ANALYSIS OF THE DISSOLUTION OF SILICA NEAR HLW REPOSITORIES

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Introduction

Silica is a common mineral in most repository rocks. Its presence in rocks of the type found near the sites of several of the proposed HLW repositories have led to concerns that there might be a significant change in porosity caused by the dissolution of silica in the flowing groundwater. A numerical experiment was devised which would test this hypothesis for typical to conservative conditions expected near HLW repositories. This report describes the numerical experiment and its results, and the impact of the results on the definition of the Disturbed Zone. The techniques describes might be useful for dissolution of other types of minerals, but each case should be considered carefully.

Description of the Heat Transfer Model

The heat transfer model has been taken from Ref 1. The repository is assumed to be a thin rectangular plate parallel to the surface of the earth as shown in Fig. 1. Heat transfer is considered to be totally by conduction with constant thermal conductivity and heat capacity. Heat is being generated by 10 year old spent fuel, uniformly distributed across the area of the repository. Coefficients of the heat transfer model are given in Table 1.

Table 1 - Parameters of Repository Model

Repository length = 1600 m

Repository width = 1200 m

Depth of repository below earth's surface = 1200 m

Coefficient of Heat Transfer = 7.25×10^7 joules/(m yr °c)

Heat capacity of rock = 2.77×10^6 joules(m^3°c)

Initial Heat load = 4.41×10^8 joules /(m^2 yr)

Groundwater flux = 1 meter/year

Ambient Temperature = 30° C, 50°C

Density of Rock = 2.2 gm/cc

Transport Model

Groundwater is assumed to be moving in a straight line through a thin stream tube at a flux U meters/years, as shown in Fig. 1. The stream tube is aligned in one of two ways:

1. Parallel to the x axis (horizontal) passing through the point $y = 0$, $z = z_1$, or

2. Parallel to the z axis (vertical), passing through the point $x = 0$, $y = 0$.

Temperature along the stream tube is a function of time determined by the heat transfer model.

Mass Transfer Model

A mass balance on the segment of the stream tube of cross section A , as shown in Fig. 2, from x to x + Δx is used to develop the relationship for the dissolution of silica:

Mass of silica entering at $x = U\ A\ C_x\ \Delta t$ (1)

Mass of silica leaving at $x + \Delta x = U\ A\ C_{x+\Delta x}\ \Delta t$ (2)

Change in mass of solid silica in time $\Delta t = \Delta M$ (3)

The change in porosity is taken as the change in the silica mass ΔM divided by the original silica mass in the segment, M_0:

$$M_0 = A \rho \Delta x \tag{4}$$

where ρ is the density of the silica

The change of porosity at a point is therefore:

$$\Delta M/M_0 = \int_0^t (U/\rho)\ (\partial C/\partial x)\ dt \tag{5}$$

The equilibrium concentration of silica in water can be described by an empirical relationship (Ref. 2):

$$K = 10^{(a + b\ T + c/T)}\ \text{moles/liter} \tag{6}$$

where T is the absolute temperature degrees Kelvin, and a, b, and c are constants which depend on the crystalline form. Coefficients are given in Table 2 for several phases of silica.

Table 2 - Coefficients in Solubility Equation for Four Silica Phases

Phase	a	b	c	K at 100°C	$\partial K/\partial T$ at 100°C
Quartz	1.881	2.028×10^{-3}	-1560	8.75×10^{-4}	1.85×10^{-5}
Alpha-Cristobalite	-.0321	0	-988.2	2.08×10^{-3}	3.41×10^{-5}
Beta-Cristobalite	-.2560	0	-793.6	4.13×10^{-3}	5.43×10^{-5}
Amorphous	.3380	-7.889×10^{-4}	-840.1	6.19×10^{-3}	7.48×10^{-5}

Method of Solution

The heat transfer model was run to develop temperatures at points along the stream tube from times of 1 to 10,000 years. Time was calculated on a logarithmic scale $\tau = \ln t$, in order to take the conditions over a wide range of time into account. The temperature gradient is expressed by the first order difference between two points. Equation (5) in solved for $\Delta M/M_0$ in time at points midway between the temperature points using the trapazoidal rule:

$$(\Delta M/M_0)^{\tau+\Delta\tau}_{i+\frac{1}{2}} = (\Delta M/M_0)^{\tau}_{i+\frac{1}{2}} + (U\Delta\tau/2\Delta x\rho)\ (f_{i+\frac{1}{2}}(\tau) + f_{i+\frac{1}{2}}(\tau+\Delta\tau)) \qquad (7)$$

where $f_{i+\frac{1}{2}}(\tau) = (C_{x_{i+1}}(\tau) - C_{x_i}(\tau))\ e^{\tau}$,

$\tau = \ln t$

The concentration C is assumed to be determined by the equilibrium coefficient:

$$C_x(\tau) = K\ (T(x\ ,\ \tau)) \times 0.06009, \qquad (8)$$

where the constant 0.06009 is a conversion factor from moles/liter to gm/ml.

