are being developed for the “passive” treatment of metalliferous mine waters. Such systems use a variety of (bio)geochemical engineering approaches to achieve immobilisation of metals, including: precipitation, adsorption, microbiological reduction or oxidation and pH manipulation. Thus these technologies potentially offer low intensity harvesting of metals from legacy mine waste and would simultaneously achieve: (i) eventual decontamination of the mine waste, (ii) protection of the environment from metal pollution and (iii) recovery of the metals. However, further research is required to design systems that capture metals in forms that are directly amenable to recycling.

6. Conclusions and implications

There are numerous drivers for the reclamation of legacy mine sites. Many wastes are likely to be causing significant breaches of water and soil quality guidelines in the UK and the mobilisation of these pollutant metals may be negatively impacting surrounding ecosystems. When considering site reclamation strategies a balance needs to be achieved, however, between protecting human, water and ecological receptors that may be at risk from metal pollution from mine wastes and designations that are dependent upon it. In addition, the simultaneous recovery of economically valuable metals from the mine wastes during site remediation may provide a useful mechanism to offset the cost of such activity.

This study has determined the physical and chemical composition of several prominent legacy metalliferous mine tailing waste piles in SW England and Wales across a range of parameters, including metal content, mineralogy, paste pH, particle size distribution, total organic carbon and total inorganic carbon. The co-location of cultural and ecological designations with the mine wastes have also been determined. The following can be concluded:

1) Several mine wastes investigated contain a number of different economically valuable metals (namely Cu, Pb and Sn) at concentrations close to or greater than typical minimum ore grade;
2) Several mine wastes investigated contain a number of different pollutant metals (namely Cr, Ni, Zn, As, Cd, Pb) at concentrations exceeding Soil Guideline Values; and

3) Most of the case study sites receive some form of protection either due to their historical significance, rare species assemblages or geological characteristics which may limit the potential for resources recovery and rehabilitation.

Results demonstrate that it is unlikely that the potential economic gain of extracting valuable metals from the mine waste will constitute a sole driver for intervention. Instead it is suggested that this value could be considered as a useful mechanism to offset site rehabilitation costs. A substantial number of mine sites in SW England and Wales are co-located with cultural or ecological designations, many of them due to the mining activities. These unique geological, ecological and cultural resources will act as a significant constraint to mine waste remediation and site reclamation if the existence of these features were to be adversely affected by such activities. This paper has demonstrated that an integrated assessment methodology for assigning and evaluating resource value is necessary to allow appropriate evaluation of resource potential. It is clear that further work is urgently required to apply similar holistic resource value determination approaches at other legacy mine sites in the UK and world-wide. This will enable the establishment of a reliable methodology for the quantitative assignment of resource value (economic, cultural, environmental, etc.) at such sites. In turn this will enable prioritisation of mine sites in most urgent need of rehabilitation, but also enable such rehabilitation and remediation processes to be conducted via methodology that is both at appropriate cost and disturbance to existing environmental and cultural designations.

