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Mass Transport of Soluble Species Through Backfill into Surrounding Rock

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용해도가 큰 핵종의 충전물질에서 주변 암반으로의 이동 현상

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Abstract

Some soluble species may not be solubility-limited or congruent-released with the matrix species. For example, during the operation of the nuclear reactor, the fission products can be accumulated in the fuel-cladding gap, voids, and grain boundaries of the fuel rods. In the waste package for spent-fuel placed in a geologic repository, the high solubility species of these fission products accumulated in the "gap", e.g. cesium or iodine are expected to dissolve rapidly when ground water penetrates fuel rods.

The time and space dependent mass transport for high solubility nuclides in the gap is analyzed, and its numerical illustrations are demonstrated. The approximate solution that is valid for all times is developed, and validated by comparison with an asymptotic solution and the solution obtained by the numerical inversion of Laplace transform covering the entire time span.

요 약

처분된 폐기물에서 용해도가 큰 핵종이 침출될 때, 그 핵종의 용해도에 의해 조절되거나 조화 용해하지 않는 경우가 있다. 예를 들면 원자로 운영시 핵분열 생성물의 일부는 그레인 경계나 핵연료와 피복재 사이의 틈새에 축적될 수가 있다. 사용후 핵연료 처분장에서 이와 같이 축적된 핵분열 생성물중 세슘이나 요오드와 같이 용해도가 큰 핵종은 용기가 부식되면 지하수내에 급격하게 녹게 된다. 이와 같이 틈새에 녹아있는 용해도가 큰 핵종의 이동현상을 시간 및 공간의 함수로 모사하고 그 수치 결과를 제시하였다. 전구간에서 유효한 근사해를 제시하고 이를 초기 및 후기 접근해와 Laplace 변환을 수치 재변환으로 얻은 해들과 비교함으로 검증하였다.

1. Introduction

The dissolution rate of solubility-limited species or congruent-released species in the waste package for spent fuel have been studied previously [1]. However some soluble species may not be solubility-limited or congruent-released with the matrix species. For example, during the operation

of the nuclear reactor, the fission products can be accumulated in the fuel–cladding gap, voids, and grain boundaries of the fuel rods. In a spent–fuel waste package placed in a geologic repository, the high solubility species in these fission products accumulated in the "gap", e.g. cesium or iodine are expected to dissolve rapidly[2] when the ground water penetrates fuel rods. The previous mass transfer analysis[3] for spent fuel package without backfill shows that this soluble "gap activity" of cesium or iodine is the greatest contributor to fractional release rates for these radionuclides into surrounding rock, in qualitative agreement with laboratory experiments on spent–fuel rods with locally perforated cladding[4]. In the following, the mass transfer analysis in a water filled void is extended to include diffusion of soluble species through a backfill into surrounding rock in one–dimensional planar geometry.

2. Theoretical Analysis

2.1 Governing Equations and Solutions

The governing equations for the backfill and rock region are expressed in equations (1) and (2), respectively (see Figure 1).

$$\frac{\partial N_1}{\partial t} = D_1 \frac{\partial^2 N_1}{\partial x^2} - \lambda N_1, -L < x < 0, \quad t > 0 \quad (1)$$

$$\frac{\partial N_2}{\partial t} = D_2 \frac{\partial^2 N_2}{\partial x^2} - \lambda N_2, \quad x > 0, \quad t > 0 \quad (2)$$

where the subscripts 1 and 2 represent the backfill and rock, respectively, and

$$D_1 \equiv \frac{D_f}{K_1} \quad (3a)$$

$$D_2 \equiv \frac{D_f}{K_2} \quad (3b)$$

$N \equiv N_1(x, t)$, and $N_2 \equiv N_1(x, t)$ are radionuclide concentrations in the backfill region of thickness L and the semi–infinite rock region, respectively which have retardation coefficients K_1 and K_2. D_f is the species' diffusion coefficient in the water saturated media, and λ is the decay constant.

The side conditions are

$$N_1(x,0) = 0, \quad -L < x < 0 \quad (4a)$$

$$N_2(x,0) = 0, \quad x > 0 \quad (4b)$$

$$N_1(0,t) = N_2(0,t), \quad t > 0 \quad (5)$$

$$-\epsilon_1 D_f \frac{\partial N_1}{\partial x} = -\epsilon_2 D_f \frac{\partial N_2}{\partial x}, \quad \text{at } x = 0, \quad t > 0 \quad (6)$$

$$N_2(\infty, t) = 0, \quad t > 0$$

where ϵ_1, ϵ_2 are the porosities of the regions.