Model Results

The model was run for the horizontal and vertical stream tubes using a flux of 1 meter per year and a time limit of 10,000 years. The ambient temperature was taken to be 30°C and 50°C. The amorphous silica phase was used as the base mineral because it is the most soluble form. Results of these runs are shown in Figs. 3 and 4. In the horizontal stream tube case shown in Fig. 3, the maximum occurs close to the upstream edge of the repository. The peak values of $\Delta M/M_0$ are approximately 0.0006 and 0.0007 for T_o = 30°C and 50°C respectively.

No silica would dissolve downstream of the repository center, $x = 0$. Because of symmetry and the assumption of equilibrium. The model would predict precipitation of an equal amount of silica dissolved downstream from the repository centerline.

In the vertical stream tube case shown in Fig. 4, the maximum $\Delta M/M_0$ for $U = 1$ meter/year occurs at the intersection with the repository plane, and is about 0.0005 and 0.0006 for the cases of T_0 = 30°C and 50°C respectively. The vertical stream tube differs slightly from the horizontal case because the fluxes may be upward or downward, and the temperature is not symmetrical around the plane $z = z_1$, because of the geothermal gradient.

An increase in ambient temperature of 20°C caused only about a 20% increase in maximum dissolution, however, so the geothermal gradient, which is on the order of 5°C per 1000 meters, would not affect the results significantly.

In both cases, dissolution is directly proportional to the groundwater flux. An increase in the flux to 10 meter/year (3.2×10^{-7} m/sec) would therefore increase the maximum $\Delta M/M_0$ to 0.007 and 0.006 for the horizontal and vertical stream tubes respectively.

Simplified Model

The results of the model presented above indicate that silica dissolution is greatest where the temperature gradient is steepest, which is at the interface between the repository and the surrounding rock. In addition, the peak dissolution calculated for the horizontal and vertical stream tubes were roughly equal, even though the repository was represented as a thin plate horizontal to the earth's surface. These observations lead to the development of a simpler model which can be used for quick estimates of the maximum dissolution. Consider the case of the vertical stream tube, with flow along the z axis. By applying the chain rule, the concentration gradient in Eq. 5 can be rewritten:

$$\partial C/\partial z = (\partial C/\partial T)\ (\partial T/\partial z) \tag{9}$$

Equation (5) becomes

$$\Delta M/M_0 = \int_0^t (U/\rho)\ (\partial C/\partial T)\ (\partial T/\partial z)\ dt \tag{10}$$

For an infinite horizontal plane source, Conductive heat flux away from the upper and lower surfaces of the repository is $2k\ \partial T/\partial z$, where k is the thermal conductivity. The model assumes chemical equilibrium, so $C = 0.06009\ K$ as stated by Eq. 8.

Therefore $$\partial C/\partial T = 0.06009\ \partial K/\partial T \tag{11}$$

If we assume that $\partial K/\partial T$ can be represented by an average value β in Eq. 8:

$$\beta(\bar{T}) = (\partial K/\partial T)_{\bar{T}} \tag{12}$$

and therefore taken outside of the integral, Eq. 10 becomes

$$\Delta M/M_0 = 0.06009\ U\ \beta(\bar{T})/(2\ \rho k) \int_0^t 2k\ \partial T/\partial z\ dt = 0.06009\ \beta(\bar{T})\ Q(t)/2\rho k \tag{13}$$

where Q(t) is the integrated heat load to time t per square meter of repository (top) area.

The coefficient β can be derived by differentiating Eq. 6, and is shown for in Fig. 5 for amorphous silica. Note that β changes by less than a factor of 2 between 300 and 373.1 °K, which is within the expected operating temperatures of planned HLW repositories. Taking outside of the integral would not therefore lead to a great error. The integrated heat load can be expressed as

$$Q(t) = Q_0 \, f(t) \tag{14}$$

where Q_0 is the initial surface heat load, joules/(m^2 yr) and $f(t) = \int_0^t Q/Q_0 \, dt$. The function f(t) is shown graphically in Fig. 6 for 10 year old spent fuel.

Equation 13 is conservative because it considers only the steepest temperature gradient. The thermal gradient is also maximized because heat transfer is considered in only one dimension which fails to take heat loss perpendicular to the z axis into account. A conservative value of β must be chosen, however. A suggested value of $\bar{T}$ which has been shown to give conservative results is

$$\bar{T} \, (°K) = (T_0 + 100)/2 + 273.1 \tag{15}$$

where T_0 is the ambient temperature at the repository level, °C.

This model should be applicable to horizontal flows as well, since the silica dissolution fractions predicted from the numerical models of the previous section gave roughly equal results for the vertical and horizontal cases.

Example

Consider the repository presented in the previous section (Table 1). Calculate $\Delta M/M_0$ at 1000, 10,000 years, for T = 30°C.

