Prediction of the long-term performance of abandoned lead zinc mine tailings in a Welsh catchment

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Abstract

In this study we investigated the sulphidic mine tailings from Frongoch and Grogwynion, two abandoned lead zinc mines in mid Wales, UK. Despite falling within the same orefield the mine waste characterisation has identified differences in the tailings from the two sites. Bulk concentrations range from 10 to 52 g kg^{-1} for Pb, 1.1 to 2.9 g kg^{-1} for Zn in Grogwynion and from 1.0 to 130 g kg^{-1} for Pb, 11 to 110 g kg^{-1} for Zn in Frongoch. An experimental (European standard leaching tests TS 14429 and TS 14405) and geochemical modelling approach was used to study the leaching composition as a function of pH and liquid/solid ratio. There was little correlation between the tailings bulk metal concentrations and the leachate composition, but variations in Pb and Zn concentrations were found to be consistent with control of dissolved Pb and Zn by secondary minerals and the mechanisms of dissolution/precipitation/sorption involving them. Specifically, the Grogwynion mine tailings with near-neutral pH have predominant lead and zinc carbonates controlling Pb and Zn solubility in the leachates, whereas the Pb and Zn concentrations in Frongoch leachates are best modelled with a surface complexation model for metal sorption to oxyhydroxides. The different speciation results in a greater sensitivity of Grogwynion tailings to acidification with a potential release of Pb in solution up to 10 times higher than in Frongoch, despite similar bulk Pb concentrations. At acid pH, Zn is similarly dissolved to a greater extent in Grogwynion than in Frongoch tailings. There was no evidence of sulphide oxidation during the batch and column leaching tests and the suitability of using these European leaching standards for the characterisation of sulphidic mine waste materials for waste management purposes has been considered.

Keywords: mine waste characterisation, abandoned metal mine, leaching test, sequential extraction, geochemical modelling, Wales.

1. Introduction

Lead and zinc mining has a long history in the Ystwyth catchment of mid Wales. Lead mining near Cwmystwyth may well have started in pre-Roman times with sporadic activity throughout the Middle Ages. The advent of the Society of Mines Royal in the sixteenth century, with the emphasis on silver production, saw mining become a major contributor to the Welsh economy. In the mid-Wales area Pb and Zn mining continued from this time through to the early part of the twentieth century.

In a recent report (Welsh Assembly Government, 2005) it was estimated that over 4% of surface waters in west Wales were at risk or probably at risk due to diffuse source pressures related to mining and mine water impacts. The Environment Agency (EA) for England and Wales, in its Metal Mines Strategy for Wales (EA, 2002) focussed on the top 50 abandoned mine sites, which were recognised as having the greatest environmental impact on surface waters. One of the longer term objectives of the EA's study was to scope remedial options. Two of the abandoned mines prioritised by the EA, Frongoch and Grogwynion, are the subject of this paper.

According to Lewis (1967), Grogwynion was certainly active in 1637 and was still in profit in 1879. The lease on Frongoch was first taken up in 1759 and the mine was worked for Pb ore until the 1870's and then subsequently until the turn of the century for zinc blende. In his account of Frongoch's history Bick (1996) describes how, after the closure of Frongoch in 1904, the mine remained abandoned until a company was set up in the 1920's to exploit the zinc blende on the dumps, this continued until 1930 when activity essentially ceased.

A contemporary account published by the French mining engineer Moissenet (Moissenet, 1866) describes the ore processing at Frongoch in some detail and gives an insight into how process waste from the operations was discharged into the environment. He describes a series of workshops arranged on a slope at the mine and powered by water in which the crushing, jigging and separation of the ore were carried out hydraulically by gravity separation to concentrate the Pb and Zn minerals. The tails were discharged from the final stage Lisburn buddle to waste.

Environmental impacts of mining were of national concern at this time and the River Pollution Commissioners report (Rivers Pollution Commission, 1874), approximately contemporaneous with Moissenet's visit, describes Pb mining as causing some of the most serious pollution of rivers in the country and during periods of flooding producing damage to vegetation and the occasional poisoning of cattle and poultry through over bank deposition and subsequent ingestion of contaminated sediments by animals. The elaborate ore treatment, requiring large volumes of water to aid the process of jigging, and through which a large proportion of the ore was wasted, was blamed for water pollution and the turbid, whitened state of the Ystwyth. In the same report the Commissioners present an analysis of muds and slimes from the Frongoch Mine that contained over 100 g kg^{-1} Pb and nearly 90 g kg^{-1} Zn. Griffith (1919) recognised that surface drainage from mine waste heaps, wind blown redeposition of sand and slime dust on adjacent lands, erosion from farm roadways constructed with mine wastes, leat overflows, adit discharges, and flood deposition of Pb and Zn contamination were the main causes of soil infertility in Cardiganshire. He described how horses and sheep were particularly vulnerable having poor condition and reduced life expectancy due to ingestion of contaminated particulate material. Poultry were particularly sensitive because of their grit-eating nature, producing shell-less eggs; all fish life in the affected rivers had been destroyed. Davies (1987) has estimated that approximately 35% of the ore raised to the surface was lost during ore dressing operations.

More recently the European Mine Waste Directive (EC, 2006) has introduced new requirements for mine waste management including that resulting from the legacy of historical mining. The challenge in implementing the European Directive is to develop a national or pan European, harmonised, risk-based inventory of abandoned mines in order to prioritise sites for remediation based on a common set of criteria. The characterisation of the mine waste in its physical and chemical properties in the short and long term forms the basis for such risk-based classification of abandoned mine sites. The prediction of the longer term reactivity of tailings and mobility of contaminants in response to changes in environmental factors such as those that might be expected by climate change effects requires an understanding of the essential geochemical processes controlling the waste behaviour. To achieve this objective the authors have tested the feasibility of using a combined experimental and geochemical modelling approach which was described by Kosson et al. (2002); van der Sloot (2002); van der Sloot et al. (2006), for the characterisation of the long term leaching behaviour of waste materials. This approach, based on the European CEN/TC292 leaching test methods, has been used successfully to predict the leachate quality of municipal solid waste incinerator bottom ash (Dijkstra et al., 2006; Meima and Comans, 1997, 1998) and contaminated soils (Dijkstra et al., 2004). Understanding the geochemical processes governing the release of contaminants from the waste as a function of pH and liquid/solid (L/S) ratio forms the basis for predicting the longer term release behaviour and assessment of impact and the best waste disposal/remediation scenarios. In this paper, the leaching behaviour of Pb and Zn over a range of pH and as a function of the L/S ratio is investigated using Grogwynion and Frongoch mine tailings.

2. Materials and Methods

2.1 Site Description and Sampling

Frongoch is situated in the catchment of the Nant Cwmnewydion, a tributary of the Ystwyth, while Grogwynion is located on the north bank of the Ystwyth River, which flows west towards the Irish Sea (Fig. 1). The British Geological Survey's mine entrances database indicates that there are about 87 abandoned mine entrances in this

193 km^2, medium sized catchment that might possibly be contributing to the pollution load; at least 20 of these correspond to Frongoch and Grogwynion abandoned mines. Grogwynion tailings occupy the valley floor immediately behind a bund constructed of mine waste. Land immediately to the west of Grogwynion comprises the former Gwaithgoch Dressing Mill, which utilised flotation techniques and was designed to carry out secondary processing of mine waste from both Grogwynion and Frongoch and it is suspected that the tailings from this process were deposited on the Grogwynion tailings site. In the vicinity of Grogwynion the steep valley sides are largely forested, but contain numerous former mine workings that are mostly free of vegetation. There are areas of open cut along east to west- trending mineral veins that are associated with the Ystwyth Fault, towards the top of the ridge behind Grogwynion. The Frongoch site is surrounded by pasture land to the north, south and east, with further mine workings to the west. Although the Frongoch mine workings have been abandoned the site has remained in industrial use as a saw mill.

Mineralization is hosted by the Silurian Devil's Bridge Formation at Frongoch and the older Rhayader Mudstones at Grogwynion (Davies et al., 1997). The Devil's Bridge Formation comprises interbedded thin turbidite sandstones and thicker turbidite mudstones with phosphatic pockets. The Rhayader Mudstones comprise very thinly interbedded turbidite mudstones and thicker mudstone units. The mineralised veins are dominated by quartz, with two generations of carbonate being evident, an early phase of ferroan dolomite and a later one of calcite. Typical of the Pb-Zn deposits of the mid-Wales ore field, the mineralization at both sites is concentrated on east-northeast-trending normal faults. The currently accepted model of ore genesis is one of metals leaching from the Lower Palaeozoic during dewatering and low grade metamorphism (Raybould, 1974; Davies et al., 1997).

Mining impacted stream sediments in the Ystwyth Valley and its tributaries are still evident (BGS, 2000). High Pb concentrations in stream sediments are recorded downstream from the main mines, for instance 430 m below the discharge point of the stream draining from Frongoch into the Nant Cwmnewydion the Pb concentration is 10.0 g kg^{-1} and Zn concentration is 2.96 g kg^{-1} decreasing to 2.20 g kg^{-1} Pb and 2.14 g kg^{-1} Zn in the Nant Magwr, approximately 1.5 km upstream from its junction with the Ystwyth. In a small stream draining through the Grogwynion site the sediment Pb concentration is lower at 2.90 g kg^{-1}, but is still very high when compared to Pb values from non-mined areas of the catchment that are generally less than 0.10 g kg^{-1}. Water quality is also impacted in the vicinity of abandoned mines and the British Geological Survey's baseline study of surface water quality (BGS, 1999) indicates high Pb concentrations of 320 µg l^{-1} associated with Cwmystwyth Mine upstream from Grogwynion. High dissolved Zn concentrations (>300 µg l^{-1}) are also reported, with the highest value of 3 mg l^{-1} from the Nant Cwmnewydion below Frongoch. There are extensive deposits of mine waste at both sites. The mine waste can be subdivided into coarser waste rock and fine-grained tailings. This study has concentrated on the mine tailings at each of the sites. At Frongoch, where the tailings occupy a former lagoon area of approximately 120 m x 70 m, the lateral and vertical variability of the tailings was confirmed with three exploratory trial trenches, excavated to depths of between 1.65 m and 3.50 m. The findings of the trial trenches were used to produce the profile presented in Fig. 1. Data from trial trench FRS 3001 forms the subject of this paper. Six disturbed samples were collected from this trench at each visible change in lithology (Table 1). The Grogwynion site was investigated by sampling from profiles revealed by hand augering and digging to depths of approximately 2 metres (Table 2). Hand augered samples comprised a composite of sample material from 5 auger holes at the corner and centre of a 5 x 5 m square. Groundwater was not encountered at Grogwynion, however it is suspected that groundwater in the tailings is in hydraulic continuity with the river. At Frongoch perched groundwater was encountered at 1.10 m depth, with a second strike at 3.35 m depth.

2.2 Analytical methods

Samples of tailings were air-dried and sieved to <2 mm. Total element content of the <2 mm fraction was obtained by inductively coupled plasma atomic emission spectroscopy (ICP-AES) after sample digestion with a mixture of hydrofluoric, perchloric and nitric acids. The pH was measured in 0.01M $CaCl_2$ solution at a liquid to solid ratio of 2.5 $l\ kg^{-1}$. The organic matter content of each sample was estimated by measuring the weight loss (LOI) after heating to a temperature of 450°C. Mineral identification was achieved by X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) on the heavy mineral fraction (density > 2.89 $g\ cm^{-3}$). Further chemical characterisation of the mine waste was carried out using the sequential extraction and leaching test methods described below.

2.3 Sequential Extraction

The sequential extraction method used has been previously described by Cave and Wragg, (1997). The method relies on a seven duplicate step extraction scheme using increasing concentrations of aqua regia for each pair of extractions. Approximately two g of <2 mm material was accurately weighed into Whatman ‘Vectaspin 20’ centrifuge tubes with polypropylene filter inserts (pore size 0.45 μm). 10 ml aliquots of extractant were added to the tubes and the vessels centrifuged for 10 minutes at 1034 G, where the extracts were removed and stored in 30 ml polystyrene Greiner® tubes prior to analysis. The process was repeated sequentially until all 14 extracts, each of volume 10 ml, had been processed. The extractants used were deionised water and increasing concentrations of aqua regia (0.01, 0.05, 0.10, 0.50, 1.0 and 5.0 M). For the 0.1, 0.5, 1 and 5 M acid extracts, 0.25, 0.50, 0.75 and 1 ml, respectively, of hydrogen peroxide were also added to each extractant before making up to 10 ml volume. The solutions obtained were analysed for major and trace elements by ICP-AES.

