Addition of a Rate Limit to a Shrinking Core Oxidation Model for Predictive Modeling of Mine Water Quality

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Abstract One of the more difficult problems in predictive modeling of mine water quality is accurate representation of sulfide mineral oxidation and the associated leaching of acid, metals, and other constituents. Shrinking core models (SCM) of sulfide oxidation are often used to represent oxidation kinetics; however, the SCM cannot represent increasing oxidation rates observed in laboratory tests. Addition of a rate limiting term to the SCM overcomes this limitation and allows modeling the full range of rate behavior. The resulting model provides more accurate representation of rate behavior of different lithologic materials, resulting in more accurate water quality predictions.

Keywords Sulfide oxidation modeling, rate limit, mine water quality

Introduction

Shrinking core models of pyrite oxidation (Davis and Ritchie 1986a-c) are widely used to represent the kinetics of sulfide mineral oxidation for predictive modeling of water quality in mine dumps, tailings impoundments, and mine pits. Recently there has been increased scrutiny of mine water quality predictions and the current state of predictive modeling of mine water quality. A key limitation of the classic SCM is the assumption that the sulfide oxidation rate can only decrease over time as oxidation progresses. This assumption is based on the theory that oxygen diffusion to reaction sites will be the primary limiting factor at the mine scale, where an abundance of sulfide minerals typically creates an oxygen demand in excess of the oxygen diffusion rate. However, in cases when oxygen availability is not the limiting factor (*e.g.* laboratory tests, near-surface environments, and where advection or convection occurs) oxidation rates are sometimes observed to increase with time, typically accompanied by a decrease in pH and a dramatic increase in acid and metals release. In these cases, the classic SCM will under-predict the degree of oxidation and associated release of acid and metals.

In the classic SCM (Davis and Ritchie 1986a-c; Homma *et al.* 2004) reaction rates are limited only by two-stage diffusion of oxygen to a reaction site. In the first stage, oxygen diffusion through air-filled pores or fractures in mine materials is constrained by a diffusion coefficient representative of the porous media (D1). In the second stage, diffusion to a reaction site within a mineral grain is constrained by a second diffusion coefficient representing an oxidized rind (D2). The SCM will generate an infinite rate on a fresh surface; as a result, an initial oxidized thickness must be set. As oxidation progresses an increasingly thick rind forms as the unreacted core shrinks, resulting in a decreasing oxidation rate. However, in laboratory tests oxidation rates are observed to increase over time in some materials as pH decreases, a behavior that cannot be represented by the SCM.

During laboratory humidity cell tests (HCT), one commonly observed behavior is consistent with the assumptions of the classic shrinking core model. In these instances, the release of iron, sulfur and acidity decreases over time, creating cumulative release plots that approach an asymptote as oxidation progresses toward 100 % (Fig. 1a; HCT 9). It is hy-

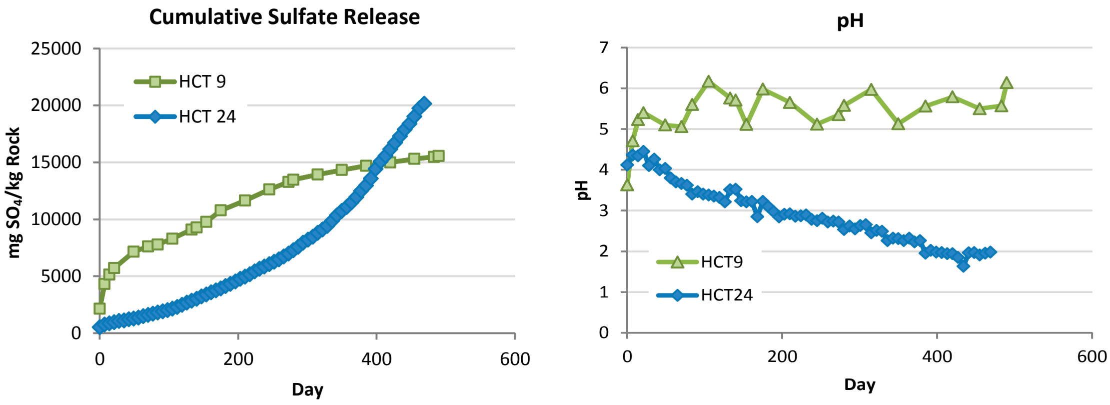

Fig. 1 *Cumulative sulfate release (a, left) and pH (b, right) in decreasing (HCT 9) and increasing (HCT 24) rate humidity cell tests*