Solution

The representative temperature lies between ambient and boiling:

$$\bar{T} = (30°C + 100°C)/2 + 273.1 = 338.1°K$$

From Fig. 4, $\beta = 5.85\text{x}10^{-5}$ moles/liter °K

(a) for t = 1000 years, from Fig. 5, f(t) = 119, so:

$$\Delta M/M_0 = \frac{1.0 \times 5.85\text{x}10^{-5} \times 4.41\text{x}10^{8} \times 119 \times 0.06009}{2 \times 2.2 \times 7.25\text{x}10^{7}} = 5.8\text{x}10^{-4}$$

(b) for t = 10,000 years, f(t) = 275, so:

$$\Delta M/M_0 = 1.34\times10^{-3}$$

The result at 10,000 years is about double the dissolution predicted by the numerical model of the previous section. The largest discrepancy is probably caused by the conservative choice of $\overline{T}$. Figure 7 shows the time dependent temperature rise above ambient at the repository center predicted by the numerical temperature model, indicating that the average temperature is probably considerably less than 338.1 ° K. The approximate solution is reasonable considering its simplicity.

Significance of Silica Dissolution

Silica dissolution will increase the porosity and hydraulic conductivity of the rock, thereby increasing the groundwater flux through the affected region. For an equal value of $\Delta M/M_0$, rock with initially small porosity would be more greatly affected than rock with large initial porosity.

A reasonable estimation of the importance of silica dissolution can be made by considering the case a repository with the bare minimum specifications of a 100 year travel time and distance to the accessible environment of 2000 meters horizontally. Travel time t, distance L, porosity n and Flux U are related by the following equation:

$$U/n_0 = L/t = 2000 \text{ meters}/100 \text{ years} \qquad (16)$$

The change in the porosity relative to the initial porosity n_0 can be derived from Eq. 13:

$$\Delta n/n_0 = (\Delta M/M_0)/n_0 = (UQ_0\ f(t) \times 0.06009)/n_0\rho k \qquad (17)$$

Conservatively assuming the same conditions as in the previous example for 10,000 years,

$$\Delta n/n_0 = \frac{(2000 \times 5.85\mathrm{x}10^{-5} \times 4.41\mathrm{x}10^{8} \times 275 \times 0.06009)}{2 \times 2.2 \times 7.25\mathrm{x}10^{7}} = 0.027$$

The porosity for the present case therefore would change less than 3% over a 10,000 year period. If the common parallel-plate laminar flow model for groundwater movement is adopted (Ref. 3), the groundwater flux would be proportional to the pore width cubed, providing that the hydraulic gradient and other properties remain the same:

$$\Delta U/U = (1 - \Delta n/n_0)^3 - 1 \qquad (18)$$

The flux through the affected area would therefore increase by about 8 percent in the present example.

The above analysis is conservative for the following reasons:

1. Equilibrium between water and silica is assumed at all times, with no consideration given to the rates of dissolution, which could be limiting in some circumstances;
2. The most soluble form of silica was assumed;
3. A known conservative value of the solubility coefficient was used in the dissolution model;
4. The simplified model overestimates dissolution and considers only its highest value;
5. Minimum specifications on travel time and distance to the accessible environment were used to estimate the ratio U/n_0.

If the $\Delta M/M_0$ from the numerical model (Eq. 7) were used, along with a more reasonable 1000 year groundwater travel time, less than a 1/2% increase in flux would be predicted.

Conclusions

The importance of the dissolution of silica to the integrity of a repository was explored with several simple models. The models assumed conductive heat transfer only, and that groundwater was always saturated with silica at a concentration determined by an empirical function of temperature. Maximum dissolution ratio occurred where temperature gradients were greatest which was at the edges of the repository, and were directly proportional to the groundwater flux.

The importance of the silica dissolution was determined for a conservative case of a repository barely meeting the requirements of groundwater travel time and distance to the accessible environment. Conservative coefficients were used in a conservative, simplified model to predict that porosity would increase by less than 3% and groundwater flux by 8% over 10,000 years. More reasonable estimates of the coefficients indicate much smaller increases. It can be generally concluded from these results that increased porosity caused by silica dissolution is not a major consideration in the transport of groundwater or radionuclides near a HLW repository, and may therefore be neglected from consideration in defining the disturbed zone. This may not necessarily be the case for dissolution or phase change of other minerals, however. It will be necessary to perform an analysis for other types of minerals on a case-by-case basis. The techniques employed in this report may be useful for other minerals, especially if the change in $\Delta M/M_0$ is by dissolution or another process controlled by temperature gradient alone.

REFERENCES

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3. R. B. Bird, W. E. Stewart, E. N. Lightfoot, Transport Phenomena, John Wiley and Sons Inc., New York, 1960.

