MATHEMATICAL SIMULATION OF A WASTE ROCK HEAP[1]

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Abstract: A computer model has been developed to simulate the generation of acidic drainage in waste rock piles. The model considers the kinetic rates of biological and chemical oxidation of sulfide minerals (pyrite, pyrrhotite) present as fines and rock particles, as well as chemical processes such as dissolution (kinetic or equilibrium controlled), complexation (from equilibrium and stoichiometry of several complexes), and precipitation (formation of complexes and secondary minerals). Through mass balance equations and solubility constraints (e.g., pH, phase equilibria) the model keeps track of the movement of chemical species through the waste pile and provides estimates of the quality of seepage (pH, sulfate, iron, acidity, etc.) leaving the heap. The model has been expanded to include the dissolution (thermodynamic and sorption equilibrium), adsorption and coprecipitation of uranium and radium. The model was applied to simulate waste rock heaps in British Columbia, Canada and in Thüringia, Germany. To improve the accuracy and confidence of long-term predictions of seepage quality, the entire history of the heaps was simulated. Cumulative acidity loads and water treatment considerations were used as a basis for evaluation of various decommissioning alternatives. Simulation of the technical leaching history of a heap in Germany showed it will generate contaminated leachate requiring treatment for acidity and radioactivity for several hundred years; cover installation was shown to provide a significant reduction of potential burdens, although chemical treatment would still be required beyond 100 years.

Additional Key Words: computer model, waste rock model, technical leaching, prediction, uranium.

Introduction

Acidic drainage from waste rock containing sulfide minerals is a serious environmental problem. The accurate prediction of the potential magnitude and duration of the contaminant loading is of concern to both mine operators and regulatory agencies. Mathematical modeling is a recommended tool for evaluating the extent of the problem and for providing direction for assessing management and decommissioning strategies.

A computer model has been developed to simulate the generation of acidic drainage in waste rock piles (SENES 1993). The model simulates the waste rock pile as an equivalent rectangle of specified depth and surface area. The depth is then subdivided into 20 horizontal layers, forming a series of interconnected modeling units. Water infiltrating the waste rock is assumed to flow downwards and exit as seepage at the base of the waste rock pile. The void space within the unsaturated waste rock pile is assumed to contain a small amount of pore water associated with the surface of the rock particles. The waste rock particles are characterized as being either fines or rocks (figure 1).

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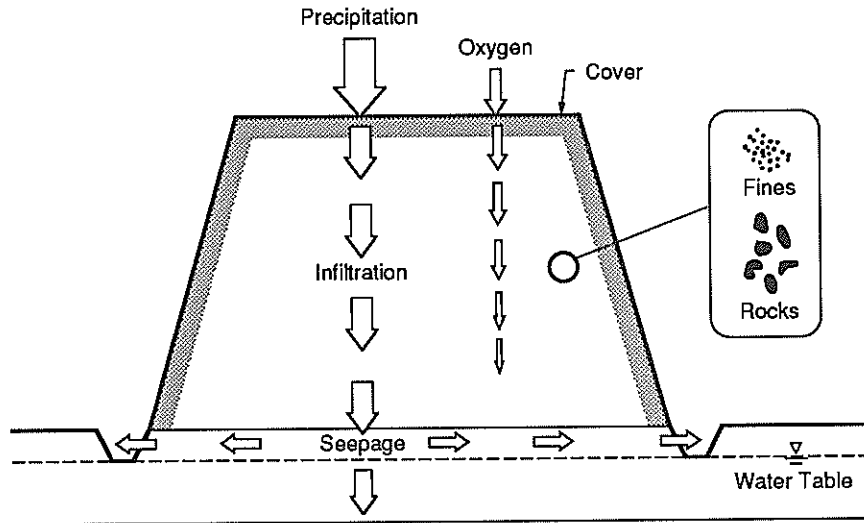
Figure 1. Concepts adopted for modelling of waste rock piles.

Model Structure

The computer model is comprised of seven main modules as shown in figure 2. The **Initial Inventory Module** assigns the initial concentrations and calculates the internal geochemical, kinetic, and physical parameters used in the subsequent modules. The theoretical basis for the model and the equations describing sulfide oxidation, oxygen transport, enthalpy (temperature) transport, pH calculation and aqueous speciation, and dissolution-precipitation reactions were previously described by Scharer et al. (1992).

