# Mine Waste Resource Assessment and Appraisal of Recovery via Mine Water

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**Abstract** In recent years, mine wastes have increasingly become targets for metals recovery. This paper discusses techniques to make preliminary resource value assessments and considers appropriate technology for metals recovery focussing on the passive cementation of copper on to zerovalent iron. The Parys Mountain legacycopper mine in the UK is used as an example where UAV photogrammetry, LiDAR and portable XRF were used to make volume and resource estimates. The cementation reaction is demonstrated to be capable or removing the majority of the Cu in an economically useful form from the mine water within a time period suitable for incorporation within a passive treatment/capture system.

## Introduction

There are many reasons why metal mine wastes may be considered as suitable targets for metals recovery, some important examples are as follows: (i) Reworking of mine wastes and tailings where historic beneficiation processes were inefficient or metal prices have changed significantly such that that present-day reworking of the wastes is now economically viable; (ii) Reworking of mine wastes for metals which were not the original target of exploitation and are present at economic levels in the material. For example there has been recent interest in the so-called “E-tech” elements (Co, Te, Se, Nd, In, Ga, heavy rare earth elements) whose security of supply is an issue in addition to them being essential for current and future technologies. (iii) Site remediation and reclamation to prevent harm to human health and environment from historic mine wastes. It is very well known that many mine wastes can pose significant threats to the environment through AMD/ARD-ML (acid mine drainage, acid rock drainage and metal leaching) and/or airborne dust release. Drivers in the European Union include meeting the requirements of the Water Framework Directive (2000/60/EC) and the Mine Waste Directive (2006/21/EC). It is also noteworthy that recent economic assessment frameworks which take into account damage to the provisioning of ecosystems services may provide additional incentives to ensure prevention of pollution from mine sites. (iv) There is potential for the current regulatory perspectives on the acceptability of long-term risk to environment posed by mine waste to change, such that current mine waste management practices e.g. cover/liner systems are considered to no longer provide sufficient protection of human health and the environment far enough into the future. This would mean that the removal of leachable metals from mine waste becomes a more favourable risk reduction strategy than containment. (v) That given long-term demand for metals and depletion of exisiting ores, what consitutes ecomonic grades continues to decline into the future such that, (i) above becomes viable for currently produced mine wastes.

All of these reasons point towards the importance of turning our attention to examining mine wastes as a resource. Thus some of the questions that follow on naturally from this are:

what techniques are currently available to make low cost and rapid resource assessments for mine wastes? And what practicable and economically viable techniques can be devised for extracting metals and/or remediating sites? A third interesting question not discussed further here is: (iii) should potential future resource recovery plans be "designed" into current mine closure planning?

## Approaches for Resource calculations for waste piles

Given these drivers for recovering metals from mine wastes and the vast number of mine waste dumps located all over the world (over 8,000 in the UK alone), techniques which allow their rapid assessment are required for screening and initial assessments made which can then be used to explore the resource potential of mine wastes and/or their pollution potential. Such site-based studies will necessarily be followed by more detailed and costly investigations. In this paper we draw from work on Parys Moutnain (UK) as a case study sites which is part of a much wider resource assessment (see Crane et al, 2016). There is no planned work at Parys Mountain but it serves as a useful UK example to consider when developing strategies for resource recovery from mine wastes. Parys Mountain Mine is located in North West Wales, at the north east of the island of Anglesey, near the towns of Amlwch and Pen-Y-Sarn. Parys Mountain is an example of a VMS (Kuroko-style) deposit and is now abandoned but was extensively worked, particularly in the 18$^{th}$ century. It was at its zenith the largest copper mine in the world. AMD now drains from the site via an adit into the Afon Goch river.

