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Two dimensional movements of a redox front downstream from a repository for nuclear waste

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ROYAL INSTITUTE OF TECHNOLOGY
Dept. of Chemical Engineering

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SUMMARY

A broken canister with radioactive waste from nuclear power plants is assumed to have come in contact with water. Radiation (mainly α) will radiolyze the water to form the main products: hydrogen and hydrogen peroxide. The rate of the radiolysis decreases with time. The hydrogen is not very reactive and will diffuse away. The hydrogen peroxide will oxidize ferrous iron in the backfill and rock matrix to ferric iron. Normally there is a reducing environment in the bedrock, but with the migration of the hydrogen peroxide into the bedrock it will change to an oxidizing environment. The hydrogen peroxide is very reactive and cannot coexist with ferrous iron. Thus a sharp front between oxidizing and reducing conditions is developed. This redox front moves very slowly in comparison with the movement of the radionuclides in the fissure. Some of the nuclides (Np, Tc and U) have a much lower solubility under reducing conditions than under oxidizing conditions. These will precipitate at the redox front to the solubility concentration.

A model with diffusion in the axial and transverse directions, advection in the axial direction and diffusion into the rock matrix is used in a numerical computation to describe the movement of the redox front. An analytical solution with advection only in the fissure has also been used.

Christensen and Bjergbakke (1982b) have computed the production rate of the oxidizing agents. From these computations two cases have been studied: a probable case with a production of 144 moles H_2O_2 in one million years and a hypotetical maximum case with a production of 29 000 moles H_2O_2. In the first case the canister is assumed to be intersected by one fissure and in the other by five fissures.

The computations for the probable case give an extension of the redox front in the direction of flow 6,8 m in one million years, compared with 6 m obtained by the analytical solution. The extension in the transverse direction from the centre line has been calculated to be at most 1.6 m. The penetration into the rock matrix at the inlet of the fissure has been calculated to be $3.7 \cdot 10^{-2}$ m.

1. Background

The canister with radioactive waste in a final repository is assumed to have been penetrated. Radiolysis of water by radiation (mainly α) from the radioactive material occurs and produces reducing species (hydrogen gas) and oxidizing species (mainly hydrogen peroxide). The hydrogen gas is not very reactive and will diffuse away. The hydrogen peroxide, which is very reactive, will attack the canister material and oxidize ferrous iron in the backfill and will finally diffuse into the bedrock where it will oxidize the ferrous iron.

The amount of ferrous iron in the backfill is limited and the redox front quickly penetrates this to the bedrock. In an initial period the transport into the bedrock adjacent to the backfill is faster than the transport into the flowing water in the fissures of the bedrock. After some time, when the bedrock nearest the backfill is oxidized and the distance for diffusion into the bedrock has increased, the H_2O_2 migration into the flowing water in the fissures will dominate.

Some nuclides (Np, Tc, U) have a much lower solubility under reducing conditions (normally bedrock conditions) than under oxidizing conditions. These nuclides will precipitate at the redox front.

2. Formulation of the problem

The oxidizing agent (OA) released from the fuel diffuses out through the backfill and into water flowing in a fissure intersecting the repository hole. The OA is released at a known rate which is changing with time. Figure 1 shows the fissure intersecting the repository hole. Figure 2 shows the streamlines along the fissure and how the cylindrical hole is replaced by a plane source to simplify the computations. Figure 3 shows the expected movement of the redox front along the fissure and into the rock matrix.

The change in concentration of OA in the water can be described by the advection dispersion equation in two dimensions.

$$\frac{\partial c}{\partial t} = -u \frac{\partial c}{\partial z} + D_z \frac{\partial^2 c}{\partial z^2} + D_y \frac{\partial^2 c}{\partial y^2} + \frac{D_e}{b} \left. \frac{\partial c_p}{\partial x} \right|_{x=x_0} \qquad (2.1)$$

The last term accounts for the diffusion into the rock matrix.

The OA which goes into the matrix reacts very fast with the reducing agent (RA) in the matrix. OA and RA cannot coexist. A sharp front will develop: on one side there is OA, on the other there is the full concentration of RA. Figure 4 shows the movement of the redox front for a case when there is a large surplus of RA.

It has been shown by Neretnieks (1974) that when $q \gg c_s$ the concentration gradient is constant from the surface and into the front at x_b. The rate of movement of the front is small in relation to the time constant for diffusion of OA. For this case the rate of movement of x_b is obtained by stochiometric mass balance:

$$\frac{dx_b}{dt} = - \frac{D_e}{q_0 f} \frac{\partial c_p}{\partial x} = \frac{D_e}{q_0 f} \frac{c_s}{x_b} \qquad (2.2)$$

The reaction is:

$$OA + \frac{1}{f} RA = (RA)_{\frac{1}{f}} OA \qquad (2.3)$$

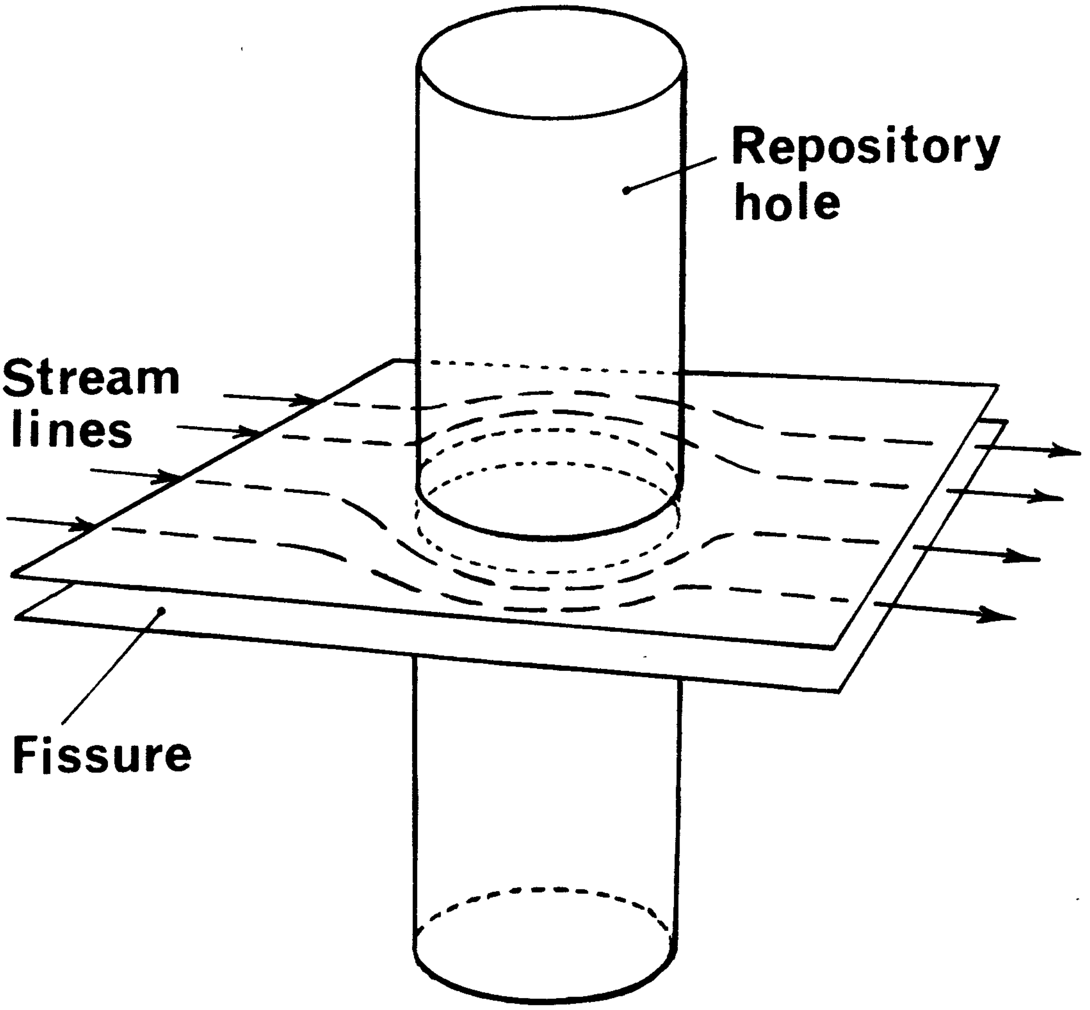


Figure 1. A fissure with flowing water intersects a repository hole containing a waste cylinder.

