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SOLUBILITY LIMITED RADIONUCLIDE TRANSPORT THROUGH GEOLOGIC MEDIA

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Prior analyses for the migration of radionuclides neglect solubility limits of resolved radionuclide in geologic media.But actually some of the actinides may appear in chemical forms of very low solubility. In the present report we have proposed the migration model with no decay parents in which concentration of radionuclide is limited in concentration of solubility in ground water. In addition, the analytical solutions of the space-time-dependent concentration are presented in the case of step release, band release and exponential release.

Keywords; Migration, Radionuclide, Solubility Limit, Geologic Media, Transport, Analytical Solution Step Release, Band Release, Exponential Release Ground Water

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溶解限を考慮した地層中の放射性核種の移行

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放射性核種の地中移行に関する従来のモデルでは，固化体から核種が浸出する際，水理系での核種の溶解度に限界がないとして，取り扱ってきている。しかし，実際には，核種の種類や同一核種の場合にもその存在する化学形態によって，それぞれ溶解限が存在することがわかっている。この報文では，親核種－核種について，溶解限を考慮した地中移行モデルを提案し，ステップリリース，バンドリリースそして，エキスポーネンシャルリリースにおける，時間，場所の関数として，核種の濃度を求める解析解を導出した。

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1. Introduction

Prior analyses(1) which neglect solubility limits can overestimate the concentrations of these radionuclides in groundwater. When the radionuclides encapsuled in a canister begin to dissolve in groundwater, some radioactive elements such as plutonium may appear in chemical forms of very low solubility(2) even with the dissolution of the canister material. The purpose of this section is to make a more realistic measure of the actual hazard from radioactive waste. In this report we present the space-time-dependent concentration of a radionuclide with no decay parents, which is limited in concentration by solubility in the groundwater. The other assumptions used here are

(i) No dispersion
(ii) Local equilibrium
(iii) Precipitate does not move
(iv) Step, Band and Exponential release modes

2. Mass transport

2.1 Transport equation

In this model the governing equation can be written as follows

$$K \frac{\partial N}{\partial t} + V \frac{\partial N}{\partial z} + \lambda K N = 0 \tag{1}$$

where N : Concentration of nuclide in aquifer phase (g/cm^3)
K : Overall sorption coefficient (-)
V : Velocity of water (cm/yr)
λ : Decay constant of nuclide (1/yr)

From equation (1)

$$\frac{\partial N}{\partial t} + v \frac{\partial N}{\partial z} + \lambda N = 0 \tag{2}$$

where v : Effective migration velocity of nuclide (cm/yr)

2.2 Material balance at a source

Here we consider the material balance of nuclide at a source (z=10)

$$\frac{dM_p(t)}{dt} = m(t) - N^*V - \lambda M_p(t) \tag{3}$$

$$m(t) = C_1 e^{-\lambda t} \tag{4}$$

where M_p : g of atom precipitate / cm^2 of total cross sectional area (g/cm^2)

$m(t)$: Dissolution rate of nuclide from the source ($g/yr \cdot cm^2$)

N^* : Solubility limit (g/cm^3)

C_1 : Dissolution rate of atom of total cross sectional area ($g/yr \cdot cm^2$)

In the case of step release mode, we assume the constant dissolution rate i.e. $C_1 = m_o$ (constant).
From equations (3) and (4)

$$\frac{dM_p(t)}{dt} = m_o e^{-\lambda t} - N^*V - \lambda M_p(t) \tag{5}$$

Initial condition $M_p(0) = 0$
Solving the differential equation (5), we can get

$$M_p(t) = m_o t e^{-\lambda t} - \frac{N^*V}{\lambda}(1 - e^{-\lambda t}) \tag{6}$$

In the case of band release mode, the constant dissolution rate C_1 is denoted by $\frac{M_o}{T}$. Here M_o (g/cm^2) is the initial amount of nuclide at the source at $t = 0$ and T (yr) is leach time. The initial concentration of the nuclide is $\frac{M_o}{VT}$ in aquifer phase at $z = 0$.
Then

$$M_p(t) = \frac{M_o}{T} t e^{-\lambda t} - \frac{N^*V}{\lambda}(1 - e^{-\lambda t}) \tag{7}$$

