

## Dissolved metals and As from metal mine waste - Laboratory vs. field determination

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Leachates from aged mine waste tips at two abandoned metal mines in south west England were investigated in order to determine the scale and mechanisms of ecotoxic element release and assess the advantages and limitations of field and laboratory methods. Tip drainage waters were sampled in streams and shallow groundwater and master variables were determined *in situ*. In the laboratory, mine waste samples were extracted in batch experiments (acetic acid, MilliQ H<sub>2</sub>O and MgCl<sub>2</sub>) and the European dynamic up-flow percolation test (CEN TS14405). A range of metals, metalloids and anions was analysed in water samples and mineralogy (XRD, SEM-EDX) and particle size of mine waste was determined.

Waste tip material contained a small proportion (<5%) of primary sulphide ore minerals, and Pb, Cu, Zn, Mn and As were associated with abundant secondary Fe phases and clays. Fractional release of elements from the mine waste was generally observed in column and field leachates. At low concentrations (<5  $\mu\text{mol L}^{-1}$ ), selective metal adsorption onto secondary Fe phases was implied in the order of affinity of Pb>Cu>Mn>Zn>Cd> Ni.

Under oxic conditions, element release from the waste material was controlled by the interplay of dissolution and sorption processes. Column and batch extractions with MilliQ H<sub>2</sub>O provided a good approximation of metal concentrations observed in the field when the L:S ratio was representative of field conditions, i.e. low and high L:S ratio for perched water tables within tips and shallow groundwaters, respectively. However, metal and As behaviour at the solid-solution interface was very sensitive to pH change. Leachate As concentrations were higher in the field (up to 380  $\mu\text{mol L}^{-1}$ , pH 5.0-5.3) than in the laboratory experiments (up to 41  $\mu\text{mol L}^{-1}$ , pH 4.0-4.5), reflecting the greater mobility of oxyanions at higher pH values. Conversely, Pb concentrations were lower in the field (up to 2.8  $\mu\text{mol L}^{-1}$  pH 3.2-5.6) compared to laboratory leachates (up to 81  $\mu\text{mol L}^{-1}$ , pH 1.9-2.6). Batch extractants that amend the eluent pH also resulted in discrepancies between field and batch leachates. This highlighted the importance of maintaining pH conditions representative of field pore waters in column and batch extractions. Nevertheless, when applied to representative samples, carefully constrained laboratory experiments can aid the prediction of pollutant fluxes in the field.

## Fluoride removal from solution by calcite — pCO<sub>2</sub> sorption kinetics

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Effective remediation modeling and design depends on the ability to predict the rate at which a pollutant will be removed from a system. It is important therefore, to model the sorption *rate* rather than equilibrium sorption. Here we establish the time dependence of F sorption under various conditions.

The kinetics of fluoride removal by calcite as a function of pCO<sub>2</sub> (mol%), initial fluoride concentration and calcite surface area were analysed according to pseudo- first and second order reaction kinetics. If pseudo-second order kinetics are applicable, a plot of  $t/q_t$  against  $t$  should be a linear relationship, from which the initial sorption rate constant ( $h$ ), can be determined from the slope and intercept of the plot.

Free drift experiments were carried out in a constant temperature room utilizing a gas glovebox connected to commercially prepared CO<sub>2</sub>/N<sub>2</sub> mixtures. Solutions of F (as KF) were equilibrated in the CO<sub>2</sub>/N<sub>2</sub> atmosphere prior to the addition of calcite of known mass and size (<150  $\mu\text{m}$  & +1.18-2.36mm). pH and F<sup>-</sup> ion selective electrodes were used to follow the reaction in at one minute intervals.

It was found that the pseudo-second order reaction kinetic model provided the best correlation to the data in all cases ( $r^2 > 0.99$ ). Plots of the sorption rate constant ( $\log(h)$ ) vs pCO<sub>2</sub> show that for the same initial [F], the <150 $\mu\text{m}$  fraction (larger SA) has a larger rate constant as larger SA dissolves quicker. Particles with the same SA however show a significant difference in the sorption rate with changes in initial [F]. The fact that  $h$  increases with increasing [F], is surprising given that previous findings[1] show the larger the initial concentration the slower the reaction rate as it takes longer to reach equilibrium

The major advantage of these results is the possibility of obtaining generalized predictive expressions which can be used directly to derive the amount of fluoride removed at any given concentration, pCO<sub>2</sub> and reaction time without the necessity of developing complicated theoretical models.

[1] Plazinski, W. *et al.* (2009) *Advances in Colloid and Interface Science* **152**(1-2), 2–13.