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ABSTRACT

In a KBS-3 repository for spent nuclear fuel, radiolysis can occur if canisters are breached and water comes into contact with the fuel. The oxidants produced by radiolysis may migrate into the clay surrounding the canister and change the redox conditions from reducing to oxidizing. If much oxidants are produced, they can migrate to the water flowing in the fractures in the rock. Some of the oxidants also may oxidize the uranium and other nuclides in the fuel and make them more soluble. The nuclides will then migrate out in a higher oxidation state and may precipitate at the redox front.

Calculations were done for a production of 144 moles of oxidants in one million years. A higher and a much lower production were also considered. It was assumed that the canister is either totally or locally corroded. The results show that, for the most probable production rate, a large fraction of oxidants would be consumed in the clay. If the corrosion is local and there is a fracture opposite the damage, the amount of oxidant transported into the fracture would be significant. Here the advance of the redox front in the fracture would be some tens of metres. For the lowest production rate, the oxidants never reach the fractures in the rock. Only with improbably high production rates could the tips of the redox front move very long distances in isolated channels that are not part of a network.

CONTENTS

SUMMARY

In a KBS-3 repository for spent nuclear fuel, radiolysis can occur if and when the canisters are breached and water comes into contact with the fuel. The oxidizing agents produced by radiolysis of the water can migrate into the clay (bentonite) buffer around the canister and oxidize the reducing minerals. If much oxidant is produced, they can migrate further out into the rock matrix and into the water flowing in the fractures. Some of the oxidants also may oxidize the uranium and other nuclides in the fuel and make them more soluble. These nuclides will then migrate out in a higher oxidation state and themselves act as oxidants. They may be reduced again and precipitated at the redox front when they come into contact with the reducing minerals in the rock.

The production of oxidants by radiolysis is estimated at 144 moles in one million years. In the calculations of the redox front, two other levels of radiolysis production rate were considered. In the first hypothetical situation, iron is not present and no recombination of the radiolysis products takes place. The high production rate gives a total production of 29 000 moles of oxidants in one million years. In the second situation, a smaller production rate is assumed to occur, owing to limitations in the water availability. This is possible when there is only localized damage in the copper canister. Then the over pressure in the canister prevents water flowing into the canister. This reduced production rate is estimated to be about 100 times lower than the low production rate.

The calculations were made by considering two types of damage in the canister. One is when the canister is completely corroded and the other is when the canister has a small hole in the wall. With the reduced production rate the redox front never reaches the rock surrounding the repository hole; the front is confined within the clay. With the low production rate and when all the clay is reached by the oxidants (canister totally corroded), the redox front takes about one million years to reach the water flowing in the fractures in the rock. When only a small fraction of the clay can be reached by the oxidants (local corrosion), the redox front reaches the rock in some tens of thousand years. For the hypothetical high production rate, the clay is oxidized in a short time.

Once the front reaches the rock, the oxidants may find a water-bearing fracture and be carried away by the flowing water. They also may diffuse into the rock and into the still unoxidized clay. The fraction that is taken up by the flowing water will determine the advance of the redox front in the fracture. This fraction was less than 0.1 for the low production rate and less than 0.6 when a high production rate was assumed.

When the oxidants are transported away in the fracture, they may diffuse from the fracture into the rock and react with the reducing species in the rock. For the low production rate and with the canister locally corroded, the redox front will move only a few tens of metres. This applies for the channels with the fastest flow rates. For channels with smaller flow rates, the tip of the redox front is found much nearer the canister. For improbably high production rates, the tips of the redox front could move

large distances if the channels were isolated and not part of a network. This situation is unlikely.

There are many uncertainties concerning the rate of radiolysis, the geometry of the flow paths and the availability of reducing species in the clay and in the rock. Despite these uncertainties, it is unlikely that the redox front will ever pass the clay. If it does, the tips of the redox front will probably move less than a hundred metres, even in a channel with a high flow rate.

1 INTRODUCTION

In Sweden, storage of radioactive waste from nuclear power plants will be in a final repository at a depth of 500 m in crystalline rock. The waste will be sealed in copper canisters. The canister may be breached at some future time, allowing water to come in contact with the fuel. Radiation, especially α-radiation, will act by radiolysis and produce hydrogen and hydrogen peroxide (oxidants). The hydrogen is not very reactive and may diffuse away. But the hydrogen peroxide, which is a strong oxidizing agent, will change the redox conditions around the canister from reducing to oxidizing conditions.

The oxidizing agents around the canister may react with reducing species in the canister and around it, such as the Fe(II) minerals in the clay and rock. Oxidizing species that do not react in the clay may be transported to the water flowing in fractures in the rock around the repository hole. The oxidants may then move with the flowing water in the fractures and change the redox state from a reduced to an oxidized state. This would influence the solubilities and sorption properties of many radionuclides.

Some hydrogen peroxide may oxidize the uranium and other nuclides in the waste. These nuclides will act as oxidants when they encounter reducing minerals in the clay and rock. In the following discussion, the migration of oxidants includes all species in higher oxidation states that can change the redox potential of the water from "reducing" to "oxidizing".

The aim of this report is to study the movement of the redox front in relation to the type of corrosion to which the canister is subjected and to the various estimated levels of oxidant production. The canister is considered to be both locally and totally corroded. The advance of the redox front is evaluated for two levels of oxidant production, a hypothetical level (high production rate) and a more realistic level (low production rate) (Christensen and Bjergbakke, 1982). A third level will be also included, the reduced production rate (Neretnieks and Faghihi, 1991). For each type of corrosion, several pathways for the oxidizing species are discussed. Oxidizing agents remaining after the Fe(II) in the clay has been oxidized may diffuse directly into the rock and react with the Fe(II) in it, or they may diffuse into fractures and be removed by the flowing water.

2 PROCESSES IN THE CANISTER DEPOSITION HOLE

When the canister is pierced, water may flow into it and move into the gaps between the fuel rods and the zircaloy cladding. The water will be split by radiolysis into reducing (hydrogen) and oxidizing components (mainly hydrogen peroxide). The hydrogen is not very reactive and may escape. But the oxidizing agents may react, first with the reducing species in the canister and later with the reducing species in the clay around the canister. When the oxidants reach the rock, they may diffuse into the rock or be removed by the flowing water in the fractures.

In this model, it is assumed that oxidants do not react with the canister material. They will, however, oxidize uranium (IV) oxide to uranium (VI), and other redox–sensitive elements to their higher oxidation states. These species are more soluble in their higher oxidation state, and some may dissolve completely. The dissolved species diffuse out from the damaged canister. Some oxidants may not react with the fuel, and it is assumed that these diffuse out from the canister. Both the original oxidants and the oxidizing nuclides are assumed to be sufficiently reactive to oxidize the reducing agents, Fe(II) minerals, in the clay and rock outside the canister. The nuclides then revert to a lower oxidation state. Some of them may then precipitate because of their lower solubility in the lower oxidation state.

2.1 Alpha-radiolysis

Christensen and Bjergbakke (1982) calculated the hydrogen production resulting from α-radiation and α- and β-radiation in water penetrating a copper canister. In their calculations, they assumed that all the spaces between the fuel pellets and the zircaloy cladding are evenly filled with water. The water volume is 4.3 litres distributed over an area of 144 m^2.

They also found that for simultaneous α- and β-radiation, the β-radiation produces a great number of radicals that aid the recombination of hydrogen and hydrogen peroxide. Fe^{2+} and Fe^{3+} in the water act together with OH^- as catalytic scavenger pairs for the oxidants. For the conditions studied, the most probable production by radiolysis with a 0.03 mm film of water is 1 mole each of H_2O_2 and H_2 per square meter of wetted pellet surface in one million years. This gives 144 moles of H_2O_2 in one million years. A hypothetical situation is also calculated in which there is no iron present in solution and no recombination takes place. Here the production of oxidants would be increased to 200 moles/m^2 during the same period. This would result in a total production of nearly 29 000 moles of H_2O_2 in one million years.

A third situation will be also explored, where the production of hydrogen is reduced because of limitations in the water availability. If the canister has been locally corroded, then radiolysis in the interior of the canister causes the pressure to rise. This raised pressure is due to the hydrogen gas formed by the radiolysis of water. The pressure reduces the volume of water that penetrates the canister, and so the volume of water to be radiolysed is reduced (Neretnieks and Faghihi, 1991). The production of oxidants is reduced by a factor 100. This is called the reduced production rate.

Table 1 Hydrogen production in water irradiated with mixed α- and β-radiation, emitted by fuel from a boiling water reactor (BWR) with a burn–up of 33 MWday/tonne fuel. (The data are currently rough estimates only.)

Breaching time t_1, [a]	Production rates (N^c), [moles/a] "Low"	"High"	Integrated production, [moles] "Low"	"High"
100	$8.3 \cdot 10^{-4}$	3.6	0.054	260
300	$6.7 \cdot 10^{-4}$	2.5	0.2	860
10^3	$4.6 \cdot 10^{-4}$	1.17	0.6	2 100
10^4	$2.5 \cdot 10^{-4}$	0.25	3.84	8 600
10^5	$1.8 \cdot 10^{-4}$	0.013	23	20 600
10^6	$0.9 \cdot 10^{-4}$	0.006	144	29 000

The starting point for the modelling is the breach point of the canister at time t_1. Once the canister has been breached, α-radiation breaks down water molecules to produce oxidants, mainly hydrogen peroxide, and reducing agents, mainly hydrogen. The hydrogen is assumed to diffuse away. It is further assumed that no accumulation of oxidants takes place within the canister. The production rate of oxidants is found directly from Table 1. The oxidants are further assumed to react quickly with any reductant they encounter. These assumptions mean that a mass balance suffices to determine the amount of reductant that has reacted at any moment. For the sake of simplicity, the production rate is expressed as a function of the time. It forms an approximately straight line on a log-log plot and may be written as

$$N^c(t) = a_N \, t^{-b_N} \qquad b_N > 0 \tag{1}$$

where the coefficients a_N and b_N are parametres needed to fit the lines. Figure 1 shows the production rates from Table 1 (Christensen and Bjergbakke, 1982) and the lines fitted by using Equation (1). The parameter a_N was corrected to yield the total production shown in Table 1 for a time of one million years.

