SENSITIVITY OF MINE SPOIL HEAPS FROM AN ABANDONED LEAD MINE IN MID WALES (UK) TO CHANGES IN pH OF NATURAL WATER SYSTEMS IN THE CONTEXT OF CLIMATE CHANGE

Barbara Palumbo-Roe, Vanessa Banks, Séan Quigley and Ben Klinck
British Geological Survey, Kingsley Dunham Centre, Keyworth, Nottingham, UK NG12 5GG

Abstract

A case study of cerussite-dominated mine tailings (5-7 wt% Pb) from the former lead-zinc Grogwynion Mine, Mid Wales (UK), is presented with the objective of providing an improved understanding of the chemical speciation that controls element release from the waste in the short and long term. An experimental and modelling approach was used to examine the effects of pH changes in fresh waters interacting with the waste heaps and of the projected increase over time of atmospheric $P\mathrm{CO}_2$ on Pb mobility. Results of pore water analysis and pH-dependent leaching experiments indicated that cerussite controlled Pb solubility in the pore waters and leachates, maintaining concentrations < 10 mg L^{-1} at $\mathrm{pH} > \sim 6$. As pH decreased upon acid addition the cerussite mineral phase dissolved. The precipitation of anglesite in the acid domain of the experiment had a negligible effect in reducing the concentration of dissolved Pb deriving from cerussite dissolution, as a result of the limiting concentrations of SO_4 in solution. The output from the simulation of the projected $P\mathrm{CO}_2$ increase on the solubility of cerrussite in equilibrium with freshwater suggested a limited increase in Pb solubility. Other factors such as changes in temperature and the intensity of microbial activity and related CO_2 production may also influence the solubility changes of such carbonate systems. Clearly, an understanding of the integrated effects of projected climate changes for a given environment is required to quantify the potential impacts of climate change scenarios on mine contaminated environments.

Introduction

A legacy of nineteenth century mining in Mid Wales is the occurrence of lead rich tailings and contaminated soils. Old spoil deposits have arisen from crude ore processing methods developed many decades ago, and often contain concentrations of metals that might be of significance both environmentally and commercially. Such spoil has typically been deposited in heaps or lagoons with little or no regard for the exposure of the local environment to higher levels of toxic metals.

UK climate change scenarios developed by the Hadley and Tyndall Centres (Hulme et al., 2002) have underpinned much research on climate change impacts on the environment. In river catchments affected by mine pollution, it is possible that climate change will affect metal mine pollutant loadings via a number of influences, in particular in the unsaturated zone, river basin dynamics and possibly also in aeolian transport. Elevated maximum summer temperatures increase the potential for capillary rise, facilitating mineral precipitation. Indicative of this has been the recent observation of bianchite (zinc sulphate hexahydrate) on surface tailings at one of the Mid-Wales mine sites under study. Efflorescent minerals such as these are rapidly dissolved by subsequent rainfall events. Furthermore, elevated summer temperatures and consequential drying increase the sediment available for aeolian mobilisation and the impact on biogeochemical processes such as sulphide oxidation. The consequences of increased rainfall intensity are likely to include: periodic sediment mobilisation as a consequence of increased run-off (punctuated erosion events), thereby increasing water course loading and also the leaching potential by moving sediment from the anaerobic to aerobic environment. However, off-set against this is the potential for dilution. For example, Arnell and Reynard (1995) have modelled the potential changes in river flow, demonstrating that annual run-off will increase more than 20% by 2050 in the wetter catchments of Great Britain, while drier catchments will show a decline by a similar percentage. Clearly, a full understanding of these changes for a given catchment is required to quantify the potential impacts of climate change on catchments affected by mine pollution.

Among the most important impacts of climate change is the potential lowering of surface water pH as a consequence of increases in concentrations of atmospheric CO_2. This is particularly significant in the context of mine waste that does not support vegetation. The decrease in pH will alter the saturation state with respect to carbonate minerals and it is this aspect of climate change that forms the focus of this study of cerussite-dominated mine waste from Grogwynion Mine. The mine is a former lead-zinc mine and one of the fifty Welsh sites prioritised by the Environment Agency for remediation. An experimental and modelling approach was used in order to describe the chemical speciation that controls element release from the waste and to address the effects on metal mobility of pH changes of fresh waters and of the projected increase over time of atmospheric $P\mathrm{CO}_2$.