A data-processing algorithm, the Chemometric Identification of Substrates and Element Distributions (CISED) (Cave et al., 2004), was used to identify the number of components extracted, their composition and the proportion in each extract. The chemometric data-processing is based on the assumption that the material is made up of a mixture of discrete physico-chemical components characterised by a distinct element composition. Under increasing acid concentration each physico-chemical component will dissolve according to its degree and rate of solubility. By taking into account the solubility of minerals and their composition it is possible to assign each CISED component to a certain physico-chemical phase, e.g. exchangeable fraction, carbonates, Fe-Mn oxides, organic matter, sulphides, and silicates.

2.4 Leaching tests

In order to provide a better understanding of the chemical speciation and leaching behaviour that controls constituent release from the waste under changing environmental conditions a pH-dependent leaching test and a percolation test, as described in the European standards TS 14429 and TS 14405, (CEN/TC292, 2004; CEN/TC292, 2005) respectively, were performed on composite samples representative of the whole depth-profile for the Grogwynion and Frongoch tailings. All leaching tests were performed in duplicate.

The pH-dependent leaching test TS 14429 was performed over a range of pH values from acid to alkaline at a L/S ratio of 9 (15 g of solid in 135 ml of solution) for a period of 48 hours. Nitric acid and sodium hydroxide were used to give a final solution pH in the desired range. The filtered leachate solutions were analysed for major and trace elements by ICP-AES. The test provides metal release information as a function of pH and, in addition, the acid neutralisation potential is derived from this procedure.

The percolation test TS 14405 was run as an up-flow column test with the pH allowed to float to a natural value when de-ionised water was used as leaching agent. The columns, with a length of 150 mm and an inside diameter of 50 mm, were slowly saturated with deionised water at a constant flow rate equivalent to a leachant linear velocity of 15 cm day^{-1} using a peristaltic pump. This flow rate allowed the test to be conducted within a manageable time-span of 3 weeks, while apparently fulfilling local equilibrium conditions. The eluates were collected at specific L/S ratios between 0.1 and 10. The pH of the leachates was measured straight after sample collection. The leachates were then filtered through a 0.45 μm filter before being preserved for chemical analysis. Redox potential during the experiment ranged from 400 to 450 mV.

2.5 Geochemical modelling

Geochemical modelling, consisting of solution speciation and batch reaction modelling, was used to assist in the understanding of the processes governing the release of Pb and Zn as a function of pH and L/S ratios, reflecting the variables that are most sensitive to potential change associated with either proposed remedial measures, or the impacts of climate change. Solution speciation and batch reaction modelling was performed using PHREEQC (Parkhurst and Appello, 1999) and the WATEQ4f database (Ball and Nordstrom, 1991). The mineral Hydrozincite ($Zn_5(OH)_6(CO_3)_2$) (Preis and Gamsjäger, 2001) was added to the thermodynamic database for our calculations.

Input files to calculate saturation indices of potential solubility controlling phases consisted of the measured total element concentrations in the solutions extracted in the pH-dependent and percolation tests, with each solution pH fixed at the measured value. The precipitation of all solids was suppressed. Only saturation indices of the phases which were likely to be present in the mine waste or possibly formed during the experiment were considered, namely Al $(OH)_3$(a), Alunite ($KAl_3(OH)_6(SO_4)_2$), Anglesite ($PbSO_4$), Bianchite ($ZnSO_4 .6H_2O$), Calcite ($CaCO_3$), Cerussite ($PbCO_3$), $Fe(OH)_3$(a), Galena (PbS), Goslarite ($ZnSO_4 .7H_2O$), Gypsum ($CaSO_4 .2H_2O$), Hydrozincite ($Zn_5(OH)_6(CO_3)_2$), Jarosite ($KFe_3(OH)_6(SO_4)_2$), $Pb(OH)_2$, Pyrite (FeS_2), Smithsonite ($ZnCO_3$), Sphalerite (ZnS), Zincite (ZnO) and ZnO (a), where (a) stands for amorphous.

The pH-dependent leaching results were compared with the prediction of a batch reaction model simulating mineral dissolution/precipitation and adsorption to reactive surfaces present in the mine waste as a function of pH. The simulated system was an open system in equilibrium with atmospheric CO_2. The leachate composition in equilibrium with the mine waste at different pH was modelled by simulating a titration with HNO_3 and NaOH of a solution with a composition corresponding to the initial leachate solution in the pH-dependent test (prior to addition of acid or base). In the input files it was assumed equilibrium of the aqueous solution with potential solubility controlling mineral phases, chosen on the basis of evidence of mineralogical and chemical sequential extraction analyses. Kinetic rates were not included in the model. Experimental L/S ratio conditions were simulated. To enhance the model, the role of surface complexation was investigated by adding the Generalised Two Layer Model of Dzombak and Morel (1990). The recommended specific surface area of 600 $m^2 g^{-1}$ was used to calculate site densities for amorphous Fe hydroxide (HFO). The estimated amount of HFO that served as input in the adsorption model was derived from the concentration of Fe extracted up to the 5 M aqua regia extraction step in the CISED extraction protocol and these values recalculated to represent the amount of sorbent minerals at a L/S ratio of 9 l kg^{-1}. In FRS 3001, where amorphous Al hydroxides were considered present as additional sorbent minerals, HFO was taken as a surrogate for amorphous Al hydroxides (assuming 1 mol Fe hydroxide = 1 mol Al hydroxide), following the approach of Meima and Comans (1998) .

3. Results and Discussion

3.1 Mineralogical and geochemical characterisation

Grogwynion tailings (GWS 101 profile) were mainly composed of quartz, chlorite, mica and feldspar, representative of the gangue minerals, with traces of calcite and dolomite. All samples contained cerussite (typically 3-4 wt%), 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 in the heavy mineral fraction by SEM analysis. Traces of pyrite, chalcopyrite and sphalerite were locally present in the heavy mineral fraction and appeared to be fresh and unaltered.

Results of the mineralogical analysis of Frongoch profile FRS 3001 indicated a gangue assemblage comprising quartz, feldspar, mica and chlorite. All samples in this profile contained an appreciable proportion of sphalerite (1-20 wt%), being notably higher at a depth of 74-100 cm. Galena was present from 74 cm depth and enriched (around 10 wt%) at 140-165 cm depth. Traces of anglesite were detected from 74 to 140 cm depth. A surface efflorescence of bianchite was observed during the particularly dry summer conditions of 2006.

The chemical composition of the two profiles varies reflecting the variation in mineralogical composition of the tailings layers. It is shown as a function of profile depth in Fig. 2. In profile GWS 101 the pH ranged from 5.9 to 6.7. Lead concentration, ranging from 9.95 to 52.4 g kg^{-1}, had its maximum at a depth of 75-125 cm, at around the midpoint of the core, which corresponded to the lowest pH value and max S concentration. Zinc concentrations decreased from 2.87 g kg^{-1} down the profile, to a minimum of 1.09 g kg^{-1}. Organic matter content ranged between 1.3 to 1.9 wt%. In profile FRS 3001 Pb concentrations ranged from 1.01 to 127 g kg^{-1}, Zn from 10.6 to 112 g kg^{-1}, Cd from 0.019 to 0.402 g kg^{-1}. Organic matter content ranged between 0.2 to 0.7 wt%, except for the bottom horizon with a value of 6.6 wt%, due to the presence of pockets of peat towards the base of the stratum. The pH increased down the profile from 3.9 to 6.2 at a depth range of 140-165 cm and decreased again at the bottom horizon of 165-220 cm corresponding to a higher organic matter content, Al, and Fe. Zinc, Cd, Cu, Pb and S showed an enrichment at 74-100 cm and 140-165 cm, suggesting enrichment in sulphides in these intervals.

3.2 Sequential extraction results

Fig. 3 shows the leached concentration of Pb and Zn, against the extraction steps 1 to 14 for both GWS 101 and FRS 3001 profiles. Under increasing concentration of aqua regia each element will dissolve according to its degree and rate of solubility, related to mineralogical phase and sample texture. In order to aid in the data interpretation a selection of pure mineral phases occurring in mine tailings were subject to the same sequential extraction procedure and their extraction profiles are illustrated in Fig. 4. The extraction profiles of Pb in GWS 101 all showed a main, sharp peak at step 5 (0.05 M aqua regia), where the cerussite pure mineral phase was mainly removed (Figs. 3-4). In FRS 3001 the Pb extraction peak was generally broader and shifted towards stronger acid conditions, where galena and anglesite are leachable. Some differences throughout the various horizons of each profile were, however, evident and will be the focus of the following paragraphs.

Zinc was mostly extracted over the step range 3 to 7 (0.01- 0.1 M aqua regia) in GWS 101. It is suggested that this represents Zn carbonate, associated with cerussite. A subordinate portion of the Zn was also extracted at step 13-14 (5 M aqua regia) in the first 100 cm of the profile, which Fig. 4 suggests is related to sphalerite dissolution. In FRS 3001 Zn was mostly leached at step 13-14 (5 M aqua regia) with the exception of the top and bottom horizons. In the top horizon an appreciable amount of Zn was determined in the deionised water extraction. This suggests that the upper layers in the tailings are characterised by soluble Zn salts, likely to be a Zn sulphate phase. In the bottom horizon at 165-220 cm depth the Zn extraction window fell in the range 3 to 7 (0.01- 0.1 M aqua regia).

The CISED chemometric data-processing of the sequential extraction results helps to elucidate the observed leaching patterns and to discern the metal speciation in the tailings sample and mineral reactivity. Figures 5 to 7 illustrate the composition and extraction profiles of the CISED extracted components with their geochemical assignments for horizon 0-20 cm in profile GWS 101 and horizons 0-17 and 165-220 cm in profile FRS 3001. Fig. 8 summarises the solid phase partitioning of Pb and Zn in the same tailings horizons. In the near neutral pH condition of Grogwynion most Pb and Zn is present as carbonates. Subordinate Pb phosphate (pyromorphite), Pb and Zn associated with Mn/Fe-rich oxyhydroxides and Zn sulphide phases were also identified by the CISED extraction. This complements the XRD analysis results with information on mineralogical phases that are present, but whose abundance was below the XRD detection limit. In the acidic Frongoch tailings Pb and Zn carbonates were rarely developed, while primary sulphides and secondary sulphates of Pb and Zn were the main phases. Significant differences between the top and lowest horizons of profile FRS 3001 were in the presence of large amounts of Zn, as Zn sulphate, in the pore water of the top horizon and the presence of “exchangeable” Zn and Pb, coupled to Pb Zn Al rich phases, probably Pb Zn rich Al hydroxides, in the lowest horizon.

3.3 Leaching test results

3.3.1 Percolation test

The leaching tests were carried out on composite samples representative of the whole profile as this was considered to be a practical basis for characterisation as part of risk assessment. The composite sample of Grogwynion GWS 101 tailings consisted of: 107 g kg^{-1} Al, 1.22 g kg^{-1} Ca, 0.005 g kg^{-1} Cd, 63.9 g kg^{-1} Fe, 21.9 g kg^{-1} K, 1.06 g kg^{-1} Mn, 32.2 g kg^{-1} Pb, 2.05 g kg^{-1} S and 1.82 g kg^{-1} Zn. The Frongoch composite sample composition was 46.5 g kg^{-1} Al, 0.339 g kg^{-1} Ca, 0.184 g kg^{-1} Cd, 24.9 g kg^{-1} Fe, 11.0 g kg^{-1} K, 0.243 g kg^{-1} Mn, 30.6 g kg^{-1} Pb, 30.4 g kg^{-1} S and 50.5 g kg^{-1} Zn. Fig. 9 shows the results of the percolation test, run in duplicate, as the leachate concentrations (mg l^{-1}) of Pb, Zn, S and pH in each pore volume fraction (PV) for Grogwynion (GWS 101) and Frongoch (FRS 3001) composite tailings samples. The leachate pH ranged between 6.2 - 6.9 for Grogwynion tailings and 5.6 - 6.4 for Frongoch tailings. The Pb leached from Grogwynion tailings was fairly constant with concentration between 1.3 to 3.0 mg l^{-1}. Zinc release decreased ten fold with the progress of the leaching from 56 to 5.7 mg l^{-1}. In FRS 3001 both Zn and Pb concentrations decreased over the leaching period from 480 to 20 mg l^{-1} for Zn, from 25 to 4.5 mg l^{-1} for Pb. Despite Frongoch leachates starting with much higher concentrations of Pb and Zn than Grogwynion leachates, the concentration-time trends for both tailings types generally converged towards similar values at the end of the leaching, showing little correlation with Pb and Zn bulk concentrations in the tailings material.

