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Some mechanisms which may reduce radiolysis

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SUMMARY

In previous assessments of the rate of radiolysis in the KBS 3 concept, it has been assumed that free liquid water will intrude the canister and form a film around the uranium oxide pellets in the gap between the pellets and the zircaloy tube. The initial water film thickness was further assumed to be maintained forever. The alpha radiation which is emitted from the uranium oxide pellets will radiolyze the water which is dissociated to oxidizing and reducing components. It has, also, been assumed that the reducing components which mostly consist of hydrogen are much more mobile than the oxidizing species and can leave the system either by diffusion or by gas flow.

The studies of the rate of radiolysis, in KBS 3 (1983) , indicated that its value is so high that the release rate of the nuclides can be considerably enhanced.

In this report two mechanisms which may considerably decrease the rate of radiolysis are studied. The first main effect is that capillary forces in the very fine pores of the bentonite which surround the canisters do not permit the release of water if there is a gas over pressure inside the canister. Some possible bypassing mechanisms such as gas and surface diffusion are discussed. As long as there is gas inside the canister the gap will partly be gas filled and the alpha-particles will have less water to radiolyze. Because some hydrogen will be dissolved and will escape by diffusion, a rate of radilolysis will be maintained which balances the rate of diffusion. This in turn will be influenced by the geometry of the diffusion path. The size of the hole in the copper canister seems to be one of the critical items which determine the escape of the hydrogen and thus the rate of radiolysis.

The other main effect which will reduce the radiolysis is the accumulation of the corrosion products in the gap. This reduces the water content in the gap. Consequently there will be less water which can be radiolyzed. The presence of corrosion products which have a higher density than water will also consume the energy of the alpha-particles faster.

Both effects seem to, independently, have a potential of reducing the rate of radiolysis by a few orders of magnitude.

1 BACKGROUND

In Sweden the high level nuclear waste in the form of spent fuel placed in copper canisters which are surrounded by compacted bentonite are deposited in deep geological repositories at 500 m depth. Groundwater may corrode the copper canisters and water may come in contact with the spent nuclear fuel. The radioactive materials may form soluble corrosion products which may diffuse out of the canister (Neretnieks, 1983).

The used fuel contains mainly UO_2, fission products of uranium and higher actinides. Interaction of the uranium dioxide waste form with groundwater yields soluble radionuclide components. The groundwater at repository depth is reducing but oxidizing conditions at the fuel surface can be produced by the radiolysis of water. Under oxidizing conditions many of the nuclides, including the uranium in the waste matrix itself are more soluble than under reducing conditions.

The effects of gamma and beta radiolysis of water are of little importance compared to the alpha radiation. This is the dominant factor in the long-term stability of the disposed fuel as the fields of radiation remain high enough to be of importance after many thousands of years.

During radiolysis of water by alpha radiation equal amounts of oxidizing and reducing molecules are produced. We exemplify the oxidizing components by H_2O_2, although they are made up of a multitude of species. The reducing components are exemplified by H_2. The oxidation of UO_2 in water is faster by H_2O_2 than by dissolved oxygen at the same concentration (Shoesmith et al , 1985). Other radionuclides can also be oxidized and become more soluble and more mobile.

A novel idea which may reduce the radiolysis is presented and investigated. The water in the gap is exposed to both the radiation and chemical reactions with the structural materials. It is the formation of hydrogen gas from the radiolysis combined with the capillary forces in the system at the interface between the bentonite clay backfill and the corrosion products that might strongly decrease the rate of radiolysis by preventing water to enter to replenish the water lost by radiolysis.

This process strongly limits the access of water to the fuel's surface, thereby decreasing the amount of water exposed to α-radiation, and consequently the rate of radiolysis. The mechanism of interest is that the compacted bentonite clay surrounding the canister has very small pores which are much smaller than most other porous materials.

If the hydrogen produced by radiolysis forms a gas phase, the water from the fine capillaries in the bentonite clay cannot enter the larger pores of the corrosion products or the even larger gap between the fuel pellets and the zircaloy which holds the pellets. See Figure 1.