Finally a simple mass balance of the gap region equates the rate of change of the radionuclide mass flux through the gap–backfill interface of surface area S and the rate of decay of the specie in the gap volume V bounded by S. On the assumption that the nuclide concentration is uniform throughout the gap and equal to $N_1(-L, t)$

$$-V \frac{\partial N_1(-L,t)}{\partial t} = -D_f \epsilon_1 S \frac{\partial N_1(-L,t)}{\partial x} + \lambda V N_1(-L,t), \quad t > 0 \quad (8)$$

The initial gap concentration is taken to be

$$N_1(-L,0) = N^o \quad (9)$$

Equations (1) through (9) formulate the mathematical problem.

The quantity of principal interest, however, is the mass flux of the radionuclide at the backfill–rock interface

$$\dot{M}(0,t) = -D_f \epsilon_1 S \frac{\partial N_1(0,t)}{\partial x}, \quad t > 0 \quad (10)$$

To find a solution, take a Laplace transform with respect to the t variable, and there results with side conditions and a mass balance equation

$$\dot{m}(0,p) = K_1 \epsilon_1 N^o S \frac{2}{(1+\delta)(q_1+\gamma_o)} \frac{e^{-q_1 L}}{1 - \sigma e^{-2q_1 L}} \quad (11)$$

where

$$\sigma \equiv \frac{1-\delta}{1+\delta}\frac{q_1-\gamma_o}{q_1+\gamma_o}$$

$$\delta \equiv \frac{\epsilon_1}{\epsilon_2}\sqrt{\frac{K_1}{K_2}} \tag{12}$$

$$q_1^2 \equiv \frac{p+\lambda}{D_1}$$

$$\gamma_o \equiv K_1\epsilon_1\frac{S}{V}$$

This complicated function can be inverted numerically [5]. However, it is also possible to obtain approximate solutions for small and large times as well as an approximate solution covering the entire time range. For early and moderately large time, expand equation(11) in power of e^{-2q_1L}. Hence the mass flux is with the $\mathcal{L}^{-1}$ symbol denoting the inverse Laplace transform

$$\dot{M}(0,t) = K_1\epsilon_1 N^oS\frac{2}{1+\delta}\mathcal{L}^{-1}\left\{\frac{1}{q_1+\gamma_o}\sum_{n=0}^{\infty}\left[\frac{1-\delta}{1+\delta}\right]^n \times\left[\frac{q_1-\gamma_o}{q_1+\gamma_o}\right]^n e^{-(2n+1)q_1L}\right\},\ |e^{-2q_1L}|<1 \tag{13}$$

Since the early time behavior corresponds to $|q_1|\to\infty$, the term $(q_1-\gamma_o)/(q_1+\gamma_o)$ in equation (13) is approximated by unity. On inversion and return to the original parameters, these results

$$M(0,t) \simeq K_1\epsilon_1 N^oS\frac{2e^{-\lambda t}}{1+\delta}\sum_{n=0}^{\infty}\left\{\left[\sqrt{\frac{D_1}{\pi t}} - \gamma_oD_1H(\beta_n^2)\right]\exp\left[-\frac{[2n+1]^2L^2}{4D_1t}\right]\right\} \times\left[\frac{1-\delta}{1+\delta}\right]^n,\quad \text{valid for small } t \tag{14}$$

where

$$H(z^2) \equiv e^{z^2}\,\mathrm{erfc}(z)$$

$$\beta_n \equiv \frac{(2n+1)L}{2\sqrt{D_1t}} + \gamma_o\sqrt{D_1t} \tag{15}$$

For moderate time range the term $(q_1-\gamma_o)/(q_1+\gamma_o)$ in (13) is replaced by (-1) then an approximate solution is obtained. It is discovered that this approximation solution covers the entire time range of physical interest to a satisfactory degree [5], and this will be shown in the numerical illustrations. Hence for this case

$$\dot{M}(0,t) \simeq K_1\epsilon_1 N^oS\frac{2e^{-\lambda t}}{1+\delta}\sum_{n=0}^{\infty}\left\{\left[\sqrt{\frac{D_1}{\pi t}} - \gamma_oD_1H(\beta_n^2)\right]\exp\left[-\frac{[2n+1]^2L^2}{4D_1t}\right]\right\} \times\left[\frac{\delta-1}{\delta+1}\right]^n,\quad \text{applicable for } t\geq 0 \tag{16}$$

The numerical values of equations (14) and (16) happen to coincide for small t because only the first term ($n=0$) dominates in both series and these terms are identical.

