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### Publication Date

2003-12-20

# Pore-Water Concentrations Determined from Leached Salts in Fractured Rock

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**Abstract.** This paper presents a quantitative approach to estimate chemical concentrations and their uncertainties in pore waters from analyses of leached salts. The method was applied to samples derived from welded tuffs in the unsaturated zone at Yucca Mountain, Nevada, a proposed underground repository site for storing high-level radioactive waste. Distributions of aqueous species such as chloride have been useful in identifying unsaturated zone percolation patterns and flow behavior, which are crucial issues in assessing repository performance (Sonnenthal and Bodvarsson, 1999; Wu et al., 2003). However, because the welded fractured tuffs have low porosities and low water content, it has been difficult to extract sufficient pore water for chemical analyses. One approach used for determining  $^{36}\text{Cl}/\text{Cl}$  ratios in pore waters has been to leach soluble components from rock samples using deionized water (Fabryka-Martin et al., 1997). However, determination of the actual chemical concentrations in the pore waters from leachate analyses is complicated by factors that include specific leaching time and uncertainties in rock physical properties (such as porosity, saturation and rock density). In this paper, we describe a model to estimate the effect of incomplete leaching on the measured concentration. These uncertainties in the estimated pore water concentrations derived from leachate concentrations are then quantified using the perturbation method.

Key words: leaching; chloride; pore water; fractured rock; tuffs; Yucca Mountain

## 1. Introduction

Yucca Mountain, Nevada, located in a semi-arid region in the western U.S., is a proposed site for the U.S. Department of Energy's high-level nuclear waste repository. The geological formations at Yucca Mountain consist of alternating layers of welded and nonwelded ash-flow and ash-fall tuffs. Geological formations have been grouped into stratigraphic units based on the degree of welding, in descending order from the land surface as follows: the Tiva Canyon welded tuff (TCw), the Paintbrush nonwelded tuff (PTn) hydrological unit, the Topopah Spring welded tuff (TSw), and the mostly nonwelded and sometimes altered Calico Hills Formation (CHn). Lying on the ground surface is a discontinuously distributed quaternary alluvial deposit (Q).

In general, pore-water geochemistry at Yucca Mountain has been studied by using pore-water extraction, involving triaxial compression from relatively high-porosity rock samples of the PTn and CHn tuffs without much difficulty (Fabryka-Martin et al., 1997). However, since the welded tuffs in the TCw and TSw units typically have low porosity and low water content, pore-water salts were extracted by leaching from drillcores or tunnel walls (Fabryka-Martin et al., 1997). Because the leaching of the rock samples is incomplete, the actual pore water concentrations in these samples are unknown. Thus, current pore water concentration profiles along boreholes are incomplete, with data missing from the corresponding TCw and TSw tuffs.

Quantification of pore water concentrations from leached salts involves uncertainties arising from leaching processes, which involve physical properties such as rock density, porosity, and saturation. The objective of this paper is to describe an approach to estimate the original pore-water concentrations and the associated uncertainties and apply it to samples from the fractured welded tuffs at Yucca Mountain.

## 2. Mathematical Model of Leaching

We made some general, defensible assumptions regarding this leaching experiment. No chemical reactions that would change Cl and Br are involved. Leaching is a physical process that usually lasts a short time (less than a few days), and therefore the effect of dissolution of minerals on salt concentrations in the volcanic rock can be ignored. Chlorine salts on the fracture surfaces are considered together with the pore water Cl (Lu et al., 2003).

We introduce a time-dependent leaching factor  $\gamma(t)$  to account for the progressive leaching process of chemical components in a laboratory leaching experiment. During leaching, the pore-water concentration decreases while the leachate concentration increases; eventually, the two concentrations approach the same value. We use the following relationship to describe the evolution of leachate concentrations:

$$\gamma(t) = \frac{C_{eq}}{C_x(t)} \quad t > 0 \quad (1)$$

where  $\gamma(t)$  is the leaching factor,  $C_{eq}$  is the equilibrium concentration for a specific component, and  $C_x(t)$  is the leachate concentration at time  $t$ . Since  $C_x(t)$  increases over time as more mass leaches into the leachate, the leaching factor  $\gamma(t)$  decreases, eventually reaching an equilibrium value after sufficient leaching time.