***Fig 1**. UAV (drone) photograph of Great Open cast at Parys Mountain taken in 2016.*

## Preliminary Volume and Resource Calculation at Parys Mountain

Fig 1 shows a UAV (Unmanned Arial Vehicle) photograph of the Parys Mountain site. LiDAR (Light Detection and Ranging) data and satellite maps were initially consulted to identify the principal features, this was followed by identification of 11 prominent spoil tips during a site walkover. A UAV Photogrammetry Survey was conducted. Photogrammetry is the process of spatially referencing overlapping stereo digital photographs in order to create 3D spatial data. The software used in this investigation was Photoscan (designed and licensed by Agisoft Ltd). The UAV used in this investigation was a Phantom 3 Professional, equipped with a 12 M pixel camera at fixed 20 mm focal length. Three basepoints across the site were established (one for each UAV flight) to allow optimum coverage of the area. The UAV flight time was approximately 15 minutes (due ot battery life). Each flight aimed to capture as many overlapping images of the site features from different angles and at different elevations..

Following the UAV survey, software was used to first align photographs to requisite quality, and then from these produce a dense cloud of x,y,z points to build a mesh to create a heightfield surface and a digital elevation model (DEM). Once a fully-meshed 3D model was completed it was georeferenced. Whilst the software exports the camera location data, which is archived during the UAV survey, and provides an approximate georeference automatically during the photo alignment stage, a higher degree of accuracy is demanded when attempting to calculate volume of features and structures. To increase accuracy, ground control points (GCPs) were taken. Agisoft recommends 9 to 10 GCPs in order to fulfil the georeferencing task. In this instance, 7 sample points, determined by GPS, together with LiDAR data was used to determine the elevation and an additional 3 Ordnance Survey trig points were included which together provide the 10 GCP for an accurate georeferenced model. To determine the volume of a feature, it is necessary to remove all “secondary faces” using the “closed model volume” method, which automatically fills in hollow spaces to produce a base plane. This method does have limitations, for example, the base plane cannot be manual set to a referenced elevation, or a specific dip, but this process is possible with companion software to edit the mesh cloud.

From the UAV results with the Agisoft software a total volume of the 11 tips considered was determined to be 953,510m$^3$ this is considered a conservative estimate because of the assumption is that the ‘close hole’ feature represents the correct planar surface underlying the spoil tip, because the exact depth to the base is unknown. Furthermore, the incomplete UAV coverage of the site resulted in modelling and scaling errors in Agisoft, primarily concerning tip two of the mine waste piles. The failure to acquire imagery of the South slope led to gaps in the dense cloud point. However, all other areas of the site had excellent coverage at different angles and elevations. The calculated total volume of 953,500 m$^3$ was used with in situ density measurements to produces a conservative tonnage estimate of 1,935,600 tonnes. Alternative approaches were also used based on calculating volume from LiDAR or Satellite data for the 11 tips, assuming a base elevation and calculating a volume using either trapezoidal or Simpson’s rule to determine a volume from the measured area and LiDAR elevation data. The total spoil calculates to a volume of 3,200,000 m$^3$ and satellite data 1,032,532 m$^3$. The satellite and Agisoft volume estimates were surprisingly similar, despite employing a very different method to calculate volume. The variation in results between photogrammetry and LiDAR is due in large part to the methods of calculating volume where the method of determining the depth to base of each individual spoil tip. Some spoil tips were located on hillsides, with a sloping topography resulting in a non-linear base, the LiDAR volume calculations were based on the lowest point of elevation of the identified boundary of the spoil tip and produced a horizontally-planar base for the model. The base plane likely intersects regolith and bedrock (beneath the waste pile) and therefore represents an overestimate of the pile size.

For measuring the chemical composition of mine wastes XRF is useful for rapid in field screening has been assessed by numerous authors (e.g. Kalnikcy and Singhvi 2001; Kilbride et al. 2006; McComb et al. 2014). Based on 12 portable XRF readings the average copper concentration was 1,500 mg/kg and as such approximately 2,900 tonnes of Cu is estimated to be present. Whilst not all of this could be recovered, if 30% recovery, expected from an inefficient dump leaching operation (e.g. Petersen, 2015) to 50% recovery gives 870 – 1450 tonnes which at current (April 2017) market value is worth within the region of £4-6M. Whilst these calculations are clearly very preliminary this is a very useful exercise as a means to get a first estimate of the mass of resources contained within mine wastes and can be used to immediately inform decisions regarding the economic viability of the recovery of such resources.

