

Integration of Field Data and a Geochemical Transport Model to Assess Mitigation Strategies for an Acid-Generating Mine Rock Pile at a Uranium Mine

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Abstract

Mine rock at a uranium mine in northern Saskatchewan, Canada, was evaluated for mine closure planning. The rock pile contains 7 million tonnes of reactive material. The pile was sampled by excavating trenches with a backhoe to depths of 15 m. Samples were processed to quantify chemicals of concern (including nickel, sulphur and uranium) in both the solid and water-soluble forms. The mass of water-soluble constituents ranged from 17% (for nickel) to 29% (for uranium) of the total mass initially available in the solids. The soluble inventory was interpreted to represent the oxidative reaction products that were generated in the more than 15 years of storage within the pile. Kinetic reaction terms for oxidative leaching were calculated for the chemicals of concern and were used to develop kinetic modules in the PHREEQC chemical equilibrium code that also incorporates mass transport. The kinetic terms were assessed to show that oxidation rates were not transport-controlled in the pile. The model was run in the kinetic mode and the output provided loading rates for the chemicals of concern at the base of the pile. Model simulations were also conducted to evaluate the effectiveness of constructed cover options for closure. This approach can be applied when oxygen transport is not rate limiting and can provide a simpler alternative to complex kinetic and transport codes that may not have had the critical review that public domain codes are generally subjected to. In general, most mine rock piles where modelling is required for environmental assessment will be in the class of "not oxygen transport limited".

INTRODUCTION

Prediction of water quality effects in the downstream receiving environment from mine rock drainage is an integral part of waste management and mine closure planning. Prediction techniques cover a wide range of methods and approaches that include simple scale-up calculations based on laboratory kinetic test results to complex models involving water, gas, mass and heat transport coupled with chemical reactions.

The objective of this investigation was to develop a model to assess the potential environmental impact of a rock stockpile. The stockpile under investigation originated from a uranium operation and the key chemicals of concern included, nickel, uranium and acid. A field investigation was conducted to assess the current status of acidification and metal leaching in the stockpile and to provide data that could be used to develop a geochemical and mass transport model. In this case, the basis of the

waste rock model was a public domain code (PHREEQC, Parkhurst and Appelo, 1999) that is a standard in geochemical practice.

COMPONENTS OF A KINETIC-BASED MODEL

A kinetic-based model for the geochemical evaluation of mine rock should include three main concepts. The first concept involves the identification and quantification of rates for oxidation, neutralization and metal release reactions. The second concept involves equilibrium controls for key geochemical processes that occur in the pile, such as neutralization and sorption reactions, gypsum precipitation/dissolution (for Ca and SO₄ concentrations) and iron precipitation/dissolution (for Fe concentration and pH). This also includes an assessment of pH values that result from acid production (oxidation) and neutralization reactions. The third concept involves the mass balance, flow of infiltrating water and transport of dissolved constituents vertically downward in the pile. These concepts

were combined to produce an overall model for the source term in the rock stockpile. The geochemical model program PHREEQC (Parkhurst and Appelo, 1999) was used to simulate chemical reactions and one-dimensional transport through the pile. PHREEQC calculates chemical equilibrium and allows simultaneous calculation of kinetic reactions such as sulphide oxidation, mineral dissolution and metal release. The chemical calculations can be conducted in “cells” that act as mixed reactors for which the solids or mineral characteristics can be defined. The model also considers flow and transport of dissolved constituents between cells so that the rock stockpile can be modelled in one-dimension as a series of cells in which the key reactions and flow rates can be defined.

Kinetic Controls

Geochemical models that describe the oxidation process in rock piles should include the mechanisms for rate controls. The model should also consider the oxygen uptake rates or sulphide mineral reaction rates for the calculation of overall production of oxidation products in the rock pile. In rock stockpiles, the rates of oxidation can vary significantly.

Fast Kinetics

When the sulphide content of the solids material is high, there can be a large oxygen demand and oxidation rates can be very high. These high rates can induce oxygen concentration gradients that can lead to diffusion control through the pore spaces and in some, more extreme cases, if the reaction rates are high enough, can cause heating and gas convection to occur.

Complex models are required to provide a basis to investigate complex interrelationships in rock piles that generate heat and in which air-flow is induced during sulphide mineral oxidation. In these cases, however, there is little doubt that rapid rates of reaction exist and water quality will be problematic, and the need for modelling is generally outweighed by the need for remedial action.