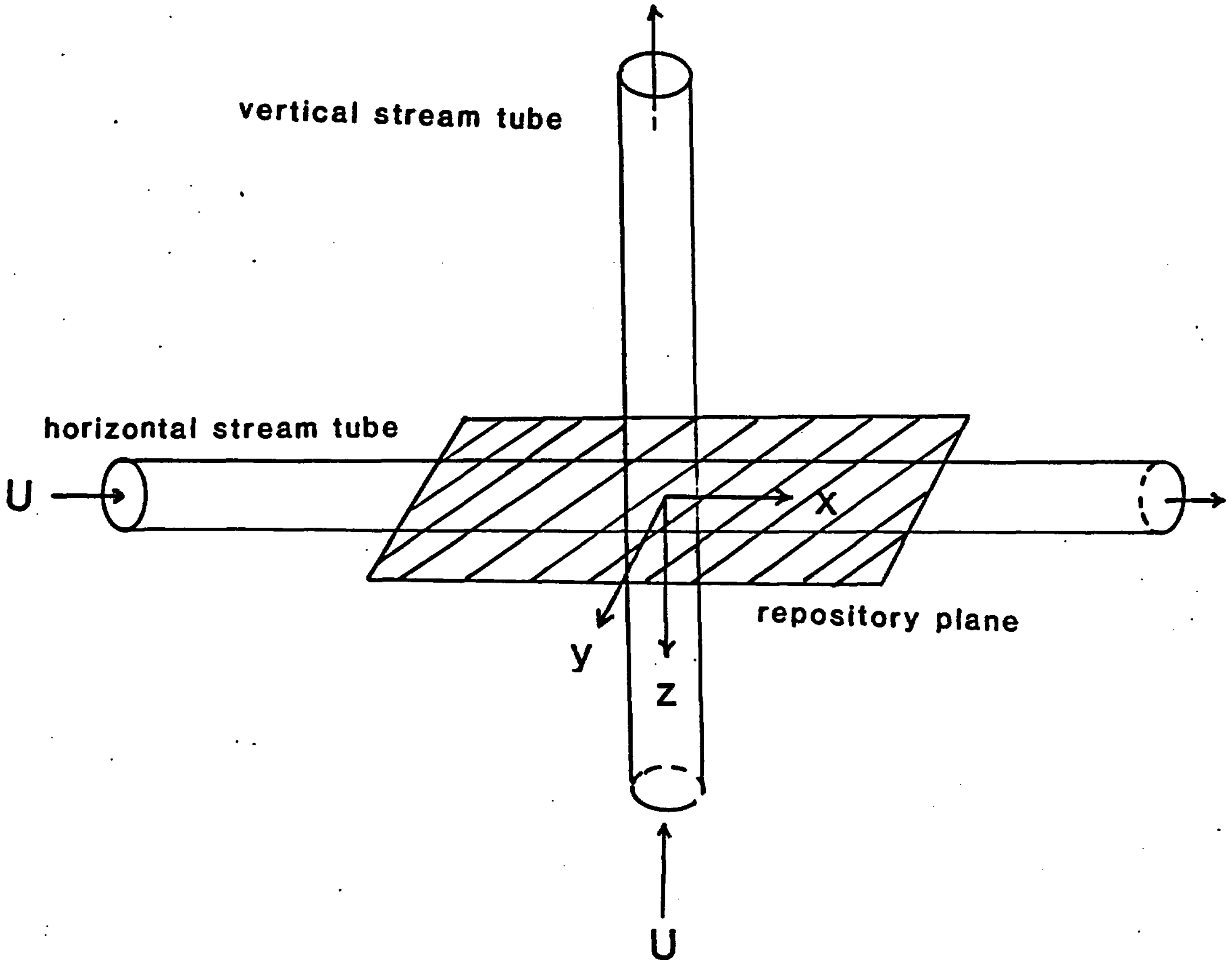

FIGURE 1 - REPOSITORY WITH VERTICAL AND HORIZONTAL STREAM TUBES

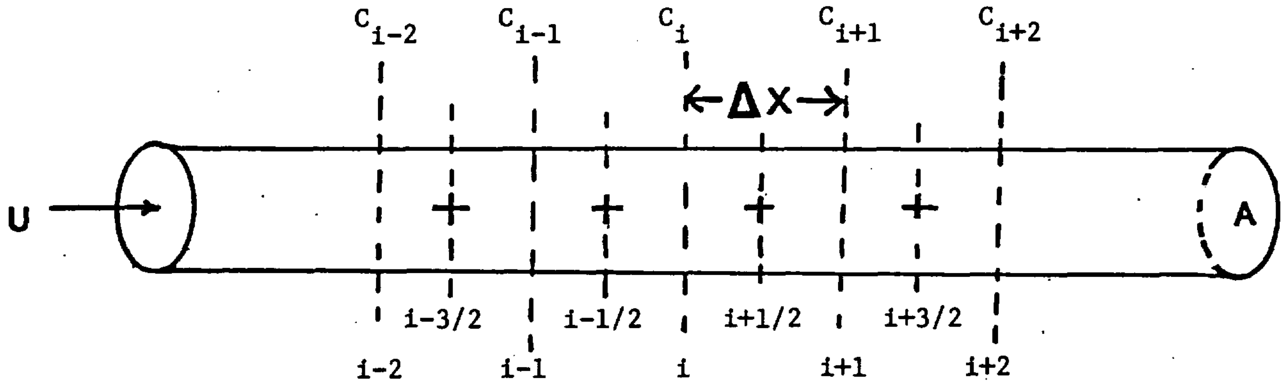

