



The nature of waste associated with closed mines in England and Wales

Minerals & Waste Programme
Open Report OR/10/14



MINERALS & WASTE PROGRAMME OPEN REPORT OR/10/14

The National Grid and other Ordnance Survey data are used with the permission of the Controller of Her Majesty's Stationery Office. OS Topography © Crown Copyright. All rights reserved. BGS 100017897/2010

Keywords
Abandoned mine waste facilities;
England and Wales; mineral
deposits; environmental impact;
European Mine Waste Directive.

Front cover Graiggoch Mine (SN 7040 7410), Ceredigion, Wales.

Bibliographical reference Palumbo-Roe, B and Colman, T with contributions from Cameron, D G, Linley, K and Gunn, A G. 2010. The nature of waste associated with closed mines in England and Wales. British Geological Survey Open Report, OR/10/14. 98pp.

Copyright in materials derived from the British Geological Survey's work is owned by the Natural Environment Research Council (NERC) and the Environment Agency that commissioned the work. You may not copy or adapt this publication without first obtaining permission. Contact the **BGS** Intellectual Property Rights Section, British Geological Survey, Keyworth, e-mail ipr@bgs.ac.uk. You may quote extracts of a reasonable length without prior permission, provided a full acknowledgement is given of the source of the extract.

The views and statements expressed in this report are those of the authors alone and do not necessarily represent the views of the Environment Agency.

Environment Agency Contact: Hugh Potter

The nature of waste associated with closed mines in England and Wales

Palumbo-Roe, B and Colman, T

Contributor/editor

Cameron, D G, Linley, K and Gunn, A G

Keyworth, Nottingham British Geological Survey 2010

BRITISH GEOLOGICAL SURVEY

The full range of our publications is available from BGS shops at Nottingham, Edinburgh, London and Cardiff (Welsh publications only) see contact details below or shop online at www.geologyshop.com

The London Information Office also maintains a reference collection of BGS publications, including maps, for consultation.

We publish an annual catalogue of our maps and other publications; this catalogue is available online or from any of the BGS shops.

The British Geological Survey carries out the geological survey of Great Britain and Northern Ireland (the latter as an agency service for the government of Northern Ireland), and of the surrounding continental shelf, as well as basic research projects. It also undertakes programmes of technical aid in geology in developing countries.

The British Geological Survey is a component body of the Natural Environment Research Council.

British Geological Survey offices

BGS Central Enquiries Desk

Tel 0115 936 3143 Fax 0115 936 3276

email enquiries@bgs.ac.uk

Kingsley Dunham Centre, Keyworth, Nottingham NG12 5GG

Tel 0115 936 3241 Fax 0115 936 3488

email sales@bgs.ac.uk

Murchison House, West Mains Road, Edinburgh EH9 3LA

Tel 0131 667 1000

Fax 0131 668 2683

Fax 029 2052 1963

email scotsales@bgs.ac.uk

Natural History Museum, Cromwell Road, London SW7 5BD

Tel 020 7589 4090 Fax 020 7584 8270

Tel 020 7942 5344/45 email bgslondon@bgs.ac.uk

Columbus House, Greenmeadow Springs, Tongwynlais, Cardiff CF15 7NE

Tel 029 2052 1962

Maclean Building, Crowmarsh Gifford, Wallingford

OX10 8BB

Tel 01491 838800 Fax 01491 692345

Geological Survey of Northern Ireland, Colby House, Stranmillis Court, Belfast BT9 5BF

Tel 028 9038 8462 Fax 028 9038 8461

www.bgs.ac.uk/gsni/

Parent Body

Natural Environment Research Council, Polaris House, North Star Avenue, Swindon SN2 1EU

Tel 01793 411500 www.nerc.ac.uk Fax 01793 411501

Website www.bgs.ac.uk

Shop online at www.geologyshop.com

Foreword

This report was commissioned by the Environment Agency to inform their work to create an inventory of closed and abandoned mining waste facilities which are causing serious negative environmental impacts or are a serious threat to human health. This work is being carried out for Article 20 of the Mining Waste Directive (2006/21/EC).

Acknowledgements

Our thanks to Neil Breward for reviewing the report. We are also grateful for guidance and encouragement from the BGS Mineral and Waste programme and for the financial support to the Environment Agency.

Contents

Fo	rewor	'di
Ac	know	ledgementsi
Co	ntent	Si
Ex	ecutiv	ve Summaryv
1	Intr	oduction1
	1.1	Scope of the review
	1.2	Methodology2
	1.3	The Mine Waste Directive
	1.4	Extraction of information from the 2006 BGS report
	1.5	The character of mine waste
	1.6	Waste characterisation4
	1.7	Data sources and limitations
	1.8	Definitions and terminology
2	Env	ironmental hazards associated with abandoned mining waste facilities11
	2.1	General assessment 11
	2.2	Hazard source characterisation and transfer mechanisms at metalliferous mine sites. 12
	2.3	Visual environmental impact
	2.4	Physical Hazards
	2.5	Risk
3	Non	-metalliferous mine waste facilities19
	3.1	Sand and gravel
	3.2	Crushed rock and building stone
	3.3	Chalk
	3.4	Silica sand

	3.5	Common clay and shale / fireclay	24
	3.6	Slate	33
	3.7	Coal	33
	3.8	Peat	37
	3.9	Industrial clays	38
	3.10	Gypsum and anhydrite	39
	3.11	Salt	40
	3.12	Potash	40
4	Meta	ılliferous mine waste facilities	43
	4.1	Introduction	43
	4.2	Granite-associated tin-copper fissure vein mineralisation south west England	48
	4.3	Lower palaeozoic shale-hosted crosscourse lead and zinc veins in southwest Englar	1d55
	4.4	Carbonate-hosted lead, zinc, fluorspar and baryte mineralisation	
	4.5	Other carbonate-hosted lead-zinc orefields	63
	4.6	Lower Palaeozoic Volcanogenic massive sulphide copper mineralisation in Angleson	ey64
	4.7	Lower Palaeozoic volcanic-associated copper-lead-zinc mineralisation	65
	4.8	Lower Palaeozoic shale-hosted lead-zinc and baryte veins	67
	4.9	Precious - metal vein mineralisation	72
	4.10	Sediment-hosted red-bed copper deposits	73
	4.11	Copper mineralisation in Dinantian limestone	73
	4.12	Merioneth manganese deposits	73
	4.13	Iron ore deposits	73
5	Conc	clusions	77
Ap	pendi	x 1 Extracts from Council Directive 91/689/EEC	78
	ANN	EX II of Council Directive 91/689/EEC	78
	ANN	TEX III on hazardous waste of 91/689/EEC	79
Glo	ssary		80
D	n		

FIGURES

Figure 1 Coverage of G-BASE sediment and soil sampling	10
Figure 2 Main mineral deposit types and potential environmental issues	11
Figure 3 Closed sand and gravel (9084 sites), bedrock sand (3754 sites) and silica sand operations (367 sites).	25
Figure 4 Closed limestone (11641 sites), dolomite (1745 sites) and chalk (4298 sites) mines a quarries.	
Figure 5 Closed igneous rock quarries (2694 sites).	27
Figure 6 Closed sandstone mines and quarries (24927 sites)	28
Figure 7 Closed common clay and shale mines and quarries (12604 sites)	29
Figure 8 Closed slate mines and quarries (2863 sites).	30
Figure 9 Closed deep coal mines (7626 sites).	31
Figure 10 Closed surface coal (764 sites) and fireclay (384 sites) mines and quarries	32
Figure 11 Coal and waste output. Richards, Morehead and Laing (1996)	35
Figure 12 Closed anhydrite, ball clay, china clay, gypsum, peat and salt mines and quarries	41
Figure 13 Closed china clay and ball clay mines and quarries	42
Figure 14 Metal mining fields in England and Wales	45
Figure 15 Abandoned metalliferous mines and quarries in England and Wales (Nos of sites 1 Table 6).	
Figure 16 Closed mines in south west England.	50
Figure 17 Closed metal mines in northern England	57
Figure 18 Closed metal mines in the Southern Pennine Orefield.	62
Figure 19 Calcite-rich tip at Snailbeach mine in 1980s before reclamation	68
Figure 20 Closed metal mines in Wales and Shropshire	69
Figure 21 Closed hematite (40 sites) and ironstone (1589 sites) mines and quarries	75

TABLES

Table 1 The EWC 2000 codes for wastes from the extractive industry	. 6
Table 2 Estimated mineral waste production in the UK (Source: DEFRA, 19.6.2003)	. 8
Table 3 Potentially harmful elements associated with major metalliferous orefields in England and Wales	
Table 4 Relative toxicity values for different environmental and habitat situations (Mhairtin et a 2009)	
Table 5 Source-pathway-receptor analysis of a simple conceptual model	18
Table 6 Summary of closed mines and quarries in England and Wales (Source: BGS BritPits Database)	19
Table 7 Assessment of non-metalliferous waste products by commodity	20
Table 8 Main metalliferous deposit types in England and Wales with associated elements and minerals	47
Table 9 Estimated metal and waste production of the main metal deposit types	48
Table 10 Largest mines of the Northern Pennine Orefield (Dunham, 1990)	58
Table 11 Recorded metal production from Central Wales (Jones, 1922)	71
Table 12 Summary statistics of geochemical data for 823 stream sediment samples from the Central Wales mining field (British Geological Survey, 2000)	71
Table 13 Key features of all the ironstones of England and Wales	76

Executive Summary

This report has been prepared for the Environment Agency (EA) to provide information on mineral waste associated with closed mining and quarrying sites in England and Wales as part of the provisions of the EU Mine Waste Directive 2006 (MWD). The Environment Agency is the regulatory body for England and Wales (E&W) responsible for producing an inventory of closed mining waste facilities, including abandoned waste facilities, as required by Article 20 of the European Mine Wastes Directive, by May 2012.

The report builds upon the information on non-metalliferous sites from a study of waste from active mineral workings in the UK (Colman et al., 2006) with much additional material on metalliferous mine sites.

The report uses BGS and other datasets to provide generalised maps showing the locations of closed mineral workings and hence associated waste tips. Estimates of mineral production for each area are also given. Waste production figures are not available as waste has generally not been recorded in any official statistics; existing figures are generalised from estimated mineral to waste ratios that are highly variable, especially with regard to metalliferous mines.

The report summarises the various types of mining in England and Wales and provides generic qualitative characterisation of the waste associated with former workings of the following mineral commodities and deposit types: crushed rock, sand and gravel, building stone, silica sand, clay and shale, fireclay, slate, china clay, ball clay, fuller's earth, gypsum/anhydrite, salt, potash, fluorspar, barytes, limestone/dolomite, peat, coal and metalliferous deposits.

Geoenvironmental models of metalliferous mineralisation are used to classify the types of mineralisation occurring in England and Wales into a small set of mineral deposit types. Each deposit type has certain specific geochemical characteristics that enable broad generalisations to be made concerning each type's mineral content, host rock and general geological setting. These in turn have relevance to the degree of environmental problems likely to be associated with specific deposit types.

Metalliferous mining has been an important industry in many more remote areas of England and Wales, commonly in areas of high scenic value. It has been carried out over thousands of years but the main period of working was between 1700 and 1900 with the exception of tin and copper in southwest England, fluorite and baryte in the Pennine orefields and ironstone which were worked throughout the 20th Century. The minerals worked were generally those of copper, iron, lead and zinc sulphides with substantial amounts of tin (as cassiterite, SnO₂), fluorite and baryte. No metal mines are currently active in England and Wales, though minor amounts of lead are recovered from small-scale fluorite and baryte mining in the Southern Pennine Orefield. Large amounts of various iron minerals have also been mined.

Mineral wastes are associated, to a greater or lesser extent, with the extraction and processing of almost all of the minerals produced in England and Wales.

Chemical hazards associated with closed mine waste facilities may include the toxicity of certain mine spoil and of any other materials which may have been deposited on site. Some sites might have been used for fly-tipping and may have received material more toxic than the spoil itself. Additionally, some mineral processing operations can give rise to slags and ashes, gaseous and particulate emissions through, for example, grinding and ore roasting and smelting.

The waste from active non-metalliferous workings, apart from that associated with deep coal mining, was generally not considered to cause significant environmental effects. Slate and china clay waste may give rise to visual and stability problems.

At abandoned metalliferous mine sites, acid mine drainage and metal-rich drainage that develops as a consequence of the weathering of sulphide-rich wastes may represent one of the main contaminant sources along with the legacy of past mineral processing activity. The presence of acid drainage from a mine site is largely dependent on the availability of water, presence of pyrite and the absence of a neutralising host/country rock. Pyrite is the main acid producing mineral; other acid forming sulphide minerals include arsenopyrite, marcasite and pyrrhotite. Not all mine sites will generate acid mine drainage as a result of the neutralisation capacity of the host rock containing carbonates, such as limestone, or because pyrite may not be present in significant concentrations.

Different orefields are associated with particular suites of minerals and elements and there are large variations in actual concentrations. The most significant elements associated with the major orefields are reported. Metalliferous mineral veins in England and Wales are principally characterised by elevated concentrations of lead and zinc with variable concentration of cadmium, barium and fluorine. Other types of mineralisation such as in SW England have high concentrations of copper and arsenic. Soils and spoils of mine waste facilities will contain concentrations of contaminants derived from the mined ore or commodity which may be considerably elevated above local background concentrations and therefore likely to be present at environmental significant levels. The occurrence of elevated concentrations of harmful or toxic elements in the environment does not, however, indicate that there is a significant risk as this will depend on a number of factors including their chemical form, concentration, behaviour and bioavailability, the size of the mineral particle in which the element occurs, the pH of the water or soil and, very importantly, the presence and type of pathways and receptors.

1 Introduction

1.1 SCOPE OF THE REVIEW

This report has been prepared for the Environment Agency (EA) to provide information on waste associated with closed mining and quarrying sites in England and Wales as part of the provisions of the European Council Directive 2006/21/EC, the Mine Waste Directive (MWD).

The purpose of this report is to inform the EA on the approximate numbers of mine waste facilities, their location, the nature of their contained waste, the potential hazards they pose to the environment and human health and likelihood of release of contaminants. Of particular relevance are the water, soil and sediment related impacts associated with the abandoned mine waste facilities.

A generic qualitative characterisation of the waste associated with former workings of various groups of deposit types will be derived.

The Environment Agency is the regulatory body for England and Wales (E&W) responsible for producing an inventory of closed mining waste facilities, including abandoned waste facilities, as required by Article 20 of the European Mine Waste Directive, by May 2012. This document builds upon the information on non-metalliferous sites from a report on waste from active mineral workings in the UK (Colman et al., 2006) with much additional material on metalliferous mine sites.

The total number of closed and abandoned onshore mining and quarrying sites in England and Wales is unknown, but estimates range into the hundreds of thousands of which many thousands produced significant quantities of 'waste' (sensu lato) that may be subject to some or all of the provisions of the Mine Waste Directive. They encompass a wide variety of metalliferous, construction, industrial and energy minerals.

The amount of mineral produced has been reasonably well recorded over many years. However, waste has not been recorded to the same standards, although coal and some other industries do have reasonable recent records of 'mine waste' or 'arisings'. This has caused considerable difficulties in assessing the volume and types of waste at abandoned sites as required under the MWD.

Many waste tips, especially those associated with the coal and ironstone industries, have been reused as brownfield sites for later developments such as industrial estates. The tips have been levelled and covered with topsoil before buildings are erected.

A relatively small proportion of the waste facilities, are very large, exceeding 5 Million m³; these are generally associated with china clay, slate and deep mined coal extraction. Most are less than 500 000 m³. The ratio of mineral to waste varies very widely, even for the same commodity, and can range from around 50 to 1 to less than 1 to 1. Much of the waste, especially that produced by non-coal and non-metalliferous mines and quarries, is inert.

The 'vein minerals' of fluorite and baryte were described separately in the report by Colman et al. (2006), as there were no active metal mines at that time. However, they properly form part of the metalliferous mineralisation, with which they are intimately associated, and are therefore described here alongside the relevant metalliferous deposit types.

1.2 METHODOLOGY

The methodology of this report is based on a hierarchical approach with a series of steps involved in determining the nature of waste produced by closed mineral workings. The assessment is carried out distinguishing the mine waste facilities associated with a) non metalliferous mineral deposits and b) metalliferous mineral deposits.

The steps are as follows:

- 1. Extraction of relevant information from the 2006 BGS report 'Study to assess the nature of the waste produced by active mineral workings in the UK' (Colman et al., 2006) as the waste produced by active or closed workings is similar. However, this report did not cover metalliferous mining as no metal mines were active in the UK at that time.
- 2. Extraction of the numbers of closed sites in England and Wales and the minerals / rock types produced using the current BGS BRITPITS database, supplemented by the BGS Mineral Occurrence Database. The classifications of the minerals worked at the sites are those used in the BGS Directory of Mines and Quarries publication (and also in the BGS 2006 report mentioned above) based on mineral commodity worked.
- 3. Provision of information on metalliferous mining in England and Wales. No metal mines are currently active; most have been closed for over 100 years, but substantial amounts of waste remain. This has used a variety of sources, chiefly BGS reports on economic minerals dating from the 1920s to the 1990s.
- 4. Classification of metallic mineral deposits within current generally accepted 'mineral deposit type' classes. The published United States Geological Survey (USGS) classifications have been used as defined in the mineral deposit models of Cox and Singer (1986). The models group mineral deposits by means of their contained metals, host rocks and geological setting. They also contain information on associated elements, some of which may be potentially harmful. Use of the models and their extension into geoenvironmental models (Seal and Foley, 2002) gives information on the likely characteristics of the mined minerals and associated waste rocks.
- 5. Characterisation of the mine waste. Chemical composition, toxicity of constituents and volume of waste determine the hazard of mine waste. The characterisation comprises four key parts:
 - Description of mode and occurrence of the worked mineral and associated gangue/waste minerals:
 - Description of extraction and processing methods;
 - Identification of key constituents of potential environmental significance on the basis of hazardous properties and relative mobility in the waste stream type;
 - Information on the amount of waste material produced is provided, where available. This is necessarily qualitative or, at best, semi-quantitative, as there is little published data and some of the underlying assumptions on which the quantities are estimated are highly generalised.
 - Environmental signature assessment. The likelihood of release of contaminants from the mine waste facilities is crucial in the assessment of potential environmental impacts. This is to be considered at site specific level and it is therefore outside the terms of reference of this report. Nevertheless evidence of contaminant releases from mine waste facilities is gathered through consultation of BGS geochemical maps of sediments and waters (GBASE Atlases), where available.

The degree of detail given is dependent on the level of information available. A premise of this approach is that it is possible to estimate the key environmental characteristics of mine wastes

from a consideration of ore type, composition and the ore processing methods combined with knowledge of element geochemical properties and dispersion behaviour.

6. Classification of the mining waste into one of the three classifications, namely 'hazardous' and 'inert', and 'non-inert non-hazardous'. The definitions of each class will be discussed further in paragraph 1.6.1. This classification is based on an overview of each mineral commodity and as such site-specific issues could not be considered.

1.3 THE MINE WASTE DIRECTIVE

The European Mine Waste Directive seeks to mitigate the environmental effects of mine waste, encourage the reuse and minimisation of mine waste and to prevent the occurrence of major accidents associated with tailings dams and other waste containment structures. The MWD has numerous Articles dealing with these matters. The current project is concerned with Article 20 – Inventory of closed waste facilities in England and Wales.

Article 20 of the Mine Waste Directive, states that 'Member States shall ensure that an inventory of closed waste facilities, including abandoned waste facilities, located on their territory which cause serious negative environmental impacts or have the potential of becoming in the medium or short term a serious threat to human health or the environment is drawn up and periodically updated. Such an inventory, to be made available to the public, shall be carried out by 1 May 2012, taking into account the methodologies as referred to in Article 21, if available.'

To implement the provisions of this article the location of all abandoned mines in England and Wales, or at least as many as is practical, must be known before they can be prioritised into those causing or likely to cause serious negative environmental impacts and those that do not cause such impacts. This requires lists of abandoned extractive sites and knowledge of their waste products. The BGS BRITPITS database contains over 110 000 entries covering all types of extractive industries, including quarries and mines, and classifies Open, Dormant, Closed and Abandoned sites. However, it does not hold information on waste.

1.4 EXTRACTION OF INFORMATION FROM THE 2006 BGS REPORT

The information regarding the character of mine waste in the 2006 report (Colman et al., 2006) remains valid. However, this did not consider waste from metalliferous mines as none were active at the time of the report. To enable the current report to be read as a 'stand alone' document, the Character and Amount of Waste descriptions from Section 3 and the Data Sources and Limitations from Section 2 of the 2006 study are reproduced in this report, with additions or corrections as necessary.

1.5 THE CHARACTER OF MINE WASTE

The waste produced by the extraction of minerals in England and Wales consists principally of naturally occurring materials, such as overburden, interburden (rock interbedded with the useful mineral) and the residues left after the initial processing of the extracted mineral to produce a saleable product. Extraction and processing waste thus consists essentially of:

- a) Overburden and waste rock, including soil;
- b) Fine-grained materials derived from mineral processing and separation techniques to remove unwanted material, such as unmineralised waste rock, silt and clay.

It is important to note that the waste material, although composed of the same mineral substances as the soil and solid rock from which it is derived, is not in the same physical condition. It may have been disaggregated, mixed and moved to a different location under different hydrological

conditions. The surface area of the material will be increased by reducing the particle size and some dense minerals may concentrate in certain areas of settling ponds or lagoons. The material may also have been exposed to the atmosphere and to surface and/or groundwater. This can cause chemical and physical transformations, some of which may be detrimental to the environment.

This assessment has excluded waste from the following sources:

- Active workings of all types.
- On- and offshore hydrocarbon, water and mineral drilling operations.
- Offshore marine dredging of aggregates.
- Processing of imported mineral ores, such as bauxite for alumina, lead and zinc concentrates and iron ores for smelting.
- Downstream mineral processing operations, such as dimension stone cutting and polishing, additional treatment of aggregates remote from the operating site, wharves and railhead depots, chemical and fertiliser production from minerals such as salt, potash, phosphate, gypsum and limestone and plasterboard operations.
- Mine water, resulting from the pumping of active and dormant operations.

Mineral wastes are associated, to a greater or lesser extent, with the extraction and processing of almost all of the minerals produced in England and Wales. Most are subsequently used to restore worked out sites, but in some cases, e.g. china clay, slate and colliery spoil, where the ratio of waste to mineral is high, or where the worked-out void is allowed to collapse as in deep coal mines, it is not feasible to return waste to the working quarry or mine and waste accumulates as large surface tips. In addition, slimes and other fine-grained residues resulting from washing and mineral processing operations are usually stored in lagoons or tailings dams where they settle out from process water, which can be re-used. In all cases good mining practice calls for the minimisation of waste products as they are, by definition, unsaleable and therefore do not contribute to profits. In the past mine wastes were not subject to any regulation and may have been dumped on any convenient adjacent piece of land to the mine or quarry. These dumps may have been used at intervals, following the mine or quarry closure, as a convenient source of cheap aggregate or fill. Some metal mine dumps, especially in the Pennine orefields, have been reworked to extract formerly worthless minerals such as barytes or fluorspar.

1.6 WASTE CHARACTERISATION

In the following paragraphs a summary of the information required on waste characterisation for active mining is provided. This will also guide the assessment and collection of data related to the abandoned mine waste facilities, as the aim of both is the same, i.e. prevention of major accidents and harm to human health and the environment.

Waste characterisation in accordance with Annex II of the MWD for active mine waste facilities requires that the waste to be deposited in a facility shall be characterised in such a way as to guarantee the long term physical and chemical stability of the structure of the facility and to prevent major accidents. Also "The waste characterisation shall include, where appropriate and in accordance with the category of the waste facility, the following aspects:

- (1) description of expected physical and chemical characteristics of the waste to be deposited in the short and the long term, with particular reference to its stability under surface atmospheric/meteorological conditions, taking account of the type of mineral or minerals to be extracted and the nature of any overburden and/or gangue minerals that will be displaced in the course of the extractive operations;
- (2) classification of the waste according to the relevant entry in Decision 2000/532/EC, with particular regard to its hazardous characteristics;
- (3) description of the chemical substances to be used during treatment of the mineral resource and their stability;

- (4) description of the method of deposition;
- (5) waste transport system to be employed".

1.6.1 The European Waste Catalogue EWC 2002, Decision 2000/532/EC

The European Waste Catalogue (EWC) (EWC 2002, Decision 2000/532/EC) lists waste materials according to generic industry, process or waste type.

The EWC was transposed into English & Welsh law by regulation 19 of the Landfill Regulations (England & Wales) 2002. Under the Landfill Regulation 2002 for wastes destined for landfill, the waste producer's obligations include undertaking fundamental characterization of the waste prior to transport and disposal. They have to code their waste streams according to the EWC and characterize their waste streams to assess whether they meet the relevant waste acceptance criteria (WAC) for acceptance at hazardous, non-hazardous or inert landfills.

Similarly, as a result of the implementation of the MWD pursuant to Annex II(2), a classification of the extractive waste according to the relevant entry in Decision 2000/532/EC will have to be provided, with particular regards to its hazardous characteristics.

The EWC 2000 codes for wastes from the extractive industry are reported in Table 1. The EWC 2002 defines wastes according to their known hazard characteristics, any waste whose six-digit code is marked with an asterisk (*) is a hazardous waste; however, there are two types of hazardous waste entries in the catalogue: "Absolute entries": those entries with an asterisk (*) and without a specific or general reference to "dangerous substances". Wastes covered under these entries are hazardous waste regardless of the concentration of any "dangerous substance" within the waste. "Mirror entries": those entries with an asterisk (*) and with a specific or general reference to "dangerous substances", which are generally identified by the word "containing" in the description. These "mirror entries" cover wastes that have the potential to be either hazardous or nonhazardous depending on their actual composition and the concentrations of "dangerous substances" within the waste.

For the purpose of EWC 2000 'dangerous substance' means any substance that has been or will be classified as dangerous in Directive 67/548/EEC and its subsequent amendments; 'heavy metal' means any compound of antimony, arsenic, cadmium, chromium(VI), copper, lead, mercury, nickel, selenium, tellurium, thallium and tin, as well as these materials in metallic form, as far as these are classified as dangerous substances (Decision 2000/532/EC, Annex, point 5). Decision 2000/532/EC also states that if a waste is identified as hazardous by a specific or general reference to dangerous substances, the waste is hazardous only if the concentrations of those substances are such (i.e. percentage by weight) that the waste presents one or more of the properties listed in Annex III to Council Directive 91/689/EEC (Appendix 1).

The full list (Annex II to Council Directive 91/689/EEC) of constituents of the wastes which render them hazardous when they have the properties described in Annex III to Council Directive 91/689/EEC is attached in Appendix 1. Among them, "heavy metals ", as defined in the previous paragraph, inorganic sulphides, inorganic fluorine compounds excluding calcium fluoride (the Fluorite mineral), inorganic cyanides, acidic solutions, basic solutions, phosphorus compounds excluding mineral phosphates are of relevance for the extractive industry.

In the EWC only "acid-generating tailings from processing of sulphide ore" with the code 01 03 04* is classified as absolute hazardous waste, regardless of any threshold concentrations. Other tailings (code 01 03 05*) or waste (code 01 03 07*) containing dangerous substances from physical and chemical processing of metalliferous minerals, or wastes (code 01 04 07*) containing dangerous substances from physical and chemical processing of non-metalliferous minerals have mirror entries and are classified as hazardous waste if dangerous substances are present above threshold concentrations.

The EWC is, however, a non-exhaustive list of waste types. It does not contain any reference to gypsum or peat extraction and associated waste.

Table 1 The EWC 2000 codes for wastes from the extractive industry

EWC CODE 01 - Wastes Resulting from Exploration, Mining, Quarrying, and Physical and Chemical Treatment of Minerals:
and Chemical Treatment of Minerals.
01 01 wastes from mineral excavation
01 01 01 wastes from mineral metalliferous excavation
01 01 02 wastes from mineral non-metalliferous excavation
01 03 wastes from physical and chemical processing of metalliferous minerals
01 03 04* acid-generating tailings from processing of sulphide ore
01 03 05* other tailings containing dangerous substances
01 03 06 tailings other than those mentioned in 01 03 04 and 01 03 05
01 03 07* other wastes containing dangerous substances from physical and chemical processing
of metalliferous minerals
01 03 08 dusty and powdery wastes other than those mentioned in 01 03 07
01 03 09 red mud from alumina production other than the wastes mentioned in 01 03 07
01 03 99 wastes not otherwise specified
01 04 wastes from physical and chemical processing of non-metalliferous minerals
01 04 07* wastes containing dangerous substances from physical and chemical processing of
non-metalliferous minerals
01 04 08 waste gravel and crushed rocks other than those mentioned in 01 04 07
01 04 09 waste sand and clays
01 04 10 dusty and powdery wastes other than those mentioned in 01 04 07
01 04 11 wastes from potash and rock salt processing other than those mentioned in 01 04 07
01 04 12 tailings and other wastes from washing and cleaning of minerals other than those mentioned in 01 04 07 and 01 04 11
01 04 13 wastes from stone cutting and sawing other than those mentioned in 01 04 07
01 04 99 wastes not otherwise specified
01 05 drilling muds and other drilling wastes
01 05 04 freshwater drilling muds and wastes
01 05 05* oil-containing drilling muds and wastes 01 05 06* drilling muds and other drilling
wastes containing dangerous substances
01 05 07 barite-containing drilling muds and wastes other than those mentioned in 01 05 05 and
01 05 06
01 05 08 chloride-containing drilling muds and wastes other than those mentioned in 01 05 05
and 01 05 06
01 05 99 wastes not otherwise specified.

1.6.2 Definition of inert waste and non inert-non hazardous waste

As a result of the EWC classification, mine waste can be attributed to the "hazardous waste" or "non hazardous waste" category. The non-hazardous waste category includes the following subcategories: "inert" and "non inert-non hazardous", to which correspond different requirements of the MWD.

Non inert - non hazardous waste, in the interpretation adopted in this report, is waste that is not in the hazardous list, but cannot be classified as inert.

Inert waste as defined in Article 3 (1) of Council Directive 2006/21/EC means "waste that does not undergo any significant physical, chemical or biological transformations. Inert waste will not dissolve, burn or otherwise physically or chemically react, biodegrade or adversely affect other matter with which it comes into contact in a way likely to give rise to environmental pollution or harm human health. The total leachability and pollutant content of the waste and the

ecotoxicity of the leachate must be insignificant, and in particular not endanger the quality of surface water and/or groundwater".

The Commission Decision of 30 April 2009 (2009/359/EC) completing the definition of inert waste of Article 22(1)(f) defines the criteria to be fulfilled by inert waste.

- a) the waste will not undergo any significant disintegration or dissolution or other significant change likely to cause any adverse environmental effect or harm human health;
- b) the waste has a maximum content of sulphide sulphur of 0.1 %; or the waste has a maximum content of sulphide sulphur of 1 % and the neutralising potential ratio, defined as the ratio between the neutralising potential and the acid potential, and determined on the basis of a static test prEN 15875, is greater than 3;
- c) the waste presents no risk of self-combustion and will not burn;
- d) the content of substances potentially harmful to the environment or human health in the waste, and in particular As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, V and Zn, including in any fine particles alone of the waste, is sufficiently low to be of insignificant human and ecological risk both in short and long term and or does not exceed national threshold values for sites identified as not contaminated or relevant national natural background levels;
- e) the waste is substantially free from products used in extraction or processing that could harm the environment or human health.

1.7 DATA SOURCES AND LIMITATIONS

Data on the location and type of mines and quarries are taken from the BGS corporate **BRITPITS** database, which contains information on over 110 000 mineral sites including active, inactive, closed and abandoned sites as well as selected wharves, secondary aggregates sites and other locations. The database is believed to be the most definitive source of information on mineral workings for the UK. It is continually modified to take account of changes in the industry and new sites, but can never be absolutely up-to-date. The data is updated from BGS's own extensive records, a wide range of contacts within the minerals industry and Mineral Planning Authorities and by both formal and informal (visits, enquiries, trade journals, etc.) means.