Slow Kinetics

If the sulphide content is low and, consequently, the oxygen demand is low, diffusion through the pile can be rapid enough to maintain oxygenated

conditions throughout the pile. In this case, the rates of reaction will not be limited by oxygen diffusion or transport through the pore spaces but only by the kinetics of the oxidation reaction on the rock particles.

This class of rock can be difficult to assess because there may be a significant time lag between rock placement and the onset of metal leaching or the decrease in pH associated with acidic drainage.

Selecting an Appropriate Kinetic Model

One of the key factors of applying a kinetic model is determining the rate limiting step in oxidation reactions. This question needs to be addressed in the context of best estimates of the release rates and transport in water moving through the rock pile and the near-field environment.

Ritchie (1994) provided a means to determine if oxidation rates are controlled by oxygen transport or by the intrinsic oxidation rate (IOR). His results show that oxidation within a rock pile will not be oxygen transport controlled if a characteristic diffusion length is not exceeded. The characteristic diffusion length, L_c , is given by:

$$L_c = (2DC_0/S^*_o)^{1/2}$$

where: D = diffusion coefficient for O_2 (m^2/s)

C_0 = O_2 concentration in air (kg/m^3)

S^*_o = max. IOR ($kg-O_2/(m^3s)$)

If L_c is greater than the height of the pile then oxygen transport is not likely to be limiting and oxygen can be replaced in the pile at a faster rate than it is consumed. In this case, the oxidation rate for the overall pile can be calculated from the intrinsic oxidation rate directly. In order to avoid the use of gas diffusion controls in the waste rock model, L_c must be greater than the height of the pile being evaluated.

Determining the Kinetics of Reactions

The reaction rate for the oxidation of sulphide minerals can be determined in several ways. When a historical stockpile is being evaluated, there will be valuable information contained within the pile, and appropriate sampling can provide results that can be utilized to establish key kinetic relationships for model development. For example, the mass of soluble sulphate produced over the history of the pile can be

quantified. If a first-order reaction is assumed, in which the rate is proportional to the sulphide content in the solid phase, the rate constant can be determined. The rate constant (k) can be calculated by estimating the original mass of sulphide present (M_0), the existing mass of sulphide (M) and the elapsed time for the reaction. The decay equation:

$$M = M_0 \exp(-kt)$$

can be used and the rate constant derived. The rates of metal leaching can be treated in a similar way to that of sulphide oxidation. Neutralization reactions may also be kinetically controlled. In waste rock that has developed acidic conditions, the rate of neutralization can be proportional to the rate of sulphide oxidation (or acid generation).

For neutralization reactions, a surrogate solid, (e.g. $Ca_xMg_{1-x}CO_3$), can be used to represent all neutralization reactions and the rate of dissolution calculated from apparent steady-state cation release rates observed in kinetic tests (column or humidity cell studies) and sulphate release rates according to:

$$R_{\text{diss}}(CaMgCO_3) = R_{\text{ox}}(FeS_2) \times R(\text{cations})/R(SO_4)$$

where:

$R_{\text{diss}}(CaMgCO_3)$ = Ca Mg- CO_3 Dissolution Rate in the pile

$R_{\text{ox}}(FeS_2)$ = FeS_2 Oxidation Rate in the pile

$R(\text{cations})$ = cation release rate in kinetic tests

$R(SO_4)$ = SO_4 release rate in kinetic tests

Equilibrium Controls

In sulphide-bearing rock, there are several common equilibrium reactions that are likely to occur. These involve mineral precipitation and dissolution reactions involving gypsum and ferric oxyhydroxides, sorption reactions on iron oxides and others.

As a minimum, the following equilibrium reactions have been considered: gypsum equilibrium (initial mass in solids specified), $Fe(OH)_3$ (as Ferrihydrite) equilibrium, open system equilibrium with oxygen ($P_{O_2} = 0.21$), open system equilibrium with carbon dioxide ($P_{CO_2} = 0.01$ atm), and equilibrium sorption onto hydrous ferric oxide (HFO). In addition, precipitation of metal hydroxides can occur if the pH is sufficiently high.