FIGURE 2 - STREAM TUBE TRANSPORT MODEL

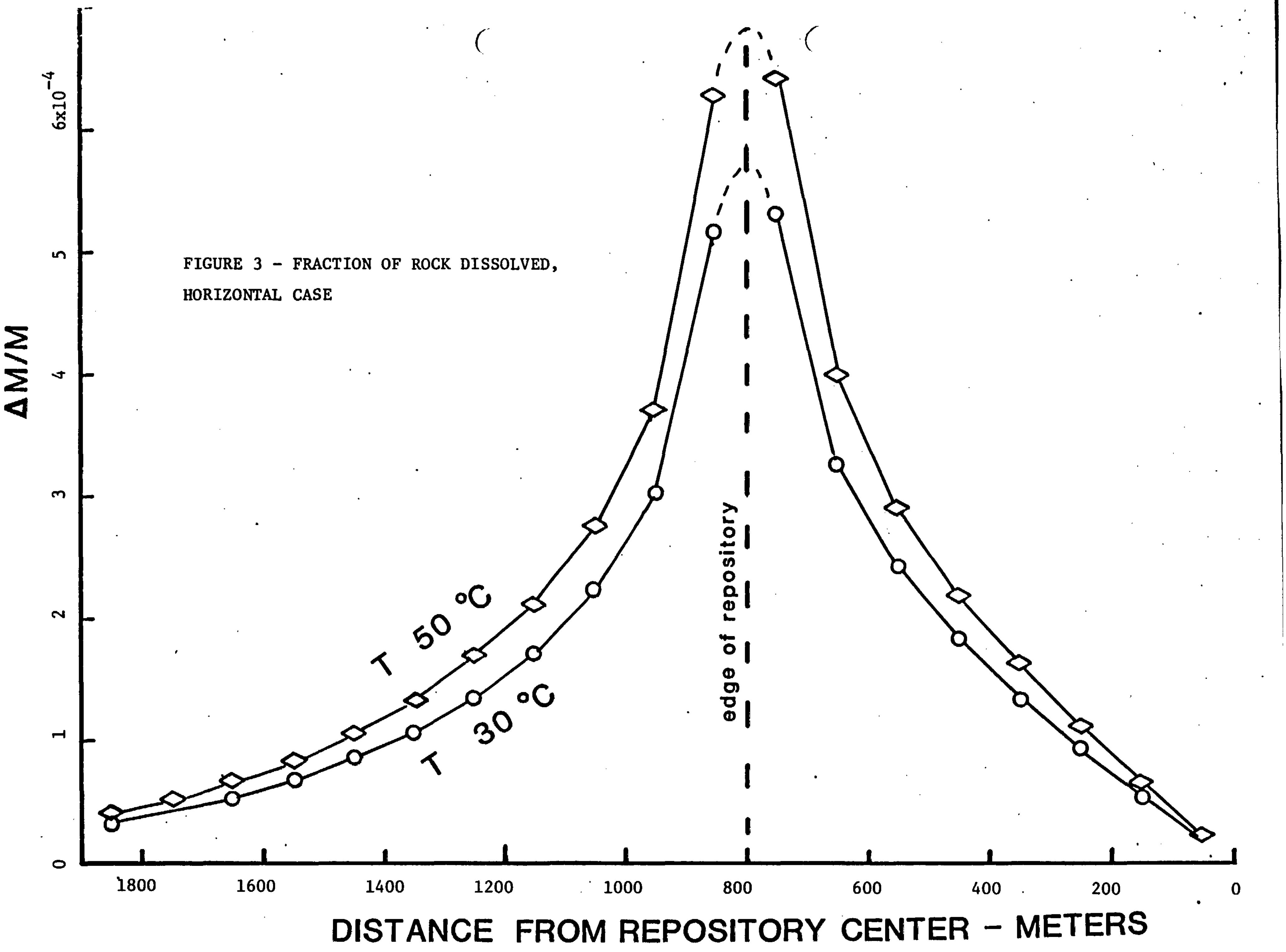

FIGURE 3 - FRACTION OF ROCK DISSOLVED, HORIZONTAL CASE