UAV photogrammetry is a rapidly improving technology and holds great promise in the surveying of large areas of mine wastes. But caution should be exercised because the accuracy of volume estimation depends on the time taken in post-processing to edit mesh fields, produce high-quality dense point clouds and correctly align hundreds of images with the use of GCPs. The use of LiDAR data in GIS packages such as ArcGIS and Surfer 11 provides faster and easier estimations of volume but both techniques are also constrained by the requirement to determine an accurate determination of the topography of the mine waste pile floor. More recent sites may have accurate maps outlining the original surface but often with historic mines the original level of the base of the dump is lost to history. In such cases geophysical surveys (such as Electrical Resistance Tomography and ground penetrating radar) can provide a cost effective means to accurately map the base of the dumps.

## Metal Recovery

When considering metal recovery from low-grade material the boundary between what is feasible is controlled by what is technically achievable and the economically viability. Due to the thermodynamics of separation of chemical mixtures (Gutowski 2011; Valero et al 2015), an increase in the exergy cost for extraction is imposed as the target becomes more dilute within a mixture. This is reflected in the economics of ore processing and is why *in situ* mining and heap/dump leaching, which keep energy costs to a minimum by negating the large energy requirements of conventional mining and processing are favoured for low-grade ores (Sapsford et al 2016). There can also be other constraints which would curtail the use of physical "dig and process" remaining technology, for example in the UK a large number of historic mines have protected designations e.g. Sites of Special Scientific Interest, or Scheduled Ancient Monuments which would heavily constrain or prevent invasive resource recovery practices (see Crane et al, 2016). For these reasons, metal recovery using *in situ*, or heap/dump leaching would be favourable technology to utilise if conducted at sufficiently high environmental standards. AMD/ARD-ML could be considered as a passive version of dump leaching and there is interest in capturing metals from AMD/ARD-ML. There are difficulties with this approach however, firstly the level of metals required to make AMD/ARD-ML environmentally devastating can be far lower than the amount which constitutes a viable resource. Take the example of Parys Mountain, it is often reported that the discharge is the single largest contributor of Cu and Zn to the Irish Sea, discharging 24 tonnes of Zn and 10 tonnes of Cu every year, whilst the environmental impact of this is significant the value of this even if it could be 100% recovered as pure metals would be < £100,000, much less than the costs involved in capturing and refining the metal to sell in this form. This also highlights another problem for capturing metals from AMD/ARD-ML – the process chosen to capture the metals is heavily constrained by the infrastructure, experience and technology available locally. One of the only options currently meets this criteria in the UK is the cementation of Cu onto zerovalent iron ($Fe^o$) – a passive method which can create a product with a market (metal salvage/recyling companies).