pothesized that in these cases the decrease in rate corresponds to an increasing limitation of diffusion to deliver oxygen across an increasingly thick oxidized rind consistent with SCM assumptions.

Occasionally, increasing oxidation rates are observed in kinetic tests (Fig. 1a; HCT 24). In this example, as pH decreases to 3 and below (Fig. 1b; HCT 24) a corresponding exponential increase in the release of sulfate and iron is observed. There are a number of possible explanations for increased rates observed at lower pH, including dissolution of secondary oxide mineral phases, increased bacterial populations and activity, and increased oxidation by ferric iron. Here it is hypothesized that pH decreased to a point capable of dissolving secondary oxide minerals, thereby eliminating the oxidized rind around the unreacted core. Under these conditions, the oxidized rind ceases to be the rate-limiting factor assumed in the shrinking core model, and abundant dissolved ferric iron is suddenly available to facilitate oxidation.

None of these potential behaviors are captured in the SCM, where the rate can only decrease over time as the unreacted core shrinks and oxygen must traverse a thicker and thicker rind of oxidized material to reach a reaction site.

Williamson and Rimstidt (1994) presented pyrite oxidation rate laws derived from laboratory experiments as functions of H^+, dissolved oxygen, and dissolved ferric and ferrous iron concentrations. More recently, Rimstidt and Vaughan (2003) and Lapakko and Antonson (2006) presented comparisons of rate law predictions to observed oxidation rates in laboratory experiments, with the latter describing how rates observed in humidity cell tests tended to be closer to rate law predictions above pH 6 and 2 to 8 times faster than predicted at pH 3.3 to 5.0. These results indicate that the aqueous rate laws also do not fully capture the range of behavior observed in HCTs.

Methods

An empirically fit rate limiting term was added to the SCM to account for the initial oxidation rate of a fresh surface and allow for an increasing rate as oxidation progresses. Results of adding a rate limiting term to the shrinking core model include the ability to model the full range of behavior observed in materials during humidity cell testing, including both decreasing rates resulting from diffusion across an increasing distance to the unreacted core, and increasing rates resulting from decreasing pH and associated dissolution of secondary oxide minerals.

An implementation of the Davis-Ritchie shrinking core model (Davis and Ritchie 1986a-c; Molson *et al.* 2005) was coded in Mi-

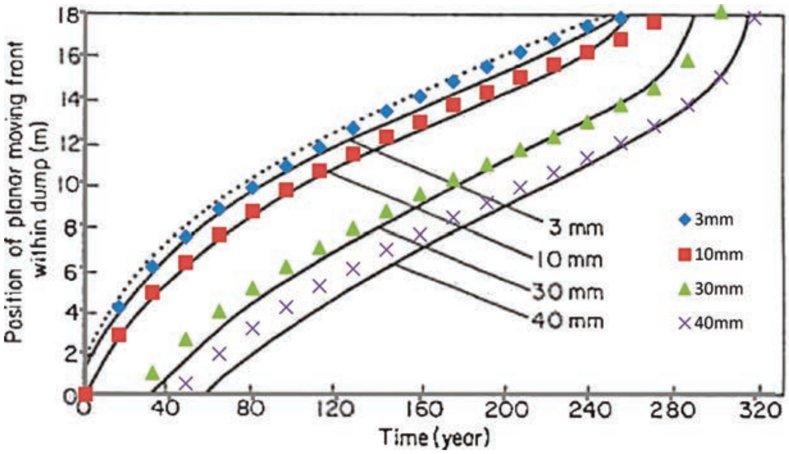

Fig. 2 *Model verification (symbols) over base plot from Davies Ritchie 1986a Fig. 3*

crosoft Visual Basic for Applications in Microsoft Excel using a novel numerical implementation that allows the addition of a simple rate limit term to the formulation. The model code was verified against the original Davis-Ritchie code and reproduced the original results satisfactorily (Fig. 2).