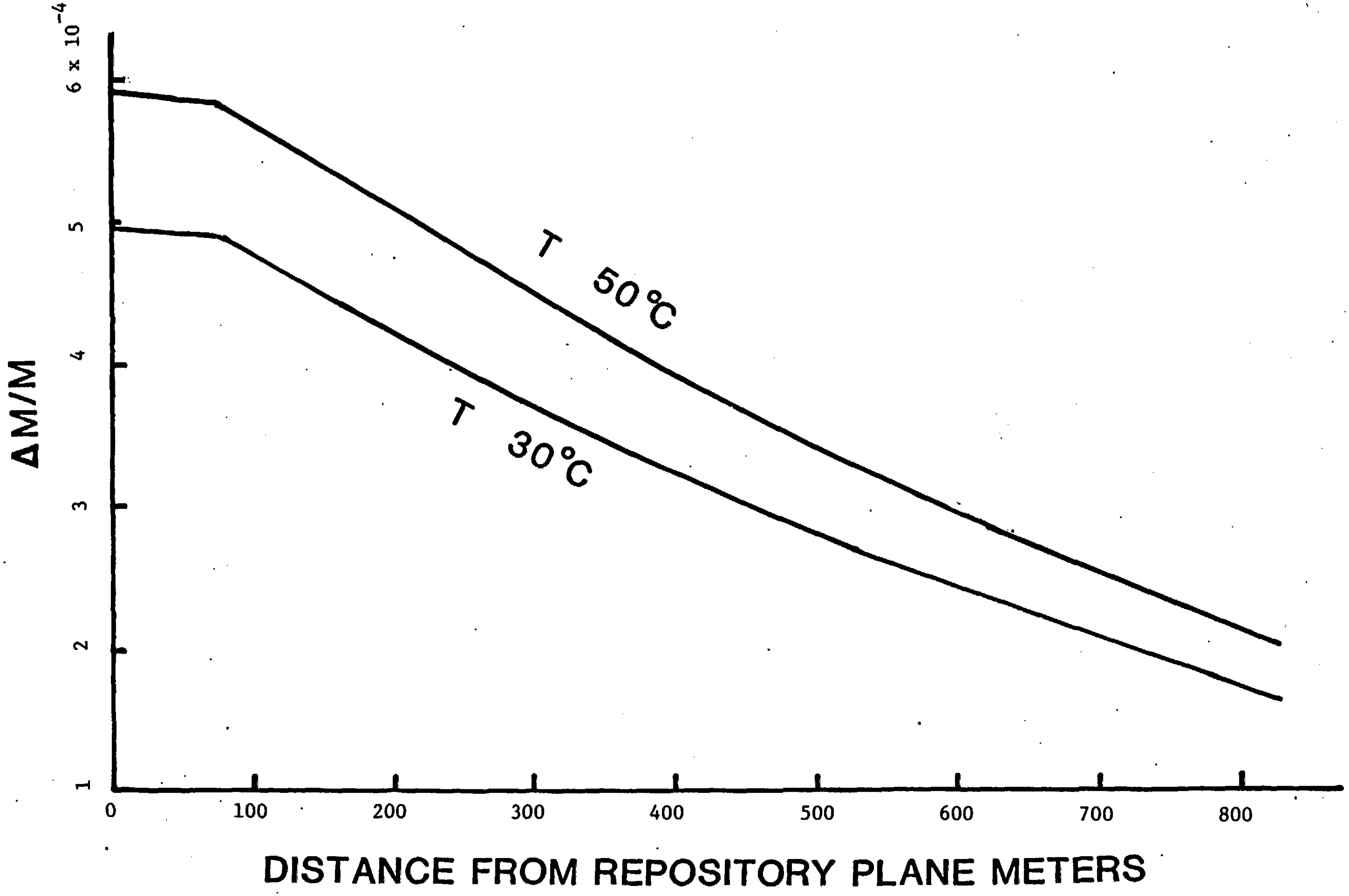

FIGURE 4 - FRACTION OF ROCK DISSOLVED, vertical case

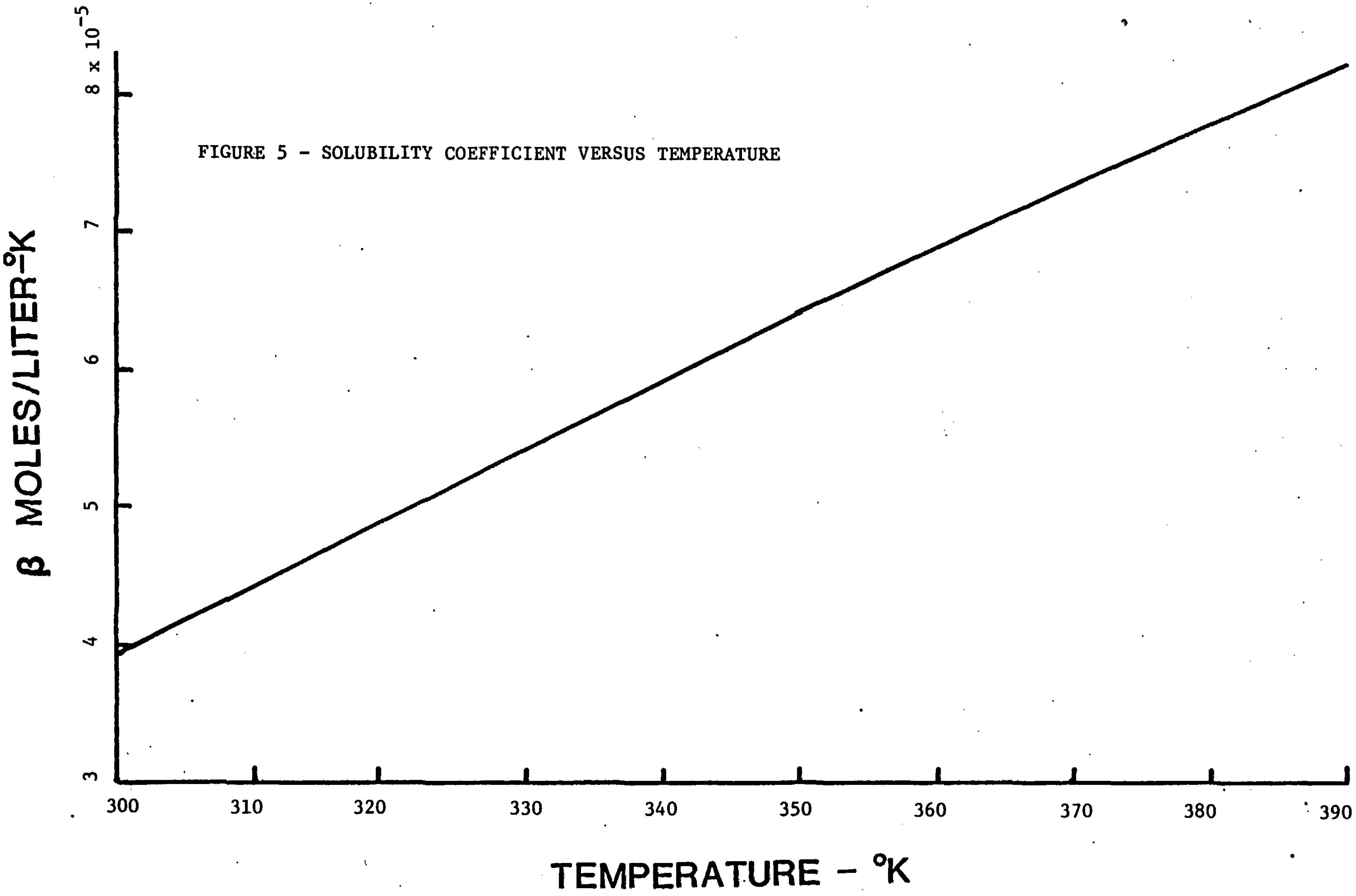

