

Resolving the scale discrepancy in laboratory and field weathering rates

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ABSTRACT: Results from tracer studies in hydraulically-unsaturated column reactors containing mine rock demonstrate that significant mass of pore water is relatively immobile. This water mass is retained within stagnant zones that do not contribute to advective transport of solutes in reactor effluent. Solutes other than the inert tracer in the reactor effluent arise from chemical dissolution of minerals that compose the mine rock. Results demonstrate that the weathering rates of individual minerals can be quantified, if the effect of aqueous speciation, heterogeneous chemical equilibria and retention of solutes within stagnant zones are all considered. These results support the hypothesis that retention of solutes within stagnant zones at field sites contributes to the commonly observed discrepancy in weathering rates determined at laboratory and field scale.

1 INTRODUCTION

1.1 Mine sites as geological observatories

Source term modeling is a critical part of environmental risk assessment for mine water pollution. Such modeling requires the prediction of the rate of mineral weathering reactions that generate and attenuate the dissolved load of metals from mine water discharges. A long-standing discrepancy in observed weathering rates between observations made in laboratory experiments on single minerals and weathering at catchment scale (e.g. White & Peterson 1990) is also observed for mine sites (Strömberg & Banwart 1994). For all of these weathering systems, rates observed in field systems are typically $10^2 - 10^3$ times greater than those observed in laboratory studies. This discrepancy is important to resolve because it creates significant uncertainty, both in the conceptualization of reactive transport processes, and consequently in the quantitative prediction of contaminant source strength and attenuation that underpins environmental assessment.

One consequence of this discrepancy for mine sites is their suitability as geological observatories to study weathering processes in detail. If the discrepancy can be resolved for mine sites, this will shed light on factors that are potentially general and thus significant for catchments and aquifers as well. An important factor is the level of mineralogical detail that is usually available for metal mine sites in order to identify zones above and below the economic cutoff in ore quality.

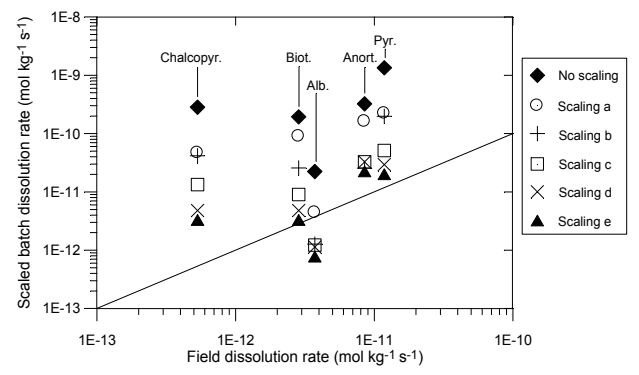


Figure 1. The cumulative effect of scaling dissolution rates from laboratory batch reactors to the field site. The solid line denotes the ideal case of “perfect prediction”, where the scaled laboratory rate equals the observed field rate. The symbol (\blacklozenge) shows the prediction in the absence of any adjustment for the scaling factors considered. The cumulative impact of considering the following effects in turn is shown: a) environmental temperature (\circ), b) pore water pH ($+$), c) particle size distribution (\square), d) reactive mineral content (\times) and e) water flow patterns (\blacktriangle). Individual minerals are noted as albite (Alb), anorthite (Anort), biotite (biot), chalcopyrite (chalcopyr) and pyrite (Pyr).

1.2 Resolving the scale-dependence of weathering rates

Malmström et al. (2000) demonstrated that the discrepancy in scale-dependent weathering rates could be resolved for a mine waste deposit, by accounting for the effect of a few bulk physical-chemical parameters. Figure 1 shows that weathering rates ob-

tained from laboratory studies using 0.15kg of rock could be successfully extrapolated to field scale in order to quantify the flux of solutes arising from mineral weathering within a mine waste deposit containing 9.5×10^{10} kg of rock. The parameters used to account for the 100-fold difference in mass-normalized weathering rates (mole/kg-s) between lab and field scale for this site included

- a) Environmental temperature,
- b) Pore water pH,
- c) Particle size distribution,
- d) Reactive mineral content, and
- e) Water flow patterns.