In the case of exponential release mode, the nuclide is leached at a fractional rate k (1/yr) from the source.
The amount of $M_s(t)$ within the source at time t satisfy;

$$\frac{dM_s(t)}{dt} = -(\lambda + k)\, M_s(t) \tag{8}$$

Initial condition $M_s(0) = M_o$

From the equation (8) we can get

$$M_s(t) = M_o e^{-(\lambda+k)t} \tag{9}$$

So leach rate

$$k\, M_s(t) = kM_o e^{-(\lambda+k)t} \tag{10}$$

In this case, the equation (3) becomes

$$\frac{dM_p(t)}{dt} = kM_o e^{-(\lambda+k)t} - N^*V - \lambda M_p(t) \tag{11}$$

Initial condition $Mp(0) = 0$

Solving the differential equation (11), we can get

$$M_p(t) = \left(\frac{N^*V}{\lambda} + M_o\right)e^{-\lambda t} - M_o e^{-(k+\lambda)t} - \frac{N^*V}{\lambda} \tag{12}$$

2-3 Solution of transport equation

(a) Step release mode

(1) $Mp(t) > 0,\ N(z=0,t) = N^*$ at $t^* \geq t \geq 0$

Initial condition $N(z,t=0) = 0$ (13)

Boundary condition $N(z=0,t) = N^*$ (14)

Equation (2) is transformed with respect to t

$$sn - N(z,o) = -v\frac{dn}{dz} - \lambda n \tag{15}$$

$$\therefore\ n(z,s) = ce^{-\frac{s+\lambda}{v}z} \tag{16}$$

Taking Laplace transform of boundary condition

$$n(o,s) = \frac{N^*}{s} \tag{17}$$

$$n(z,s) = \frac{N^*}{s}e^{-\frac{s+\lambda}{v}z} \tag{18}$$

Inverse transform of above equation is

$$\underline{\underline{N(z,t) = N^* e^{-\frac{\lambda}{v} z} h\left(t - \frac{z}{v}\right)}} \tag{19}$$

(2) $M_p(t) = 0, \; N(z=0,t) \le N^*$ at $t>t^*$

Let $t' = t - t^*$ $(t' \ge 0)$: $t = t^*$ $(\ne 0)$ is a root of equation

$$M_p(t) = 0$$

Initial condition $$N(z,t'=0) = N^* e^{-\frac{\lambda}{v} z} h\left(t^* - \frac{z}{v}\right) \tag{20}$$

Boundary condition $$N(z=0,t') = \frac{m_o}{V} e^{-\lambda(t'+t^*)} \tag{21}$$

From equation (15)

$$sn - N^* e^{-\frac{\lambda}{v} z} h\left(t^* - \frac{z}{v}\right) = -v \frac{dn}{dz} - \lambda n \tag{22}$$

$$\therefore \frac{dn}{dz} + \frac{s+\lambda}{V} n = \frac{N^*}{v} e^{-\frac{\lambda}{v} z} h\left(t^* - \frac{z}{v}\right) \tag{23}$$

Taking Laplace transform with respect to z

$$p\tilde{n} - n(o,s) + \frac{s+\lambda}{v} \tilde{n} = \frac{N^*}{v} \int_o^\infty e^{-pz} e^{-\frac{\lambda}{v} z} h\left(t^* - \frac{z}{v}\right) dz \tag{24}$$

here

$$n(o,s) = \frac{m_o}{V} e^{-\lambda t^*} \frac{1}{s+\lambda}$$

$$\therefore \tilde{n}(p,s) = \frac{1}{p + \frac{s+\lambda}{v}} \left\{ \frac{m_o}{V} e^{-\lambda t^*} \frac{1}{s+\lambda} + \frac{N^*}{v} \frac{1}{p + \frac{\lambda}{v}} \left(1 - e^{-(p+\frac{\lambda}{v}) v t^*}\right) \right\} \tag{26}$$

Inverse transform above equation with respect to z

$$n(z,s) = \frac{m_o}{V} e^{-\lambda t^*} \frac{1}{s+\lambda} e^{-\frac{s+\lambda}{v} z}$$
$$+ \frac{N^*}{s} \{ e^{-\frac{\lambda}{v} z} - e^{-\frac{s+\lambda}{v} z} - e^{-\frac{\lambda}{v} z} h(z - vt^*)$$
$$+ e^{-\frac{\lambda}{v} z} e^{(t^* - \frac{z}{v}) s} h(z - vt^*) \} \tag{27}$$

