Geochemical Sources and Long-Term Implications of Mine Waste Weathering, Cwmystwyth Mine, Wales

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Abstract

Evaluation of the distribution and leaching potential of lead, cadmium, and zinc from the Cwmystwyth Mine has been undertaken along with surface grab sample mineralogy. Metal concentrations and pH were evaluated respectively, in which a general weak association between these two factors was found. Using these two parameters, a Ficklin diagram was created to assess the type of drainage being produced at the Cwmystwyth Mine, which indicated that metal leaching neutral mine drainage is being generated.

Discharge water from mine workings, waste materials and outcrop generated some variations in terms of pH and metal concentration, with most samples showing alkaline results but higher metals from water that flows through the mine (Nant y Gwaith).

Given the extensive mining history at Cwmystwyth, it is no wonder that metals are finding their way through the environment, heavily exceeding the EQS set out by the European Commission. Lead concentrations in all samples but one exceeded the EQS range, and dissolved metal concentrations in the water samples significantly increased downstream. Zinc concentrations are uniformly high, reflecting the higher mobility of zinc over lead and secondary zinc minerals are much rarer than lead sulfate or lead carbonate phases. Cadmium geochemistry appears controlled by zinc mobility and secondary phases.

In summary, the mine is heavily contaminating the Ystwyth catchment, with high levels of Pb, Zn, Cd, and other transition metal(loids) are contributing to this contamination such as Mn and As. As proved to be leaching, but it still meets the EQS. Contamination in the river is attributed to the water discharge and perhaps seepage from different mine tailings, adits and underground workings.

It is very unlikely that the site will be remediated by cover or removal of mine waste or by using passive treatment due to its topographical complexity, and the sensitive nature of the site, being within a protected Site of Special Scientific Interest (SSSI). Moreover, the data suggests that there have not been any improvements in terms of dissolved metals in the water when data was compared to historic values; hence the mine remains a potential source of metals to the catchment.

Keywords: Mine Waste Geochemistry, Reclamation

Introduction

The Cwmystwyth mine in central Wales has been exploited for a period of over 2000 years through to final abandonment in the early 1950s chiefly for lead and silver but in later years from the 1880s onwards for zinc as well (Bick, 1993; Meek, 2014). The mine occupies a precarious location on steep slopes and the formally glaciated valley falls sharply to the Ystwyth River with little or no flat ground between the mine workings and the river, indeed the lowest adit occurs at river level (Fig.1).

The presence of transition metals in the mine waste and soils has resulted in significant impacts to the Ystwyth catchment particularly with release of cadmium and zinc but also copper and lead (Jones & Erichsen 1958; Fuge *et al*. 1993; Mighall *et al*., 2002; Edwards & Williams, 2016). This has led to studies evaluating metal removal from water and attenuation mechanisms in the impacted soils in the area. Cwmystwyth is a hydrologically complex site, with mining activity having had a significant impact on the natural regime. The River Ystwyth receives all surface and sub-surface drainage from the mine, causing it to fail European Water Framework Directive (WFD) standards for zinc, lead, and cadmium. The subsurface workings are drained via Pugh's, Gill's Lower and Kingside adits. Pugh's Adit is the largest point source of metals from the site, whilst Gill's Lower and Kingside are collapsed and emerge as small upwellings. There are also numerous other minor upwellings of contaminated groundwater.

In addition, a number of streams draining the plateau high above Cwmystwyth flow down through the site, eroding and mobilising sulfate and metals from the extensive waste tips and are then lost to ground as they pass over the site through mine waste or through the workings. Mine drainage is also influenced by the large Ystwyth Fault (fig.1) which runs in a northeast to southwest trend, bisecting the River Ystwyth. It is thought that contaminated groundwater from the sub-surface workings discharges directly into the river through this fault zone.

