Surface observations applied to the interpretation of unsaturated column experiments

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Abstract Results from unsaturated column experiments on spoil from lead mines are presented and the extent to which interpretation of leachate water analyses can lead to an array of equally valid but indistinguishable conclusions is examined. Candidate phases for equilibrium control on lead and zinc concentrations were identified using geochemical modelling. This exercise provided a number of possible control phases including smithsonite, willemite and cerussite. However, it was not possible to uniquely identify either the control phases or the precise locations of these phases using column effluent chemistry alone. Without this information it is not possible to apply laboratory results to field conditions. Surface analysis techniques, including SEM, were therefore used to both identify and locate secondary phases. Samples from both the laboratory experiment and the field site were examined using these methods and the differences between them are discussed with respect to the problems of scaling laboratory results to field scale.

Key words lead; laboratory study; minewater; scaling; secondary minerals; unsaturated; zinc

INTRODUCTION

Mining related pollution contaminates thousands of kilometres of waterway worldwide (e.g. Banks et al., 1997) yet little is known of the processes controlling geochemical characteristics and longevity of discharges. Field studies suffer from difficulties with characterization resulting from the heterogeneous nature of many sites; laboratory studies, on the other hand, allow more detailed measurement of primary parameters but problems with scaling to field conditions are significant. One important issue is the degree to which processes occurring in the field are replicated in laboratory situations, given the differences in parameters such as temperature and experimental time scale.

Samples of ore-bearing limestone from a 200 year old lead mine in Derbyshire, UK, were leached in unsaturated columns and studied using SEM (scanning electron microscopy) to identify reactions controlling zinc and lead concentrations in column effluents. Results were then compared to those from unreacted material and field site discharges.

EXPERIMENTAL AND ANALYTICAL METHODS

Sample preparation and characterization

Twenty kilograms of galena (PbS), sphalerite (ZnS) and barytes (BaSO₄) bearing limestone was collected from an old (>100 years) spoil heap close to the field site. This material was jaw-crushed to a median grain size of 1 mm and the grain size...
distribution was determined. Mineralogy and mineralogical relationships were determined by optical examination of polished sections. Major and trace element composition were analysed by XRF (X-ray fluorescence) at the British Geological Survey, Keyworth. SEM (scanning electron microscopy) with facilities for qualitative identification of elemental composition was performed on polished sections and column material both before and after the run.

**Unsaturated columns**

Two columns were constructed from 10 cm diameter UPVC drainpipe (Fig. 1), of lengths 25 (2D) and 50 (3D) cm and filled with the crushed ore limestone. De-ionized water was pumped, using a peristaltic pump, onto a sintered glass disc on the top of the column. Low influent flow rates (0.9–2.7 cm$^3$ cm$^{-2}$ day$^{-1}$) gave unsaturated flow conditions. After passing through the spoil the effluent entered low-volume Teflon flow cells containing pH and redox probes. Effluent then discharged into a receiving vessel, from which samples were taken daily, filtered and analysed for cations using ICP-AES (inductively coupled plasma atomic emission spectroscopy) at the Assay Office, Sheffield, and anions using Dionex ion chromatography at the Groundwater Laboratory at the University of Sheffield. Over the course of the six-month experimental run, flow rates were varied, columns were flooded and drained and tracer tests were performed.

![Fig. 1 Schematic diagram of the experimental set-up.](image)

**RESULTS**

Figure 2 illustrates the variation in calcium, zinc and lead concentrations and pH with time. pH remains relatively steady throughout the run, with values from column 2D exceeding those of the longer column 3D. This, in conjunction with the higher alkalinity values measured in effluent from 3D, is consistent with a higher partial pressure of CO$_2$ at the base of the taller column. Calcium and zinc levels are both higher in the taller column, but lead levels are lower. The higher calcium and zinc levels could be explained by kinetic dissolution of calcium and zinc bearing minerals,
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in which case the longer residence time of influent within the longer column would lead to elevated concentrations of dissolved constituents. Alternatively, it could be explained by equilibrium mineral dissolution, but with absolute quantities governed by parameters differing within the two columns such as pH or redox potential, which would be controlled at least partially by the extent to which the column acts as an open or closed system with respect to atmospheric oxygen and carbon dioxide. The higher lead levels found in the shorter column may reflect equilibrium dissolution controlled by such parameters, or they may indicate differences in the average composition of the material filling the columns. Repeat analyses of column material suggests that the second explanation is unlikely.

GEOCHEMICAL MODELLING AND INTERPRETATION

To distinguish between these possibilities, saturation state indices for common lead- and zinc-bearing minerals were calculated for the columns using concentrations measured at the end of periods of steady flow rate, which are thought to represent steady state or quasi steady state concentrations, and for the minewater discharge which will eventually be modelled using the column data. Calculations were made using Phreeqc (Parkhurst & Appelo, 1999), utilizing the Phreeqc database, which is essentially the same as that for PhreeqE (Parkhurst et al., 1980) but with minor modifications to achieve consistency with the data of Nordstrom et al. (1990) and Ball & Nordstrom (1991). Figure 3 illustrates saturation indices for these minerals for the column effluents and the minewater discharge.

