Applied Geochemistry 89 (2018) 160–172

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Diavik waste rock project: A conceptual model for temperature and sulfide-content dependent geochemical evolution of waste rock – Laboratory scale

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ARTICLE INFO

Handling Editor: Dr. R. Seal.

Keywords:
Reactive transport
Sulfide oxidation
Scale-up
Shrinking core model

ABSTRACT

The Diavik Waste Rock Project consists of laboratory and field experiments developed for the investigation and scale-up of the geochemical evolution of sulfidic mine wastes. As part of this project, humidity cell experiments were conducted to assess the long-term geochemical evolution of a low-sulfide waste rock. Reactive transport modelling was used to assess the significant geochemical processes controlling oxidation of sulfide minerals and their dependence on temperature and sulfide mineral content. The geochemical evolution of effluent from waste rock with a sulfide content of 0.16 wt.% and 0.02 wt.% in humidity cells was simulated with the reactive transport model MIN3P, based on a conceptual model that included constant water flow, sulfide mineral content, sulfide oxidation controlled by the availability of oxidants, and subsequent neutralization reactions with carbonate and aluminosilicate minerals. Concentrations of Ni, Co, Cu, Zn, and SO_4 in the humidity cell effluent were simulated using the shrinking core model, which represented the control of oxidant diffusion to the unreacted particle surface in the sulfide oxidation process. The influence of temperature was accounted for using the Arrhenius relation and appropriate activation energy values. Comparison of the experiment results, consisting of waste rock differentiated by sulfide mineral content and temperature, indicated surface area and temperature play important roles in rates of sulfide oxidation and release of sulfate and metals. After the model was calibrated to fit the effluent data from the higher sulfide content cells, subsequent simulations were conducted by adjusting only measured parameters, including sulfide mineral content and surface area.

1. Introduction

Laboratory-scale experiments such as humidity cells are often used to characterize the geochemical evolution of sulfidic waste rock and the associated impacts on effluent water quality (i.e., decreased pH and increased solute concentrations) generated as part of mine operations (Lapakko, 2003; Ardau et al., 2009; Sapsford et al., 2009). The mineral leaching rates derived from humidity cell experiments are commonly extrapolated to anticipate the geochemical evolution of full-scale waste-rock piles using empirical scale factors, a process typically referred to as scale-up. Scale factors usually incorporate one or more parameters understood to influence effluent quality, such as pH, grain or particle size distribution, moisture content, temperature, oxygen availability, and mineral surface area (Kempton, 2012; Amos et al., 2015). Site-specific heterogeneities in physical and geochemical characteristics often render empirically based scale-up methods ineffective for accurate prediction of effluent quality (Amos et al., 2015). The capacity of reactive transport models to account for site heterogeneity and coupled geochemical processes leads to the potential to address scale-up using a detailed, mechanistic, and quantitative approach.

The Diavik Waste Rock Project (DWRP) was developed, in part, to assess scale-up techniques through the implementation of laboratory- and field-scale experiments conducted using sulfidic mine waste rock produced at Diavik Diamond Mine (Diavik), Northwest Territories, Canada. DWRP experiments involve small-scale (1-kg sample) humidity cells, medium-scale (~9300 kg) *in situ* collection lysimeters, large-scale ($\sim 8.2 \times 10^7$ kg) densely instrumented waste-rock test piles, and instrumentation within the full-scale waste-rock pile, thus providing detailed datasets specifically designed to quantify scale-up processes.

Scale-up studies already conducted as part of the DWRP include

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https://doi.org/10.1016/j.apgeochem.2017.12.007
Received 30 May 2017; Received in revised form 20 November 2017; Accepted 5 December 2017

preliminary calculations summarized by Bailey (2013) and Sinclair et al. (2015). Bailey (2013) normalized sulfide oxidation rates from the humidity cell experiments to sulfide mineral surface area to estimate the mass loading expected from the *in situ* collection lysimeters. This approach was determined to be relatively accurate for more conservative parameters (e.g., Cu and Zn) but less suitable for estimation of solutes involved in multiple coupled processes (e.g., Fe and Al). Sinclair et al. (2015) developed a loading-rate model to evaluate hypotheses regarding the geochemical evolution of pore water in one of the waste-rock test piles (15-m scale) and indicated this approach can be used to simulate the migration of solutes not affected by secondary mineral formation at the larger field scale.

The DWRP humidity cell experiments were conducted over a period of approximately nine years using run-of-mine waste rock collected at Diavik. The waste rock is sorted into three types according to sulfur content: Type I $<$ 0.04 wt.%, Type II 0.04 to 0.08 wt.%, and Type III $>$ 0.08 wt.% S (Smith et al., 2013). The experiments were conducted as one component in a strategy to quantify the primary geochemical mechanisms controlling effluent quality from waste rock at the mine site.

The reactive transport model MIN3P (Mayer et al., 2002) was used to simulate the effluent geochemistry resulting from the humidity cell experiments and allow assessment of the primary weathering processes involved. The simulations were used to develop an integrated robust conceptual model of the geochemical evolution of the Diavik waste rock, which was applied to all of the humidity cell experiments to account for a range of sulfide contents and temperatures. This paper presents a conceptual model of metal sulfide weathering in low sulfide waste rock using the results of humidity cell effluent quality sampling, the resulting estimated weathering rates, and mineralogical and hydraulic properties from the DWRP humidity cell and field-scale experiments. The simulations provide a geochemical conceptual model that can subsequently be adapted for simulations of the larger scale field experiments towards the development of an integrated conceptual model of sulfide weathering.