There is little comprehensive information on the quantities of waste produced by mineral working, except for some specific minerals such as china clay or coal, as it has generally been of no interest to the statistical or planning community, having by definition no commercial value. Mine and quarry waste is not classed as 'controlled waste' and is, therefore, not regulated by the controlled waste legislation. The few published statistics on the quantities of waste involved are mainly based on estimates calculated using an arbitrary ratio of waste / product for a specific mineral (e.g. Gutt et al., 1974; Whitbread et al.,1991; Arup, 1991). The Environment Agency has estimated that 97 million tonnes of mine and quarry waste were produced in 2003 (Table 2).

The BGS Mineral Occurrence Database (MOD)

The MOD database has been used to supplement information on closed mines from BritPits. The MOD has over 12000 records of mineral occurrences throughout Great Britain. These range from records of gold grains panned from a stream to minerals associated with metal mines. The database holds the location of each record but information on each occurrence is widely variable and is dependent on the available data at the time of entry.

BritPits and the MOD have both been used to derive information for the images of mines and quarries but both are still incomplete.

The British Geological Survey Regional Geochemical Atlases

The British Geological Survey Regional Geochemical Atlases have been consulted to assess the environmental signatures inherent in metalliferous mines in England and Wales. These atlases are based on analysis of stream sediments and waters collected at an average sampling density of 1 per 2 km² during field campaigns from 1969 to 2008, and ideally taken from 1st or 2nd order

streams, and based on the work of the Geochemical Baseline Survey of the Environment (G-BASE) project. Further information on these and other published atlas areas can be obtained on the BGS webpage under http://www.bgs.ac.uk/gbase/home.html. Figure 1 shows the coverage of G-BASE stream sediment and soil sampling points.

Although relative large number of investigations have been made on sites affected by mining, mostly from metalliferous mining, a comprehensive review of these sources of information is outside the remit of this report. Site specific assessments were outside the scope of the review and the extent of contamination and variety of environmental issues within and between sites belonging to the same mineral deposit type may vary considerably.

This overview desk study report cannot cover the complete Source – Pathway – Receptor scenario generally used in risk assessments because it is drawn from current information available to us and applies a generic, rather than a site-specific, view of the potential risk posed by the waste produced by each mineral sector.

Table 2 Estimated mineral waste production in the UK (Source: DEFRA, 19.6.2003)

1.8 Waste minerals (Thousand tonnes) Category											
Year	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000
² Colliery	36,450	36,679	32,900	25,229	15,927	17,575	16,112	15,141	12,543	10,444	8,806
3 Opencast	9,932	10,423	9,347	8,871	8,559	8,944	9,292	9,107	8,094	8,095	7,181
⁴ China Cla	27,339	26,205	22,526	22,156	22,778	23,283	20,537	26,648	21,608	20,745	21,790
⁵ Clay	19,756	16,335	15,172	13,799	15,174	16,725	14,507	13,791	14,110	13,560	14,205
⁶ Slate	7,180	7,200	6,520	9,240	8,040	5,500	8,180	6,940	9,000	7,220	7,200
7 Quarrying	54,814	51,039	48,416	49,466	53,057	51,558	48,677	47,380	35,602	46,619	33,595

Source: Defra.

- 1 Estimates are based on the production data in UK Minerals Year Book, published by British Geological Survey
- 2 Colliery waste estimate is based on deep-mined coal assuming a ratio of waste to saleable product of 1:2
- 3 Coal waste is based on opencast and other coal production and is also based on a 1:2 ratio
- 4 China clay waste is estimated on the ratio of waste to saleable product of 9:1 5 Clay waste is estimated on the ratio of waste to saleable product of 9:1
- 6 Slate waste is estimated on the ratio of waste to saleable product of 20:1
- 7 Quarrying waste is estimated on the ratio of waste to saleable product of 1:9
- 8 Figures are provisional

1.8 DEFINITIONS AND TERMINOLOGY

The following are the most important terms used in the report.

Article 20 Inventory of closed waste facilities: "Member States shall ensure that an inventory of closed waste facilities, including abandoned waste facilities, located on their territory which cause serious negative environmental impacts or have the potential of becoming in the medium or short term a serious threat to human health or the environment is drawn up and periodically updated. Such an inventory, to be made available to the public, shall be carried out by 1 May 2012, taking into account the methodologies as referred to in Article 21, if available".

Dam (definition from Article 3 (11) of the MWD) means an engineered structure designed to retain or confine water and/or waste within a pond.

Hazardous waste: Defined in Article 3(2) of the MWD which refers to Article 1(4) of Council Directive 91/689/EEC on hazardous waste.

Heap (definition from Article 3 (10) of the MWD) means an engineered facility for the deposit of solid waste on the surface.

Leachate (definition from Article 3 (14) of the MWD) means any liquid percolating through the deposited waste and emitted from or contained within a waste facility, including polluted drainage, which may adversely affect the environment if not appropriately treated.

Mine: site which is worked to produce minerals by underground methods. However, the term 'Opencast Mine' is often used for surface coal or iron workings.

Mineral: Article 3 (5) of the MWD (Directive 2006/21/EC) gives the definition of a mineral as 'a naturally occurring deposit in the earth's crust of an organic or inorganic substance, such as energy fuels, metal ores, industrial minerals and construction minerals, but excluding water'.

Pond (definition from Article 3 (12) of the MWD) means a natural or engineered facility for disposing of fine-grained waste, normally tailings, along with varying amounts of free water, resulting from the treatment of mineral resources and from the clearing and recycling of process water.

Quarry: site which is worked to produce minerals from a surface operation.

Tailings (definition from Article 3 (9) of the MWD) means the waste solids or slurries that remain after the treatment of minerals by separation processes (e.g. crushing, grinding, size-sorting, flotation and other physico-chemical techniques) to remove the valuable minerals from the less valuable rock.

Waste: Defined in Article 3(1) of the MWD which refers to Article 1(a) of Directive 75/442/EEC which states that 'waste' shall mean any substance or object in the categories set out in Annex I which the holder discards or intends or is required to discard.

Waste facility: according to Article 3 (15) of the MWD 'waste facility' means any area designated for the accumulation or deposit of extractive waste, whether in a solid or liquid state or in solution or suspension, for the following time-periods:

- no time-period for Category A waste facilities and facilities for waste characterised as hazardous in the waste management plan;
- a period of more than six months for facilities for hazardous waste generated unexpectedly;
- a period of more than one year for facilities for nonhazardous non-inert waste;

mineral, for rehabilitation and construction purposes.

— a period of more than three years for facilities for unpolluted soil, non-hazardous prospecting waste, waste resulting from the extraction, treatment and storage of peat and inert waste. Such facilities are deemed to include any dam or other structure serving to contain, retain, confine or otherwise support such a facility, and also to include, but not be limited to, heaps and ponds, but excluding excavation voids into which waste is replaced, after extraction of the

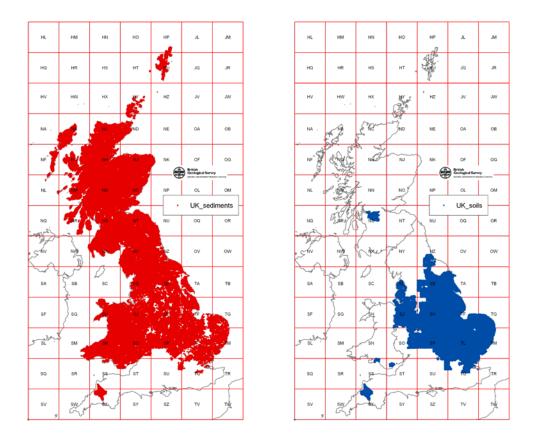


Figure 1 Coverage of G-BASE sediment and soil sampling.

2 Environmental hazards associated with abandoned mining waste facilities

2.1 GENERAL ASSESSMENT

Figure 2 groups the mineral deposits and commodities into classes, depending on the mineral mined and the likely environmental problems they may cause.



Figure 2 Main mineral deposit types and potential environmental issues.

2.2 HAZARD SOURCE CHARACTERISATION AND TRANSFER MECHANISMS AT METALLIFEROUS MINE SITES

The source characterisation is very much dependant on the past history of the site. The most common sources of contamination related to mining and mineral processing are mine wastes in the form of waste rock, tailings, water discharges or process water. Chemical hazards include the toxicity of the mine spoil and of any other materials which may have been deposited on site. Some sites might have been used for fly-tipping and may have received material more toxic than the spoil itself. Additionally some mineral processing operations can give rise to slags and ashes, gaseous and particulate emissions through, for example, grinding and ore roasting and smelting.

At abandoned mine sites, acid mine drainage and metal-rich drainage that develops as a consequence of the weathering of sulphide rich wastes may represent one of the main contaminant sources along with the legacy of past mineral processing activity.

Soils and spoils of mine waste facilities will contain concentrations of potentially harmful elements (PHE) derived from the mined ore or commodity which may be considerably elevated above local background concentrations.

Different metalliferous orefields are associated with particular suites of minerals and elements and there are large variations in actual concentrations. Table 3 lists the most significant PHEs associated with the major orefields. The orefields are shown in Figure 14.

Table 3 Potentially harmful elements associated with major metalliferous orefields in England and Wales

Area	Main Associated Elements
North Pennines	Pb, Zn, F, Cd, Ba
Lake District	Cu, Pb, Zn, As
South Pennines	Pb, Zn, F, Cd, Ba
North Wales	Pb, Zn, Cu, Cd, As, Ba
Central Wales	Pb, Zn, Cd, Ba
Mendips	Pb, Zn, Cd
Southwest England	Sn, Cu, As, Pb, Zn
West Shropshire	Pb, Zn, Ba

2.2.1 Waste rocks and tailings

In general the first stage of mineral processing involves reducing the size of the mined material so that the economic mineral grains are no longer locked in a rigid aggregate of gangue, the waste being dumped or used as mine backfill. The second stage of mineral processing involves the separation of the mineral grains from the gangue, which may proceed via physical, surface chemical or bulk chemical means. In the past such treatments were physical relying on crushing and ore washing. The waste products from these operations would generally have been piped to a tailings dam facility. One of the outcomes of ore crushing and a major contributing factor to possible environmental impact is the greatly increased surface area of the mined material that potentially leads to an increase in chemical reactivity and weathering rates.

In the mines of SW England and the Pennines techniques used were very similar. On larger mines mechanical crushers or stamps would have been used whereas on smaller mines hand cobbing was more likely. The ore was cleaned on dressing floors that consisted of riffles or buddles that relied on gravity separation in water. The more efficient operations were able to win a high percentage of the ore, while in less efficient operations a lot of mineral went to waste in the slimes.

The sulphide content of the tailings is of environmental concern as result of sulphide oxidation once these wastes are exposed to atmospheric oxygen and water. The weathering of sulphide minerals in tailings heaps promote acid mine drainage (AMD) and the release of contaminants to surface and groundwater. Pyrite is ubiquitous in most metal sulphide and coal deposits and may exist in association with other chalcophile elements such as As, Bi, Cd, Co, Cu, Ga, In, Hg, Mo, Pb, Sb, Sn, Te and Zn. Pyrite oxidation occurs according to this simplified scheme (Stumm and Morgan, 1996):

$$2FeS_2 + 2H_2O + 7O_2 = 2Fe^{2+} + 4SO_4^{2-} + 4H^+$$

Further partial oxidation of ferrous to ferric iron consumes protons:

$$4Fe^{2+} + 4H^{+} + O_2 = 4Fe^{3+} + 2H_2O$$

Ferric iron may act as an electron acceptor for further pyrite oxidation, or hydrolysis may occur, both processes releasing further protons:

$$FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$

$$Fe^{3+} + 3H_2O = Fe(OH)_2 + 3H^+.$$

Micro-organisms often drive the oxidation reaction (Nordstrom and Alpers, 1999).

Many factors may affect the leaching characteristics of tailings heaps. These factors have to be taken into account to explain the often limited correlation between metal contents in the tailings and in the leachate. They are reviewed by Merrington and Alloway (1993) and summarised as follows:

- -Particle size of ore minerals is one important factor. Mineral processing practices such as crushing and grinding ensure that a large surface area of the ore particles in mine tailings is exposed to oxidative processes.
- -Microbial oxidation can increase the rate of chemical oxidation of ionic species by five to six orders of magnitude.
- -The presence of pyrite in tailings greatly increases the release of metals from other sulphides, such as chalcopyrite (CuFeS₂) and sphalerite (ZnS), while its own dissolution is suppressed.
- -Temperature has a significant effect on ore weathering with increasing rate at higher temperature.
- -The rate of water flow through tailings and the contact time between the leaching solution and the solid phases greatly influences the solution chemistry of the leachate.
- The formation of secondary minerals, particularly insoluble Fe(III) species, may reduce metal concentration in the leachate through the formation of sealed coatings around ore particles.

The acidity generated by sulphide oxidation only results in a very low pH in the mine water when it exceeds the alkalinity in the system. Such alkalinity may be available as bicarbonate in groundwater or in the form of mineral phases such as calcite. This buffering reaction has been observed at many sites where the tailings are dominated by the presence of calcite as the gangue mineral (Germain et al., 1994; Blowes et al., 1998). Acid neutralisation in the tailings causes a reduction in the concentrations of dissolved metals (Al et al., 2000), because the neutral pH enhances precipitation and adsorption processes. Evidence from humidity cells tests carried out by Holmström et al. (1999) has shown that addition of carbonates in sulphidic tailings not only reduces the solubility of heavy metals by maintaining a high pH, but also decreases the oxidation rate of sulphides.

2.2.2 Secondary minerals

A significant fraction of the metals released by sulphide oxidation can be retained within the secondary mineral precipitates in the tailings deposits and underlying soils.

Secondary minerals formed by sulphide weathering and leachate-host rock interaction include Fe and aluminium hydroxides and hydroxyl sulphates that are significantly less soluble than

efflorescent sulphate salts. Important Fe^{3+} minerals are ferrihydrite ($Fe_5HO_8\cdot 4H_2O$), schwertmannite ($Fe_8O_8(OH)_6SO_4\cdot nH_2O$), jarosite ($KFe_3(SO_4)_2(OH)_6$), and goethite (α -FeO(OH)). The secondary iron hydroxides are important because they can sorb significant quantities of trace metals and remove them from solution, the sorption capacity being pH-dependent.

The analysis of secondary minerals can give an indication of the pore-water chemistry at the time of formation and of the solid phases that are potentially controlling solute concentrations in the pore solution. Hydrous ferric oxide and iron hydroxysulphate minerals, such as ferrihydrite and schwertmannite, precipitate from acidic to near-neutral mine- and natural- drainage water, while jarosites tend to form in low-pH (1.5 to 3.0), high-sulphate (>3000 mg/l) environments (Bigham and Nordstrom, 2000). Aluminium hydroxysulphate minerals, including basaluminite (Al₄(SO₄)(OH)₁₀·5(H₂O)) and jurbanite (Al₄(SO₄)(OH)·5(H₂O)), precipitate from water having pH between 4.5 and 5. Jarosite is slightly soluble and can, therefore, produce acidity (Alpers et al., 1994).

The evaporative concentration of sulphate in mine tailings can produce a series of highly soluble secondary metal-bearing sulphate salts. Evaporative processes can operate during hot arid conditions, or in tailings piles beneath snow packs. Common secondary sulphate salts in mining environments include melanterite (FeSO₄7H₂O), rozenite (FeSO₄4H₂O), halotrichite (FeAl₂(SO₄)₄22H₂O), alunogen (Al₂(SO₄)₃17H₂O, copiapite (Fe²⁺Fe³⁺₄((OH)(SO₄)₃)₂20H₂O), goslarite (ZnSO₄7H₂O) and chalcanthite (CuSO₄5H₂O), among numerous others. The "efflorescent" salts temporarily sequester acidity and metals for later dissolution during rain events or snowmelt. Gypsum is a common secondary sulphate, which can contribute dissolved solids, but it does not store acidity or metals.

2.2.3 Heterogeneity of tailings heaps

In the environmental management of old mining sites it is important to recognise that the heaps are not homogeneous in either composition or permeability. Changes due to geological and economic factors in the grade and types of ores mined during the nineteenth century gave rise to highly variable ore production, affecting the characteristics of the produced tailings in terms of particle size, permeability, secondary mineral formation and concentration of heavy metals.

Spoil heaps are generally characterised by an upper oxidised zone and a lower reduced zone. The weathering and mobility of minerals differs in the two zones.

Of particular importance is the occurrence of impermeable layers in the tailings heaps. These layers affect the infiltration of rain water and reduce the volume of tailings exposed to oxidising conditions. The occurrence and effects of impermeable layers in tailings heaps in UK have been described by Merrington and Alloway (1993). Relative to the composition of the bulk tailings material, elevated concentrations of heavy metals were found in fine-grained material layers in the tailings profiles at a Pb-Zn-Cu mine in Cornwall and a Pb-Zn mine in Mid Wales. The anomalous zones were characterised by the accumulation of fine particles of sulphide minerals stabilised by the reducing conditions developed in these fine-grained, impermeable layers. The increased risk due to release of heavy metals in the leachate from the heaps associated with the disturbance of the impermeable layers is the most important consideration.

2.2.4 The effects of vegetation on the leaching of contaminants from mine tailings

One method of stabilising and reclaiming mining areas is revegetation since proper soil cover can eliminate surface erosion and infiltration. However, there is evidence that direct contact between plant roots and contaminated material may increase the probability of leaching heavy metals. Organic compounds exuded by plants and rhizosphere microbes may increase heavy metal solubility by forming stable aqueous complexes. Batch and column experiments carried out by Burckhard et al. (1995) confirmed that geochemical modelling can predict the capability of organic ligands found in the rhizosphere to complex and increase the solubility of zinc from

mine tailings. Similar results were observed by Zhu et al. (1999) confirming that topsoil cover has the potential to mobilise zinc and cadmium, while there is less impact on lead. The insensitivity of lead to the presence of a topsoil cover suggests that, although top soils could accelerate microbial oxidation of mine tailings and subsequent mobilisation by organic acids—metal complexes, the sparingly soluble lead phosphates or carbonates may be overriding all other influences.

2.2.5 Chemical hazard

Chemical hazard can be subdivided into different categories, as chemical conditions often pose a different hazard to human than to flora and fauna.

Table 4 reports the relative toxicities of metals in soil and sediments for human ingestion/inhalation and livestock receptors, and of metals in surface water and groundwater for livestock and aquatic life receptors. These relative toxicity values are extracted from Mhairtin et al. (2009) in their inventory and risk classification study of historic mine sites of Ireland.

Table 4 Relative toxicity values for different environmental and habitat situations (Mhairtin et al. 2009)

Relative Toxicity Values						
	Soil and sedi	Surface water and groundwater				
Element	Human ingestion & inhalation	Livestock	Eco Aquatic	Eco Salt - Aquatic	Livestock	
Aluminium	N/A	N/A	0.1	0.1	0.01	
Antimony	10	0.1	0.1	0.1	0.1	
Arsenic	10	0.1	0.01	0.1	0.01	
Barium	0.01	0.01	0.001	0.001	0.1	
Cadmium	10	10	10	1	10	
Chromium	10	0.1	0.1	0.1	0.1	
Copper	0	0.1	1	1	0.1	
Iron	0.001	0.01	0.01	0.01	0.01	
Lead	10	1	1	1	1	
Manganese	0.1	0.001	0	0	0.001	
Mercury	10	1	10	10	1	
Nickel	10	0.1	0.1	1	0.1	
Selenium	0.1	1	1	0.1	1	
Silver	0.1	0.01	10	10	0.01	
Thorium	10	0.01	0.01	0.01	0.01	
Uranium	10	0.01	0.01	0.01	0.01	
Vanadium	0.1	0.1	0	0	0.1	
Zinc	0.01	0.01	0.01	0.1	0.01	

The effect of potentially harmful elements on humans depends on the type and extent of exposure and whether they are ingested, adsorbed through the skin or inhaled in dust. In humans cadmium may progressively and irreversibly impair kidney functions. Exposure of young children to lead can permanently impair mental functions. High concentrations of arsenic in the diet can cause severe skin problems, whilst chronic exposure to lower doses of arsenic may lead to the development of lung and skin cancer. Copper appears to have a low toxicity to humans. Soil copper concentrations even in areas of copper mining are unlikely to result in exposure limits being exceeded. Copper phytotoxicity could occur in plants grown on mine spoil tips. Copper has a relatively high toxicity to aquatic life. High concentrations of zinc in soil are known to inhibit plant growth and in animals can cause severe anaemia. Inhibition of plant growth may also be caused by elevated concentrations of nickel, cobalt and chromium in soil.

2.2.6 Transport mechanisms

The redistribution of potentially harmful elements into drainage sediments, soils and waters occurs as a result of physical and chemical weathering and a variety of dispersion processes. Factors which will influence the dispersion via a range of pathways include:

- Grain size of mineral particles;
- The pH of water and soils;
- Solubility and chemical speciation of the contaminant source minerals and their weathering products;
- Type and density of vegetation covering contaminated mine spoils;
- Rainfall;
- Wind direction and strength;
- Slope stability;
- Drainage;
- Connectivity between abandoned mine workings and surface waters.

2.2.6.1 FLUVIAL DISPERSION

Fluvial action will redistribute contaminants from mineral veins and abandoned mine waste facilities downstream from the source. Major mechanisms of fluvial dispersion are as dispersion in detrital particles and in solution. Contamination is not restricted to the drainage channels, but it also affects overbank sediments and alluvial sediments during periods of inundation (Macklin and Ridgway, 1994).

2.2.6.2 Atmospheric dispersion

Contaminant-enriched fine dust particles on unvegetated spoil tips are very susceptible to transport and dispersion by the wind. The moist, cool maritime climate of the UK tends to mitigate this potential problem. Nevertheless, there are periods of low rainfall, when the tip surface can dry out and dust can be blown from the tip. For example, this was seen as a potential hazard at the Snailbeach tip in Shropshire, where around 1 Mt of waste from the local lead mines was situated in the centre of the village (Figure 19). The tip consisted mainly of the limestone hostrock, together with small amounts of lead, zinc and iron minerals, as well as unrecovered barite and calcite. It has now been largely covered with soil which has stabilised it against wind erosion and restricts rain water ingress.

2.2.6.3 GRAVITATIONAL DISPERSION

Surface creep on the unstable slopes of mine spoils is an important dispersion mechanism. Migration down slopes may occur naturally or can be caused by restoration or reclamation works or a change in land use. This might have a significant effect on water quality if erosion of mine spoils results in contamination of receiving stream water and sediments.

2.3 VISUAL ENVIRONMENTAL IMPACT

Mine waste tips can be visually intrusive. This can be due to their shape, for example the conical tips of the china clay industry in SW England; many coal mine tips were sited on relatively flat ground and thus stood out from the surrounding landscape. Their colour can also be at variance with the local environment. The stark white of the china clay tips led to their informal name of the "The Cornish Alps" and the black or dark grey colour of coal tips contrasts strongly with the surrounding green vegetation. In both cases, an answer to the problem has been to attempt to reduce their height and make smoother, rounded or flattened shapes. The remodelled tips have then been sown with various grasses to make them visually indistinguishable from the surrounding fields. This approach has been variably successful in different parts of Britain. It

suffers from the disadvantage that it uses more surface area than the previous conical tip approach, but is visually more acceptable to the planning community.

2.4 PHYSICAL HAZARDS

Physical hazards associated with a mine waste facility are principally related to mine workings, buildings and processing areas and are likely to include: shafts, adits and open stopes; unstable buildings; unstable ground; tanks, channel and ponds containing waters. In the past, before the advent of more effective and efficient tipping procedures and coal preparation plants, many coal tips contained enough fine coal and oxidising pyrite that they commonly caught fire, releasing large amounts of smoke into the environment.

For stability hazards the areas most affected by tips on steep slopes are the South Wales coalfield and the North Wales slate industry. The geology, topography and high rainfall of South Wales causes a relatively common incidence of natural slope failures. This, combined with the former practice of uncontrolled coal waste tipping on the hills and slopes above the colliery settlements, makes the area prone to stability problems. The worst accident caused by coal waste tip failure in the UK was that at Aberfan in South Wales on October 21st 1966, when 144 people, mainly children in a primary school, were killed by a slurry of water-saturated waste descending a steep hillside. The accident was caused by the sudden failure of Tip No 7 of Merthyr Vale Colliery due to tipping over a concealed spring. Abnormally heavy rain caused the base of the tip to fail (Woodland, 1969). That accident led directly to the passing of The Mines and Quarries (Tips) Act 1969. Since 1967 dangerous occurrences involving tips must be reported to the Mines Inspectorate. Between 1969 and 1989 out of 110 "falls of ground" reported none were attributed to the collapse of a spoil tip. This may have been due to increased vigilance and remedial actions taken following the Aberfan disaster. However, there were 74 "dangerous occurrences" involving spoil tips with 1 in 3 involving damage to property, though no loss of life was reported (DETR, 1999).

2.5 RISK

The occurrence of elevated concentrations of harmful elements in the environment does not, however, indicate that there is a significant risk as this will depend on a number of factors including their chemical form, concentration, behaviour and bioavailability, the size of the mineral particle in which the element occurs, the pH of the water or soil and the presence and type of pathways and receptors.

A hazard only presents a risk to receptors (in no order of priority: children, adults, livestock, controlled waters, the terrestrial and aquatic ecosystems and property), if specific pathways are present to link them. The generally accepted source – pathway –receptor paradigm used in risk assessment methodologies that underpins the Environment Protection Act 1990 provides a site-specific view of the risk posed by mine waste (Table 5). The risk posed by any particular mine waste or waste facility will be site specific and will depend on the linkage between the source of contamination and potential receptors.

In terms of human health risk assessment there are three main exposure pathways for a given contaminant. The largest area of concern is the oral/ingestion pathway followed by the dermal and respiratory exposure routes. In England and Wales, concern in respect of oral ingestion pathway is often focussed on the potential for exposure of children and other sensitive individuals to contaminated soil and derived dusts. This is principally because of a well distributed, regulated and managed mains water and food supply system. However, an increasing trend towards a preference for private household water supply means that this exposure route should not be necessarily discounted. Whether contaminated soils and/or derived dusts pose a risk to human health depends on the potential of the contaminant to leave the soil and enter the human bloodstream or to be concentrated in foodstuffs. The use of total contaminant concentration provides a conservative approach in this context as it assumes that all of the

OR/10/14

contaminant present in the soil and/or food is available for uptake in the human gut. However additional and more specific analyses (e.g. Physiologically Based Extraction Tests (PBET) (Cave et al., 2003)) have been developed and adopted to determine more precisely the fraction of contaminant that is available for uptake, be it from food or from the inadvertent ingestion of soils and dusts. The use of such testing, in conjunction with similar tests that have been developed to estimate the leachability of mine wastes and its bioavailability to plants and ecosystems is an essential component in quantitatively estimating the risks associated with mine waste.

Table 5 Source-pathway-receptor analysis of a simple conceptual model

SOURCE	PATHWAY	RECEPTOR
Waste Rock and tailings	Airborne, deposition and inhalation.	Agricultural land, surface water, livestock and humans
Acid Mine and Acid Rock Drainage	Surface and groundwater flow	Groundwater, surface water, agricultural produce through irrigation and humans through ingestion
Contaminated soils	Ingestion and leaching	Human, agricultural produce
Contaminated food	Ingestion	Humans and animals
Contaminated water	Irrigation and ingestion	Human and agricultural produce

3 Non-metalliferous mine waste facilities

The summary of closed pits (mines and quarries) in Table 6 incorporates information available within the Britpits database to December 2009. The database is under continuous revision and updating. The maps (Figures 3 to 21) show the location of the individual mines and quarries. Information on the amount of waste material produced is provided in Table 7. The numbers of sites, particularly of metalliferous mines, is not yet comprehensive and significant numbers of sites require to be located and added to the database. This work is ongoing as resources permit. However, there are numerous sites within each of the orefields of England and Wales and so no significant area of mineralisation is omitted.

Table 6 Summary of closed mines and quarries in England and Wales (Source: BGS BritPits Database)

Commodity	No of closed
	sites
Sand and Gravel	9084
Sand	3754
Silica Sand	267
Silica Rock	100
Igneous Rock	2694
Sandstone	24927
Chalk	4298
Dolomite	1745
Limestone	11641
Ball Clay	63
China Clay	217
Clay	12604
Fireclay	384
Slate	2863
Anhydrite	7
Gypsum	109
Salt	49
Opencast Coal	764
Deep mined Coal	7626
Peat	54
Iron Ore - Hematite	49
Iron Ore - Ironstone	1589
Iron Ore - Ochre	12
Vein Minerals	
Baryte	29
Copper	205
Fluorite	58
Lead	620
Tin	335
Witherite	12
Zinc	5
Vein Minerals (undifferentiated)	705

Table 7 Assessment of non-metalliferous waste products by commodity

Mineral	Estimated Cumulative Mineral Production Mt	Estimated Cumulative Waste Production Mt	Estimated area of waste tips Ha
Coal	26000	3600 including reclaimed tips 2000 on 560 tips	22000 in 1966 Currently 2-4000 Ha in England
China Clay	150	280 600	800 (Gutt el al., 1974) 2000 (Arup, 1991)
Slate	36	500-700	1500
Constructional minerals	4300 limestone	0	
Gypsum	200	0	0

3.1 SAND AND GRAVEL

Sand and gravel are materials of specific particle size, generally between 0.0625 mm and 4 mm for sand and between 4 mm and 64 mm for gravel, suitable for combining with coarser aggregates and cement to form concrete. They are also used for a variety of other filling and levelling applications. They are mainly composed of quartz (SiO₂), together with a variety of hard and durable silica-rich fragments of sandstone, quartzite, flint and igneous (mainly granitic) rocks. Two main categories are identified according to their source, 'superficial' and 'bedrock'.

There are 9084 superficial and 3754 bedrock sand and gravel quarries that are closed; a few worked both categories (Figure 3).

3.1.1 Superficial deposits

Character and amount of waste

Waste from working these deposits consists of a) overburden and b) 'fines' comprising clay and silt. The amount of waste produced varies considerably depending on the specific character of the site, but will range from a few per cent up to around 30% of the total material quarried. The fine material is stored in lagoons that are generally restored to some form of productive use by covering with soil.

Classification

The waste from the vast majority of sand and gravel facilities is non-hazardous and can be classified to the EWC 2002 entry: 01 04 12- Tailings and other wastes from washing and cleaning of minerals other than those mentioned in 01 04 07 and 01 04 11. However, there are no published systematic compilations of data on the mineral contents of waste lagoons and other sites and their relationship with the local environment. The waste from the vast majority of sites is inert according to the current interpretations in operation in England and Wales.

3.1.2 Bedrock deposits

Mode of occurrence

These deposits are of considerable importance in England and consist of relatively unconsolidated sandstones from which construction sands can be readily produced. Some may contain sandy pebble beds or conglomerates from which gravel can be produced. The most important bedrock sand and gravel deposits occur within the Triassic Sherwood Sandstone

Group, notably in the English Midlands. Important sources of construction sand are the Lower Greensand in East Anglia and south-east England and the Permian Yellow Sands in north-east England and Tertiary sands in the South East.

Character and amount of waste

Waste from these deposits can be quite variable in type and quantity. The Sherwood Sandstone tends to have a large number of cobbles in it, which are derived from a number of sources, mainly hard and well-indurated sandstones, greywackes, quartzites and igneous rocks from the west and north of the UK. There may also be considerable amounts of fine material that is unsaleable

Classification

The majority of the waste produced is non-hazardous entries and typically inert, classified with codes 01 04 08, 01 04 09 and 01 04 12. However, there are no published systematic compilations of data on the mineral contents of waste lagoons and other sites and their relationship with the local environment.

3.2 CRUSHED ROCK AND BUILDING STONE

This is the most varied class of deposits in terms of their origin and occurrence. Crushed rock is worked to provide hard rock aggregates for concrete and base material for road building as well as other applications. They are sourced from a variety of igneous, metamorphic and sedimentary rocks, but the main requirements are hardness, resistance to abrasion and availability in quantity in the right locations. Building stones are worked from rocks of many different types and ages. They must possess the ability to be split or sawn into the required shapes and to possess the right colour, appearance and durability. The main rock types used for these applications are limestone, sandstone and igneous and metamorphic rock.