2.2. Study for Limiting Cases

The approximate solutions for the mass transfer rate into the surrounding rock, $\dot{M}(0, t)$ are given by equations (14) and (16). These approximate solutions reduce to the exact solution for certain limiting cases of parameter values. For some special cases of these results are derived here.

i) With identical rock and backfill properties, i.e., $K=K_1=K_2$ and $\epsilon=\epsilon_1=\epsilon_2$, the results reduce to those of a single region problem. With these conditions, every term in the summation in equations (14) and (16) vanishes except for $n=0$. The mass transfer rate becomes

$$\dot{M}(0,t) = K\epsilon N^0S\left[\sqrt{\frac{D}{\pi t}} - \gamma_oDH(\beta^2)\right]\exp\left(-\left[\lambda t + \frac{L^2}{4Dt}\right]\right),\quad t\geq 0 \tag{17}$$

where β and D are defined by

$$\beta = \frac{L}{2\sqrt{Dt}} + \gamma_o\sqrt{Dt}$$

$$D = \frac{D_f}{K} \tag{18}$$

ii) For the case without backfill, the mass transfer rate at the gap/rock interface can be computed by setting $L=0$. Then the equation (17) becomes

$$M(0,t) = \tag{19}$$

$$K\epsilon N^0 S\, e^{-\lambda t} \left[\sqrt{\frac{D}{\pi t}} - \gamma_o DH(\gamma_o^2 Dt) \right], \quad t \geq 0.$$

This expression is exactly same as that employed in the previous analysis [3].

3. Illustrations

To illustrate the results, it is assumed that groundwater rapidly fills the void in the waste package for spent fuel and water contacts the interior of spent-fuel rods, and one percent of the total inventory of cesium and iodine is rapidly dissolved into the "void-water". The "void-water" is the volume of 0.45 m^3, which is equal to the difference of the volume of the waste canister and the total volume of enclosed fuel rods [6]. The area of the gap/backfill interface area is 6.1 m^2 [6]. Ground water flow is assumed to be small enough so that the mass transfer through backfill and rock is controlled by a molecular diffusion, and the value of the diffusion coefficient is assumed to be 10^{-5} cm^2/sec for both backfill and rock. The thickness of backfill is assumed to be 15 cm and the porosities of the backfill and rock are assumed 0.3 and 0.01 [7], respectively. The fractional release rates at the backfill/rock interface normalized to the initial inventory are computed as a function of time after container failure.

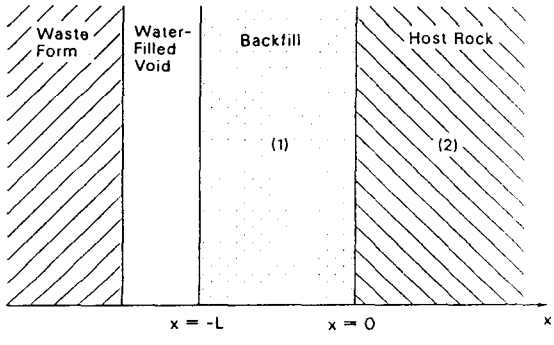

Fig. 1. Geometry.

In Figure 1 the approximate solution (16) is compared with the early time approximate solution (14), the large time asymptotic solution [5], and the numerical inversion of the Laplace transform [5]. In Figure 2 and Figure 3, the fractional release rate for stable nuclide are plotted as a function of time after container failure with the assumption of the same retardation coeffcient in backfill and rock. A solid line, a dotted line, a dashed line, and bullets in Figures 1 to 3 represent the approximate solution, the early time approximate solution, the large time asymptotic solution, and the numerical inversion of Laplace transform, respectively.