The observed decreasing leaching patterns of Pb, Zn, as well as S, suggest a very slow oxidation rate, even negligible, of the Pb and Zn sulphides in the column experiment, consistent with an advective supply of dissolved O_2 dominating over diffusion, due to the low diffusivity of O_2 in saturated columns. The lack of observed significant amounts of pyrite in both tailings types and associated Fe oxyhydroxide weathering products further limits the sulphide oxidation through the Fe(III) oxidation pathway (Malmstrom et al., 2006).

The fairly constant concentration of leached elements can be due to surface kinetics (mineral dissolution at a rate controlled by surface kinetics processes) or mineral equilibrium processes (Evans et al., 2006). Saturation index calculations suggested that concentration of Pb was controlled by chemical saturation with respect to the secondary mineral cerussite (for PV > 0.1) in Grogwynion tailings. Under these conditions the concentration of Pb remains constant as long as the factors affecting mineral solubility (pH, T, solution composition) and mineral phase activity remain constant. The decline in leachate Pb concentrations with time observed in Frongoch leachates might either reflect wash-out of pore water solutes present in the tailings prior to the start of the experiment or dissolution/depletion of the secondary mineral anglesite as the leachates went from supersaturated to slightly undersaturated with respect to anglesite during the experiment. All leachates were slightly undersaturated with respect to various sulphate, carbonate or hydroxide phases of Zn included in the WATEQ4F database (Ball and Nordstrom, 1991), making it difficult to infer the importance of either washout of pore water or mineral phase dissolution in the control of decreasing Zn release in both tailings types.

3.3.2 pH-dependent leaching test

Fig. 10 shows the pH-dependent leaching data for Pb, Zn, Cd, Ca and S in Grogwynion and Frongoch composite samples.

The pH-dependent test procedure was also used to generate the acid neutralisation capacity (ANC) curve of the material, an indicator of the buffering capacity of the waste. The ANC curve (Fig. 10) represents acid/base added per kg of material (calculated as mol H^+ kg^{-1} with base addition expressed as a negative value) against pH. The curve for GWS101 showed a drop in pH from the natural pH of 6.8 (at L/S ratio of 9) to 5.7 on the first addition of 13 mmol H^+ kg^{-1} material and a rather slower decrease from 5.7 to 5.1 following the addition of ~ 60 mmol H^+ kg^{-1}. In Frongoch tailings the acid buffering capacity was lower than for Grogwynion tailings. The acid addition to obtain a pH of 3.8 from the natural pH of 5.8 (at L/S ratio of 9) was 36 mmol H^+ kg^{-1}.

The leaching of Pb and Zn was strongly dependent on the pH for both Grogwynion and Frongoch composite samples, with leachate metal concentrations decreasing from acid to neutral pH then slightly increasing again towards strongly alkaline pH. The solubility of Pb was higher at acid pH in Grogwynion tailings samples and lower at alkaline pH, compared to Frongoch tailings. At low pH the dissolved Zn concentrations were of the same order of magnitude in both tailings types, despite the greater enrichment in total Zn of Frongoch tailings. In particular Zn concentrations seemed to level off at a pH below 5.3 in Frongoch tailings. Under alkaline conditions Zn, behaving similarly to Pb, was leached to a greater extent in Frongoch than in Grogwynion tailings. The sulphur leaching pattern was almost pH independent at alkaline pH reaching a plateau of 20 mg l^{-1} for Grogwynion and of 150 mg l^{-1} for Frongoch.

Over the acid pH range Grogwynion leachates were saturated with respect to anglesite while becoming saturated in cerussite at alkaline pH. They were generally undersaturated with respect to Zn secondary minerals with the exception of willemite (Zn_2SiO_4) at alkaline pH The Frongoch leachates were generally calculated to be undersaturated with respect to Pb and Zn oxides, carbonates, sulphates and phosphates, over the acid pH range, except for anglesite, while they were saturated or oversaturated at alkaline pH with respect to willemite, Zn (hydroxy) carbonates, ZnO(a) and cerussite. This information serves as a basis for constraining the modelling of the pH-dependent leaching data.

3.4 Results of batch reaction modelling

Experimental and simulated Pb and Zn leaching from pH 4 to 9 are shown in Fig. 11. Table 3 summarises the model inputs and assumptions.

For Grogwynion three simulations were performed and compared with the experimental curves: (1) assumed equilibrium with atmospheric P_{CO2}, and carbonate minerals of Pb and Zn (cerussite and hydrozincite), on the basis of XRD evidence and the sequential extraction data. Hydrozincite, a common secondary mineral from the weathering of sphalerite in mine dumps of the Central Wales orefield, was chosen as representative of the Zn carbonate phases. The concentration of each mineral phase was estimated from the maximum metal leached at acid pH of the leaching test, based on the assumption that carbonate phases will all be dissolved at a pH of around 4. In model (2) anglesite precipitation was allowed and in model (3) surface complexation was also included, as the CISED extraction suggested the subordinate presence of Pb Zn rich-Fe oxyhydroxides along with the metal carbonate phases.

The leaching of Pb was adequately described above pH 6.6 by the solubility of cerussite (model 1). The model, however, overestimated the leaching of Pb at more acid pH. One possible explanation might be due to dissolution kinetics of cerussite not accounted for in the model. Allowing for anglesite precipitation led to lowering the dissolved Pb at equilibrium (from 300 mg l^{-1} in model 1 to 150 mg l^{-1} in model 2) over the acid pH range. In model (3) surface complexation on Fe oxyhydroxides (HFO) was included, estimating the amount of HFO from the CISED extraction. The sorption was, however, insignificant. Improvement of model prediction was observed by introducing surface complexation with Fe oxyhydroxides using a much higher input of HFO (0.25 g l^{-1}).

Although the shape of the hydrozincite solubility curve (model 1) qualitatively follows the pattern of the leaching data with a minimum at around pH 8, measured Zn concentrations were up to 1 order lower than the model predicted. The use of the surface complexation model improved the prediction, only if one assumed large amounts of sorbent minerals (0.5 g l^{-1} HFO), which are not present in the natural system.

The model findings confirmed that cerussite largely controlled Pb solubility in the experimental leaching of Grogwynion tailings. The modelling results for Zn are, however, inconclusive. Surface precipitation on hydrous oxides has been considered to explain the Zn leaching from Municipal Solid Waste Incinerator bottom ash by Meima and Comans (1998) and Dijkstra et al. (2002). The use of surface precipitation rather than surface complexation is suggested by Dzombak and Morel (1990) and Zhu (2002) to interpret data at high sorbate/sorbent ratios when all surface sites become saturated and surface precipitates form on Fe oxyhydroxides. However, the importance of the role of Fe oxyhydroxides over mineral carbonate solubility in controlling the leaching behaviour of Zn in this material needs further study and the surface precipitation model on Fe oxyhydroxides has not been applied in this modelling.

In a system containing carbonates, as observed in the tailings of Grogwynion, 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. By comparing the release pattern of Pb and Zn as a function of pH and the titration curve (Fig. 10) in Grogwynion tailings, it is apparent that below a pH of approximately 5.7 the cerussite present, together with the subordinate Zn carbonates, is buffering the pH, via dissolution, which results in a very gradual change in pH and a large rise in dissolved Pb and Zn (up to 330 and 55 mg l^{-1}, respectively, at pH 5). At Frongoch the modelling approach included dissolution/precipitation coupled to surface complexation (Table 3). First, equilibrium with anglesite and bianchite was modelled, with concentrations estimated assuming all dissolved Pb and Zn were derived from the respective sulphate mineral dissolution. The solubility curve of anglesite is clearly shown to be independent of the pH for neutral to acid pH (Fig. 11), while Zn sulphate is highly soluble throughout the pH range, suggesting that other mechanisms rather than sulphate mineral dissolution are responsible for the observed leaching patterns. To allow for surface complexation, the available concentrations of elements for sorption were derived from the results of the lowest pH value in the pH-dependent leaching test, assuming sorption processes are less significant at acid pH. The concentration of HFO surface was used as a fitting parameter starting from the estimated value from the CISED extraction. The predicted Pb and Zn concentrations based on the surface complexation model with an estimated HFO of 0.06 g l^{-1} were respectively, 1 and 2 orders of magnitude higher than the measured concentrations of Pb and Zn (Fig. 11). The use of a higher sorbent concentration (0.2 g l^{-1} HFO) described reasonably well the Pb leaching, while modelled Zn was still 1 order of magnitude higher than measured concentrations and only the use of large amounts of sorbent minerals (0.5 g l^{-1} HFO) improved the data fitting.

We emphasise that we did not take into account the possible metal complexation by dissolved organic carbon, based on the DOC analysis in the mine waste water extracts of a separate study (Palumbo-Roe, unpublished results). These concentrations were lower than 1 mg l^{-1} and were therefore assumed not to be significant.

Sulphide oxidation was also excluded in the model. One could wonder if the release of Pb and Zn at acid pH is due to the oxidation of galena and sphalerite or alternatively mineral dissolution and desorption of adsorbed Pb and Zn as result of pH decrease. A number of factors seem to suggest a greater contribution to Pb and Zn release from a more labile fraction than from sulphides in the experimental condition of the pH-dependent test:

- A lack of correlation between dissolved Pb, Zn and S was observed across the experimental pH range. The observed pattern of higher S concentration at alkaline pH would also be inconsistent with known faster oxidation rates of sulphides at acidic pH (Gleisner and Herbert, 2002);
- Although galena and sphalerite are thought to be degradable by acid attack (Stanton et al., 2008), it is plausible that the short duration of the experiment reduced the significance of the sulphide dissolution.

It should be noted that the model predictions shown are based on applying the PHREEQC model with no calibration, using a standard set of binding sites and parameters derived in the laboratory for well-characterised materials. This lack of calibration introduces uncertainties as conditions in mine tailings may be very different from those modelled and highlights the limitations of the model. Nevertheless, the modelling predictions compared with the experimental results provide increased insights into the processes affecting the leaching behaviour of mine waste.

4 Summary and Conclusions

The XRD results coupled with the complementary CISED sequential extraction have indicated the nature of Pb and Zn phases in Grogwynion Pb-rich and Frongoch Pb-Zn-rich mine tailings. Grogwynion tailings mineralogy is dominated by the occurrence of Pb and associated Zn carbonate minerals with subordinate Pb and Zn sulphides. In the more acidic Frongoch tailings Pb and Zn carbonates are not present and there appears to be a clear vertical differentiation of Pb and Zn mineral phases through the studied profile. In the surface zone water leachable Zn sulphate is present along with the primary Pb and Zn sulphides. The basal section is characterised by the predominance of Zn/Pb Al-hydroxide phases along with Pb/Zn sulphides, which are spatially related to the occurrence of the peat layer in the succession. Solute transport in the tailings is governed by unsaturated flow and is controlled by the seasonal precipitation – evapotranspiration cycle. It is envisaged that the seasonal movement of the saturated /unsaturated surface (the zero flux plane) in the tailings in response to seasonal capillary pressure changes is responsible for causing the zonation seen today, in particular the surficial enrichment of soluble Zn sulphate as bianchite at Frongoch during dryer periods.

The feasibility of using the European standards TS 14429 and TS 14405 developed in CEN/TC292 for the characterisation of the leaching behaviour of waste material, in the case of sulphidic mine waste, has been tested. These standards represent a step forward towards the harmonisation of tests for environmental risk assessment of waste. Geochemical modelling has proved useful to interpret the leaching behavior in the controlled experimental conditions. The results of the percolation tests and pH-dependent leaching test are consistent with control of Pb and Zn concentrations by mechanisms of dissolution/ precipitation/ sorption, whereas there is no evidence of sulphide oxidation during the leaching. This is probably due to a combination of kinetic controls and the short duration of the tests. The differences in the secondary mineral phases of Pb and Zn in the two mine tailings types explain the different responses to pH variations and emphasise the relationships between solid state speciation and element mobility. Cerussite controls Pb solubility in Grogwynion leachates, maintaining concentrations less than 10 mg l^{-1} at pH greater than ~6 . As pH decreases upon acid addition the cerussite mineral phase dissolves and Pb is largely released in solution. Although the modelling of Zn data is inconclusive, the evidence of the CISED results and similarities in the Pb and Zn pH-dependent leaching pattern suggests that dissolved Zn concentrations in Grogwynion leachates are controlled by Zn carbonates. The Pb concentration in Frongoch leachates is, instead, modelled with a surface complexation model for metal sorption to oxyhydroxides. However, the existing thermodynamic database for Zn is unable to accurately reproduce the Zn leaching data. The column leaching tests indicate that both tailings types have a high capacity to generate high Pb and Zn concentration leachates, which is maintained for up to forty pore water volumes. The significance of this is that the tailings, after well over a century of mine closure, generate Pb and Zn rich leachates. The percolation test best describes the seasonal flushing of the secondary minerals, products of metal sulphide oxidation, from the surface layers of the tailings at Frongoch and Grogwynion, whereas it does not address the sensitivity to redox changes of the waste. This aspect becomes significant during periods of exposure of the tailings to alternating wet and dry periods and should be considered further by using humidity cells, unsaturated column leaching and field sampling. Nevertheless, the data presented provide a useful baseline against which to model any proposed changes to the site, for example any proposed remedial works. Used in conjunction with hydrological data the modelling offers the potential to provide a useful insight into the impacts of seasonality on contaminant migration through the mine tailings.