The **Case-Specific Module** contains the instructions for simulation of timed events and specific scenarios, such as construction of the waste pile (i.e., placement of lifts, reprofiling, installation of a cover) and changes in the nature of the infiltration flow (i.e., infiltration rate, recirculation of leach solution). These activities are simulated by making changes to the corresponding model parameters (e.g., infiltration flows, mineralogy, oxygen diffusion coefficient, moisture content).

The **Kinetics Module** contains all of the equations for evaluating sulfide oxidation, oxygen transport, and temperature. The stoichiometric equations for the oxidation of iron sulfides, pyrite and pyrrhotite into their reaction products have been reviewed (Lowson 1982, Nordstrom 1982). The abiotic oxidation of sulfide minerals is modeled by the following relationship (Moses and Herman 1991, McKibben and Barnes 1986):

$$k_c = A \ (0.33 \ pH)^{0.7} \ e^{-\frac{E_a}{RT}} \ [O_2] \tag{1}$$

where: k_c = chemical surficial reaction rate constant (mol m^{-2} s^{-1}),
E_a = Arrhenius activation energy (J/mol),
$[O_2]$ = oxygen concentration (mol/m^3),
A = Arrhenius pre-exponential factor,
R = molar gas constant (J mol^{-1} K^{-1}),
T = temperature (K).

The preexponential factor (A) for the chemical rate constants is dependent on the pyrite/pyrrhotite content. The chemical reaction rate has been shown to be a weak function of the pH (McKibben and Barnes 1986). The

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biological oxidation rate, however, includes both temperature and pH dependence in the following manner (Scharer et al. 1991):

$$k_B = B\left[\frac{1}{1+10^{2.5-pH}+10^{pH-4}}\right]e^{-\frac{E_a}{RT}} \qquad (2)$$

where: B =   biological scaling factor, and

k_B =   biological surficial reaction rate constant $(mol\ m^{-2}\ s^{-1})$

The constant "B" in equation 2 is the biological scaling factor (SENES and Beak 1988) used to fit site specific data and is, in turn, a function of moisture content, nutrient levels, and the partial pressure of oxygen and carbon dioxide. Bacterial oxidation becomes significant at pH values below 4; at pH 2 to 3, the biological oxidation rate is approximately 16 to 35 fold greater than the abiological rate. The waste rock is assumed to consist of fine grained and coarse rock particles. The specific reaction rate $(mol\ kg^{-1}\ s^{-1})$ for fine particles is calculated from the abiological and biological oxidation rates as follows:

$$R_{s,p} = (k_c + k_B)a/\rho \qquad (3)$$

where: $R_{s,p}$ =   overall specific reaction rate $(mol\ kg^{-1}\ s^{-1})$ - fine particles,

a   =   specific surface area of sulfide minerals (m^2/m^3), and

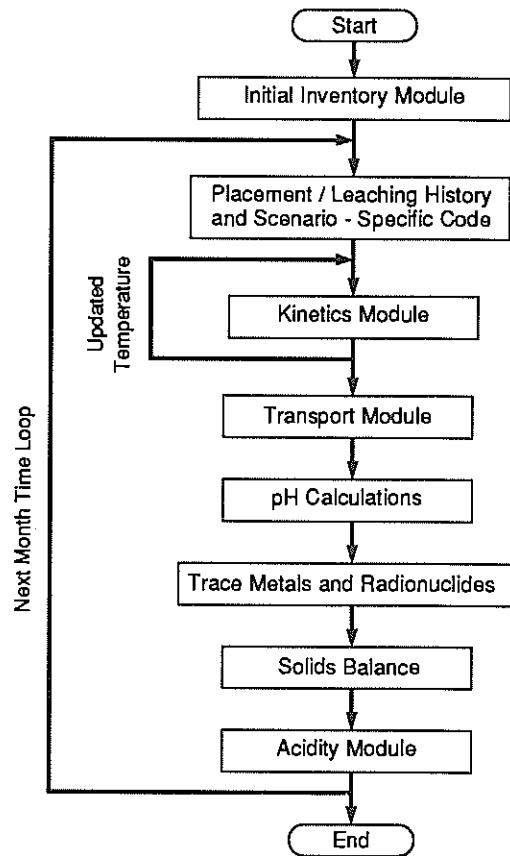ρ =   density of the sulfide mineral (kg/m^3).