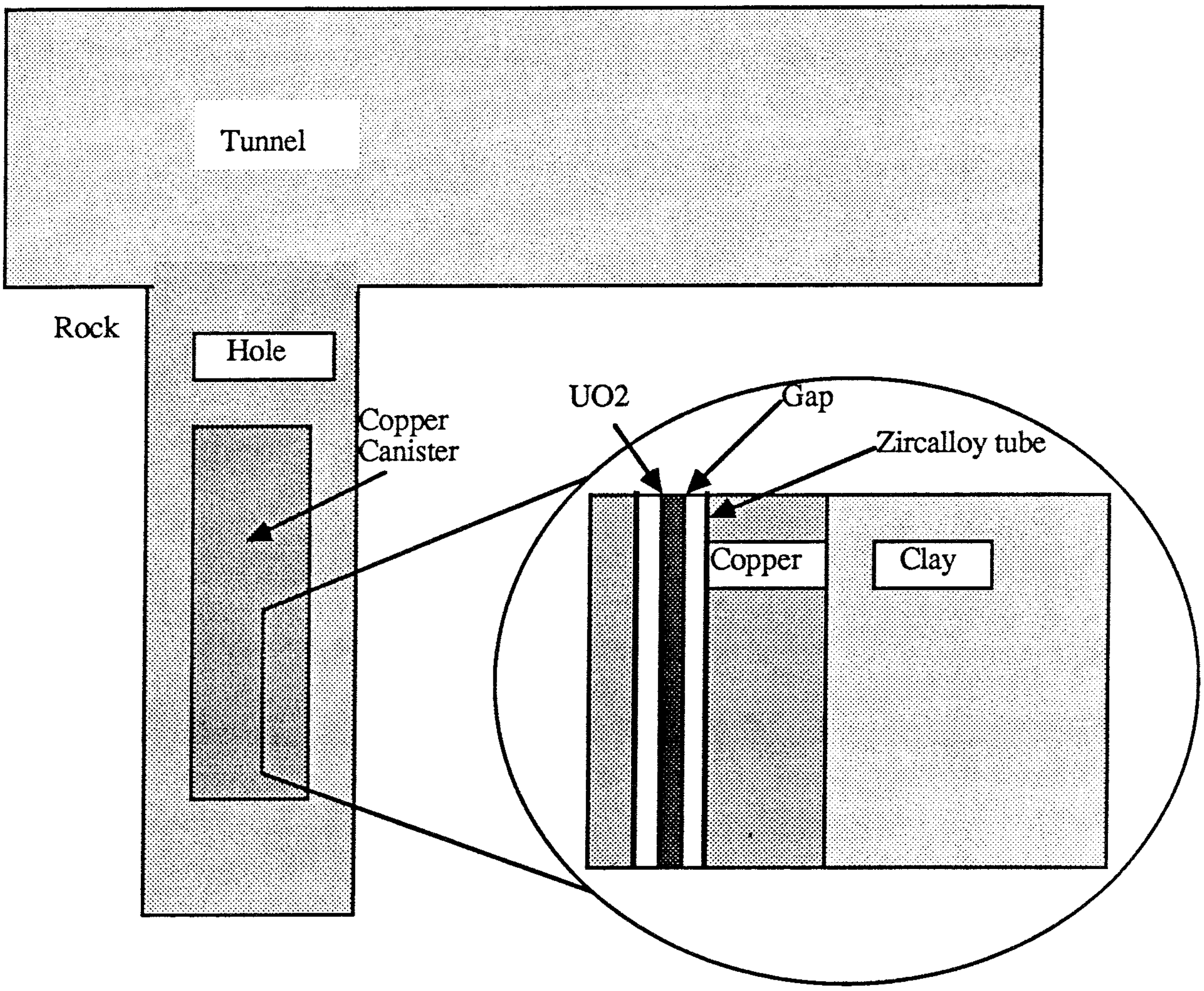

Figure 1 Tunnel with repository hole and copper canister surrounded by bentonite. The spent fuel in zircaloy tubes is inside the copper canister. Only one of many tubes is shown.

Another mechanism, due to the formation of corrosion products in the gap which reduces the rate of radiolysis, is also explored.

Originally, the width of the gap is 30 μm which coincides with the penetration depth of alpha particles in water (Christensen et al, 1982). As the corrosion of zircaloy and uranium oxide takes place, the corrosion products will expand into the gap. This will, eventually, cause the corrosion products to accumulate in the gap and decrease its size. Consequently, if the amount of water in the gap decreases, then the radiolysis will proportionally decrease as well.

We will attempt to describe the process of the formation of corrosion products that will reduce the amount of water which can be radiolyzed by being exposed to the alpha particles.

We will also investigate how the amount of water which may fill the voids might not be replenished, once the radiolysis starts and hydrogen forms. The hydrogen gas may form such an over pressure that it will prevent the water to be liberated from the small pores in the bentonite clay, where the water is bound strongly by capillary forces.

2 GAS TRANSPORT FROM THE CANISTER

2.1 Physical model for capillary bound water

Physically, porous media can be regarded as a connected system of capillary channels of varied sizes and shapes. The highly compacted bentonite surrounding the copper canister is such a medium. It contains pores with very small apertures which give rise to strong capillary forces. The pores of compacted bentonite have radii typically of sizes $5 \cdot 10^{-8}$ m (Pusch and Forsberg, 1983), but also contain many smaller pores. To illustrate the mechanism of capillary forces, we use a simplified model of a circular tube first before proceeding to the more complex pores of porous media.