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Captions

Fig. 1. Location of the Frongoch and Grogwynion abandoned mines in Wales. Profile of the tailings at Frongoch and plan of the tailings at Grogwynion.

Fig. 2. Soil pH and element (g kg^{-1}) depth profiles of the Frongoch (FRS 3001) and Grogwynion (GWS 101) tailings.

Fig. 3. Pb and Zn sequential extraction profiles for Frongoch (FRS 3001) and Grogwynion (GWS 101). Zn* secondary axis for horizon 0-17 and 165-220 cm in Profile FRS 3001.

Fig. 4. Sequential extraction profiles for selected Pb and Zn minerals.

Fig. 5. CISED components from horizon 0-20 cm in GWS 101. A tentative assignment of mineralogical phases is based on chemical composition and extraction pattern. Total extracted solids in g kg^{-1}.

Fig. 6. CISED components from horizon 0-17 cm in FRS 3001. A tentative assignment of mineralogical phases is based on chemical composition and extraction pattern. Three lead sulphate-rich (Pb Sulphate (1), Pb Sulphate (2), Pb Sulphate (3)) and two Pb Sulphide- rich (Fe Pb Zn Sulphide (1) and Fe Pb Zn Sulphide (2)) components are identified. Total extracted solids in g kg^{-1}.

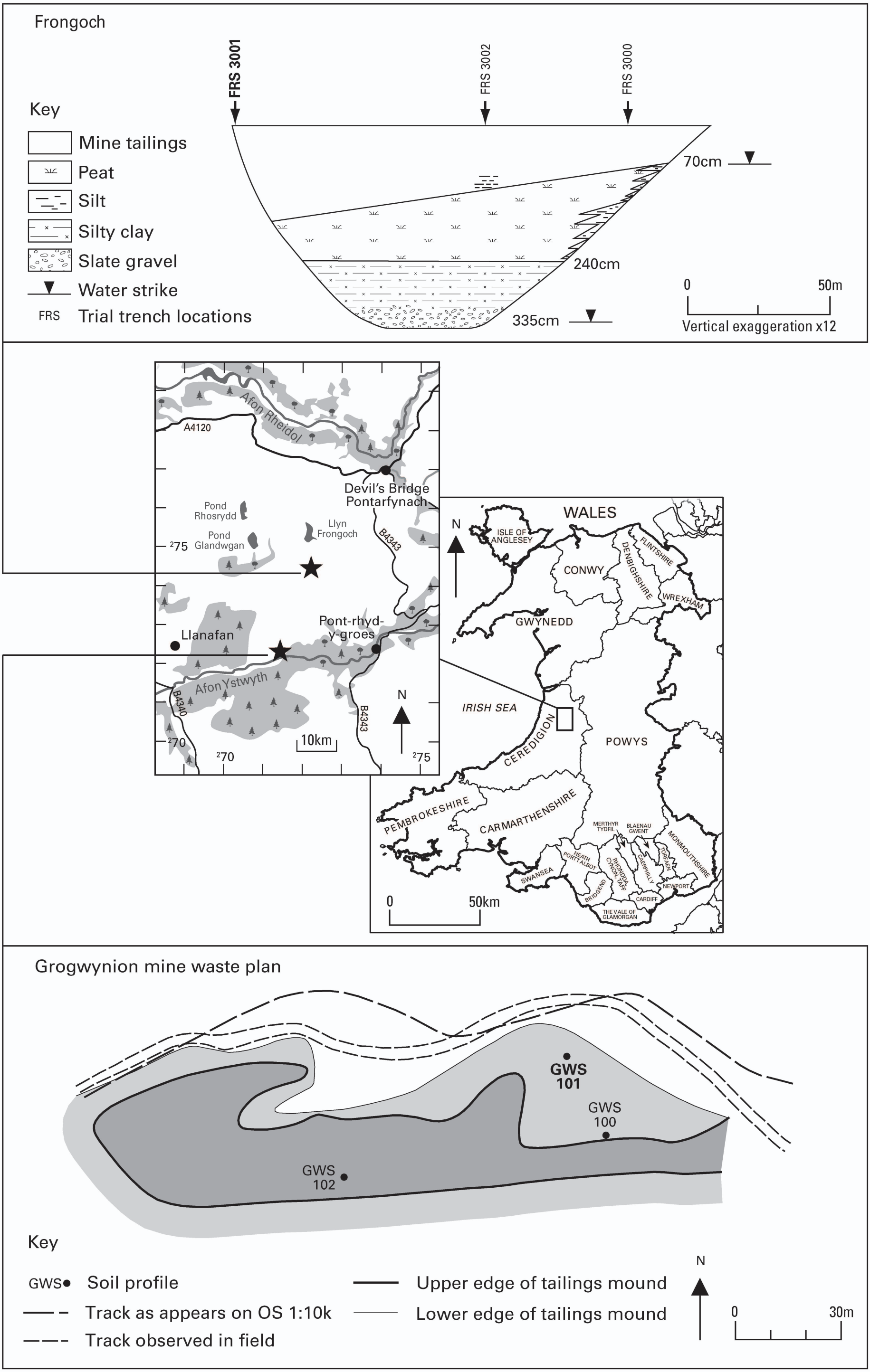
Fig. 7. CISED components from horizon 165-220 cm in FRS 3001. A tentative assignment of mineralogical phases is based on chemical composition and extraction pattern. Total extracted solids in g kg^{-1}.

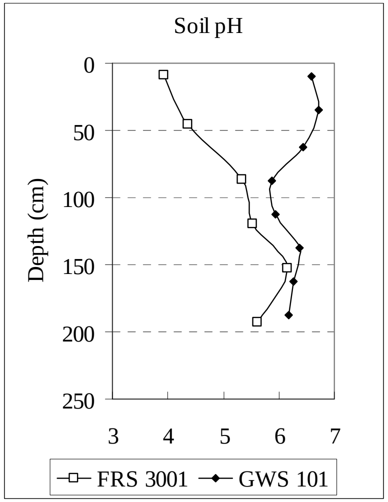
Fig. 8. Solid phase distribution of Pb and Zn in selected tailings horizons from Grogwynion and Frongoch based on the CISED results.

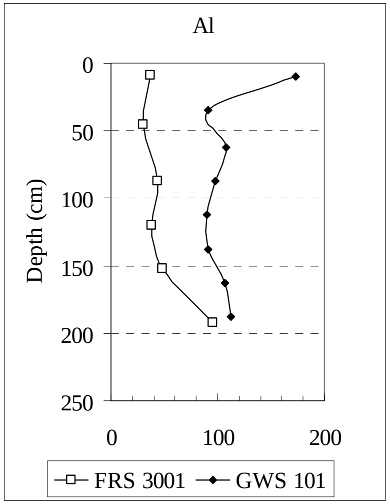
Fig. 9. Leachate evolution during the percolation test (PV: pore volume).

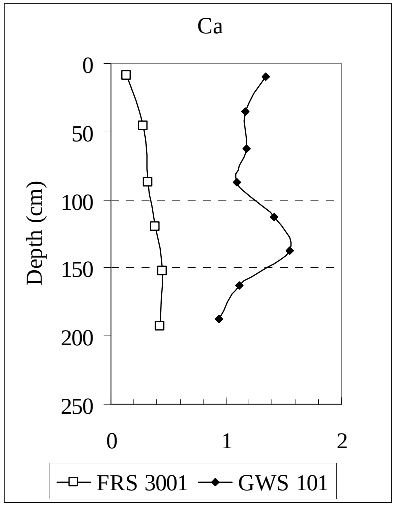
Fig. 10. Element release as a function of pH during the pH-dependent leaching test. The acid neutralisation curve (ANC) is also shown.

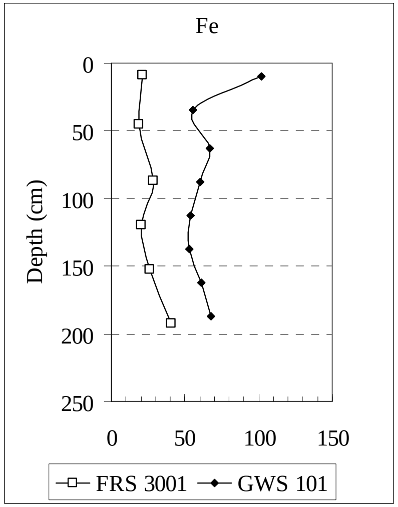
Fig. 11. Dissolved Pb and Zn in Grogwynion and Frongoch tailings as function of pH and PHREEQC modelling results.

Frongoch
Key
Mine tailings
Peat
Silt
Silty clay
Slate gravel
Water strike
FRS Trial trench locations
FRS 3001
FRS 3002
FRS 3000
70cm
240cm
335cm
0
50m
Vertical exaggeration x12
A4120
Afon Rheidol
Devil's Bridge
Pontarfynach
Pond
Rhosrydd
Pond
Glandwgan
Llyn
Frongoch
B4343
²75
Llanafan
Pont-rhyd-y-groes
Afon Ystwyth
B4340
B4343
N
10km
²70
²70
²75
WALES
N
ISLE OF ANGLESEY
CONWY
DENBIGHSHIRE
FLINTSHIRE
WREXHAM
GWYNEDD
IRISH SEA
CEREDIGION
POWYS
PEMBROKESHIRE
CARMARTHENSHIRE
MERTHYR TYDFIL
BLAENAU GWENT
MONMOUTHSHIRE
TORFAEN
CAERPHILLY
RHONDDA CYNON TAFF
NEATH PORT TALBOT
SWANSEA
BRIDGEND
CARDIFF
NEWPORT
THE VALE OF GLAMORGAN
0
50km
Grogwynion mine waste plan
GWS 101
GWS 100
GWS 102
Key
GWS● Soil profile
Track as appears on OS 1:10k
Track observed in field
Upper edge of tailings mound
Lower edge of tailings mound
N
0
30m