Based on mass balance, the initial Cl concentration in the pore water of a rock sample is equal to the sum of mass remaining in the rock and mass leached out into the leachate. We have the following mass balance equation:

$$\frac{C_0 \theta S M}{d \sqrt{\tau}} = C_x (M_w / d_w - \frac{\theta (S_{1x} - S) M}{d \sqrt{\tau}}) + C_{1x} \frac{\theta S_{1x} M}{d \sqrt{\tau}} \quad (2)$$

where subscript 1 denotes rock matrix, subscript  $w$  stands for leachate, and subscript  $x$  is used for quantities at a specific time. Specifically,  $C_0$  is the initial pore water concentration (in mg/L),  $C_x$  is the leachate concentration at a specific time (mg/L),  $C_{1x}$  is matrix pore water concentration at a specific time (mg/L),  $S$  is initial saturation,  $S_{1x}$  is rock saturation under leaching at a specific time,  $\theta$  is rock-matrix porosity,  $M$  is rock mass (kg) with bulk density  $d$  ( $\text{kg}/\text{dm}^3$ ), and  $M_w$  is the initial leachate mass with density of  $d_w$  ( $\text{kg}/\text{dm}^3$ ). The symbol  $\tau$  represents tortuosity and is defined as the square of the ratio of the shortest distance to the effective path in a porous medium. Tortuosity (as a factor) is incorporated into the equation to reflect the increase of pore volume caused by pore-system tortuosity of the rock, which accounts for the pore geometry (Grathwohl, 2000). The term  $(S_{1x} - S)$  on the right side of Equation (2) is the amount of water that has soaked into the rock matrix.

The equilibrium concentration of leaching can be obtained from Equation (2) by letting  $C_x = C_{1x} = C_{eq}$ :

$$C_{eq} = \frac{C_0 \theta S M}{M_w \sqrt{\tau} d / d_w + \theta S M} \quad (3)$$

In Equation (2), the variable  $C_{1x}$  is not a quantity directly measured from the leaching experiment. Therefore, we need to express it in terms of other variables. In terms of mass balance, at a specific time of leaching, the mass to be leached out from the rock pores is equal to the mass to be gained in the leachate until equilibrium. We can write another equation for mass balance:

$$\frac{(C_{1x} - C_{eq})\theta_1 S_{1x} M_1}{d_r \sqrt{\tau_1}} = (C_{eq} - C_x) \left[ M_w / d_w - \frac{\theta_1 (S_{1x} - S_1) M_1}{d_r \sqrt{\tau_1}} \right] \quad (4)$$

Finally, combining Equations (1) and (4) with Equation (3), we derive the following equation for quantifying the Cl concentration in the rock sample:

$$C_0 = C_x \gamma \left[ M_w d \sqrt{\tau} / (d_w \theta S M) + 1 \right] \quad (5)$$

### 3. Uncertainty Analysis

For the following analysis, we manipulate the mathematical derivation in the perturbation method. We write terms for concentration and physical properties as the sums of their means and fluctuations, taking initial pore-water concentration as an example:

$$C_0 = \langle C_0 \rangle + C'_0 = C_0^0 + C'_0 \quad (6)$$

where (in the following text) angular brackets  $\langle \rangle$  indicate a mathematical expectation (ensemble mean) (also expressed with superscript 0), and the primed quantity is the zero mean fluctuation.