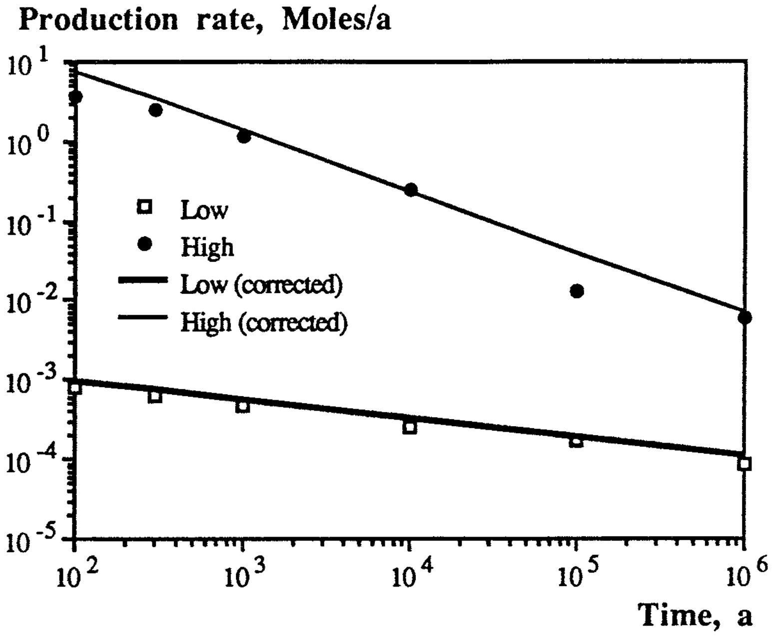


Figure 1 Production rates of hydrogen and hydrogen peroxide, with and without recombination. The straight lines show the fit used in the modelling.

2.2 The oxidation of Fe(II) in the clay

In the system, there are two large sources of reducing agents that are assumed not to participate in the reactions. The uranium oxide itself in one canister has a reducing capacity of about 10 000 equivalents when U(IV) is oxidized to U(VI). The copper canister can have over 10 tonnes of copper, depending on the wall thickness chosen. It would have 15 750 equivalents of reducing capacity per tonne of copper if oxidized to Cu(I), and twice the amount if oxidized to Cu(II). Both these potentially strong sinks are assumed not to react.

The oxidants and oxidized nuclides diffuse into the clay. They react with the ferrous iron, Fe(II), which is the main reducing agent in the clay and in the rock. The reaction between the oxidants and Fe(II) is written

$$2\,Fe^{2+} + H_2O_2 + 2H^+ \Longrightarrow 2\,Fe^{3+} + 2H_2O \qquad (2)$$

The various oxidants, including the oxidized nuclides, are collectively denoted by hydrogen peroxide, H_2O_2. It is assumed that the oxidation reaction is so fast that the two species (oxidants and reductants) cannot be present at the same time. Therefore a very sharp redox front will form, separating the reduced zone from the oxidized zone.

The oxidation of the Fe(II) in the clay is studied for two situations: a) the canister is completely corroded, and b) the breaching is local, corrosion taking place only at one point on the canister surface. Figure 2 shows views of both situations.

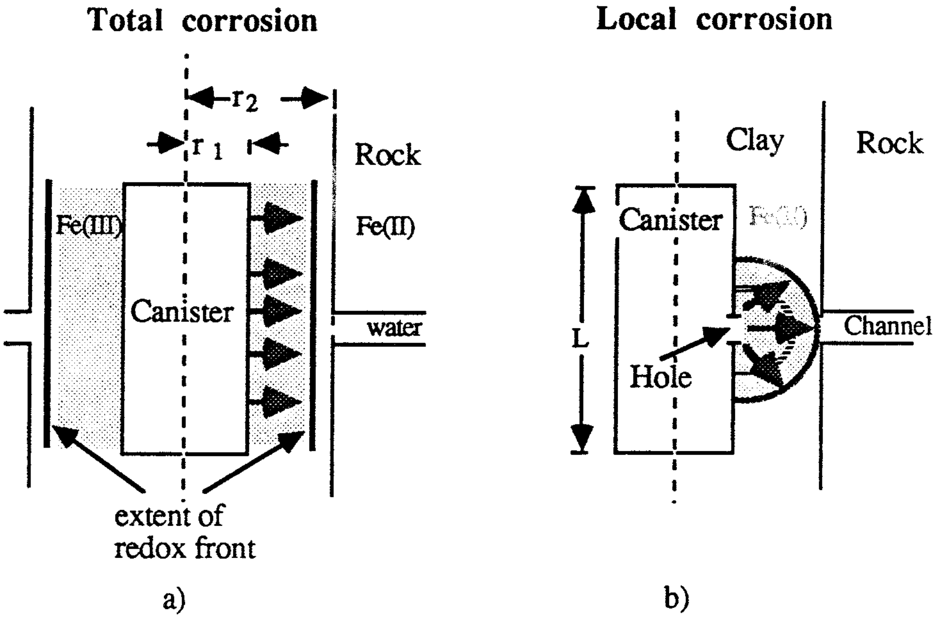


Figure 2 Two types of corrosion and advance of the redox front. The arrows indicate the direction of the spread of the redox front.

Calculations are first performed for total corrosion of the canister. Local corrosion is discussed later, as it is more complicated. Evaluating the release of oxidants into the water in a fracture requires some assumptions about the location of the hole in relation to the fracture, and if there are one or several holes.

In both types of corrosion, the solutions are similar; only the geometry is different. It is assumed that the oxidation reaction is very fast, that the oxidants do not react inside the canister, and that there is no accumulation of oxidants in the system. A material balance may then be found between the oxidants produced by radiolysis and the reducing species that are oxidized.

Oxidants are only produced after the canister is breached. For example, Table 1 shows that if the canister breaches after 10^5 years, the total production to one million years will be 121 moles (144 - 23 moles). The content of reducing species in the clay, Fe(II), may vary over a wide range. So the calculations are done for two concentrations of Fe(II) in the clay, 0.1 and 1.0 % by weight. The reducing capacity of the clay is calculated as

$$\text{Reducing capacity} = V_c \cdot q_o \cdot f \tag{3}$$

where V_c is the volume of clay, q_0 is the concentration of the reducing species in the clay, and f is the stoichiometric factor for the redox reaction.

a) <u>The canister surface is totally corroded</u>

This is illustrated in Figure 2a. Here it is assumed that the release of oxidants from the canister into the clay starts after the canister is totally corroded. If the concentration in the clay is 0.1 % by weight, the reducing capacity of the clay is equivalent to a production of 120 moles of oxidants. From the production data (Table 1) for the most probable production rate, the low production rate, the total production of oxidants over one million years is slightly larger than the reducing capacity of the clay. This means that during the period $0.8–1 \cdot 10^6$ years, all the clay is oxidized. For the high production rate, the clay is completely oxidized in a very short time.

The reduced production rate, defined in Section 2.1, is less probable here. This scenario is based on the assumption that the access of water to the canister is limited by the over pressure in the canister. This would not be so if the canister were totally corroded. However, if this scenario is valid, the oxidizing species are not sufficient to oxidize all the reducing species in the clay. About 1.0 % of the clay will be oxidized in one million years.

The time needed to oxidize the reducing species in the clay is greatly increased if the concentration of Fe(II) in the clay is 1.0 % by weight. The reducing capacity of the clay will be equivalent to a production of 1 200 moles of H_2O_2. The ferrous iron in the clay would be completely oxidized only with the high production rate. This time is calculated by a mass balance between the reducing capacity of the clay and the production of oxidants, for the time interval between a canister breach and a given time. The production of oxidants is

$$P = \int_{t_1}^{t_2} N^c(t)\,dt \tag{4}$$

where P is the total production of oxidants from time t_1, the time at which the release of oxidants starts (canister breach) to time t_2, the time at which the redox front reaches the rock. This integral is solved analytically and the time t_2 is obtained as

$$t_2 = \left[\frac{q_0\, f\, (1-b_N)}{a_N} V_c + t_1^{(1-b_N)} \right]^{\frac{1}{(1-b_N)}} \tag{5}$$

where V_c is the volume of clay to be oxidized. Here, only the clay radially surrounding the canister is considered. The clay above and below is not included. If it is, the amount of clay is more than doubled.

Table 2 shows the time interval (t_2-t_1) that the redox front takes to reach the interface between clay and rock. The calculations were made for concentrations of 0.1 and 1.0 % by weight of Fe(II) in the clay, and for different breaching times for the three radiolysis production rates discussed in Section 2.1.

For the high production rate, the time needed to reach the rock is very short for both 0.1 and 1.0 % by weight of Fe(II) in the clay. For the most probable production rate (low production rate) and 0.1 % by weight of the reducing species in the clay, the time is about one million years. Otherwise this time is very long; during the first million years only a small part of the clay is oxidized.

Table 2 Canister is totally corroded. Times (t_2-t_1) that the redox front takes to reach the rock, for various breaching times and production rates of oxidant. The oxidized volume of clay is 6.63 m^3.

	Time that the redox front takes to reach the rock, (t_2-t_1) [a]					
Production rates	Reduced		Low		High	
Fe(II) in clay	0.1 %	1.0 %	0.1 %	1.0 %	0.1 %	1.0 %
Breaching time t_1 [a]						
10^2	$> 10^6$	$> 10^6$	$0.78 \cdot 10^6$	$> 10^6$	17	280
10^3	$> 10^6$	$> 10^6$	$0.78 \cdot 10^6$	$> 10^6$	93	1260
10^4	$> 10^6$	$> 10^6$	$0.81 \cdot 10^6$	$> 10^6$	525	6300
10^5	$> 10^6$	$> 10^6$	$1.00 \cdot 10^6$	$> 10^6$	3000	33000

b) The canister surface is locally corroded

Here, corrosion takes place only at one point. It is assumed that the hole in the canister wall is exactly opposite a water-bearing fracture. It is also assumed that the hole diameter is small compared with the dimensions of the canister. The volume of clay to be oxidized, before the oxidants reach the fracture, was approximated by a sphere centred on the small hole. The radius (r_2-r_1) of the sphere is the distance between the small hole and the rock. The volume of clay to be oxidized is less than the 2 % of the clay surrounding the canister, approximately 0.12 m^3. The time at which the oxidants reach the water flowing in the fracture, t_2, is calculated by using Equation (5). This time is much shorter than before, because the volume of clay to be oxidized is much smaller than when the canister is totally corroded (see Figure 2b).

For an Fe(II) content in the clay of 0.1 % by weight, the reducing capacity of the clay is equivalent to a production of about 2.5 moles of H_2O_2. Thus for the reduced production rate (1.4 moles in one million years) there are not enough oxidizing agents to oxidize the clay between the hole in the canister and the fracture in the rock. The reduced production rate is the most probable if the canister is locally corroded and the water availability is very limited.