Malmström et al. (2000) developed a relatively simple mathematical algorithm to scale laboratory rates to field conditions by accounting for the various factors as follows. The effect of environmental temperature was accounted for by considering activation energy effects as quantified by the Arrhenius equation. The effect of pore water pH was accounted for by considering the reaction order with respect to protons for the kinetic rate expression associated for the dissolution of each mineral. The particle size effect was accounted for by considering the differences in particle size distribution whereby at field scale the presence of 80% of rock mass was contributed by relatively large particles (nominal size > 4mm) that contributed relatively little geometric surface area. The reactive mineral content accounted for the relative content of the dominant sulfide and silicate minerals. Water flow patterns were accounted for by considering the relative mass of mobile and immobile water within the reacting system.

This study demonstrated for the first time that the impact of water flow patterns contributed significantly to the apparent weathering rate at field sites. This arises due to the presence of immobile water where reaction with source minerals causes the accumulation of solutes that are not flushed from the system. These solutes thus do not contribute significantly to the solute mass flux measured in site drainage. It is this mass flux upon which the field-scale weathering rates are based, which is also often the case for weathering studies in catchments.

Based on these studies, further work to quantify the impacts of water flow patterns has been carried out. The objectives of these experiments are

1. To develop experimental methods to study weathering under hydraulically-unsaturated conditions,
2. To quantify the relative contribution of mobile and immobile water under steady flow conditions
3. To quantify solute fluxes in these systems
4. To account for slow mass transfer of solutes from immobile water to column effluent

2 EXPERIMENTAL METHODS

A description of the design and application of unsaturated column experiments is presented by Banwart et al. (2002). The column, a PVC pipe, had a length of 25cm and an inner diameter of 10cm. The reacting rock was sandstone collected from the surface of a coal mine waste rock deposit. The modal mass composition determined by XRD and XRF data was estimated as 65% quartz with 20% illite clay, 8% kaolinite and a number of minor phases including 0.6% pyrite and 0.6% calcite. The porous medium was sieved, uniformly packed and tamped lightly into the column to a bulk density of 1.846 g cm^{-3} . The material exhibited a millimeter to sub-millimeter grain size with rounded quartz grains.

Solute flux was determined by measuring the water mass flow rate and solute concentration of the column effluent. Effluents drained through tubing through flow cells in which dissolved O_2 , redox potential and pH were determined. Effluent drained under gravity into acidified collection flasks and was analyzed using ICP-AES for total dissolved element concentrations, and IC for anions.

The modeling code PHREEQC (Parkhurst 1999) was used to develop a 1-D reactive transport model to represent coupled physical and chemical processes within the column. In addition to advection and dispersion, aqueous speciation and heterogeneous equilibria with ion exchange surfaces and mineral phases within the column were considered. Mass transfer rates were determined for phases known to be present and exhibiting substantial undersaturation with respect to influent test solutions. Tracer tests using bromide ion as an inert anion in the influent solution were used to assess the relative mass of mobile and immobile water.

3 RESULTS

Figure 2 shows the comparison between measured concentration of inert tracer and the values simulated using the PHREEQC code when considering both immobile and mobile water. The agreement between modeled and measured values is significantly better than that shown in Figure 3 which neglects immobile water. The results demonstrate that the role of immobile water is to retard advective solute transport, due to diffusion of solute mass into stagnant zones when the tracer front passes. Diffusion of solutes from stagnant zones then results in a relatively long tail of significant solute concentrations long after the tracer peak has eluted from the column.

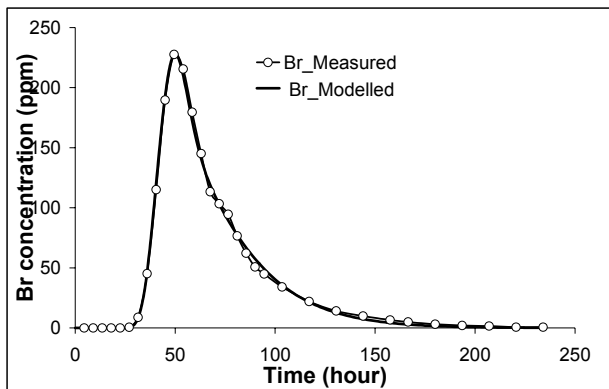


Figure 2. Measured bromide ion concentration with time compared with reactive transport model simulation using PHREEQC and considering the flow domain to behave as a dual porosity porous medium; i.e. with mobile and immobile water within the column reactor.