3.2.1 Limestone

Mode of occurrence

Limestone is a sedimentary rock composed mainly of calcium carbonate CaCO₃. Where the rock comprises between 10 and 50 % of the mineral dolomite (CaMg(CO₃)₂), it is known as dolomite or dolomitic limestone (formerly magnesian limestone). Dolomite is found in some areas of Carboniferous limestone and also in the Permian Magnesian Limestone of the East Midlands and north-east England. Limestones suitable for crushed rock occur in the north and west of England and Wales, as far south as the Peak District and the Mendips. They mainly occur in rocks of Silurian and Lower Carboniferous age as thick beds (up to 25 m) of nearly pure CaCO₃ with minor amounts of clays, cherts and volcanic ash. Their lateral extent can be many kilometres. Generally, the worked beds will be semi-horizontal, though some inclined beds were mined in the West Midlands. Limestones of Carboniferous age are the most important source of crushed rock aggregate in England despite their relatively limited distribution. They typically form thick, uniform deposits of relatively hard limestone and dolomite ideally suited to the production of crushed rock aggregates. They yield relatively strong, low porosity aggregates suitable for a wide range of construction uses, except road surfacing because of their poor skid resistance. Carboniferous limestones are also an important source of calcium carbonate for a range of industrial applications, for use as agricultural lime and for cement manufacture. There are approximately 13386 closed limestone and dolomite quarries (Figure 4).

Character and amount of waste

Limestone quarries produce very variable amounts of waste, depending on the local topography and geology. There may be significant quantities of overburden to be moved. Much of this will be used for restoration of the quarry on completion, depending on the requirements of the rehabilitation plan in the mineral permission. Within the limestone body there may be significant amounts of chert (very fine grained SiO₂), and/or clay. These will be disposed of as waste, which may be classified as inert.

Much of the waste produced in sub-surface mines for building stones is stowed underground and never reaches the surface. Surface quarries for building stone may generate significant amounts of waste from defective blocks and trimmed pieces from production blocks. However, it will be roughly the same material as the saleable product and therefore inert.

Classification

The waste from the vast majority of limestone quarries can be classified as inert. The EWC 2000 codes are 01 04 10 - Dusty and powdery wastes other than those mentioned in 01 04 07, and 01 04 13 - Waste from stone cutting and sawing other than those mentioned in 01 04 07.

3.2.2 Igneous and metamorphic rock

Mode of occurrence

A wide variety of different types of igneous rocks of various ages are quarried, principally as a source of aggregate. Resources are mainly located in the north and west of the country (Figure 4). Extrusive igneous rocks tend to be of more variable quality than intrusive bodies and production is mainly located on the latter. Intrusive igneous bodies are of very variable size, ranging from large granitic intrusions up to tens of kilometres in surface dimensions, to relatively small mafic intrusions, particularly dolerite sills. Metamorphic rocks, having generally been derived from sedimentary rocks, tend to occupy larger areas, within which there may be selected sections, which possess the right characteristics for a particular product. There are approximately 2700 closed igneous and metamorphic rock quarries (Figure 5).

Character and amount of waste

The overall amount and character of waste varies widely between quarries. The two main waste products are very large oversize blocks and very fine undersize particles. The actual properties and amounts of these depend on the products of the individual quarry.

Classification

The waste from all the workings is non-hazardous entries and likely to be inert, with codes 01 04 10 - Dusty and powdery wastes other than those mentioned in 01 04 07, and 01 04 08 -Waste gravel and crushed rocks other than those mentioned in 01 04 07. However, there are insufficient data regarding the mineralogy and interaction with the local environment to unequivocally state that no quarries contain any hazardous minerals or materials.

3.2.3 Sandstone

Mode of occurrence

A wide range of ages and types of sandstone have been quarried in England and Wales at nearly 25000 sites for use as aggregates and building stone (Figure 6). The main groups of rocks from which sandstone was extracted are:

- i. Carboniferous sandstones, especially the Pennant Measures of South Wales and the Millstone Grit and Coal Measure sandstones of the Pennines.
- ii. Permian sandstones in the north of England, especially the Vale of Eden.
- iii. Lower Palaeozoic greywackes in the north and west of England and Wales.

The sandstones occur in bedded, lenticular deposits with vertical dimensions ranging from metres to tens of metres, and lateral dimensions extending to several kilometres or more in all directions.

Character and amount of waste

Waste generally consists of overburden and oversize and undersize sandstone blocks and particles.

Classification

Waste from all sites is non-hazardous and is likely to be inert, classified with codes 01 04 10 - Dusty and powdery wastes other than those mentioned in 01 04 07, and 01 04 08 - Waste gravel and crushed rocks other than those mentioned in 01 04 07.

3.3 CHALK

Mode of occurrence

Chalk is as a relatively soft, very fine grained, white limestone consisting mainly of the debris of planktonic algae. The Cretaceous chalk occurs extensively in southern and eastern England and may be up to 450 m thick. The lowest part of the Chalk (Grey Chalk) is characterised by a higher clay content. The overlying White Chalk is of higher purity (93 – 98 % CaCO₃) and contains abundant flint (amorphous silica) nodules. There are approximately 4300 closed chalk quarries (Figure 4).

Character and amount of waste

The waste is mainly flint nodules, chalk fragments and clay.

Classification

The waste is classified as inert with codes 01 04 08-Waste gravel and crushed rocks other than those mentioned in 01 04 07, and 01 04 09-Waste sand and clay.

3.4 SILICA SAND

Mode of occurrence

Silica (industrial) sand occurs as disaggregated quartz-rich sand deposits and weakly cemented sandstones of various ages ranging from Carboniferous to the present. It is used in a variety of industrial processes, mainly glassmaking and foundry sand. Production of silica sand is around 4 million tonnes a year. Unlike construction sands, which are used for their physical properties alone, silica sands are valued for both their chemical and physical properties and it is on a combination of properties that their industrial applications are based. There are 367 closed silica sand and silica rock mines and quarries (Figure 3).

Character and amount of waste

Waste from silica sand mining operations consists of clay and silt and other unsaleable materials that are generally used for restoration purposes. The waste produced from acid leaching silica

sand for colourless glass manufacture is neutralised with lime to produce gypsum, which is disposed of in lagoons, along with silts and clays.

Classification

It can be classified as inert with the EWC 2002 entry as 01 04 12 - Tailings and other wastes from washing and cleaning of minerals other than those mentioned in 01 04 07 and 01 04 11. Sites that used acid leaching produced gypsum-rich waste, which is non-inert non-hazardous.

3.5 COMMON CLAY AND SHALE / FIRECLAY

Mode of occurrence

Clay and shale are bedded sedimentary rocks consisting mainly of fine particles of clay and other minerals. They occur in almost every geological period. However, the predominant formations used for clay and shale extraction are the Jurassic Oxford Clay, the Carboniferous Coal Measures and Etruria Formation and the Triassic Mercia Mudstone. They are mainly used to make fired products, such as bricks and tiles. Fireclays are non-marine, sedimentary mudstones that occur as seatearths, the fossil soils on which coal-forming vegetation once grew, and which underlie most coal seams. Fireclay resources are, therefore, mainly confined to coal-bearing strata. They are valued principally as a premium-quality brick clay. Fireclay beds are comparatively thin (normally <1 m) and production is now almost entirely confined to opencast coal sites. However, in the past fireclay was even extracted from underground mines. There are approximately 13000 closed clay and fireclay mines and pits (Figure 7).

Character and amount of waste

The thickness of overburden ranges from 1 m to exceptionally a few tens of metres. The waste consists of overburden, together with variable amounts of inferior quality clay and interbedded sand. Generally the ratio of useful clay to waste is high, so relatively little waste is produced. Only small quantities of fireclay are generally recovered from open-cast coal sites. Overburden is similar to that principally associated with coal extraction.

Classification

Waste products from these operations are likely to be mainly inert and falling into the EWC category 01 01 02.

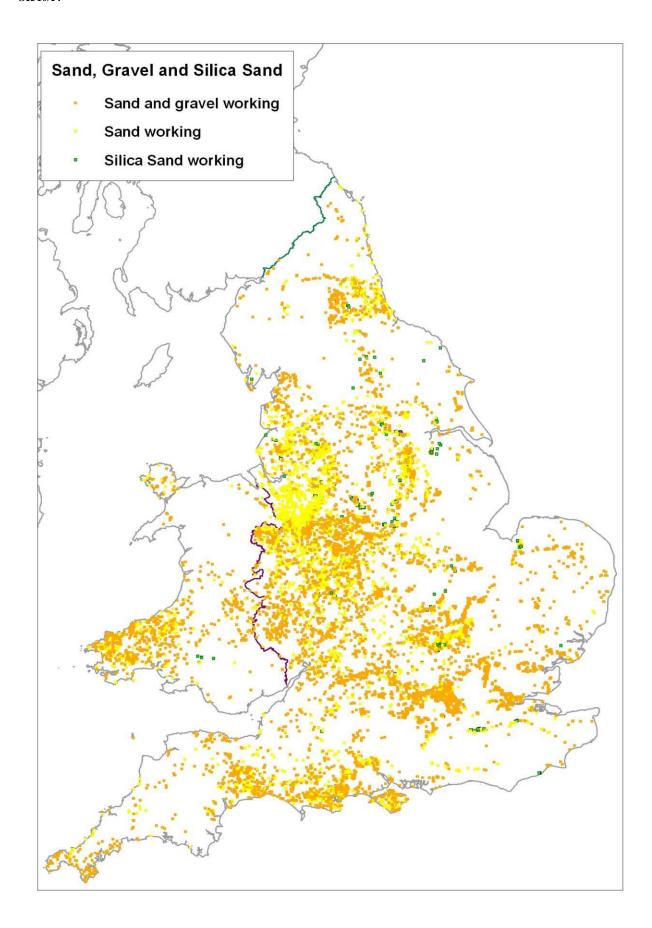
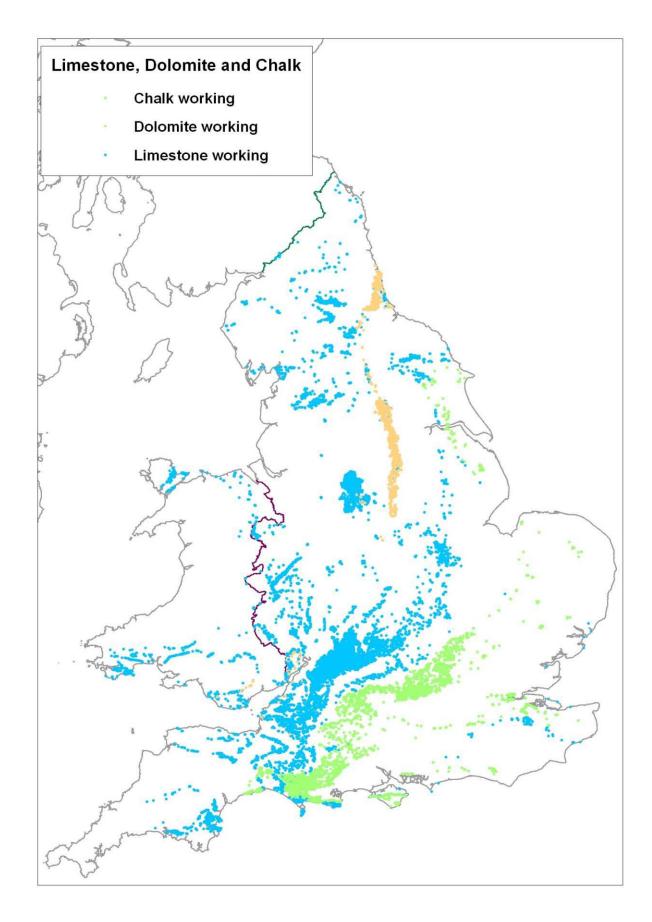


Figure 3 Closed sand and gravel (9084 sites), bedrock sand (3754 sites) and silica sand operations (367 sites).



 $Figure\ 4\ Closed\ limestone\ (11641\ sites),\ dolomite\ (1745\ sites)\ and\ chalk\ (4298\ sites)\ mines\ and\ quarries.$

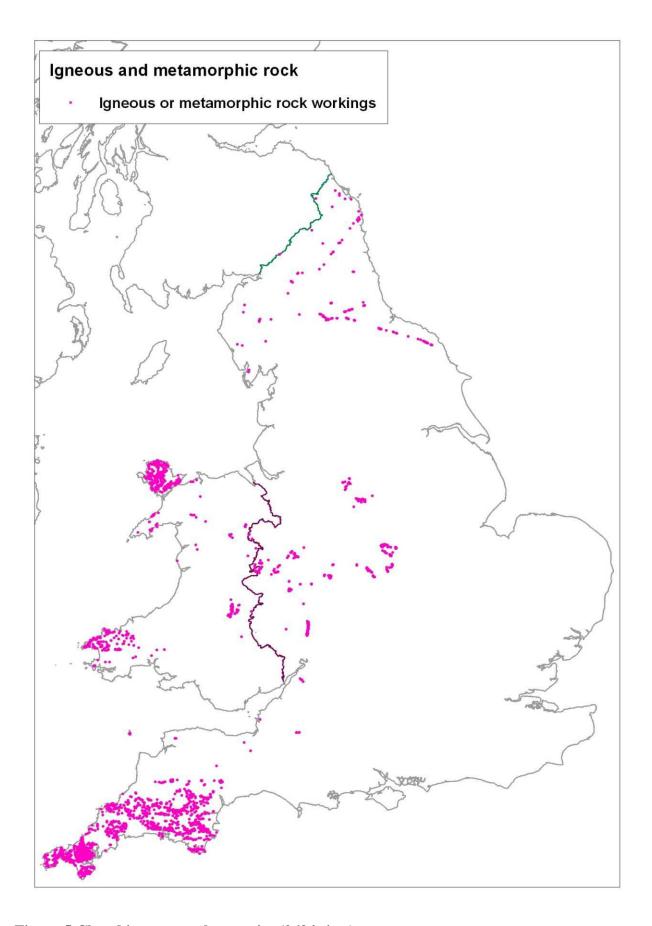


Figure 5 Closed igneous rock quarries (2694 sites).

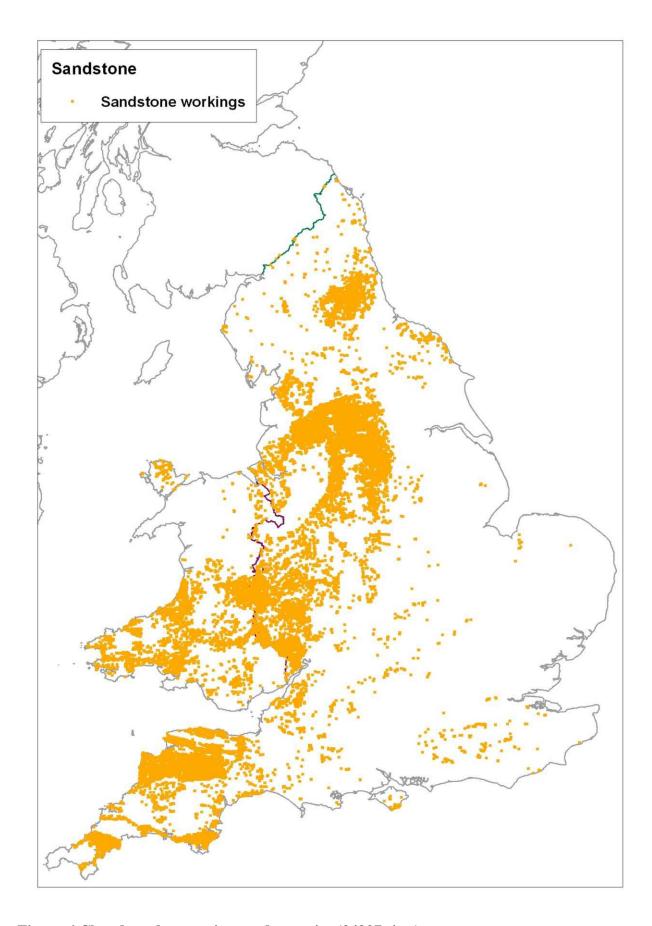


Figure 6 Closed sandstone mines and quarries (24927 sites).

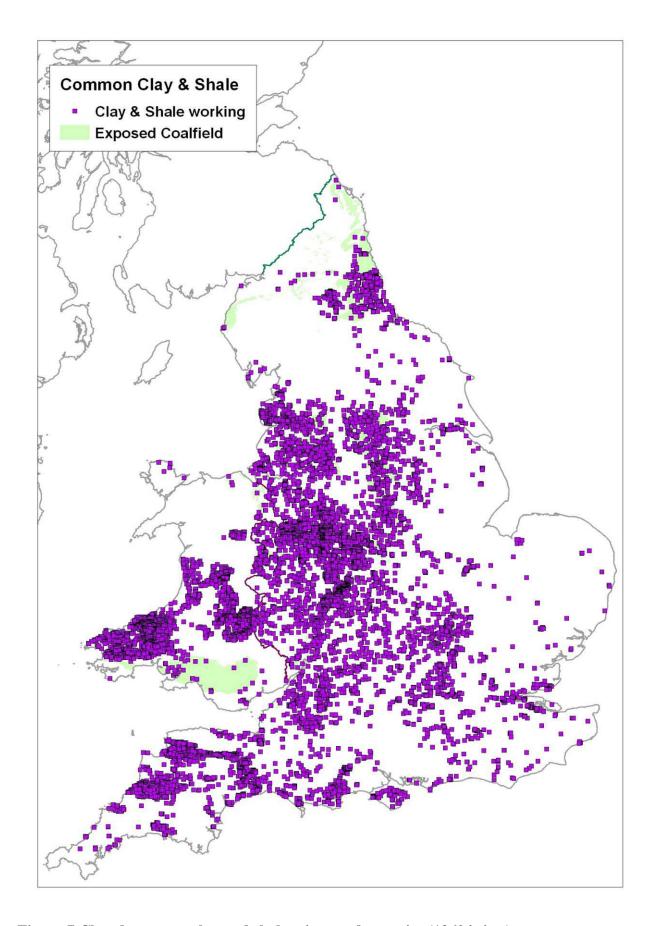


Figure 7 Closed common clay and shale mines and quarries (12604 sites).

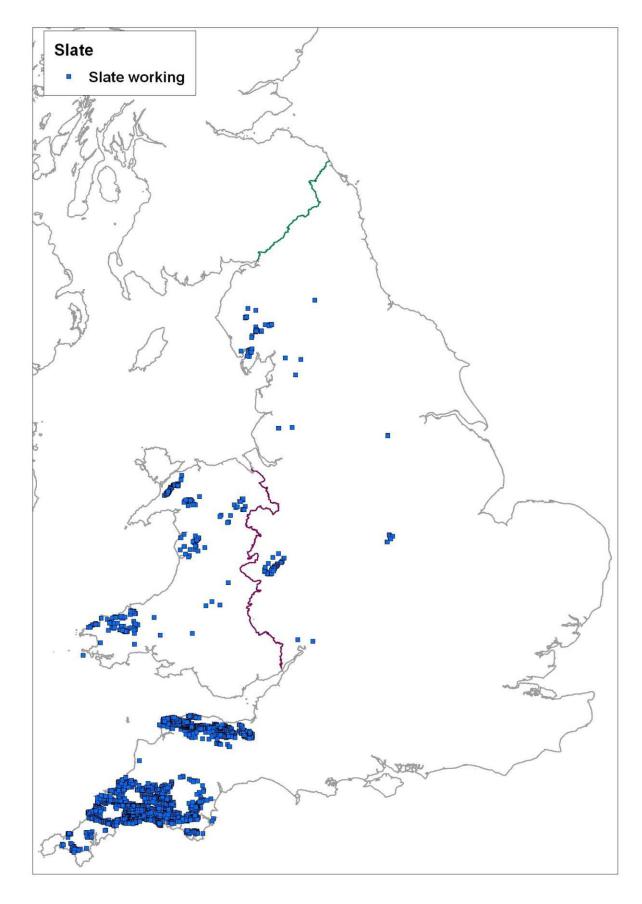


Figure 8 Closed slate mines and quarries (2863 sites).

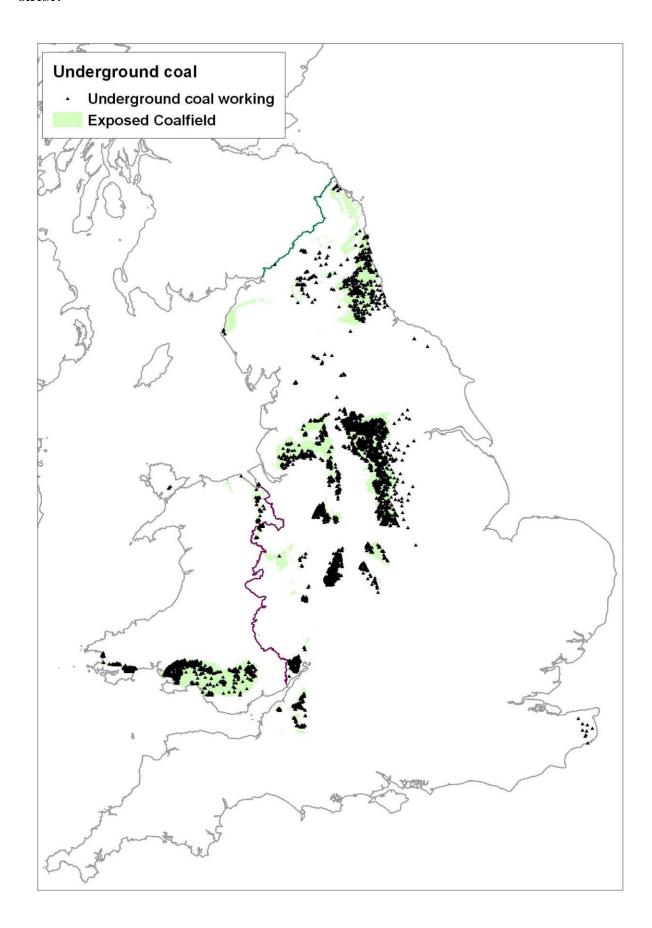


Figure 9 Closed deep coal mines (7626 sites).

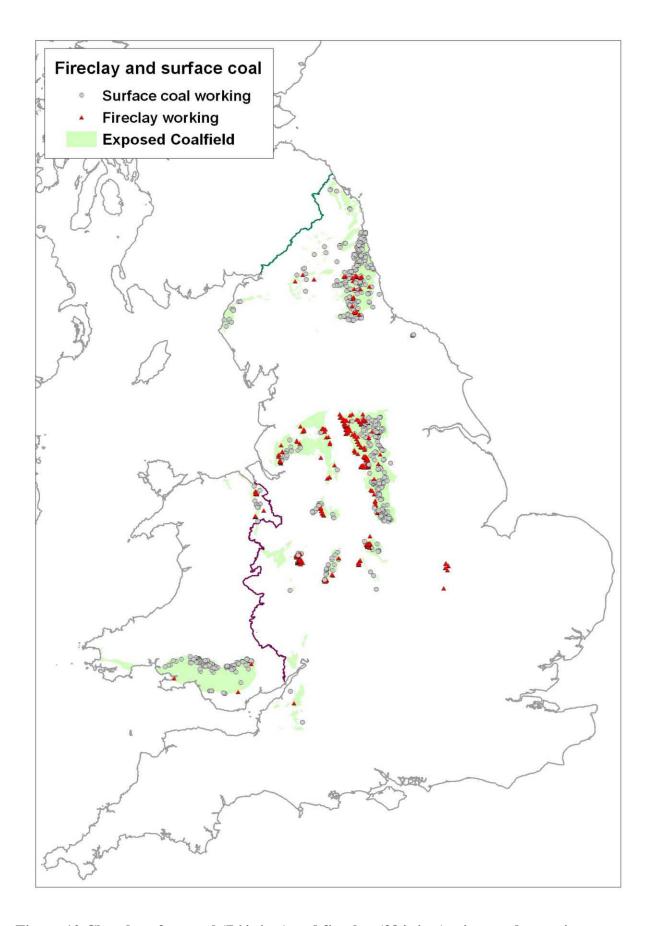


Figure 10 Closed surface coal (764 sites) and fireclay (384 sites) mines and quarries.

3.6 SLATE

Mode of occurrence

Slate is a very fine-grained sedimentary or volcanic rock, which has been altered by heat and pressure (metamorphism) to produce a slaty cleavage whereby it splits easily along a particular direction. It is used for roofing and, increasingly, slate powder is used as a filler and insulating material. Slates in England and Wales are restricted to formations of Lower Palaeozoic age or older. Cambrian and Ordovician rocks are the most important sources. Slates occur as beds of fissile rock, which are generally in the range of 1 to 10 m thick and are usually steeply inclined. The main areas for slate mining are North Wales and the Lake District. There are approximately 2900 closed slate mines and quarries (Figure 8).

Character and amount of waste

The slate industry has always produced very large quantities of waste. Estimates range up to 20 tonnes of waste per tonne of finished slate. This has been reduced with increased mechanisation; using chain saws instead of blasting in one North Wales quarry reduced the waste factor from 87:1 to 12:1 (Crockett, 1975). One estimate of the amount of waste in the active and former areas of production in Cornwall, the Lake District, North and South Wales is 500 million tonnes (Richards and others., 1995). Currently over 1 million tonnes of slate are quarried in North Wales each year. The waste tends to be of all sizes, from blocks weighing several tonnes to dust from the slate cutting processes. Slate waste tips were often deposited on steep slopes, though they are generally stable unless disturbed having settled over many decades. New waste tips are engineered in compliance with The Mines and Quarries (Tips) Regulations, 1971 and subsequent Quarries Regulations 1999. The waste is free draining and the tips are largely unaffected by the passage of water. The composition of the waste is essentially the same as the slate produced which is valued for its durability and resistance to weathering. Small quantities, up to 1-2% but usually much lower, of pyrite crystals may occur locally. These are mainly locked within the rock fragments, but crystals exposed to the atmosphere will produce small amounts of acid drainage from the waste pile and iron ochre staining. The main problems with slate tips relate to their visual impact.

Classification

It is inert and classified mainly as 01 01 02 - Wastes from mineral non-metalliferous excavation and, also, as 01 04 13 - Waste from stone cutting and sawing other than those mentioned in 01 04 07.

3.7 COAL

Coal occurs in layers (seams) in sequences of sedimentary rocks. Individual coal seams in England and Wales may be up to 3.5 m thick, although exceptionally thicker seams may also occur. All onshore coal resources in England and Wales occur in strata of Carboniferous age (300 - 330 million years old). These rocks have been subjected to folding and faulting and now occur at varying depths below the surface. Most of the coal in England and Wales is bituminous coal and is used chiefly in electricity generation. A small amount of anthracite, which has a higher calorific value and a lower volatile content, is mined in South Wales. Coal is worked either from surface pits (opencast) or deep mines. Coal mines can produce large amounts of waste rock. They may also produce large amounts of drainage water, which may contain dissolved elements, including metals. These metals may be deposited as the mine water reaches the surface or may be transported over considerable distances depending on circumstances.

Coal has been produced in Britain since Roman times. The industry's growth accelerated from the late eighteenth century with the Industrial Revolution, reaching a peak annual production of 293 Mt in 1913. It has then declined steadily to 100 Mt in 1984 before a dramatic decline to the current levels of 7 Mt from underground mines and 8 Mt from opencast pits. The coal waste problem was relatively small when all coal was mined by hand and as little waste as possible was raised for tipping. Even so, with so many collieries in the last century (over 3700 individual pits in 1881 (Hull, 1881)), small tips were created round every mine. The waste was relatively coarse and therefore free draining. As the mines expanded their production overhead bucket conveyors were used to carry spoil to the tip, creating conical mounds. These older tips often contained a significant amount of coal, up to 10 % in some cases, and due to the method of tipping, were not consolidated which allowed air to circulate within them. Oxidising pyrite raised the temperature sufficiently for coal to start burning. This caused a common problem of tips igniting spontaneously to form burnt or partially burnt spoil. This changed the physical and chemical characteristics of the tip material, often fusing large amounts into brick-like substance and releasing fumes. In 1967, out of over 2000 colliery spoil tips owned by the then National Coal Board (NCB), over 50 % were burning and 15 % were burnt out. This was a generalised estimate with no specific locations. There are approximately 7626 closed mines and 764 closed opencast sites in BRITPITS (Figure 9 and Figure 10).

In 1930 about 7 Mt of waste or 'spoil' was produced with an annual coal production of 200 Mt (Thomson and Rodin, 1972). In 1970 about 60 Mt of waste was produced with an annual coal production of 140 Mt, illustrating the problem of increased waste production with increased mechanisation which started about 1950. Figure 11 below shows the historic production of coal in the UK and the rise in waste production from the 1920s. In 1981/82 the proportion of waste to coal ranged from 29 % to 79 % with an average of 55 % (DOE. 1988). This machine-won waste was usually finer than the hand-won waste and with the development of coal separation plants increased amounts of very fine waste were produced. This was disposed of in settling ponds or lagoons. In 1979-80 the amounts of waste from different mining activities was:

- -Coal face (roof, seam and floor) 35 Mt (52 %)
- -Face rippings 10 Mt (15 %)
- -Development driving 10 Mt (15 %)
- -Roadway repairs 6 Mt (9 %)
- -Ad hoc waste production 6 Mt (9 %) (Blelloch, 1983).

Of the total of 67 Mt about 11 Mt or about 16 % was left underground or incorporated in the saleable coal. About 80 % of the waste was defined as coarse discard with a particle size between 0.5 mm and 150 mm. The remainder was classed as fine discard with a particle size of less than 0.5 mm and much of this is less than 10 µm in size. Fine discards are generally produced during flotation of the coal in the coal preparation plant and are usually pumped to tailings lagoons (Richards, Morehead and Laing. 1996). The waste may also contain demolition rubble, steel materials, wood and other waste, including boiler ash, especially in the older tips. It may also be mixed with blast furnace slag if the colliery was adjacent to an iron or steel works. By 1998 the waste production had been reduced to about 12 Mt / yr. In 1992 1 Mt of coal was won by reworking old waste tips (Richards, Moorehead and Laing, 1996).

Nearly all coal mine waste is disposed of by surface tipping. A study in 1961 estimated that there were 2000 colliery tips in England and Wales alone, covering 12150 hectares (James et al., 1961). However, only 560 tips were known in 1990 as many had been reclaimed or revegetated. In some coastal areas, especially in County Durham in north-eastern England, most waste was disposed of by tipping in the sea with over 5 Mt being disposed of in this way in 1972 (Gutt et al., 1974). These mines have now closed and the tipping ceased.

There was little or no control over the sites of colliery waste tips and tipping activities. For example, the Town and Country Planning General Development Order in 1950 allowed tipping on sites used on or before July 1 1948 to continue without further permission and without restrictions on the height or area of the tip. This applied to the majority of pits then in operation

and in 1971 only 35 % of waste from deep mined operations was deposited on tips subject to planning control. However, following the Aberfan disaster of 1966 the Mines and Quarries (Tips) Act 1969 was passed to strictly control and monitor the siting, design, operation and aftercare of all mine waste tips. Further regulations and internal NCB guidelines have subsequently been introduced.

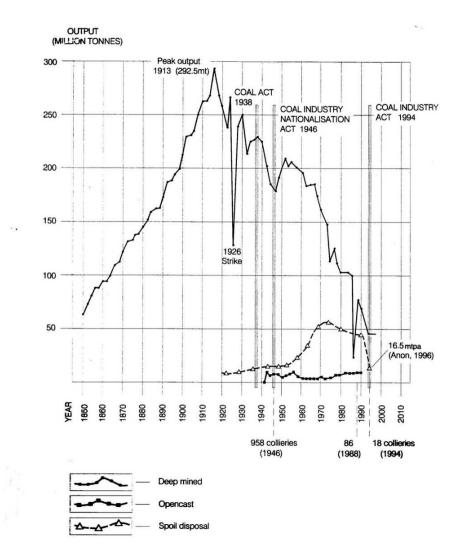


Figure 11 Coal and waste output. Richards, Morehead and Laing (1996).