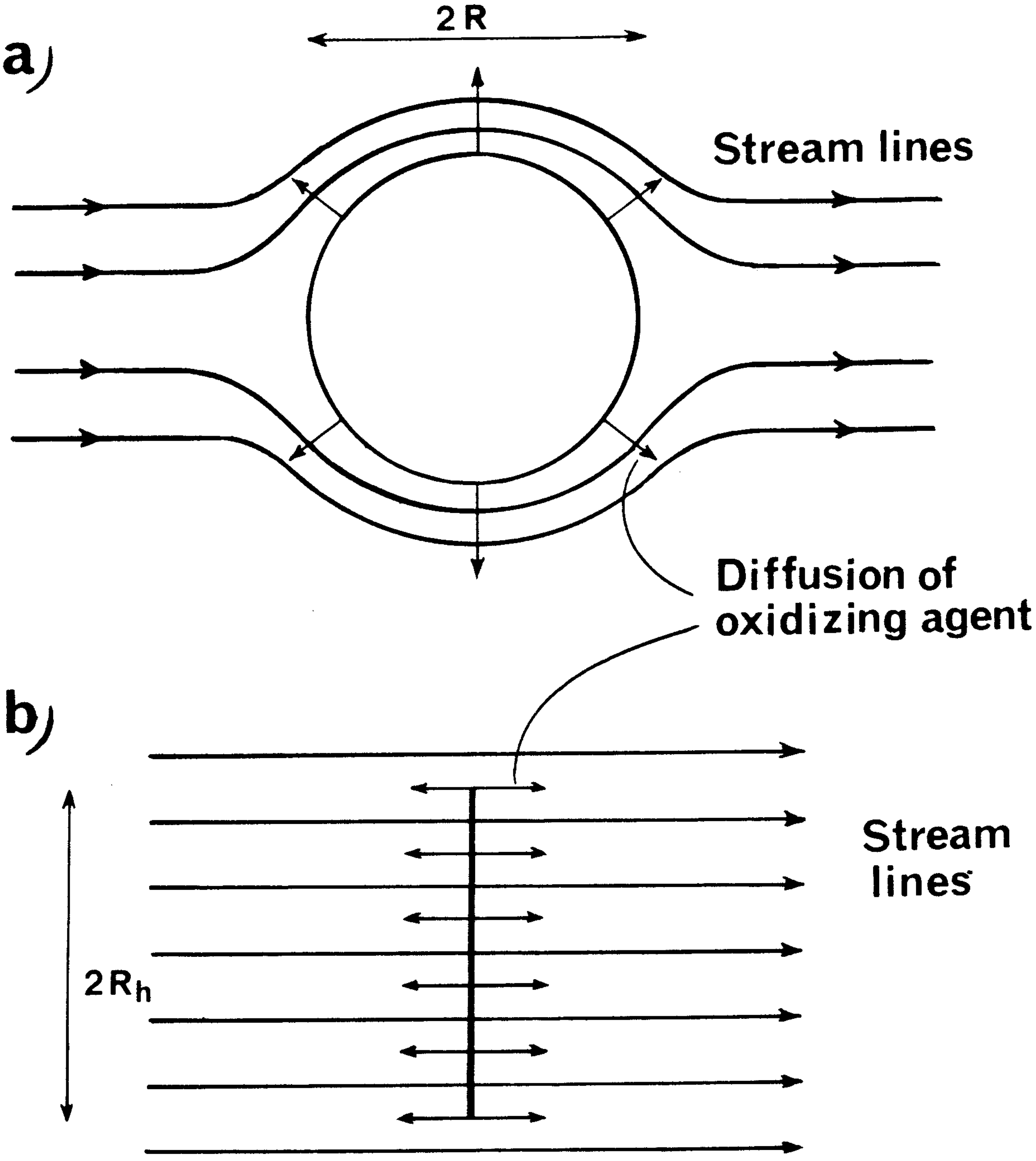
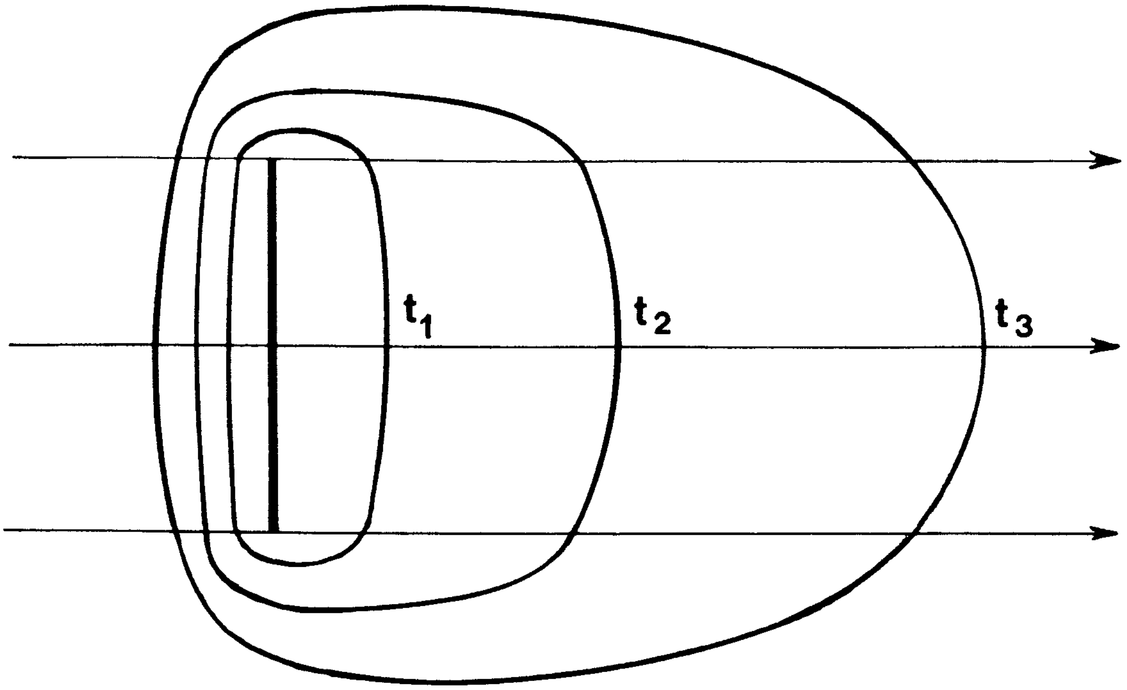
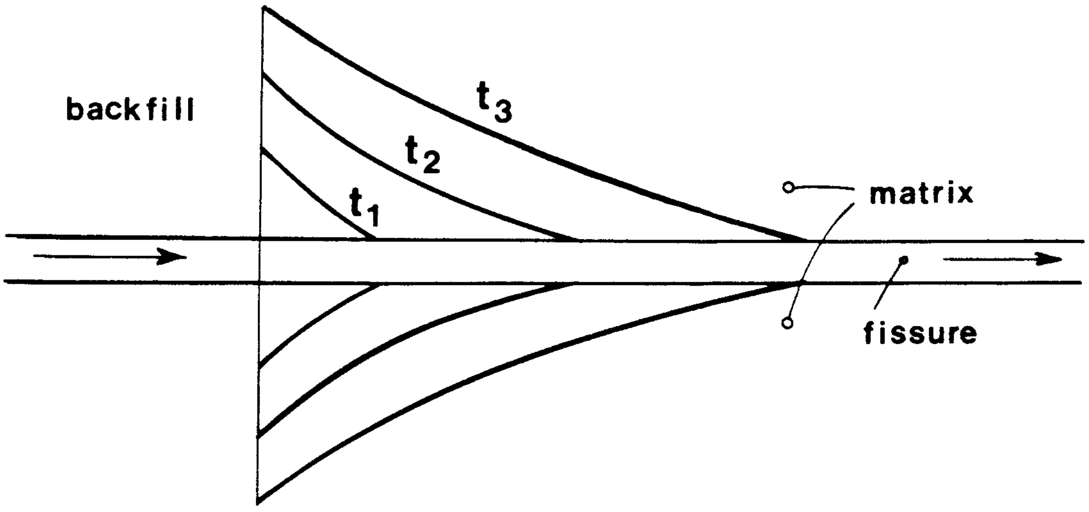


Figure 2. a) "Real" situation. Release of OA around the full circumference of the cylinder $2\pi R$.

b) Simplified case. Release only downstream from a plane source of length 2 R_h. The same rate of OA release in both cases.



a) Redox front in fluid



b) Redox front in matrix

Figure 3. The movement of the redox front downstream from the release zone.

a) view of the fissure
b) view of the matrix.