The classic shrinking core model requires that a pre-existing oxidized rind exists on the grains being modeled in order to avoid an infinite oxidation rate at the model start, generally applied as an unoxidized radius of 0.95 (5 % oxidized initial condition). This approach does not allow for modeling of fresh sulfide surfaces commonly found in material ground for humidity cell tests and in recent mine materials. Alternate rate limiting was added to the model code by including a rate limit term that is invoked if the rate limit is less than the rate calculated from the D2 diffusion coefficient, local oxygen content, and thickness of the oxidized rind. The rate limit is incorporated as an initial rate representing 0 % oxidation, and an ending rate representing the rate at 100 % oxidation. The instantaneous rate is linearly interpolated as oxidation proceeds from 0 to 100 %.

There are two instances where the alternate rate limit may be invoked; first, when the shrinking core code generates an unrealistically high oxidation rate if the oxidized rind is thin or non-existent. In this case, a standard oxidation rate from literature or calibration to a HCT is used to set the initial rate. Second, if the calibration data set demonstrates an increasing rate over time the alternative rate limit is invoked to represent the rate of sulfide oxidation at the grain scale (*e.g.* replacing the D2-derived rate). Under the alternative rate limit, the local availability of oxygen still limits the overall maximum rate of oxidation (*i.e.* diffusion at the dump scale limited by D1 is an overriding control on oxidation rate).

Model parameters are presented in Table 1 for the two HCTs (9 and 24) examined here. Model results demonstrate that with the alternate rate limit added, the model is capable of fitting both increasing (Figs. 3–4) and decreasing rates observed during kinetic tests (Figs. 5–6).

Fig. 3 illustrates an increasing rate over time accompanied by a decrease in pH from 4 to 2 (Fig. 1b) which appears to have resulted in dissolution of secondary oxide minerals re-

HCT	Pyrite wt. %	D2 (m^2/d)	Initial Rate Limit (mg py/kg-day)	End Rate Limit (mg py/kg-day)
HCT 9	4	7.4E-8	200	-
HCT 24	2.3	-	8	112

Table 1 *Model Parameters.*

sulting in an exponential rate increase. Other factors that may contribute to the increasing rate include greater activity of oxidizing bacteria at lower pH and increased oxidation by ferric iron.

Fig. 4 illustrates the close agreement between the rate limit model results and the actual cumulative sulfur release data from HCT24. It should be noted that the shrinking core model is not capable of creating an upward inflecting curve. There has been discussion in mining and regulatory circles regarding how long HCT tests should run. In a minimum 20 week test (140 days) it would be possible to approximate a shrinking core model fit to the early time data that would predict a decreasing rate beyond 140 days. As can be seen in Figs. 3 and 4, a shrinking core model with a decreasing rate would greatly underestimate the ultimate production of acid and metals from this material.

Figs. 5 and 6 illustrate a fit of the classic shrinking core model to an HCT with a higher sulfide content (4 %) but higher effluent pH