Table 7 shows that approximately 22000 Ha were classified as colliery spoil waste in 1966 in the whole of Great Britain. Since official statistics on waste reclamation have been compiled, approximately 8768 Ha of areas affected by deep mined coal operations, which may include surface plant areas as well as waste tips, had been reclaimed by 1988 and a further 2280 Ha remained derelict. A further study in 1996 for England and Wales (Richards, Morehead and Laing. 1996) estimated that 14 520 Ha of colliery waste tips had been reclaimed (by 1994 in England and 1988 in Wales) and a further 6557 Ha require reclamation as waste disposal ends due to planned pit closures. It is not clear if this estimate includes waste tips at pits which were working at the time of the survey, many of have subsequently closed. The rate of reclamation from 1988 to 1993 was about 260 Ha per year (Wickens and others, 1995). Thus the total area remaining in England and Wales may be as little as 2000 Ha. The locations of current managed and mapped tips can be obtained from the records of the Coal Authority. However, there appears to be relatively little documentation of older tips (pre-Aberfan). For example, an enquiry some years ago to the Coal Authority for current and historical coal mines and tips around Leeds produced a total of around 2500 'mine entries' and 10 tips with maps of their locations.

3.7.1 Deep-mined Coal

Mode of occurrence

Worked coal seams in England and Wales are mainly restricted to beds of the Carboniferous Lower and Middle Coal Measures. These occur in many areas of England and Wales but active deep coal mines are restricted to Yorkshire, Nottinghamshire, Warwickshire and South Wales, with a few very small operations elsewhere. In deep mines, coal is extracted from strata 200 m below the surface to depths of up to 1200 m. Workable coal seams generally exceed 1 m in thickness.

Character and amount of waste

The amount of waste is highly dependent on the amount of non-coal mineral (mainly shale and sandstone) within the coal. This can vary from negligible quantities up to 50 % or more if the coal is split into thinner beds with bands of shale between. Estimates generally use a ratio of 1 to 2 for waste to saleable coal. The waste mainly consists of clay, shale and sandstone, rocks composed of mostly inert silicate minerals. However, there is usually up to 2 or 3 % pyrite (FeS₂) within the coal and some of this will occur in the waste. Modern practice is for the waste to be tipped and compacted in engineered, benched mounds, which are restored to productive use as soon as possible. The problem of acid mine drainage, resulting from the oxidation of pyrite within the tip, remains a possibility.

Classification

Due to the ubiquitous presence of pyrite any coal waste tips may generate acid drainage, though the amount will vary with local conditions and the original concentration of pyrite within the tip. The waste is classified according to the EWC 2002 codes as 01 04 07* - Waste containing dangerous substances from physical and chemical processing of non metalliferous minerals with a hazardous mirror entry. However, the risk posed by individual tips cannot be determined due to the lack of detailed information on the chemistry and the interaction of the tips with the environment. Waste tips can also cause physical problems as evidenced by the catastrophic failure of the Aberfan tip in South Wales, which killed 144 people in 1966.

Stringent regulations (The Mines and Quarries (Tips) Regulations, 1971 and subsequent Quarries Regulations 1999) have since helped to make sure that tips are properly designed, constructed and maintained (Richards et al., 1996). Older abandoned tips should also have been inspected and remediated (from the point of view of stability) since the Aberfan disaster. Many tips have been reused as brownfield sites for other developments, such as industrial estates. In these cases the waste has been levelled and covered with topsoil before buildings are erected. The waste is considered to be potentially hazardous although current requirements for monitoring and management should ensure that the environment outside the waste facility is fully protected against the egress of any harmful leachates.

3.7.2 Opencast coal

Mode of occurrence

Opencast coal is worked in areas of exposed Coal Measures in the same general areas as deepmined coal.

Character and amount of waste

Generally the coal is cleaner and less pyritic than deep-mined coal. Almost all the waste produced during the overburden stripping and mining operations is used to restore the site to its former condition as the aggregate thickness of coal seams taken is generally less than 5 % of the

total thickness of the material quarried. The coal may be taken to a preparation plant for the removal of any in-seam shale, but is normally sold as dug because it is of high quality. Younger and Sapsford (2004) prepared a document for SEPA (Scottish Environment Protection Agency) that provides a framework for assessing the risk of release, by weathering, of List 1 and List II substances (European Directive on Groundwater [80/68/EEC]) from soils and rocks disturbed by opencast coal mining in Scotland. The document identified that iron, manganese, aluminium and sulphate are present in leachates derived from many opencast coal sites in Scotland; zinc, nickel, ammonium and occasionally copper occur less commonly. Younger and Sapsford (2004) describe the way in which water infiltrating waste may be in insufficient quantities to remove oxidation products, thereby allowing the accumulation of hydroxysulphate evaporate minerals (efflorescent salts) in specific compartments of the waste. Younger and Sapsford (2004) note that although it has been reported that the release of mercury and cadmium might be anticipated, there is an absence of mineral sources for mercury and there is only one recorded occurrence of greenockite (CdS) in the Scottish Coal Measures rocks. Furthermore, no coal mine-waste related drainage with mercury and cadmium concentrations in excess of the detection limit has been encountered by these authous. It should also be noted that Younger and Sapsford (2004) emphasise the influence of the geological setting on the occurrence of sulphide minerals, with higher concentrations of the minerals being associated with the marine bands, thus requiring sitespecific conceptual modelling of the geochemistry.

Consideration has been given to the potential for the self-combustion process, which has occurred historically as a consequence of the exothermic reaction that results from oxidation of pyrite. It has been concluded that the fine-grained nature of the raisings from current coal processing activities and the engineering of the waste piles prevents the oxidation process.

Classification

The continuous nature of the mining and restoration means that there is relatively little surface expression of waste. However, the gross disturbance resulting from quarrying at such sites may significantly alter the pathways by which groundwater may be exposed to leached pollutants, should they be present. The waste from coal preparation plants, which is placed in lagoons, as with the deep-mined coal, is potentially hazardous as it may contain small amounts of pyrite and is considered to be hazardous (classified with code 01 04 07* - Waste containing dangerous substances from physical and chemical processing of non metalliferous minerals) although current requirements for monitoring and management should ensure that the environment outside the waste facility is fully protected against the egress of any harmful leachates.

3.8 PEAT

Mode of occurrence

Peat occurs in many parts of the UK as post-glacial, unconsolidated deposits of compressed plant remains in a water-saturated environment. Lowland Raised Bogs, which are the main source of peat, occur in flat-lying areas, mainly on low plains or broad valley floors. There are 54 closed peat workings in the BRITPITS database (Figure 12).

Character and amount of waste

Peat is one of the most absorptive natural substances and can concentrate many elements, including potentially toxic trace elements under particular circumstances. However, the peat currently worked on an industrial scale in England and Wales is considered very unlikely to have acquired any such elements due to their location away from natural sources of these elements. Very little waste is generally produced during peat extraction and processing operations and consists of clay and fine sand.

Classification

Peat is specifically excluded from some provisions (7.8, 11.1, 11.3, 12, 13.6, 14 and 16) of the Mine Waste Directive (Article 2 (3)). The waste from peat operations, provided it consists of clay and sand as noted above is inert. The classification is code 01 01 02 - Wastes from mineral non-metalliferous excavation.

3.9 INDUSTRIAL CLAYS

3.9.1 China Clay

Mode of occurrence

China clay, or kaolin, is a commercial clay composed mainly of the hydrated aluminosilicate clay mineral kaolinite. China clay in England and Wales is restricted to the exposed granite areas of Cornwall and Devon where they have been hydrothermally altered to change some of the constituent feldspar into kaolinite. The deposits are irregular in form, but are commonly funnelshaped and can extend to over 300 m in depth with lateral dimensions of up to 2 km. The main area of working is the western half of the St Austell Granite, but important deposits also occur on the south-western edge of the Dartmoor Granite (Figure 12).

Character and amount of waste

The extraction and processing of china clay involves the production of very large quantities of waste. For each tonne of china clay recovered typically 9 tonnes of waste, comprising 4 tonnes of granular waste (china clay sand), 2.5 tonnes of rock waste (stent), 1.5 tonnes of overburden and 1 tonne of micaceous residues, are also produced (Highley, 1984). Total industry waste arisings are about 10 million tonnes a year. The total industry stockpile has been estimated at over 600 million tonnes.

The waste produced is of two main types: coarse material comprising sand (mainly quartz) and rock waste, which if not sold is disposed of in large tips; and a fine slurry waste called mica residue which is disposed of in large lagoons and abandoned china clay pits. The micaceous residue consists mainly of mica, but with some quartz, feldspar and coarse kaolinite. As a result of the overlap in particle size between kaolinite and mica there is some loss of the coarser kaolinite particles into the oversize fraction. This oversize material is recovered by ultrafine flotation allowing the coarse kaolinite particles formerly rejected to be recovered. This is followed by low-solids sand grinding to break down the kaolinite aggregates to maximise recovery. Some mica residues are also being reworked. Small amounts of china stone, which is essentially unkaolinised granite with low levels of iron, are produced for use as a flux in ceramic glazes and as a mild abrasive. Any waste produced is comparable to that produced in the china clay operations. There are 217 closed china clay sites (Figure 8)The waste tips have been extensively remodelled in recent years to reduce the heights of the conical tips that were formerly used and replace them with less visually intrusive shapes.

Classification

The china clay waste is considered to be inert and classified with a code $01\ 04\ 12$ - Tailings and other wastes from washing and cleaning of minerals other than those mentioned in $01\ 04\ 07$ and $01\ 04\ 11$.

3.9.2 Ball Clay

Mode of occurrence

Ball clay is a fine-grained, highly plastic sedimentary clay, which fires to a light or near-white colour. The clay mineral kaolinite is the key component, though mica and quartz are also important constituents. Ball clay in England and Wales occurs in the Wareham area of Dorset and the Bovey and Petrockstow basins in Devon (Figure 12 and Figure 13). There are 63 closed sites. It occurs as sedimentary layers of Tertiary age within a complex package of sands, silty clays and lignites. Ball clays are derived from deep tropical weathering profiles developed on a variety of rocks, including mudstones and sandstones. Intense chemical alteration resulted in the formation of kaolinite, which was subsequently eroded, transported and deposited. Some of the ball clays in the Bovey Basin were derived from the deep weathering and alteration of the nearby Dartmoor Granite. The Bovey Basin is the most important producing area and contains over 40 ball clay beds ranging between 1 and 6 m in thickness.

Character and amount of waste

The ratio of waste (overburden and interburden) is very variable from deposit to deposit, but is greatest in the Bovey Basin, which is the principal source of ball clay. The waste consists of silt, sand, lignite and clays that have too high a carbon and iron content for economic use. This is unlikely to cause any significant problems.

Classification

The waste is classified as inert with a code 01 04 09 - Waste sand and clays.

3.10 GYPSUM AND ANHYDRITE

Mode of occurrence

Gypsum (CaSO4.2H2O) and anhydrite (CaSO4) are, respectively, the hydrated and anhydrous forms of calcium sulphate. The former is economically the most important. They occur as beds and nodular masses up to a few metres thick and are the products of the evaporation of seawater. The amount of natural gypsum extracted in England and Wales has declined appreciably in recent years due to the availability of substantial amounts of desulphogypsum derived from flue gas desulphurisation (FGD) plants at coal-fired power stations.

In England and Wales, gypsum and anhydrite normally occur in strata of Permo-Triassic and Jurassic age. The current production areas are Nottinghamshire, Leicestershire, Staffordshire, Cumbria and East Sussex (Figure 12). There are 109 closed gypsum sites and 7 closed anhydrite mines. Gypsum is formed by the hydration of anhydrite at or near the surface, but passes into anhydrite generally at depths greater than 40-50 m, although this depends on local conditions. Anhydrite is, therefore, very much more extensive at depth than gypsum.

Character and amount of waste

Opencast working produces temporary waste that consists mainly of the surface soil and beds above and between the gypsum seams. There is only one small opencast working in England and Wales. Underground mining produces little or no waste, as all the operations are in-seam.

Classification

The little waste produced is non hazardous but if gypsum is present is classed as non-inert with the code 01 01 02- Wastes from mineral non-metalliferous excavation.

3.11 SALT

Mode of occurrence

Salt (sodium chloride, NaCl), occurs in nature in solid form as rock salt (halite), or in solution as brine. Rock salt occurs in beds, commonly associated with mudstone, ranging in thickness from a few centimetres up to several hundred metres. The purity of individual salt beds depends on the extent of interbedded mudstone. Natural brine is produced by the dissolution of salt-bearing strata by circulating groundwater. Brine may also be produced artificially by injecting water into salt beds and pumping out the resulting solution. In England and Wales salt occurs in beds of Permian and Triassic age and is produced in Cheshire, the North York Moors National Park and Northern Ireland (Figure 12). There are 49 closed salt sites.

Character and amount of waste

Mining of rock salt and subsequent processing, which involves crushing and treating the salt to keep it free-flowing, does not produce any waste. The brine produced by brine pumping requires purification before it can be used either as a chemical feedstock (for chlorine /caustic soda, and soda ash manufacture) or for the production of white salt by an evaporation process. The purification process involves precipitating out calcium sulphate, magnesium hydroxide and calcium carbonate. These insoluble wastes are disposed of into worked out salt cavities. The waste is subject to the provisions of the Landfill Directive, and the landfill tax - at the lower rate of £2/t applying to inactive or inert waste. Total production of these wastes is estimated to be of the order of 60 - 100000 tonnes per year. The underground rock operations produce no waste at the mine site.

${\it Classification}$

The waste is classified as non-hazardous non-inert with the entry 01 04 11 - Wastes from potash and rock salt processing other than those mentioned in 01 04 07.

3.12 POTASH

There are no abandoned potash mines in England and Wales. The only site of potash extraction in England and Wales is the operating Boulby Mine in the North York Moors National Park.

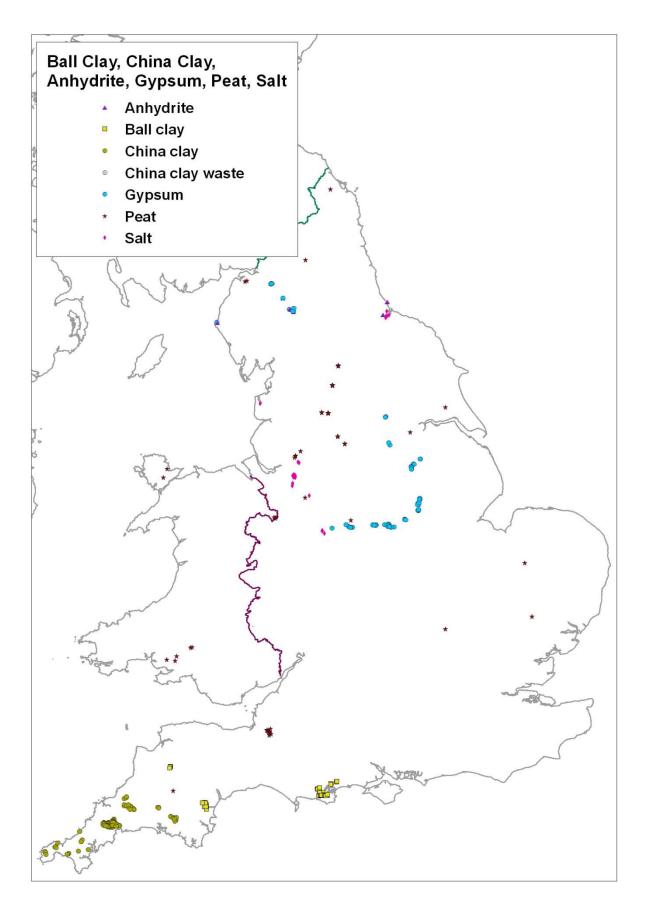


Figure 12 Closed anhydrite, ball clay, china clay, gypsum, peat and salt mines and quarries.

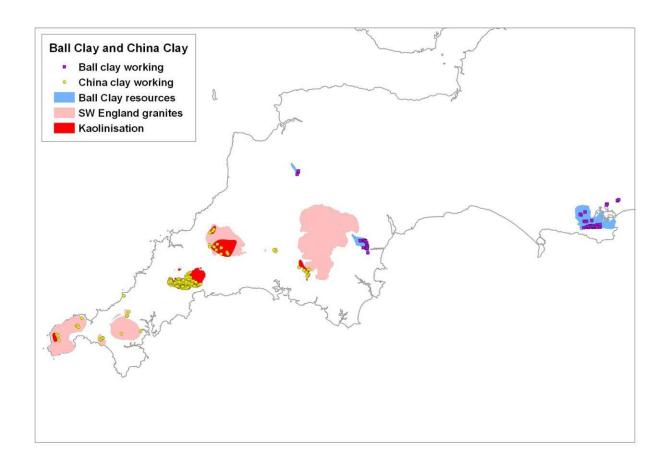


Figure 13 Closed china clay and ball clay mines and quarries.

4 Metalliferous mine waste facilities

4.1 INTRODUCTION

Britain has a legacy of metalliferous mining going back to pre-Roman times and the mining and processing of metal ores has inevitably caused some effects on the environment. The main period of production was from the first part of the 18th century to the end of the 19th century, associated with the Industial Revolution. There has been very little metal mining in Britain, with the exception of tin and copper in Cornwall and iron ore in Cumbria, Glamorgan and the East Midlands since the late 19th century. There are tens or possibly hundreds of thousands of abandoned metal mines in England and Wales. However, the scale of mining that was formerly carried on was vastly different to today's highly mechanised and productive mines elsewhere in the world. Many of the old mines were very poorly capitalised and operated on a hand to mouth basis with frequent periods of inactivity. Outputs were often no more than a few tonnes per year. Local laws and customs meant that in the Southern Pennine Orefield of Derbyshire, for example, mine titles were measured in 'meers' of 28 to 32 yards with at least one shaft in every meer along a vein. Each shaft might be worked by a different partnership and any vein might have a number of differently named mines along it, worked over a period of several hundred years. Mining was undertaken by hand, with very little machinery, apart from simple mechanical pumps, until the latter half of the 19th century.

Even with very simple equipment some substantial metal mine operations were carried out. In Anglesey the Parys and Mona mines probebly mined over 3 million tonnes of rock to produce around 130000 tonnes of copper metal. The Ecton copper mines of Staffordshire, that were worked out by about 1880, probably mined over 100000 tonnes of rock to produce 15000 tonnes of copper. Recording of the output was very sporadic and unsystemmatic until the middle of the 19th century when Robert Hunt began to compile his annual Mineral Statistics of the United Kingdom of Great Britain and Ireland. Similarly deposition of abandoned mine plans was only made mandatory in 1872 with no requirement for any common standard of presentation.

Modern mining categorises material as 'ore' and 'waste' with separate treatment for the two types of material. Underground historic mining was largely carried on literally in the dark, with limited understanding of the ore bodies being worked. All the material mined had to be manhandled several times as it was hauled to surface and so there was a strong incentive to mine as little as possible while still acheiving a profitable output. Definite waste material, from the driving of non-mineral tunnels and other access developments, was commonly stacked underground in any convenient empty space. These spaces grew as the mine expanded. 'Ore' was brought to surface in man-handleable lumps that were then hand picked and hammered to extract the profitable minerals. The rejected rock was dumped in any nearby convenient place. No plans were kept of the waste unless it impinged on some other activity of the mine and had to removed.

The character of waste has changed with evolving technologies. The first waste from a mine may be relatively large pieces of unmineralised rock from the development of a shaft or adit. Initially, hand-worked ore would be hand cobbed to remove the valuable minerals and so again the pieces of reject 'waste' would be relatively large. The resulting waste pile would be free-draining and with a small surface area. If output increased mechanical crushing, and later grinding machinery would be installed. This would give rise to a larger amount of smaller particles of waste with a larger surface area and more likely to retain water and oxidise any sulphides, such as pyrite.

Mine 'waste' was of no interest, was not recorded and was generally disposed of in as cheap and simple a method as possible, commonly by dumping it in a convenient river. Many tips were used as local quarries with 'stone' being carried away for a variety of purposes. The 'mundic' problem of Cornwall arose from the common practice from the early 1900s of using mine waste

as aggregate in concrete for buildings. Much of the waste contained pyrite that oxidised in the presence of water and air, causing the concrete to degrade and fail. The arsenical tips of the Devon Great Consols mine near Gunnislake in Cornwall found a ready local market as path gravel as it was a natural weedkiller. Much of the waste material from the Ecton copper mine in Staffordshire was used as basecourse for local roads and as ballast for the Leek and Manifold Light Railway in the early 1900s. Thus mine 'waste' has historically been unrecorded and ignored, other than when it caused a problem due to pollution or stability or could be profitably used for some other purpose.

Today there is still no national inventory of waste products and there was no national understanding of possible environmental impacts until very recently, except in certain local, very extreme examples. There have been numerous surveys of 'derelict land' that may include mine waste and the British Geological Survey routinely mapped mine waste under a general title of 'made ground' that included various types of material, not just mine waste.

4.1.1 Metalliferous mining areas in Britain and main characteristics of mineral deposits

At the present time there are no metalliferous mines active in England and Wales; though small amounts of lead and zinc are recovered as by-products of fluorspar and baryte mining in Derbyshire. However, metalliferous mining was carried out extensively in South-West England (Alderton, 1993), the Northern and Southern Pennine Orefields (Ixer and Vaughan, 1993), the Mendips (Green, 1958), North Wales (Earp, 1958), Central Wales (Jones, 1922) and the Lake District (Firman, 1978). Mining for ironstone was carried out in many areas, especially Cumbria, North Yorkshire, South Wales and the East Midlands (Slater and Highley, 1980). The principal areas of metalliferous mineralisation and former mining are shown in Figure 14 and the abandoned mines are shown in Figure 15.

The main environmental hazards deriving from mines and mine tailings are: discharge of acid mine drainage to surface and groundwater, and the contamination of soils through associated industrial activity. Discharges can contain very high concentrations of potentially harmful elements, such as lead, arsenic, mercury, cadmium, copper and zinc derived from sulphide ores and associated gangue minerals and this concentration of contaminants in soils can pose a serious health risk. Abandoned mines, tailings piles and associated, untreated, acid mine drainage constitute an important source of contamination to the biosphere. Wastes are a possible threat to the quality of life of local inhabitants and possibly affect their health, and can inhibit development of affected areas (brown field sites).

The environmental signatures of mine waste associated with different metalliferous mineral deposits are highly variable. Nevertheless, some general observations can be drawn. The pyrite contents of ore and the carbonate contents of ore / host rock principally determine the pH and contaminant content of mine waters, seepage from mine waste piles and tailings. Mine waste that contains abundant pyrite and base metal sulphide minerals relative to carbonate minerals, also surrounded by rocks with low acid-buffering capacity, have enhanced potential for associated acidic mine drainage water containing elevated abundances of dissolved harmful and toxic elements. On the other hand, water draining pyrite and carbonate-rich mine waste associated to ore hosted by carbonate-bearing rocks tends to be near-neutral; this mine drainage type can, however, be enriched in zinc and manganese above water quality thresholds, depending on the trace element content of the ore and derived waste. These contaminants remain mobile, either in solution or as colloids, for long distance downstream of the mine sites.

The various types of mineral deposits worked in Britain may be broadly classified in terms of the currently accepted 'Mineral Deposit Types' that have been developed in the past 30 years (e.g. Cox and Singer, 1986). These mineral deposit models were largely developed for assisting with mineral exploration as guides to finding new deposits. They have been further developed into 'Geoenvironmental Models of Mineral Deposits' (Seal and Foley, 2002) as a natural extension to take account of the environmental effects of the working of mineral deposits.

A table of the generalised elements and minerals from the principal classes of metalliferous mineral deposits in England and Wales in the past is given in Table 8. Table 9 presents a summary estimate of metal production and associated waste production.

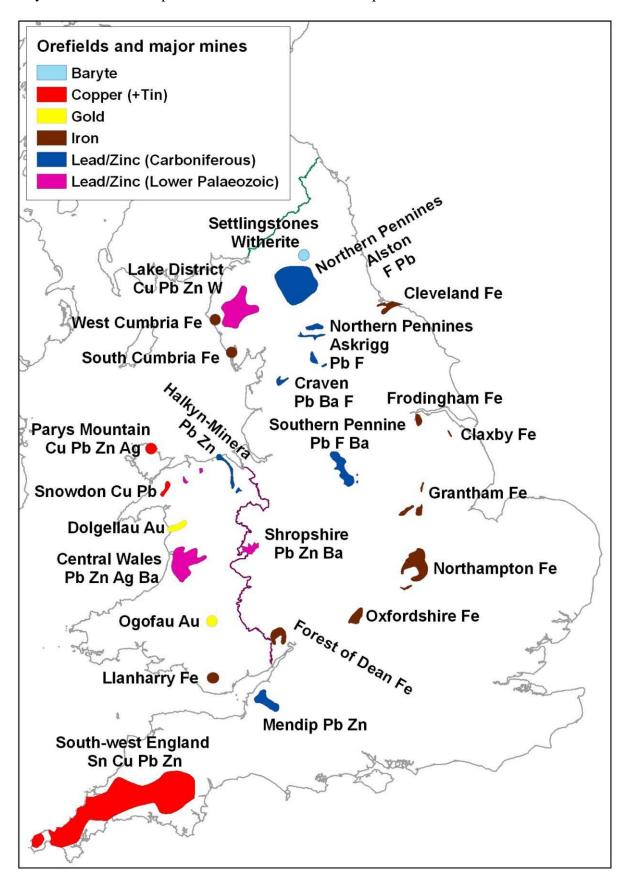


Figure 14 Metal mining fields in England and Wales.

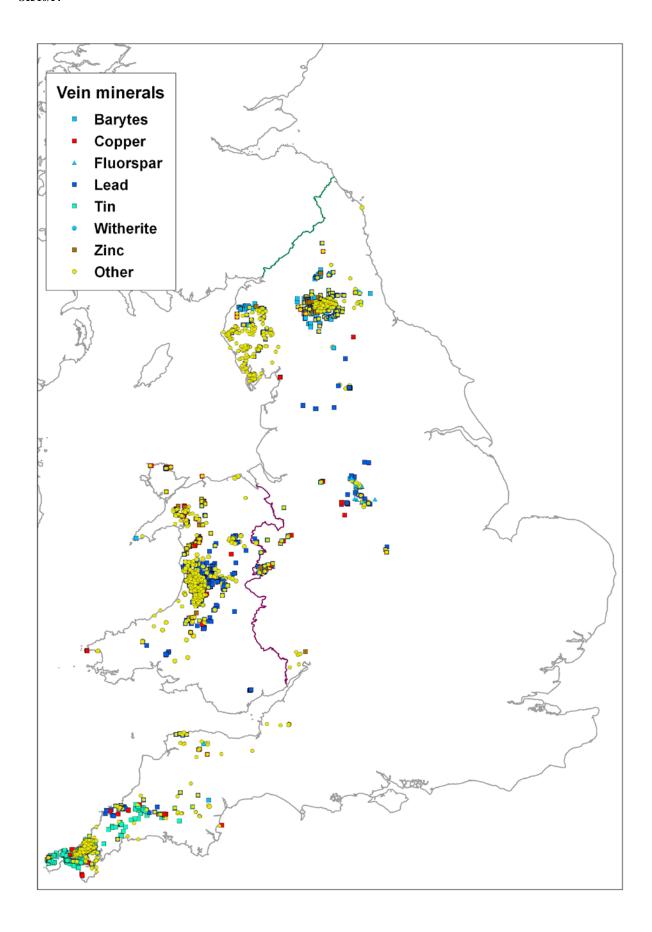


Figure 15 Abandoned metalliferous mines and quarries in England and Wales (Nos of sites from Table 6).

Table 8 Main metalliferous deposit types in England and Wales with associated elements and minerals

Deposit type adapted from Cox and Singer (1986)	Main area	Main Associated Elements	Trace to minor elements	Main minerals	Trace to minor minerals	Gangue minerals
Granite-associated tin-copper fissure vein mineralisation	Southwest England	Sn, Cu, As, Pb, Zn, W, Fe	Ag, Bi, F U, Ni	Cassiterite, Chalcopyrite, Arsenopyrite, Galena, Sphalerite, Wolframite, Pyrite	Fluorite, Uraninite	Quartz, Feldspar, Chlorite
Lower Palaeozoic shale-hosted crosscourse lead-zinc-baryte vein mineralisation	Southwest England	Pb, Zn, Ba, Fe	Ag, Cd, Sb	Galena, Sphalerite, Baryte, Pyrite	Bournonite, Jamesonite	Calcite, Quartz
Carbonate-hosted lead-zinc- baryte-fluorite vein and replacement mineralisation	Northern and Southern Pennines	Pb, Zn, F, Ba, Fe	Ag, Cd, Ni	Galena, Sphalerite, Baryte, Fluorite, Pyrite		Calcite, Quartz
Carbonate-hosted lead-zinc vein and replacement mineralisation	North Wales and Mendips	Pb, Zn	Ag, Cd	Galena, Sphalerite, Pyrite		Calcite
Lower Palaeozoic lead-zinc- baryte shale-hosted vein	Central Wales, North Wales, Lake District and Shropshire	Pb, Zn, Ba	Ag, Cd	Galena, Sphalerite, Baryte, Pyrite, Marcasite	Chalcopyrite,	Quartz, calcite
Lower Palaeozoic volcanic- associated copper-lead-zinc massive sulphide and vein mineralisation	Lake District, Anglesey and Snowdonia	Cu, Pb, Zn, Fe, (W)	Ag, Cd, Bi, As, Ba	Chalcopyrite, Galena, Sphalerite, Pyrite, Pyrrhotite, Magnetite	Arsenopyrite, Scheelite, Wolframite	Calcite
Carbonate-hosted Bilbao-type hematite vein and replacement mineralisation	Cumbria, South Wales and Forest of Dean	Fe	Ba, F	Hematite	Fluorite, Baryte	Dolomite, Calcite, Quartz
Jurassic and Cretaceous ironstones	Cleveland, East Midlands and Oxfordshire	Fe	As, P	Chamosite	Pyrite	Quartz Calcite
Coal Measures blackband and clayband ironstones	Staffordshire and South Yorkshire	Fe		Siderite, Clay		Clay

Table 9 Estimated metal and waste production of the main metal deposit types

Deposit type	Main areas	Estimated metal production Mt	Calculated estimated waste production Mt	Calculated estimated waste area Ha
Granite-associated Sn-Cu fissure vein mineralisation	Southwest England	2 Sn 2.5 Cu	50 – 75	1500 - 2000
Lower Palaeozoic shale- hosted crosscourse Pb-Zn vein mineralisation	Southwest England	0.3 Pb	5 - 8	100 - 160
Carbonate-hosted Pb-Zn-Ba-F vein mineralisation	Northern and Southern Pennines	7.5 Pb	10 - 50	200 - 1000
Carbonate-hosted Pb-Zn vein mineralisation	North Wales and Mendips	2.1 Pb	2 – 20	40 - 400
Lower Palaeozoic volcanic-associated Cu-Pb-Zn massive sulphide and vein mineralisation	Lake District, Anglesey and Snowdonia	0.2 Pb	1 – 2	20 - 40
Lower Palaeozoic shale- hosted vein mineralisation	Central Wales and Shropshire	0.7 Pb	5 – 40	100 - 800
Carbonate-hosted Bilbao- type vein and replacement mineralisation	Cumbria, South Wales and Forest of Dean	200 Fe ore	100	490
Jurassic and Cretaceous minette ironstones	Cleveland, East Midlands and Oxfordshire	1100 Fe ore	2200	11300
Coal Measures blackband and clayband ironstones	Staffordshire and South Yorkshire	120 Fe ore	60	300

4.2 GRANITE-ASSOCIATED TIN-COPPER FISSURE VEIN MINERALISATION SOUTH WEST ENGLAND

The most important base-metal mining area in Britain was south west England which produced over 2.5 Mt of tin metal, 2 Mt of copper metal and 250000 tonnes of arsenic trioxide (Dunham et al., 1978). There are over two thousand named mines (Dines, 1956) and estimates of over 10000 shafts, many of which are poorly recorded. The mineralisation is mainly in the form of southwest-northeast steeply dipping multi-stage fissure veins associated with Variscan granite intrusions. There are also large tonnage stockworks deposits, such as those at the Hemerdon (Christoffersen and King, 1988) and Mulberry mines. The mines have been worked over many hundreds of years with the main period of working between about 1700 and 1900. Activity after 1900 was largely restricted to a few areas around Camborne-Redruth and near Land's End. The mineralisation falls within the general descriptive model (15b) of Sn veins of the USGS (Cox and Singer, 1986).