Locus of the front at various times.

where f is the stochiometric factor. Equations 2.1 and 2.2 are to be solved with the following initial and boundary conditions:

$$c = 0; \quad q = q_0 \text{ for } x > 0; \quad z > 0; \quad \text{all } y; \quad t = 0 \tag{2.4a}$$

$$c = 0; \quad q = q_0 \text{ for } x \to \pm\infty; \quad y \to \pm\infty; \quad z \to \pm\infty; \quad t > 0 \tag{2.4b}$$

$$N = N(t); \quad z = 0; \quad \text{in } -R_h \leqslant y \leqslant R_h; \quad -2b \leqslant x \leqslant 0; \quad t > 0 \tag{2.4c}$$

These conditions imply that at the beginning the water and the matrix have no OA and the matrix has a concentration q_0 of RA (2.4a). Far away from the source so it will remain (2.4b). From time zero and onwards OA is released into the water at a rate of N(t) moles/s over a distance of $2R_h$ and the width 2b of the fissure, x = 0 at one of the fissure walls.

The boundary condition 2.4c is exchanged for $N = u \cdot 2b \cdot 2R_h \cdot c_0$ in the calculations to increase stability. This makes very little difference in practice as $u\, c_0 \gg - D_z \left.\frac{\partial c}{\partial x}\right|_{z=0}$ which implies that advection dominates over diffusion to release the oxidants to the water.

As $\frac{\partial c_p}{\partial x}$ is constant over x within the diffusion front in the rock matrix

$$\frac{\partial c_p}{\partial x} = \left.\frac{\partial c_p}{\partial x}\right|_{x=0} = \left.\frac{\partial c_p}{\partial x}\right|_{x=x_b} = - \frac{c}{x_b} \tag{2.5}$$

and equation 2.1 becomes

$$\frac{\partial c}{\partial t} = - u\frac{\partial c}{\partial z} + D_z \frac{\partial^2 c}{\partial z^2} + D_y \frac{\partial^2 c}{\partial y^2} - \frac{D_e}{b} \frac{c}{x_b} \tag{2.6}$$

and equation 2.2 becomes

$$\frac{\partial x_b}{\partial t} = \frac{D_e}{q_0 \cdot f} \cdot \frac{c}{x_b} \tag{2.7}$$

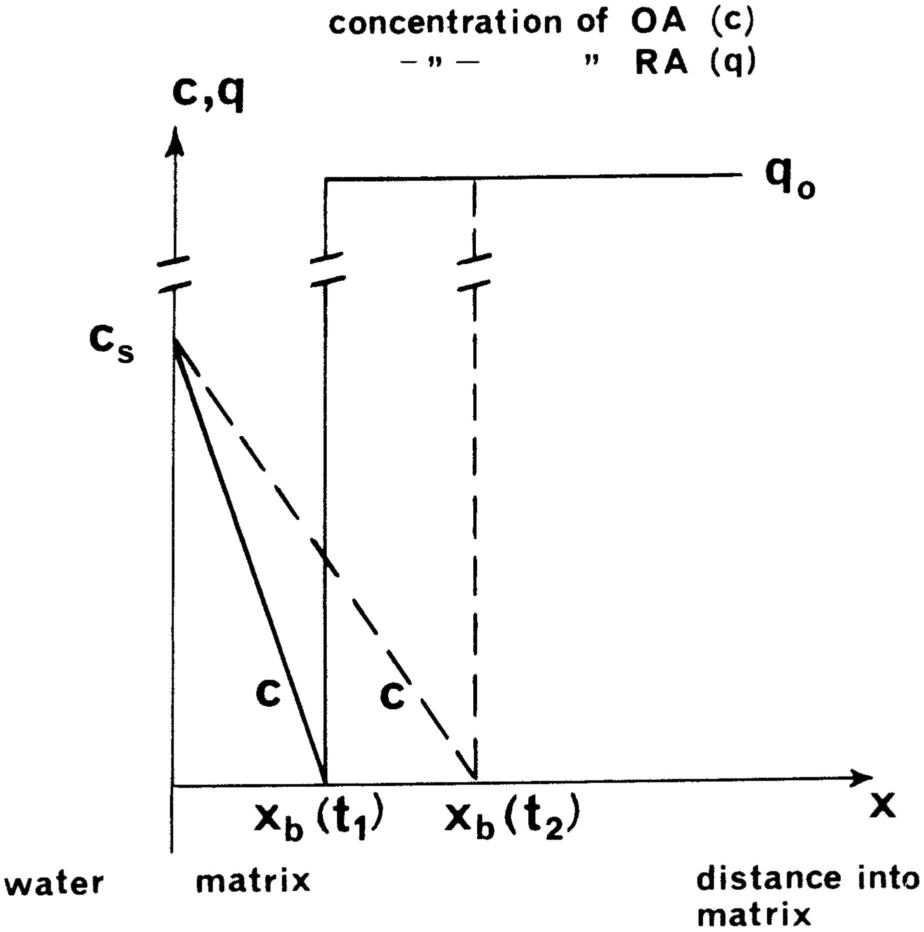


Figure 4. The movement of a redox front into the rock matrix.
c_s = concentration at rock surface of OA
q = concentration of RA in matrix

3. Method of solution

The DuFort-Frankel explicit finite difference approximation scheme in a modified form, is used to solve the problem numerically (Lapidus and Pinder 1982).

The terms in equation 2.1 are discretized as follows:

$$\frac{\partial c}{\partial t} = (c_{r+1,s,t} - c_{r-1,s,t})/2\ \Delta t \qquad (3.1)$$

$$\frac{\partial c}{\partial z} = (c_{r,s,t} - c_{r,s-1,t})/\Delta z \qquad (3.2)$$

To ascertain stability $c_{r,s,t}$ is exchanged for

$$c_{r,s,t} = \frac{\alpha}{2}\ c_{r+1,s,t} + \frac{(2-\alpha)}{2}\ c_{r-1,s,t} \qquad (3.3)$$

where $1 \leqslant \alpha \leqslant 2$ ($\alpha = 1$ gives the DuFort-Frankel scheme).

In the second derivatives the $c_{r,s,t}$ expression of 3.3 is also used and a discretization gives

$$\frac{\partial^2 c}{\partial z^2} = (c_{r,s+1,t} - \alpha\ c_{r+1,s,t} - (2-\alpha)\ c_{r-1,s,t} + c_{r,s-1,t})/\Delta z^2 \qquad (3.4)$$

$$\frac{\partial^2 c}{\partial y^2} = (c_{r,s,t+1} - \alpha\ c_{r+1,s,t} - (2-\alpha)\ c_{r-1,s,t} + c_{r,s,t-1})/\Delta y^2 \qquad (3.5)$$

The matrix diffusion term is

$$\left.\frac{\partial c_p}{\partial x}\right|_{x=0} = - \frac{c_{r,s,t}}{x_{b,r,s,t}} = - \frac{\alpha\, c_{r+1,s,t} + (2-\alpha)\, c_{r-1,s,t}}{2\, x_{b,r,s,t}} \tag{3.6}$$

Substituting the above equations into 2.1 gives

$$c_{r+1,s,t} = (B_1 c_{r-1,s,t} + B_2\, c_{r,s+1,t} + B_3\, c_{r,s-1,t} + + B_4\, (c_{r,s,t+1} + c_{r,s,t-1}))/B_o \tag{3.7}$$

where $$B_o = \frac{1}{2\Delta t} + \alpha\, (\frac{u}{2\Delta z} + \frac{D_z}{\Delta z^2} + \frac{D_y}{\Delta y^2} + \frac{D_e}{2bx_{b,r,s,t}}) \tag{3.8}$$

$$B_1 = \frac{1}{2\Delta t} - (2-\alpha)\, (\frac{u}{2\Delta z} + \frac{D_z}{\Delta z^2} + \frac{D_y}{\Delta y^2} + \frac{D_e}{2bx_{b,r,s,t}}) \tag{3.9}$$

$$B_2 = \frac{D_z}{\Delta z^2} \tag{3.10}$$

$$B_3 = \frac{D_z}{\Delta z^2} + \frac{u}{\Delta z} \tag{3.11}$$

$$B_4 = \frac{D_y}{\Delta y^2} \tag{3.12}$$

The increase in x_b according to equation 2.7 is

$$\frac{\partial x_b}{\partial t} = \frac{D_e}{q_o \cdot f} \cdot \frac{c_{r,s,t}}{x_{b,r,s,t}} \tag{3.13}$$

Assuming constant concentration an integration of 3.13 gives

$$x_{b,r+1,s,t} = [x^2_{b,r,s,t} + \frac{D_e \cdot \Delta t}{q_o \cdot f} (\alpha \, c_{r+1,s,t} + (2-\alpha) \, c_{r-1,s,t})]^{0.5}$$

(3.14)

Equations 3.6, 3.7 and 3.14 are solved by iteration.