Figure 2. Structure of model of waste rock pile.

The specific surface area of fine particles is evaluated by employing a Pareto-type distribution function (Scharer et al. 1992). The fine particles are modeled on the basis of shrinking particle kinetics. A shrinking reactive front concept is used to model oxidation of larger sulfide particles (larger than 2 mm particle size) or sulfide embedded in a rock matrix. The physical model consists of two phenomena: (1) the transport of oxygen through a liquid film and a layer of reaction products (primarily ferric hydroxide) and (2) the temporal shrinking of the reactive front as the sulfide is being oxidized. It can be shown that the overall oxidation rate per unit surface area is given by the combination of the two phenomena:

$$k_r = \frac{C}{\gamma}\left(\frac{1}{\frac{C}{\gamma(k_c+k_B)} + \frac{\Delta x}{D}}\right) \qquad (4)$$

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where:
k_r	=	overall specific reaction rate of rock surfaces (mol m^{-2} s^{-1}),
γ	=	stoichiometric constant relating oxygen uptake to mineral oxidation,
Δx	=	thickness of layer surrounding the particle (m),
C	=	local concentration of the oxygen in the pore space (mol/m^3), and
D	=	diffusion coefficient of oxygen through the liquid film and layer of reaction products (m^2/s).

The transport of oxygen through the pore space is widely regarded as a rate controlling process (Cathles and Schlitt 1980, Davis and Ritchie 1986, Scharer et al. 1991). The principal mode of oxygen transport is molecular diffusion in open (i.e. non water filled) zones. The advective transport of oxygen in the percolating pore water is considered to be less significant (Scharer et al. 1991). The differential equation describing the transport process is the following:

$$\frac{\partial C}{\partial t} + D_e \frac{\partial^2 C}{\partial z^2} + vK_H \frac{\partial C}{\partial z} - \gamma \bar{R}_s = 0 \qquad (5)$$

where:
$\bar{R}_s$	=	volume average sulfate oxidation rate (mol m^{-3} s^{-1}),
C	=	concentration of oxygen in the pore space (mol/m^3),
D_e	=	effective diffusion coefficient of oxygen through the waste rock (m^2/s),
z	=	depth into matrix (m),
t	=	time (s),
v	=	water infiltration rate (m/s), and
K_H	=	modified Henry's law constant (mol/m^3 oxygen in liquid per mol/m^3 oxygen in the gas phase).

In some situations, the convective transport of gaseous oxygen may be important. Since gas flow rates are usually not known, an effective dispersion coefficient is estimated and employed instead of diffusion in equation 5. The volume average sulfide oxidation rate is a function of the local oxygen concentration. Equation 5 possesses highly variable, both spatial and temporal, coefficients. For this reason, the equation is solved numerically using finite difference methods.

The temperature has a profound effect on both the chemical and the biological oxidation rates. To calculate the temperature, a simple enthalpy balance is employed. Since it is difficult to construct a global enthalpy model, the monthly temperature at various depths is evaluated as a temperature increment (ΔT) resulting from enthalpies of sulfide oxidation reactions:

$$\rho_B \, C_P \, \frac{\partial \Delta T}{\partial t} + k \, \frac{\partial^2 \Delta T}{\partial z^2} + F_W C_W \, \frac{\partial \Delta T}{\partial z} = Q_{RX} - \Delta H_V E_W \qquad (6)$$

where:
ΔT	=	temperature rise in the material (K),
C_p	=	heat capacity of the solids (J kg^{-1} K^{-1}),
ρ_B	=	bulk density (kg/m^3),
k	=	thermal conductivity (J m^{-1} K^{-1} s^{-1}),
F_W	=	vertical water flux (mol m^{-2} s^{-1}),
C_W	=	molar heat capacity of water (J mol^{-1} K^{-1}),
Q_{RX}	=	sulfide reaction enthalpy generation (J m^{-3} s^{-1}),
ΔH_V	=	enthalpy of evaporation (J/mol), and
E_W	=	evaporative water loss (mol m^{-3} s^{-1}).