4.2.1 Nature of ore

The main mineral in the veins is quartz, with smaller amounts of tourmaline and chlorite, together with variable amounts of fluorite and muscovite. The main economic minerals were those of copper (mainly as chalcopyrite), tin (mainly as cassiterite), and arsenic (as arsenopyrite).

Pyrite was ubiquitous though most common in the mines around Callington and Gunnislake. Zinc (as sphalerite) was produced as a co-product of tin extraction at Wheal Jane mine in Cornwall until it closed in 1991. Wheal Jane mine was neglected for many years, due to the high content of fine-grained pyrite which made economic recovery of tin difficult, until it was reopened in 1971. Pyrite was recovered from many mines and used in the production of sulphuric acid from the middle of the 19th century. Dines (1956) records a total production of 150000 tons from the whole orefield. Much more was probably discarded as waste.

The veins are mainly less than 1 km long, around 1-2 m wide and have been worked to several hundred metres depth. The deepest operation was at Dolcoath Mine, near Camborne, which reached a depth of 550 fathoms (over 1500 m). In many places, such as the Redruth – Camborne area of Cornwall, there are many sub-parallel veins in close proximity. These have been worked and reworked from a multitude of shafts and connecting underground drives. In many cases tin mineralisation occurred below that of copper and so many mines changed from copper to tin production during their working lives.

4.2.2 Hostrocks

The main hostrocks of the mineralisation in southwest England, and therefore an important constituent of the waste heaps, are coarse grained granite and fine grained 'killas'. The latter are metamorphosed sediments, mainly mudstones or sandstones. Granite and killas both give rise to slightly to strongly acidic groundwater that is not buffered by the surrounding rocks. There are some thin calcareous horizons in the killas called 'calc-flintas'. These are likely to neutralise acid groundwater, but are neither voluminous nor extensive. There are also numerous granite dykes, locally known as 'elvan', that are often associated with the mineralised fissures.

4.2.3 Mine centres

The mines are mainly clustered around the 'emanative centres' of the underlying granitic source rocks. The principal areas are Camborne-Redruth associated with the Carn Brea and Carnmenellis Granites, St Just associated with the Land's End Granite and Callington associated with the Kit Hill Granite (Figure 16Figure 16. The largest mines were around Camborne-Redruth. For example the Dolcoath mine produced 350000 tons of copper ore ranging between 6 and 7.3 per cent metal and over 80000 tons of black tin (70% Sn) (Dines, 1956) and the South Crofty mine over 60000 tons of tin in the Redruth area. Geevor mine near St Just produced over 50000 tons of black tin from 1900 to 1990.

Many of the mines also produced arsenic, especially in the Callington and Tavistock areas. The main producer was the Devon Great Consols mine near Callington with a recorded output of over 70000 tons between 1848 and 1909 (Dines, 1956). In the 1870s half the world's production was estimated to come from half a dozen mines in the area, including Devon Great Consols. Other centres of arsenic production included the Cambourne - Redruth area where the South Crofty, Dolcoath and East Pool mines all produced significant amounts and the Levant mine on the Land' End peninsula (Dewey, 1920). The smelting of arsenical ores to produce white arsenic for weedkillers and insecticides in the 19th century contaminated large areas downwind of smelters in the region (Abrahams and Thornton, 1987). Small amounts of antimony were produced in the Wadebridge area of north Cornwall.

A few mines were also worked for uranium as a colouring agent, and later as a source of radium, in the first part of the 20th century (Dines, 1956). The most important of these was the South Terras mine, near St Austell, which produced 736 tons of 'uranium ore' containing around 11% the uranium minerals Pitchblende Uraninite U_3O_8 from or (UO₂), $(Ca(UO_2)_2(PO_4)_2.11H_2O)$, Torbernite $(Ca(UO_2)_2(PO_4)_2.12H_2O)$ and Zippeite $(K_4(UO_2)_6((OH)_{10})_1)_1$ (SO₄)₃) 4H₂O). Smale (1993) suggests that the mine produced both uranium and radium. The small waste tip has been used as a natural analogue for radionuclide mobility (Hooker et al., 1989).

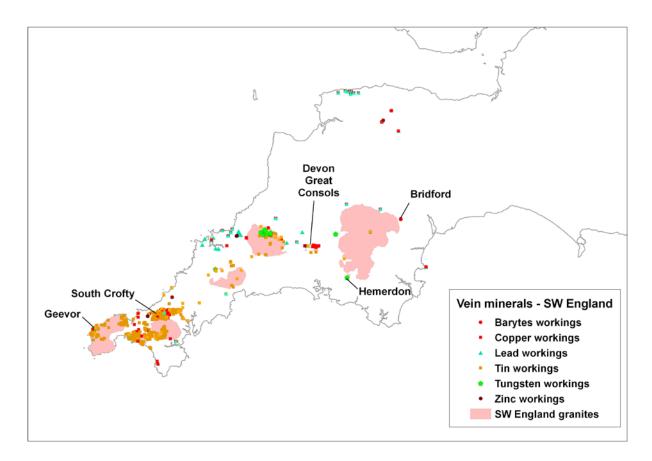


Figure 16 Closed mines in south west England.

4.2.4 Methods of extraction and processing.

These methods generally apply to all the orefields in Britain that worked semi-vertical veins with lengths of hundreds to thousands of metres, widths of less than 10 metres and depths of tens to hundreds of metres.

During the main productive phase from 1750 to 1900 the main exploration methods were:

- Costeaning or trenching to expose a vein at surface.
- Sinking an exploratory shaft from surface on or close to the vein; exploratory core drilling only became common in the latter half of the last century.
- Driving sub-horizontal tunnels from the shaft to the vein. These are usually at 10 to 30 m intervals down the shaft.
- Driving along a vein in the hope of finding payable ore as most veins only contained economically recoverable ore over 25 to 50% of the length and width of the vein.
- Driving a crosscut normal to the vein from existing underground workings in the hope of intersecting a parallel structure.

The mining methods mainly used hand-driven drilling to make holes for explosives, before the introduction of the rock drill in the mid to late 1800s. There was thus a strong incentive to minimise the amount of rock extracted and many veins were 'slit' to just extract the portion containing tin or copper minerals and to allow physical access. Much of the vein was often left behind, though later, more mechanised mining involved more complete extraction of the vein materials for processing on surface. "Payable ore" was often only 30 % of the overall content of the vein.

The main mining method was overhand stoping by driving sub-horizontal levels along the vein at about 10 m intervals vertically. Holes were drilled up into the ore from the level below and the

ore blasted down and removed. Underhand stoping was the reverse, with holes drilled down into the ore. Timbering and waste was then be used to raise the working level so that another set of holes could be drilled. The process was repeated until the level above was reached and removed. This created high narrow stopes (open spaces) that were generally timbered to prevent their collapse during the working life of the mine unless they were strong enough to stand without timbering.

The use of mechanised equipment such as locomotives or trackless load-haul-dump machines in the second half of the 20th century increased the size of the underground workings from perhaps a metre wide and under two metres high using manual labour alone, to two metres or more in each direction to enable the use of this equipment. This increase in size of the workings usually resulted in the extraction of additional unwanted host rock which often contained some low-grade and unprofitable mineralisation with an attendant increase in the waste production. Prior to mechanised mining, the material raised to the surface would have been hand cobbed to separate the economic minerals of the time, while the waste material would be discarded in heaps close to the shaft. The early waste dumps were therefore often of coarse chippings and thus free draining and with a relatively small surface area. This restricted access of water and oxygen to the sulphide minerals.

Following the development of the steam-driven Cornish stamp mill in the 1850s, which pulverised vein material to much finer grain sizes, all the ore mined was treated and thus the amount of waste increased. The material was treated by simple gravity processes such as buddling, jigging and shaking tables that used water to separate the denser economic minerals from the lighter waste. The unwanted slimes and sand-size material resulting from these processes were dumped on convenient open spaces near to the mine site. As time went on and mineral throughput increased, these became dedicated tailings dams with stone or coarse waste used to build retaining walls. This fine-grained material has a much greater surface area and therefore is more likely to react with surface water to produce acid mine drainage (AMD).

Every mine has some form of waste tip. Obviously larger mines will tend to have larger tips, roughly proportional to their metal output. Unusually, the Geevor mine near Land's End in Cornwall, being sited on a cliff, tipped most of its waste directly into the sea. There are thus thousands of individual heaps of discarded material throughout the mining districts. Much of it has been reworked or redistributed for a variety of purposes, including road building and aggregate – see the mundic problem below.

Only a few metal mines in Cornwall survived long enough to use froth flotation technology which requires a very finely ground ore as feed to the flotation tanks. This produces even finer grained slimes that require a properly established and engineered 'tailings facility'. Mines that used froth flotation include the Wheal Jane (closed 1992) and South Crofty (closed 1998) mines in the Camborne-Redruth area and Geevor mine (closed 1990) near Land's End.

4.2.5 Waste production in south west England

There are no definitive figures for waste production but a production record for Cornwall of 90 years from 1815 to 1905 (the main period of activity in the area) shows that over 8 Mt of copper ore were mined to produce 571 000 t of copper metal (Dewey, 1923). This gives a run-of-mine grade of about 7.1 % copper at 100% recovery. The main copper mineral was chalcopyrite which contains around 33 % copper. This means that about 20 to 25 % of the ore was copper mineral or 'ore' leaving perhaps 75 to 80 % as 'waste', i.e. an ore to waste ratio of perhaps 1:4. This would imply that about 6 Mt copper mine waste was produced for the area and time mentioned. There would be additional waste rock from underground development, shaft sinking and other activities that might amount to another few million tonnes. For the total production of 2 Mt copper this would indicate an overall waste production for the copper mines of around 20 to 25 Mt. Tin mine

waste would be greater than for copper as the ore grade is usually lower (around 2% Sn in the main period of working, though this declined in the later years of the industry) although the tin content of the main ore (cassiterite) is higher at around 70 % Sn. At an estimated average grade of 2 % tin this would give an estimated tin mine waste tonnage of around 100 Mt. However, many mines produced both metals and so the figure may be somewhere between 50 and 75 Mt. This gives a total waste production for the whole south-west England mining field of around 75 to 100 Mt. Using an assumption that 1 Mt of waste covers 20 Ha to a depth of 2 m (assuming a waste density of 2.5 t/m³) this would indicate a total area of about 1500-2000 Ha. However, many tips are less than 2 m high and therefore the area could have been greater. In 1990 it was estimated that metalliferous mining spoil heaps covered 1620 Ha in Cornwall (Mitchell, 1990). This indicates a figure with a similar order of magnitude to that calculated above. These figures are necessarily uncertain but are included to give a picture of the amount of waste in the region. The waste was never analysed, except in some cases to ascertain how much tin or copper was being lost to the tailings, and hence the proportions of potentially harmful elements, such as arsenic, within any particular waste tip are unknown.

A detailed survey of a 30 km² area in one of the most heavily mineralised parts of Cornwall (Holt, 1992) found that the area contained over 3000 shafts, 436 km of lode and 142 km of mine adits. This study investigated the effects of mining from the point of view of subsidence and contamination. It did not, however, provide detailed information on the mining wastes even in this relatively small survey area. The actual amount and area of mining waste in south west England thus remains unknown.

An initial investigation using current and historic Ordnance Survey maps shows that it is difficult to 'map' the extent of current or former waste tips in the area. Older maps simply show named mines or old shafts sometimes surrounded by an indication of waste ground, but not necessarily mine waste. For example in the United Downs area the old maps show areas of mines and waste ground of about 80 Ha around the United Mine and 65 Ha around the Great Consolidated Mine. In contrast the current 10K OS map shows an area of about 15Ha as 'Hale Hills Tailings Dams' in the same location. These are the more modern tailings dams used by the South Crofty and other mines in the area from the 1960s to the 1990s. The South Crofty Mine near Redruth has an area of around 12 Ha, including mine buildings, while the old South Tolgus Mine in the same area covers about 13 Ha. Thus while current and historic mapping may be useful in indicating areas of former mine working, it should not be taken as definitive in any way as it may distort the actual 'on the ground' situation. Similarly air- or space-borne imagery, while very useful in classifying some areas, is not a definitive technique as many tips have been vegetated and do not show unique characteristics to enable them to be distinguished (Fleming et al., 2003).

During the period 1900–1950, readily-available mine waste, specifically vein material containing pyrite (mundic) and killas rocks, were used as aggregates in concrete in order to keep building costs low. Unfortunately both these materials, especially in Cornwall and Devon, deteriorate with exposure to the atmosphere and give rise to serious structural faults. Some buildings have had to be demolished because they were unsafe.

4.2.6 Characterisation of the waste and environmental signature.

4.2.6.1 POTENTIAL CHEMICAL HAZARD

The chemical hazard represented by the mine waste associated with this deposit type is generally dependent on the sulphide mineral content and related acid mine drainage potential together with the presence of harmful elements. The principal sulphide minerals that have significant acid generation potential in the deposit type are pyrite, chalcopyrite and arsenopyrite. The majority of deposits are in host rocks consisting of plutonic granitic rocks and pre-intrusive clastic sedimentary or metasedimentary rocks that have low acid buffering capacity, amplifying the problem of acid mine drainage.

The solubility of cassiterite (SnO₂) is very low with a consequent low environmental signature.

Elements as Cu, As, Pb, Zn and Fe associated with the main mineral ore are likely to be present at environmental significant levels in the mine waste. Among them arsenic represents a major hazard in the region.

Potential hazards also include possible elevated concentrations of uranium and thorium in mill tailings and smelter waste due to primary enrichments of these elements in host rock and ore and the gravity and magnetic separation methods used in milling, which concentrate high specific gravity minerals. Radon is a naturally occurring gas which is formed in the decay series of ²³⁸U. It is a colourless and odourless gas, which is very dense and chemically unreactive. Radon decays to highly radioactive heavy metallic daughter products, some of which decay by alpha particle emission. These daughter products, if retained in the lung through inhalation, will irradiate lung tissue by alpha particle emission.

4.2.6.2 Drainage signatures

Mine drainage is generally characterised by a low pH due to the presence of abundant pyrite and arsenopyrite coupled with host rocks lacking significant acid-buffering capacity and is enriched in contaminants. Acidic mine waters from the Levant mine, Cornwall, showed concentrations up to 665 mg/l Cu, 41 mg/l Zn, 76 mg/l Mn, 6 mg/l Co and >2500 mg/l total Fe (Bowell and Bruce, 1995). The production of acid rock drainage and leaching of metals can be related to sulphide oxidation. Precipitation of iron oxyhydroxides, caused by a pH increase, was shown to cause coprecipitation of other metals, including Cd, Co, Pb, Mn, Ag and Zn, thus limiting the release of dissolved metals in solution from the mine. However, the release of suspended metal-rich ochres in mine discharge waters (with high Pb, Zn, Cd, Mn, Ni, Sn, Sb, As, Bi, Cu, Co and Ag) still presents a potential environmental hazard.

The followings are example of underground mine waters extracted from the BGS database (unpublished data):

Mount Wellington Mine. The mine connected to Wheal Jane underground and was last reworked between 1970 and 1991. Mine water with pH 2.8, contains about 600 mg/l SO₄, 2 mg/l Mn, 100 mg Fe, 26 mg/l Al, 0.15 mg/l both Co and Ni, 1.2 mg/l Cu, 6 mg/l Zn, 0.05 mg/l As.

Cligga Head Mine. The mine was last worked in the 1950s (by Geevor). The mineralisation consists of numerous veins (in parts a stockwork) cutting greisenised granite comprising cassiterite, wolfram and mixed sulphides in a quartz (+/- chlorite, tourmaline) gangue. Uranium minerals (including torbernite) are present. Mine water has near neutral pH (6.5), 0.4 mg/l Cu, 1.2 mg/l Zn, 0.05 mg/l As (also high in chloride).

Frementor Mine. The mine was worked until 1919 (and from 1925 to 1929) for tin and tungsten. Minor chalcopyrite and arsenopyrite is present in the ore which is hosted in greisenised granite. Mine waters have a pH around 5, low sulphate concentrations less than 20 mg/l, high F up to 5.5 mg/l and As 0.2 mg/l.

Wheal Fanny. Devon Great Consols Wheal Fanny Section waters with pH 3.1 contain up to 140 mg/l SO₄, around 4 mg/l Mn and Fe, 9 mg/l Cu, 0.5 mg/l Zn and 0.2 mg/l As.

Arsenic distribution patterns reported by a study of Aston et al. (1975) in the waters of the Tamar, Lyhner and Tavy catchments indicated the incidence of high As concentrations of over 250 μ g/l in the Gunnislake region of the Tamar and its tributaries and concentrations of 10-50 μ g/l As in the River Lyhner. The area has long been associated with the mining and smelting of arsenopyrite and contains four main centres of mining: Gunnislake, Latchley, Luckett and Devon Great Consols, Tavistock and Sydenham-Damarel.

4.2.6.3 ARSENIC MOBILITY FROM SOLID MINE SPOILS

Arsenic represents a major hazard associated with the waste from the Cu-Sn mines in south west England. Arsenopyrite (FeAsS) exposed to atmospheric weathering mainly produces scorodite (FeAsO₄.2H₂O) and fine-grained, secondary Fe(III) oxides/hydroxides (ferrihydrite, goethite) and sulphates (jarosite), forming weathering crusts during periods of low rainfall. Scorodite is metastable under most conditions and may break down further to the ultimate products of goethite and soluble arsenate (Roussel et al., 2000). The occurrence of ferrihydrite / goethite or jarosite depends on the local buffering capacity of the pyrite-bearing rock, i.e. presence of gangue minerals such as calcite and siderite, with ferrihydrite precipitating under pH-neutral, oxidising conditions, whereas jarosite is stable only under acidic oxidising conditions and requires a source of potassium. These Fe(III)-rich weathering products are efficient scavengers of arsenic oxyanions. Consequently, arsenic is concentrated in weathering products relative to whole rocks and its concentration in the weathering products generally increases with increasing total iron content. The presence of the secondary ferric oxide and jarosite precipitates is important with regard to the environmental impact of the contaminated soils, since long term stability may be affected by locally anoxic conditions leading to the reductive dissolution of less stable Fe oxyhydroxides and basic sulphates and consequent release of the heavy metals and metalloids adsorbed or coprecipitated.

The mobility of arsenic in the mine spoils and contaminated soil depends on many factors including redox potential, pH, clay mineralogy, the presence of competing oxyanions for retention sites and the presence of iron and aluminium oxides (Corwin et al., 1999). The investigations carried out on arsenic sorption indicate that the effect of pH on As sorption varies with the nature of the As species, mainly arsenate or arsenite. According to Smith et al. (1999) the sorption of As(V) on soil is generally higher than As(III) and soils high in oxide mineral contents adsorb three times more As(V) than soils containing small amounts of oxide minerals. The pH does not have an effect on As sorption by soils low in oxide minerals, while in highly oxidic soils sorption of As(V) decreases with increasing pH. This decrease is attributed to the increasing negative surface potential of variable charge soils. Sorption of As(III) was not found to increase with increasing pH. The retention of arsenic on soils is also dependant on the quantity and type of clay. Soils with higher clay content adsorb more arsenic than soils with a lower clay content. The order of arsenic sorption given by Dickens et al. (1967) is as follows: kaolinite> vermiculite> montmorillonite. Arsenate sorption is also influenced by the presence in solution of phosphate and molybdate oxyanions that can compete for retention sites on the mineral surfaces of soils.

The capacity of secondary minerals to incorporate arsenic influences its mobility in the mine waste and soils with the retardation of arsenic movement. Erosion from mining areas may, however, introduce metals in particulate forms to aquatic environments. These particulates contain metal forms that are stable only under the geochemical condition of the mine site. Observations from Savage (2000) suggest that the capacity of these minerals to retain arsenic, once deposited in the aquatic environment, depends on the local pH and redox conditions. In general, goethite can retain adsorbed arsenic except under reducing conditions of sediment burial, whereas jarosite is not stable under any reservoir conditions and can be expected to release arsenic into the dissolved phase.

Arsenic bioaccessibility. Results of arsenic bioaccessibility in 109 soils from Devon Great Consols Mine, an abandoned Cu-As mine in Devon, indicate a median value of the percent bioaccessible As of 15%, showing that relatively little of the total As is present in a bioaccessible form. Mine soils showed overall higher As bioaccessibility than other mineralised soils not affected by mining activities and background soils within the Tamar Catchment whose percent bioaccessible As median values were 9% (Palumbo-Roe and Klinck, 2007).

4.2.6.4 SOIL/SEDIMENT CONTAMINATION

Soils surrounding tailings deposits are recipients of metals released in acid mine drainage or dispersed by wind erosion and may provide a further source of contamination even after the exhaustion of sulphides in the rock dump. Various district councils in south west England have wide experience of problems associated with high levels of arsenic contamination in the context of land use planning. As with other contaminants, the problem concerns the toxicity of the topsoil and its health implications for the food chain. Although substantial areas in Devon and Cornwall have arsenic contamination above the UK soil guideline value (SGV) of 32 mg/kg for residential use, very high concentrations 10 to 40 times over the SGV are common in mining areas.

A soil geochemical survey of the 920 km² Tamar catchment in south west England undertaken by the British Geological Survey (Rawlins et al., 2003) demonstrated that approximately 60% of the sites throughout the catchment had total soil As values above 20 mg/kg. The most contaminated land was in the south of the catchment, in the Kit Hill/Gunnislake and Tamar Valley areas, in areas of intense former mining activity, including smelting.

The risk associated with liming practice to remediate arsenic contaminated soils and mine tailings is highlighted by Jones et al. (1997), due to the pH dependence of As sorption reactions on oxide minerals.

Mitchell et al. (1995) review the significance of public exposure to arsenic in SW England, where mining legacy combined with the natural processes of pedogenesis has resulted in a significant area of arsenic contaminated wastes and soils. Possible pathways of exposure to arsenic such as contaminated food stuff and soil ingestion are considered in this review.

Li and Thornton (1993) indicate that direct ingestion of soil can be a major source of dietary arsenic for grazing livestock. The average intake of soil by cattle was estimated to be from 1 to 10% of the total dry matter intake. However, only 1% of the arsenic in the soil was actually adsorbed by cattle. Consequently, cases of toxicity are uncommon.

4.3 LOWER PALAEOZOIC SHALE-HOSTED CROSSCOURSE LEAD AND ZINC VEINS IN SOUTH WEST ENGLAND

4.3.1 Nature of ore

A number of north-south 'cross-course' fissure veins in south west England (Figure 16) been worked for lead and zinc over many hundreds of years. The last mines closed in the early 19th century. The 'cross-courses', so called as they are generally normal to the main tin-copper fissure veins, can be up to 15 m wide and are often brecciated with fragments of the country rock mixed with quartz and ore minerals. The main ore minerals were galena and sphalerite with subsidiary sulphosalts such as antimonite, bournonite and tetrahedrite (Dines, 1956). Native silver and antimonial silver or pyrargyrite also occur in some mines, such as Ludcott. The principal gangue mineral was quartz with subsidiary calcite, ankerite, fluorspar and dolomite. The galena was particularly silver-rich averaging 40 oz per ton (~1200 g/t). Mines of this type near Wadebridge produced minor amounts of antimony from jamesonite and bournonite. Total production was around 300000 t of 'lead ore' containing 60–75% Pb (Dines, 1956). Significant amounts of baryte were produced in the Teign Valley in Devon from similar cross-course veins cutting Carboniferous Culm Measures. The largest mine, Bridford, produced over 450000 t of baryte.

4.3.2 Host rocks

The deposits usually occur more than 1 km from the major granite intrusions and are generally deposited from lower temperature fluids (Alderton, 1993). The host rocks are the 'killas' or metamorphosed mudstones and sandstones with some volcanic rocks. The Teign Valley mines,

which were largely worked for baryte, though some did also produce lead, occurred in Carboniferous Culm Measures of interbedded sandstones, shales and cherts with some volcanic rocks.

4.3.3 Mine Centres

The main areas of cross-course lead mineralisation are in the Liskeard and Callington areas where the Herodsfoot and Mary Ann mines each produced around 1 million ounces of silver and 20-30000 tons of lead concentrate. The Wadebridge area mines were notably antimony-rich, though production was relatively small with a recorded output of 300 tons. Baryte was largely restricted to the Teign Valley mines.

4.3.4 Methods of extraction and processing

The mines all worked relatively narrow steeply inclined veins and the mining methods were similar to those used elsewhere in Britain. Early surface workings were followed downwards from the outcrop of the vein for a few metres. Shafts were then sunk alongside the vein and working levels driven from the shafts to the vein. The ore was then extracted, usually by overhand stoping working up to the next level. Horizontal adits were driven from valleys to intersect the workings for drainage and haulage where possible.

4.3.5 Waste production and character of the waste

Waste production is difficult to quantify as it was not generally recorded. However, metal production figures do enable some estimate of the amount of waste to be calculated. Given that the total production of lead was 300000 tons of lead ore at 60 - 70 % lead and assuming an average grade of around 7% Pb for the mine output (comparable to other, similar lead mines elsewhere, e.g. Greenside in the Lake District), this would mean that the ore contained about 10% galena with the rest as waste. This would give a very rough estimate of about 3 million tons of waste or enough to cover an area of 60 Ha to a depth of 2m.

Referring to the Teign Valley barytes mines, Dines (1956) records that 15% of the baryte was lost in slimes during the mineral processing with a total recovery of between 80 and 83% of the baryte in the vein. If these have not been recovered since the mine closed this implies that there is up to 90000 tonnes of baryte in the tips, much of it finely ground, as well as sub-percent levels of galena, sphalerite, fluorspar and pyrite mixed in with the waste country rock. The Frankmills and Exmouth mines in the same area also produced significant amounts of lead. Dines (1956) states for the Frankmills mine 'The waste dumps are large and contain weathered siderite and cherty vein quartz, both with scattered crystals of galena and blende, and a later generation of comby quartz penetrating the siderite. The tailings dumps are also extensive and grab samples from these are said to have shown 8 to 10 per cent barytes and 1 per cent galena'. This is one of the few contemporary references to the waste tips of a metal mine. The production figure of about 500000 tonnes for the area implies that waste production was perhaps as high as 5 million tonnes. Various attempts have been made to recover lead and baryte from the dumps. The current and historic OS maps show that Bridford Mine has an area of about 5 Ha, Frankmills 4 Ha and Reed 2 Ha, including the mine buildings and any waste areas.

4.4 CARBONATE-HOSTED LEAD, ZINC, FLUORSPAR AND BARYTE MINERALISATION

The main areas of production are the Northern Pennine Orefields, split into the northern Alston and southern Askrigg areas, and the Southern Pennine Orefield in Derbyshire (Figure 14, Figure 17 and Figure 18). Mineralisation generally occurs as fracture-hosted mineralisation in Carboniferous late Dinantian to early Namurian platform carbonates adjacent to Carboniferous shale-dominated basins. The mineralisation comprises large numbers of long (up to several kilometres), narrow (less than 10 metres), steeply-dipping oreshoots of limited vertical extent

confined to a small number of massive limestone or sandstone beds. Galena and fluorite are the main ore minerals. These are accompanied by subsidiary, but locally important, baryte, sphalerite, witherite and chalcopyrite. The economic minerals are accompanied by variable amounts of quartz and calcite. Mineralisation probably occurred during early Permian times. Dunham (1983) considers Pennine-style mineralisation to be a fluoritic subtype of the Mississippi Valley Type of carbonate-hosted lead-zinc deposits (Cox and Singer, 1986). There are a number of significant replacement orebodies, some of which were only partly investigated and/or extracted due to the technologies of the time and the concentration on richer and more easily worked vein deposits. Minor elements are commonly included within the main ore minerals. Sphalerite generally contains around 0.1 to 0.2% cadmium; pyrite can contain arsenic, antimony, cobalt and nickel and baryte and witherite can contain strontium. Any of these minor elements may be present in small quantities in the mine waste.

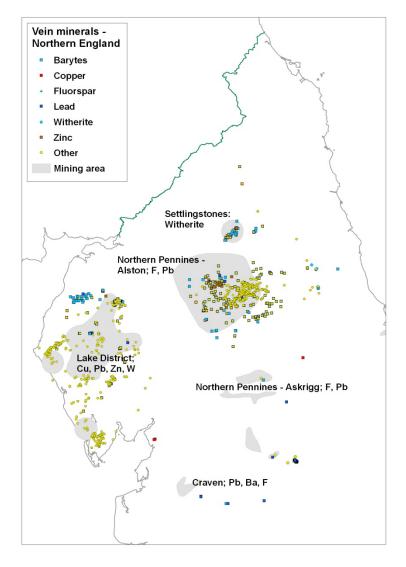


Figure 17 Closed metal mines in northern England.

4.4.1 Northern Pennine Orefield

The most important areas are around Rookhope and Stanhope in Weardale and around Alston and Nenthead in Tynedale areas (Dunham, 1990) and around Greenhow in the Askrigg area (Dunham and Wilson, 1985). Mining finally ceased in Weardale in 1998. Fluorite occurs in oreshoots within major veins up to 20 km long and 10 m wide, and also in stratabound replacement orebodies (flats) adjacent to veins as well as numerous minor veins (Greenwood and Smith, 1977). The predominant directions of the veins are west-northwest and east-northeast.

The former can be continuous structures up to 20 km long. The Alston area shows pronounced zonation of some of the ore minerals. Fluorite dominates the inner zone with calcite and then baryte towards the margins of the mineralised area. This zonation is coincident with the subcrop of the concealed high heat production Caledonian Weardale granite.

Table 10 shows the twenty largest mines in the North Pennine orefield in terms of total recorded output of all minerals produced.

Table 10 Largest mines of the Northern Pennine Orefield (Dunham, 1990)

						Total
	Lead	Fluorspar	Baryte	Witherite	Ironstone	tons (all
Mine	tons	tons	tons	tons	tons	minerals)
Grove Rake	24550	695341				719891
Settlingstones	16902			630000		646902
Carricks	6766				500000	506766
Cambokeels	2866	474633				477499
Stanhopeburn	24000	380000				404000
Blackdene	4500	364406				368906
Stotfield Burn	9957	330667				340624
Redburn	3000	328805				331805
Closehouse	15000		310000			325000
Cowgreen	1600		300000			301600
Silverband	7500		290000			297500
Allenheads	260000	10000				270000
Burtree Pasture	150000	100000				250000
South Moor Colliery				237000		237000
New Brancepeth Colliery			221659			221659
Sedling	17 455	166 241				183696
Crawley / Hope	8 571	163 000				171571
Heights	7 470				141491	148961
Boltsburn	127 785	7 299				135084
Fallowfield	11 196			105000		116196

4.4.1.1 METHODS OF EXTRACTION AND PROCESSING.

The mineral deposits of the Northern Pennine Orefield have been worked over thousands of years from pre Roman times to the end of the last century. The main period of production of lead was from around 1750 to 1920 and for fluorspar from 1900 to 2000. Outcropping veins were initially worked down from the surface in narrow open pits as the vein walls were generally strong enough to stand without support. As the workings increased in depth underground working became necessary with access by shafts and adits. Some of these could be several kilometres in length. The Alston orefield in particular was mainly worked by two companies during the main period of production; the London Lead Company and the Beaumont Company.

The average grade of lead ore was around 7% lead (Dunham, 1990), though this would have been very variable, depending on the thickness and continuity of the ore shoot worked and the mining methods in place at the time. Given that galena contains around 75% Pb this implies that the grade was around 10% galena with 90 % waste host rock. Some of this waste from the lead mines would have been fluorite which may have been reclaimed during later retreatment of the lead mining waste. Thus the waste from the estimated lead production of 4 Million tonnes could have been between 4 and 36 Mt, though the lower figure is more likely due to selective mining

and storage of waste underground. The fluorspar operations mined a much higher grade of ore than those for lead with a minimum of around 25% CaF₂ though it was often much higher at closer to 40 or 50% CaF₂. The recorded fluorspar production of 2.5 Million tonnes may have generated around 2 to 3 Mt of waste, though the figure is likely to be much lower due to the successive retreatment and extraction of fluorspar from pre-existing lead mining waste dumps. The Askrigg orefield had a much smaller production of around 1 million tonnes of lead with around 140 000 tonnes of fluorspar and minimal zinc and baryte.