FIGURE 5 - SOLUBILITY COEFFICIENT VERSUS TEMPERATURE

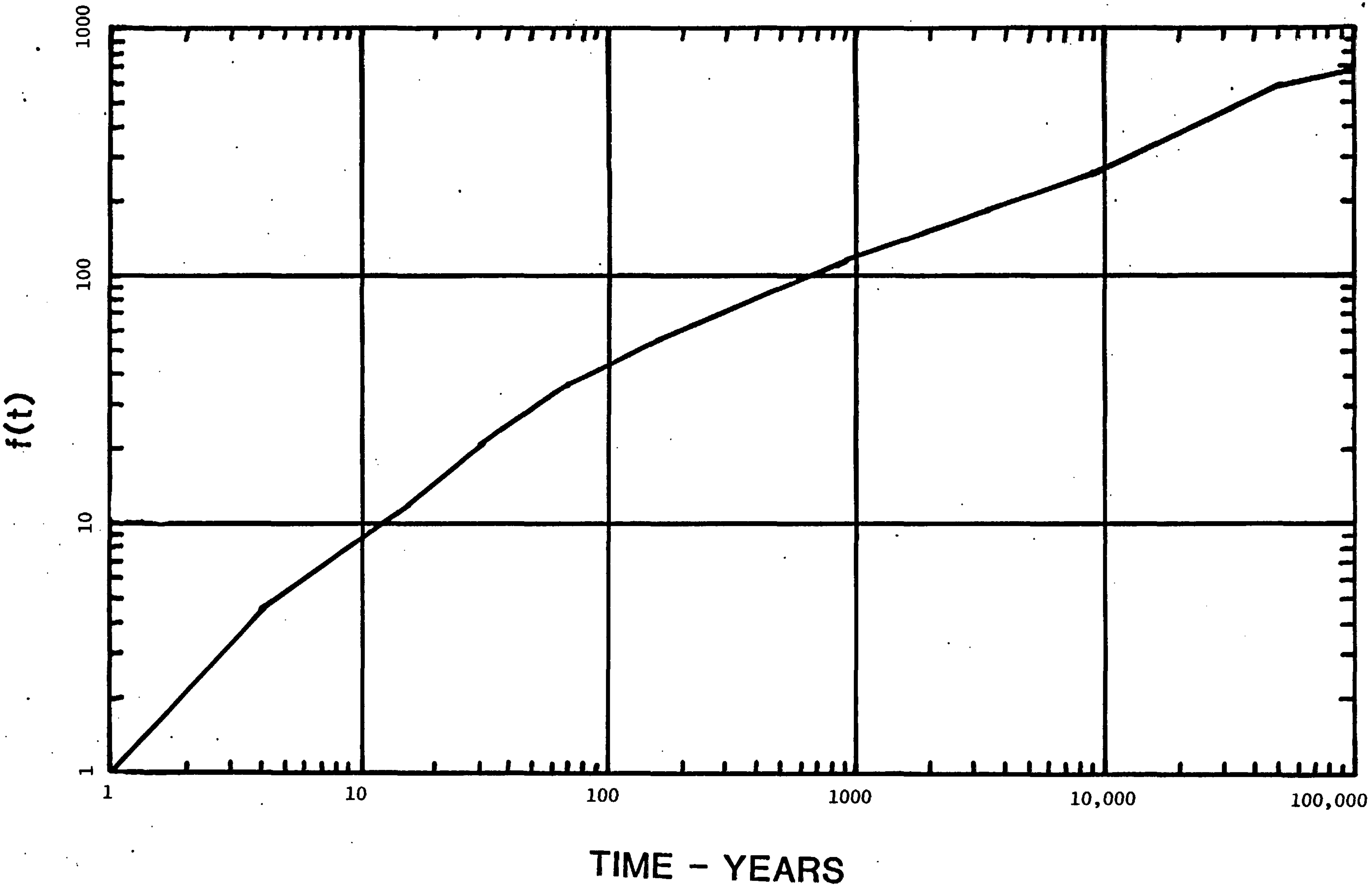

FIGURE 6 – FUNCTION f(t) VERSUS