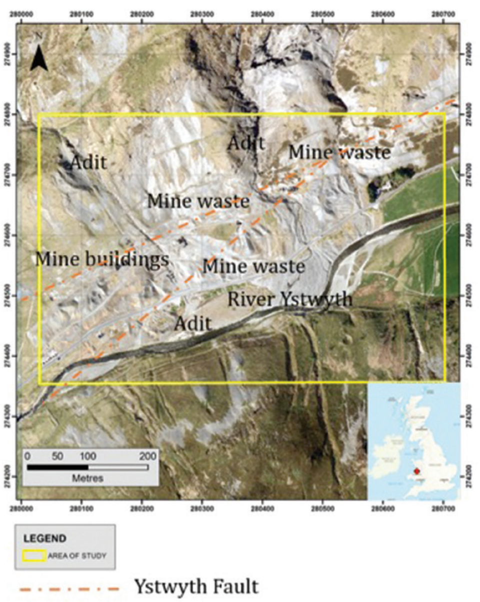


Figure 1 *Study area and main mine facilities at the Cwmystwyth Mine. Insert shows location with respect to the British Isles (Digimap and ArcMap).*

Methodology

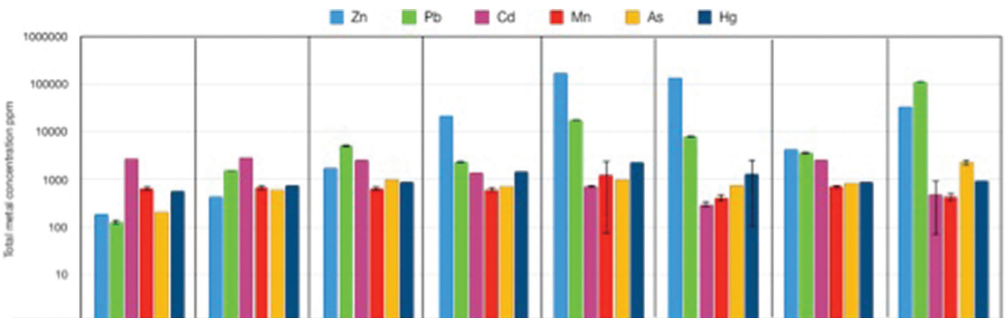
The sampling strategy used in the site aimed to characterise areas where waste dump was deposited, and the potential pathway of the transition metals reaching the waters of the River Ystwyth, based on factors discussed in the literature review (Marquinez, 2019). This strategy could provide evidence to determine the mobility of metals in the ground and how its concentration changes downslope. A summary of methods employed is provided in Table 1. Water samples were collected from the Ystwyth River and other local streams and drainage running through the Cwmystwyth Mine. The sampling strategy was based on gathering samples from the confluent and effluents of the streams in the area to visualise changes as the water flows downstream and through the mine. A carbonate rating test was carried out with the purpose of finding out the percentage of carbonate in each sample, which will be subsequently used in a Neutralisation Potential test. Dump waste material was crushed to 4mm chips according to BS EN 12457.

These results have been mapped and compared to in-situ pH data collected in the field from these dump materials. For the purpose of this paper only lead, cadmium, manganese, arsenic, and zinc are described in detail. The heat maps showing metal distribution for these elements and paste pH are provided in Figure 3.

The maps illustrate that high metal bearing material is present at the lower adit adjacent to Ystwyth river as reflected in the hot spots for lead and arsenic at the lower Gill adit (fig.3). By comparison zinc is most anomalous in the wash-out sediment from the Hugh adit and the higher elevation workings where it appears to have been transported (fig.3). Apart from the Pugh adit

Table 1 *Summary of samples collected on site.*

Sample type	Number of samples	Testwork Undertaken
Water samples	7	ICP-MS for dissolved metals/pH
Solid Waste samples	20	XRF/XRD/Leaching test/Carbonate rating/ Neutralisation Potential/pH