The Settlingstones area in Northumberland was a major source of witherite (BaCO₃) with a total production of 740000 t (Dunham, 1990). Several deposits were also worked in the Durham coalfield, to the east of the Northern Pennine Orefield, with a total production of 264000 t of witherite and 234000 t of baryte (Dunham, 1990). Witherite is a hazardous mineral, though there was relatively little waste rock in the mining areas due to the purity of the baryte and witherite vein deposits. Nevertheless some witherite and baryte will have been lost to the waste tips as no recovery process is 100% efficient. Significant amounts of host rock, with minor lead, zinc and barium minerals, were produced during the driving of access adits, shaft sinking and other non-productive mining activities. Small amounts of galena and sphalerite also occurred with the barium minerals and may not have been recovered.

Some of the coal mines in the area also had problems with barium-rich groundwater and a blanc-fixé plant operated for a number of years from 1933 to 1969 at the Eccles colliery (Gray and Judd, 2003) producing around 3000 tons of BaSO₄ per year. Radium pollution from uranium associated with barium in Carboniferous coal mine drainage is a serious problem in Poland (Pluta, 2001). It is not known if any radium occurred in the barium-rich waters in Durham.

4.4.2 Southern Pennine Orefield.

Galena-fluorite-baryte mineralisation occurs in major east-west veins (rakes) and stratabound replacement deposits (flats) together with some cave fill deposits (pipes). The richest mineralisation is concentrated in the uppermost Dinantian limestones beneath Namurian shales on the east side of the Dinantian outcrop (Ford and Ineson, 1971; Ford, 1976). Current production is mainly from open-pit operations and is principally confined to the north-eastern part of the orefield between Eyam and Bradwell. This area is almost entirely within the Peak District National Park. Substantial (in excess of several hundred thousand tonnes) replacement fluorspar orebodies have been worked, adjacent to major veins, such as Dirtlow Rake in the Bradwell area (Butcher and Hedges, 1987) and Masson near Matlock (Dunham, 1952). The most important metal mine was the Millclose Mine near Darley Dale in the south-east of the orefield where over 400000 tons of lead concentrates and 90000 tons of zinc concentrates were recovered from a remarkable orebody where natural upgrading of galena in a cave system produced very high grades of mineralisation (Varvill, 1959). The Millclose tips have been reworked and are now the site of the Enthoven lead smelting works recovering lead from car batteries. The Millclose site covers an area of about 30 Ha, including the recycling plant. However, the 1939 OS map only shows an area of about 6 Ha around the mine. Current production from the Southern Pennine Orefield is almost wholly treated by Glebe Mines' Cavendish Mill near Stoney Middleton.

Total production from the Southern Pennine Orefield is estimated at 2.5 million tonnes of lead and 4.3 million tonnes of fluorspar.

4.4.3 Characterisation of the waste and environmental signature in the Pennine orefields.

The amount of waste is very difficult to determine, due to inadequate records and the retreatment of many dumps, sometimes several times, as well as their physical removal to other treatment plants before the residue is dumped there. There were several central processing plants, such as Broadwood and Blackdene, in the Northern Pennine Orefield during the later years of the fluorspar production period in the last half of the 20th century. These processed ores from a

number of mines and produced a uniformly sized fine-grained waste of limestone and silica with small amounts of fluorspar and metallic elements, mainly lead and zinc. Their waste products were stored in tailings ponds close to the plants. The estimated production of around 4 Mt of lead from the Alston area of the Northern Pennine Orefield could have generated up to 36 Mt of waste if the overall lead grade was 7%. This is likely to be an upper estimate as much waste was left underground and much has been removed from the tips for various purposes, including recovery of fluorspar.

The waste production of the Southern Pennine Orefield is again conjectural, due to the paucity of records recording this activity during the main producing phase from 1700 to 1850. The fluorspar production again used a much higher grade of ore than the lead production with a minimum of around 25% CaF₂ compared to around 7% Pb. The fluorspar grade would often have been much higher at closer to 40 or 50% CaF₂. Thus the waste from the estimated lead production of 2.5 Mt could have been between 2 and 20 Mt, though the lower figure is more likely due to selective mining and stowage of waste underground. The recorded fluorspar production of 4.3 Mt may have generated around 4 to 5 Mt of waste, though the figure is likely to be lower due to the successive retreatment of dumps and the extraction of fluorspar from pre-existing lead mining waste dumps. For example the Cavendish Mill operation currently extracts as much 'waste material' for further processing and extraction of minerals from the current Blakedon Hollow tailings dam as it deposits in them (Colman et al., 2006). The area of the Cavendish Mill and associated tailings dams is estimated at around 20 Ha.

4.4.3.1 Drainage signatures

Northern Pennines

Low amounts of pyrite, coupled with large amounts of acid-buffering minerals associated with this deposit type are reflected in low potential for acid metal-rich mine drainage generation. Zinc is relatively highly soluble throughout a range of pH values at which lead and copper are entirely or mostly sorbed. As a result, zinc is the dominant base metal in all of the mine-drainage water sampled in the northern Pennines.

Leachate composition determined at seepage from mine tips in the area of Rookhope, Weardale, indicate maximum concentrations of 150 mg/l SO₄, 0.3 mg/l Pb, 1 mg/l Zn, 1.9 mg/l F and a neutral pH. Metal mobility is however limited by the abundance of carbonate rock, except for zinc.

Extensive literature is available, however, for the purpose of this report only a few examples are reported to illustrate the environmental impacts. A survey of 190 streams distributed within five main areas of the orefield (Allendale, Alston Moor, Derwent Catchment, Teesdale, Weardale) during 1974 and 1975 indicated many sites with levels of zinc above 0.1 mg/l and 20 streams with more than 1 mg/l mostly in the Nent valley of Alston Moor (Say and Whitton, 1981). Accounts of the ecological impact of mining in the Northern Pennine Orefield are given by Abel and Green (1981) on the Rivers East and West Allen in Northmberland, joining to form the River Allen, a tributary of the South Tyne.

Mine waters emerging from adits which were used to dewater the underground mine workings can be a source of elevated zinc, derived by the oxidising effects of meteoric waters passing over fissures of rocks containing sphalerite. The mine waters are characterised by high pH and alkalinity. The levels of lead are generally low due to its low solubility at alkaline pH. The WHO guideline of 1.50 mg/l F is exceeded in many mine waters of the northern Pennine area. In humans fluorine is an essential element to the proper formation of bones, especially teeth. However, excess fluorine (doses of 20-80 mg per day) can result in severe bone deformities, which are irreversible, and severe lesions of the gums and tooth root structure.

Karst, where present, can impose significant control on the local hydrologic regime because of its ability to channelize ground water for long distances from mine sites.

Southern Pennines

The hydrogeochemistry of groundwaters in the Derbyshire Dome has been studied by Edmunds (1971). The author reports on how the groundwater flow in the Carboniferous Limestone is strongly influenced by historical human activities associated with base-metal mining. The storage capacity of the limestone has been significantly increased during the past 200 years by the excavation of large quantities of ore and gangue along veins which followed the principal vertical fractures and bedding surfaces. Drainage of the mining areas by the driving of tunnels, locally termed "soughs", provided new outlets for the water with consequent lowering of the water table. Over 230 soughs are recorded and more than seventy of these still carry water either seasonally or continuously (Edmunds, 1971). Mine drainage waters are distinguishable from the limestone background in their content of Pb, Ni, Fe, Zn and F. Often the concentration is only two or three times the background and this enrichment potentially in potentially harmful elements, such as lead, zinc or fluorine, is low when compared with values from other areas. The rather low enrichment factor in the Derbyshire waters is due principally to the buffering effect of the limestone which maintains pH greater than 7, restricting the mobility of some elements.

Banks et al. (1996) have described the uses and positive functions of mine drainage waters in central and eastern England. Water from lead mine soughs in the Carboniferous Limestone of Derbishire (Meerbrook Sough, Hillcarr Sough, Mandale Sough, Magpie Sough, Waterloo Inn Sough) are exploited for public water supply (Edmunds et al., 1989).

4.4.3.2 MINE WASTE CHARACTERISATION AND SOIL /SEDIMENT CONTAMINATION

The results of a survey of 24 old metalliferous spoil tips sites associated with abandoned mine workings in the west of Co. Durham and south Northumberland are reported in Cooke and Morrey (1981). They are characterised by pH range 3.6-7.4, Pb 288-127500 mg/kg, Zn 340-51200 mg/kg, Cu 27-192 mg/kg, Cd 7-44 mg/kg, Ni 12-82 mg/kg, K 100-20000 mg/kg, P 15-870 mg/kg, N 70-670 mg/kg, F 3410-196000 mg/kg, Ba 12100-16100 mg/kg.

Lead sulphides such as galena may persist at alkaline pH in the mine waste with the formation of protective low-solubility coatings consisting of anglesite (PbSO₄), cerussite (PbCO₃) or pyromorphite (Pb₁₀(PO₄)₆Cl₂), depending on the supply of dissolved SO_4^{2-} , CO_3^{2-} or PO_4^{3-} . Under acid condition galena weathering may give rise to high concentrations of lead in receiving stream water downstream mine sites. However, lead mobility is restricted by sorption on clays, organic matter or iron oxyhydroxides or the formation of secondary low solubility Pb minerals (anglesite, cerussite, or pyromorphite).

Lead bioaccessibility is an important factor to consider in assessing the human health hazard of lead rich mine waste from the Pennine orefields. The mineralogic form of lead has been recognised as an important factor controlling Pb bioaccessibility. As the solubility of ingested lead phases is dependent on the mineral forms, encapsulation of lead phases within alteration and precipitation products limits the availability of the Pb-bearing phases as they traverse the gastrointestinal (GI) tract. Solid phases in mining soils are typically less soluble than the oxidised Pb compounds emitted from active smelters (Griffin et al., 1991). The theoretical geochemistry controlling chemical alteration and dissolution of lead in soils has been described for oxides, sulphides, carbonates, phosphates and silicates (Lindsay, 1979). Palumbo and Klinck (2002) investigated the risks of accidental ingestion of lead mining contaminated soils by humans using a physiologically based extraction test (PBET) which measures the bioaccessibility of a particular element of a contaminated soil once it has been ingested. The bioaccessibility of lead in the mine waste was dependent on lead mineralogy, with cerussite more bioaccessible (48% total lead) than anglesite (5% total Pb). Thornton et al. (1994) related Pb bioavailability factors to the mineralogy, particle size and associations of Pb-bearing soil particles. Analysis of particulate material collected on handwipes was undertaken in Winster, a Derbyshire mining village with a high soil and dust lead content (5610 mg/kg and 1870 mg/kg,

respectively). An amorphous form of the Pb phosphate was found to be a common constituent of the Pb bearing solid phase. Pyromorphite is believed to have formed in Winster soils as the end-product of the weathering of lead compounds. It has an extremely low solubility in neutral $(K_{sp}=10^{-84.4})$ and acidic environments $(K_{sp}=10^{-25.8})$, lower than other common lead minerals. Uptake in humans is likely to be controlled by the acid conditions (pH 1-3) of the human stomach. Thus the low solubility of pyromorphite would account for the normal lead concentrations found in children living in the study area, despite the evidence of an elevated intake of lead.

Levels of fluorine in soil around mine sites in the Pennines are potentially very high, up to 2 % with much higher levels in the spoils itself (20%). Fluorine is generally present as insoluble calcium fluoride and in this form is not readily taken up by plant roots. These soils could potentially provide a toxic dose to a child by direct ingestion or cause fluorosis to grazing livestock.

High concentrations of lead, zinc, copper and cadmium have been reported in stream sediments, soils and herbage of the south Pennines (Ineson, 1981). Toxic effects and deaths have been reported in a wide range of animals, but new-born lambs and calves are more susceptible.

In-situ smelting operations, particularly those from 1720 to 1920, have appreciably increased the lead and zinc contents of the top layer of the soil, especially on the high ground.

Pollution from historic metal mining in the Pennine orefields on river sediment has been reported (Macklin et al., 1997).

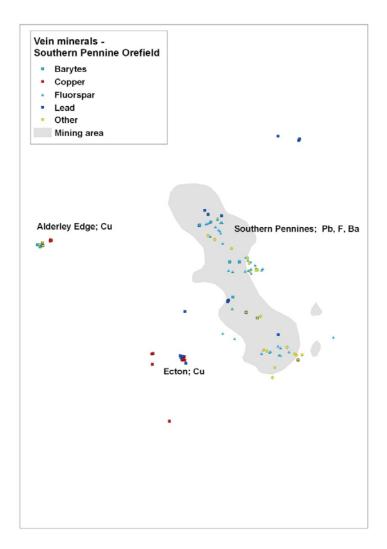


Figure 18 Closed metal mines in the Southern Pennine Orefield.

4.5 OTHER CARBONATE-HOSTED LEAD-ZINC OREFIELDS

4.5.1 North-west Wales

The Halkyn-Minera mining field in north-east Wales (Figure 20) was worked by the Romans, and the early mining history of the area is described by Smith and Mudder (1991). The mineralisation occurs over an area of about 100 km² along the eastern margin of the Dinantian limestones which rest unconformably on, or are faulted against, Silurian sediments. Mineralisation occurs as a series of veins around 0.2 to 0.3 m wide occupying a radial pattern of east-northeast and northwest normal faults which pass into the underlying unmineralised Silurian shales. Some sub-horizontal 'flats' also occur, as in the Jamaica mine which may have been infills of solution cavities in the limestone (Smith, 1991); some also occur in shattered chert horizons adjacent to faults. The veins carry a simple mineralogy of calcite, sphalerite and galena with up to 550 mg/kg Ag. Quartz, fluorite and baryte occur sporadically. Greenockite (CdS) has been recorded at Halkyn. Galena is the dominant sulphide in the main north-south limestone outcrop; sphalerite becomes more important to the east and at depth and is the dominant sulphide in the eastern part of the Minera vein (Earp, 1958). Traces of pyrite and chalcopyrite are common. The main gangue mineral is calcite, but quartz is locally dominant at the Minera mine. Fluorite only occurs in a few mines and baryte is rare. The main ore-bearing zones occur in the upper part of the Dinantian limestone below an 8 m thick shale horizon (the Main Shale) which probably acted to concentrate mineralisation beneath it (Dunham et al., 1978). Some mineralisation also occurred in the overlying Namurian Cefn-y-Fedw sandstone. The Minera veins in the south of the area, were up to 4 m wide (Earp, 1958) and have a mainly quartz gangue. Additional information on the mining district is given in Warren (1984).

Total production for the Halkyn and Minera areas has been estimated at 1900000 t of lead concentrates (75-80 % Pb) and 346500 t of zinc concentrates (45 % Zn). Burt et al. (1992) have published detailed production (but not waste) statistics for many of the mines of North Wales. Waste production is again difficult to quantify but can be estimated from 2 to 20 Mt. This would cover an area from 40 to 400 Ha to a depth of 2m.

4.5.1.1 THE ENVIRONMENTAL LEGACY OF METAL MINING IN THE HALKYN MOUNTAIN AREA.

Two major studies on the environmental aspects of the mines of Halkyn Mountain were carried out in 1983 by Dr Brian Davies, University College of Wales, Aberystwyth and in 1986 by the Robinson Jones Partnership Ltd. The first study concluded that contamination of soils by lead was very widespread on the mountain and that vegetables and blood lead levels were elevated in some instances. Halkyn Mountain area contained a mosaic of wastes comprising not only lead and zinc but also other elements discarded within non-commercial minerals associated with the ore, cadmium being the most important in terms of contaminants. Their environmental significance derives from their potential toxicity to plant and animal life. The significance of these hazards was magnified in Halkyn Mountains because of the relative large local population and because of the adjacent productive agricultural land. The second report by the Robinson Jones Partnership Ltd recommended a systematic selective programme of reclamation works to achieve significant reductions in contamination. Cadmium shows an anomaly in stream water south-west of Minera, while there are no high concentrations associated with the mineralisation and mining in the Halkyn area.

4.5.2 South Wales

In south Wales, numerous small lead-zinc veins have been worked in the Carboniferous Limestones which form a narrow outcrop around the South Wales coalfield (Foster-Smith, 1981) (Figure 20). The workings occur mainly on the southern side of the coalfield, between Porthcawl and Bridgend, and their recorded total production since 1845 has been very small. Fluorite has

been reported from the Beaufort Consols mine on the Mumbles peninsula. The mineralisation is mainly confined to the Carboniferous Limestone but does extend into the unconformably overlying Trias and Lower Jurassic sediments as minor veins and disseminations in a few places such as Ogmore (Fletcher, 1988) and Llantrissant (Bowler and Kingston, 1971).

4.5.2.1 ENVIRONMENTAL SIGNATURE

As in all mining areas, the stream sediments show geochemical anomalies which are partly natural (i.e. due to mineralisation) and partly anthropogenic, related to the ore mining (British Geological Survey, 2000). In the stream sediments zinc values around 2000 mg/kg are associated with very high barium and lead concentrations in the area of mineralised carboniferous limestone south of Bridgend (British Geological Survey, 2000).

4.5.3 Mendip orefield

This orefield has been worked over a long period of time, though it has been largely derelict for well over 100 years (Figure 14). Economic mineralisation occurs in Carboniferous Limestone and the unconformably overlying Triassic Dolomitic Conglomerate (Green, 1958). The mineralisation is mainly structurally controlled, with few replacement orebodies in contrast to the Pennine deposits. It occurs in swarms of short northwest-southeast or west-northwest-east-southeast striking veins and in pore-space infilling within the Dolomitic Conglomerate (Ixer, 1993). Most traces of mining have disappeared with only a few areas of waste heaps and the remains of vein workings. The main mining areas were around Chewton Warren and Rowberrow-Shipham.

The main mineral mined was galena but secondary zinc minerals such as smithsonite (ZnCO₃) were mined for use in brass production in Bristol. Calcite was the dominant gangue mineral with some baryte; fluorite is very rare.

Total production is difficult to estimate, but the orefield may have produced in excess of 200000 tonnes of lead with some zinc (Green, 1958). Waste production is again very difficult to quantify with such a long history of working and reworking and very sparse records of production.

The village of Shipham gained some notoriety in the 1970s following the publication of the Wolfson Atlas (Webb et al. 1978) that showed high cadmium concentrations in the local soils. The cadmium was thought to have been derived from the oxidation of sphalerite. This was followed up by Philipp and Hughes (1982) who found that a known cancer risk was unlikely to be explained by the presence of cadmium.

4.6 LOWER PALAEOZOIC VOLCANOGENIC MASSIVE SULPHIDE COPPER MINERALISATION IN ANGLESEY

The Parys Mountain Cu-Pb-Zn deposit in Anglesey (Figure 20) is the largest volcanogenic massive sulphide (VMS) deposit known in Britain. It was discovered in 1768 (though it may have been worked in Roman, or even pre-historic times) and cumulative production exceeds 130000 tonnes of copper from underground workings and open pits obtained from a total estimated ore production of 3 Million tonnes. The main period of production was during the late eighteenth and early nineteenth centuries. Modern exploration started in 1955 and since then a number of companies have drilled about 300 surface and underground holes for a total length exceeding 60 km. Originally described as a vein-like structure, it was reinterpreted as Ordovician volcanogenic mineralisation of Kuroko-style by Pointon and Ixer (1980). The deposit is hosted in hydrothermally altered acid and basic volcanic and sedimentary rocks of Ordovician and early Silurian age (Tennant and Steed, 1997). Massive bedded sulphides and disseminated "feeder" veins and stockwork mineralisation occur over a zone 2 km long and up to 500 m wide. The property is currently under active exploration by Anglesey Mining plc who sank a 300 m deep exploration shaft at the western end of the deposit (Morfa Ddu) in 1990 to investigate drill-indicated reserves of 4.8 Mt at 1.5% Cu, 3.0% Pb, 6.0% Zn, 57 g/t Ag and 0.4 g/t Au. About 1

km of underground development and a large programme of underground drilling was carried out, while a small pilot plant proved the amenability of the ore to conventional processing from the production of about 2000 tonnes of material at 10% combined copper, lead and zinc that was sent to Avonmouth for smelting. Further drilling has since been carried out and the mineralised zones are still open to the north and east. Additional resources of over 30 Mt grading 0.76% Cu were indicated by earlier exploration to the north-east of the shaft site.

The main minerals are pyrite, chalcopyrite, galena and sphalerite with many other minor sulphide phases and also secondary sulphates and carbonates resulting from weathering of the insitu and waste heap sulphides. Galena and sphalerite mineralisation that occurred in so-called "bluestone" was fine-grained and intimately intergrown. The miners during the main phase of working found this impossible to treat economically and, if mined with the copper ore, was probably discarded on the tips. The whole site is covered with various thicknesses and size fractions of waste. There has also been extensive and long-lived production of small amounts of copper using precipitating ponds. The entire site covers an area of about 130 Ha and consists of two large open pits up to 300m long by over 100m wide surrounded by numerous shafts and adits and with a ring of shallow copper precipitating ponds around most of the site. These wooden-lined pits used scrap iron to precipitate copper metal. This was periodically removed and the soluble ferrous sulphate allowed to flow into the natural drainage. The open pits and underground mines were water-filled. However, in 2003 the Environment Agency and Anglesey County Council pumped all the water out of the underground workings and the open pits and now the entire site drains to the north through the Dyffryn Adda adit.

Waste production at Parys Mountain is difficult to quantify as the entire site is covered with some form of waste following two hundred years of exploitation. Some ore was calcined on site to remove or reduce the sulphur content and to produce 'copperas' (hydrated ferrous sulphate) and sulphuric acid. The whole area of 130 Ha may have some form of mine waste on it.

4.6.1 Environmental signature

Volcanogenic massive sulphide deposits are among the most likely of all deposits types to cause significant environmental problems, particularly highly acid and metal-rich mine drainage, due to the high iron sulphide mineral contents and the presence of host rocks with low buffering capacity.

The Regional Geochemistry Stream Water Atlas (British Geological Survey, 1999) indicates highly acid (pH 2.5) waters with very high concentrations of harmful elements (Cd 0.05 mg/l, Pb up to 0.170 mg/l, Ni up to 0.190 mg/l, U up to 0.012 mg/l, Zn up to 25 mg/l) at Parys Mountain and in the tributaries of the Afon Alaw which flows west from Parys Mountain towards Holyhead. High concentrations of contaminants in the waters are associated with high concentrations in stream sediments (e.g. 1469 mg/kg Zn, 11 mg/kg Ag, 3000 mg/kg Pb, 1467 mg/kg Cu).

4.7 LOWER PALAEOZOIC VOLCANIC-ASSOCIATED COPPER-LEAD-ZINC MINERALISATION

4.7.1 Lake District

The largest metal mine in the Lake District (Figure 17), Greenside above Ullswater, produced over 200000 tonnes of lead at an average grade of about 7% (Gough, 1965) from a single vein in the Ordovician Borrowdale Volcanic Formation. The mineralisation consists of galena with subsidiary sphalerite and minor chalcopyrite. The mine was worked to a final depth of 600 m before final closure in 1962. Chalcopyrite, with quartz, pyrite, arsenopyrite and, locally, some magnetite and Co-Ni-As sulphides, has been worked from several sites, most productively in the Coniston area. The mineralisation at Coniston occurs in breccia veins also in the Borrowdale Volcanic Formation (Stanley and Vaughan, 1982; Millward et al., 1999). The mineralisation is

complex; the main minerals are chalcopyrite and pyrite, but significant amounts of magnetite and arsenopyrite also occur together with galena, sphalerite, barite and fluorite and traces of antimony and other elements. Numerous other small metal mines were worked in the Lake District, especially in the Caldbeck Fells, where over 100 mineral species have been reported www.mindat.org (usually in trace amounts). They include a wide variety of antimony, arsenic, copper, iron, lead and zinc secondary arsenates, carbonates, phosphates and sulphates.

Carrock Fell mine worked several small quartz-greisen veins in Caledonian Skiddaw granite and Ordovician Skiddaw slates with a minor production of tungsten from scheelite and wolframite. This site has now been completely restored since final closure of the mine in the early 1980s.

The Greenside production figure implies a waste production of around 2 million tonnes covering an area of 40 Ha to a depth of 2 m. The Greenside site covers about 11 Ha on the current 10K OS map which in reasonable agreement with this figure as the waste tips are significantly higher than 2 m. The Greenside tips are directly above Ullswater and abnormal rainfall could cause significant erosion of the tailings into the lake. Coniston mine produced around 4500 tonnes of copper from 53000 tonnes of ore grading 5 to 13 % Cu (Dunham et al., 1978), implying a waste production of up to 500000 tonnes. The Coniston site, including the waste tips, covers about 5 Ha.

4.7.2 Characterisation of the waste and environmental signature

Very high lead level (many > 5000 mg/kg) associated with high arsenic, cadmium and zinc are present in stream sediments around the former mine workings of Carrock, Drygil, Driggith, Hay Gill and Roughton Gill in the Caldbeck Fells from the Eycott volcanic group outcrop.

Force Crag has numerous large areas of mine spoil, containing significant amounts of veinstone. Fine-grained mill tailings are also common. Dumps are enriched in: baryte, todorokite, sphalerite, galena, bournonite, native antimony, chalcopyrite, pyrite, siderite, cerussite, fluorite, malachite and native silver.

Coniston copper mine contains extensive workings and spoil heaps over large area enriched in Cu, As, Pb, Zn, Ni, Co, Bi, Te. Outcrops and dumps contain quartz, chlorite, chalcopyrite, arsenopyrite, tennanite, pyrite and magnetite. Also bismuth and nickel minerals are present. Tailings flush into streams which drain into Levers Water reservoir.

Greenside mine at Glenridding was one of the last mines to close in Cumbria in 1962 (Denny, 1981). The author reported at the time of his study elevated levels of metals, especially lead, in the aquatic ecosystem of the receiving waters of Ullswater lake.

4.7.3 Snowdonia

A number of minor Cu-Pb-Zn volcanogenic vein and stockwork deposits occur within the Snowdon caldera (Reedman et al., 1985) in Ordovician volcanic and Cambrian and Ordovician sedimentary rocks. They are interpreted as filling volcano-tectonic faults. Production has been minimal and waste tips are small, though the terrain means that they are spread downwards on slopes from the mine entrances and are extensively weathered. The mineralisation consists of pyrite, pyrrhotite, chalcopyrite, galena and sphalerite in quartz. Calcite occurs in a few mines.

The largest area is in the Nantlle valley, associated with the workings of the Drws-y-Coed copper mine in Cambrian quartzites (Figure 20). This has been worked over hundreds of years to a maximum depth of 480ft (Bick, 1982). Total production is likely to have been less than 100000 tonnes of ore. A Kuroko-style massive pyrite deposit at Cae Coch, north-east of Snowdon, produced about 200 000 tonnes of pyrite for sulphur during World War I and II (Ball and Bland, 1985). The high-grade massive pyrite orebody produced relatively little waste material but this is

spread thinly over several hundred metres of a steep hillside and is pyrite-rich. The total area of the Cae Coch mines and waste is about 2 Ha from the 1920s OS map.

4.7.4 Characterisation of the waste and environmental signature

Spoil from the mining of the Snowdon mining field has had a strong impact on the geochemistry of the surface environment (British Geological Survey, 2000).

The mines in the central Snowdonia copper mining area (around Cwm Pennant), Beddgelert and Snowdon show a strong copper signature in the stream sediments, several sites giving values in excess of 900 mg/kg. Although the area around Snowdon was predominantly a copper-mining district, lead and zinc ores were also present in some quantity and are responsible for the Pb anomalies in stream sediments in the area (e.g. 4818 mg/kg near the old Lliwedd mine, 4000 mg/kg near Hafod-y-llan mine and crushing mill). These mines tipped tailings directly into the adjacent watercourses. Low anomalies of pH values at Beddgelert correspond to acid mine drainage associated with Sygun copper mine.

The extent and intensity of contamination depends on many factors, including the type of waste material, the topography of the local area, the size and velocity of the local streams and proximity of the tips to the stream.

4.7.5 Llanwrst

The Llanwrst mining field (Figure 20) has produced tonnes of lead and tonnes of zinc from more than 20 mines over an area of 20 km² working veins up to 20 m wide in Ordovician volcanic and sedimentary rocks. The dominant minerals are galena, sphalerite and pyrite in a quartz gangue. The two largest mines are Trecastell and Parc. Trecastell produced an estimated 6552 tons of lead concentrates and 12 716 tons of zinc concentrates between 1893 and 1913. Parc finally closed in 1962.

4.7.6 Characterisation of the waste and environmental signature

Very high levels of lead (up to 16200 mg/kg) are present in the sediments associated with high Ag, Cd, Cu, Sb and Zn (in many sites more than 4000 mg/kg) at the Llanwrst Pb-Zn mining field (British Geological Survey, 2000). Many sites show high zinc concentrations in stream water ranging from 25 to 3000 μ g/l in neutral pH water (British Geological Survey, 1999).

4.8 LOWER PALAEOZOIC SHALE-HOSTED LEAD-ZINC AND BARYTE VEINS.

4.8.1 West Shropshire

The West Shropshire mining field covers an area of about 40 sq km from Shelve to Habberley, southwest of Shrewsbury (Figure 20). The largest mines were Snailbeach and Huglith, with over 40 smaller mines. The area has produced over 235650 tonnes of lead and 18994 tonnes of zinc between 1845 and 1913 and 566 505 tons of baryte between 1860 and 1944 (Dines, 1958).

The mines worked narrow veins in Precambrian and Lower Paleozoic sedimentary and volcanic rocks. Most metal mines were in the Lower Palaeozoic Ordovician Mytton Flags, a thick series of mudstones. The main baryte mines were in late Precambrian Longmyndian sandstones. The main ore minerals were galena and sphalerite, with some baryte and minor witherite, in a calcite gangue. The silver content of the galena was relatively low at around 50 g/t of lead.

The Snailbeach mine was worked to a total depth of 552 yards (about 500 m) and produced 131913 tons of lead ore, 4392 tons of zinc ore and 42327 tons of baryte. The main vein was generally less than 3 m wide though occasionally it was over 7 m wide. The Huglith mine worked almost massive baryte (75-95 % BaSO₄) in an east-west vein up to 6 m wide

accompanied by minor quartz and traces of copper minerals, such as chalcocite, malachite and azurite, and bitumen. Huglith produced a total of 295108 tons of baryte.

4.8.1.1 CHARACTERISATION OF THE WASTE AND ENVIRONMENTAL SIGNATURE

The Snailbeach mine had a landmark white tip, consisting mainly of calcite, but with significant quantities of sphalerite, galena and other sulphides (Figure 19). Following concerns of metal-rich dust and drainage the tip was landscaped and remodelled in the late 1990s by Shropshire County Council to cover most of the exposed waste material, leaving a small portion for mineral collecting.

To the north of the Shelve district, lead concentrations in stream water between 35 and 90 μ g/l were reported at 5 sites along a 9 km reach of Rea Brook, which passes through areas of former metal mining, including Callow Hill, Wrentnall, Batholes and Snailbeach (British Geological Survey, 1999). These are also associated with a cluster of high cadmium values (5-21 μ g/l). Pennerley, Snailbeach, Tankerville, White Grit sites showed anomalously high zinc concentrations (>1 mg/l) in near neutral pH water.

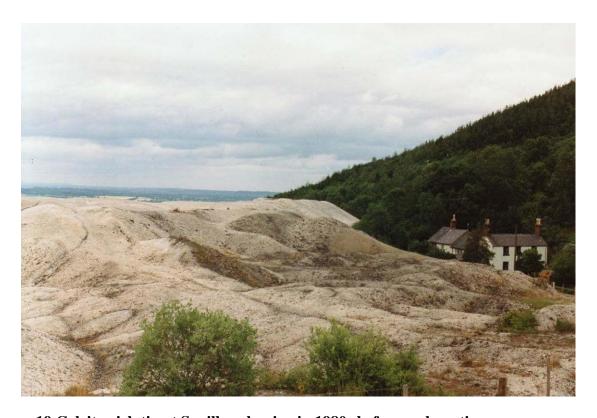


Figure 19 Calcite-rich tip at Snailbeach mine in 1980s before reclamation.