Material and Methods

Located by National Grid Reference SN 714723, the Grogwynion site occupies a valley side setting, immediately to the north of the River Ystwyth, a westerly flowing river that meets the sea at Aberystwyth. The River Ystwyth is deeply incised, from a valley floor elevation of approximately 90 m AOD, ground level rises steeply to at least 320 m AOD. The valley sides are largely forested, but contain numerous former mine workings, which are mostly free of vegetation. Mine waste and tailings occupy the valley floor immediately behind a bund constructed of mine waste, to the north of the river. Following a walk-over survey and site investigation two principal waste types were identified: an area of fine-grained tailings in the centre- north of the site, which is surrounded by coarser material that comprises the majority of the site (Fig. 1). Two number two-metre depth profiles, one of the fine grained tailings (profile GWS 101) and the other of the coarser waste spoil (profile GWS 102), were collected by hand augering to provide the material for the geochemical characterisation and leaching tests. Each leaching test sample comprised a composite of material from auger flights taken from 5 holes distributed within an area of 5 square metres. All samples, other than those used for leaching tests, were air-dried and sieved to <2 mm. Total element content of the <2 µm fraction was obtained by inductively coupled plasma emission spectroscopy (ICP-AES) after digestion of the samples with a mixture of hydrofluoric, perchloric and nitric acids. The pH was measured in 0.01M $CaCl_2$ solution and the cation exchange capacity (CEC) determined by titration. Whole-rock X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) on the heavy mineral fraction (density > 2.89 g cm^{-3}) were carried out. Soil pore water was extracted by centrifugation at 14000 rpm for 35 mins at 5°C. After centrifugation, the solution was passed through 0.45 µm filters and analysed by ICP-AES. The pH-dependent leaching test (as described in CEN standard PrEN 14429), was performed on composite samples representative of the whole depth-profile of the coarse waste rock and the fine tailings. The leaching test was performed in duplicate over a pH range of 5 to 8 at a liquid to solid (L/S) ratio of 10 for a period of 48 hours at 20 ºC. Nitric acid and sodium hydroxide were used to give a final solution pH in the desired range. The filtered leachate solution was analysed for major and trace elements by ICP-AES. Geochemical modelling was carried out using PHREEQC (Parkhurst, 1995) with the WATEQ4F (Ball and Nordstrom, 1991) thermodynamic database. All mineral stability diagrams were calculated using Geochemist's Workbench (Bethke, 1998) with the thermodynamic database thermo.dat.

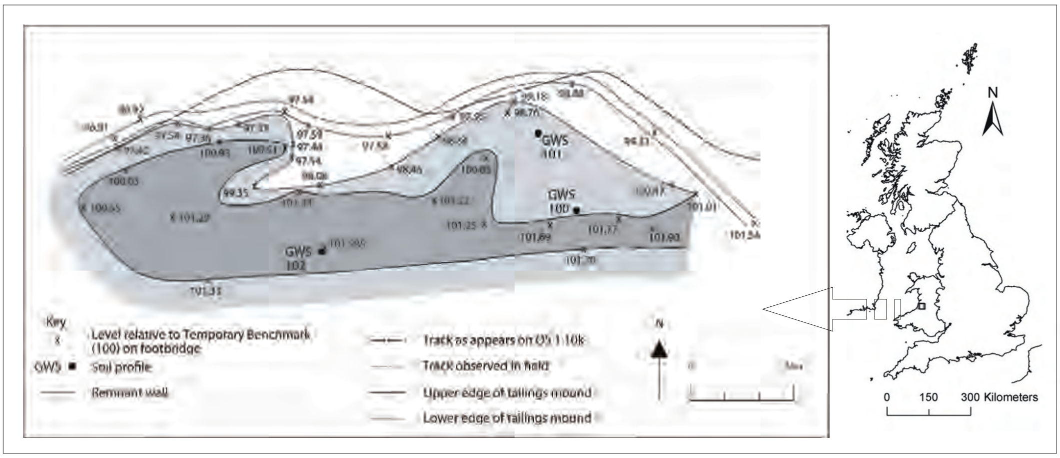


Figure 1. Study area with location of the sampling points (darker shaded area represents area of higher relief coarser-grained material).