Inverse transform above equation with respect to t'

$$N(z,t') = \frac{m_o}{V} e^{-\lambda(t'+t^*)} h(t' - \frac{z}{v})$$
$$+ N^* e^{-\frac{\lambda}{v}z} [\{1-h(t' - \frac{z}{v})\}-\{1-h(t'+t^* - \frac{z}{v})\}h(z-vt^*)$$

(28)

$$N(z,t) = \frac{m_o}{V} e^{-\lambda t} h(t-t^* - \frac{z}{v})$$
$$+ N^* e^{-\frac{\lambda}{v}z} [\{1-h(t-t^* - \frac{z}{v})\}-\{1-h(t - \frac{z}{v})\}h(z-vt^*)$$

(29)

(b) Band release mode

(1) $M_p(t) > 0$, $N(z=0,t) = N^*$ at $t^* \geq t \geq T$

Initial condition $N(z,t=0) = 0$ (30)

Boundary condition $N(z=0,t) = N^*$ (31)

Then

$$N(z,t) = N^* e^{-\frac{\lambda}{v}z} h(t - \frac{z}{v})\{1-h(t - \frac{z}{v} - T)\} \quad (32)$$

(2) $M\ (t) = 0$, $N(z=0,t) \leq N^*$ at $t>T>t^*$

Let $t' = t-t^*$ $(t' \geq 0)$; $t=t^*$ $(\neq 0)$ is a root of equation $M_p(t) = 0$

Initial condition $N(z,t'=0) = N^* e^{-\frac{\lambda}{v}z} h(t^* - \frac{z}{v})$ (33)

Boundary condition $N(z=0,t') = \frac{M_o}{VT} e^{-\lambda(t'+t^*)} [1-h\{t'-(T-t^*)\}]$

(34)

Then

$$N(z,t) = \frac{M_o}{VT} e^{-\lambda t}\{h(t-t^* - \frac{z}{v}) - h(t - \frac{z}{v} - T)\}$$
$$+ N^* e^{-\frac{\lambda}{v}z} [\{1-h(t-t^* - \frac{z}{v})\}-\{1-h(t - \frac{z}{v})\}h(z-vt^*)]$$

(35)

(c) Exponential release mode

(1) $M_p(t) > 0$, $N(z=0,t) = N^*$ at $t^* \geq t \geq 0$

Initial condition $N(z,t=0) = 0$ (36)

Boundary condition $N(z=0,t) = N^*$ (37)

Then

$$N(z,t) = N^*e^{-\frac{\lambda}{v}z} h(t - \frac{z}{v}) \tag{38}$$

(2) $M_p(t) = 0$, $N(z=0,t) \leq N^*$ at $t > t^*$

Let $t' = t-t^*$ $(t' \geq 0)$: $t=t^*(\neq 0)$ is a root of equation $M_p(t) = 0$

Initial condition $$N(z,t'=0) = N^*e^{-\frac{\lambda}{v}z} h(t^* - \frac{z}{v}) \tag{39}$$

Boundary condition $$N(z=0,t') = \frac{M_o}{V} ke^{-(k+\lambda)(t'+t^*)} \tag{40}$$

Then

$$N(z,t) = \frac{M_o}{V} k\ e^{-(k+\lambda)t}\ e^{k\frac{z}{v}} h(t-t^* - \frac{z}{v}) + N^*e^{-\frac{\lambda}{v}z} [\{1-h(t-t^* - \frac{z}{v})\}-\{1-h(t - \frac{z}{v})\}h(z-vt^*)] \tag{41}$$