Table 3 Canister is locally corroded. Times (t_2-t_1) that the redox front takes to reach the rock, for various breaching times and production rates of oxidant. The oxidized volume of clay is 0.12 m^3.

	Time that the redox front takes to reach the rock, (t_2-t_1) [a]					
Production rates	Reduced		Low		High	
Fe(II) in clay	0.1 %	1.0 %	0.1 %	1.0 %	0.1 %	1.0 %
Breaching time t_1 [a]						
10^2	$> 10^6$	$> 10^6$	$4.4 \cdot 10^3$	$0.81 \cdot 10^5$	0.3	3
10^3	$> 10^6$	$> 10^6$	$4.8 \cdot 10^3$	$0.83 \cdot 10^5$	1.6	16
10^4	$> 10^6$	$> 10^6$	$6.9 \cdot 10^3$	$0.92 \cdot 10^5$	9.1	92
10^5	$> 10^6$	$> 10^6$	$11.2 \cdot 10^3$	$1.23 \cdot 10^5$	52.0	525

Calculations were made for various breaching times and concentrations of 0.1 and 1.0 % by weight Fe(II) in the clay for the three radiolysis production rates. Results for the time that the redox front takes to reach the interface between clay and rock are shown in Table 3. For the high production rate the times to reach the fracture are very short, less than 1 000 years. For the low production rate these times are also short (less than 12 000 years), unless an Fe(II) content of 1.0 % by weight is used in the calculations. For the reduced production rate the times are very long.

3 FRACTION OF OXIDANTS REACHING THE FRACTURE

3.1 General considerations

The transport of oxidants into the water in the fracture begins when the redox front has reached the mouth of the fracture at time t_2. At this time, not all the oxidant produced in the canister by radiolysis diffuses into the fracture. The amount diffusing into the fracture depends mainly on the amount of oxidant diffusing into the rock from the clay and on the amount of oxidant reacting with the Fe(II) in the zone of clay not yet oxidized. For times greater than t_2, there are several possible pathways. The relative importance of these pathways is determinated by their resistance to the transport.

For example, if the canister is totally corroded, two pathways can be distinguished: diffusion into the water in the fracture and direct diffusion into the rock from the clay. Initially, the resistance to the diffusion into the rock is small compared to the resistances for diffusion into the fracture inlet and into the flowing water in the fracture. A concentration profile is rapidly formed in the water that flows around the canister deposition hole in the fracture. The resistance to diffusion into the rock progressively increases, because the rock nearest the clay is oxidized and this increases its diffusion length. A centimetre of rock has the same diffusion resistance as 50 centimetres of clay.

If there is no accumulation of oxidants in the oxidized region and within the canister, the amount of oxidants per unit time passing into the fracture in the rock, N^f, may be expressed as

$$N^f = K \cdot \left(c(t) - c_\infty\right) \tag{6}$$

where K is a mass transfer coefficient, c(t) is the concentration in the clay, and c_∞ is the concentration in the water far from the repository hole (assumed to be zero).

The method for determining c(t) is as follows. In the rock matrix, the rate of uptake from the clay depends on the concentration c(t) at the interface and on how far the rock has already been oxidized. The concentration drop from c(t) to zero over the thickness of the oxidized rock determines the gradient for further transport of oxidants into the rock. For the oxidizing agents passing into the water in the fracture, the rate of transport also will depend on c(t) at the fracture mouth and on the mass transfer coefficient. The latter is expressed as an equivalent flow rate, Q_{eq}. The complication is that the rate of transport in both pathways depends on c(t), which in turn is determined by the two diffusion rates. The equations for the transport rates thus must be solved simultaneously. The rate of transport to the fracture, N^f, is

$$N^f = Q_{eq} \cdot c(t) \tag{7}$$

The rate of transport into the rock, N^r, is

$$N^r = -D_e \cdot A \cdot \left(\frac{d\,c(t)}{dx}\right)_{x=0} = D_e \cdot A \cdot \frac{c(t)}{x_r} \tag{8}$$

for the pseudo steady-state approximation possible here (Neretnieks, 1983). The intruding oxidizing agent will oxidize more rock, and the redox front will move with a rate $\frac{dx_r}{dt}$ so that N^r becomes

$$N^r = \frac{dx_r}{dt} \cdot A \cdot q_o \cdot f \tag{9}$$

Combining Equations (8) and (9) and integrating gives the momentary location of the redox front $x_r(t)$

$$x_r(t) = \left(\frac{2\,D_e}{q_o \cdot f} \cdot \int_{t_2}^{t} c(t)\,dt\right)^{1/2} \tag{10}$$

It is possible to account for the diffusion resistance in the clay as well. This was actually done in the computations. It was found that this resistance was noticeable only when the penetration depth into the rock was very slight. The full equations for this resistance are not given here. When the whole canister is degraded, the contact area with the rock (A) is taken as the mantel area of the hole with the same height as the canister. If the concentration is the same throughout the clay, a mass balance of an elemental volume in the clay (Figure 3) gives

$$V \cdot \frac{d\,c}{dt} = N^c - Q_{eq} \cdot c(t) - N^r \tag{11}$$

where V is the water volume in the clay. An expression for N^r can be obtained from Equations (8) and (10) as

$$N^r = D_e \cdot A \cdot c(t) \cdot \left(\frac{2D_e}{q_o \cdot f} \int_{t_2}^{t} c(t)\,dt\right)^{-1/2} \tag{12}$$

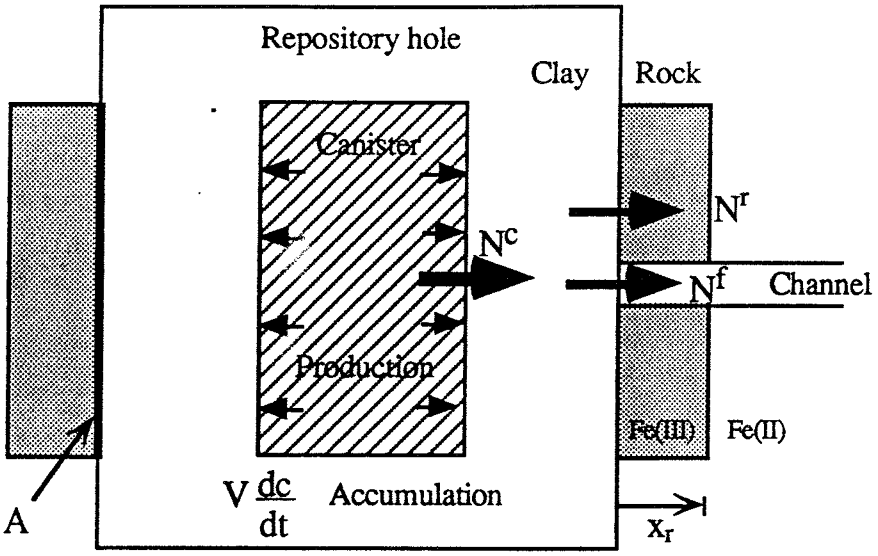


Figure 3. Production, accumulation and uptake in rock and water in a fracture.

The value of c(t) can now be found. Equations (11) and (12) form a combined differential and integral equation that is solved numerically for c(t). Analysis of Equation (11) shows that the accumulation term $V\frac{dc}{dt}$ is very small compared to any of the terms on the right-hand side. Neglecting this term considerably simplifies the solution of Equation (11) and has very little influence on the results. The simplified equation was therefore used in the calculations. The value of N^f is then directly obtained from Equation (6). The fraction of oxidant produced that enters the water in the fracture is expressed by the ratio

$$N^f/N^c = \varphi(t) \qquad (13)$$

If the canister is locally corroded, the geometry of the oxidized zone (Figure 2b) is simplified to a cylinder as shown in Figure 4. The cylinder at the initial time (t_2) has a volume of 0.12 m^3, equivalent to the volume of clay oxidized when the redox front reaches the fracture. Three pathways indicated by the arrows in Figure 4 are identified: to the still unoxidized clay, to the rock, and to the fracture. For times larger than t_2, the cylinder grows in the direction of the unoxidized clay (radial direction) and in the direction of the rock (axial direction).

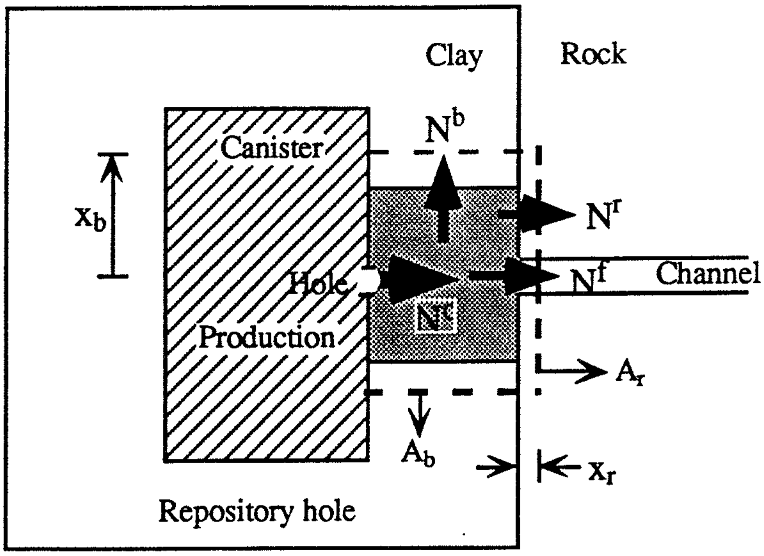


Figure 4. Production of oxidants, oxidation of clay, and uptake in water in a fracture and in rock. The dashed lines indicate the growth of the cylinder into the clay and rock.

For local corrosion, the further oxidation of the clay is estimated, as well as the uptake into the rock and fracture. Then if N^b is the flow rate to the unoxidized clay and the concentration throughout the clay is the same, a mass balance of an elemental volume in the clay gives

$$V \cdot \frac{dc}{dt} = N^c - Q_{eq} \cdot c(t) - N^r - N^b \qquad (14)$$

As before, Equation (14) is simplified by assuming no accumulation in the clay. The transport of oxidants is governed by the relative resistances between the pathways. In the calculations of the resistances in the various pathways, the areas of contact are not constant. They grow with the penetration into the rock (x_r) or into the clay (x_b). In Figure 4, A_b is the contact area between oxidized and unoxidized clay, and A_r is the contact area between oxidized and unoxidized rock. The gradients for transport to the clay and rock are taken over the distances x_b and x_r in the figure.