The monthly baseline temperatures are used as the first estimate for the monthly temperatures in the Kinetics Module. The temperature rises are calculated and the entire Kinetics Module is then repeated using the updated temperatures.

The **Transport Module** estimates the movement of aqueous species through each of the 20 simulated layers using material balances. The reaction stoichiometry and the overall sulfide oxidation rate determined in the kinetics module are used to calculate the sulfate and iron concentrations. The iron is partitioned into ferrous and ferric forms according to the pH and oxygen conditions. Other major aqueous species (e.g., uranium, calcium, radium, potassium, aluminum) are determined, and the model checks for the formation of secondary minerals (e.g., jarosite) and performs an inventory of minerals in each layer (e.g., calcite, gypsum, siderite, aluminum hydroxide, iron hydroxide).

The **pH Module** performs the complexation-speciation of numerous dissolved constituents and calculates the pH using published thermodynamic data and algebraic algorithms (Parkhurst et al. 1980, Motekaitis and Martell 1988). The pore water pH is estimated by solving for electroneutrality.

The **Trace Metals and Radionuclides Module** determines the concentrations of dissolved radionuclides (uranium and radium). The uranyl ion concentration is first estimated from thermodynamic data considering equilibrium with respect to uranite and uranyl carbonate (Mocker 1992). After calculating the various complexed species, the total uranium in solution is obtained. The sorption equilibrium on solid ferric hydroxide, aluminum hydroxide, and organic surfaces is estimated simultaneously, and the lower of the two concentrations (solubility versus sorption equilibrium) is used as the representative concentration. As time progresses the predominance of solubility equilibrium may "switch" to sorption equilibrium. At low pH values, neither solution nor sorption equilibrium is anticipated (SENES 1985, Byerley et al. 1987). Unlike uranium, radium-226 is not expected to form a pure solid phase. Rather, the coprecipitation of radium-226 sulfate with gypsum is modeled as a nonideal solid solution (SENES 1988). The sorption of dissolved radium-226 on solid surfaces is calculated simultaneously and compared with predictions from coprecipitation theory. The estimation of radium concentration also includes radioactive decay.

The **Solids Balance Module** evaluates the extent of secondary mineral formation and dissolution. Solid-liquid material balances are utilized with thermodynamic data to establish the concentrations of aluminum hydroxide, calcite, dolomite, ferric hydroxide, gypsum, jarosite, siderite, and metal sulfides in each layer.

The **Acidity Module** estimates the acidity of the seepage from the waste rock pile. Acidity of an aqueous solution may be defined as the capacity to accept hydroxyl (OH^-) ions in a basic titration from an ambient pH to pH of 8.5. In the simulated pore water, the dissolved complexes of iron, aluminum, copper, and zinc are the principal OH^--accepting species. The acidity can be conveniently expressed as the difference in equivalents between nonaccepting anions and cations (Stumm 1992):

$$Acidity = [Cl^-] + 2[SO_4^{2-}] + [NO_3^-] - [Na^+] - [K^+]$$
$$- 2[Ca^{2+}] - 2[Mg^{2+}]$$

(7)

The total acid production for the entire waste rock pile is calculated from the acid production flux in the bottom layer which is assumed to exit as seepage flow. The total acidity is evaluated as a "running average" annual acidity, expressed as kilograms $CaCO_3$ equivalent acidity per annum.

Model Development and Calibration

In a previous application (Knapp et al. 1992, SENES 1991b), the model was adapted to simulate the continuous deposition of fresh waste rock onto existing waste rock piles at a silver mine in British Columbia, Canada.