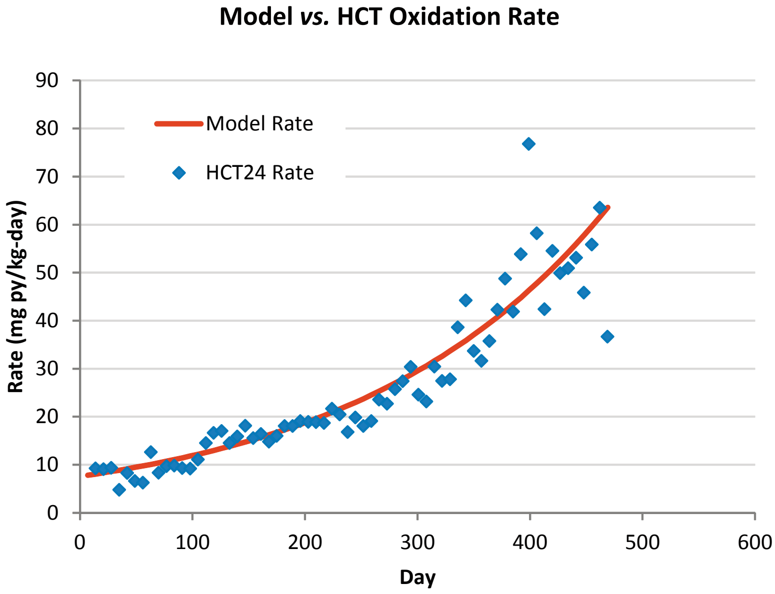

Fig. 3 *Rate limit model fit to increasing rate HCT24*

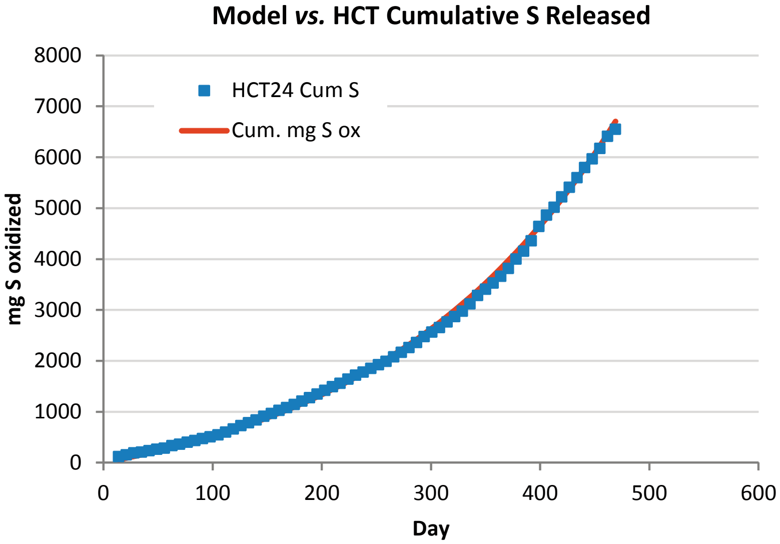

Fig. 4 *Rate limit model fit to cumulative sulfur release in HCT24*

(generally 5–6; Fig. 1b) that appears to have allowed formation of secondary oxide mineral rinds. These conditions do not violate the assumptions of the SCM and a reasonable fit can be achieved. In this example, the oxidation rate started out very high (Fig. 5), decreasing over time. This behavior is also apparent in the shape of the cumulative sulfur release curve, which rises steeply before inflecting convexly toward the limit imposed by the total sulfur content of the material.

Conclusions

Oxidation rate behavior is dependent on pH, with strongly acidic conditions (pH 2–3) associated with increasing rates over time and mildly acidic conditions (pH 5–6) generally associated with decreasing rates over time. In between, a variety of rate behaviors can occur including relatively constant rates and transitioning from one behavior to another. Increasing oxidation rates violate the simplifying assumptions of the SCM, which is unable to model anything but a decreasing rate as ox-