3.2 Calculating the fraction of oxidants entering the fracture

The resistance of the pathway into the fracture is made up of three resistances: that for the transport by diffusion through the clay, that for the transport from the clay into the fracture mouth, and that for the transport into the flowing water in the fracture, which is represented by a film resistance.

The fraction of oxidant entering the water in the fracture depends on the production rate and the concentration of Fe(II) in the clay and in the rock. This fraction will be calculated as a function of time. When the redox front reaches the fracture, the transport pathways that have to be considered are: oxidants diffusing into the fracture, oxidants diffusing into the rock from the clay, and oxidants diffusing into the unoxidized clay when the canister is partially damaged.

The relative mass flow of oxidants into the water in the fracture is independent of the oxidant concentration. It depends only on the relative values of the resistances for the various pathways, because there is no accumulation of oxidants in the pore water. The data used in the calculations are shown in Table 4.

Table 4 Data used to calculate the fraction of oxidants entering the water in the fracture.

Variable	Units	Clay	Rock
Effective diffusivity, D_e	m^2/s	$2.5 \cdot 10^{-12}$	$5.0 \cdot 10^{-14}$
Concentration of Fe(II)	% by weight	0.1-1.0	1.0-8.0
Volume of clay, V_c	m^3	6.6	
Average water flux, u_0	$l/m^2 \cdot a$	0.1	
Fracture aperture, δ	m	10^{-4}	
Radius of the repository hole, r_2	m	0.75	
Radius of the canister, r_1	m	0.375	
Length of the canister, L	m	5.0	
Diffusivity in water, D_w	m^2/s	$3.9 \cdot 10^{-9}$	

<u>Canister totally corroded</u>

Here it is assumed that all the clay surrounding the canister has been oxidized. Two transport pathways are distinguished: one into the fracture and the other into the rock surrounding the repository hole. The fraction of oxidants that diffuses into the water in the fracture is calculated by considering the relative resistances for these two pathways.

Some simplifying assumptions are made. For example, the resistance to the transport of oxidants into the rock is calculated by considering the whole cross section of the clay. In reality, each pathway uses only a fraction of this area for diffusion. This assumption is only valid for slight penetration of oxidants into the rock.

Figure 5 shows the fraction of oxidants that diffuses into the water in the fracture and into the rock, for various penetrations into the rock. These relationships depend on the geometry of the system and on the water flow rate in the fracture. Initially, when the redox front has just reached the rock, the fraction of oxidants passing into the water in the fracture is negligible. The resistance to the transport of oxidants into the rock increases with the penetration of oxidants into the rock. So the fraction of oxidants transported into the fracture begins to increase. For example, for a penetration of 50 cm into the rock, 40 % of oxidants diffuse into the fracture.

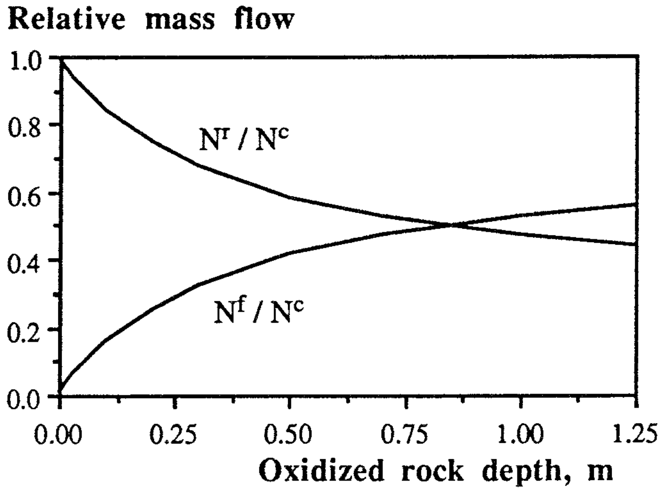


Figure 5 Fraction of oxidants that diffuses into the rock surrounding the canister deposition hole and into the water in the fracture. The average flow rate of water in the fracture was 8.5 l/a.

The variation in oxidant fraction for two concentrations of Fe(II) in the rock is shown in Figure 6 for a high production rate and a breaching time of 10 000 years. The figure on the right shows the penetration of oxidants from the clay into the rock. For a totally corroded canister and low production rates, most of the oxidants are consumed by the clay. Over one million years the penetration in the rock is very small, and therefore the fraction of oxidants into the water is small, see Figure 5.

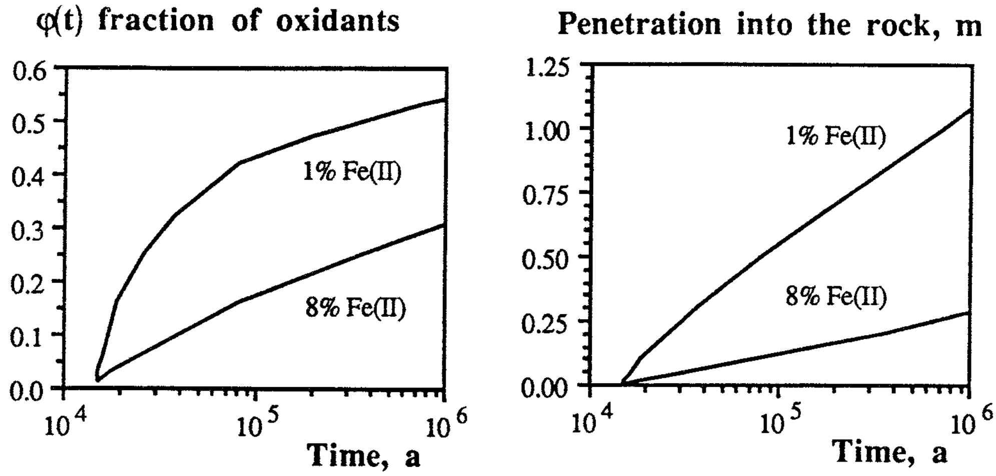


Figure 6. High production rate. Fraction of oxidants entering the water in the fracture and penetration of oxidants from the clay into the rock, for two concentrations of Fe(II) in the rock and an average water flow rate in the fracture of 8.5 l/a.

Canister locally corroded

When the redox front reaches the fracture, only a small part of the clay has been oxidized. About 98 % of the ferrous iron in the clay has not yet been oxidized. This means that a significant part of the oxidants produced will be consumed by the clay.

The calculations are similar to those for a totally corroded canister. The situation is more complex, however, because diffusion into the unoxidized clay must be included. The oxidants are thus transported through three pathways. The first goes into the water in the fracture, the second goes into the rock, and the third corresponds to the fraction of oxidants that reacts with the still unoxidized clay. Some assumptions must be made for the geometry of the contact areas between oxidized and reduced clay, and between the oxidized clay and the rock. The geometry is simplified to a cylinder as before.

The pathway into the unoxidized clay is the most important, because the diffusion in the clay is about 50 times larger than the diffusion in the rock. When the volume of oxidized clay is small, most of the oxidants diffuse into the unoxidized clay. Then the fraction that diffuses into the fracture is small. When all the clay is oxidized (up to a limit of 6.6 m^3), the situation is quite similar to a totally corroded canister.

Figures 7 and 9 show the fraction of oxidants passing through the various pathways for low and high production rates respectively. They also show the average penetration into the rock from the clay. The flow rate of oxidants and the cumulative mass of oxidants into the water in the fracture are shown in Figures 8 and 10. The calculations were done for an average flow rate of water in the channel of 8.5 l/a and a breaching time (t_1)

of 1000 years. The time at which the oxidants reached the fracture mouth (t_2), was 1 016 years for the high production rate and 84 000 years for the low production rate, see Table 3.

With a low production rate the clay consumes a large part of the oxidants. Then the fraction of oxidants entering the fracture is very small, reaching only about 10 % after one million years. As shown in Figure 8, the amount that has actually entered the fracture is about 5 % after one million years. For a high production rate, the fraction is much larger; 30 % after one million years.

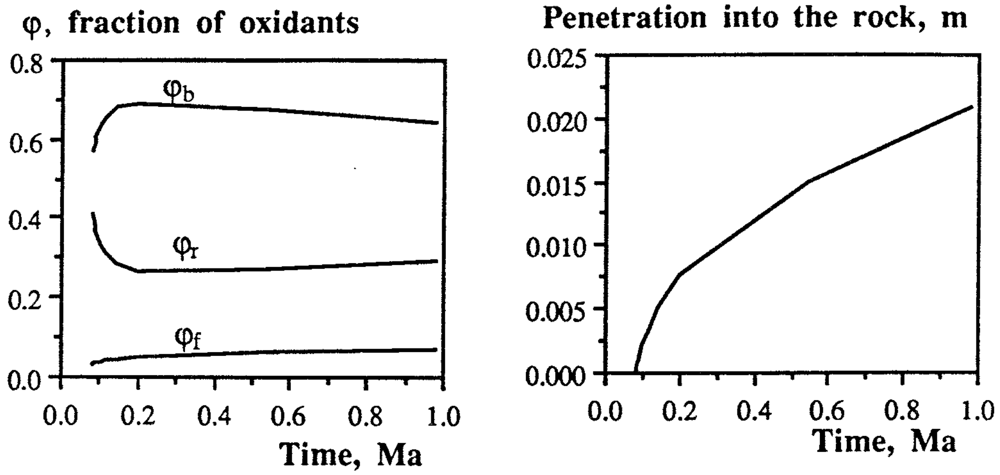


Figure 7. Low production rate. Fraction of oxidants entering the water in the fracture and penetration of oxidants from the clay into the rock, for an average water flow rate in the fracture of 8.5 l/a and for an Fe(II) concentration of 1.0 % by weight in clay and 8.0 % by weight in rock. φ_b = fraction entering unoxidized clay; φ_r = fraction entering the rock; φ_f = fraction entering the fracture.