Results and Discussion

1. Geochemical characterisation

Both the coarse mine waste and the fine tailings were mainly composed of quartz, chlorite, mica and feldspar, representative of the gangue minerals, with traces of calcite and dolomite. SEM analysis of the heavy mineral (HM) fraction revealed that samples all contained abundant cerussite (typically 20-40% in the HM fraction), which predominantly occurred as a secondary cement phase binding composite grains including fragments of silicates. Only minor amounts of galena with surficial encrustation of cerussite were observed. Minor amounts of other sulphides (pyrite, chalcopyrite and sphalerite) were locally present and appeared fresh and unaltered. Dolomite was generally absent within the heavy mineral fraction of the fine tailings profile whereas it was abundant in the coarse mine waste profile. The overall greater abundance of calcium carbonate minerals in the coarse grained waste was reflected in larger concentrations of Ca (0.17 – 0.79 wt%) and higher pH (6.20-7.35) in these samples compared to the fine tailings samples (Ca 0.09 - 0.12 wt% and pH 5.87-6.72). Fine tailings samples were also relatively higher in sulphur (S 0.07-0.36 wt% and 0.06-0.13 wt%, respectively, for the fine tailings and the coarse waste samples) and overall metal concentrations. The Pb concentration (up to 5.20 wt%) of the whole spoil material was invariably higher than that of Zn, Cu and Cd (Zn 256-3600 mg kg^{-1}, Cu 106-531 mg kg^{-1}, Cd 0.5-5.64 mg kg^{-1}). The Fe concentration ranged between 5 to 10 wt% in both profiles.

Pore water extracts from the fine tailings profile GWS 101 were mainly Ca-SO_4 type waters with pH ranging from 6.4 to 6.9, whereas the composition of pore water solutions in GWS 102 profile, the coarse mine waste, was mostly of Ca-HCO_3 type with pH of 7.06- 7.94. This latter composition is consistent with mine water forming from rock that contains few sulphides or with no sulphide oxidation in progress. Pore water composition of the fine tailings is instead indicative of acid mine drainage neutralised by carbonate host rocks. Trace metal concentrations of pore water extracts were generally higher in profile GWS 101 than profile GWS 102, with Zn concentrations (up to 29 mg L^{-1}) greater than those of Pb (up to 460 µg L^{-1}), Cu (up to 170 µg L^{-1}) and Cd (up to 100 µg L^{-1}). Measurements of saturation indices for a range of common Pb and Zn compounds suggested the near saturation state of pore water extracts with respect to cerussite, smithsonite ($ZnCO_3$), calcite, dolomite and $Fe(OH)_{3(a)}$.

2. Leaching tests

Although both profiles were subject to the leaching tests, this discussion is mainly focused on the fine tailings material. This is because the coarse mine waste yielded a level of Pb <0.1 mg L^{-1} in most of the leachates.

The acid neutralisation capacity (ANC) curve and the element release as a function of pH diagram for the fine tailings are shown in Figures 2 and 3, respectively. The pH of each leachate solution in the pH-dependent test was used to generate the ANC curve of the material. The titration curve (Fig. 2) represents acid/base added per kg of soil (calculated as mol H^+ kg^{-1} with base addition expressed as negative value) against pH. It showed a drop in pH from the natural pH of 6.76 to 5.74 on the first addition of 13 mmol H^+ kg^{-1} soil and a rather slower decrease from 5.74 to 5.09 following the addition of ~ 60 mmol H^+ kg^{-1} soil. In a system containing carbonates, as in the mine waste samples, a decrease in pH due to incremental addition of acid shifts the equilibrium of the dissolved inorganic carbon species with an increase in $CO_2(aq)$ and HCO_3^- against a decrease of CO_3^{2-}, causing undersaturation of carbonate minerals and carbonate dissolution. The dissolution of carbonate minerals follows the order of solubility with dissolution of the most soluble carbonate phases (Stumm and Morgan, 1996), in the sequence calcite, smithsonite and cerussite.