The concentration at the canister can be computed from

$$c_o(t) = N(t)/2 \cdot u \cdot \Delta y \cdot 2b \cdot y_{nr} \qquad (3.15)$$

$N(t)$ = production rate of OA moles/year

$2y_{nr}$ = number of Δy occupied by the canister

$2\Delta y \, y_{nr} = 2R_h$ = equivalent flow width (m)

The numerical scheme does not give a sharp front beyond which the concentration is zero. The concentration drops continuously although very sharply in the transverse as well as in the axial direction. Typically it will drop ten orders of magnitude over 5 elements in the transverse direction in the region where the zero concentration boundary is expected to be. The location of the boundary can be found with sufficient accuracy for the present purpose by the following consideration: In the element where the boundary is, there is an influx of mass by flow and diffusion in the water to just compensate the influx by diffusion into the matrix $\frac{\partial c}{\partial t} = 0$ in equation 2.1. Transport by diffusion in the z direction can be neglected compared to flow. By approximating $\frac{\partial c}{\partial z} = \frac{c_{n+1,m} - c_{n,m}}{\Delta z}$ we find that $\frac{\partial c}{\partial z} = - c_{n,m}/\Delta z$ as $c_{n+1,m} = 0$. If the diffusive transport in the y-direction also is neglected equation 2.1 gives

$$x_b = \frac{D_e}{u \cdot b} \cdot \Delta z \qquad (3.16)$$

4. Calculated example

Christensen and Bjergbakke have calculated the effects of α-radiation (1982a) and α- and β-radiation (1982b) from spent fuel on water which has penetrated into the fuel rods in one copper canister of the proposed Swedish design. In their calculations they assume that all the voids between the fuel pellets and the zircaloy cladding is evenly filled with water (4.3 l). This gives a water film about 0.03 mm thick on the outer surface (144 m^2) of the pellets. That is also the effective range of α-particles in water. This amount of water is certainly exaggerated as there are bound to be expanded corrosion products from the copper and zircaloy which will intrude into the original free voids. Christensen and Bjergbakke (1982b) found that when there is simultaneous α- and β-radiation the β-radiation produces a significant number of radicals which will aid the recombination of produced hydrogen and hydrogen peroxide. This is also aided considerably by the presence in the water of Fe(II) and Fe(III) which together with the OH-radical act as a catalytic scavenger pair for hydrogen and hydrogen peroxide. Christensen and Bjergbakke (1982b) concluded that the most probable production of radiolysis products is 1 mole each of H_2O_2 and H_2 per square meter of wetted pellet surface with a 0.03 mm film of water in one million years (case 1). In the hypothetical case (case 2) in which there is no iron present the production of H_2 and H_2O_2 may increase to 200 moles/m^2 in 10^6 years. In table 1 and 2 the production rate and the integrated production up to one million years are given for the two cases according to Christensen and Bjergbakke (1982b).

TABLE 1. Hydrogen production in water irradiated with mixed alfa- and beta-radiation from BWR fuel with a burn-up of 33 MWd/t. (Case 1.)

Storage time years	Production rate moles/year	Integrated production moles
100	8.3 E-4	5.4 E-2
300	6.7 E-4	2.0 E-1
1000	4.6 E-4	6.0 E-1
10^4	2.5 E-4	3.84
10^5	1.8 E-4	23
10^6	0.9 E-4	144

TABLE 2. Irradiation of pure water with mixed alfa- and beta-radiation. BWR fuel. (Case 2.)

Storage time years	Production rate moles/year	Integrated production moles
100	3.6	260
300	2.5	860
1000	1.17	2100
10^4	0.25	8600
10^5	1.3 E-2	20600
10^6	0.6 E-2	29000

The ferrous iron content of some Swedish crystalline rocks has been measured and values between 1 and 7 % by weight (Torstenfelt et al. 1983) have been found. In the examples 1 % is used. With a rock density of 2700 kg/m^3 the 144 moles H_2O_2 in case 1 would be able to oxidize 288 moles of Fe(II) to Fe(III). This is equivalent to 0.60 m^3 of rock. In the other case, the 29 000 moles H_2O_2 would be able to oxidize a rock volume of 60 m^3.

The flow rate of water in the bedrock (u_0) may be expected to be less than 0.3 l/m^2,year (Bengtsson et al. 1983). In the computation 0.1 l/m^2,year was used. Assuming that the effective fissure spacing (S) is 5 m so that only one fissure (0.5 mm wide) intersect the 5 m long canister (L), then the equivalent flow rate (Q_{eq}) which must carry the produced H_2O_2 is 0.67 l/year•canister, as calculated by the near field model (Neretnieks 1982). In the fissure the water downstream from the canister would have an equivalent flow width 2 R_h with a concentration $c_0(t)$ of the oxidizing agents when leaving the vicinity of the canister, see figure 5. The equivalent flow width can be evaluated from

$$2\ R_h = \frac{Q_{eq}}{L \cdot u_o} \qquad (4.1)$$

$$u = \frac{u_o}{\varepsilon} \qquad (4.2)$$

TABLE 3. Values for cases 1 and 2.

		Case 1	Case 2
Production of OA in 10^6 years (moles)		144	29 000
Number of fissures per canister		1	5
Fissure width, 2b, (m)		$5 \cdot 10^{-4}$	$1 \cdot 10^{-4}$
S	(m)	5	1
$\varepsilon = \frac{2b}{S}$		10^{-4}	10^{-4}
R_h	(m)	1.34	1.34
Q_{eq}	(l/year•canister)	0.67	0.67
u_o	($l/m^2 \cdot$year)	0.1	0.1
u	(m/year)	1	1

If there is no diffusion or dispersion in the axial and transverse directions the movement of the redox front may be calculated by analytical methods (Neretnieks 1982b). This is done in appendix 1. In case 1 the redox front is calculated to have moved 5.8 m downstream from the canister in the fissure and $3.7 \cdot 10^{-2}$ m into the rock matrix at the inlet to the fissure ($z = 0$), in one million years. In the other case the redox front is calculated to have moved 16.6 m in the fissure and 0.5 m into the rock matrix at the fissure inlet. The effective diffusivity in the bedrock is taken to be $D_e = 5 \cdot 10^{-14}$ m^2/s (Skagius and Neretnieks 1982).

For the very low velocity in the fissure the dispersion in the axial direction is dominated by molecular diffusion (Fried 1971). The dispersion in the transverse direction then also would be due to molecular diffusion. The molecular diffusivity for small molecules in water is around $D_v = 2 \cdot 10^{-9}$ m^2/s (Perry and Chilton 1973).

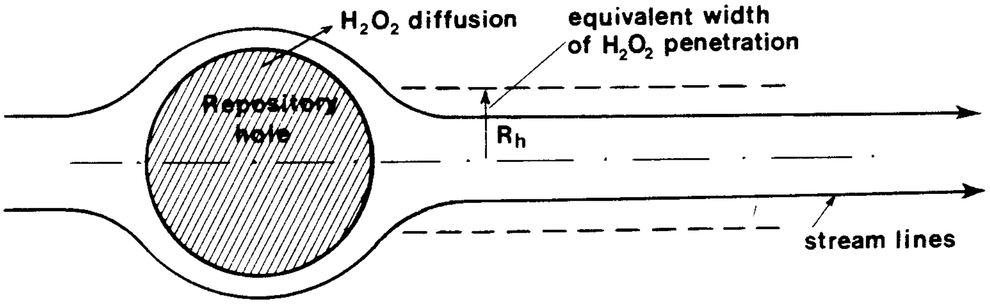


Figure 5. The water which passes the repository hole will pick up oxidizing agent to an equivalent depth of R_h with a concentration $c_0(t)$.

The numerical method described previously is used to solve this problem. Equation (3.16) is used to localize the redox front (x_b (case 1) = $3.2 \cdot 10^{-3}$ m and x_b (case 2) = $2.3 \cdot 10^{-2}$ m with eq (3.16)). In the computations the following steps in time and space were used:

	Case 1	Case 2
Timestep Δt (years)	5000	1000
Spacestep Δy (m)	0.34	0.34
- " - Δz (m)	0.50	0.73

The front extends 6.8 m in the flow direction and 1.6 m from the centre line at the widest place for case 1. In the other case it extends 18 m in the flow direction and 2.4 m at the widest place. The redox boundary along the fissure plane is shown for case 2 in figure 6.

The penetration of the redox front into the rock matrix at the inlet of the fissure is computed in case 1 to be $3.7 \cdot 10^{-2}$ m and in case 2 to be $S/2 = 0.5$ m. In figures 7 and 8 the redox front extension in the flow direction as well as in the transverse direction in the rock matrix is shown.

Upstream from the canister the redox front has in case 1 moved 0.9 m and in case 2 1.5 m in one million years.