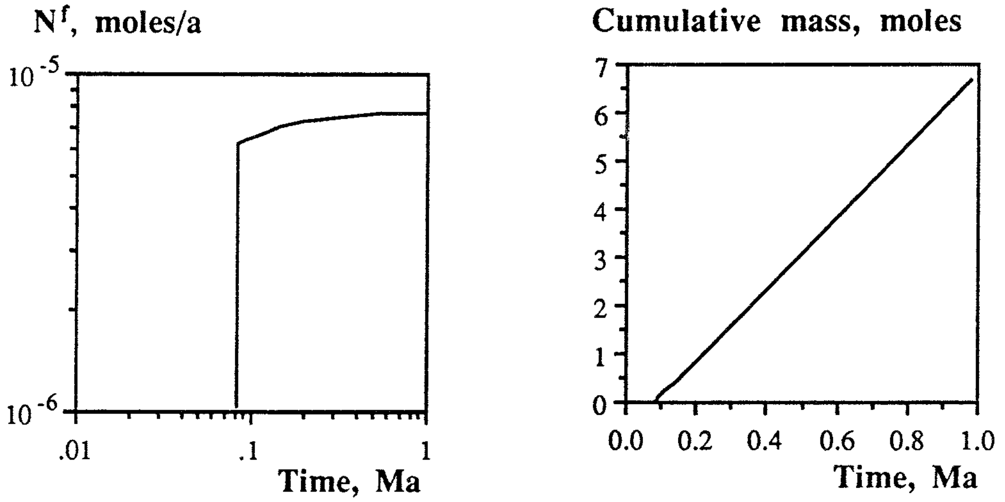


Figure 8. Low production rate. Flow rate and cumulative mass of oxidants entering the water in the fracture, for an average water flow rate in the fracture of 8.5 l/a and for an Fe(II) concentration of 1.0 % by weight in clay and 8.0 % by weight in rock.

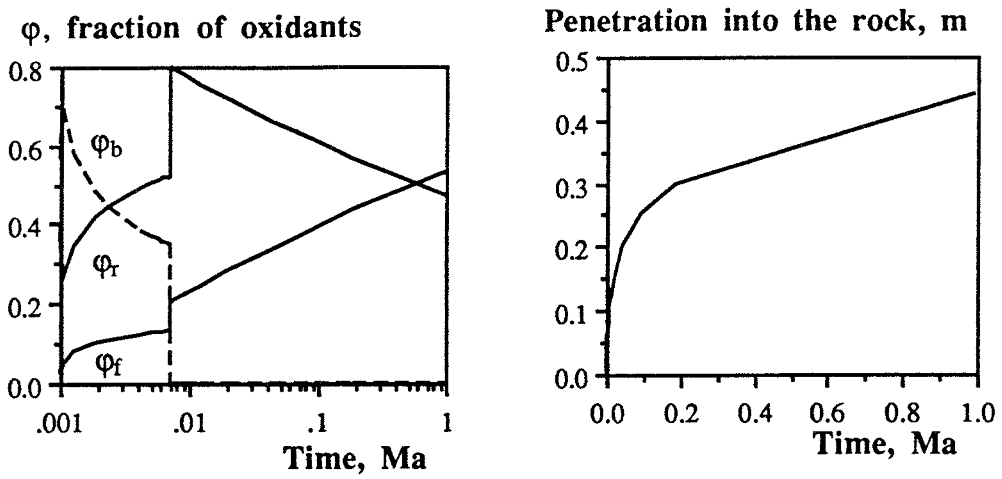


Figure 9. High production rate. Fraction of oxidants entering the water in the fracture and penetration of oxidants from the clay into the rock, for an average water flow rate in the fracture of 8.5 l/a and for an Fe(II) concentration of 1.0 % by weight in clay and 8.0 % by weight in rock. φ_b = fraction entering unoxidized clay; φ_r = fraction entering the rock; φ_f = fraction entering the fracture.

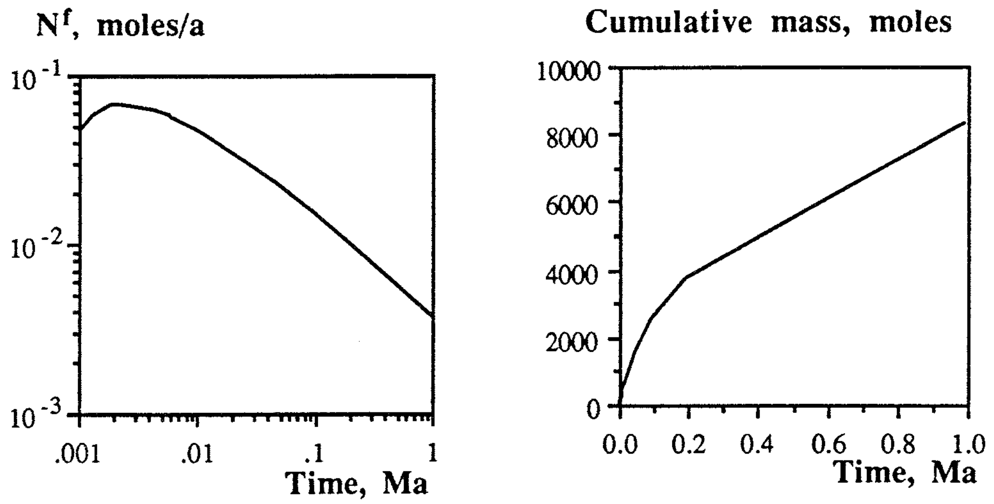


Figure 10. High production rate. Flow rate and cumulative mass of oxidants entering the water in the fracture, for an average water flow rate in the fracture of 8.5 l/a and for an Fe(II) concentration of 1.0 % by weight in clay and 8.0 % by weight in rock.

4 PROCESSES IN THE FRACTURED ROCK SYSTEM

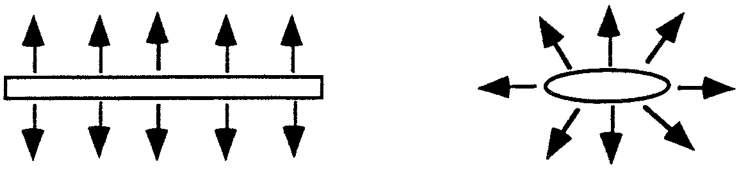
The oxidants that reach the mouth of the fracture will diffuse into the flowing water. A concentration profile will develop in the water, which will become deeper the further along the fracture the water has flowed. When the water leaves the canister hole, it has picked up some oxidants. A solution for the diffusion equation in the flowing water is available for flat surfaces (Bird et al., 1960, p. 537) and is used here as an approximation for the curved surface

$$N = Q'_{eq} \cdot c(t) = 4 \cdot \delta \cdot \sqrt{D_w \cdot U \cdot r} \cdot c(t) \qquad (15)$$

where r is the radius of the hole, U the water velocity in the fracture, δ the fracture aperture and D_w the diffusivity of the oxidants in water. For the sake of simplicity, it is assumed that the oxidants do not react in the fracture and do not diffuse into the rock bordering the fracture near the deposition hole; they all enter the flowing water. Further downstream, the oxidants may react with reducing species on the fracture surface or diffuse into the rock matrix to react with the Fe(II) in the rock.

The transport of oxidants in fractured rock has been modelled by using a quasi-steady state in the rock matrix, as developed by Neretnieks (1983) and Romero et al. (1992). They solved the model by using a constant concentration at the fracture mouth. Here, this concentration varies with time. The rock is modelled as a fractured medium with sparse channels in the fracture planes. The oxidants are transported by the water flowing in these channels. The oxidants may diffuse into the rock matrix and react with the reducing species present in the rock, Fe(II). Initially, the diffusion in the rock is limited to locations close to the fracture, in the order of millimetres or centimetres. If the width of the channel is much larger than the penetration length, then the diffusion may be described as diffusion perpendicular to the fracture plane and a system of rectangular axes can be used. After long times, the diffusion is no longer perpendicular to the fracture plane, but radial. Then the diffusion into the rock is better described as diffusion from a cylindrical surface. Figure 11 shows these two situations.

In this report, the calculations are performed for times up to one million years. These times are not long enough to justify the use of cylindrical coordinates, because the channels are thought to have widths of tens of centimetres or more. In these calculations, it is assumed that the channel width is 1 metre. If the penetration length is comparable to the channel width, the difference between the rectangular and the cylindrical model is small. In some situations, the penetration into the rock may reach some tens of centimetres.



Wide channel and
short penetration depth
gives lineal diffusion

Narrow channel
gives radial diffusion

Figure 11 Diffusion process of the oxidants in wide and narrow channels.

The oxidants released from the clay into the fracture will be transported into the 1–meter–wide channel downstream. Then the time-dependent concentration of oxidants at the inlet can be calculated from the fraction of oxidants that actually diffuses into the fracture and the water flow rate in the channel

$$c_f(t) = \frac{N^f}{Q_{ch}} \tag{16}$$

where N^f is the release rate of oxidants entering the fracture and Q_{ch} the water flow rate in the channel. With rectangular coordinates, the advective transport of a species along a fracture (neglecting axial dispersion) is given by Neretnieks (1983) as

$$\frac{\partial c^f}{\partial t} + u\frac{\partial c^f}{\partial z} + \frac{f}{m}\frac{\partial q}{\partial t} = 0 \tag{17}$$

The last term accounts for the diffusion into the rock, c^f is the oxidant concentration in the water in the fracture, u is the water velocity in the fracture, f is the stoichiometric factor for the oxidation reaction, q is the average concentration of reducing species Fe(II) in the rock, and m is the ratio of the water volume in the fracture to the solid volume of the rock.

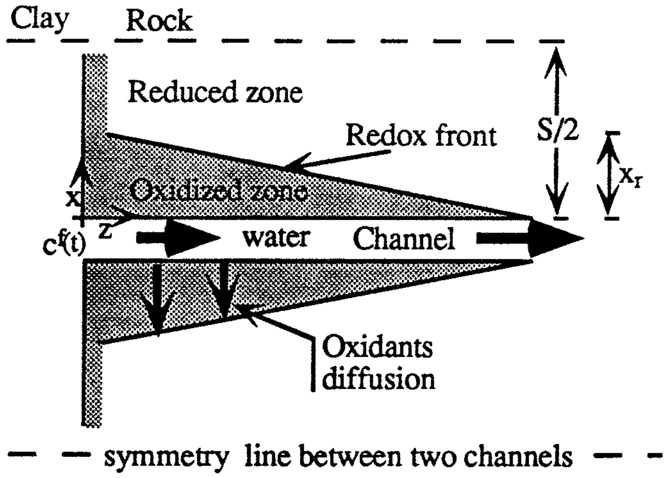


Figure 12 View of the advance of the redox front. The oxidants diffusion is shown by the arrows perpendicular to the channel.