SAMPLE	CS1 (ppm)	CS3 (ppm)	CS7 (ppm)	CS10 (ppm)	CS15B (ppm)	CS18 (ppm)	CS19 (ppm)	CS20 (ppm)
Pb	125.5	1532.5	5006	2293	17558	7869.5	3605	111400
Zn	188	422	1702	21080	171400	140750	4146	33750
Cd	2800	2900	2600	1362.5	709	296.5	2600	493.5
Mn	642.5	662.5	633	596	1249	413.5	694.5	420
As	204	607	987.5	693	972	750.5	859	2274
Hg	568.5	732.5	887.5	1461.5	2300	1346.5	910.5	931.5

***Figure 2** XRF results for selected sites to illustrate range of concentrations in mine waste.*

mouth arsenic shows elevation in more acidic soils and is antipathetic to cadmium and manganese which show a visual correlation to high pH.

Assessment of Carbonate Buffering

The carbonate test results have proved a small, insignificant amount on carbonate in each sample with typically less than 1% total carbonate and only a few samples reported any calcite present, and this is reflected in the widely acidic pH of surface soils on site and reflects the local geology that is comprised of arenite and argillite host rocks (Mason, 1994).

Leached Metals

Using the results of the BS EN 12457 testwork, interpolated heat maps were derived to analyse the spatial distribution of the soluble metals that have potential to leach into the environment and cause serious harm (fig 4). These results portray the potential labile nature of the metals from surface material. Cadmium and manganese show similar trends and are most labile in the area of Gill's lower adit in the south west of the map. Lead and zinc are most labile in the sediments associated with Hugh adit whilst arsenic shows a hot spot on the side of the hill where

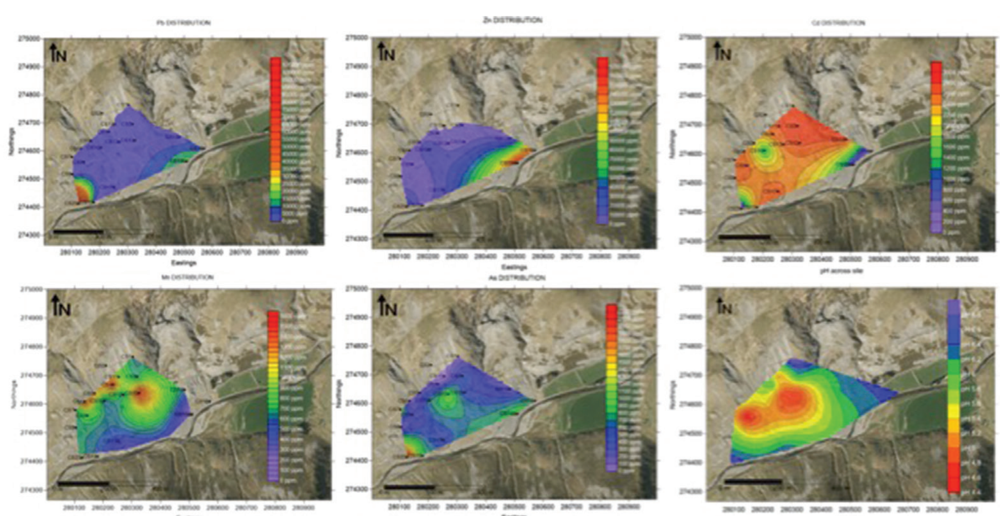


***Figure 3** Heat maps showing total element distribution for Pb, Zn, Cd, Mn, & As as well as paste pH for the area of study shown in Figure 1.*