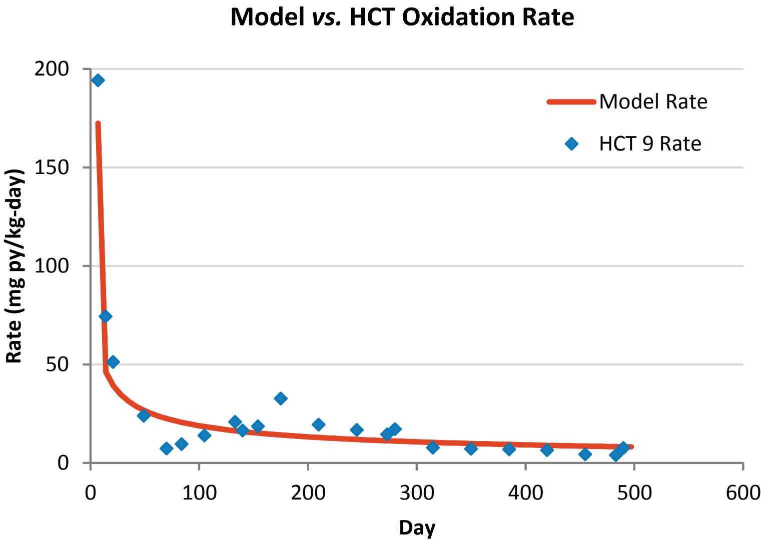

Fig. 5 *Shrinking core model fit to decreasing rate HCT9*

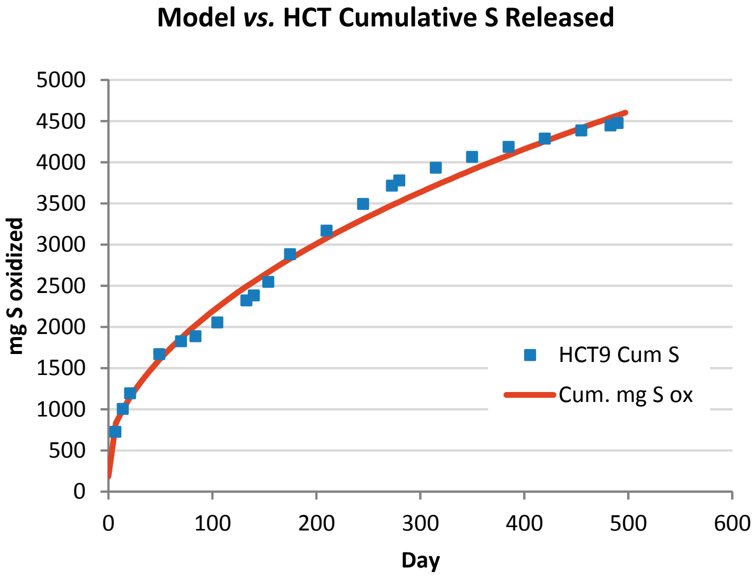

Fig. 6 *Shrinking core model fit to cumulative sulfur release in HCT9*

idation progresses. As a result, the classic SCM may under-predict acid and metal release from the most reactive materials, particularly in the later stages of oxidation. It is hypothesized that the different rate behaviors are primarily related to pH and the solubility of secondary oxide minerals. In the case where secondary oxide minerals accumulate in a rind around unreacted sulfide grains, the assumptions of the classic SCM are met and reasonable fits to data can be obtained. However, in cases where pH decreases sufficiently to partially or completely dissolve secondary oxide minerals, or prevent their precipitation entirely, oxidation rates are observed to increase. In order to model this behavior, it is necessary to add a rate limit function to the shrinking core model. This addition allows fitting of both increasing and decreasing rates, as well as transitional behaviors between these end points.

Reproducing kinetic test results (HCTs) is a simple test of an oxidation model that indicates whether the numerical model is capable of reproducing the full range of oxidation behavior observed in different mine materials. Given the considerable uncertainties already inherent in scaling from laboratory to field scale, it is important to verify that a model can accurately represent more controlled laboratory tests. Accuracy and utility of mine water quality predictive modeling depend on how well the model implementation reflects the actual conditions being modeled. In the case of oxidation modeling of sulfide-bearing mine materials, introducing a rate limit term to the SCM can simulate the varied oxidation kinetics of different lithologies and alteration types observed in HCTs, increasing the accuracy of water quality predictions.

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