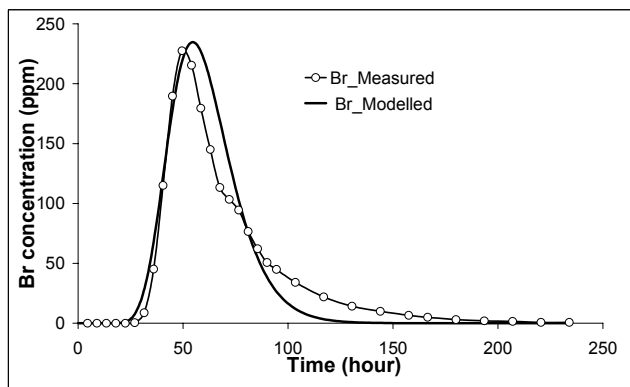


Figure 3. Measured bromide ion concentration with time compared with reactive transport model simulation using PHREEQC and considering the flow domain to behave as a homogeneous porous medium; i.e. with uniform distribution of flow.

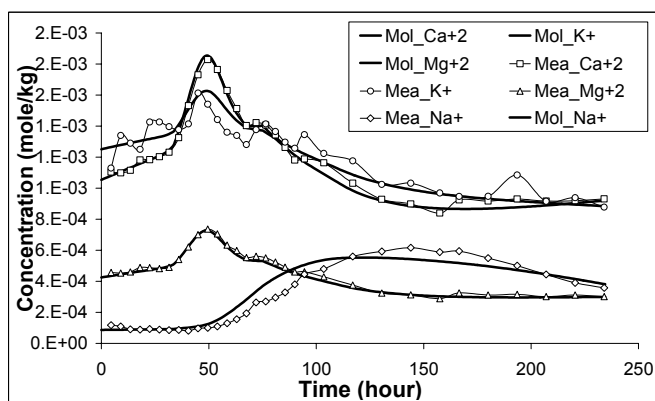


Figure 4. Measured cation concentrations with time compared with reactive transport simulation using PHREEQC and considering the flow domain to behave as a dual porosity porous medium.

Table 1 lists the transport model parameter values used to obtain the curve plotted in Figure 2. The model assumes a linear mass transfer rate law; i.e. a first-order rate coefficient, to explain the diffusion of solute mass into and from the stagnant zones. The model results suggest that the mass of immobile water is significant, and is approximately one-half that of the mobile water.

Table 1. Transport parameter values for dual porosity model.

Parameter	Value
Pore water velocity	14.5 cm d ⁻¹
Diffusion coefficient	2.02x10 ⁻⁹ m ² s ⁻¹
Dispersivity	0.0012 m
First-order mass transfer rate	2.0x10 ⁻⁶ s ⁻¹
Porosity of mobile domain	0.23
Porosity of immobile domain	0.11

Figure 4 compares the measured and simulated concentrations with time of cations within the column. The dynamics of solute concentrations in the column effluent depend not only on the time-dependence of weathering reactions, but also the time-dependence of the Na⁺ peak that enters the column as the cation co-solute with the bromide tracer. This results, for example, in displacement of other cations from the exchange surfaces within the columns. This is shown by the delay in the Na⁺ peak compared to that of bromide (Fig. 2), and the associated peak in released Ca²⁺, K⁺ and Mg²⁺ that coincides with the arrival of the bromide peak. The dissolution of calcite was necessary to include in order to simulate calcium ion dynamics while dissolution of illite was necessary to explain the dynamics of potassium ion.