Mass Transport

One-dimensional advection-dispersion can be incorporated into the model to simulate the transport of constituents through the pile to the ground water system below the pile. Although waste rock piles are typically unsaturated, flow and transport of infiltrating water can be assumed to occur through a “saturated” medium with porosity equivalent to the volumetric moisture content of the pile that is typically less than 10% by volume. Transport can then be coupled with chemical reactions to simulate the interaction between infiltrating water, reactions in the pile and constituent loadings reporting to the base of the pile. The conceptual scheme, used as the basis for PHREEQC modelling, is illustrated in Figure 1.

DATA REQUIREMENTS AND INTERPRETATION FOR MODEL APPLICATION

An historic stockpile of mine rock was investigated to evaluate closure plan options. Existing monitoring data suggested that drainage from the pile had resulted in elevated levels of sulphate, nickel and uranium and depressed pH in groundwater at the toe of the stockpile. A sampling program was designed and initiated to collect data that could be used to predict future loading rates for constituents of concern and to evaluate reclamation strategies.

The stockpile of mine rock originated from a uranium operation. The pile contained about 7 million tonnes over an area of about 26 ha and with an average height of about 16 m.

A sampling program of the rock stockpile was conducted and rock samples were collected from selected locations in depth profiles for solids geochemistry, rinse water dissolved solids, and material for column and humidity cell tests (CRI, 2001). The data were interpreted in terms of the inventories of the total reactive constituents in the solids, stored inventories of soluble oxidation products and the remaining inventories of potentially leachable constituents of concern in the solid phase.

Solids chemistry results showed relatively consistent values over the area of the pile and with depth for most constituents, and average values were considered to be representative of solids concentration in the pile for the

constituents of concern. The average concentrations of selected parameters are provided in Table 1.

TABLE 1: Solids concentration of selected parameters.

Constituent	Content (mg/kg)
S (%)	0.27
Ni	46
U	83

Solids samples were also submitted for SWEP analysis to determine the soluble mass of constituents in the pile. Average values (n=11) are provided as mass of soluble constituent per kg of rock (Table 2) and effectively represent the mass of soluble reaction products that have accumulated in the pile since the rock was deposited.

TABLE 2: Soluble masses from kinetic tests and SWEP analyses (mg/kg).

TEST	SO ₄ (as S)	Ni	U
SWEP TESTS			
Trench 1 (n=7)	585	7.4	8.1
Trench 3 (n=4)	355	1.4	6.5
<i>SWEP Tests Avg.</i>	501	5.2	7.5
KINETIC TESTS			
Column 1	587	14	35
Humidity Cell 1A	681	17	42
Humidity Cell 1B	691	12	29
Column 3	382	1.7	32
Humidity Cell 3	544	2.0	30
<i>Kinetic Tests Avg.</i>	577	9.3	34

The SWEP (Province of British Columbia, 1992) and kinetic test results indicate that gypsum dissolved in the tests and the observed sulphate load was used quantitatively as an indicator of sulphide oxidation history for the average 15-year age of the pile.

This provides an average oxidation rate over the 15-year period and rates would likely have been

higher at early times during the onset of oxidation. This oxidation rate, however, gives a reasonable value to assess the rate control mechanisms within the pile. Table 2 shows that the soluble sulphate produced from the waste rock over the 15-year period is about 577 mg/kg as "S". This is equivalent to 1.89 kg-O₂ /m³ (consumed to oxidize the sulphide to sulphate) over the 15-year period of oxidation and translates to an average intrinsic oxidation rate (IOR) of 4 x 10⁻⁹ kg-O₂ /(m³s). The characteristic diffusion length therefore varies between 17 and 27 m for the 15-year average oxidation rate. This suggests that the Claude pile, that has an average depth of 16 m, has an oxidation rate close to a value that will allow oxygen to diffuse into the pile to depths of 17 to 27 m without causing oxygen gradients to occur and without limiting oxidation rates by oxygen transport into the pile.

The soluble load of selected metals to the pore water in the rock was estimated from dissolved or soluble mass in the column and humidity cell leachate data and the initial quantities of the constituents of concern were also estimated. These initial masses were used with the current known masses in the solids to estimate the rate constants for each of the constituents. Simple first order reaction kinetics were assumed for the Basecase, and the kinetic relationships were defined in the kinetic subroutines in the PHREEQC model.