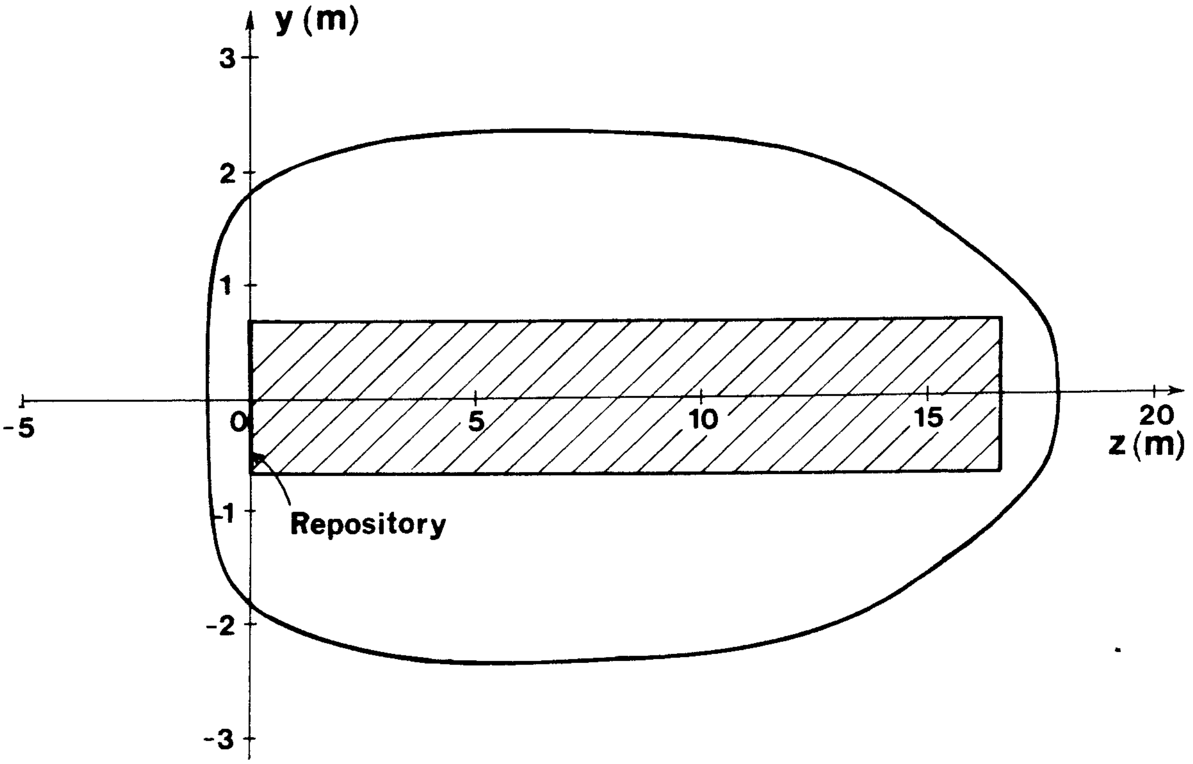


Figure 6. The extension of the redox front in a single fissure. Production 5800 mol in 10^6 years. $u_0 = 0.1$ l/m^2 year. (Case 2.) Redox front with advection only according to the analytical solution is marked with lines.

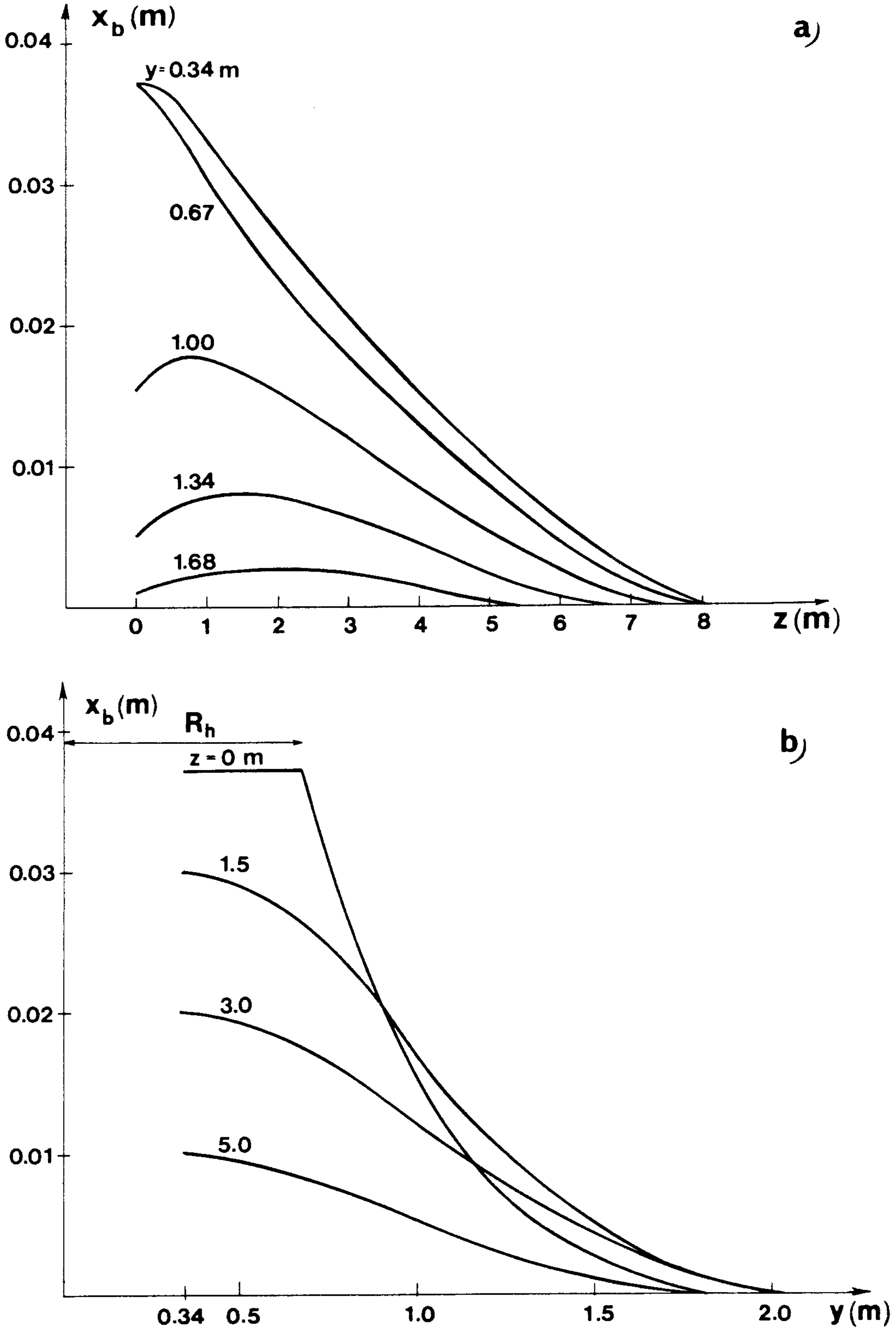


Figure 7. Penetration of the redox front into the rock matrix. (Case 1.)

a) In the flow direction (z) for different y.

b) In the transverse direction (y) for different z.

x_b = penetration depth.