The model was used to evaluate several possible cover scenarios: compacted clay, semicompacted clay, noncompacted clay, and pervious till. The various covers were characterized in the model by specifying (1) corresponding infiltration rates and (2) the apparent oxygen diffusion coefficients (determined experimentally at University of Waterloo by Chao et al. 1991). Figure 3A shows the agreement between model predictions and field data. Figure 3B illustrates the benefits achieved through use of the various cover types.
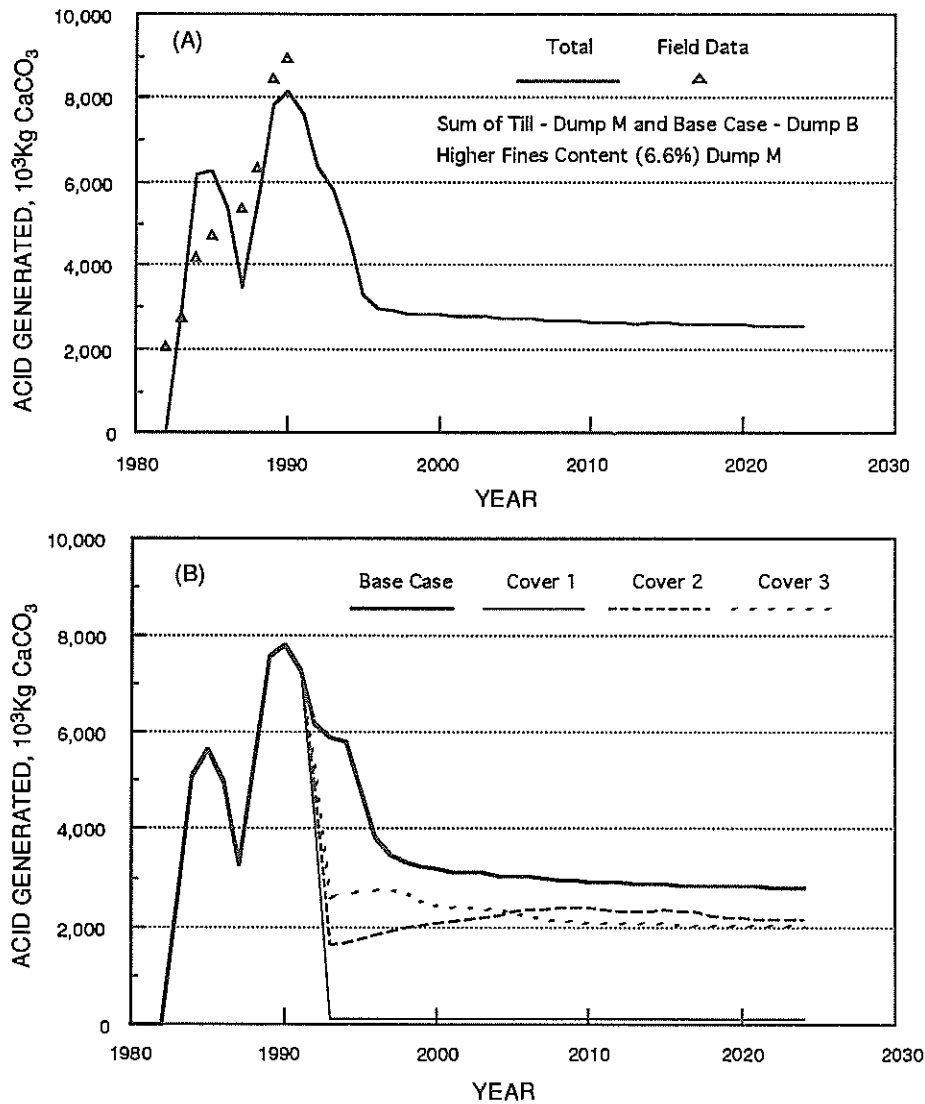
Figure 3. Acid generated, (A) and comparison of cover effectiveness (B)
at dumps M and B, British Columbia, Canada.

For the most recent application, the model was adapted to simulate the simultaneous construction and leaching of a waste rock pile at a uranium mine in Thüringia, Germany. Simulating the entire history of the waste rock pile allowed for better characterization of the current conditions which improved the confidence level for long-term predictions of seepage quality. Leaching of the waste rock pile was simulated by specifying the aqueous concentrations of the chemical species present in the infiltration flow to correspond with the assumed quality of the leach solution. The infiltration flow was then reassigned to simulate natural precipitation, as the waste rock pile currently receives infiltration from natural precipitation only. The apparent oxygen diffusion coefficient was also reassigned to correctly simulate different oxygen conditions during active leaching, following reprofiling activities which result in compacted surface layers, and the future placement of a cover.