Substituting terms in Equation (5) for the above perturbative terms, and then collecting terms with less than the second order separately, leads to

$$C_0^0 = C_x^0 \gamma^0 \left[ 1 + w d^0 \sqrt{\tau^0} / (\theta^0 S^0) \right] \quad (7)$$

$$C'_0 = \gamma^0 \left( 1 + w \frac{d^0 \sqrt{\tau^0}}{\theta^0 S^0} \right) C' + C_x^0 \left( 1 + w \frac{d^0 \sqrt{\tau^0}}{\theta^0 S^0} \right) \gamma' - w C_x^0 \gamma^0 \frac{d^0 \sqrt{\tau^0}}{(\theta^0)^2 S^0} \theta' \\ - w C_x^0 \gamma^0 \frac{d^0 \sqrt{\tau^0}}{(\theta^0 S^0)^2} S' + w C_x^0 \gamma^0 \frac{d^0 \sqrt{\tau^0}}{\theta^0 S^0} d' + w C_x^0 \gamma^0 \frac{d^0 (\tau^0)^{-1/2}}{2\theta^0 S^0} \tau' \quad (8)$$

where  $w = M_w / (d_w M)$ . Here and below, we assume, for simplicity, that the random variable  $\gamma$  is secondary stationary. Then, the covariance between concentration at location  $\mathbf{x}, \mathbf{x}'$  is given by

$$C_{C_0 C_0}(\mathbf{x}, \mathbf{x}') = \langle C'_0(\mathbf{x}) C'_0(\mathbf{x}') \rangle \quad (9)$$

$$= (\gamma^0)^2 \left( 1 + w \frac{d^0 \sqrt{\tau^0}}{\theta^0 S^0} \right)^2 C_{cc} + (C_x^0)^2 \left( 1 + w \frac{d^0 \sqrt{\tau^0}}{\theta^0 S^0} \right)^2 C_{\gamma\gamma} \\ + \left( w C_x^0 \gamma^0 \frac{d^0 \sqrt{\tau^0}}{(\theta^0)^2 S^0} \right)^2 C_{\theta\theta} + \left( w C_x^0 \gamma^0 \frac{d^0 \sqrt{\tau^0}}{\theta^0 (S^0)^2} \right)^2 C_{SS} \\ + \left( w C_x^0 \gamma^0 \frac{d^0 \sqrt{\tau^0}}{\theta^0 S^0} \right)^2 C_{dd} + \left( w C_x^0 \gamma^0 \frac{d^0 (\tau^0)^{-1/2}}{2\theta^0 S^0} \right)^2 C_{\tau\tau}$$

where the  $C$ -terms with double subscripts are the covariance of corresponding terms. Here, cross-covariance terms are eliminated because each physical property can be assumed to be

independent. This equation expresses the initial pore-water-concentration uncertainty in terms of leachate concentration measurement, the leaching process in terms of leaching factor (degree approaching equilibrium in time), and physical properties in terms of porosity, saturation, bulk density of the rock sample, and tortuosity of the pore systems.

#### **4. Application and Discussions**

We use Equations (7) and (9) to estimate the chemical concentrations of pore waters from the leachate analyses. Here, we use the leaching data and physical properties from borehole USW UZ-14 as an example (Figure 1).

In this example, the porosity distribution takes a lognormal distribution. Saturation and rock density are approximated with a normal distribution, and tortuosity is approximated by porosity (Lu et al., 2003). The resulting calculated concentrations are plotted in Figure 2, with the one standard deviation mark. In the calculation, each sample was assigned the mean and covariance obtained for corresponding layers. The results indicate that above porosities of approximately 10%, and for typical leaching times of two days, the leaching process approaches equilibrium and the pore water concentrations can be estimated directly using the saturation, rock density and porosity. For samples having porosities below about 10%, leaching is likely to be incomplete over times of less than two days and a correction such as that described here may be required.

#### **5. Conclusions**

We have developed a mathematical model to estimate the pore-water concentrations of chemical components from analyses of leached salts. The model is based on the mass balance of chemical compositions in a leaching experiment with the time factor accounted for by a leaching factor.