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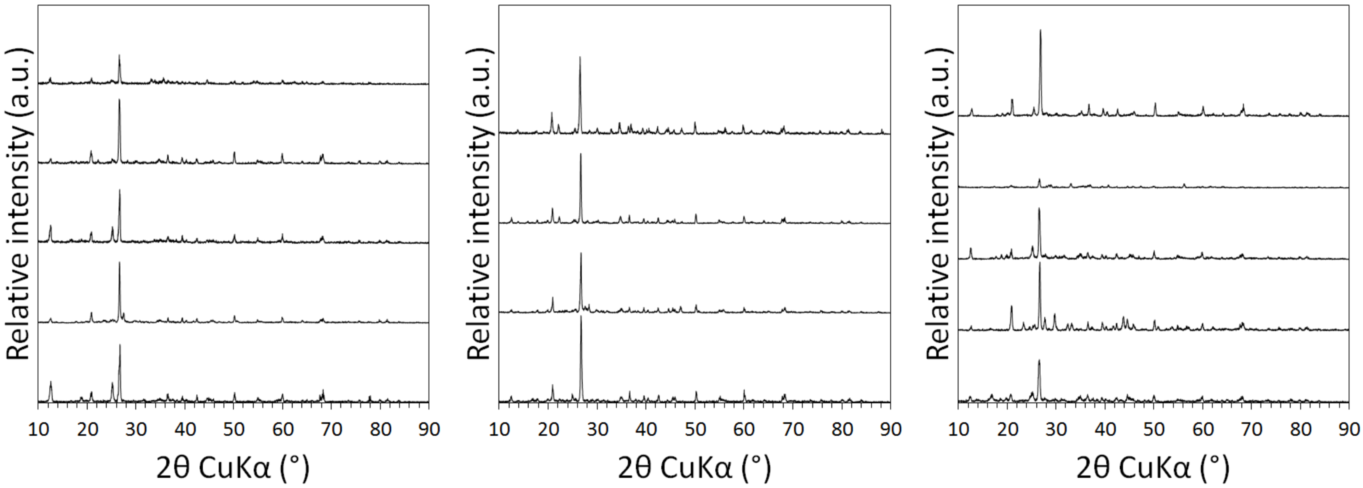
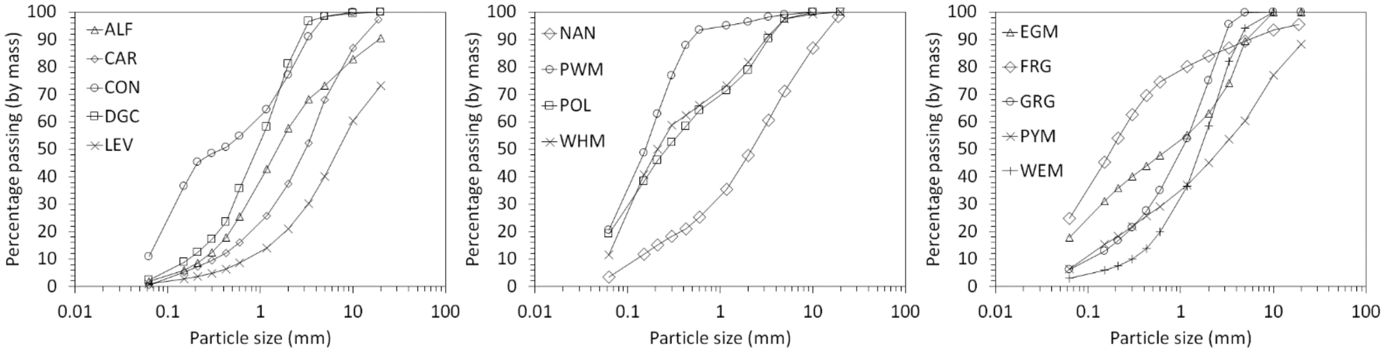
Appendix A. XRD spectra for the mine tailing composite samples. LHS (from bottom): ALF, CAR, CON, DGC, LEV; middle (from bottom): NAN, POL, PWM, WM; RHS (from bottom): EGM, FRN, GROG, PYM, WEM.



Appendix B. Particle size as a function of cumulative volume for the composite mine tailing samples



Appendix C. Number of non-active mines by commodity in each type of geological, ecological and cultural designation in the South West of England

Commodity	Number of mines in each designation													
	Total	LNR	NNR	SSSI	SAC	SPA	AW	PH	OMH	AONB	NP	SM	WHS	More than 1 designation (%)
Antimony	6	0	0	0	0	0	0	0	0	2	0	0	0	2 (33%)
Arsenic	1	0	0	0	0	0	0	1	0	0	1	0	0	1 (100%)
Arsenic Copper	13	0	0	1	1	0	5	4	1	13	0	2	13	13 (100%)
Barytes	2	0	0	0	0	0	0	1	0	0	2	0	0	2 (100%)
Celestite	20	0	0	0	0	0	0	1	0	0	0	0	0	1 (5%)
Copper	55	0	0	9	8	0	6	16	3	24	1	0	21	38 (69%)
Gold	2	0	0	0	0	0	2	0	0	0	0	0	0	2 (100%)
Iron ore	57	1	1	7	7	0	5	12	2	3	27	2	0	40 (70%)
Ironstone	124	3	0	27	27	3	41	47	1	18	1	3	0	79 (64%)
Lead	15	0	0	2	0	0	0	2	0	11	0	0	0	11 (73%)
Lead Antimony	2	0	0	0	0	0	0	2	0	2	0	0	0	2 (100%)
Lead Copper	1	0	0	0	0	0	0	1	0	0	0	0	0	1 (100%)
Lead Silver	11	0	0	0	0	0	0	0	0	1	1	0	0	2 (18%)
Manganese	11	0	0	0	0	0	3	3	0	1	0	0	0	5 (45%)
Tin	225	3	0	8	1	0	4	46	22	81	5	6	101	173 (77%)
Tin Copper	147	2	0	5	0	0	0	29	21	31	0	10	61	99 (67%)
Tin Tungsten	9	0	0	5	0	0	0	5	0	8	0	0	0	8 (89%)
Tungsten	1	0	0	0	0	0	0	1	0	1	0	0	0	1 (100%)
Vein Minerals (e.g. Pb, Zn, Cu, Sn)	11	0	0	5	0	0	2	2	2	7	2	0	1	9 (82%)
Zinc	3	0	0	0	0	0	0	0	0	0	0	0	0	0 (0%)
Zinc Copper Tin	1	0	0	0	0	0	0	0	0	0	0	0	0	0 (0%)
Grand Total	717	9	1	69	44	3	68	12	52	203	40	23	197	489 (68%)