A summary of the concentrations of constituents of concern in the solid phase and as soluble mass is presented in Table 3. These values were used to estimate the initial concentrations in the solid phase prior to reactions in the waste rock pile. The percentages of soluble or reacted mass in relation to the original values shows that between 4 and 29% of the available mass has reacted over the 15-year period. The uranium was the most reactive and nickel was the least reactive of the selected constituents. On average, the data suggest that about 20% of the original mass of these constituents has leached to date or that 80% remains as potentially leachable material. The calculated rate constants and the equivalent half-lives of the leaching (or

oxidation) reactions are shown for selected constituents in Table 4.

Leaching and oxidation rates provide for the release of acidity and selected constituents over time. The kinetic release rates of U and Ni were also used in individual subroutines in PHREEQC. These metals were represented as “dummy” solids UO_2 and $NiCl_2$ in the model and the calculation of the release rates followed those discussed in a previous section.

Table 4: Kinetic parameters used for Basecase scenario

Constituent	Rate Constant (1/s)	$t_{1/2}$ (yr)
U	7.2×10^{-10}	30
Ni	3.9×10^{-10}	60
S	4.4×10^{-10}	50

MODEL APPLICATION

Three scenarios were modelled. These included a Basecase to represent current and ongoing conditions in the pile with no remediation and two scenarios involving soil covers.

The Basecase scenario was developed using the observed conditions in the pile. The initial pore water concentrations were assumed to equal the soluble constituent concentrations derived from the kinetic test results and the concentrations of solids that can dissolve kinetically over time were assumed to equal the solids concentrations observed in the pile at the time of sampling (1999). The initial pore water pH for the Basecase was adjusted to yield a value between 3.0 and 4.0 after equilibrium with solids and sorption sites to reflect the values that were observed for rinse pH in the field and those measured in leachate from the column and humidity cell tests.

The time step used for PHREEQC calculations was calculated from infiltration rates and the measured resident pore water volume or moisture content per cubic metre of waste rock. The average moisture content of the stockpile was approximately 5% by weight or approximately 8.75% by volume (assuming a bulk density of $1,750 \text{ kg m}^{-3}$). Therefore, the resident pore volume was 0.0875 m^3 per cubic

metre of waste rock, or 262 mm of equivalent infiltration per cell with a 3 m depth. It requires approximately two years to replace one resident pore volume based on an average infiltration rate of 127 mm/yr and this was the time step used for the Basecase. The time step is also required in the kinetic expressions so that the appropriate mass of solids react and the products get transferred to the solution phase during each time step.

Cover Scenarios and Assumptions

Two scenarios were considered for mitigation of the pile, both based on a two-layer cover incorporating reworked and compacted rock and local sand till. One cover scenario represented a 1 m layer of till overlying a 0.2 m layer of compacted waste rock. The other scenario consisted of a 1 m layer of till over a 0.3 m layer of compacted waste rock. The covers reduce both the diffusion of oxygen into the pile (affecting oxidation and metal release rates) and infiltration rates. Adjusting the time step in the model simulated the lower infiltration rates and the reaction rates for solids were adjusted to reflect lower diffusion rates of oxygen into the pile.

The decrease in oxygen flux through the covers is lower than the unhindered flux through the waste rock and acts to control the ingress of oxygen and the overall oxidation rate in the pile. This oxygen restriction will affect rates of sulphide oxidation and metal leaching (that is an oxidative process). In contrast to the Basecase, leaching or reaction rates were assumed to be constant with time (or zero-order) for the cover scenarios. A constant rate was assumed because the oxygen flux, that drives the oxidative dissolution reactions as well as the oxidation of sulphides, is constrained by the covers. The rate of sulphide oxidation was assumed to be controlled by the oxygen flux through the covers, and therefore the IOR was adjusted to agree with the flux value for each cover that limits the global rates of oxidation. The metal leaching rates were assumed to be linearly related to the oxygen flux. By using a constant rate, adjusted for the decrease in oxygen flux relative to the Basecase, it was assumed that the leaching and oxidation reactions occur as fast as

oxygen is allowed into the waste through the cover. The reaction rates were estimated to be the initial rates at time zero for the Basecase divided by the flux reduction factor for each cover. The flux reduction factors are the ratios of the equivalent oxygen flux for Basecase conditions divided by the flux for each cover scenario. A summary of the flux values and reduction factors are presented in Table 5.