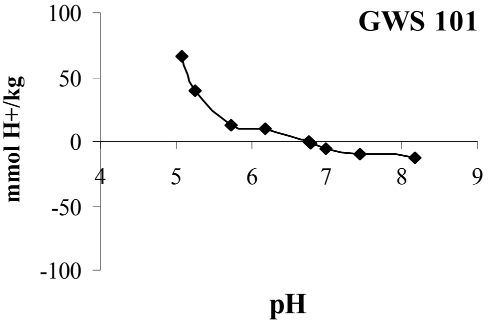


Figure 2. Acid neutralisation capacity curve for the fine tailings material.

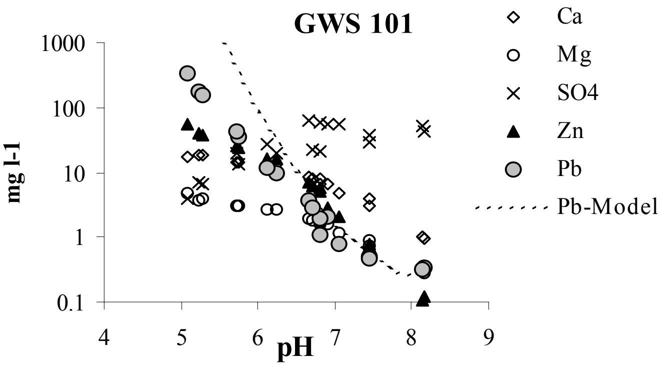
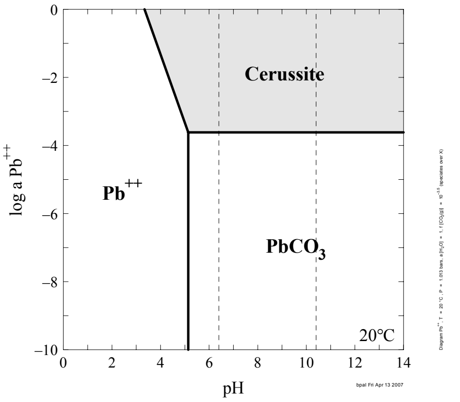


Figure 3. Lead, Zn and Ca leaching from the fine tailings material as a function of pH (dashed line: model simulation using PHREEQC).

By comparing the release pattern of Ca and Pb as a function of pH (Fig. 3) and the titration curve (Fig. 2), it was apparent that below pH of approximately 5.7 the cerussite present, together with the calcium and calcium-magnesium carbonates, was buffering the pH, via dissolution, which resulted in a very gradual change in pH and a large rise in dissolved Pb (up to 330 mg L^{-1}) along with Ca and Mg. The presence of moderate amounts of calcite in profile GWS 101 initially provided an effective buffer against the mobilization of Pb and Zn, by maintaining a circumneutral pH. Following the exhaustion of calcite, further acid addition caused Zn and Pb carbonate dissolution. Therefore, the geochemical evolution of these metal carbonate-rich tailings and the metal release rates cannot be assumed to be linear over time, as they depend on the amount and type of buffering minerals available.

3. Model results

Figure 3 shows the simulation results of dissolved Pb concentration changes during the pH-dependent test assuming a solution with a composition corresponding to GWS 101 pore water in equilibrium with cerussite and atmospheric $P\mathrm{CO}_2$ (in the model anglesite was allowed to precipitate if SI >1). The model findings confirmed that cerussite controlled Pb solubility in the studied samples (the discrepancy between experimental and modelling results occurring at low pH and elevated Pb concentration in solution may be due to the limitation of the experimental L/S ratio).