Sources: mine data from BRITPITS Licence No. 2014/098BP ED British Geological Survey © NERC. All rights reserved. Local Nature Reserve (LNR), National Nature Reserve (NNR), Site of Special Scientific Interest (SSSI), Special Area of Conservation (SAC), Special Protection Area (SPA), Ancient Woodland (AW), Priority Habitat (PH), Open Mosaic Habitat on Previously Developed Land (OMH), Area of Outstanding Natural Beauty (AONB) and National Park data © Natural England copyright. Contains Ordnance Survey data © Crown copyright and database right 2016. Scheduled Monument and World Heritage Site © Historic England 2016. Contains Ordnance Survey data © Crown copyright and database right 2016. The Historic England GIS Data contained in this material was obtained on 29th June 2015. The most publicly available up to date Historic England GIS Data can be obtained from HistoricEngland.org.uk.

Appendix D. Number of non-active mines by commodity in each type of geological, ecological and cultural designation in Wales

Commodity	Total number of mines in each designation														
	Total	LNR	NNR	SSSI	SAC	SPA	AW	PH[1]	OMH	AONB	CP	NP	SM	WHS	LHI	More than 1 designation (%)
Barytes	3	0	2	2	0	0	0	3	0	0	0	0	0	0	2	2 (67%)
Barytes Lead	4	0	0	0	0	0	0	4	0	0	0	0	0	0	1	1 (25%)
Copper	213	2	13	58	41	3	16	212	0	6	4	120	10	0	117	195 (92%)
Gold	74	0	0	17	9	3	7	70	0	12	1	62	2	0	52	74 (100%)
Gold Copper	19	0	0	0	6	0	7	18	0	0	0	19	0	0	18	19 (100%)
Iron Ore	60	0	0	5	3	0	9	59	0	1	0	0	1	0	20	31 (52%)
Ironstone	178	5	0	10	8	5	10	177	22	2	4	19	0	9	75	100 (56%)
Lead	1847	0	5	425	269	29	160	1791	23	375	7	260	27	0	474	1199 (65%)
Lead Copper	5	0	0	0	0	0	3	5	0	0	0	0	0	0	0	3 (60%)
Lead Copper Zinc	1	0	0	0	0	0	0	1	0	0	0	0	0	0	1	1 (100%)
Lead Silver	55	0	0	31	20	0	0	54	4	37	0	0	0	0	1	37 (67%)
Lead Silver Copper	1	0	0	0	0	0	1	1	0	0	0	0	0	0	1	1 (100%)
Lead Zinc	1	0	0	1	0	0	0	1	0	1	0	0	0	0	0	1 (100%)
Manganese	113	0	0	31	21	17	1	112	0	27	0	71	1	0	56	112 (99%)
Vein Minerals	775	1	11	109	48	43	102	749	3	12	0	74	35	0	441	575 (74%)
Zinc	1	0	0	1	0	0	0	1	0	0	0	0	1	0	1	1 (100%)
Grand Total	3350	8	31	690	425	100	316	3258	56	473	16	625	77	9	1260	2352 (70%)

[1] Priority habitat data in Wales is presented as the area within a 1.6 km (1 mile) grid square so the location of the mine cannot be said to be accurately co-located with the habitats. SSSI=Site of Special Scientific Interest, AW=Ancient Woodland, PH=Priority Habitat PH, OMH=Open Mosaic Habitat on Previously Developed Land, SAC=Special Area of Conservation (European), SPA=Special Protection Area, AONB=Area of Outstanding Natural Beauty, NP=National Park, CP=Country Park, SM=Scheduled Monument, WHS=World Heritage Site, Landscape of Heritage Interest; Sources: mine data from BRITPITS Licence No. 2014/098BP ED British Geological Survey © NERC. All rights reserved. All other data © Natural Resources Wales copyright. Contains Ordnance Survey data © Crown copyright and database right 2016.