Table 5: Summary of cover oxygen flux values and flux reduction factors

Scenario	Oxygen Flux kg-O ₂ /(m ² s)	Flux Reduction Factors for Covers
Base Case	7.3 x 10 ⁻⁸	-
20 cm Cover	3.5 x 10 ⁻⁹	21
30cm Cover	1.5 x 10 ⁻⁹	49

The restriction of oxygen flux through a cover also has an additional effect on the reaction progress over time. The smaller flux of oxygen through the cover allows oxidation in the topmost zone below the cover initially. As the sulphide or other metals become depleted, the oxygen can move downward to react with sulphide and/or metals that remain available at deeper locations in the pile. This concept is consistent with observations in diffusion-controlled systems and can be referred to as a moving reaction front. This process was simulated for the stockpile by specifying that oxidation or leaching reactions only occurred in the topmost layer or cell that contained residual (unleached) material. After the top cell becomes depleted, the reaction starts in the next cell, maintaining the constant reaction rate (and oxygen flux), until that cell becomes depleted, initiating the reaction in the next cell. In this way, the moving reaction front was simulated for the cells that comprised the rock pile.

RESULTS

Basecase Results

The results of interest from the modelling study are represented by the concentrations and loading rates from the base of the pile. The loading rates, were calculated from the predicted concentrations in the water flowing from the base of the pile and the total flow rate that was

estimated from the rate of infiltration and the total area of the rock pile.

The loading rates for selected constituents of interest at the base of the stockpile were evaluated. These loadings consist of two components. One component results from the existing soluble mass that occurs as dissolved constituents in the pore water in the pile. The second component of loadings is represented by the new mass that is released from the solids over time as a result of ongoing oxidation and metal leaching. The loading rates for the Basecase are presented in Figure 2, showing the releases of the soluble mass alone and the total mass for sulphate uranium and nickel.

The chemistry of the exiting pore water is characterized by low pH (trending from 3.1 to 4.3) and sulphate loadings that peak at almost 550 tonnes/yr before declining. The uranium and nickel loadings peak near values of 20 and 11 tonnes/yr, respectively, before declining. Peak loadings were calculated to occur between 15 and 25 years after the start of the simulation. The Basecase (no cover) results reflect trends in concentrations such as low initial values, peak values within tens of years and rapid declines to near zero values within 200 years for Ni. All constituents became depleted from the solids within a few hundred years. The small differences in behaviour for sulphate resulted from reactions involving gypsum.

Cover Scenarios

The results of the cover simulations differ from those of the Basecase, with much lower peak concentrations of all constituents of interest. The loading rates as a function of time are shown in Figure 3. The sulphate loadings were of the order of 80 tonnes/yr for the 20 cm cover and about one-half of that value (40 tonnes/yr) for the 30 cm cover. Peak uranium loadings remained high for both covers, nearing 10 and 13 tonnes/yr from the 30 cm and 20 cm scenarios, respectively. Peak concentrations for nickel in both cover scenarios were similar with values of about 3 tonnes/yr or one quarter of the peak from the Basecase.

These results show that the mass loadings for the cover scenarios were similar and both covers

exhibited significant decreases in loadings compared to the Basecase. The covers effectively reduced the peak loadings of all constituents of concern by factors of between two (U) and ten (SO₄). The 30 cm cover exhibited slightly better performance (greater reductions in peak values) compared to the 20 cm cover but the differences between covers is small compared to the incremental benefit of either cover compared to the Basecase.

SUMMARY AND CONCLUSIONS

Geochemical characterization of the historic uranium mine rock showed that the masses of constituents of concern are partitioned into soluble and solid components. Release rates were estimated from field and laboratory data, including chemical characterization of pore water and solids, and kinetic tests that were conducted for about 35 weeks. The geochemical speciation model PHREEQC was applied to predict the release of key chemical constituents from the rock to drainage over time with vertical transport of leachate to the watertable. The PHREEQC model could be applied to prediction of sulphide oxidation in the rock stockpile because the oxidation rate was demonstrated to be kinetically-controlled and not dependent on gas diffusion in the stockpile.