t FOR 10 YEAR OLD SPENT FUEL

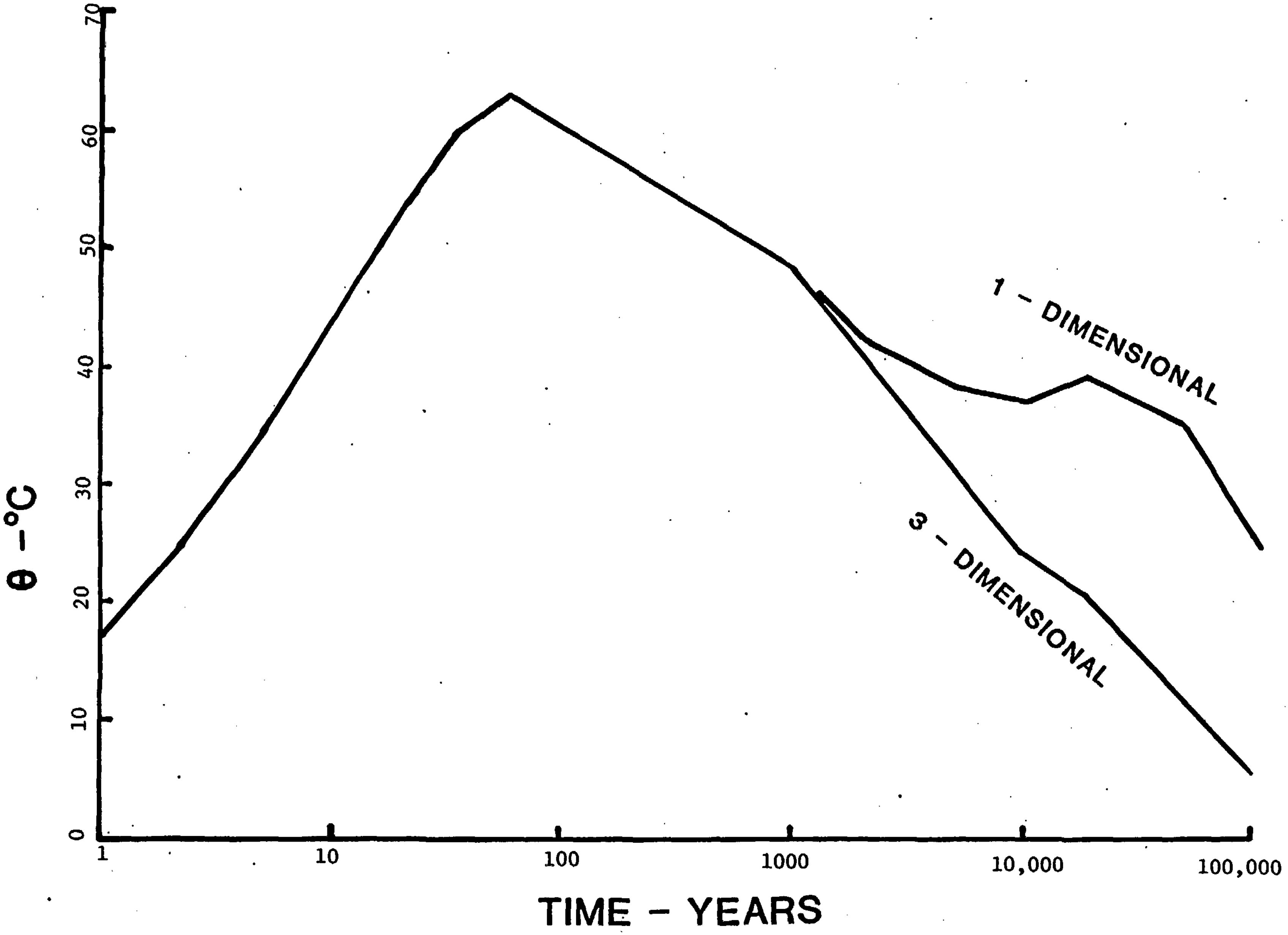

FIGURE 7 – TEMPERATURE AT CENTER OF REPOSITORY, 1-D AND 3-D MODELS