Soil pH
Depth (cm)
0
50
100
150
200
250
3
4
5
6
7
FRS 3001
GWS 101


Al
Depth (cm)
0
50
100
150
200
250
0
100
200
FRS 3001
GWS 101


Ca
Depth (cm)
0
50
100
150
200
250
0
1
2
FRS 3001
GWS 101


Fe
Depth (cm)
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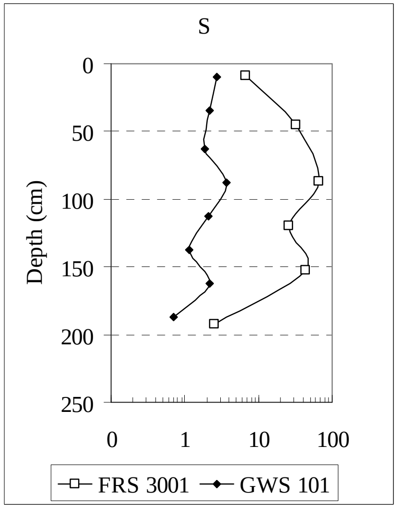
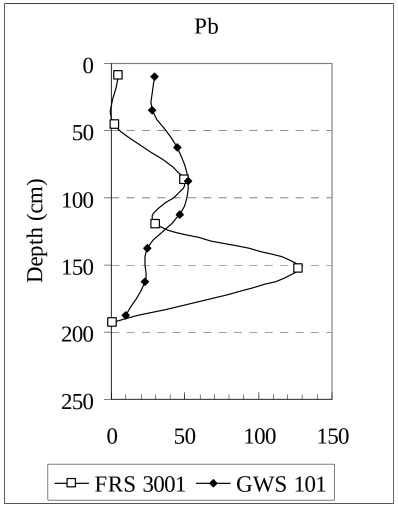
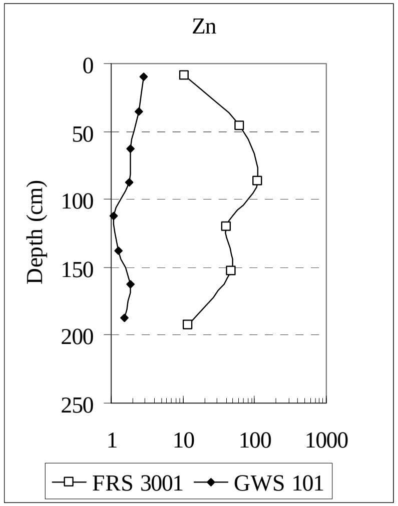
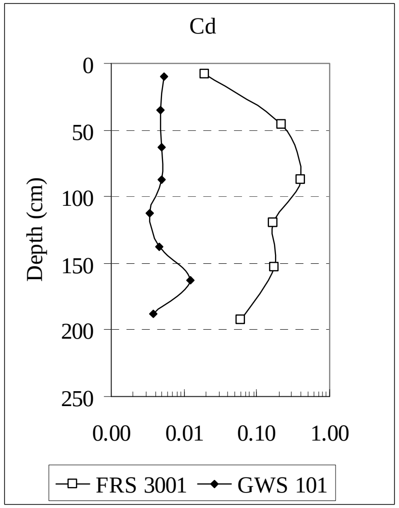
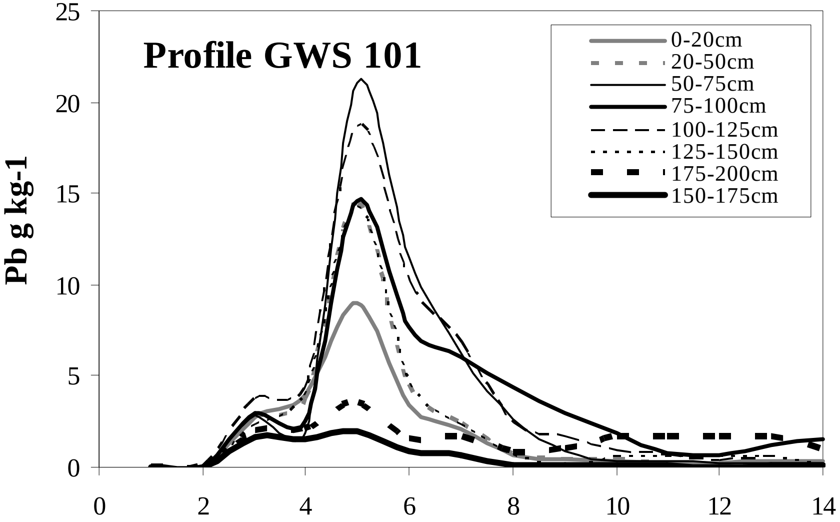
50
100
150
200
250
0
50
100
150
FRS 3001
GWS 101

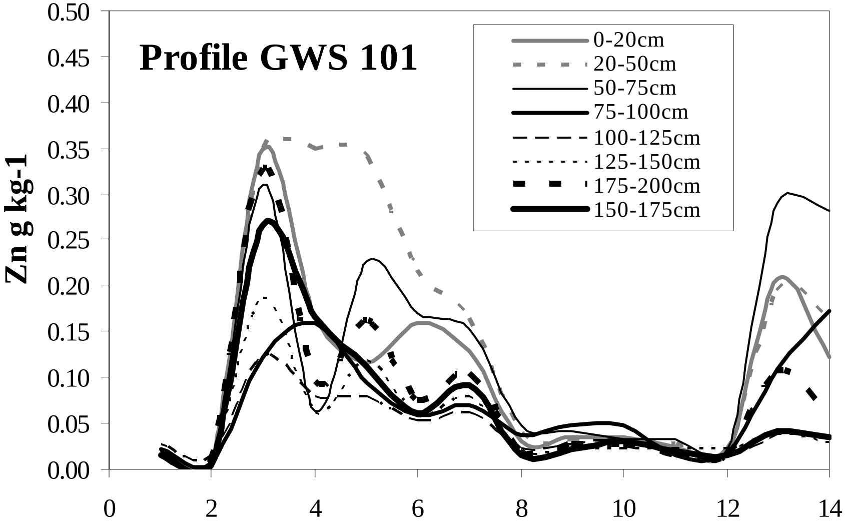

S
Depth (cm)
0
50
100
150
200
250
0
1
10
100
FRS 3001
GWS 101

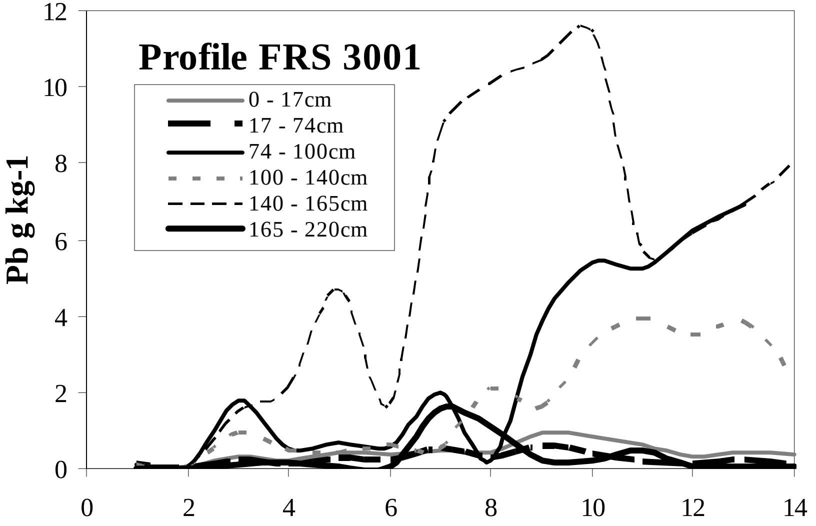

Pb
Depth (cm)
0
50
100
150
200
250
0
50
100
150
FRS 3001
GWS 101

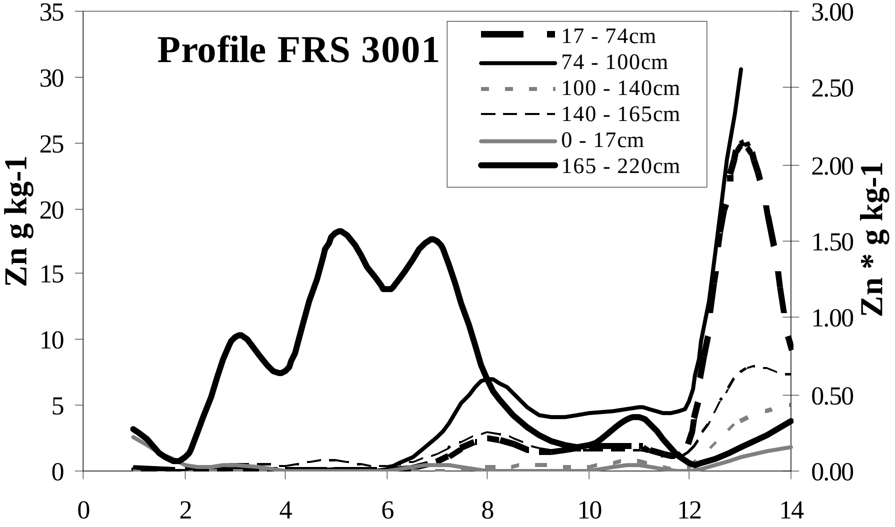

Zn
Depth (cm)
0
50
100
150
200
250
1
10
100
1000
FRS 3001
GWS 101

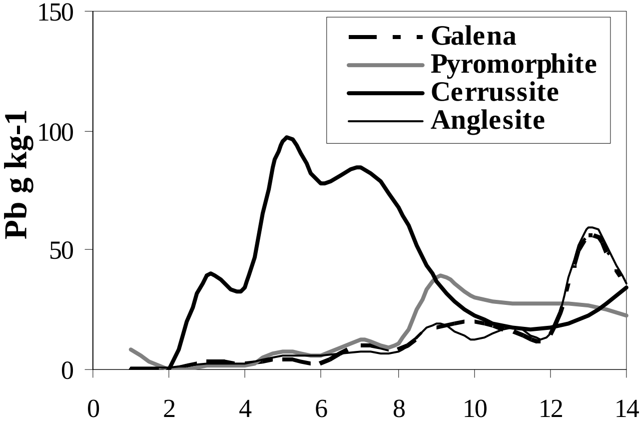

Cd
Depth (cm)
0
50
100
150
200
250
0.00
0.01
0.10
1.00
FRS 3001
GWS 101

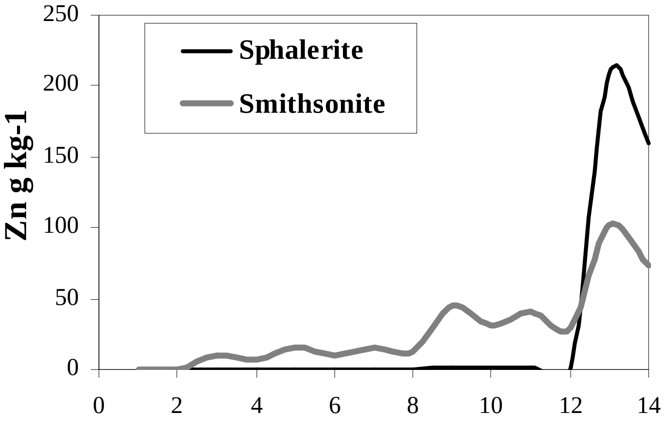

Profile GWS 101
Pb g kg-1
0
5
10
15
20
25
0
2
4
6
8
10
12
14
0-20cm
20-50cm
50-75cm
75-100cm
100-125cm
125-150cm
175-200cm
150-175cm


Profile GWS 101
Zn g kg-1
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
0.50
0
2
4
6
8
10
12
14
0-20cm
20-50cm
50-75cm
75-100cm
100-125cm
125-150cm
175-200cm
150-175cm


Profile FRS 3001
Pb g kg-1
0
2
4
6
8
10
12
0
2
4
6
8
10
12
14
0 - 17cm
17 - 74cm
74 - 100cm
100 - 140cm
140 - 165cm
165 - 220cm

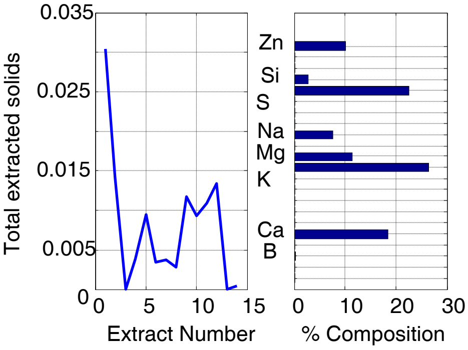

Profile FRS 3001
Zn g kg-1
Zn * g kg-1
0
5
10
15
20
25
30
35
0.00
0.50
1.00
1.50
2.00
2.50
3.00
0
2
4
6
8
10
12
14
17 - 74cm
74 - 100cm
100 - 140cm
140 - 165cm
0 - 17cm
165 - 220cm


Pb g kg-1
150
100
50
0
0
2
4
6
8
10
12
14
Galena
Pyromorphite
Cerrussite
Anglesite