## Copper removal from Parys Mountain mine water by cementation

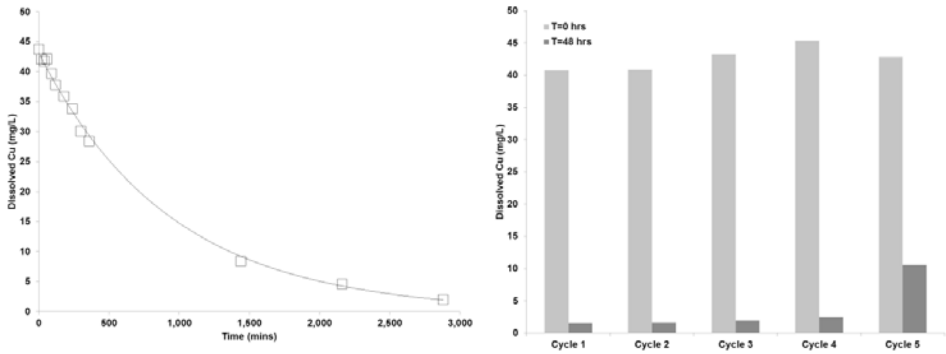
The cementation reaction of Cu onto $Fe^o$ (or other more electropositive metal e.g. Zn or Al) occurs passively. Typically (as was used in the past at Parys Mt.) scrap iron/steel was used as the $Fe^o$ source for the reaction as follows: $Cu^{2+} + Fe^o_{(s)} = Cu^o_{(s)} + Fe^{2+}$ By stoichiometry 55.8 kg of $Fe^o$ produces 65.5 kg of $Cu^o$ but in practice typical consumptions were 1.5 kg of scrap $Fe^o$ for every kg of Cu; due to oxidation and other reactions in the pond. Typical composition of the precipitate is 85%-90% Cu, 0.2-2% Fe, 0.5% $SiO_2$+$Al_2O_3$, remainder oxygen. (Biswas & Davenport, 1976). The standard operation for cementation was to simply run the pregnant solution through ponds (as used at Parys Mt.) or a launder with scrap $Fe^o$ housed on gratings; which allows room for the Cu precipitate to collect under the grating. Labour intensive and inefficient, launder precipitators were superseded by vertical cone separators (e.g. the Kennecott Cone Precipitator) which could improve Cu yield significantly through using turbulent flow to remove the Cu which precipitates over the scrap $Fe^o$ (Biswas & Davenport 1976).

Cu cementation on to scrap $Fe^o$ was a process extensively used at Parys Mountain throughout the mines working history[1] and finally stopped in the middle of the 20th century. Interestingly, the water feeding the ponds was deliberately washed through the spoil tips, recovering up to 50 tonnes of Cu a year (Younger and Potter 2012). Further value was recovered by selling iron precipitated ochre as pigment. The recirculation of mine water through mine workings has been practised in other locations for enhanced metal recovery and is a process option on a spectrum between the AMD/ARD-ML drainage and dump leaching. If this process could be done without risk of harm to the environment it may provide a means through which metal concentrations in mine water can be enhanced to a level by which metal recovery from the mine water becomes viable as a revenue stream to pay for, or at least offset the costs of mine water treatment. A related example is documented in Tucci and Gammons (2015), where over 9 years, 1700t of copper were recovered from the Berkeley Pit Lake, Montana by pumping the deep pit water through a cementation based Cu-recovery

1 http://www.amlwchhistory.co.uk/parys/timeline.htm

circuit, resulting in a decrease in Cu concentrations from an average of >150 mg/L in 2002 to roughly 50 mg/L in 2012.

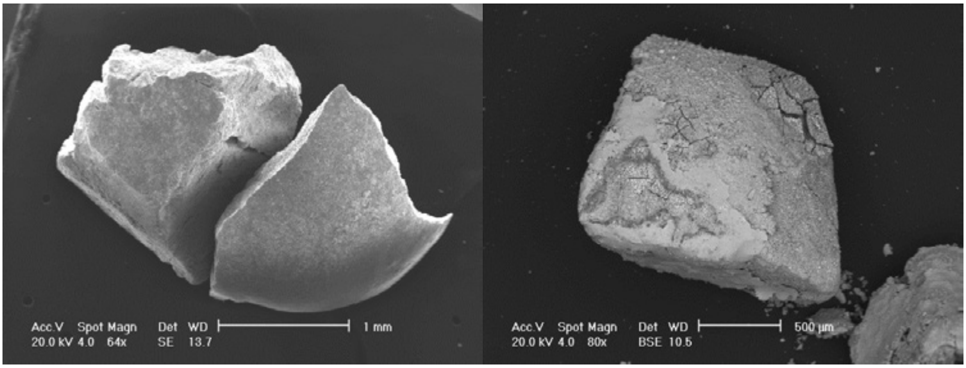
The aim of the current study was to re-examine the mechanism and kinetics of the cementation of Cu in the Parys Mountain mine water with $Fe^{o}$ to assess the potential for incorporating the process into a modern treatment system. 140L of Parys Mt. mine water was collected from the Dyffryn Adda adit before it reaches the Afon Goch Gogledd River. The water was collected in containers which were fully submerged in order to minimise oxygen ingress and refrigerated on return to the laboratory (within 12 hrs of sampling). Cementation experiments were conducted as follows: 1g of $Fe^{o}$ filings were added to a 500 mL of mine water and agitated for 48 hrs with aqueous samples being periodically extracted and analysed for dissolved Cu and Fe concentrations. After 48 hrs the mine water was then decanted (i.e. completing one cementation cycle) and fresh mine water was then added. This was repeated 5 times. Figure 2 displays Cu concentration data recorded throughout the experiment.