Calibration entails "tuning" the model to simulate the behavior of the waste rock pile over the period of time for which operating data are available. The usual calibration data includes measured temperature and oxygen profiles, recorded flow measurements, pH and chemical analyses of seepage reporting to the collection ditches. Certain key parameters and scaling factors are assumed to be distributed and are systematically sampled until reasonable agreement between predictions and current field data is obtained. Some of the modeling parameters are based on "best estimates" derived by previous calibration of several tailings sites (SENES 1985, 1991a, Scharer et al. 1992) and waste rock heaps (SENES 1991b). Numerical estimates of rate constants are usually based on laboratory and field experiments performed at different temperatures, pH's, and with bacteria (SENES 1985). In the current case, the primary calibration data were seepage data for pH, sulfate, iron, and uranium. The simulated calibration curves show good agreement with the available field data (fig. 4).
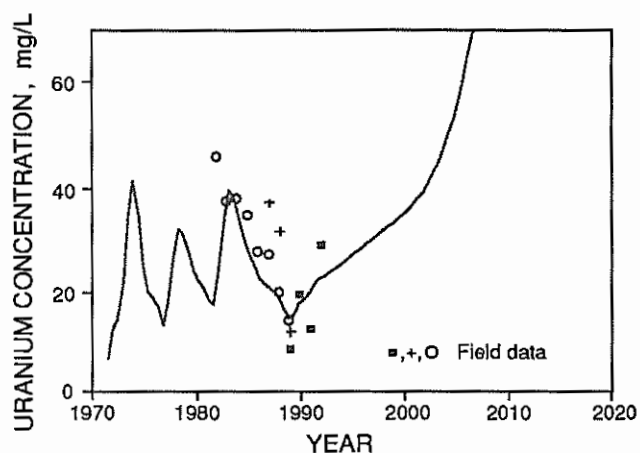

Figure 4. Calibration: predicted uranium for heap leach outflow.

Results of Modeling Scenarios

The simulation of the base case scenario (no remedial measures) shows the current pH of 2 to 3 will be maintained for next 100 years due to the buffering provided by secondary minerals (e.g., jarosite and iron hydroxide). Around 2100, the pH rises quickly to neutral, as jarosite and iron hydroxide have been depleted; the profiles of sulfate and iron also decrease to lower long-term values around 2100. Acidity calculations begin at the cessation of technical leaching, and the acidity shows a gradual overall decline until neutral pH conditions are achieved around 2100.

The broad uranium peak around 2025 (fig. 5) is due to continued release of uranium through oxidation of pyrite and dissolution of uranium-bearing secondary minerals while the flow through the heap is greatly reduced. The uranium predictions are also shown as a loading (kilograms/year) to take into account the difference in seepage rates during and after the active leaching phase (fig. 6); the broad uranium peak is actually much less in terms of uranium load than uranium removed during active leaching. The simulation shows that there may be considerable uranium remaining which has been made more susceptible to oxidative dissolution through the leaching activity; this uranium would be expected to be released from the waste heap in the future.

The radium profile (fig. 7) shows three plateaus which indicate radium levels are being controlled by a solid phase (e.g., adsorption onto a secondary mineral and/or coprecipitation with gypsum). Radium is quickly mobilized as these solid phases dissolve. The first plateau of 6 Bq/L is due to adsorption of radium onto gypsum. The second plateau is due to adsorption onto iron hydroxide. While the third long-term plateau of 8 Bq/L is controlled by adsorption onto the organic carbon. Only a small fraction of the total radium is leached from the heap.