Figure 2 shows that the approximate solution agrees with the early time approximate solution, the large time asymptotic solution, and the numerical inversion solution, for $K_1=K_2=10$. As the

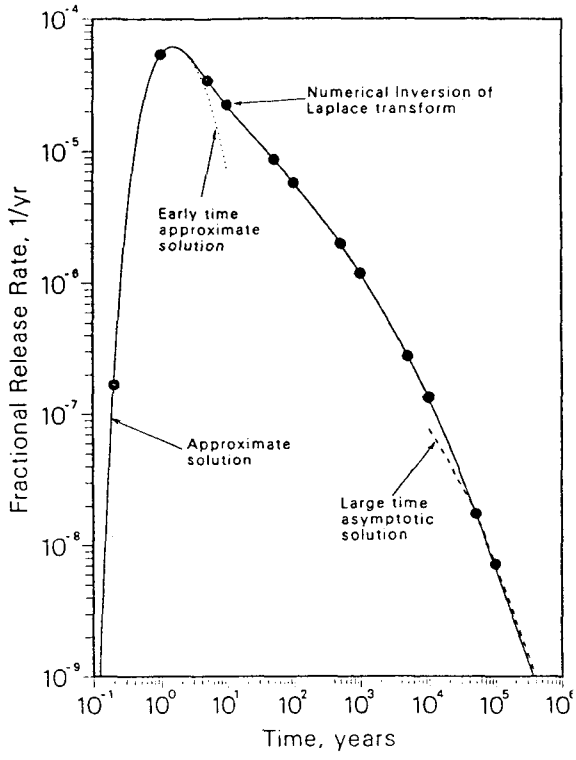

Fig. 2. Comparison of Different Solution Methods for $K_1=K_2=10$.

retardation coefficient becomes larger, the approximate solution agrees with other solution methods very well.

Figure 3 shows for the non-sorbing nuclide, i.e., unity retardation coefficient. In the early time the approximate solution agrees with the early time approximate solution and the numerical inversion solution. But as time increases, the approximate solution becomes different from the numerical inversion solution and the large time asymptotic solution, while the numerical inversion solution agrees with the large time asymptotic solution. The approximate solution gives over-estimation in the moderate time range in which the release rate is high and significant, and under-estimation in large time range in which the release rate becomes small and negligible. Thus the approximate solution can be a good tool to estimate the releases rate for all cases. Therefore the approximate solution (16) is used in next illustraions.

Figure 4 shows the fractional release rate of a stable nuclide as a function of time with the retardation cofficients of the backfill, K_1, and the rock, K_2 as parameters. Initially there is no nuclide in the backfill and rock, so it takes time for nuclide to diffuse through backfill and to reach at backfill/rock interface. Since a high K_1 means a large retardation effect in the backfill region, the nuclide with small K_1 arrives at the backfill/rock interface earlier than that with high value of K_1. This "arrival time" depends only on backfill characteristics, e.g., retardation coefficient in the backfill and the thickness of the backfill because until nuclides reach the backfill/rock interface, the rock properties do not affect the solution. Therefore, nuclides which have the different values of K_2 reach the interface at the same time if their K_1 values are the same. A high K_2 means, however, a large sorption effect in the rock region, and it

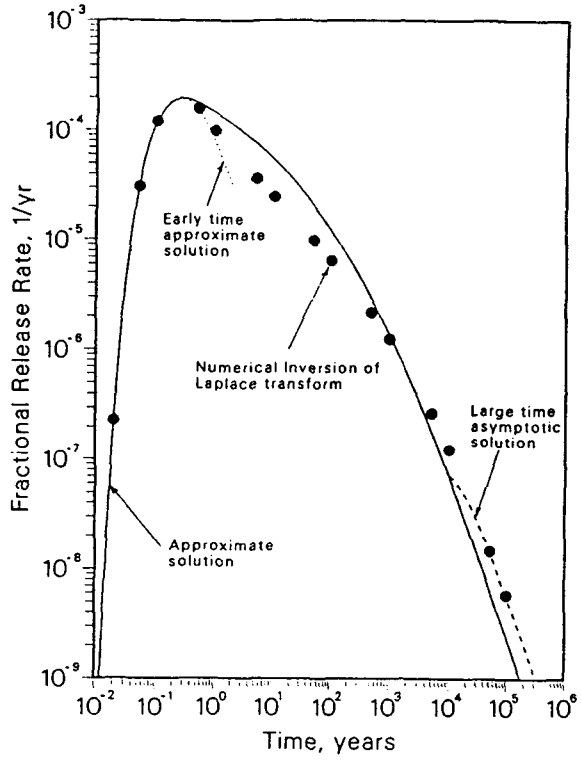

Fig. 3. Cimparison of Different Solution Methods $K_1 = K_2 = 10$.