3. Results and Discussion

Figures 1-3 show the concentration profile of N(z,t) for three release modes. As seen in these figures, the profiles of N(z,t) are changed before and after $t=t^*$. In fig.1 it is interesting that in the region of $z<v(t-t^*)$, N(z,t) is a function of only t and in the region of $v(t-t^*)<z<vt$, N(z,t) is the function of only z. This phenomenon is also observed in the case of band release mode in fig.2. According to exponential release, because of its boundary condition at $t>t^*$ and $z<v(t-t^*)$, N(z,t) increases according to the increase of z.
With this model, we can show the space-time dependent concentration of radionuclide assuming appropriate value of m(t). Now a few data is known about the solubility limit N^* of radionuclide. From the solubility curve of $Pu(OH)_4$ and Pu(IV) polymers as a function of accidity, the solubility limit of Pu(IV) nuclide is 10^{-7} moles/l at PH=7[(2)]. As the decay constant of ^{239}Pu is 2.84×10^{-5} (1/yr), the time t^* is around 1.7×10^5yr and this value does not depend on the quantity of m_0 in equation (5) of the case of step release. In future solubility limited case of two and three members chain should be solved analytically. This problem is a non equilibrium case in which solubility limited boundary must be a moving boundary according to time and space. This problem is an interesting one but it is much difficult to solve analytically.

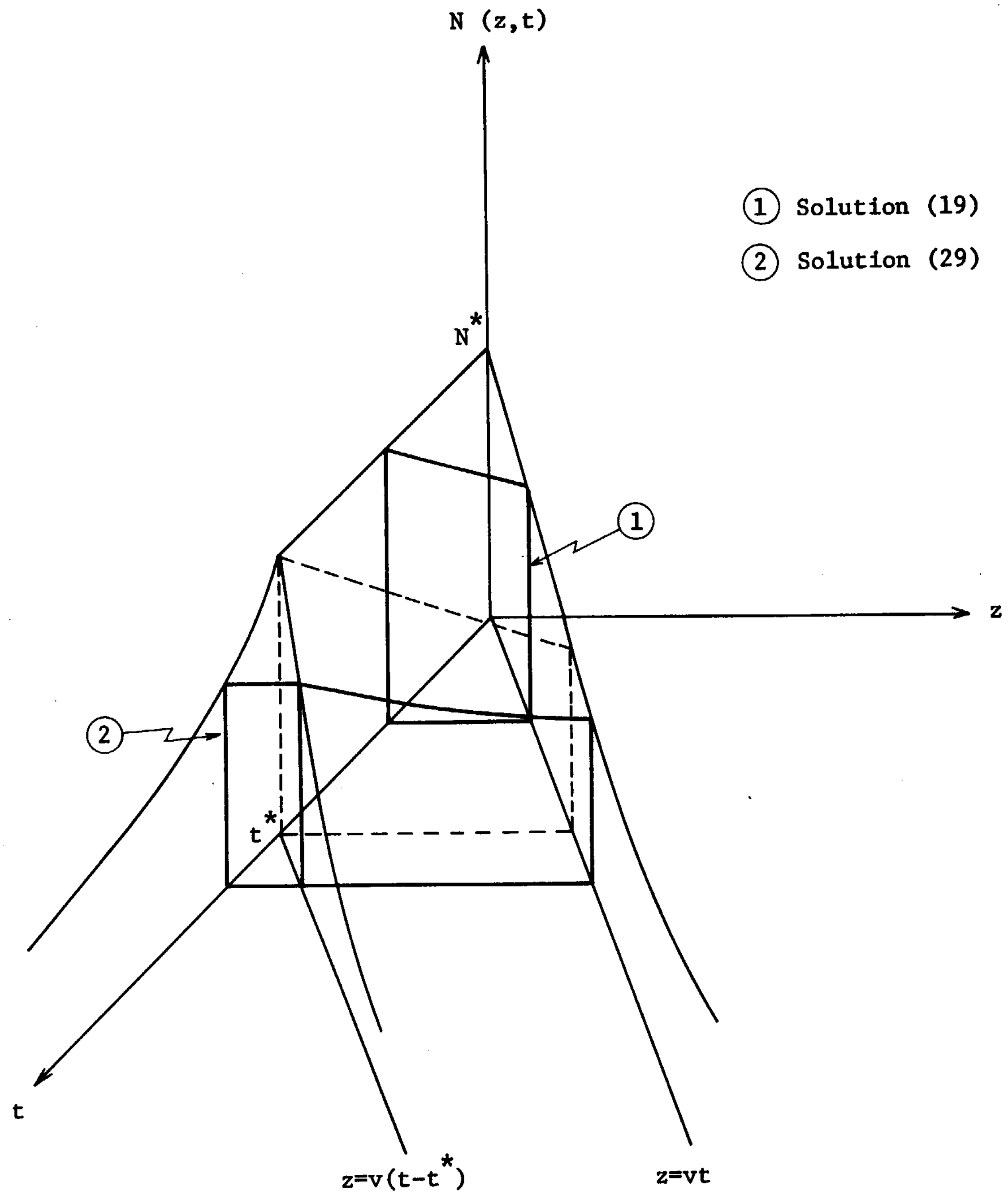

Fig. 1 Concentration profile of N (z,t)
(Step release mode)