The simulation of the various decommissioning alternatives (reprofiling plus cover) showed that there was very little observed difference between these decommissioning alternatives. The major effect was due to the installation of a cover in each case, as the cover greatly reduces the infiltration of water and transport of oxygen. A long-term pH plateau of 5 is predicted, although high sulfate levels will be maintained over the long term (fig. 8). Presumably this results from the buffering provided by dissolution of mica (sericite), which gives rise to dissolved potassium and

aluminum sulfates. The uranium peak is one third of that for the uncovered scenario and occurs 200 years later. The predicted radium levels are not significantly reduced.
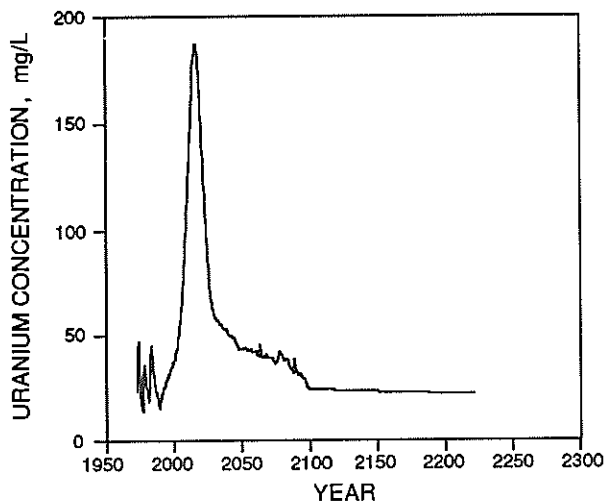
Figure 5. Base case scenario: predicted uranium for heap leach outflow.
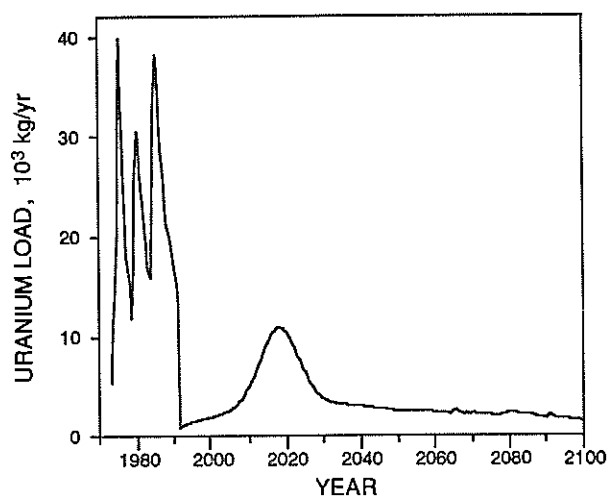
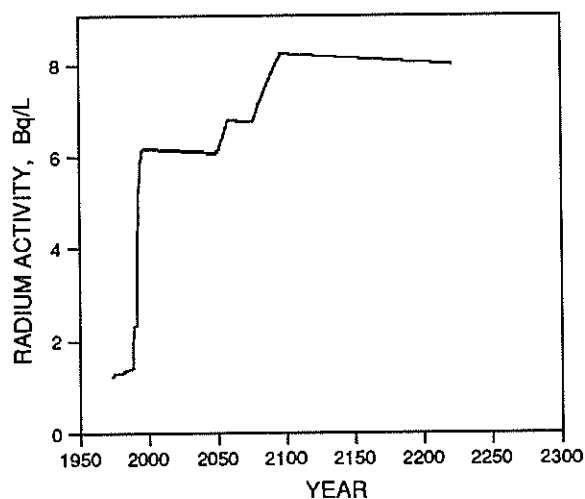Figure 6. Base case scenario: predicted uranium load for heap leach outflow.

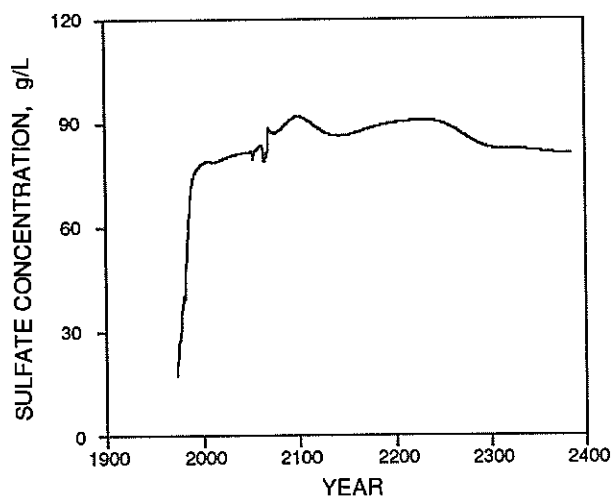Figure 7. Base case scenario: predicted radium for heap leach outflow.