We use the perturbation approach to develop and solve the mathematical model to estimate uncertainties in pore-water concentration arising from physical properties such as porosity, saturation, and bulk density in rock samples. The model was applied to borehole USW UZ-14 at Yucca Mountain to estimate the pore-water concentration of Cl<sup>-</sup> from the leached salt data. This approach provides a way to indirectly determine pore-water concentration data from analyses of leached salts for samples that have very low porosity and short leaching times..

#### **Acknowledgments**

The authors would like to acknowledge the help they received from Zhiming Lu and June Fabryka-Martin at Los Alamos National Laboratory, as well as the LBNL internal review by Quanlin Zhou and technical editing by Daniel Hawkes. This work was supported by the Director, Office of Civilian Radioactive Waste Management, U.S. Department of Energy, through Memorandum Purchase Order EA9013MC5X between Bechtel SAIC Company, LLC, and the Ernest Orlando Lawrence Berkeley National Laboratory (Berkeley Lab). The support is provided to Berkeley Lab through the U.S. Department of Energy Contract No. DE-AC03-76SF00098.

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**Figure Caption:**

Figure 1. Porosity and saturation profiles at borehole USW UZ-14. Data source: Flint (1998).

Figure 2. Corrected initial pore-water concentrations (circles) with error bars at borehole USW UZ-14. The field measured Cl<sup>-</sup> concentrations of pore water are shown as diamonds, and concentrations (filled circles) are approximated by Equation (5) with  $\gamma$  set to 1.0. Data source: Fabryka-Martin et al. (1997).

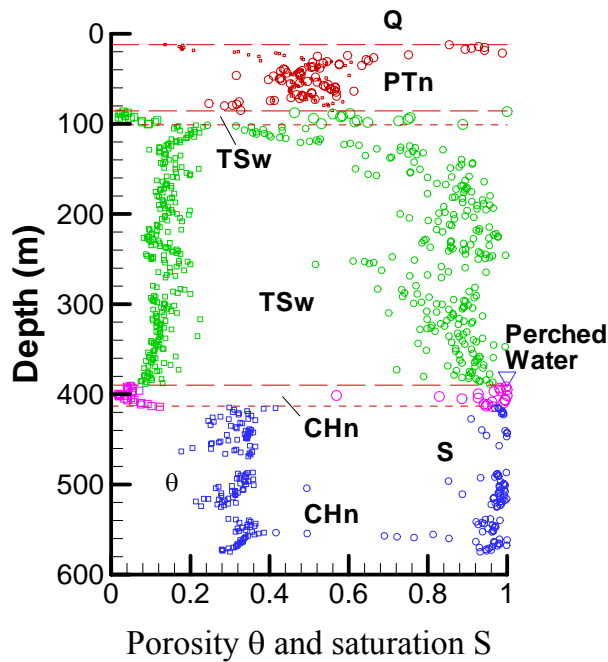


Figure 1.

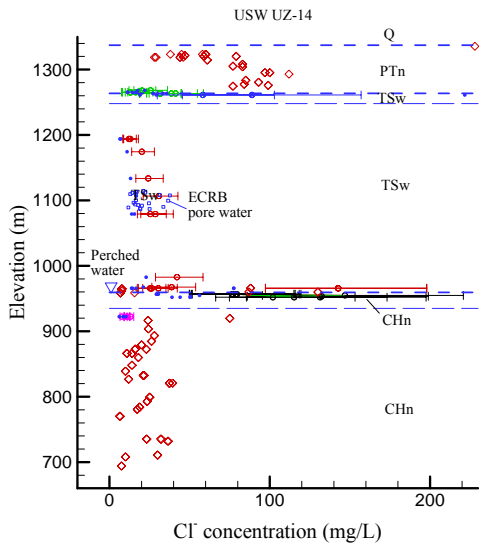


Figure 2.