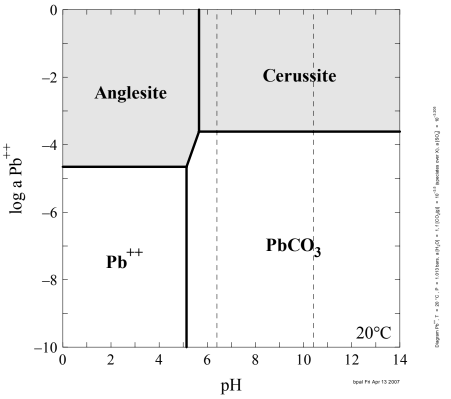
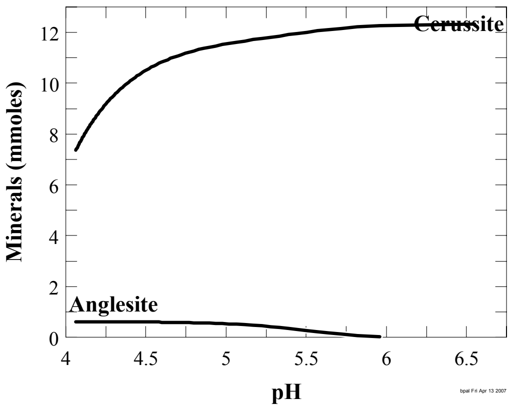


Figure 4. Solubility diagram versus pH for Pb^{2+} at 20°C in equilibrium with $CO_2(g)$ of $10^{-3.5}$ atm. Aqueous species: Pb^{2+}, $PbCO_3$. Minerals: Cerussite. Interior broken lines show mosaic boundaries for inorganic carbon species, which were allowed to speciate: subdiagrams, from left to right, are for the species $CO_{2(aq)}$, HCO_3^-, CO_3^{2}.

Figure 5. Solubility diagram versus pH for Pb^{2+} at 20°C in equilibrium with CO_2 (g) of $10^{-3.5}$ atm and containing SO_4^{2-} (60 mg L^{-1}). Aqueous species: Pb^{2+}, $PbCO_3$. Minerals: Cerussite, Anglesite.



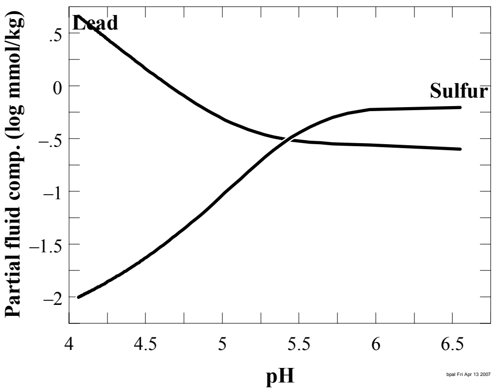


Figure 6. Modelling of mineral mass changes upon addition of 10 mmol H^+ in a system in equilibrium with atmospheric CO_2, containing cerussite and SO_4^{2-} (60 mg L^{-1}).

Figure 7. Pb and S concentrations as function of pH in the system modelled in Figure 6.

The modelled equilibrium composition of a solution in the presence of cerussite at constant partial pressure of atmospheric CO_2 ($P\mathrm{CO}_2=10^{-3.5}$), and also containing Ca and Mg in solution in equilibrium with calcite and dolomite, indicated that cerussite was the dominant stable Pb mineral phase controlling the solubility of Pb above pH of ~ 5.1 (Fig. 4). Accordingly, as the pH decreased upon acid addition to below pH 5, Pb solubility governed by cerussite increased. Figure 5 shows how anglesite becomes the stable Pb mineral phase at pH below ~ 5 in a system also containing SO_4^{2-} ions in solution. In a simplified model, as shown in Figures 6 and 7, as a consequence of 10 mmol of H^+ addition, cerussite dissolved and anglesite formed, governed by the solubility product and dissolved SO_4^{2-} ion availability. In the presence of a moderate concentration of SO_4^{2-} (~ 60 mg L^{-1}) in the pore water solution of profile GWS 101 the precipitation of anglesite, indicated by the SO_4^{2-} decrease in solution at low pH in Figure 3, had a negligible effect in reducing the dissolved Pb derived from cerussite dissolution. Similarly for Zn, the stability diagram of smithsonite (not shown) in equilibrium with atmospheric PCO_2 indicated its stability only at alkaline pH, with a sharp increase in Zn solubility as pH decreased.