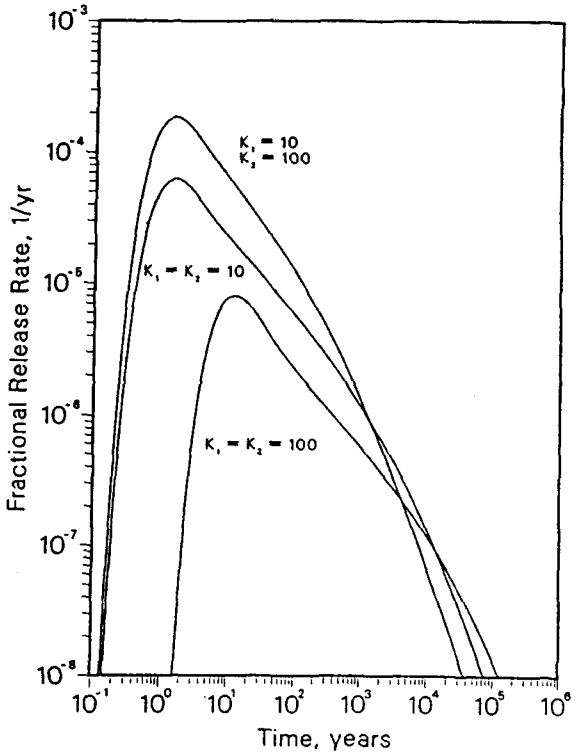

Fig. 4. Fractional Release Rate Versus Time With K_1 and K_2 as Parameter.

makes the concentration gradient near the backfill/rock interface steeper. For the nuclides with the same value of K_1, the peak value of the release rate of the nuclide with high K_2 is greater than the peak values of species with small K_2 values. On the other hand, a large retardation coefficient in the backfill means more nuclides are sorbed in the backfill, and so less nuclides reach the backfill/rock interface. Therefore for the same value of K_2, the peak value of the fractional releas rate of the unclide with small K_1 is higher than that with a high K_1 value. However, after some time period, the fractional release rates of nuclides with higher peak values become smaller than those with lower peak because more nuclides are already moved into the rock and less nuclides remain in the gap and the backfill region.

Figure 5 shows the fractional release rate of the stable nuclide with $K_1=K_2=100$ versus time with the thickness of the backfill as a parameter. For the case without backfill, the concentration gradient at the gap/rock interface is infinite at time zero. Thus the fractional release rate is very large at early times. The high release rate at early time makes the gap inventory depleted faster. Therefore the fractional release rate without backfill is less than that of a finite backfill in a later time period. Since thicker backfills delay arrival of released nuclides at the backfill/rock interface and more nuclides are used to fill up the backfill region, the peak release rate decreases. After some later time the fractional release rate of a thinner backfill becomes lower than that of thicker backfill due to the early depletion.

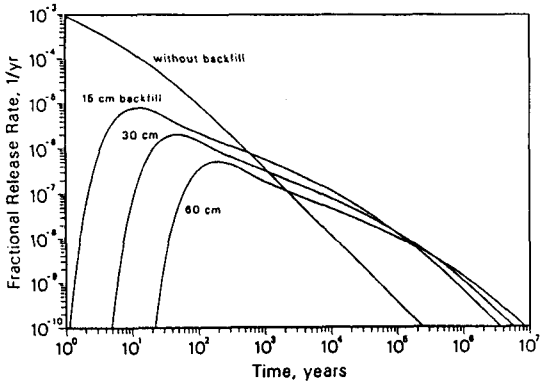

Fig. 5. Fractional Release Rates Versus Time With the Backfill Thickness as a Parameter for $K_1=K_2=100$.

Next illustrations are presented numerical illustrations of fractional release rate for typical soluble radionuclides in the nuclear waste package, e.g., cesium and iodine, into porous rock. In this calculation it is assumed that the distribution coefficient, K_d, are 100 cm^3/g for cesium and zero for iodine, the density of the solid, i.e., both rock and backfill, is 2 g/cm^3. Other parameters are the same in the previous illustrations.