Galena and sphalerite, the primary lead and zinc sulphide ores, are both massively undersaturated, as might be expected in any environment with a moderately positive redox potential. Column-derived values show very little variation; field site values are significantly higher and show considerable variation. This may be due to seasonal variation in water levels at the mine site. Willemite (ZnSiO$_4$), cerrusite (PbCO$_3$), anglesite (PbSO$_4$), smithsonite (ZnCO$_3$), lead hydroxide and zinc hydroxide are all
Fig. 3 Saturation indices of common lead and zinc bearing minerals calculated for column effluents and minewater discharges. Figures after column labels indicate flow rate in cm day⁻¹.

within error of saturation (−5 < SI < 5). The rather large range is chosen to allow for variations in solubility constant caused by differences in ordering or solid solution characteristics between this experiment and the pure phase experiments from which solubility constants were derived. Saturation indices between +5 and −5 are taken to be within error of zero and indicate that both effluent solution and minewater compositions are controlled by equilibrium with one or more of the secondary minerals identified, that is, equilibrium reactions control the composition of the effluent.

SURFACE CHEMISTRY

Unique identification of the phase or phases controlling zinc and lead concentrations in column effluent is not possible using element chemistry alone. Correct identification is necessary for robust calculations of contamination lifetimes and characteristics and for predictions of system responses to changing conditions. In addition, the location of secondary phases is important as they have been observed in some cases to form armouring on primary sulphide minerals, thus preventing further dissolution of those minerals (Benvenuti et al., 2000). Surface observation and analysis of reacted and unreacted granular material from the columns and of polished thin sections of unreacted material, was therefore undertaken using scanning electron microscopy (SEM). Lead and zinc-bearing minerals were located using back scattered electron imaging (BSE), which is sensitive to atomic weight; magnification was then increased and spot analyses were made using the qualitative energy dispersive analysis (EDX) facility. This allows sulphates and silicates to be distinguished from carbonates/hydroxides. The inability of the detector to detect elements lighter than fluorine means that carbonates and hydroxides cannot be distinguished.

Barytes (BaSO₄), a primary constituent of the rock, was the mineral most often identified on both reacted and unreacted material although angular lead carbonate/hydroxide and pyrite were also observed. It is likely that the lead phase was cerussite as secondary lead phases apart from anglesite have been shown to be kinetically inhibited.
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There was no significant difference between reacted and unreacted material suggesting either that weathering occurring on the spoil heap was of such a magnitude as to make alterations occurring within the column insignificant or that precipitation of secondary phases occurred in localized areas which were not examined. Polished thin sections of unreacted material provided more information. Figures 4(a)–(d) are photomicrographs of areas within a barytes/galena vein cutting a calcitic limestone. Figure 4(a) shows a patch of primary galena, with a clear cubic blocky cleavage. Primary barytes and calcite are also present. The particle is coated with a secondary lead phase which is probably cerussite. This phase is also identified in other areas not in direct contact with the galena, for example between calcite and barytes on the mid-left of the photograph. This area is shown at higher magnification in Fig. 4(b). Figure 4(d) shows a different lead reaction product. Within the main patch of galena (the margins of which clearly illustrate the brittle nature of fracturing preceding ore mineral precipitation), a barytes inclusion is surrounded by a reaction rim of anglesite (lead sulphate). No primary sphalerite was observed during this study, however, rims of zinc carbonate/hydroxide were observed on barytes (Fig. 4(c)).

**DISCUSSION AND CONCLUSIONS**

The results from unsaturated column experiments are consistent with control of lead, zinc and sulphate concentrations by equilibrium with secondary phases. However,
precise identification of the secondary phases responsible is impossible from effluent chemistry alone. Direct observation of the spoil material did not show a significant difference between reacted and unreacted material, but secondary lead and zinc phases were identified in four different textural locations:

- angular grains with no clear contact relationship with primary sulphides;
- reaction rims showing in situ conversion of sulphide to secondary phase (Fig. 4(a));
- rims of secondary minerals on primary minerals with which a direct genetic relationship cannot be established, e.g. zinc phase on barytes (Fig. 4(c)) or lead phase on barytes (Fig. 4(b));
- secondary minerals forming as an intermediate phase between two primary minerals, e.g. the lead sulphate seen between barytes and galena in Fig. 4(d).

The majority of lead-bearing secondary minerals observed were located within millimetres of primary minerals and lead concentrations in effluent were very low, suggesting that lead redistribution was minimal. Also, the evidence is consistent with compositional control of secondary phases by mineralogy in the immediate vicinity of precipitation, e.g. the only anglesite observed was located between a sulphate phase and a lead phase. If this is the case then gradients in chemical potential must have existed on a small scale during precipitation of these secondary minerals.

A primary aim of this study was to assess the degree to which reactions within the laboratory columns replicated those in the field before upscaling calculations commenced. Saturation indices for the relevant minerals are similar from the two situations, in spite of significant differences in certain key parameters, e.g. temperature, residence time. Surface observation and analysis has not positively confirmed that reactions occurring in the two situations are identical, but the null hypothesis that they are significantly different has been rejected.

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REFERENCES