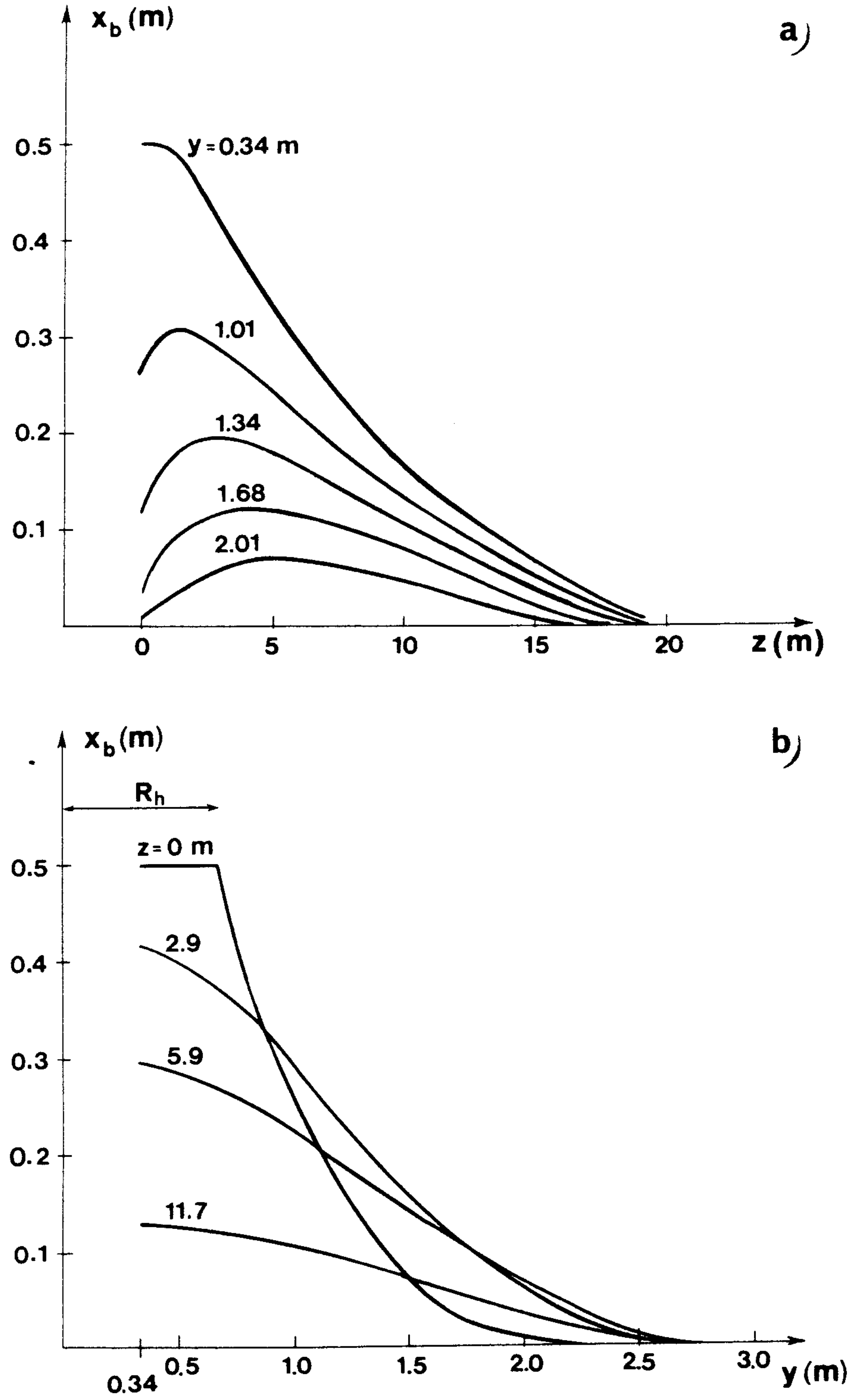


Figure 8. Penetration of the redox front into the rock matrix. (Case 2.)

a) In the flow direction (z) for different y.

b) In the transverse direction (y) for different z

x_b = penetration depth

5. The movement of a nuclide which precipitates at the redox front

Some of the important nuclides U, Np and Tc have a higher solubility in oxidizing waters than in reducing waters. Grenthe and Puigdomènech (1983) have discussed the dissolution of the fuel matrix and some of its constituents (Np, Pu) under conditions where radiolysis takes place, using a stepwise equilibrium calculation method. They assume that the oxidizing agent oxidizes the UO_2 of the matrix to the hexavalent state. This is then carried away as a carbonate complex out of the system. In the previous description H_2O_2 was used as the carrier with oxidizing power. The same would apply if UO_2^{2+} bound as some complex was the carrier with oxidizing power. The uranium would then be reduced at the redox front by reaction with ferrous iron. The minor constituents such as Tc and Np would be released congruently when the UO_2 matrix dissolves due to oxidation and complexing. Tc and Np may precipitate at the redox front because their solubility is considerably less in reducing waters. They precipitate along the whole redox front and are carried downstream from it by the water at a concentration equal to their solubility. The transverse spreading of the nuclides in the oxidized zone is fast enough to make them spread to the outer edges of the redox front (Neretnieks, Åslund 1983). If the width and the length of the redox front is known, the amount of water flowing through the oxidized region is known, the equivalent flow rate carrying the species can be computed in the following way. Figure 9 shows the oxidized region downstream from the repository. In the fissure the width 2 y_0 is oxidized and the water leaving this region has the solubility concentration of the precipitated species. The species has also penetrated a distance out into the water perpendicular to the flow direction. This can be expressed as an equivalent distance $\bar{\eta}$ (penetration thickness) with the solubility concentration (Bird, Stewart and Lightfoot 1960, p. 540 and Neretnieks 1980)

$$\bar{\eta} = 1.13 \sqrt{\frac{z_o \varepsilon}{u_o} \cdot D_v} \qquad (5.1)$$

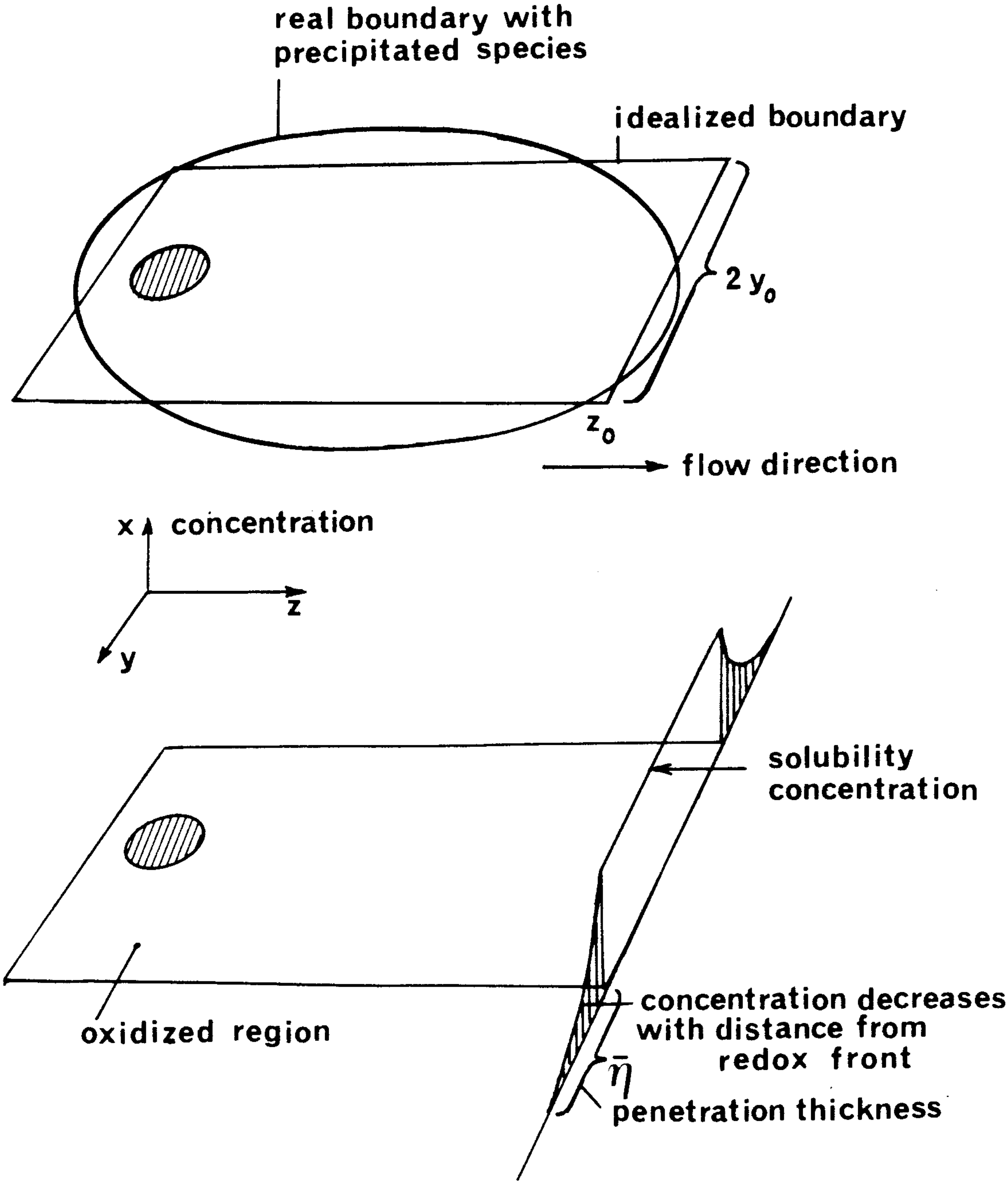


Figure 9. Shows that the water leaving the redox front has attained the equilibrium concentration c_0^{red} of the precipitated species. The species has also penetrated a distance $\bar{\eta}$ outside the front by diffusion.