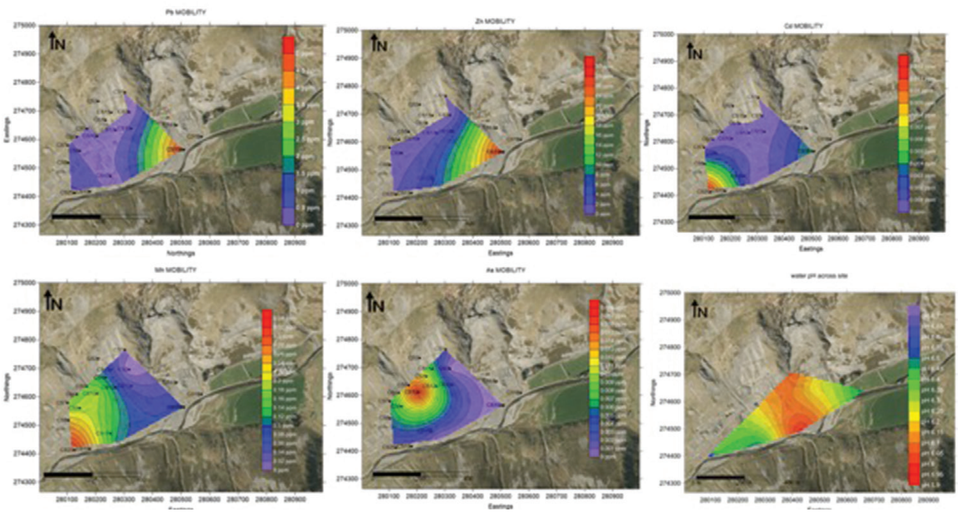


Figure 4 *Heat maps for leachable metals in EN12457 leachate and site water map.*

pH is neutral and from other data total iron content is low.

In the pH map of the River Ystwyth upstream and downstream from the mine, where acidic to neutral waters can be observed (fig.4). This indicates most of the acidic waters are coming from the Nant Y Gwaith which travels through the mine and waste dump located closer to the Ystwyth river. Regression analysis on water chemistry indicated that lead and zinc have an antipathetic relationship to pH whilst arsenic is positively correlated. Manganese and cadmium show a stronger relationship to alkalinity than pH.

Discussion

A useful visualization for mine water chemistry-pH interactions is the Ficklin diagram (Ficklin *et al.*, 1992). The plot defines fields of different water chemistry based on concentration of divalent cations and pH. The results in the Cwmystwyth mine are plotted in Figure 5, where it can be inferred that Neutral Mine Drainage (NMD) could be taking place, as most samples lie within the near-neutral/high-metal and near-neutral/low-metal zones. However, this diagram is not yet used as a formal guideline to define AMD or NMD, and due to the small number of samples this could be rather inconclusive. However, if more samples had been collected similar results could be expected.

Neutral pH in the mine could be attributed to the lack of pyrite as evidenced by the XRD results, where only sample CS10 contained less than 1% pyrite. The majority of sulfides comprise, galena and sphalerite that are both non-acid generating. According to the XRD and Carbonate Rating test, buffering is coming from silicate minerals rather than calcite, such as Albite ($NaAlSi_3O_8$) and Muscovite ($KA_{l2}(AlSi_3O_{10})(OH)_2$). Carbonate minerals generate significantly more neutralisation potential than silicate minerals, which means that the extremely low concentration of carbonate in the sample after the carbonate test indicates that there is no neutralisation potential for the studied samples, as this is directly related to the abundance of non-Fe/Mn carbonate minerals. This can be compared to a study by Jambor (2003) where it is stated that certain silicate minerals are known to buffer mine effluents at a neutral pH.

A site conceptual model of the Cwmystwyth mine (fig.6) has been developed using literature resources from a desk study and field observations. The conceptual model aims to identify and highlight the environmental linkage for the studied transition metals, which are causing the River Ystwyth to be severely contaminated.

A few sources were identified such as the mine tailings (diffuse pollution) and waste dump located near the river itself. These material dump sites are exposed to weather