The diffusion mechanism into the rock is modelled as diffusion from two water channels into a slab of thickness S. A schematic view is shown in Figure 12. The initial and boundary conditions may be expressed as follows:

Initial conditions (at $t = t_2$)

$c^f = 0$ at $z \geq 0$

$c_p, q = 0$ $z \geq 0$, and $x \geq 0$

Boundary conditions (at $t > t_2$)

$c^f = c^f(t)$ at $z = 0$

$c^f = 0$ $z = \infty$

$c_p = c^f$ $x = 0$

$c_p = 0$ $x = x_r$

From a differential mass balance, the rate of movement of the redox front perpendicular to the channel is

$$\frac{dx_r}{dt} = - \frac{D_p \cdot \varepsilon_p}{q_o \cdot f} \left(\frac{dc_p(x,t)}{dx}\right)_{x_r} \tag{18}$$

The following definitions are made for the group of variables D* and the dimensionless variables Q, C, θ, and Z:

$$D^* = \frac{D_p \cdot \varepsilon_p \cdot c_o}{(S/2)^2 \cdot q_o \cdot f} \qquad Q = \frac{q}{q_o} = \frac{x_r}{S/2} \qquad C = \frac{c}{c_o} \qquad \theta = D^*\left(t - \frac{z}{u}\right) \qquad Z = \frac{D_p \cdot \varepsilon_p}{(S/2)^2 \cdot m \cdot u} z$$

where Q is the ratio of the amount of oxidized species to the reducing species, C, θ, and Z are defined as dimensionless variables of concentration, time and distance in the fracture respectively, and c_o is an arbitrary concentration. Equation (17) may be transformed by use of the dimensionless variables to

$$\frac{\partial C^f}{\partial Z} + \frac{\partial Q}{\partial \theta} = 0 \tag{19}$$

From Equation (19), an analytical solution is obtained by following the method used by Cooper and Liberman (1970). Two situations may be distinguished, before and after the redox front has reached the centre of the slab at the inlet. The time to reach the centre of the slab is defined as the critical time (t_{cr}). This time may be calculated from Equation (18). Only times less than the critical time are considered here. Then

$$\begin{array}{lr} Q(Z,\theta) - Q(0,\theta) = -Z & \theta \le \theta_{cr} \\ Q(Z,\theta) = (1 - Z_o) - Z & \theta \ge \theta_{cr} \end{array} \tag{20}$$

where θ_{cr} is the dimensionless critical time and Z_o is defined as

$$Z_o = \int_{\theta_{cr}}^{\theta'} C^f|_{Z=0}\, d\theta$$

The penetration of the redox front into the rock at locations close to the clay-rock interface (z = 0) may be determined from

$$Q(0,\theta) = \sqrt{2\frac{D^*}{c_o}\int_{t_2}^{t} c^f(t)\, dt} \tag{21}$$

The location of the redox front along the fracture is given by

$$Q\ (Z,\theta)\ = \sqrt{2\frac{D^*}{C_o}\int_{t_2}^{t} c^f(t)\,dt}\ -\ Z \qquad (22)$$

The analytical solution was used to check the results obtained using a numerical code made for this model. This analysis shows that the solution is valid for any function that represents the concentration at the fracture inlet as a function of time. The same approach can be used for the cylindrical geometry. This derivation is shown in the Appendix.

5 THE MOVEMENT OF THE REDOX FRONT IN THE FRACTURED ROCK

In the previous sections, calculations were made to determine the time taken for the oxidants to reach the fracture. The results were shown in Tables 2 and 3 for three levels of oxidant production rates. The advance of the redox front at this stage was calculated by a simple mass balance. For the high production rate, the time to completely oxidize the clay is very short. With the other rates, the redox front probably never reaches the fracture because most of the oxidants are consumed over one million years by the clay surrounding the canister. The results showed that with the reduced production rate, all the oxidants produced are consumed by the clay (Neretnieks and Faghihi, 1991). Therefore, only the low and high production rates of oxidants are considered in further calculations.

In this section, the advance of the tip of the redox front along the fracture is calculated by using Equation (22). Equation (18) is used to calculate the penetration of the redox front perpendicular to the fracture into the rock matrix at the fracture mouth. In these equations, the inlet concentration of oxidants in the fracture, c(t), is dependent on the water flow rate in the channel. It can be found from Equation (16). The calculations will be done for periods up to one million years.

For a time scale of one million years, the amounts of oxidants entering the fracture depend on the time (t_2) at which the redox front reaches the fracture, the fraction of oxidants taken up by the rock, and the fraction taken up by the clay. This was discussed in Section 3, where it was found that the fraction of oxidants entering the water in the fracture (φ^f) increases with time, because the resistance to the transport of oxidants by the other pathways increases.

The calculations for the movement of the redox front through channels need data on flow rates through channels and the occurrence of channels in crystalline rock. Data from several tunnels in crystalline rock in Sweden show that channel widths range from a few centimetres up to one metre. The occurrence of channels ranges from 1 per 20 m^2 in Stripa (Abelin et al., 1985) to about 1 per 100 m^2 in SFR (Bolvede and Christianson, 1987). The channel flow rates vary considerably. Some data are given in Table 5.

The fracture-rock system consists of sparse independent channels with different flow rates. The calculations are made by applying the flow rates from SFR to conditions in the repository. It is assumed that the canister is intercepted by any of the channels shown in Table 5. The flow rate of water in each channel category is calculated from a flux of 0.1 $l/m^2 \cdot a$. The concentration of oxidants at the inlet of each channel may then be determined. Other data used in the calculations are given in Table 6.

Table 5 Fraction of the total flow rate in different categories of channels. Data from SFR for a mapped area of 14 000 m^2, for an average flux of 0.1 l/m^2 a.

Channel category	Number of channels	Channel fraction	Flowrate fraction	Flow rate/channel (Q_{ch}), [m^3/a]
1	2	0.012	0.131	0.0918
2	4	0.024	0.148	0.0517
3	12	0.073	0.207	0.0241
4	41	0.250	0.305	0.0104
5	38	0.232	0.126	0.0046
6	67	0.409	0.084	0.0017

Table 6 Required data for redox front calculations.

Symbol	Description	Units	Value
W	Fracture width	m	1
δ	Fracture aperture	m	10^{-4}
D_e	Oxidant diffusivity in rock ($D_p \cdot \varepsilon_p$)	m^2/s	$5 \cdot 10^{-14}$
q_o	Concentration of Fe(II) in clay	% by weight	0.1 - 1.0
	Concentration of Fe(II) in rock	% by weight	1.0 - 8.0
ρ	Clay density	kg/m^3	2 000
	Rock density	kg/m^3	2 700
	Occurrence of channels	$channels/m^2$	1/85

Fitting parametres for radiolysis production rate (Equation 1)

	Low production rate	High production rate
a_N	0.0029	249.4
b_N	0.237	0.759

5.1 Results for canister totally canister, no diffusion into the rock

The oxidants diffuse into the backfill surrounding the canister and react with the Fe(II) in the clay. The clay will be completely oxidized after a time t_2. It is assumed that the oxidants then no longer diffuse into the rock surrounding the repository hole. Therefore all the oxidants produced for $t > t_2$ diffuse into the fracture. This is a very conservative estimate, as was shown in Section 3, where the fraction of oxidants diffusing into the fracture was always less than 0.6.

The calculations are done for periods up to one million years for low and high production rates. The penetration of the tip of the redox front in the channel as a function of the water flow rate is calculated for two breaching times (t_1), the earliest and the latest (Table 2). Figure 13 shows results for the low production rate and concentrations of Fe(II) in the rock of 1.0 and 8.0 % by weight. The results for the high production rate are shown in Figure 14.

The tip of the redox front advances distances of 10 - 60 m with the low production rate. With the high production rate, the tip of the redox front can travel a large distance along an uninterrupted channel. This is unrealistic, because a channel branches after some distance and exposes a much larger rock surface to the oxidants. With the larger concentration of Fe(II) (8.0 % by weight), the tip of the redox front travels about one-third as far as with the smallest Fe(II) concentration.

The penetration of the redox front into the rock at the fracture mouth is calculated as a function of the intruding time of oxidants to the channel (t_2). Figure 15 shows the results for the high production rate and concentrations of Fe(II) in the rock of 1–8 % by weight. The curves show a very shallow penetration of the redox front into the rock matrix. The deepest penetration is 45 cm, which occurs in the channel with the smallest flow rate because of the large concentration of oxidants at the fracture mouth. This penetration is about one half of the channel width, which justifies the use of the rectangular model.

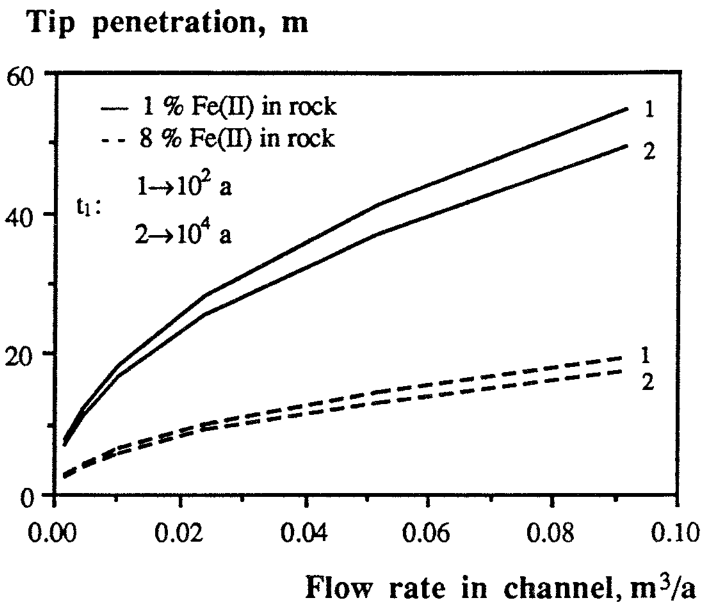


Figure 13 Low production rate and canister totally corroded. Advance of the tip of the redox front along the fracture after 10^6 years and for two breaching times t_1. See Table 2 for intruding time (t_2) to the channel.