The flow rate carrying species in concentration c_o^{red} then is

$$Q_{eq}^{red} = L \cdot (2\ y_o + 2\ \bar{\eta}) \cdot u_o \qquad (5.2)$$

where L is the length of the canister (or repository hole) 2 y_0 is the width of the redox front, z_0 its length, ε the porosity of the bedrock (2b/s) and u_0 the water flux in the bedrock. D_v is the diffusivity of the species.

For $z_0 = 7$ m, $\varepsilon = 2b/S = 5 \cdot 10^{-4}/5 = 1 \cdot 10^{-4}$, $D_v = 2 \cdot 10^{-9}$ m^2/s and $u_0 = 0.1 \cdot 10^{-3}$ m^3/m^2 year we find that $\bar{\eta} = 0.75$ m.

For L = 5 m and 2 y_0 = 3 m the equivalent oxidized crossection is 22.5 m^2 and Q_{eq}^{red} = 2.3 l/canister and year. This is 3.4 times larger than the flow rate (Q_{eq} = 0.67 l/canister,year) which carries species which do not have a solubility limitation. It can also be noted that Q_{eq}^{red} is considerably smaller than the average water flow rate per canister in the whole repository. The whole repository has an area ofabout 10^6 m^2 and contains 5000 canisters, which gives 200 m^2/canister. The average flow rate per canister is $u_0 \cdot 200$ = 20 l/canister.year. Thus only about 12 % of the water downstream from the repository is saturated with the precipitating species in this example.

6. Discussion and conclusions

In the most probable case the redox front has been calculated to move 6.8 m with the numerical method and 5.8 m with the analytical method in one million years. The numerical method takes diffusion in axial and transverse directions into consideration and has to be regarded as the more accurate method of the two. The total mass balance in the numerical method has a discrepancy of about 10 % when 360 elements and 200 time steps are used.

The penetration of the redox front into the rock matrix at the inlet of the fissure has with both methods been calculated to be $3.7 \cdot 10^{-2}$ m for the most probable case.

Gancarz and Curtis (1982b) have in a study on radiolysis effects in one of the natural OKLO reactors found surprisingly similar amounts of radiolysis products per tonne of spent fuel as is assumed to be produced in the most probable case.

In the computations the curvature of the cylinder is approximated to a plate with very little extension in the flow direction of water (z). Diffusion in the transverse direction from the plate is neglected. In the normal case species diffuse from the backfill into the rock matrix through the rock surface of the cylindrical hole that forms the repository. In our calculations diffusion into the rock matrix is assumed to begin at the inlet of the fissure.

The presence of an oxidized region gives rise to an increase of transport of those nuclides which have a higher solubility in oxidizing waters than in reducing waters. This is because they have time to diffuse from the redox front into the flowing water. The increase is moderate and only a small fraction of the water dowstream from a repository will be saturated with the nuclide.

7. Notation

$$B_o = \frac{1}{2\Delta t} + \alpha \left(\frac{u}{2\Delta z} + \frac{D_z}{\Delta z^2} + \frac{D_y}{\Delta y^2} + \frac{D_e}{2bx_{b,r,s,t}}\right)$$

$$B_1 = \frac{1}{2\Delta t} - (2-\alpha)\left(\frac{u}{2\Delta z} + \frac{D_z}{\Delta z^2} + \frac{D_y}{\Delta y^2} + \frac{D_e}{2bx_{b,r,s,t}}\right)$$

$$B_2 = \frac{D_z}{\Delta z^2}$$

$$B_3 = \frac{D_z}{\Delta z^2} + \frac{u}{\Delta z}$$

$$B_4 = \frac{D_y}{\Delta y^2}$$

b	half fissure width	(m)
c	concentration of oxidizing agent in water	$(\mathrm{mol/m^3})$
$c_o(t)$	concentration of oxidizing agent at inlet of fissure - time dependent	$(\mathrm{mol/m^3})$
c_s	concentration at surface of fissure of oxidizing agent	$(\mathrm{mol/m^3})$
$c_{r,s,t}$	concentration in element s,t at time r	$(\mathrm{mol/m^3})$
c_o^{red}	equilibrium concentration of precipitated nuclides at the redox front	$(\mathrm{mol/m^3})$
$D_e=D_p\varepsilon_p$	effective diffusivity in rock matrix	$(\mathrm{m^2/s})$
D_p	pore diffusivity	$(\mathrm{m^2/s})$
D_v	diffusivity in water	$(\mathrm{m^2/s})$
D_y	diffusivity in y-direction	$(\mathrm{m^2/s})$
D_z	diffusivity in z-direction	$(\mathrm{m^2/s})$
$D^* =$	$\frac{D_p \varepsilon_p c_o}{(S/2)^2 q_o f}$	$(\mathrm{s^{-1}})$

f	stochiometric factor	
L	length of repository hole	(m)
$m =$	$\frac{\varepsilon}{1-\varepsilon}$	
$N(t)$	production rate of oxidizing agents - time dependent	(mol/s)
$Q =$	q/q_o dimensionless concentration of reducing agent	
Q_{eq}	equivalent flow rate	(m^3/ canister•s)
Q_{eq}^{red}	equivalent flow rate carrying species in concentration c_o^{red}	(m^3/ canister•s)
q	concentration of reducing agent in rock matrix	(mol/m^3)
q_o	concentration of reducing agent in matrix at the inlet	(mol/m^3)
R	radius of cylindrical hole	
$2\ R_h$	equivalent flow width	(m)
s	fissure spacing	(m)
t	time	(s)
u	velocity of water in the fissure	(m/s)
u_o	flow rate of water in the bedrock	($m^3/m^2 \cdot s$)
x	distance into the rock matrix perpendicular to the fissure plane	(m)
x_b	distance of the redox front in the rock matrix	(m)
y	distance in the direction transverse to the flow in the fissure	(m)
$2y_o$	width of the redox front	(m)
$2\ y_{nr}$	number of Δy occupied by the canister in the numerical mesh	
z	distance in flow direction in the fissure	(m)
z_o	length of the redox front	(m)
$Z =$	$\frac{D_p \varepsilon_p z}{(S/2)^2 mu}$	
α	weighting factor in the numerical method	
ε	flow porosity of bedrock	
ε_p	diffusional porosity of rock	
$\bar{\eta}$	penetration thickness	(m)
$\Theta =$	$(t - \frac{z}{u})D^*$	

8. References

Bengtsson A, Grundfelt B, Magnusson M, Neretnieks I, Rasmuson A: Model Calculations of the Migration of Radionuclides from a Repository for Spent Nuclear Fuel. KEMAKTA Consultant Company, Royal Institute of Technology, KBS TR 83-48, May 1983.

Bird R B, Stewart W E, Lightfoot E N:
Transport phenomena, John Wiley & Sons, N Y, 1960.

Christensen H, Bjergbakke E:
Radiolysis of Groundwater from HLW Stored in Copper Canisters. Studsvik Energiteknik AB, KBS TR 82-02, 1982-06-29 a.

Christensen H, Bjergbakke E:
Radiolysis of Ground Water from Spent Fuel. Studsvik Energiteknik AB. KBS TR 82-18, November 1982b.

Fried J J, Combarnous M A:
Dispersion in Porous Media. Advances Hydroscience 7 (1971) 170.

Curtis D, Gancarz A:
Radiolysis in Nature: Evidence from the Oklo Natural Reactors, KBS TR 83-10, February 1983.

Grenthe I, Puigdomènech I, Bruno J:
The Possible Effects of Alfa and Beta Radiolysis on the Matrix Dissolution of Spent Nuclear Fuel. Royal Institute of Technology, KBS TR 83-02, January 1983.

Lapidus L and Pinder G S:
Numerical solution of partial differential equations in science and engineering. Wiley 1982.

Neretnieks I:
Adsorption of components having a saturation isotherm. Chemie Ingenieur-Technik 46, 1974, p. 781.

Neretnieks I:
Diffusion in the Rock Matrix: An Important Factor in Radionuclide Retardation? J Geophys Res 85 (1980), 4379.

Neretnieks I:
Leach Rates of High Level Waste and Spent Fuel - Limiting Rates as Determined by Backfill and Bedrock Conditions. Paper presented at the 5th International Symposium on the Scientific Basis for Nuclear Waste Management. Berlin 1982 June, Proceedings, North-Holland 1982a, p. 559-568.

Neretnieks I:
The Movement of a Redox Front Downstream from a Repository for Nuclear Waste. Royal Institute of Technology, KBS TR 82-16, April 1982b.

Neretnieks I, Åslund B:
The Movement of Radionuclides Past a Redox Front. Royal Institute of Technology, KBS TR 83-66, May 1983.

Perry R H and Chilton C H:
Chemical Engineers´ Handbook: 5th ed. 1973, McGraw Hill book company, N Y.