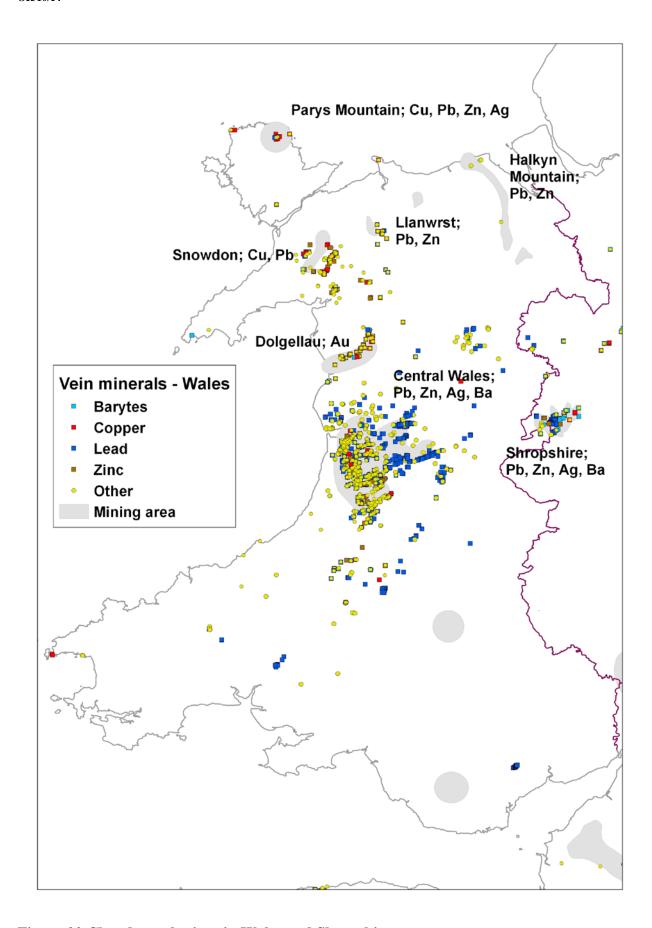


Figure 20 Closed metal mines in Wales and Shropshire.

4.8.2 Central Wales

The Central Wales mining field (Figure 20) has produced 486296 tonnes of lead concentrates averaging 75 % lead and 153193 tonnes of zinc concentrates of about 35-40 % zinc from over 250 mines in Lower Palaeozoic Ordovician and Silurian sedimentary rocks (Davies et al., 1997; Jones, 1922). The mines were worked intermittently over many hundreds of years; the main period of production and greatest output was between 1850 and 1870. Mining finally ceased in the 1920s, though attempts to recover metal from numerous waste tips continued for many years.

4.8.2.1 ORE MINERALS AND HOST ROCKS

The main host rocks to the mineralisation are Silurian mudstones and greywackes (muddy sandstones) deposited in a thick series of sediments in the Welsh Basin. The mineralisation occurs as narrow veins of quartz and sulphides, up to 2 m wide, within wider zones of faulting up to 30 m across. The veins are commonly brecciated with angular to rounded fragments of sulphides, quartz and country rock within the whole fault zone. Consequently much waste contained small amounts of unrecoverable fragments of metal sulphide. The main ore minerals were galena and sphalerite, with quartz as the main gangue mineral. Copper ore (chalcopyrite and secondary minerals such as malachite) were rare, being worked only in small quantities at Esgairfraith and in much smaller amounts elsewhere. Calcite is very rare in the orefield, only being abundant at Nantiago. The galena is notably silver-rich averaging around 100 g per tonne of lead. Cadmium occurs in association with sphalerite. Pyrite in small amounts commonly accompanied the mineralisation and was recovered at Ystumtuen mine. Baryte is not common in the orefield but over 4000 tonnes were produced from the Bryntail and Pen-y-Clun mines in the east of the district.

There were two main periods of mineralisation; an early fine-grained complex stage consisting of finely intergrown galena and sphalerite with minor amounts of copper, silver, nickel and cobalt sulphides and a later, coarse-grained galena-rich stage.

The largest mines, in terms of recorded output of combined lead and zinc, were Van, Frongoch, Logaulas, Dylife and Cwmystwyth. Frongoch was also the largest zinc producer. The recorded outputs, as with many British metal mines, may not be a true measure of the actual total output. Table 11 shows the twenty largest mines in terms of recorded output.

Waste production is again estimated using the production figures. Using the production of almost 500000 tonnes of lead concentrates the waste production can be estimated at between 1000000 and perhaps 5000000 tonnes implying a total area of waste of between 40 and 200 Ha to a depth of 2m. Significant, but unrecorded, amounts of waste have been removed by erosion and for other purposes since the mines closed so the actual area may be significantly less than these totals.

4.8.2.2 CHARACTERISATION OF THE WASTE AND ENVIRONMENTAL SIGNATURE

Zinc in stream waters near the mines Cwmystwyth, Daren, Dylife, Frongoch, Glogfawar, Goginan, Llanerchyraur has concentrations greater than 300 μ g/l in neutral pH (6.5-7.5) (British Geological Survey, 1999). Conversely, some samples near former mines have low Zn concentrations. Several cadmium anomalies are associated with Pb-Zn mineralisation and mining, notably near Llanidloes (15-30 μ g/l) downstream of the Van mine. Lead contamination in stream water is associated with former mine sites in the catchments of the Reidhol, Ystwyth and Dulas river. The highest lead concentration (3000 μ g/l) was reported in stream water of a tributary of the Afon Marchnant adjacent to the old lead mines of Esgairmwyn and South Lisburne.

Summary statistics of geochemical data for 823 stream sediment samples from the central Wales mining field (British Geological Survey, 2000) is reported in Table 12.

Table 11 Recorded metal production from central Wales (Jones, 1922)

	Lead	Zinc	Silver	Copper	
Mine	tonnes	tonnes	OZ	tonnes	
Van	96739	28424	756142		
Frongoch	57369	52854	20153		
Logaulas	39004		19668		
Dylife	35505	391	126286	1342	
Cwmystwyth	32912	18913	33509		
Goginan	25107	60	170120		
DarenEast	24460		415850	95	
Glogfawr	18520		64317		
Esgairmwyn	10430		122075		
Cwmerfin	9919	36	182594	60	
Glogfach	9880		132568		
DarenSouth	9248	196	173527	1047	
Grogwynion	8874		29322		
Bwlch	7750	6	74784		
Llanerchyraur	7198		36423		
Bronfloyd	6423		35024	23	
Cwmbrwyno	6095	796	7383		
Brynrafr	4952	8116	6886		
Dyfngwm	4930		10356	134	

Table 12 Summary statistics of geochemical data for 823 stream sediment samples from the central Wales mining field (British Geological Survey, 2000)

Element mg/kg	Mean	Maximum
Cu	59.3	7000
Pb	648	11000
Zn	265	4500
Cd	1.87	149
Ag	3.55	332
Ba	558	2669

4.8.3 Llanfair-Talhaiarn

Several mines were worked for lead – zinc and sometimes also copper in the Llanfair – Talhaiarn mining district in North Wales in Silurian sediments. The main deposits were the Llanfair mine, worked mainly for copper ore and Nant-y-Plwm lead mine. The main gangue mineral was calcite. The Pennant mine near St Asaph was worked for barite in similar rocks. There is, unusually, a comment on the waste at the Pennant mine in Dewey and Smith (1922) that "The refuse-heaps from the old lead-workings are extensive, and contain much zinc-blende (sphalerite), barytes and witherite. These dumps, ½ mile in length and about 100 feet wide, are

considered to have a total contents exceeding 100000 tons. In some places they are being worked over for barium-minerals and for what little galena can be got".

4.8.4 Lleyn Peninsula

Several small areas were worked for manganese, lead, copper, zinc and barytes in the Lleyn Peninsula in North Wales.

The Benallt and Nant mines worked a series of lenticular manganese deposits in Lower Ordovician mudstones associated with intrusive volcanic rocks. The main manganese minerals are rhodocroisite and pennantite. The mines were active between 1894 and 1928 and produced a total of around 200000 tons of ore. (Dunham et al., 1978)

The Llanengan mine worked a 5.5 km long fault zone and has a recorded production of 20570 tons of silver-rich lead ore, 2628 tonnes of zinc ore and 8254 tonnes of copper ore between 1870 and 1892. Pompren mine, near Aberdaron, produced some baryte from a lode up to 3 m wide.

4.9 PRECIOUS - METAL VEIN MINERALISATION

Several areas of Britain have produced minor amounts of gold. The most important have been the Dolgellau area of North Wales, where auriferous quartz veins in Cambrian shales have yielded a total of about 4 tonnes of gold, and the Pumpsaint area of central Wales where auriferous quartz veins cut pyritic Silurian shales.

4.9.1 North Wales

The Dolgellau Gold Belt occurs within Middle and Upper Cambrian sediments with numerous intrusions of "greenstone" (basic to intermediate volcanic rocks) on the southern and eastern flanks of the Harlech Dome. The gold is associated with massive SW-NE trending mesothermal quartz veins up to several metres wide and several kilometres long (Shepherd and Goldring, 1993). The distribution of gold is very sporadic. At Clogau St. David's mine it occurs in small, rich, steeply-dipping shoots associated with pyrite and pyrrhotite together with galena and bismuth tellurides. The veins are often auriferous where they cut graphitic shales but not where the host rocks consist of non-graphitic arenites. Grades have been poorly recorded but averaged over 30 g/t Au in 1900 with very selective mining. Gold shoots generally occur at the intersections of side lodes, where greenstone and shale form the wall rocks and at braided structures with enclosed lenses of shale (Shepherd and Goldring, 1993). The Clogau St. David's and Gwynffynydd mines have recently been further evaluated and some development has been pursued but both are now closed. Grades from bulk samples of the Clogau St. David's evaluation range up to 7.9 g/t Au (Bottrell et al., 1988). The production of 4 tonnes of gold at a historic grade of around 30 g/t, although this is difficult to quantify due to the bonanza nature of the ore shoots, implies the production of around 100 000 t of waste containing variable amounts of pyrite and other sulphides. Mercury was used to recover fine grained gold; small amounts of metallic mercury can be panned from the local streams.

4.9.2 Central Wales

The Ogofau mine near Pumpsaint has produced about 800 kg of gold from quartz veins cutting pyritic Silurian shales. Roman working is thought to have recovered about 1000 kg of gold from about 1 million tonnes of rock (Annells and Burnham, 1996). The shales are folded in an anticline and cleaved with development of crosscutting and saddle-reef quartz veins. Gold has been remobilised into some of the quartz veins and into fractures in pyrite and arsenopyrite (Annells and Roberts, 1989). Grades were around 7 g/t Au during the last period of working in 1938 but recovery was poor. Much waste rock has now been removed.

4.10 SEDIMENT-HOSTED RED-BED COPPER DEPOSITS

Several small sediment-hosted red-bed copper deposits occur in the Cheshire Basin. The largest is the Alderley Edge deposit, which produced a recorded total of about 170000 t of ore containing about 3200 t of recovered copper. The mineralisation is in Triassic sandstones and conglomerates and consists of baryte, chalcopyrite and galena impregnations and veins in areas of bleached or altered rock adjacent to faults (Warrington,1966; Carlon, 1979). Small amounts of cobalt and vanadium have also been recovered.

4.11 COPPER MINERALISATION IN DINANTIAN LIMESTONE

There are several small replacement copper deposits in Dinantian limestone at Middleton Tyas, near Ripon in northern England (MRP 54), at Ecton on the west side of the Southern Pennine Orefield (Robey and Porter, 1972) and at Llandudno on the North Wales coast (Williams, 1993). The Ecton deposit occurs within a 400 m long vertical pipe-like body of massive calcite and chalcopyrite (Critchley, 1979) and produced around 15000 t of copper in the eighteenth century. The Llandudno deposit occurs over a strike length of 100 m, with chalcopyrite mineralisation occurring as vein fillings in dolomitised limestone (Ixer and Vaughan, 1997). Waste production from all these areas is significant; for example the Ecton mine probably produced in excess of 100000 tonnes of waste, mainly as limestone, as the ore was hand-cobbed to extract as much chalcopyrite as possible. Much of the waste has been removed for various purposes.

4.12 MERIONETH MANGANESE DEPOSITS

Manganese has been produced in two areas of North Wales in the former county of Merioneth (Down, 1980). An extensive 40 cm bed of syn-diagenetic origin has been worked in Cambrian shales for rhodocroisite (MnCO₃) and spessartine (Mn₃Al₂(SiO₄)₃) around the Harlech Dome. Small veins of psilomelane and pyrolusite have also been worked in the Arenig area north-west of Bala Lake. Total production was around 60000 tonnes from over 60 small mines (Linton, 2009). The main period of working was the late 1800s; the ore was used in the steel and bleaching industries. Mining was entirely by hand from small open pit and shallow underground workings. Little or no waste was produced from these very small operations.

4.13 IRON ORE DEPOSITS

Britain has been a major producer of iron ore, but only small amounts are mined now. The main areas of production are illustrated in Figure 21. The main types of ore worked are described in the following paragraphs.

4.13.1 Bilbao-type replacement and vein hematite deposits in Carboniferous Limestone

Bilbao-type replacement and vein hematite (Fe₂O₃) deposits with grades of around 45 % Fe have been worked in Carboniferous Limestone in west and south Cumbria (Roseand Dunham, 1977; Shepherd and Goldring, 1993), in South Wales (Gayer and Criddle, 1969) and the Forest of Dean (Sibly, 1927). Total production has been about 250 Mt from the Cumbria orefields, 8 Mt from Llanharry in South Wales and 10 Mt from the Forest of Dean (Dunham et al., 1978). The amount of waste was estimated at 30 % for the Park mines in the southern Lake District (Smith, 1924). If this figure was repeated throughout the orefield this would mean a total waste output of around 80 Mt. Much of this 'waste' in the Park mine was limestone which could have been used for construction purposes. Minor amounts of fluorite and baryte occurred with the iron ores and have been found on the tips. Some of the deposits around Barrow in Cumbria, such as Hodbarrow, were notable for their formation by the dissolution of the limestone country rock.

4.13.2 Minette-type Jurassic and Cretaceous ironstones

These are Lower and Middle Jurassic bedded sedimentary low-grade (20 to 35% Fe) ironstone deposits in the East Midlands, Cleveland and Oxfordshire (Young, 1993) and similar Lower Cretaceous deposits at Caistor and Claxby, below the chalk Wolds in north Lincolnshire (Breward, 2007). These were worked on a large scale at the rate of 10 to 15 Mt/yr up to 1970 (Dunham et al., 1978). Production has now ceased. They occurred as major bedded deposits of low-grade (20-35% Fe) ore up to 10 m thick which were generally worked by open-cast methods. Underground mining was carried out in Cleveland on Teesside and at Scunthorpe and Claxby in north Lincolnshire. In some areas of opencast working the ratio of waste to ore was 18:1. In the early days of the industry large areas were left with serious problems of landscape devastation production of a "hill and vale" topography which was reclaimed by forestry. This led to the Mineral Workings Act 1951, which set up the Ironstone Restoration Fund to actively promote the restoration of former and current ironstone workings. This scheme has worked well. For example in the county of Northamptonshire 567 hectares were derelict from ironstone workings in 1952. By 1965 486 hectares of this area had been restored and the total area restored in the county, including that from operations since 1952, was more than 1620 hectares (Blunden, 1975). There is thus almost no land covered by spoil tips from ironstone mining in the East Midlands, though significant areas occur in North Yorkshire associated with the Cleveland ironstone mines and in West and South Cumbria where the Ironstone Restoration Fund did not apply.

4.13.3 Westphalian ironstones

Carboniferous (Westphalian) "Blackband" and "Clayband" bedded ironstones have been mined in many coalfields, especially North Staffordshire and the Low Moor area of South Yorkshire. The mineralisation occurred as thin bands of ironstone nodules up to 1.5 m thick associated with, or separate from, the coal seams. Mining was by hand, with little mechanised mining. Much of the ore sorting would have been done underground, thus relatively little waste was raised. There were numerous small mines, each producing a waste tip near the shaft. The main period of production was in the 19th century; mining ceased around 50 years ago (Slater and Highley, 1976). As most of the production is in, or close to, urban areas, removal and restoration of associated waste is almost complete. The total production of the Coal Measures ironstones is estimated at 211 Mt (Slater and Highley, 1976).

4.13.4 Others

There was substantial (for the time) production from vein and replacement deposits in the Northern Pennine Orefield (Dunham, 1990). A total of about 1.5 million tonnes of iron ore was produced mainly for smelting Ordovician oolitic bedded iron ores were worked in North Wales (Trythall, 1989). There are also numerous small vein and bedded deposits in Southwest England. A summary of British iron ore deposits is given in Slater and Higley (1976).

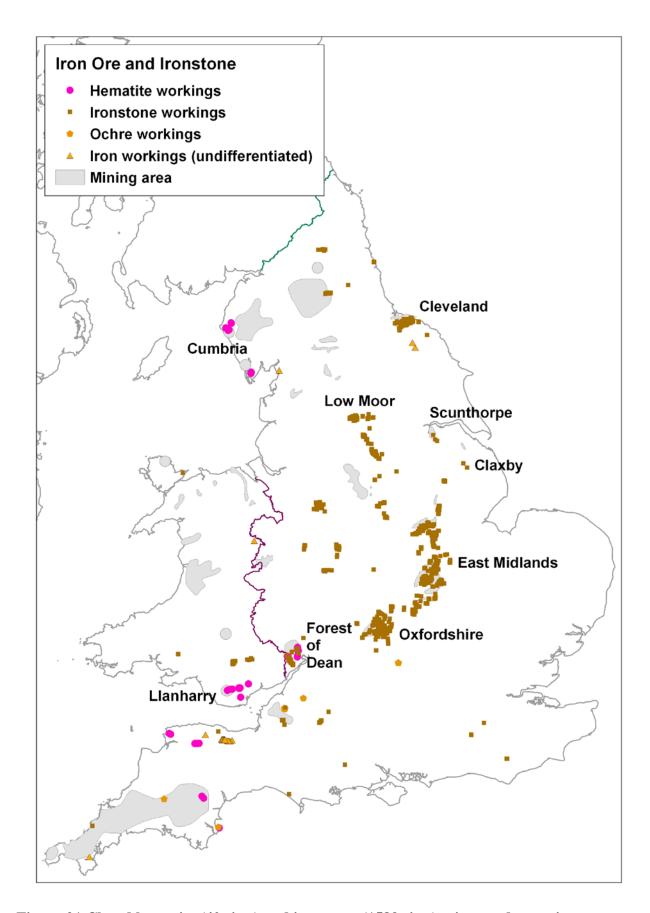


Figure 21 Closed hematite (40 sites) and ironstone (1589 sites) mines and quarries.

Table 13 Key features of all the ironstones of England and Wales

Area	Туре	Tonnage mined (est)	Waste tonnage (est)	Waste area Ha (est)	Start	Finish
Northampton Sand Ironstone	Minette	400000000	800000000	4000	1853	1974
Cleveland ironstone	Minette	371500000	743000000	3715	1850	1964
Frodingham ironstone	Minette	257000000	514000000	2570	1859	1975
West Cumberland	Bilbao	102000000	51000000	255	1855	1999
Furness and South Cumberland	Bilbao	80000000	40000000	200	1859	1968
Marlstone Rock Bed Grantham	Minette	70000000	140000000	700	1855	1980
North Staffordshire coalfield	Westphalian	65000000	32500000	163	1858	1949
Marlstone Rock Bed Banbury	Minette	32000000	64000000	320	1940	1967
South Staffordshire & Worcestershire coalfield	Westphalian	23000000	11500000	58	1858	1938
South Wales coalfield	Westphalian	17411000	8705500	44	1855	1917
Glamorgan	Bilbao	9200000	4600000	23	1859	1974
Shropshire coalfield	Westphalian	8450000	4225000	21	1858	1938
Forest of Dean	Bilbao	4763000	2381500	12	1842	1940
Westbury ironstone	Other	3100000	1550000	8	1856	1923
Northern Pennine Orefield (West Rigg)	Other	1548000	774000	4	1842	1946
North Wales coalfield	Westphalian	1360000	680000	3	1855	1911
Cornwall (Higher Ludbrook)	Other	1000000	500000	3	1855	1875
Yorkshire, Nottinghamshire & Derbyshire coalfield	Westphalian	1000000	500000	3	1800	1900
Claxby ironstone	Minette	1000000	2000000	10	1868	1969
Brendon Hills	Other	875,000	437500	2	1850	1909
Warwickshire coalfield Northumberland & Durham	Westphalian	645000	322500	2	1873	1938
coalfield	Westphalian	592000	296000	1	1869	1879
N Wales ironstones	Other	306000	153000	1	1855	1915
Perran Lode	Other Westphalian	227000	113500	1	1854	1943
Bristol & Mendip Seend ironstone	Other	213000 170000	106500 85000	0	1856 1855	1890 1874
Restormel (St Austell)	Other	130000	65000	0	1855	1910
Wealden ironstone	Other	100000	50000	0	1033	1750
Somerset & Gloucester coalfield	Westphalian	92000	46000	0	1856	1883
Great Rock, Hennock	Other	51000	25500	0	1858	1969
West Cumberland coalfield	Westphalian	25000	12500	0	1873	1909
Lancashire coalfield Minette and Bilbao estimated of	Westphalian	15000	7500	0	1874	1885

Minette and Bilbao estimated ore: waste is 1:2 Westphalian and other estimated ore: waste is 2:1

5 Conclusions

- 1. There are many thousands, probably tens of thousands of closed and abandoned mines and quarries in England and Wales; most of these will have some form of waste facility or tip.
- 2. Most of these waste facilities have been abandoned for many years, usually without a reported incident. Most metal mines and their tips have been abandoned for over 100, often over 200 years.
- 3. Many of them, especially coal and ironstone tips, located in populated area, have been reclaimed for other profitable uses as "brownfield" sites.
- 4. The amount of waste in tips was not measured as it had no value. The areas of coal tips may have been measured as land had to be bought to contain them, but it is unlikely that the volume was measured. Estimates of waste volume, and its contents of metals and other potentially harmful substances, are therefore highly subjective. On-site measurements and analyses are required to obtain the actual physical and chemical parameters of any tip.
- 5. Tips associated with construction and industrial minerals are unlikely to present any environmental problems, apart from stability and visual issues with large slate and china clay tips.
- 6. Most major coal tips have been checked and stabilised, according to the practice of the time, but some remain on unstable ground and may therefore still present a risk.
- 7. Coal mine tips may present some problems of acid drainage and minor content of hazardous elements.
- 8. Most metal mine tips may contain hazardous elements and acid-generating minerals which may pose a risk to human and animal health and to the wider environment.
- 9. The use of geoenvironmental models of metal mineral deposits can assist in the assessment of the environmental signature of abandoned mine sites. However, due to the variability of individual mineral deposits within the generic model, on-site sampling and analysis is required to decide if a particular tip requires attention or remediation.
- 10. The current project has outlined the kinds of environmental problems that may be associated with the different mineral deposit types and the locations of the main areas which may contain mine waste likely to give rise to environmental problems.

Appendix 1 Extracts from Council Directive 91/689/EEC

ANNEX II OF COUNCIL DIRECTIVE 91/689/EEC

CONSTITUENTS OF THE WASTES IN ANNEX I.B. WHICH RENDER THEM HAZARDOUS WHEN THEY HAVE THE PROPERTIES DESCRIBED IN ANNEX III (*)

- C1 beryllium; beryllium compounds;
- C2 vanadium compounds;
- C3 chromium (VI) compounds;
- C4 cobalt compounds;
- C5 nickel compounds;
- C6 copper compounds;
- C7 zinc compounds;
- C8 arsenic; arsenic compounds;
- C9 selenium; selenium compounds;
- C10 silver compounds;
- C11 cadmium; cadmium compounds;
- C12 tin compounds;
- C13 antimony; antimony compounds;
- C14 tellurium; tellurium compounds;
- C15 barium compounds; excluding barium sulfate;
- C16 mercury; mercury compounds;
- C17 thallium; thallium compounds;
- C18 lead; lead compounds;
- C19 inorganic sulphides;
- C20 inorganic fluorine compounds, excluding calcium fluoride;
- C21 inorganic cyanides;
- C22 the following alkaline or alkaline earth metals: lithium, sodium, potassium, calcium, magnesium in uncombined form;
- C23 acidic solutions or acids in solid form;
- C24 basic solutions or bases in solid form;
- C25 asbestos (dust and fibres);
- C26 phosphorus: phosphorus compounds, excluding mineral phosphates;
- C27 metal carbonyls;
- C28 peroxides;
- C29 chlorates;
- C30 perchlorates;
- C31 azides;
- C32 PCBs and/or PCTs;
- C33 pharmaceutical or veterinary coumpounds;
- C34 biocides and phyto-pharmaceutical substances (e.g. pesticides, etc.);
- C35 infectious substances;
- C36 creosotes;
- C37 isocyanates; thiocyanates;
- C38 organic cyanides (e.g. nitriles, etc.);
- C39 phenols; phenol compounds;
- C40 halogenated solvents;
- C41 organic solvents, excluding halogenated solvents;
- C42 organohalogen compounds, excluding inert polymerized materials and other substances referred to in this Annex;
- C43 aromatic compounds; polycyclic and heterocyclic organic compounds;
- C44 aliphatic amines;
- C45 aromatic amines;
- C46 ethers;
- C47 substances of an explosive character, excluding those listed elsewhere in this Annex;
- C48 sulphur organic compounds;
- C49 any congener of polychlorinated dibenzo-furan;
- C50 any congener of polychlorinated dibenzo-p-dioxin;
- C51 hydrocarbons and their oxygen; nitrogen and/or sulphur compounds not otherwise taken into account in this Annex.

ANNEX III ON HAZARDOUS WASTE OF 91/689/EEC

PROPERTIES OF WASTES WHICH RENDER THEM HAZARDOUS

H1 'Explosive': substances and preparations which may explode under the effect of flame or which are more sensitive to shocks or friction than dinitrobenzene.

H2 'Oxidizing': substances and preparations which exhibit highly exothermic reactions when in contact with other substances, particularly flammable substances.

H3-A 'Highly flammable':

- liquid substances and preparations having a flash point below 21 °C (including extremely flammable liquids), or
- substances and preparations which may become hot and finally catch fire in contact with air at ambient temperature without any application of energy, or
- solid substances and preparations which may readily catch fire after brief contact with a source of ignition and which continue to burn or to be consumed after removal of the source of ignition, or
- gaseous substances and preparations which are flammable in air at normal pressure, or
- substances and preparations which, in contact with water or damp air, evolve highly flammable gases in dangerous quantities.
- **H3-**B 'Flammable': liquid substances and preparations having a flash point equal to or greater than 21 °C and less than or equal to 55 °C.
- **H4** 'Irritant': non-corrosive substances and preparations which, through immediate, prolonged or repeated contact with the skin or mucous membrane, can cause inflammation.
- **H5** 'harmful': substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may involve limited health risks.
- **H6** 'Toxic': substances and preparations (including very toxic substances and preparations) which, if they are inhaled or ingested or if they penetrate the skin, may involve serious, acute or chronic health risks and even death.
- **H7** 'Carcinogenic': substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may induce cancer or increase its incidence.
- **H8** 'Corrosive': substances and preparations which may destroy living tissue on contacts.
- **H9** 'Infectious': substances containing viable micro-organisms or their toxins which are known or reliably believed to cause disease in man or other living organisms.
- **H10** 'Teratogenic': substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may induce non-hereditary congenital malformations or increase their incidence.
- **H11** 'Mutagenic': substances and preparations which, if they are inhaled or ingested or if they penetrate the skin, may induce hereditary genetic defects or increase their incidence.
- H12 Substances and preparations which release toxic or very toxic gases in contact with water, air or an acid.
- **H13** Substances and preparations capable by any means, after disposal, of yielding another substance, e.g. a leachate, which possesses any of the characteristics listed above.
- H14 'Ecotoxic': substances and preparations which present or may present immediate or delayed risks for one or more sectors of the environment.

Glossary

Elements and minerals

Ag – Silver. A precious metal often extracted from galena.

As – Arsenic. A poisonous carcinogenic metalloid element

Ba – Barium. A very reactive metal generally found in nature as baryte.

Baryte – a white dense mineral used in oil drilling muds, paints and paper. Consists of barium sulphate (BaSO₄).

Cassiterite – a dark brown dense mineral that is the main ore of tin. Consists of tin oxide (SnO₂)

Chalcopyrite – a yellow sulphide mineral that is the main ore of copper. Consists of copper iron sulphide (CuFeS₂)

Cd – Cadmium. A hard poisonous metal that occurs in sphalerite in concentrations up to 0.2 %.

Co – Cobalt. A hard metal associated in trace amounts with the tin – copper ores of SW England.

Cu – Copper. Red-brown, dense metal important for electrical applications due to its high conductivity. Generally extracted from chalcopyrite.

F – Fluorine. A poisonous gas, similar to chlorine, found in fluorite. Used in many chemical applications.

Fe – Iron. A dense hard metal generally extracted from hematite, magnetite or ironstone.

Fluorite – a colourless mineral that is the main ore of fluorine. Consists of calcium fluoride (CaF_2) .

Fluorspar – a commercial name for fluorite mineral.

Galena – a silvery dense mineral that is the main ore of lead. Consists of lead sulphide (PbS). Can also contain up to 0.1% silver.

Hematite – a blood-red dense mineral that is one of the main ores of iron. Consists of iron oxide (Fe₂O₃).

Magnetite – a black dense naturally magnetic mineral that is one of the main ores of iron. Consist of iron oxide (Fe_3O4)

Pb – Lead. A dense soft poisonous metal generally extracted from galena.

Pyrite – a brassy dense mineral that is responsible for generating Acid Mine Drainage (AMD) during weathering of metal mines and tips. Consists of iron sulphide (FeS₂).

Sphalerite – a variably coloured mineral that is the main ore of zinc. Consists of zinc sulphide (ZnS). Usually contains up to 0.2% cadmium and up to 10% iron.

Witherite – a rare, white, dense poisonous mineral that was used in paint manufacture. Consists of barium carbonate (BaCO₃).

Zn – Zinc. A silvery metal used in die casting and galvanising. Generally extracted from sphalerite.

Mining terms

Acid Mine Drainage (AMD) – production of sulphuric acid by the weathering of pyrite and other sulphide minerals in mines and spoil tips. Can carry heavy metals, such as copper, iron lead and zinc, in solution and deposit them away from the site of production or contaminate water courses and groundwater.

Acid Rock Drainage (ARD) – naturally occurring production of sulphuric acid from the weathering of rock containing pyrite. See also Acid Mine Drainage.

Beneficiation – the process of concentration of the valuable components of an ore or other mineral commodity. Commonly includes multiple stages such as crushing, grinding, washing, screening, flotation, roasting, etc

Bilbao-type hematite deposit – mineral deposit of massive, irregular and discordant hematite formed by the replacement of carbonate (limestone) host rocks through the action of acidic iron-rich mineralising solutions.

Buddle – circular arrangement in which finely divided ore, in water, is delivered from a central point and flows gently to the perimeter. The heaviest and coarsest particles settle, while the lightest overflow.

Buddling – to separate ore from slime or stamp work by means of a buddle.

Carbonate – a mineral characterised by a fundamental structure of CO₃. Common examples include calcite, dolomite, magnesite and siderite. Limestone and chalk are mainly composed of carbonate minerals.

Chalcophile – metals that have a low affinity for oxygen and prefer to bond with sulphur to form sulphides. They include Antimony, Arsenic, Bismuth, Cadmium, Copper, Lead, Mercury, and Zinc.

Cobbing – the breaking of rocks to gravel size (3 cm) to enable waste to be picked out.

Evaporite – a sedimentary rock composed mainly of minerals produced by evaporation, normally from an enclosed body of seawater or a salt lake. Minerals formed in this way include gypsum, rock salt, potash and various nitrates and borates.

Froth flotation – a process by which some mineral particles are induced to become attached to bubbles and thereby to float, while others sink. Thus valuable minerals in an ore are separated from other components and concentrated. The minerals must be finely ground before flotation.

Gangue – the undesirable or unwanted minerals in an ore deposit.

Host rock – the unmineralised body of rock surrounding a mineral deposit. See also wall rock.