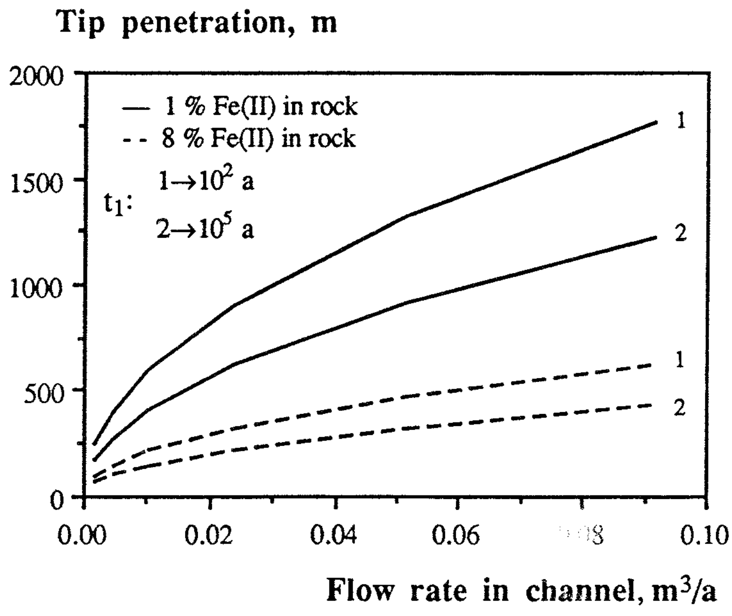


Figure 14 High production rate and canister totally corroded. Advance of the tip of the redox front along the fracture after 10^6 years and for two breaching times t_1. See Table 2 for intruding time (t_2) to the channel.

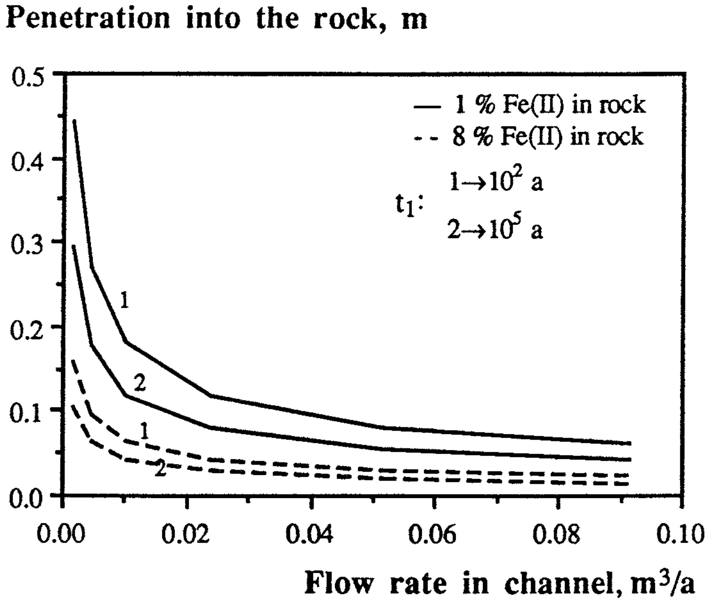


Figure 15 High production rate and canister totally corroded. Penetration in the direction perpendicular to the fracture close to the clay-rock interface vs. channel flow rate.

5.2 Results for canister totally corroded, including diffusion into the rock

The above calculations are not realistic since they do not include the uptake in the rock matrix. In practice, only a fraction of the oxidants goes into the fracture; the remainder diffuses into the rock through the clay-rock interface. Thus the amount of oxidant entering the fracture is smaller than above. Equation (22) shows that if the supply of oxidants to the fracture is reduced by a factor of 4, the distance travelled by the redox front would reduced by a factor of 2. The situation is somewhat more complex, because this fraction is a function of the time.

Figure 16 shows the distance travelled by the tip of the redox front vs. the channel flow rate, and includes the uptake of oxidants by the rock for a high production rate. Comparison with Figure 14 shows that the advance of the redox front is reduced by a factor of 2 if uptake of oxidants by the rock is considered. With the low production rate, the time for the redox front to reach the fracture mouth is very long, slightly less than one million years. Thus the production of oxidants is very small after the redox front reaches the fracture mouth. Most of the oxidants produced are then taken up by the rock, and so the fraction of oxidants entering the water in the fracture is very small.

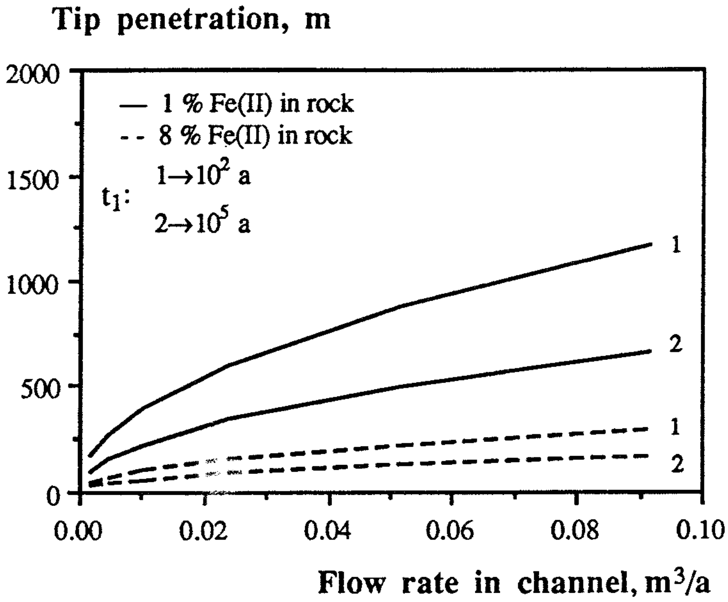


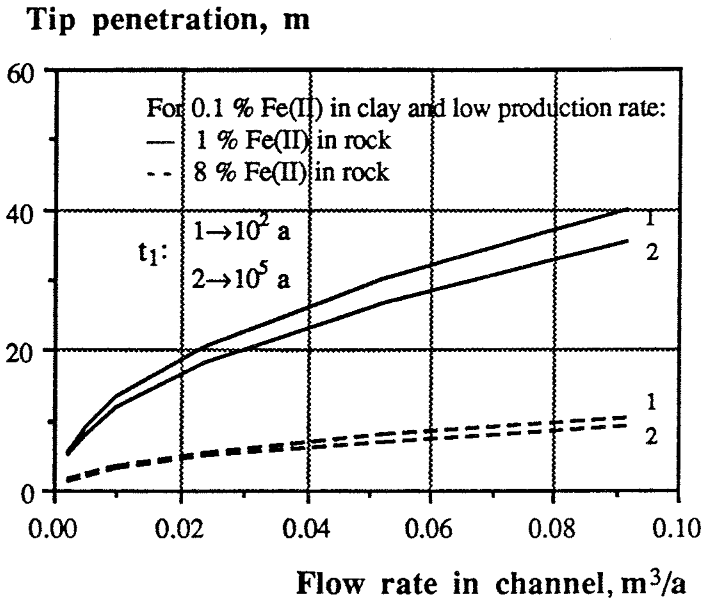
Figure 16 High production rate and canister totally corroded. Advance of the tip of the redox front as a function of the flow rate of water in the channel, see Table 5. See Table 2 for intruding time (t_2) to the channel.

5.3 Results for canister locally corroded

Here, the canister is locally damaged and a small hole is formed at the canister wall. The oxidants are transported through this hole into the clay. The oxidants react with the Fe(II) in the clay and form a small hemi-spherical zone of oxidized clay between the small hole and the fracture mouth, see Figure 2b. From this oxidized zone, the transport of oxidants takes place through three pathways: to the water in the fracture, to the rock from the clay, and to the unoxidized clay.

Calculations for low production rate and for a totally corroded canister showed that the tip of the redox front advances a few metres along the fracture. The oxidants must first oxidize all the clay before they migrate into the fracture and into the rock. When the canister is locally corroded, the transport of oxidants into the fracture begins very early compared to when the canister is totally corroded. In the fastest channel, the tip of the redox front advances into the fracture about 10-40 m after 10^6 years, depending on the concentration of Fe(II) in the rock, see Figure 17.

For a high production rate, the distances travelled by the tip of the redox front are similar to when the canister is totally corroded, see Figure 18. As was discussed above, the large distances travelled by the tip of the redox front are unrealistic.



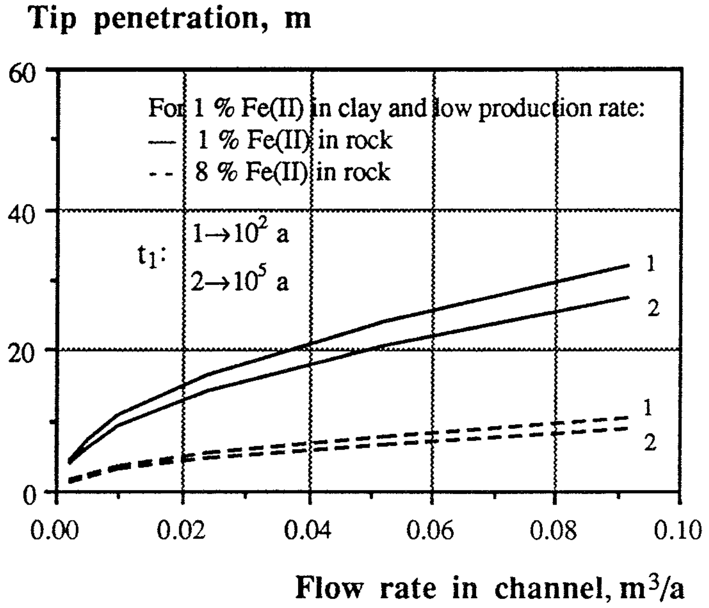


Figure 17 Low production rate and canister locally corroded. Advance of the tip of the redox front along the fracture after 10^6 years, for two breaching times (t_1) and two concentrations of Fe(II) in the clay and in the rock.