2. Humidity cell methodology

The humidity cell experiments involved a total of 36 cells, half of which were allocated to a warm cell group maintained at room temperature (approximately 22 °C) and the other half to a replicate cold cell group maintained at a lower temperature (approximately 5 °C) (Langman et al., 2014). Replicate cells were constructed within each 18-cell experiment so that both temperature groups included six cells of each of the three types (Type I, Type II, and Type III) of waste-rock material. The results of the Type II simulations are not discussed here because of their similarity to the results of the Type I simulations.

Waste rock used in the humidity cell experiments was collected in 2004 and 2005 and was characterized as approximately 75% granite (primarily quartz [SiO_2], K-feldspar [$KAlSi_3O_8$], and albite [$NaAlSi_3O_8$]), 14% pegmatitic granite, 10% biotite schist, and 1% diabase (Blowes and Logsdon, 1998; Langman et al., 2014). Biotite schist is the primary host of metal sulfide minerals at the site, and is primarily composed of albite (35–55%), quartz (20–50%), and biotite [$KMg_{1.6}Fe_{1.4}AlSi_3O_{10}(OH)_2$] (10–25%) and contains a mean sulfide content of 0.24 wt.% S (Langman et al., 2014). Pyrrhotite is the dominant metal sulfide mineral present in the waste rock wherein minor substitution of Ni and Co for Fe has occurred in the approximate ratio [$Fe_{0.852}Ni_{0.004}Co_{0.001}S$] (Jambor, 1997). Langman et al. (2014) also note smaller but significant metal sulfide contributions of chalcopyrite [$CuFeS_2$], sphalerite [ZnS], and pentlandite [$(Fe,Ni)_9S_8$]. Given the relatively low sulfide content of the waste rock, the humidity cell experiments were used to assess the potential for acid generation and the release of elevated concentrations of metals, including Fe, Ni, Co, Cu, and Zn, as well as other dissolved constituents such as sulfate [SO_4].

Initial host mineralogy of the waste rock was obtained from Jambor (1997). The mineralogical study of the Diavik waste rock included transmitted and reflected light optical microscopy to identify the silicate, carbonate, and sulfide minerals. In addition, scanning electron microscopy with energy dispersion analysis and microprobe analyses were conducted to obtain compositional data on the silicate and sulfide minerals. X-ray diffraction was used to provide quantitative estimates of the abundance of silicate minerals in the primary lithological units at Diavik. Similar analyses were conducted to identify secondary phases on a previous series of column experiments. The total S and C contents were determined by Langman et al. (2014). Additional work conducted by Langman et al. (2015) focussed on the application of synchrotron based techniques to characterize and identify secondary phases associated with the weathered sulfide minerals from the humidity cell experiment.

Each humidity cell contained 1 kg of waste rock, and was flooded on a weekly basis with deionized water following the American Society for Testing and Materials (ASTM) method D5477-96 for humidity cell testing (ASTM, 1996). Increased flooding occurred in the early stages according to the method modification described by Lapakko and White (2000). The added water was held for approximately 1 h then allowed to drain from the cells. Draining of the cells generally lasted for 4–6 h but was allowed to continue for 24 h followed by periods of dry air flow (3 d at $<$ 10% relative humidity) and humid air flow (3 d at $>$ 95% relative humidity) to complete the weekly cycle (Langman et al., 2014). Further details regarding the methodology and results of the humidity cell experiments are presented by Langman et al. (2014).

3. Conceptual model

The conceptual model presented here was developed to simulate the geochemical evolution of sulfidic mine waste rock exposed to atmospheric oxygen under wetting conditions. The conceptual model is based on the interpretation of the DWRP humidity cell experiments provided by Langman et al. (2014). Due to the relatively constant moisture and availability of oxygen within the humidity cell system, sulfide mineral oxidation is hypothesized to be the primary driver of elevated concentrations of SO_4, Ni, Co, Cu, and Zn in the humidity cell effluent. As a result, the conceptual model is focused on sulfide oxidation processes including oxidation by $O_{2(aq)}$ and Fe^{3+}. The development of the conceptual model and subsequent calibration were based on effluent geochemistry obtained from the Type I and III warm and cold humidity cell experiments (Langman et al., 2014).

Water flow through the humidity cells was simulated as continuous infiltration at a rate of 500 mL wk^{-1}, which resulted in partially saturated conditions throughout the modelled period. The humidity cells were flooded on a weekly basis (i.e., 500 mL over a period of 4–6 h); however, simulating this flow as continuous infiltration was considered a reasonable approximation because: i) fully saturated conditions represented a very low proportion of the total experiment time (2–4%) and ii) evaporation was likely limited during the weekly dry cycle and did not result in a significant reduction of moisture content.

Several key components were included in the geochemical portion of the conceptual model to create a robust, generalized set of equations to represent the oxidation of sulfide minerals in systems beyond the scope of the humidity cells and the associated DWRP field experiments. Key oxidants, including $O_{2(aq)}$ and Fe^{3+} with various microbial communities acting as catalysts (Nordstrom and Southam, 1997; Blowes et al., 2003), were included in the development of the conceptual model. Bacterial enumeration data collected as part of the DWRP humidity cell experiments (Langman et al., 2014) indicated that neutrophilic sulfur oxidizing bacteria were the dominant microbiological catalyst in the system. The pH of the Type III cells initially declined to 4–4.5 then rose slightly to 4.5–5 after a period of stabilization while the pH of the Type I cells remained circumneutral throughout the experiments (Langman et al., 2014).

Using pyrrhotite as an example, the overall oxidation reactions can