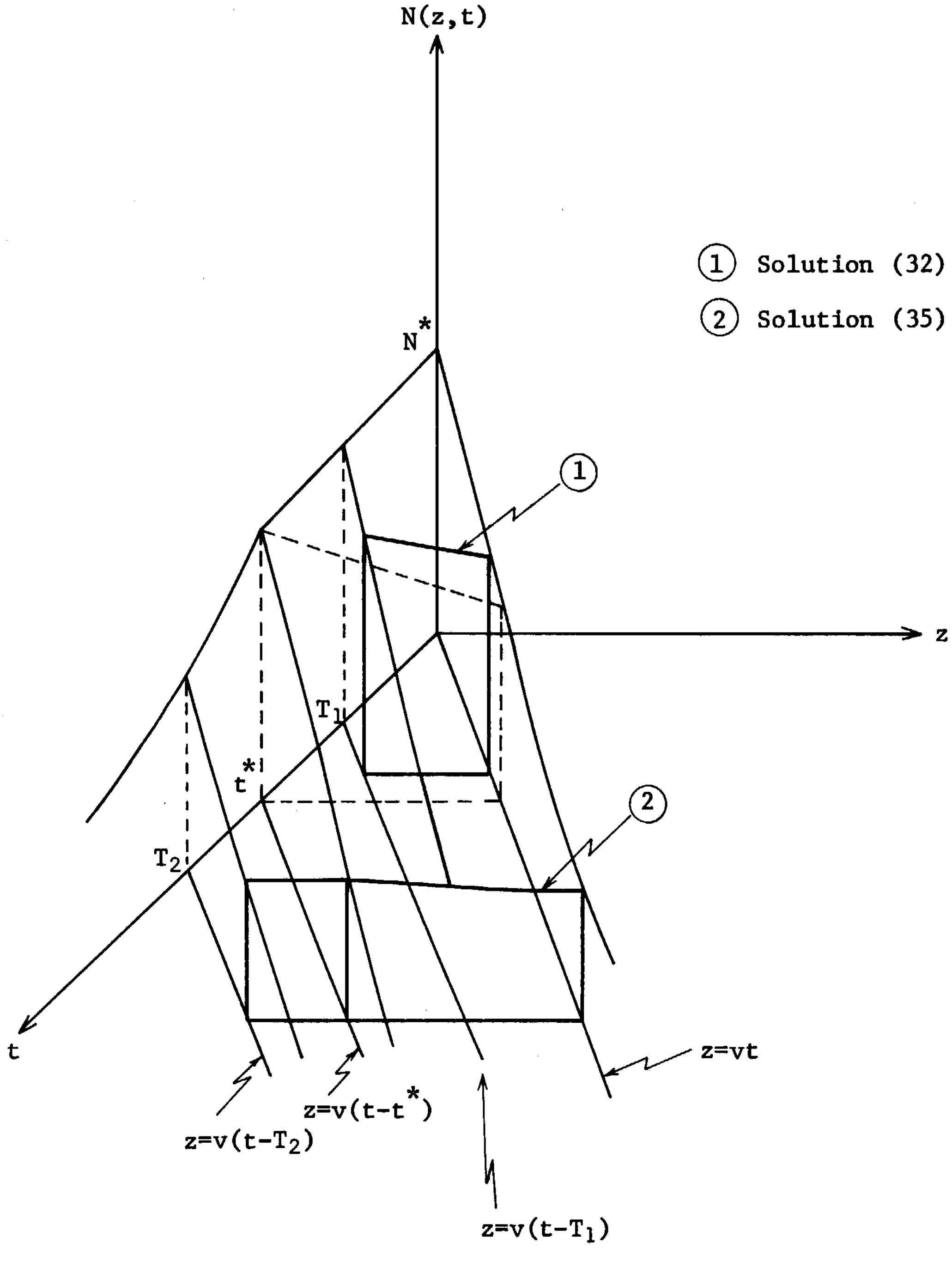

Fig. 2 Concentration profile of N (z,t)
(Band release mode)
here T_1, T_2 : leach time