Jig – a device that separates coal or ore from foreign matter, by means of their difference in specific gravity, in a pulsating water medium.

Jigging – The separation of the heavy fractions of an ore from the light fractions by means of a jig.

Karst – a distinctive landform developed on highly soluble rocks in which erosion has produced fissures, sinkholes, underground streams, and caverns

Leach – a chemical process in which certain components of the ore are dissolved to extract and concentrate valuable minerals. This can also be a natural process during the weathering of minerals in an abandoned mine or waste tip producing a leachate.

Leachate – the aqueous liquid produced during leaching. It may contain potentially harmful elements.

Lode – mining term for a mineralized *vein* (used irrespective of whether the *vein* can be economically extracted).

Massive sulphide – mining term for mineral deposit containing a major proportion (usually over 50%) of sulphide minerals. The main mineral is usually pyrite.

Minette-type iron deposit – iron deposit in Mesozoic and younger sedimentary rocks (usually Jurassic or Cretaceous) consisting of lenticular beds of iron carbonate, sililcate and oxide associated with mudstones and limestones.

Mississippi Valley type, (MVT) – a type of *stratabound* deposit of lead and/or zinc in carbonate rocks, as occurring in the Mississippi valley, USA.

Ore – rock that is profitable to mine and extract the contained minerals or metals in the economic conditions at the time of extraction.

PHE – Potentially Harmful Elements such as arsenic or lead.

Phytotoxicity – the toxic effect of a compound on plant growth. Such damage may be caused by a wide variety of compounds, including trace metals, pesticides or salinity.

Secondary minerals – minerals resulting from the weathering and oxidation of primary minerals such as metal sulphides. Generally consist of carbonates, sulphates or phosphates depending on the physico-chemical conditions under which they formed.

Slag – waste material, generally ferruginous, resulting from the smelting of metal ores.

Smelting – the reduction of metal ores to metal by high temperature reaction of the metal ore with carbon and the production of liquid metal and slag. Waste products can include SO_2 and CO_2 and dusts and vapours containing heavy metals, such as arsenic, lead and zinc. These are now largely containing by anti-pollution measures but historic processes may have released these into the local environment.

Stockwork – mining term for a zone of mineralisation consisting of a dense network of veins that are usually mined as a group, rather than individually.

Stope – mining term for the underground void left after ore extraction has taken place.

Stoping – mining term for the extraction of economic minerals in a mine leaving a void or 'stope'.

Stratabound – mineral deposit confined to a particular horizon or bed of rock.

Sulphides – general term for metal sulphide minerals.

Tailings – mining term for discarded, usually fine-grained processed ore from which the economic minerals have been extracted. Generally in engineered 'tailings ponds' where the material has been pumped in suspension and allowed to settle out.

Vein – a generally sub-vertical, tabular or sheet–like assemblage of minerals occurring in a joint or fissure in rocks.

Wall rock – an economic geology term used to describe the rock adjacent to an accumulation of ore minerals (veins, layers, disseminations, etc). See also host rock.

Workings – the current or past underground or surface openings and tunnels of a mine. More specifically, the area where the ore has been extracted.

.

References

British Geological Survey holds most of the references listed below, and copies may be obtained via the library service subject to copyright legislation (contact libuser@bgs.ac.uk for details). The library catalogue is available at: http://geolib.bgs.ac.uk.

ABEL P D AND GREEN D W J. 1981. Ecological and toxicological studies on invertebrate fauna of two rivers in the Northern Pennine Orefield. In *Heavy Metals in Northern England: Environmental and Biological Aspects*. SAY P J AND WHITTON BA (editors) Department of Botany University of Durham.

ABRAHAMS P W AND THORNTON I. 1987. Distribution and extent of land contaminated by arsenic and associated metals in mining regions of south-west England. *Transactions Institution of Mining and Metallurgy (Section B: Applied earth science)* 96 B1-8.

AL T A, MARTIN C J AND BLOWES D W. 2000. Carbonate-mineral/water interactions in sulfide-rich mine tailings. *Geochimica et Cosmochimica Acta* 64(23) 3933-3948.

ALDERTON D H M. 1993. Mineralization associated with the Cornubian granite batholith. 270-354 in Pattrick R A D and Polya D A (editors) *Mineralization in the British Isles*. (London: Chapman and Hall).

ALLEN P. M. 1980. Copper mineralisation in Great Britain. 266-276. in *European copper deposits*. Jankovic J and Sillitoe R H (editors) Special Publication Society for Geology Applied to Mineral Deposits. No. 1. - Belgrade.

ALPERS C N, BLOWES D W, NORDSTROM D K AND JAMBOR J L. 1994. Secondary minerals and acid mine water chemistry. In *Environmental Geochemistry of Sulfide Mine-Wastes*. Mineral. Assoc. Can. Short Course Handbook Ontario 22 247–270.

APPLETON J D. 1995. Potentially harmful elements from natural sources and mining areas: characteristics extent and relevance to planning and development in Great Britain. *British Geological Survey Technical Report* WP/95/3.

ANNELS A E AND ROBERTS D E. 1989. Turbidite-hosted gold mineralization at the Dolaucothi Gold Mines. Dyfed Wales United Kingdom. *Economic Geology* 84 1293-1314.

ANNELS A E AND BURMAN B C. 1995. The Dolaucothi Gold Mines 3rd Ed. (Cardiff University of Wales).

ARUP. 1991. Occurrence and utilisation of mineral and construction wastes. Department of the Environment Geological and Minerals Planning Research Programme. (London: HMSO).

ASTON S R, THORTHON I AND WEBB J S. 1975. Arsenic in stream sediments and waters of South West England. *The Science of Total Environment* Vol. 4 347-358.

BALL T K AND BLAND D J. 1985. The Cae Coch volcanogenic massive sulphide deposit Trefriw North Wales. *Journal Geological Society London* 142 889-898.

BANKS D, YOUNGER PL AND DUMPLENTON S. 1996. The historical use of mine drainage and pyrite oxidation waters in central and eastern England United Kingdom. *Hydrogeology Journal* 4 55-68.

BANKS D, YOUNGER PL, ARNESEN RT, IVERSEN ER AND BANKS SB. 1997. Mine-water chemistry: the good the bad and the ugly. *Environmental Geology* 32 157-174.

BENTLEY S P. 1996. An historical review of landslide research in the South Wales coalfield: Geological and Geotechnical Engineering 14 21-40.

BICK D. 1982. The old copper mines of Snowdonia. (Newent Glos: The Pound House).

BIGHAM J M AND NORDSTROM D K. 2000. Iron and aluminium hydroxysulfates from acid sulfate waters. In *Sulfate Minerals – Crystallography geochemistry and environmental significance*. Alpers C N. Jambor J L Nordstrom D K (eds.) Rev. Mineral. Geochem. 40 351–403.

BLELLOCH J D. 1983. Waste disposal and the environment. Colliery Guardian August 1983 392-401.

BLOWES D W, JAMBOR J L AND HANTON-FONG C J. 1998. Geochemical mineralogical and microbial characterization of a sulphide-bearing carbonate-rich gold-mine tailings impoundment Joutel Quebec. *Applied Geochemistry* 13(6) 687-705.

BLUNDEN J. 1975. The mineral resources of Britain. (London: Hutchinson).

BOTTRELL S H, SHEPHERD T J, YARDLEY B W D AND DUBESSY J. 1988. A fluid inclusion model for the genesis of the ores of the Dolgellau Gold Belt North Wales. *Journal Geological Society London* 145 139-145.

BOWELL R J AND BRUCE I. 1995. Geochemistry of iron ochres and mine waters from Levant Mine Cornwall. Applied Geochemistry 10(2) 237-250.

BOWLER C M L AND KINGSTON G A. 1971. Mineralization in the Triassic rocks of Llantrissant area Glamorgan. University of Wales Intercollegiate Colloquium. *Mineral Exploration and Economic Geology* 30-32.

Breward N. 2007. Arsenic and presumed resistate trace element geochemistry of the Lincolnshire (UK) sedimentary ironstones as revealed by a regional geochemical survey using soil water and stream sediment sampling. *Applied Geochemistry* 22(9) 1970–1993.

BRITISH GEOLOGICAL SURVEY 1999. Regional geochemistry of Wales and part of west- central England: stream water. (Keyworth Nottingham: British Geological Survey).

BRITISH GEOLOGICAL SURVEY 2000. Regional geochemistry of Wales and part of west- central England: stream sediment and soil (Keyworth Nottingham: British Geological Survey).

BURCKHARD SR, SCHWAB A P AND BANKS M K. 1995. The effects of organic acids on the leaching of heavy metals from mine tailings. *Journal of Hazardous Materials* 41 135-145.

BURT R, WAITE P AND BURNLEY R. 1992. The mines of Flintshire and Denbighshire (Exeter: University Press)

BUTCHER N J D AND HEDGES J D. 1987. Exploration and extraction of structurally and lithostratigraphically controlled fluorite deposits in Castleton-Bradwell area of Southern Pennine Orefield England. *Transactions Institution of Mining and Metallurgy (Section B: Applied earth science)* 96 B149-155.

CARLON C J. 1979. The Alderley Edge mines. (Altrincham: J. Sherrat and Son).

CAVE M R, WRAGG J, PALUMBO B AND KLINCK B A 2003. The Measurement of Arsenic Bioaccessibility in UK Soils. Environment Agency Research Report P5-062/TR02.

CHRISTOFFERSEN J E AND KING P M. 1988. Hemerdon an evaluation case history. 27-39 in Extractive Industry Geology 1985. Scott P W (editor). *Geological Society Miscellaneous Paper* No. 18.

COLMAN T, PALUMBO-ROE B AND BANKS V. 2006. Study to assess the nature of waste produced by active mineral workings in the UK. *British Geological Survey Commissioned Report* CR/06/214C.

COOK J A AND MORREY D. 1981. Heavy Metals and fluoride in soils and plants associated with metalliferous mine wastes in the Northern Pennines. 1981. In *Heavy Metals in Northern England: Environmental and Biological Aspects*. SAY PJ AND WHITTON BA (Eds.) Department of Botany University of Durham.

CORWIN D L, DAVID A AND GOLDBERG S. 1999. Mobility of arsenic in soil from the Rocky Mountain Arsenal area. *Journal of Contaminant Hydrology* 39 35-58.

COX D P AND SINGER D A. 1986. Mineral deposit models. United States Geological Survey Bulletin 1693.

CRITCHLEY M F. 1979. A geological outline of the Ecton copper mines Staffordshire. *Bulletin Peak District Mines Historical Society* 7 177-191.

CROCKETT R N. 1975. Slate. Mineral Resources Consultative Committee. Mineral Dossier No 12 (London: HMSO).

DAVIES J R, FLETCHER C J N, WATERS R A, WILSON D, WOODHALL D G AND ZALASIEWICZ J A. 1997. Geology of the country around Llanilar and Rhayader: memoir for 1:50000 geological sheets 178 and 179 (England & Wales). (Keyworth Nottingham: British Geological Survey).

DAVIS A, RUBY M V AND BERGSTROM P D. 1994. Factors controlling lead bioavailability in the Butte mining district Montana USA. *Environmental Geochemistry and Health* 16(3-4) 147-156.

DETR. 1999. Stability in surface mineral workings and tips. Department of the Environment Transport and the Regions. Mineral Planning Guidance 5 (London: DETR).

DEWEY H. 1920. Arsenic and antimony ores. Special Report on the Mineral Resources of Great Britain. *Memoir of the Geological Survey of Great Britain* No. 15.

DEWEY H AND EASTWOOD T. 1925. Copper ores of Cornwall and Devon. Special Report on the Mineral Resources of Great Britain. *Memoir of the Geological Survey of Great Britain* No. 27.

DEWEY H AND SMITH B. 1922. Lead and zinc ores in the pre-Carboniferous rocks of West Shropshire and North Wales. Special Report on the Mineral Resources of Great Britain. *Memoir of the Geological Survey of Great Britain* No 23.

DEWEY H. 1923. Copper ores of Cornwall and Devon. Special Report on the Mineral Resources of Great Britain. *Memoir of the Geological Survey of Great Britain* No 27.

DICKENS R AND HILTBOLD A R. 1967. Movement and persistence of methanearsonate in soil. Weed Science Vol. 15 299-304.

DINES H G. 1956. The metalliferous mining region of South-West England. Memoir of the Geological Survey of Great Britain.

DINES H G. 1958. The West Shropshire mining region. Bulletin of the Geological Survey of Great Britain No. 14 1-43.

DOE. 1981. Coal and the Environment. Department of the Environment (London: HMSO).

DOE. 1988. Development of evaluative framework and review of existing spoil disposal procedures. Department of the Environment Mineral Planning Research Project PECD 7/1/118-180/83. (London: HMSO).

DOE. 1990. Report of the informal working group in coal and the environment. (London: Department of the Environment).

DOE. 1991. Survey of land for mineral workings in England 1988: Volume 1 Report on survey results. Volume 2 Survey tables Analysis by mineral planning authorities national parks and areas of outstanding national beauty with regional and national totals. Volume 3 Survey tables Analysis by mineral types. Department of the Environment. (London: HMSO).

DOE. 1996. Survey of land for mineral workings in England 1994. Volume 1.- Report on survey results. Volume 2 Survey tables Analysis` by mineral planning authorities national parks and areas of outstanding national beauty with regional and national totals. Volume 3 Survey tables Analysis by mineral types. Department of the Environment. (London: HMSO).

DOMINY S C, SANGSTER C J S, CAMM G S AND PHELPS R F G. 1998. Narrow-vein stoping practice: a United Kingdom perspective. *Transactions Institution Mining and metallurgy* (Section A: Mining Industry) 107 A122-A136.

DOWN C G. 1980. The manganese mines of North Wales. British Mining 14.

DUNHAM K C. 1952. Fluorspar. 4th edition. Special Report on the Mineral Resources of Great Britain. *Memoir of the Geological Survey of Great Britain No.* 4.

DUNHAM K C, BEER K E, ELLIS R A, GALLAGHER M J, NUTT M J C AND WEBB B C. 1978. United Kingdom. 263 – 317 in Mineral deposits of Europe. Volume 1: Northwest Europe. BOWIE S H U KVALHEIM A AND HASLAM H W (Eds) (London: The Institution of Mining and Metallurgy and The Mineralogical Society).

DUNHAM K C. 1983. Ore genesis in the English Pennines: A fluoritic subtype. 86-112 in *International Conference on Mississippi Valley-type Lead-Zinc Deposits*. [Proceedings volume.] Kisvarsanyi G Grant S K Pratt W P and Koenig J W (Eds). (Rolla: University of Missouri -Rolla).

DUNHAM K C AND WILSON A A. 1985. Geology of the Northern Pennine Orefield: Volume 2 Stainmore to Craven. *Economic Memoir of the British Geological Survey*.

DUNHAM K C. 1990. Geology of the Northern Pennine Orefield: Volume 1 Tyne to Stainmore (2nd Edition). *Economic Memoir of the British Geological Survey*.

EARP J R. 1958. Mineral veins of the Minera-Maeshafn District of North Wales. Bulletin of the Geological Survey of Great Britain No. 14 44-69.

EDMUNDS W M. 1971. Hydrogeochemistry of groundwaters in the Derbyshire Dome with special reference to trace constituents. Institute of Geological Sciences London. Her Majesty's Stationery Office.

EDMUNDS W M, COOK J M, KINNUBURGH D G, MILE D L AND TRAFFORD J M. 1989. Trace element occurrences in British groundwaters. *British Geological Survey Report* SD/89/3.

ENVIRONMENT AGENCY. 2008. Assessment of Metal Mining-Contaminated River Sediments in England and Wales. *Environment Agency Science Report* SC030136/4.

FIRMAN R J. 1978. Epigenetic mineralisation. 226-241 in The geology of the Lake District. Moseley F (editor). Occasional Publication Yorkshire Geological Society No. 3.

FLEMING C, MARSH S, NOY D AND NEWSHAM N. 2003. MINEO Western European test site; contamination / impact. Mapping and modelling final report.

FLETCHER C J N. 1988. Tidal erosion solution cavitites and exhalative mineralization associated with the Jurassic unconformity at Ogmore South Glamorgan. *Proceedings Geologists Association* 99 1-14.

FORD T D AND INESON P R. 1971. The fluorspar mining potential of the Derbyshire ore field. *Transactions Institution of Mining and Metallurgy (Section B: Applied Earth Science)*80 B186-210.

FORD T D, SERGEANT W A S AND SMITH M E. 1993. The minerals of the Peak District of Derbyshire. *Bulletin of the Peak District Mines Historical Society* 12 16-55.

FORD T D. 1976. The ores of the South Pennines and Mendip Hills England - a comparative study. 161-195 in *Handbook of Strata-bound and Stratiform Ore Deposits II*. Regional Studies and Specific Deposits 5 Regional Studies. Wolf K H (editor) (Amsterdam: Elsevier).

FOSTER-SMITH J R. 1981. The non-ferrous mines of the South Wales area. British Mining 18.

GAYER R A AND CRIDDLE A J. 1969. Mineralogy and genesis of the Llanharry iron ore deposits. 605-626 in Proceedings Ninth Commonwealth Mining and Metallurgical Congress 2 (London: Institution of Mining and Metallurgy).

GERMAIN M D, TASSE N AND BERGERON M. 1994. Limit to self-neutralisation in acid mine tailings. In: *Environmental Geochemistry of Sulfide Oxidation*. American Chemical Society 365-379.

GOUGH D. 1965. Structural analysis of the ore shoots at Greenside Lead Mine Cumberland England. *Economic Geology* 60 1459-1477.

GRAY G AND JUDD A G. 2003. Barium sulphate production from mine waters in southeast Northumberland. *British Mining* 73 72-88.

GREEN G W. 1958. The Central Mendip Lead-Zinc Orefield. Bulletin of the Geological Survey of Great Britain No. 14 70-90.

GREENWOOD D A AND SMITH F W. 1977. Fluorspar mining in the Northern Pennines. Transactions Institution of Mining and Metallurgy (Section B: Applied Earth Science) 86 B181-190.

GRIFFIN S A, MARCUS SCHULZ T AND WALKER S. 1999. Calculating the Interindividual Geometric Standard Deviation for Use in the Integrated Exposure Uptake Biokinetic Model for Lead in Children. *Environ. Health Perspect* 107 481-487.

GUTT W, NIXON P J, SMITH M A, HARRISON W H AND RUSSELL A D. 1974. A survey of the locations disposal and prospective uses of the major industrial by-products and waste materials. Building Research Establishment Current Paper CP 19/74.

HEADWORTH H G, PURI S AND RAMPLING B H. 1980. Contamination of a Chalk aquifer by mine drainage at Tilmanstone east Kent U.K. *Quarterly Journal of Engineering Geology* 13 105-117.

HIGHLEY D E. 1984. China clay. Mineral Resources Consultative Committee. Mineral Dossier No 26. (London: HMSO).

HOLMSTRÖM H L,JUNGBERG J AND ÖHLANDER B. 1999. Role of carbonates in mitigation of metal release from mining waste. Evidence from humidity cells tests. *Environmental Geology* 37(4) 267-280.

HOLT D N. 1992. Investigations of ground characteristics in the area around Chacewater and St Day in the county of Cornwall. Report for the Department of the Environment. (Long Eaton Nottingham: M1 Press).

HOOKER P J, IVANOVICH M, MILODOWSKI A E, BALL T K, DAWES A AND READ D. 1989. *Uranium migration at the South Terras Mine Cornwall*. British Geological Survey Fluid Processes Series Technical Report WE/89/013.

HULL E. 1881. The coalfields of Great Britain. (London: Stanford).

HUNT C J. 1970. The Lead Miners of the Northern Pennines in the eighteenth and nineteenth centuries. Manchester University Press. 282.

IGS. 1984. South Wales coalfield landslip survey: Institute of Geological Sciences. Engineering Geology Unit Report EG80/4.

INESON P R AND FORD T D. 1982. The South Pennine orefield: its genetic theories and eastward extension. *Mercian Geologist* 8 285-303.

IXER R A AND VAUGHAN D J. 1993. Lead-Zinc-Fluorite-Baryte deposits of the Pennines North Wales and the Mendips. 355-418 in Pattrick R A D and Polya D A (Eds) *Mineralization in the British Isles*. (London: Chapman and Hall).

IXER R A AND DAVIES J. 1997. Mineralization at Great Orme copper mines Llandudno North Wales. *UK Journal of Mines and Minerals* 17 7-14.

JAMES J R, SCOTT S F AND WILLATTS E C. 1961. Land use and the changing power industry in England and Wales. *Geographical Journal* 127 286-309.

JONES O T. 1922. Lead and zinc. The mining district of North Cardiganshire and West Montgomeryshire. Special Report on the Mineral Resources of Great Britain *Memoir of the Geological Survey of Great Britain* Vol. 20.

JONES C A, INSKEEP W P AND NEUMAN D R. 1997. Arsenic transport in contaminated mine tailings following liming. *Journal of Environmental Quality* 26 433-439.

KLINCK B A, PALUMBO B, CAVE M R AND WRAGG J. 2005. Arsenic dispersal and bioaccessibility in mine contaminated soils: a case study from an abandoned arsenic mine in Devon UK. *British Geological Survey Report* Keyworth Nottingham p. 52.

LIX AND THORNTON I. 1993. Arsenic antimony and bismuth in soil and pasture herbage in some old metalliferous mining areas in England. *Environmental Geochemistry and Health* 15 135-144.

LINDSAY W L. 1979. Chemical Equilibria in Soils. New York: John Wiley & Son.

LINTON D. 2009. Website http://www.davel.f2s.com/hendrecoed/Merioneth-Manganese/index.html accessed 29 March 2010.

MACKLIN M G AND RIDGWAY J M. 1994. The use of overbank sediment for geochemical mapping and contamination assessment: results from selected English and Welsh floodplains. *Applied Geochemistry* 9(6) 689-700.

MACKLIN M G, HUDSON-EDWARDS K A AND DAWSON E J. 1997. The significance of pollution from historic metal mining in the Pennine orefields on river sediment contaminant fluxes to the North Sea. *Science of the Total Environment* Vol. 194-195 391-397

MHAIRTIN N F, STANLEY G, GALLAGHER V AND BROGAN J. 2009. Geochemistry Solid Waste Data for the Historic Mine Sites Project - Inventory and Risk Classification Volume 1. Associated datasets and digital information objects connected to this resource are available at: Secure Archive For Environmental Research Data (SAFER) managed by Environmental Protection Agency Ireland http://erc.epa.ie/safer/resource?id=18f6c6a3-8e14-102d-ba42-8e912b2741d0 (Last Accessed: 2010-04-13).

MERRINGTON G AND ALLOWAY B J. 1993. Environmental significance of heterogeneous metal distribution in historical Pb-Zn mine tailings heaps. *Trans. Inst. Min. Metall. (Sect.A: Min. industry)* 102 71-74.

MILLWARD D, BEDDOE-STEVENS B AND YOUNG B. 1999. Pre-Acadian copper mineralization in the English Lake District. *Geological Magazine* 136 159-176.

MITCHELL P. 1990. Reclaiming derelict metalliferous mining land – with particular reference to Cornwall UK. *Land & Minerals Surveying* 8 7-17.

MITCHELL P AND BARR D. 1995. The nature and significance of public exposure to arsenic: a review of its relevance to South West England. *Environmental Geochemistry and Health* 17 57-82.

NORDSTROM DK AND ALPERS C N. 1999. Geochemistry of Acid Mine Waters. In: G.S. Plumlee and M.J. Logsdon (Eds.), *The Environmental Geochemistry of Mineral Deposits, Part A: Processes, Techniques and Health Issues*, Reviews in Economic Geology Vol. 6A, Society of Economic Geologists, Inc., 133-160.

NRA. 1994. Abandoned mines and the water environment. National Rivers Authority Water Quality Series No. 14. (London: HMSO)

PALUMBO B AND KLINCK B A. 2002. The environmental impact of abandoned lead mining in mid-Wales. *British Geological Survey Internal Report* IR/02/123.

PALUMBO-ROE B AND KLINCK B A. 2007. Bioaccessibility of arsenic in mine waste-contaminated soils: A case study from an abandoned arsenic mine in SW England (UK). *Journal of Environmental Science and Health Part A* 42:9 1251 – 1261

PHILIPP AND HUGHES 1982. Morbidity and soil levels of cadmium. International Journal of Epidemiology 11 257-260.

PLUTA I. 2001. Barium and radium discharged from coal mines in the Upper Silesia Poland. *Environmental Geology* 40 (3) 345-348

POINTON C R AND IXER R A. 1980. Parys Mountain mineral deposit Anglesey Wales: geology and ore mineralogy. *Transactions Institution of Mining and Metallurgy (Section B: Applied earth science)* 89 B143-155.

RAWLINS B G O'DONNEL K AND INGHAM M. 2003. Geochemical survey of the Tamar catchment (south-west England). *British Geological Survey Report* CR/03/027 p. 232.

REEDMAN A J COLMAN T B CAMPBELL S D G AND HOWELLS M F. 1985. Volcanogenic mineralisation related to the Snowdon Volcanic Group (Ordovician) Gwynedd North Wales. *Journal Geological Society London* 142 875-888.

RICHARDS MOREHEAD AND LAING LTD. 1995. Slate waste tips and workings in Britain. Report for the Department of the Environment. (London: HMSO).

RICHARDS MOREHEAD AND LAING LTD. 1996. Restoration and revegetation of colliery spoil tips and lagoons. Report for the Department of the Environment. (London: HMSO).

ROBEY J A AND PORTER L. 1972. The copper and lead mines of Ecton Hill Staffordshire. Moorland Publishing.

ROBINSON JONES PARTNERSHIP. 1986. Halkyn Mountain Study. Delyn Borough Council Ref E1439.

ROSE W C C AND DUNHAM K C. 1977. Geology and hematite deposits of South Cumbria. Economic *Memoir of the Geological Survey of Great Britain*.

ROUSSEL C NÉELA C AND BRILA H. 2000. Minerals controlling arsenic and lead solubility in an abandoned gold mine tailings. *The Science of the Total Environment* 263 209-219.

ROY WALLER ASSOCIATES LTD. 1991. Environmental effects of surface mineral workings. Report for the Department of the Environment. (London: HMSO).

SAVAGE K S, TINGLE T N, O'DAY P A, WAYCHUNAS G A AND BIRD D K. 2000. Arsenic speciation in pyrite and secondary weathering phases Mother Lode Gold District Tuolumne Country California. *Applied Geochemistry* 15 1219-1244.

SAY P J AND WHITTON B A. 1981. Chemistry and plant ecology of zinc-rich streams in the Northern Pennines. In *Heavy Metals in Northern England: Environmental and Biological Aspects*. SAY P J AND WHITTON B A (Eds.) Department of Botany University of Durham.

SEAL R R AND FOLEY N K. 2002. Progress on geoenvironmental models for selected mineral deposit types. *United States Geological Survey Open File Report* 2002/195.

SHEPHERD T J AND BOTTRELL S H. 1993. Dolgellau Gold Belt Harlech district North Wales. 187-207 in Pattrick R A D and Polya D A (Editors) *Mineralization in the British Isles*. (London: Chapman and Hall).

SHEPHERD T J AND GOLDRING D C. 1993. Cumbrian hematite deposits North-west England. 419-445 in PATTRICK R A D AND POLYA D A (Eds) *Mineralization in the British Isles*. (London: Chapman and Hall).

SIBLY T F. 1927. Iron ores – the haematites of the Forest of Dean and South Wales. Special Report on the Mineral Resources of Great Britain. *Memoir of the Geological Survey of Great Britain No.* 10.

SLATER D AND HIGHLEY D E. 1976. The iron ore deposits in the United Kingdom of Great Britain and Northern Ireland. 393-409 in Zitzmann A (Editor). *The Iron Ore Deposits of Europe and adjacent areas*. Vol.1. (Hannover: Bundesanhalt fur Geowissenschaften und Rohrstoffe).

SMALE C V. 1993. South Terras. Cornwall's Premier Uranium and Radium Mine. *Journal of the Royal Institution of Cornwall.* New Series 1 (3) 304-321.

SMITH B. 1924. Iron ores: - Haematites of west Cumberland Lancashire and the Lake District. Special Report on the Mineral Resources of Great Britain. *Memoir of the Geological Survey of Great Britain* Vol. 8.

SMITH A AND MUDDER T. 1991. The chemistry and treatment of cyanidation wastes. (London: Mining Journal books Limited.)

SMITH E, NAIDU R AND ALSTON A M. 1999. Chemistry of Arsenic in soils: I. Sorption of Arsenate and Arsenite by four Australian soils. *Journal of Environmental Quality* 28 1719-1726.

STANLEY C J AND VAUGHAN D J. 1982. Copper lead zinc and cobalt mineralisation in the English Lake District: classification condition of formation and genesis. *Journal Geological Society London* 139 569-579.

STUMM W AND MORGAN JJ. 1996. Aquatic Chemistry. Wiley-Interscience, Hoboken, New Jersey, USA.

SZCZEPANSKA J AND TWARDOWSKA I. 1997. Distribution and environmental impact of coal-mining wastes in Upper Silesia Poland. *Environmental Geology* 38 249-258.

TENNANT S C AND STEED G M. 1997. Role of lithogeochemistry in reassessment of the geological setting of Parys Mountain polymetallic sulphide deposit Anglesey Wales. *Transactions Institution of Mining and Metallurgy (Section B: Applied earth science)* 106 B144-156.

THOMSON G M AND RODIN S. 1972. Colliery Spoil tips – after Aberfan. (London: Institution Civil Engineers).

THORNTON I, WATT J M, DAVIES D J A, HUNT A, COTTER-HOWELLS J AND JOHNSON D L. 1994. Lead contamination of UK dusts and soils and implications for childhood exposure: an overview of the work of the Environmental Geochemistry Research Group Imperial College England 1981-1992. *Environmental Geochemistry and Health* 3/4 113-122.

TRYTHALL R J B, ECCLES C, MOLYNEAUX S G AND TAYLOR W E G. 1987. Age and controls of ironstone deposition (Ordovician) North Wales. *Geological Journal* 22 31-43.

VARVILL W W. 1959. The future of lead-zinc and fluorspar mining in Derbyshire. pp.175-203 in The future of non-ferrous mining in Great Britain and Ireland: a symposium. (London: Institution of Mining & Metallurgy).

WARREN P, PRICE D, NUTT M AND SMITH E. 1984. Geology of the country around Rhyl and Denbigh. Memoir British Geological Survey sheets 95 and 107.

WARRINGTON G. 1966. The metalliferous mining district of Alderley Edge Cheshire. Mercian Geologist 1 111-129.

WEBB J S, THORNTON I, THOMPSON M, HOWARTH R J AND LOWENSTEIN P 1978. *The Wolfson Geochemical Atlas of England and Wales* 1:2 000 000. Applied Geochemistry Research Group Imperial College of Science and Technology, University of London (Clarendon Press, Oxford, 1978).

WHITBREAD M, MARSAY A AND TUNNELL C. 1991. Occurrence and utilisation of mineral and construction wastes. Report for the Department of the Environment. (London: HMSO).

WICKENS D, RUMFIT A AND WILLIS R. 1995. Survey of derelict land in England 1993. Volume 1 – Report; Volume 2 – Reference tables. Report for the Department of the Environment. (London: HMSO).

WILLIAMS C J. 1993. A history of Great Orme Mines. British Mining Vol. 52.

WOODLAND A W. 1969. Geological report on the Aberfan tip disaster of October 21st 1966. p119-127 in *A selection of reports submitted to the Aberfan tribunal*. (London: HMSO).

YOUNG T. 1993. Sedimentary iron ores. 446-483 in Pattrick R A D and Polya D A (Editors). *Mineralization in the British Isles*. (London: Chapman and Hall).

YOUNGER P L AND SAPSFORD D J. 2004. Evaluating the potential impact of opencast coal mining on water quality (Groundwater Regulations 1998). An assessment framework for Scotland. Manual prepared for the Scotlish Environment Protection Agency (SEPA). University of Newcastle Upon Tyne and NuWater Ltd, Newcastle Upon Tyne, UK. 75pp.

ZHU D, SCHWAB A P AND BANKS M K. 1999. Heavy metal leaching from mine tailings as affected by plants. *Journal of Environmental Quality* 28 1727-1732.