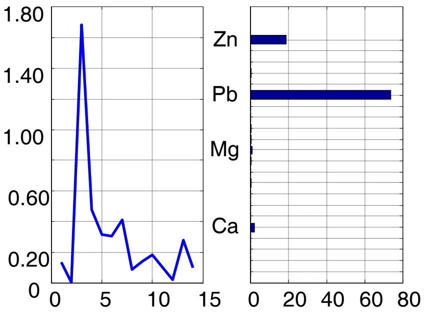

Zn g kg-1
250
200
150
100
50
0
0
2
4
6
8
10
12
14
Sphalerite
Smithsonite

GWS 101 0-20

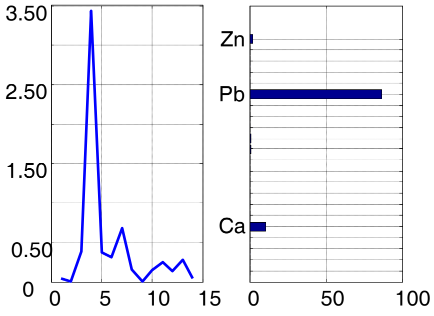
Pore Water



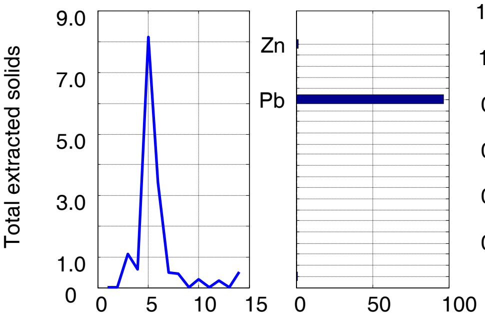
Pb Zn Carbonate



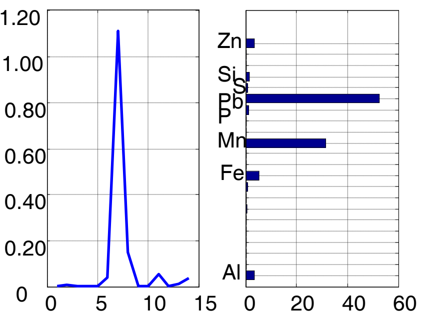
Pb Ca Carbonate



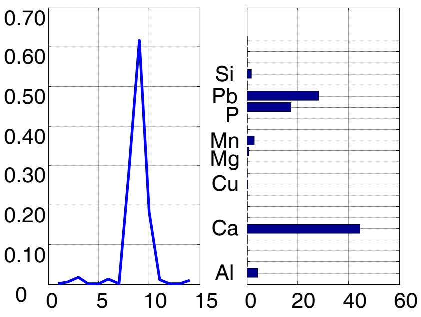
Pb Carbonate



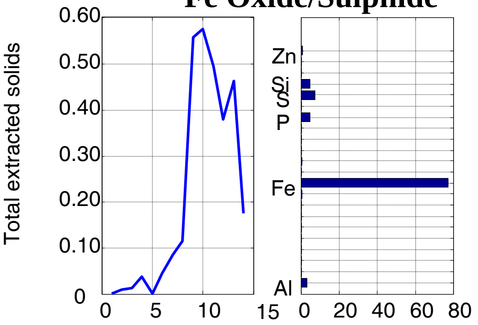
Pb Zn Mn Fe Oxyhydroxides



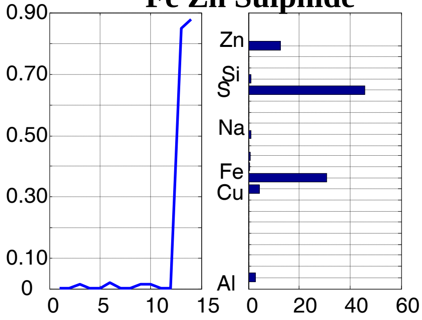
Pb Phosphate



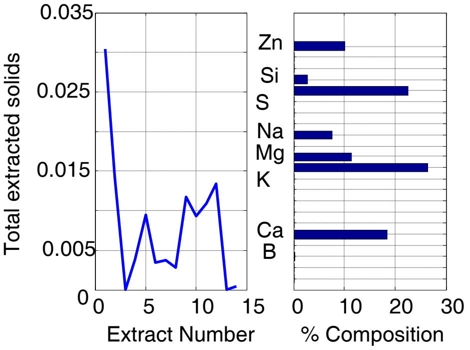
Fe Oxide/Sulphide

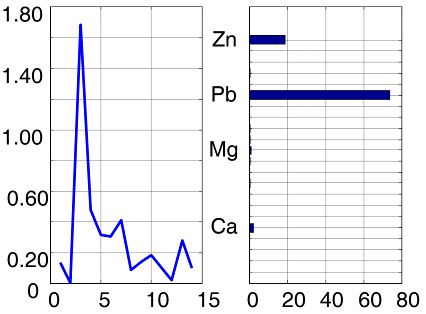


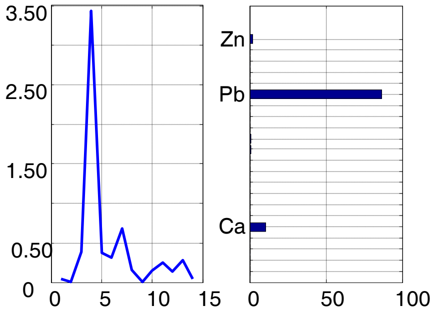
Fe Zn Sulphide

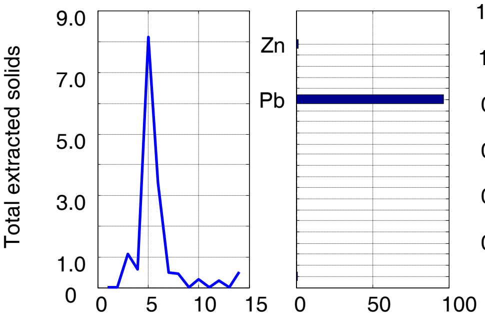


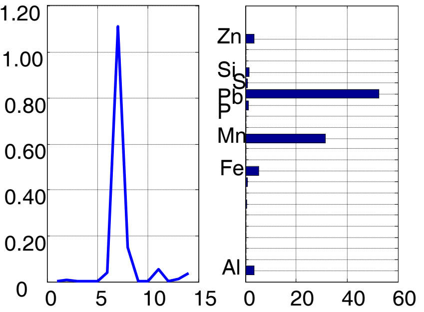
GWS 101 0-20

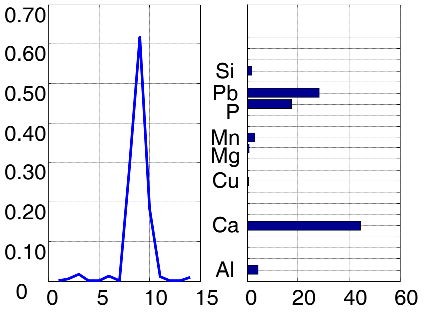

Pore Water

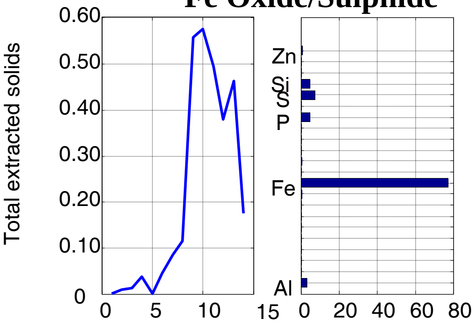

Pb Zn Carbonate

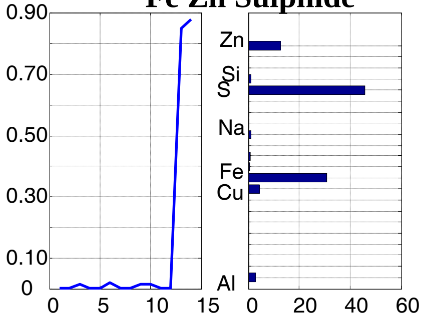

Pb Ca Carbonate


Pb Carbonate


Pb Zn Mn Fe Oxyhydroxides

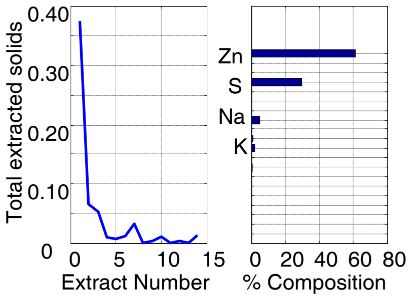

Pb Phosphate


Fe Oxide/Sulphide

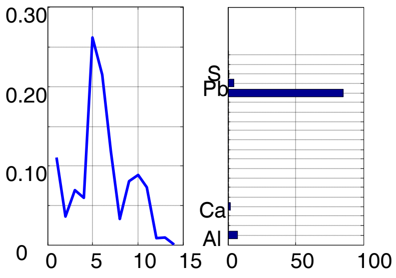

Fe Zn Sulphide

FRS 3001 0-17

Pore Water



Pb Sulphate (1)



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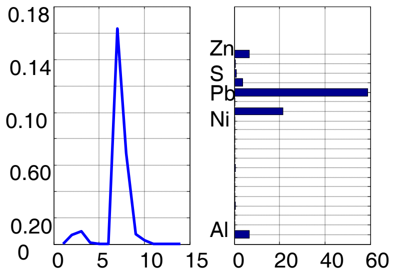
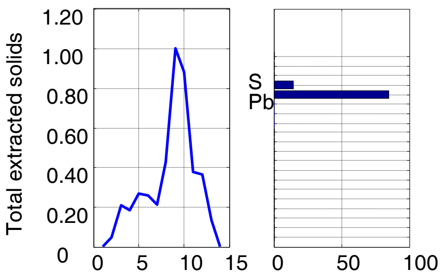
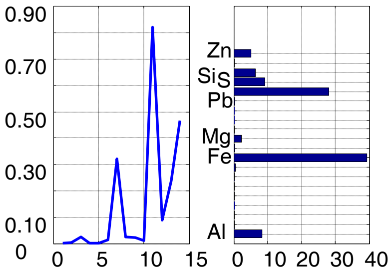


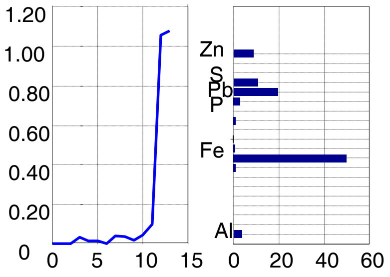
Pb Sulphate (3)



Fe Pb Zn Sulphide (1)

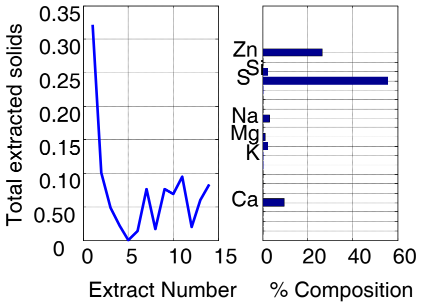


Fe Pb Zn Sulphide (2)