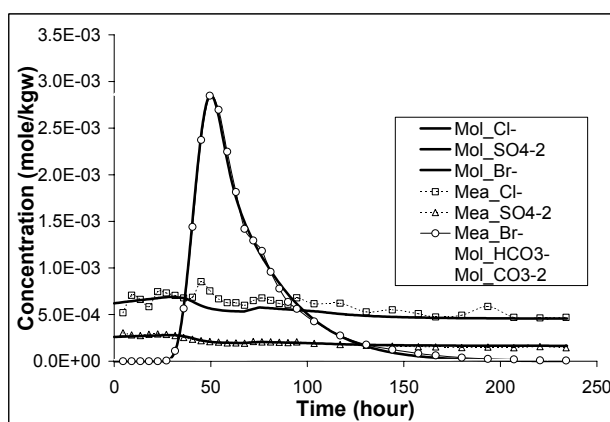


Figure 5. Measured anion concentrations with time compared with reactive transport simulation using PHREEQC and considering the flow domain to behave as a dual porosity porous medium.

Figure 5 compares the measured and simulated concentrations of anions within the column. Bromide is added with the influent solution, while sulfate arises due to oxidative weathering of pyrite contained within the mine rock. Noting that the concentration of sulfate decreases slightly during the experiment, it was necessary to invoke slower pyrite weathering rates at the end of the experiment. This was also the case for the irreversible dissolution of silicate minerals, conceptualized as the chemical dissolution of illite. At the end of the experiment, the rates of illite and pyrite weathering required to reproduce the experimental data were respectively 1.8×10^{-9} mole $\text{kg}^{-1} \text{s}^{-1}$ and 1.8×10^{-7} mole $\text{kg}^{-1} \text{s}^{-1}$.

4 IMPLICATIONS FOR WEATHERING AT FIELD SCALE

The results presented above provide strong evidence of preferential flow and the existence of a significant mass of immobile water within a bench scale column experiment. The impact on inert tracer behavior and on reactive transport of solutes arising from irreversible weathering reactions and from heterogeneous equilibria can be accounted for using modeling codes such as PHREEQC. The existence of significant immobile water and the impact on solute transport has been demonstrated previously within mine waste rock deposits above the water table; i.e. under hydraulically unsaturated conditions (Eriksson et al. 1997).

The existence of immobile water creates another potential control on the observed rates of weathering. Rate control occurs at grain scale, if irreversible chemical dissolution of mineral phases is slower than diffusive mass transfer away from the grain surface. The rate of the chemical reaction controls the overall flux of solutes from the weathering system; i.e. the column reactor for the experiment described above. If the reacting grain is located within a zone of stagnant water, an additional rate control may exist, namely, the slow mass transfer by diffusion from the stagnant zone to a zone of mobile water where the solute is then relatively rapidly flushed from the system. If this diffusion is very slow, compared to chemical dissolution rates, this solute flux may be negligible, and significant mass storage of solutes and secondary minerals may occur within the stagnant zones. Solute fluxes determined for the column effluent would not reflect the rate of weathering at grain scale since significant mass of weathering products would not be accounted for. This is not the case here, since the model accounts for the diffusion of solutes into and from stagnant zones within the column reactor.

A further control on solute fluxes can occur at the largest scale of observation, i.e. the flux of mobile water from the weathering system. If flushing of

mobile water is slow is compared to chemical dissolution rates at grain scale, then solutes accumulate in pore water until equilibrium with either source minerals or secondary minerals is reached. The limiting case here would be a batch reactor. However, by designing batch experiments with low mineral:water ratios, the dilution of solutes released by dissolution reactions generally maintains the aqueous solution far from equilibrium. Laboratory data on mineral weathering in batch reactors is thus strongly biased to accurately reflect the rate of the irreversible chemical reaction, rather than reflect hydrological conditions in weathering environments at field sites.

This conceptualization of reactive transport in weathering systems clearly implies that rates of irreversible chemical dissolution are not scale-dependent. The caveat is that well-understood factors such as environmental temperature and pH, surface area effects of particle size distribution and the relative abundance of the reactive minerals are accounted for.

The additional factor that is not commonly addressed is the patterns of water flow and the potential impact this may have on the interpretation of solute fluxes for ions that arise from weathering reactions, and that are measured in site drainage at field scale. This implies that a significant factor that accounts for the apparently slower weathering rates in the field is the accumulation of solutes that are not flushed from the system and are thus not accounted for in the solute flux.

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