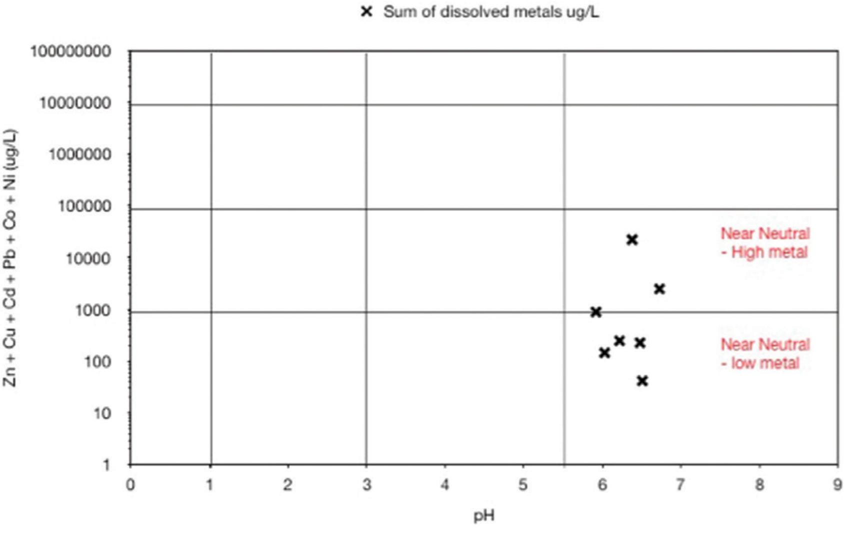


Figure 5 *Ficklin plot, Cwmstwyth mine waters.*

conditions and precipitation. Hydrological processes are a key element in this investigation, as it is expected that rainfall will infiltrate these tailings, weathering and leaching transition metals from ore deposits or mine spoil, which will consecutively seepage into the fractured bedrock reaching the water table and flowing along its direction into the receptor. The mineral lodes containing Pb and Zn underground may be a great source of contamination as the ore is being exposed to water.

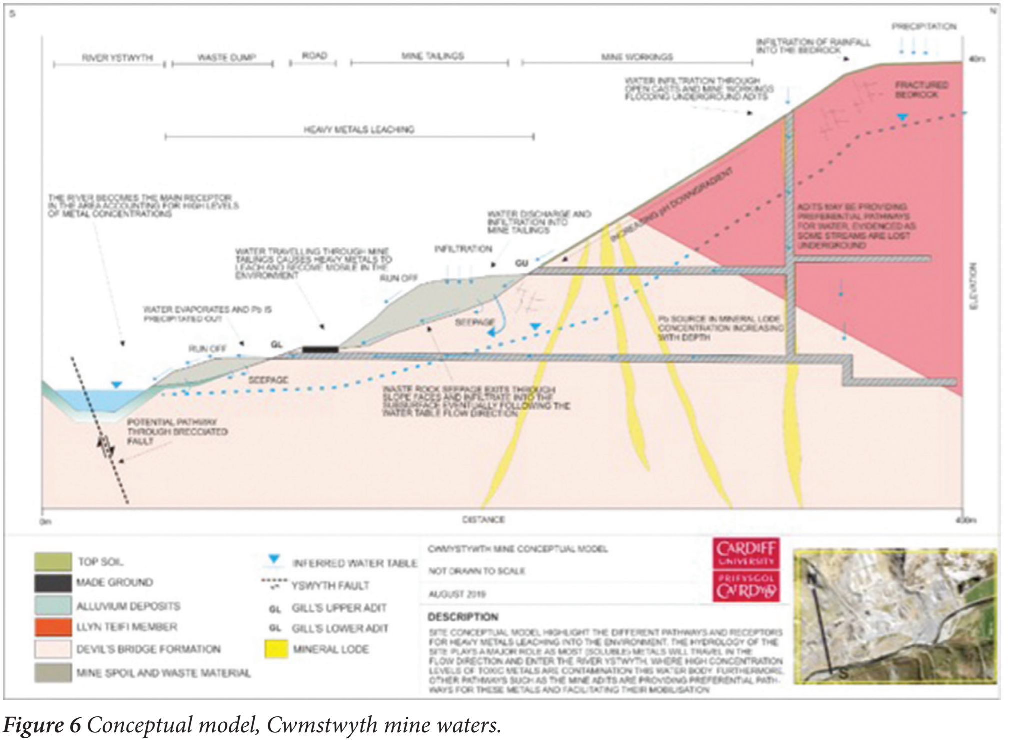


Figure 6 *Conceptual model, Cwmstwyth mine waters.*

The regulation of mine waste in the UK is managed by the Coal Authority in collaboration with the Environment Agency and Natural Resources Wales (Environment Agency, 2016). However, due to the diverse opinions of stake holders to the site and its designation as a Site of Special Scientific Interest it is highly unlikely to be remediated in the near future.