4. Sensitivity of mine waste to decreases in fresh water pH: considerations in the context of climate change

The results of the pH-dependent experiments showed that a decrease in pH gave rise to a negligible impact on Pb and Zn carbonate mineral dissolution until threshold pH values were reached. At these critical points Pb and Zn carbonates began to buffer the pH, resulting in increasing concentrations of dissolved Pb and Zn in solution. The simple model of a carbonate system in equilibrium with atmospheric CO_2 and subjected to pH changes may have its counterpart in nature should the waste come into contact with acid mine drainage or as a result of a change of disposal scenario.

In the context of climate change, we modelled the effects of the projected PCO_2 increase on the solubility of cerussite. For the simulation we used a representative fresh water composition (pH = 8, major element concentrations: SO_4^{2-} $3x10^{-4}$ M, Cl^- $2.4x10^{-4}$ M, Ca^{2+} 10^{-3} M, Mg^{2+} $3x10^{-3}$ M, Na^+ $2.5x10^{-4}$ M, Alkalinity $2x10^{-3}$ M) and allowed it to equilibrate with cerussite and the present PCO_2 of $10^{-3.5}$ atm, followed by a step-wise increase in PCO_2 to the value projected for the year 2100 (PCO_2 of $10^{-3.3}$ atm) (IPPC projection). The simulation showed that for the given water composition and atmospheric PCO_2 change, dissolved Pb would increase from 3.15 mg L^{-1} at an equilibrium pH of 6.72 to 3.61 mg L^{-1} at pH of 6.59. The modeling of pristine rain water in equilibrium with cerussite at constant PCO_2 gave very similar results. Simulation results therefore indicated a limited effect on Pb solubility with the implication that factors other than rising atmospheric PCO_2, e.g. changes in temperature and microbiological activity (microbial CO_2 production) could be more significant overall.

Concluding remarks

This study presents evidence for the influence of rising atmospheric PCO_2 and water acidification on the solubility of Pb carbonate minerals in mine waste and addresses the sensitivity of such systems.

Mine waste characterisation is considered an important tool in the assessment of the effects of climate change on the environmental risks associated with mine waste. Characterisation should include the measurement of intrinsic leaching properties in conjunction with mathematical modelling to estimate contaminant release under a range of conditions that have a significant impact on metal leaching.

Acknowledgements

This paper is published by permission of the Director, British Geological Survey. Site plan was prepared by Lauren Noakes (British Geological Survey).

References

Arnell N.W., Reynard N.S. (1996) The effects of climate change due to global warming on river flows in Great Britain. Journal of Hydrology 183 (3-4), 397-424.

Ball J.W., and Nordstrom D.K. (1991) User's manual for WATEQ4F,with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters. US Geological Survey Open-File Report, 91–183.

Bethke C.M. (1996). Geochemical Reaction Modeling. Oxford Press, 397 pp.

Hulme M., Jenkins G.J., Lu X., Turnpenny J.R., Mitchell T.D., Jones R.G., Lowe J., Murphy J.M., Hassell D., Boorman P., McDonald R., Hill S. (2002). Climate change scenarios for the UK: the UKCI02 Report. Norwich, UK: Tyndall Centre for Climate Change research, School of Environmental Sciences, University of east Anglia; 120 pp.

IPCC (2001). Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change [J.T. Houghton, Y. Ding, D.J. Griggs, M. Noguer, P.J. van der Linden, X. Dai, K. Maskell and C.A. Johnson (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 881 pp.

Parkhurst D.L. (1995). User's Guide to PHREEQC- a computer program for speciation, reaction-path, advective transport, and inverse geochemical calculations. US Geological Survey, Water-Resources Investigations Report, 95–4227.

PrEN14429 (2002). Characterisation of waste: Leaching behaviour tests- pH dependence test with initial acid/base addition. CEN/TC 292 WG6.

Stumm W., Morgan J.J. (1996). Aquatic Chemistry. John Wiley & Sons, Inc. New York.