Figure 6 shows the time-dependent fractional release rate of ^{135}Cs, ^{137}Cs and ^{129}I at the backfill /rock interface, normalized to initial inventory of each species. The non-sorbing ^{129}I arrives at the backfill/rock interface earlier than strong sorbing cesium as discussed before. ^{135}Cs and ^{137}Cs arrive simultaneously, and the release rates are almost the same in early times because they have the same retardation coefficients. However, because the half-life of the ^{137}Cs is much shorter than that of ^{135}Cs, the release rate of ^{137}Cs decreases rapidly as time goes on. In the early time the release rate of ^{129}I is higher than that of ^{135}Cs, but after about 1000 years, the releases rate of ^{135}Cs becomes higher than that of ^{129}I as discussed in context

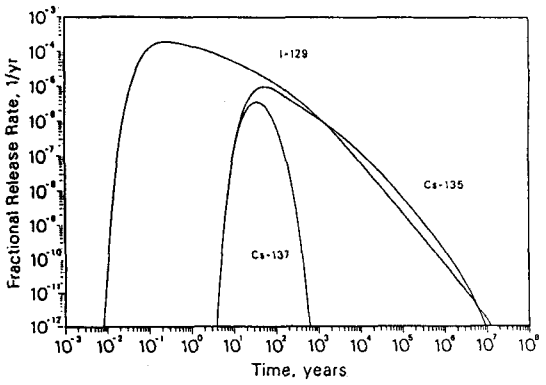

Fig. 6. Fractional Release Rates for Various Nuclides.

with in Figure 6. At later times, i.e., $t>5\times10^6$ years ^{129}I release rate becomes larger again, because the half life of ^{129}I is longer than that of ^{135}Cs and ^{135}Cs decays more rapidly than ^{129}I.

Figure 7 shows the fractional release rate of ^{137}Cs, normalized to its initial inventory, as a function of time with the backfill thickness as a parameter. As stated before, the release rate of the case without backfill is very large at early time but due to the early time depletion, the release rate is less than that of the case for finite thickness backfill at a later time period. Thicker backfills delay arrival at the backfill/rock interface and also allow greater decay in the backfill, and so the peak release rate decreases. For the relatively thicker backfill, however, early depletion effects cannot be observed because most of the nuclides decay in the backfill. Thus the release rate for a thicker backfill is smaller than that of thinner backfill for all time.

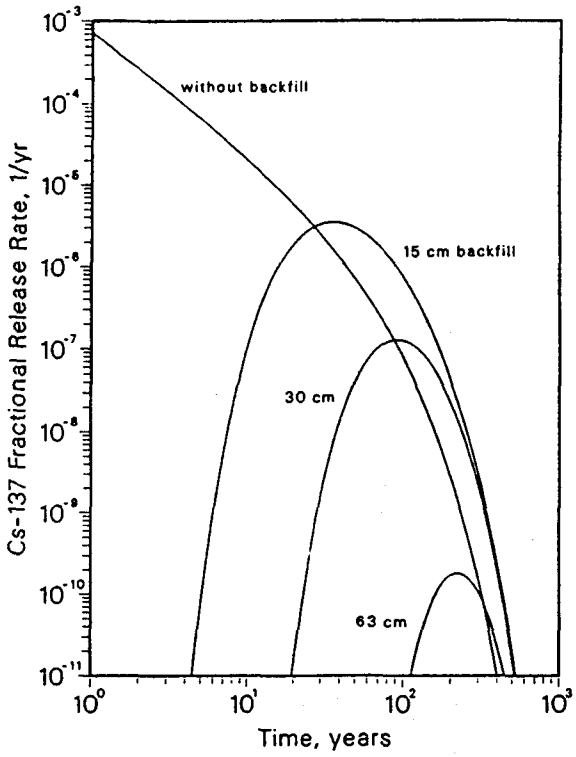

Fig. 7. Cesium-137 Fractional Release Versus Time With Backfill Thickness as a Parameter.

4. Conclusions

The transient mass transport of a soluble species released from the gap through a backfill into a surrounding rock is studied. The approximate solution that is valid for all time is developed. This approximate solution is compared with the early time approximate solution, the large time asymptotic solution, and the solution obtained from the numerical inversion of Laplace transform covering the entire time span. The approximate solution agrees with the other solutions very well except for a non-sorbing nuclide. For the non-sorbing nuclide, the approximate solution gives an over-estimation in the moderate time range in which the release rate is high and significant, and an under-estimation in the large time range in which the release rate become small and negligible. Thus the approximate solution can be a good tool to estimate the release rate for all cases.

In this study the mass transport from the waste form is neglected. Neglecting the contribution of mass transport from the waste form may be valid when the solubility of the matrix is low. If the solubility of the matrix species is high enough, e.g., uranium in a oxidation condition, then the mass transport from waste form may also be considered.

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