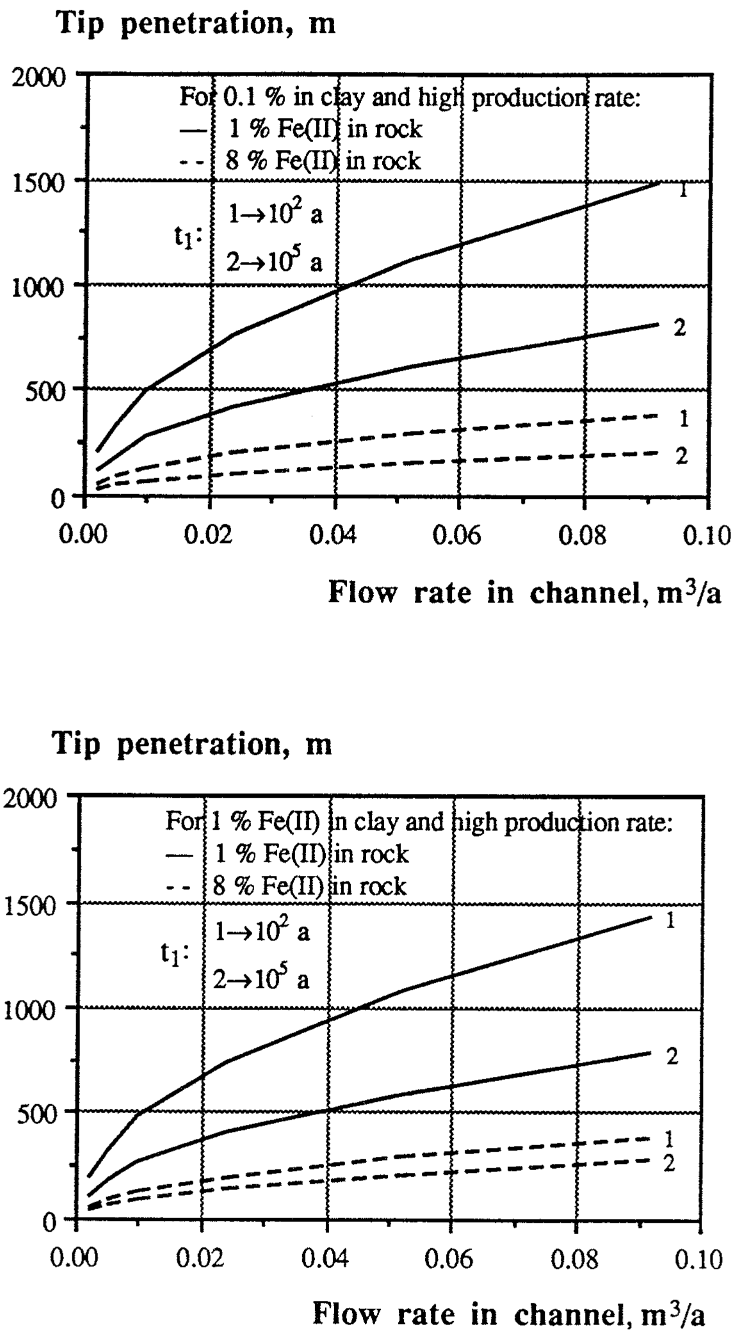


Figure 18 High production rate and canister locally corroded. Advance of the tip of the redox front along the fracture after 10^6 years, for two breaching times (t_1) and two concentrations of Fe(II) in clay and in rock.

6 DISCUSSION AND CONCLUSIONS

One of the main uncertainties in the calculations is the rate of radiolysis. The high production rate is unlikely, because it is based on the assumptions that there is no recombination of the radiolysis products formed and that all fuel pellets are fully exposed to water. Such high rates of radiolysis would have been noticed around uranium ore bodies. Even at the OKLO natural reactors, only very slight evidence of radiolysis could be found (Gancarz and Curtis, 1983). The low or possibly even the reduced rate is deemed more reasonable.

This study considers one situation where the copper canister is completely degraded. This is highly improbable because the copper is very corrosion resistant. It is conceivable that if a hole is present in the copper canister at an early stage, then the oxidants would oxidize the copper before moving further out. The oxidants would then be neutralized by the copper and unable to oxidize the clay and rock. If a canister has a hole, any hydrogen produced will escape through the hole and into the clay. The high capillary forces in the clay may lead to a pressure rise in the canister that prevents the water from entering. For the radiolysis to attain the rates given in this paper, there must be sufficient water in contact with the fuel. The corrosion products which form on the surface of the fuel decrease the available water considerably. It has been estimated that the last two effects reduce the rate of radiolysis by a factor of up to one hundred (Neretnieks and Faghihi, 1991). The most probable rate of radiolysis is somewhere between the low and the reduced rates.

With such a low rate, it would take a long time for the front to oxidize the clay and reach the rock. The front would only reach a fracture if that fracture happened to be in the part of the rock occupied by the front. It is unlikely that a channel in the rock is located exactly opposite the damage in the canister. A much larger amount of clay than that used in the calculations must be oxidized before the oxidants can reach the mobile water in a fracture. When the redox front reaches the mouth of a channel, only a fraction of the oxidants enter the water. The rest goes to the still unoxidized clay and to the rock. The oxidants that enter the water will move downstream with the water. In the calculations, the front moves some 50 m in the channels with the largest water flow rates. However, there are many uncertainties in the movement of the front along the channels. The magnitude of the channel surfaces is poorly known. A channel width of 1 metre has been used here. The channel width may well be less and the front would then move further. On the other hand, individual channels are probably not continuous for long distances but are part of a complex network. Channels branch into other channels, which gives the oxidants more flow wetted surfaces for them to diffuse into the rock. The network effects cannot be quantified yet.

Although there are many uncertainties concerning the rate of radiolysis, the geometry of the flow paths, and the availability of reducing species in the clay and in the rock, it is unlikely that the redox front will ever move past the clay. If it does, the tips of the redox front may move less than hundred metres, even in channels with high flow rate.

NOTATION

A	Cross section area for diffusion	m^2
a_N	Parameter used to fit the line for production rate	-
b_N	Parameter used to fit the line for production rate	-
c	Concentration of oxidants in liquid	mol/m^3
c_f	Concentration of oxidants in the fracture	mol/m^3
c_p	Concentration of oxidants within the pores of the rock	mol/m^3
c_o	Arbitrary concentration of oxidants	mol/m^3
C	Dimensionless concentration	-
D_e	Effective diffusivity	m^2/a
D_p	Pore diffusivity	m^2/a
D_w	Diffusivity in water	m^2/a
D^*	Group of variables	a^{-1}
f	Stoichiometric factor for the oxidation reaction	-
K	Mass transfer coefficient	m^3/a
L	Length of the canister	m
m	Ratio of flowing fluid to the solid	m^3/m^3
N^c	Production rates in the canister	mol/a
N^f	Flow rate of oxidants into the fracture	mol/a
N^r	Flow rate of oxidants into the rock	mol/a
P	Production of oxidants	mol
q	Concentration of the oxidized species in the solid	mol/m^3
q_o	Concentration in the solid of the reducing species	mol/m^3
Q	Dimensionless ratio of the amount of oxidized species to the reduced species	-
Q_{ch}	Water flow rate in the fracture	m^3/a
Q_{eq}	Local equivalent water flow rate	m^3/a
r	Distance in the direction of the transport by diffusion	m
r_o	Inner radius	m
r_{out}	Outer radius	m
r_b	Location of the redox front	m
r_1	Radius of the canister	m
r_2	Radius of the repository hole	m
S	Thickness of the slab or spacing between fractures	m
t	Time	a
t_1	Breaching time of the canister	a
t_2	Time at which the redox front reaches the fracture	a
u	Velocity of the water in a fracture or hole	m/a
u_o	Darcy velocity	$m^3/m^2 \cdot a$
V_c	Volume of clay to be oxidized	m^3
W	Width of the channel	m

x	Distance in the direction of the transport by diffusion	m
x_b	Penetration of the oxidants into the unoxidized clay	m
x_r	Penetration of the oxidants into the rock	m
z	Distance in the direction of the flow of water	m
Z	Dimensionless distance	-
δ	Fracture aperture	m
ε_p	Rock porosity	-
φ	Fraction of oxidants entering the fracture	-
θ	Dimensionless time	-
θ_{cr}	Dimensionless critical time	-
ρ	Density	kg/m^3

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APPENDIX: Derivation of equations for the movement of the redox front in a cylindrical geometry

After long times and near the edge of the channel, the diffusion is radial to the fracture plane rather than perpendicular. The oxidized zone gradually becomes oval and finally circular.

The space between the fracture walls is approximated to an annular body with the same section area and the same perimeter as the fracture. Diffusion occurs from the surface of the exterior cylinder, radius r_o, into the rock matrix. The system is defined by $z \geq 0$ and $r_o < r < r_{out}$, where r_{out} is the distance to where redox fronts from two adjacent channels meet.

The initial and boundary conditions for this situation may be written as:

Initial conditions (at $t = t_2$)	c^f	$= 0$	at $z \geq 0$
	c_p, q	$= 0$	$z \geq 0$, and $r \leq r_{out}$
Boundary conditions (at $t > t_2$)	c^f	$= c^f(t)$	at $z = 0$
	c^f	$= 0$	$z = \infty$
	c_p	$= c^f$	$r = r_o$
	c_p	$= 0$	$r = r_b$

By assuming a semistationary process ($\partial c_p/\partial t \approx 0$), the concentration gradient in the rock matrix is obtained. The velocity of the redox front in the rock is then

$$\frac{dr_b}{dt} = \frac{D_p\,\varepsilon_p}{q_o\,f}\,\frac{c^f(t)}{r_b \ln\left(\frac{r_b}{r_o}\right)}$$

Integrating the above equation gives the radial penetration distance (r_b) of the redox front

$$\frac{r_b^2}{2}\ln\left(\frac{r_b}{r_o}\right) + \frac{r_o^2 - r_b^2}{4} = \frac{D_p \cdot \varepsilon_p}{q_o \cdot f}\int_{t_2}^{t'} c^f(t)\,dt$$

The following dimensionless variables and group of variables are defined:

$$Q = \frac{q}{q_o} = \frac{r_{out}^2 - r^2}{r_{out}^2 - r_o^2} \quad , \quad C = \frac{c}{c_o} \quad , \quad \theta = D^* \left(t - \frac{z}{u}\right) \quad , \quad Z = \frac{D_p \cdot \varepsilon_p}{r_o^2 \cdot m \cdot u} z$$

$$D^* = \frac{D_p \cdot \varepsilon_p \cdot c_o}{r_o^2 \cdot q_o \cdot f} \qquad B = \left[\left(\frac{r_{out}}{r_o}\right)^2 - 1\right]$$

The governing equations can be expressed in terms of these dimensionless variables:

$$\frac{\partial C^f}{\partial Z} + \frac{\partial Q}{\partial \theta} = 0 \qquad \frac{dQ}{d\theta} = \frac{C^f}{\frac{B}{4} \ln (QB + 1)}$$

For times less than the critical time ($\theta \leq \theta_{cr}$), the solution of the above equations is

for $QB \leq 1$

$$\frac{B}{4} \sum_{0}^{\infty} \frac{(-1)^{(n+1)}}{n^2} \left[\left(Q(Z,\theta)*B\right)^n - \left(Q(0,\theta)*B\right)^n\right] = -Z$$

for $QB > 1$

$$\frac{B}{4} \left\{\frac{1}{2}\left[\left(\ln (Q(Z,\theta)*B\right)^2 - \left(\ln (Q(0,\theta)*B\right)^2\right] + \sum_{0}^{\infty} \frac{(-1)^{(n+1)}}{n^2} \left[\left(Q(Z,\theta)*B\right)^{-n} - \left(Q(0,\theta)*B\right)^{-n}\right]\right\} = -Z$$

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