Conclusions

The aim of this research entailed the evaluation of the distribution and leaching potential of transition metals in the Cwmystwyth Mine. Along with this, mineralogy was investigated to determine whether pyromorphite could have an influence in the natural attenuation of lead to prevent its mobility in the environment.

Metal concentrations and pH were evaluated respectively, in which a general weak association between these two factors was found. Using these two parameters, a Ficklin diagram was created to assess the type of drainage being produced at the Cwmystwyth Mine, which indicated that neutral mine drainage is taking place due to the low to high metal concentration and the near-neutral pH linked with the site.

In summary, the mine is heavily contaminating the Ystwyth catchment, with high levels of Pb, Zn, Cd, and other transition metals are contributing to this contamination such as Mn and Ni. As proved to be leaching, but it still meets the EQS. Contamination in the river is attributed to the water discharge and perhaps seepage from different mine tailings, adits and underground workings. The metals leaching are found in favourable conditions which are facilitating their migration into the River Ystwyth such as topography, high rainfall, high exposure to air and water etc. increasing its potential to oxidise and become mobile. Collecting field data during different seasons throughout the year could potentially show a variation in results in terms of dissolved metals being loaded into the catchment.

Reference

Atkins (2008) Metal Mine Monitoring Project 2006/07 Cwmystwyth Mine Site Monitoring Summary Report. Prepared for Environmental Agency Wales

Bick, D.E, (1993) The Old Metal Mines of Wales, Parts 1-6. Pound House, Newent.

Edwards P, Williams T (2016) Abandoned Mine Case Study: Cwmystwyth Lead Mine. June 2016, 2p. Natural Resources Wales.

Ficklin WH, Plumlee GS, Smith KS, McHugh JB (1992) Geochemical classification of mines drainages and natural drainages in mineralized areas. Proc 7th International Symposium on Water-Rock Interaction, Park City, 13-18 July 1992 V1, P381-384. Rotterdam: A A Balkema, 1992

Fuge R, Pearce FM, Pearce NJ, Perkins WT (1993) The geochemistry of cadmium in the secondary environment near abandoned metalliferous mines, Wales. Applied Geochemistry 2: 29-35.

Jambor, J.L., (2003) Mine-Waste Mineralogy and Mineralogical Perspectives of Acid-Base Accounting. In: J.L. Jambor, D.W. Blowes and A.I.M. Ritchie (Eds.), Environmental Aspects of Mine Wastes, Short Course Series Vol. 31, Mineralogical Association of Canada, 117-146.

Jones, J.R. Erichsen (1958). "A Further Study of the Zinc-Polluted River Ystwyth". Journal of Animal Ecology. 27 (1): 1–14.

Mason, J.S. (1994) A regional paragenesis for the Central Wales Orefield. Unpublished M.Sc. thesis, University of Wales.

Mighall TM, Abrahams PW, Grattan JP, Hayes D, Timberlake S, Forsyth S (202) Geochemical evidence for atmospheric pollution, Cwmstwyth, mid-Wales. Science of the Total Environment, 292:69-80.

Meek, J. (2014). Cwmystwyth Mines, Ceredigion: Management and Protection Plan. Dyfed Archaeological Trust.

Warrender R, Pearce NJ, Perkins WT, Florence KM, Brown AR, Sapsford DJ, Bowell RJ, Dey BM (2011). Field trails of low cost Reactive Media for Passive Treatment of Circum-neutral Metal Mine Drainage in Mid-Wales, UK. Mine Water & Environment 30:82-89