(a) (b)

***Fig 2***. *Results of cementation experiment (a) Dissolved Cu versus time for 1 cycle (b) Dissolved Cu concentration before (T = 0) and after (T = 48hrs) for each of the 5 cycles.*

Figure 2 (a) demonstrates that the cementation reaction is capable of removing dissolved Cu from the levels of 43.7 mg/L to 1.98 mg/L in the Parys Mine water (with the exponential fit of the data indicating the kinetics are first order with respect to dissolved Cu). Figure 2 (b) demonstrates that 1g of $Fe^{o}$ filings can be reused for continual removal of Cu from the mine water (recall the expected iron consumption during cementation noted above). However, the efficiency of Cu removal does begin to decrease, becoming more notable by the $5^{th}$ cycle. This is due to the Cu metal (and other reaction products) accumulating on the surface of the $Fe^{o}$ particles and passivating the $Fe^{o}$ surface. This can be observed in Fig 3, with the fresh ZVI surface shown in (a) and the reaction products (confirmed by EDX) shown in Fig 3 (b). In practice these reaction products would need to be removed via agitation in order to maintain high Cu removal efficiency. Other experiments (data not shown) also demonstrated that lower alkali doses (to pH 9) were required in order to precipiate the remaining dissolved metals following the cementation process presumably due to a proportion of the mine water acidity being consumed by the $Fe^{o}$ during its corrosion.




(a) (b)

***Fig 3**. SEM images of (a) Fe0 filing before cementation, and (b) after 5 x 48hr cycles of cementation in Parys Mountain mine water. Note flaky exterior which was demonstrated to be largely Cu by EDX analysis.*

## Conclusions

Mine waste resource assessment and appraisal of resource recovery from mine water is becoming an important research topic in response to numerous drivers including resource scarcity and environmental protection. This paper has outlined the use of UAV photogrammetry and LiDAR in making accurate volume assessments. The preliminary work highlights the problems encountered with accurately determining the physical base of tips where no records exist, and highlights non-invasive geophysical surveys as a useful and quick way to delineate subsurface features. Such low cost and rapid estimates of the total metal resource present at sites are useful for informing preliminary stage discussions concerning the economic viability of resource recovery from mine wastes and could be made at a regional or national level and to influence policy in this regard. Consideration of the resource recovery technology is equally important as the resource assessment and here we demonstrate that cementation reaction of Cu from mine water on to $Fe^0$ can remove Cu to relatively low levels in a time frame appropriate to incorporate into passive treatment system (aqueous Cu concentration was 1.98 mg/L after 48 hr reaction with 2 g/L $Fe^0$ particles). The relatively low aqueous Cu concentrations in the mine water (~40 mg/L) may not be sufficient to be an economically viable waste stream but copper concentrations could be increased by recirculation of the mine water through the workings as was practised historically, raising the interesting prospect that by intentionally making the mine water quality "worse", it might be able to improve environmental outcomes by providing a way to offset the cost of remediation through recovery of copper.

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