Skagius K, Neretnieks I:
Diffusion in Crystalline Rocks. Paper Presented at the 5th International Symposium on the Scientific Basis for Nuclear Waste Management. Berlin, June 1982. Proceedings, North-Holland 1982, p. 509-518.

Torstenfelt B, Allard B, Ittner T:
Iron Content and Reducing Capacity of Granite and Bentonite. Chalmers University of Technology, KBS TR 83-36, April 1983.

APPENDIX 1

The analytical solution of the movement of the redox front when there is no diffusion or dispersion in the axial and transverse directions.

The solution is given by Neretnieks (1982a).

When there is no film resistance the simplified equations can be used

$$Q(\Theta,Z) = \sqrt{2D^{*}t} - Z \quad \text{for} \quad \Theta \leqslant \frac{1}{2} \tag{A1}$$

$$Q(\Theta,Z) = \Theta - Z + \frac{1}{2} \quad \text{for} \quad \Theta > \frac{1}{2} \tag{A2}$$

where

$$Z = \frac{D_p \varepsilon_p z}{(S/2)^2 mu} \tag{A3}$$

$$D^{*} = \frac{D_p \varepsilon_p c_o}{(S/2)^2 q_o f} \tag{A4}$$

$$\Theta = (t - \frac{z}{u})D^{*} \tag{A5}$$

$$Q = q/q_o = x_b/(S/2) \tag{A6}$$

Case 1

$D_p\varepsilon_p = 5 \cdot 10^{-14}$ m^2/s

$c_o = 0.22$ mol/m^3 (average over 10^6 years)

$S = 5$ m

$q_o f = 500$ mol/m^3

$mu \approx u_o = 0.1 \cdot 10^{-3}$ m^3/m^2.year

$Q_{eq} = 0.67 \cdot 10^{-3}$ m^3/canister.year

This gives $\Theta = 1.08 \cdot 10^{-4}$ and with eq. (A1) for $Q = 0$ $Z = 1.47 \cdot 10^{-2}$. Eq. (A3) is used to compute how far downstream from the canister in the fissure the redox front has moved in 10^6 years. This gives $z = 5.8$ m. In the rock matrix, at $z = 0$, the redox front is at a distance $x_b = 3.7 \cdot 10^{-2}$ m from the fissure plane.

Case 2

$c_o = 43.3$ mol/m^3 (average over 10^6 years)

$S = 1$ m (5 fissures/canister)

The other parameters are the same as for case 1.

This gives $\Theta = 0.55$ and with eq (A2) for $Q = 0$ $Z = 1.05$ the redox front moves 16.6 m downstream from the canister in the fissure in 10^6 years and 0.5 into the rock matrix at $z = 0$.

LIST OF KBS's TECHNICAL REPORTS

1977-78

TR 121 KBS Technical Reports 1 - 120.
Summaries. Stockholm, May 1979.

1979

TR 79-28 The KBS Annual Report 1979.
KBS Technical Reports 79-01--79-27.
Summaries. Stockholm, March 1980.

1980

TR 80-26 The KBS Annual Report 1980.
KBS Technical Reports 80-01--80-25.
Summaries. Stockholm, March 1981.

1981

TR 81-17 The KBS Annual Report 1981.
KBS Technical Reports 81-01--81-16
Summaries. Stockholm, April 1982.

1983

TR 83-01 Radionuclide transport in a single fissure
A laboratory study
Trygve E Eriksen
Department of Nuclear Chemistry
The Royal Institute of Technology
Stockholm, Sweden 1983-01-19

TR 83-02 The possible effects of alfa and beta radiolysis
on the matrix dissolution of spent nuclear fuel
I Grenthe
I Puigdomènech
J Bruno
Department of Inorganic Chemistry
Royal Institute of Technology
Stockholm, Sweden January 1983

TR 83-03 Smectite alteration
Proceedings of a colloquium at State University of New York at Buffalo, May 26-27, 1982
Compiled by Duwayne M Anderson
State University of New York at Buffalo
February 15, 1983

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Roland Pusch
Division Soil Mechanics, University of Luleå
Luleå, Sweden, 1983-02-20

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Åke Bresle
Jozef Saers
Birgit Arrhenius
Archaeological Research Laboratory
University of Stockholm
Stockholm, Sweden 1983-01-02

TR 83-06 Investigation of the stress corrosion cracking of pure copper
L A Benjamin
D Hardie
R N Parkins
University of Newcastle upon Tyne
Department of Metallurgy and Engineering Materials
Newcastle upon Tyne, Great Britain, April 1983

TR 83-07 Sorption of radionuclides on geologic media - A literature survey. I: Fission Products
K Andersson
B Allard
Department of Nuclear Chemistry
Chalmers University of Technology
Göteborg, Sweden 1983-01-31

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U Olofsson
B Allard
M Bengtsson
B Torstenfelt
K Andersson
Department of Nuclear Chemistry
Chalmers University of Technology
Göteborg, Sweden 1983-01-30

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U Olofsson
B Allard
Department of Nucluear Chemistry
Chalmers University of Technology
Göteborg, Sweden 1983-02-15

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Evidence from the Oklo natural reactors
David B Curtis
Alexander J Gancarz
New Mexico, USA February 1983

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storage of unreprocessed spent nuclear fuel
Björn Sundblad
Ulla Bergström
Studsvik Energiteknik AB
Nyköping, Sweden 1983-02-07

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properties in PWR and BWR fuel using ORIGEN 2
Ove Edlund
Studsvik Energiteknik AB
Nyköping, Sweden 1983-03-07

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concrete
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Department of Nuclear Chemistry
Chalmers University of Technology
Göteborg, Sweden 1983-01-15

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J A Marinsky
State University of New York at Buffalo, Buffalo,NY
1983-03-31

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Kristina Skagius
Ivars Neretnieks
Royal Institute of Technology
Stockholm, Sweden 1983-03-11

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crystalline rock - chemical aspects
Roland Pusch
Division of Soil Mechanics, University of Luleå
1983-03-30

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Gideå Sif Laurent
Swedish Environmental Research Institute
Stockholm, Sweden 1983-03-09

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O Landström
Studsvik Energiteknik AB
C-E Klockars
O Persson
E-L Tullborg
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Swedish Geological
K Andersson
B Allard
B Torstenfelt
Chalmers University of Technology
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Sif Laurent
Swedish Environmental Research Institute
Stockholm, Sweden 1983-03-29

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for final disposal
1 Welded copper canisters
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B Lönnerberg, ASEA-ATOM
H Larker, ASEA
L Ageskog, VBB
May 1983

TR 83-21 An analysis of the conditions of gas migration
from a low-level radioactive waste repository
C Braester
Israel Institute of Technology, Haifa, Israel
R Thunvik
Royal Institute of Technology
November 1982

TR 83-22 Calculated temperature field in and around a
repository for spent nuclear fuel
Taivo Tarandi, VBB
Stockholm, Sweden April 1983

TR 83-23 Preparation of titanates and zeolites and their
uses in radioactive waste management, particularly
in the treatment of spent resins
Å Hultgren, editor
C Airola
Studsvik Energiteknik AB
S Forberg, Royal Institute of Technology
L Fälth, University of Lund
May 1983

TR 83-24 Corrosion resistance of a copper canister for
spent nuclear fuel
The Swedish Corrosion Research Institute and its
reference group
Stockholm, Sweden April 1983

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fuel canisters
A Sanderson, T F Szluha, J Turner
Welding Institute
Cambridge, United Kingdom April 1983

TR 83-26 The KBS UO_2 leaching program
Summary Report 1983-02-01
Ronald Forsyth, Studsvik Energiteknik AB
Nyköping, Sweden February 1983

TR 83-27 Radiation effects on the chemical environment
in a radioactive waste repository
Trygve Eriksen
Royal Institute of Technology, Stockholm
Arvid Jacobsson
University of Luleå, Luleå
Sweden 1983-07-01

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U Bergström
A-B Wilkens
Studsvik Energiteknik AB
Nyköping, Sweden 1983-06-08

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Otto Brotzen
Stockholm, Sweden April 1983

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ES-konsult AB
Stockholm, Sweden April 1983

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Ulf Thoregren
Swedish Geological
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Tekniska Röntgencentralen AB
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A Lambrosa
J A Marinsky
State University of New York
Buffalo, NY, USA April 1983

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Royal Institute of Technology, Stockholm
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Swedish Geological, Uppsala
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I Neretnieks
Royal Institute of Technology
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I Grenthe
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Swedish Environmental Research Institute
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Studsvik Energiteknik AB
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I Neretnieks
Royal Institute of Technology
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Royal Institute of Technology
Stockholm, Sweden 1983-06-03

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Stockholm, Sweden May 1983

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Luleå, Sweden May 31, 1983