Figure 8. Cover scenario A: predicted sulfate for heap leach outflow.

The cover reduces the loadings; however, long-term treatment of the seepage will still be necessary. Sludge production is a major concern with long-term treatment and will vary depending upon the efficiency of the solids removal process and the chemical addition rate. Experience has shown these levels may range from 1 to 3 metric tons (mt) sludge per mt of acidity. The simulation of the base case (no remedial measures) predicts large lime demands; upwards of 500,000 mt of lime are required to treat 366,000 mt of acidity released over the next 100 years. By 2100, sulfides are depleted; however levels of uranium, iron and radium-226 are still elevated and treatment for these elements will be needed well into the future. The predicted cumulative sludge volume for the base-case scenario (no cover) is shown in figure 9 and the covered case is shown in figure 10. With cover application, the rates of acid release are predicted to decline dramatically due to greatly reduced flows. For the next 400 years, this acid production is approximately 16% of the acid produced in the uncovered case over a much shorter period (i.e. 100 years). However, contaminants are still elevated in 2400 and will continue to require treatment. Due to the much lower seepage flow, less than 100,000 mt of lime would be required over the next 400 years.
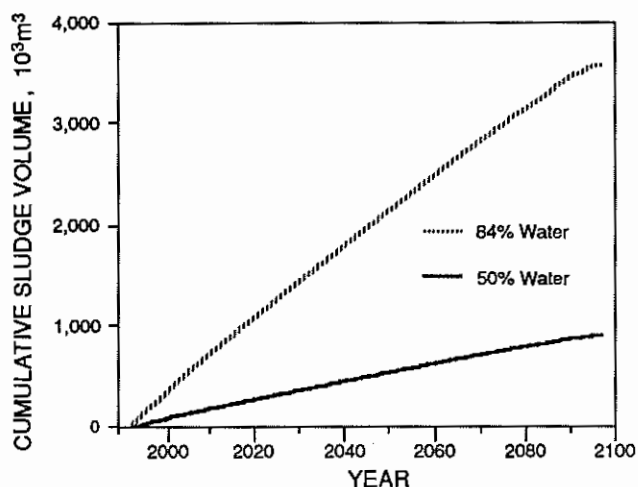
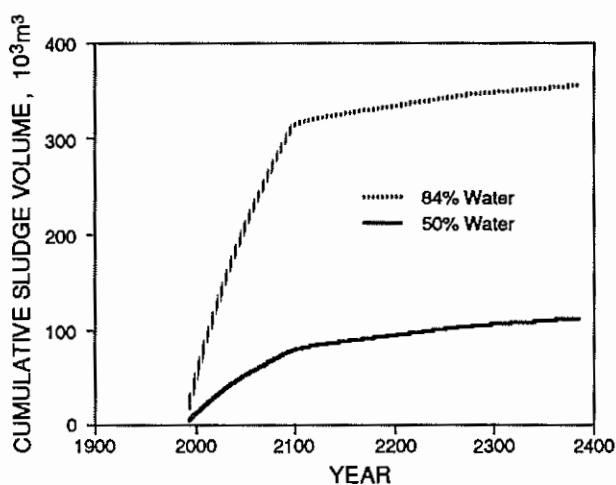Figure 9. Base case scenario: predicted cumulative sludge volume.

Figure 10. Cover scenario A: predicted cumulative sludge volume.

Conclusions

1) A model has been developed to simulate the placement and leaching history of a waste rock pile.
2) The model confirms that the existing waste rock pile will generate contaminated leachate requiring treatment for acidity and radioactivity for long periods of time.
3) Cover installation provides a significant reduction of potential contaminant burdens.
4) The cover would require care and maintenance into perpetuity, and chemical treatment would be required for a long time (beyond 100 years).
5) Treatment requirements for the uncovered pile would result in the generation of significant sludge volumes requiring future storage. Covering the waste pile would reduce this storage requirement.

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