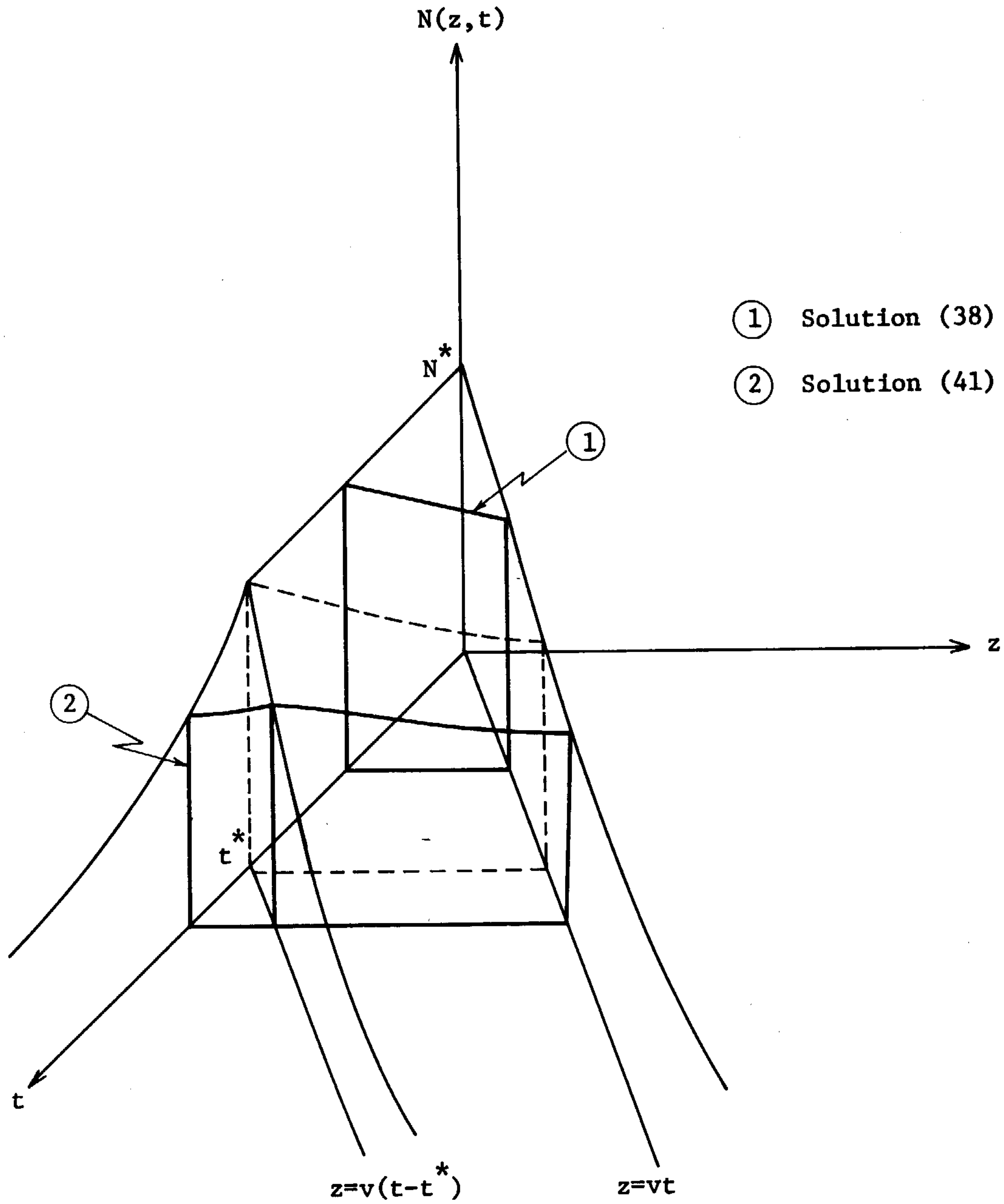

Fig. 3 Concentration profile of N (z,t)
(Exponential release mode)

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