The acquisition of data that quantified the soluble (or released) chemicals of concern together with the inventory of those chemicals

remaining in the rock provided a sound basis to develop a predictive model. The data were critical to estimate primary reaction rates associated with sulphide oxidation and secondary rates associated with neutralization. The appropriate application of the model to rehabilitation strategies allowed a quantitative comparison to evaluate future loadings of chemicals of concern to the receiving environment.

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- Province of British Columbia (1992), *Waste Management Act: Special Waste Regulation Schedule 4, Parts 1 and 2*, Queen's Printer, Victoria, BC, p72-79.

Table 3: Summary of solids and soluble mass content (mg/kg).

Constituent	Solid Mass (1999)	Soluble Mass (1999) ⁽¹⁾	Estimated Original Mass in Solids (1985) ⁽²⁾	Percent Reacted
U	83	34	117	29
Ni	46	9.3	55	17
S	2,522	577	3,099	19

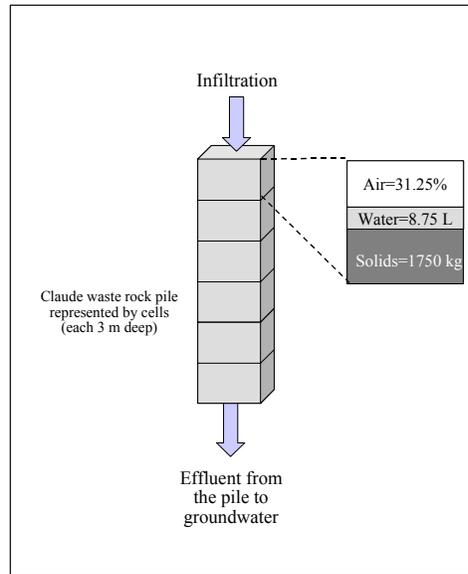


Figure 1: Conceptual model of waste rock stockpile.

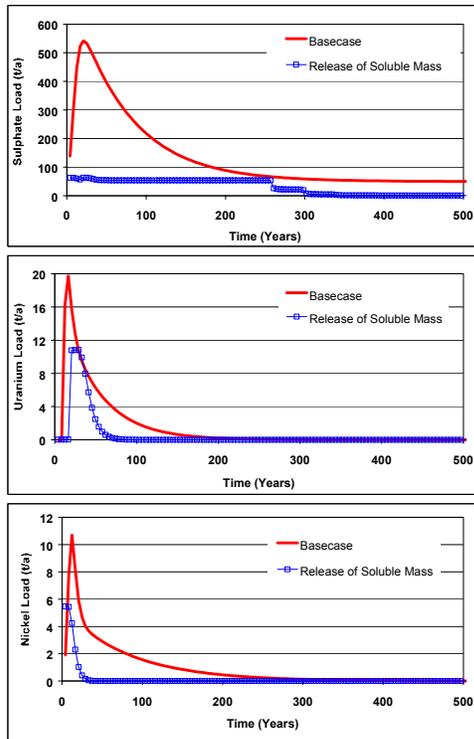


Figure 2: Annual mass loadings for the Basecase scenario and for the release of soluble mass only.

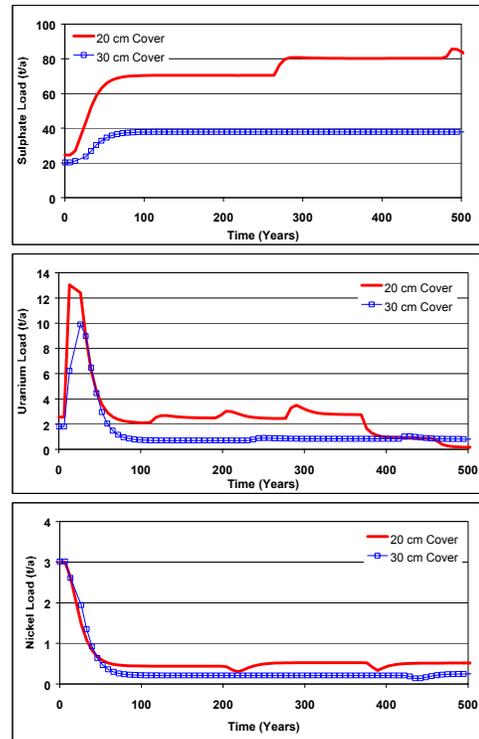


Figure 3: Annual mass loadings for the 20cm and 30cm cover scenarios.