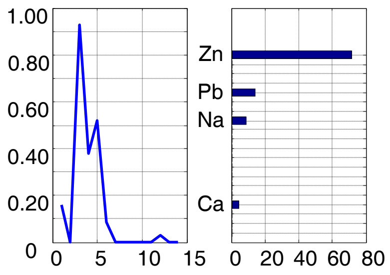


FRS 3001 165-220

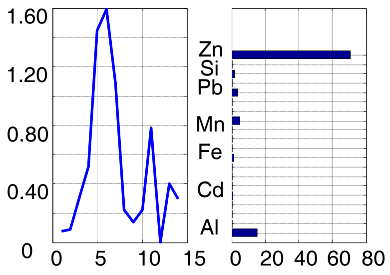
Pore Water



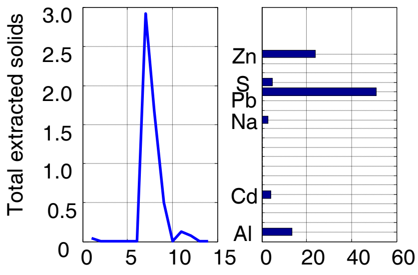
Exchangeable fraction



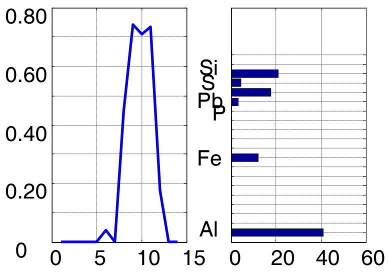
Zn Pb enriched Al Hydroxide



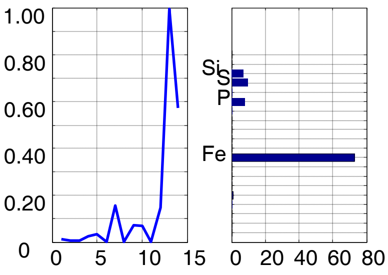
Pb Zn enriched Al Hydroxide



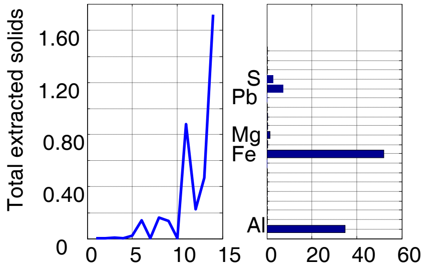
Pb Al/Fe Hydroxide



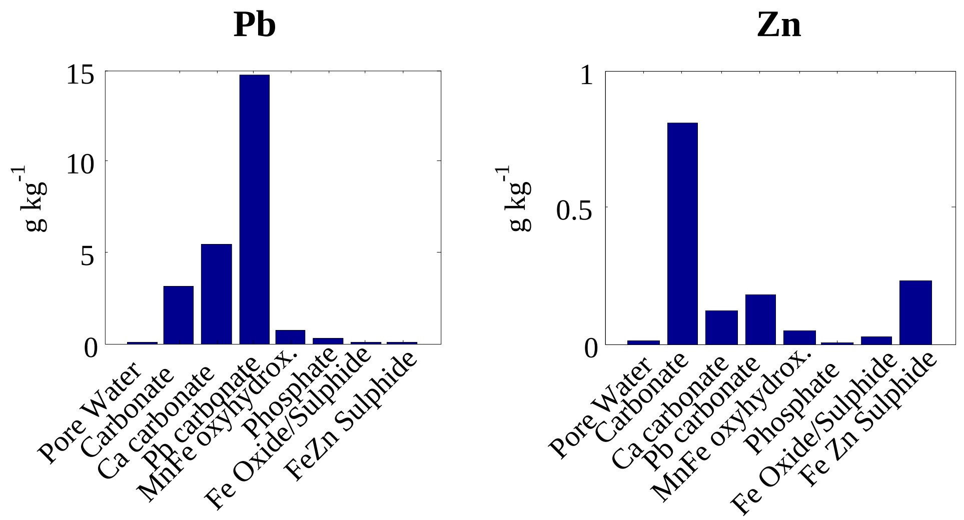
Fe Sulphide



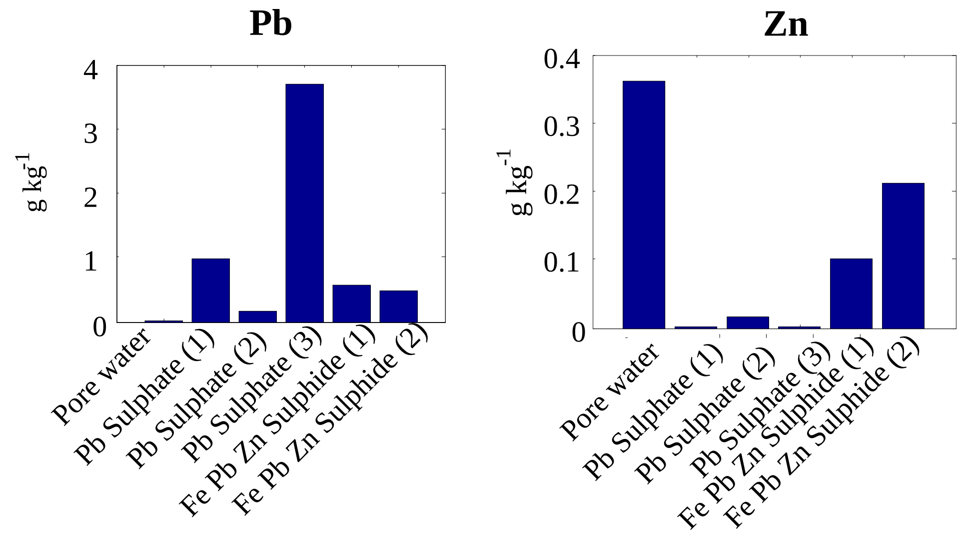
Fe Pb Sulphide/Al Hydroxide



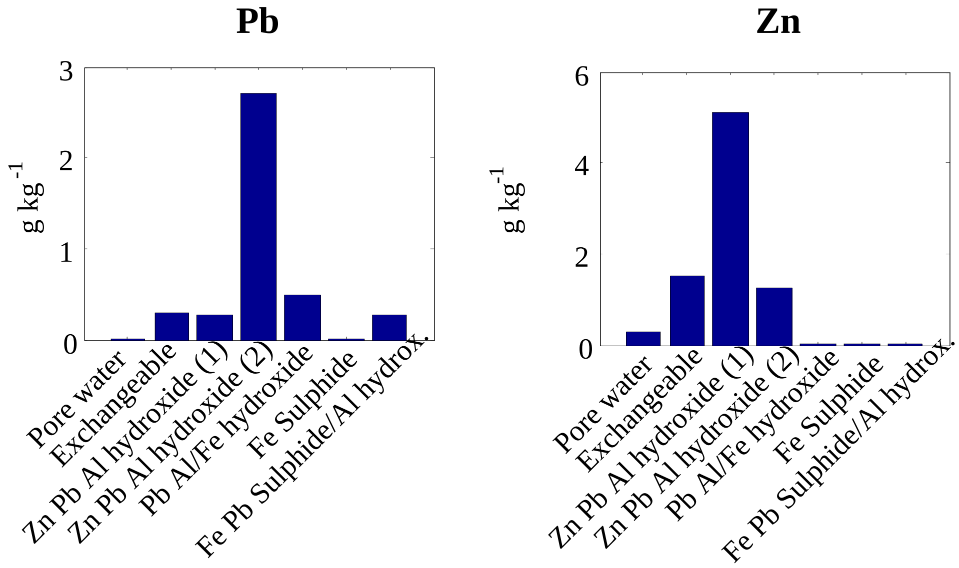
GWS 101 0-20 cm

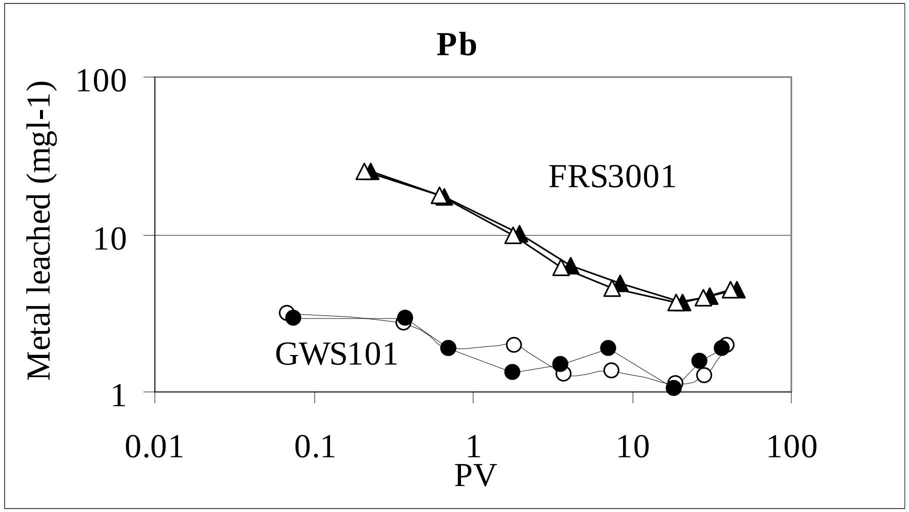


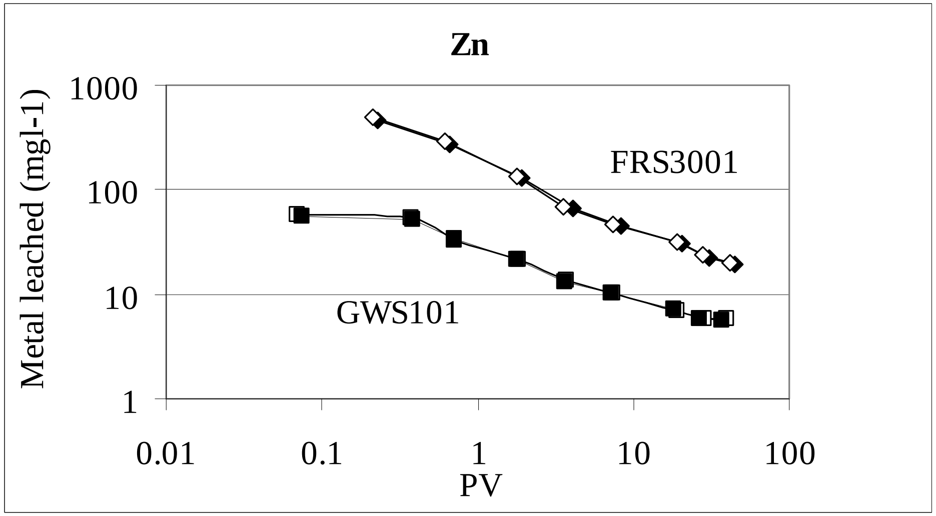
FRS 3001 0-17 cm

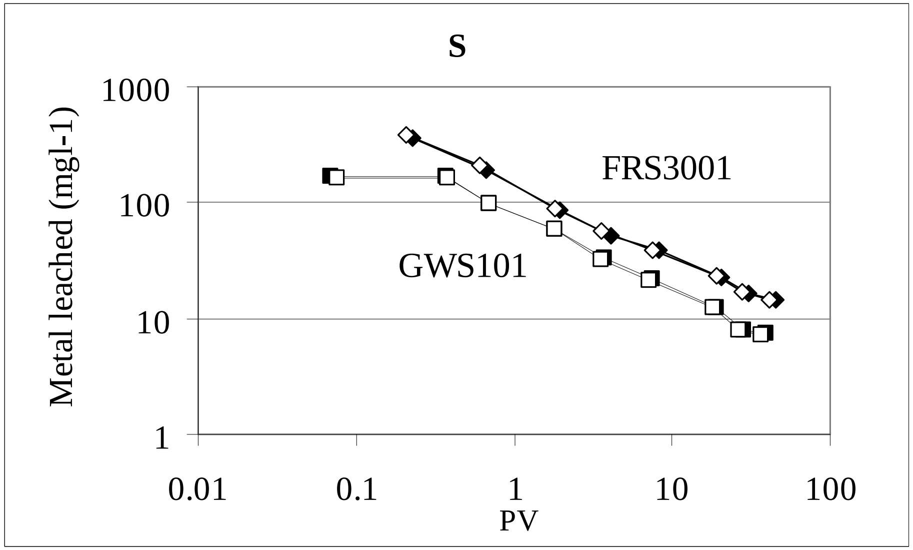


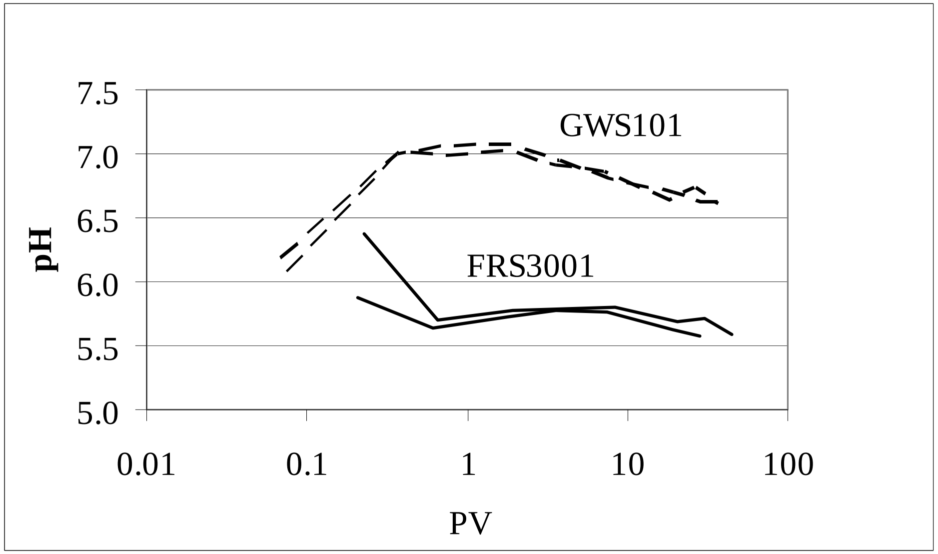
FRS 3001 165-220 cm

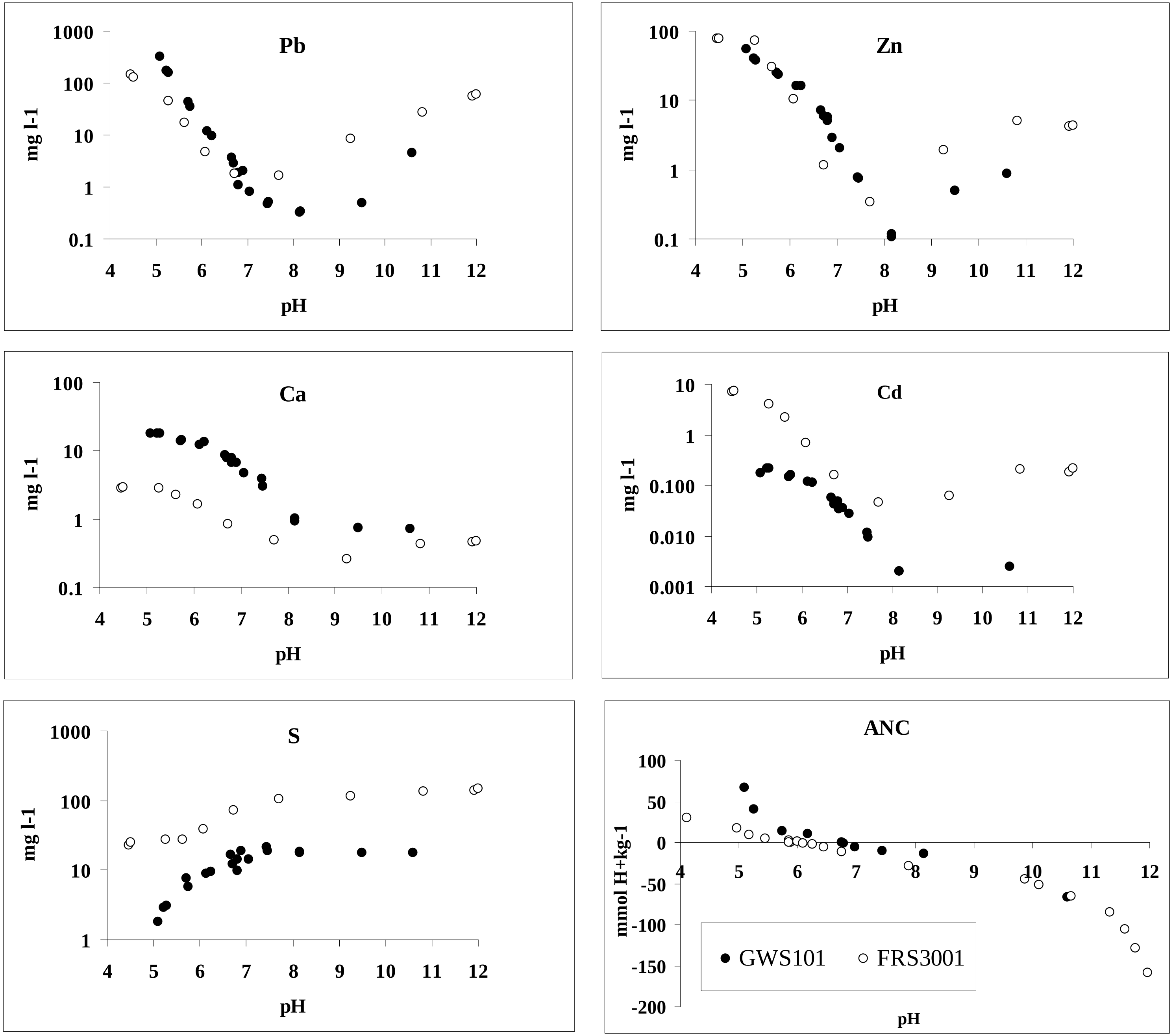


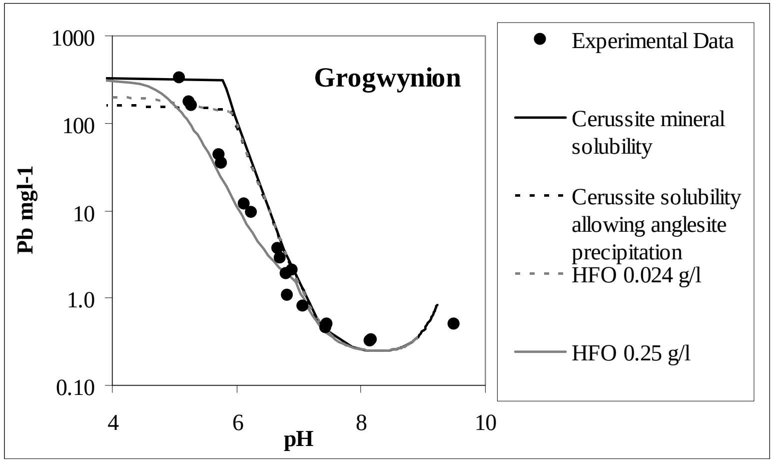

Pb
Metal leached (mgl-1)
100
10
1
FRS3001
GWS101
0.01
0.1
1
10
100
PV

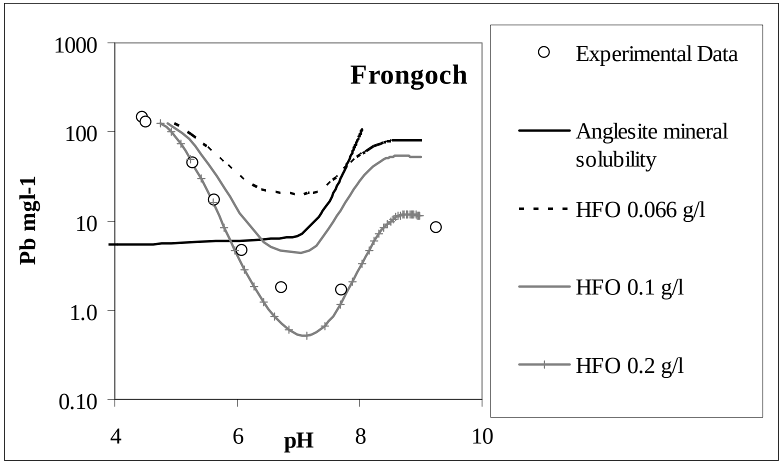

Zn
Metal leached (mgl-1)
1000
100
10
1
FRS3001
GWS101
0.01
0.1
1
10
100
PV

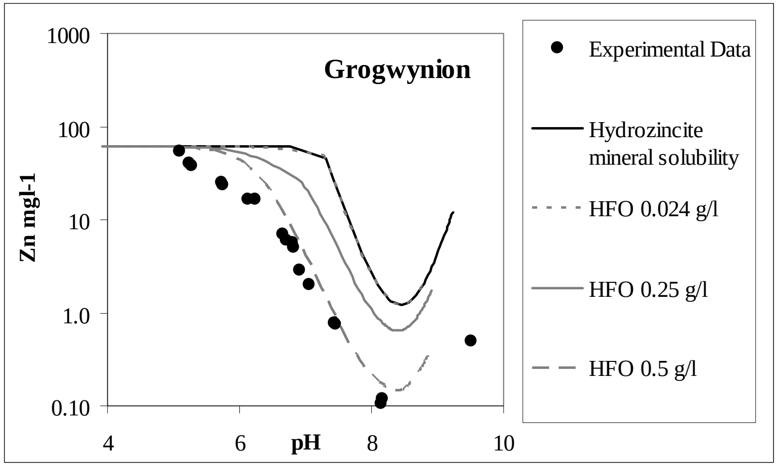

S
Metal leached (mgl-1)
1000
100
10
1
FRS3001
GWS101
0.01
0.1
1
10
100
PV


pH
7.5
7.0
6.5
6.0
5.5
5.0
GWS101
FRS3001
0.01
0.1
1
10
100
PV


Pb
mg l-1
1000
100
10
1
0.1
4 5 6 7 8 9 10 11 12
pH
Zn
mg l-1
100
10
1
0.1
4 5 6 7 8 9 10 11 12
pH
Ca
mg l-1
100
10
1
0.1
4 5 6 7 8 9 10 11 12
pH
Cd
mg l-1
10
1
0.100
0.010
0.001
4 5 6 7 8 9 10 11 12
pH
S
mg l-1
1000
100
10
1
4 5 6 7 8 9 10 11 12
pH
ANC
mmol H+kg-1
100
50
0
-50
-100
-150
-200
4 5 6 7 8 9 10 11 12
pH
● GWS101
○ FRS3001


Grogwynion
Pb mgl-1
1000
100
10
1.0
0.10
4
6
8
10
pH
Experimental Data
Cerussite mineral solubility
Cerussite solubility allowing anglesite precipitation
HFO 0.024 g/l
HFO 0.25 g/l


Frongoch
Pb mgl-1
1000
100
10
1.0
0.10
4
6
8
10
pH
Experimental Data
Anglesite mineral solubility
HFO 0.066 g/l
HFO 0.1 g/l
HFO 0.2 g/l


Grogwynion
Zn mgl-1
1000
100
10
1.0
0.10
4
6
8
10
pH
Experimental Data
Hydrozincite mineral solubility
HFO 0.024 g/l
HFO 0.25 g/l
HFO 0.5 g/l

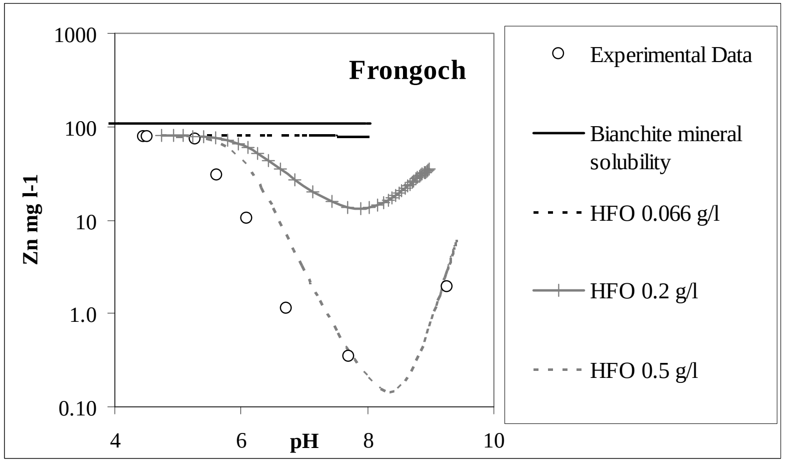

Frongoch
Zn mg l-1
1000
100
10
1.0
0.10
4
6
8
10
pH
Experimental Data
Bianchite mineral solubility
HFO 0.066 g/l
HFO 0.2 g/l
HFO 0.5 g/l

Table 1- Frongoch Profile FRS 3001

.

Depth (cm)	Description (Munsell color and texture)	Groundwater detail
0–17	Light olive brown (2.5Y 5/3) sandy very clayey SILT, with orange brown mottling towards the base.	
17-74	Dark grey (7.5YR 4/1) sandy very clayey fine SILT.	
74–100	Dark reddish grey (2.5YR 4/1) finely laminated silty CLAY, with brown to grey and orange laminae, orange brown mottling and organic fibres.	
100-140	Dark grey to black (2.5Y 2.5/1) fine gravelly, silty coarse SAND, with occasional organic fibres and including quartz grains.	Struck at 120 cm depth, standing at 150 cm depth
140–165	Soft dark slightly brownish grey and dark grey sandy (GLEY 3/1) finely laminated CLAY and SILT.	
165-220	Soft light brown and grey silty, clayey SAND with fragments of slate and occasional pockets of dark brown amorphous peat towards the base of the stratum.	

Table 2- Grogwynion Profile GWS 101

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Depth (cm)	Description (Munsell color and texture)
0–20	Grey 10YR 6/1 clayey SILT and SAND
20-50	Very dark greysh brown 10/YR 3/2 clayey SILT and SAND
50-75	Very dark greysh brown 10/YR 3/2 silty sandy CLAY
75-100	Very dark greysh brown 10/YR 3/2 CLAY with gley 5Y 5/2
100-125	Olive grey 5Y 4/2 CLAY with gley N7
125-150	Olive grey 5Y 4/2 CLAY with gley N7
150-175	Olive grey 5Y 4/2 CLAY with gley N3
175-200	Olive grey 5Y 4/2 CLAY

Table 3 – Summary of Batch Reaction Model inputs for the pH-dependent leaching simulations

		Grogwynion	**Frongoch**
Case (1)	**Infinite CO_2 reservoir with PCO_2 of $10^{-3.5}$**		
	Modelled reactions	• Mineral Equilibrium Equilibrium phases Cerussite= $2.15e^{-4}$ mol l^{-1} Hydrozincite= $2.26e^{-5}$ mol l^{-1}	• Mineral Equilibrium Equilibrium phases Anglesite= $1e^{-4}$ mol l^{-1} Bianchite= $1.6e^{-4}$ mol l^{-1}
Case (2)	**Infinite CO_2 reservoir with PCO_2 of $10^{-3.5}$**		
	Modelled reactions	• Mineral Equilibrium Equilibrium phases Cerussite= $2.15e^{-4}$ mol l^{-1} Hydrozincite= $2.26e^{-5}$ mol l^{-1} • Allowing for anglesite precipitation	• Mineral Equilibrium Equilibrium phases Anglesite= $1e^{-4}$ mol l^{-1} Bianchite= $1.6e^{-4}$ mol l^{-1}
Case (3)	**Infinite CO_2 reservoir with PCO_2 of $10^{-3.5}$**		
	Modelled reactions	• Mineral Equilibrium Equilibrium phases Cerussite= $2.15e^{-4}$ mol l^{-1} Hydrozincite= $2.26e^{-5}$ mol l^{-1} • Allowing for anglesite precipitation • Surface complexation Estimated sorbent/site concentration based on Fe extracted $1.83e^{-2}$ mol kg^{-1} material = HFO 0.024 g l^{-1}	• Mineral Equilibrium Equilibrium phases Anglesite= $1e^{-4}$ mol l^{-1} Bianchite= $1.6e^{-4}$ mol l^{-1} • Allowing for anglesite precipitation • Surface complexation Estimated sorbent/site concentration based on Al+Fe extracted $4.96e^{-2}$ mol kg^{-1} material = HFO 0.066 g l^{-1}