Assuming an initially gas filled capillary which is in contact with water, the liquid wets the tube so that it rises and forms a concave meniscus. At the interface, the excess pressure $\Delta P = P_g - P_w$ is supported by a force due to surface tension σ_s (Adamson, 1982). Setting the contact angle $\theta=0$, which is typical for water on wetting surfaces;

$$\pi r^2 (P_g - P_w) = 2 \pi r \sigma_s \cos \theta \tag{1}$$

$$\Delta P = P_g - P_w = \frac{2 \sigma_s}{r} \tag{2}$$

where r is the radius of the cylindrical tube. We find that the water may rise to a height of $\Delta P/\rho g$ m in a vertical capillary. It may also be stated that to depress the water level to the original level, an excess gas pressure of ΔP must be supplied in the capillary. For water $\sigma_s = 0.072$ N/m, and typically for a pore with radius of 200 Å ($2 \cdot 10^{-8}$ m), the capillary pressure is 72 bar.

2.2 Penetration depth of alpha particles in corrosion products

The gap between the zirconium tube and the fuel pellets will be filled with corrosion products after some time. It will mainly consist of uranium oxide with higher oxidation states of uranium. Zirconium oxide could form, but this is not as probable as formation of uranium oxides because zirconium oxide forms a protective layer from further oxidation. The alpha particles penetrate about 0.03 mm in water. In other materials the penetration depth is inversely proportional to the density of the material (Werme, 1990). An approximate penetration depth in the corrosion products, with small pores, then can be estimated by assuming that the alpha particle spends all the energy in the sum of the distances travelled in the water in the pores, and in the corrosion products. The passages in the gas filled pores will not appreciably reduce the energy of the particles and this is neglected. With a water filled porosity ε and density relative to water ρ,. the sum of the distances travelled, z, in the corrosion products with water filled pores is:

$$\frac{z}{z_o} = \frac{\varepsilon}{\rho_w} + \frac{1-\varepsilon}{\rho_{cp}} \tag{3}$$

where z_0 is the distance travelled in water (30 µm). ρ_w is 1 and ρ_{cp} =7.31 for the corrosion products which are taken to have the density of U_3O_8. Table 1 below shows the total penetration distance, and the path length travelled in water for different porosities.

Table 1. Total penetration distance z, and path length in water $z \cdot \varepsilon$.

Porosity	Total path length	Path in water	Relative rate of radiolysis
ε	z	$z\,\varepsilon$	
-	µm	µm	-
0	4.10	0	0
0.01	4.36	0.044	0.0015
0.02	4.64	0.094	0.0031
0.05	5.40	0.27	0.009
0.1	6.70	0.67	0.022
0.2	9.28	1.86	0.062
0.3	11.9	3.56	0.12
0.5	17.1	8.52	0.28
1	30	30	1

Loosely packed porous materials often have porosities in the range 0.2-0.4. Compression of porous materials as eg in forming pellets in pharmaceutical industry or in forming UO_2 pellets for nuclear reactors leads to a considerable reduction of the porosity. The formation of corrosion products due to oxidation by radiolysis products in the gap must fill the voids against considerable stress and are expected to have a considerably smaller porosity than loosely packed material.

Initially the corrosion products will form freely in the 30 µm gap, but as the corrosion proceeds there will be less and less voids to fill. The corrosion products will form and expand into the remaining voids. The growth of the crystals will eventually fill up most of the available space. As the growth proceeds, the rate of radiolysis will decrease as shown in Table 1. Already at 5 % porosity more than 99 % of the energy of the alpha particles has been lost in the corrosion products and less than 1 % in the water. At 1% porosity the rate of radiolysis will have decreased by a factor 680. The rate of radiolysis is proportional to the path length in water, therefore this rate will be decreased by a hundred-fold at this porosity. The porosity can readily decrease to less than 5 %.

When the gap has been "totally filled" with U_3O_8, formed from UO_2, the 4.3 liters of water which fill the gaps in a canister are occupied by porous U_3O_8. This is equivalent to 31.4 kg or 112 moles of uranium, if there is no porosity, and to 99.6 moles hydrogen gas formed and the same amount of oxygen equivalent to oxidize the UO_2.

If most of the oxidizing agents formed are used in oxidizing the UO_2 then the rate of radiolysis will decrease rapidly in time and the total amount of fuel oxidized will be limited to a few tens of kg. After this the rate of radiolysis would decrease by several orders of magnitude.

In addition to the water in the gap there may be some water present in the pores of the fuel pellets themselves. The mass of fuel pellets in a canister is about 1.4 metric tons. The density of UO_2 is 10 kg/l and the volume of the pellets is thus about 140 l. Assuming a pellet porosity of 1%, there may be an additional 1.4 l of water in the pellets. This will give a small addition to the water available for radiolysis.

There can, of course, be competing processes which will not permit the above scenario to develop fully. Some of the oxidizing species may escape, forming an oxidized path through which dissolving uranium oxide may diffuse out. The rate of radiolysis would then also depend on the rate of escape of the corrosion products formed.

It is reasonable to assume that if the copper canister is penetrated locally, only, the escaping dissolved uranium must first diffuse along the gap in the fuel rods to the hole in the canister and out. It will be shown below that the diffusion along the rods will be slow and not allow any substantial mass to be transported except from locations near the hole in the canister. The corrosion products formed in the gap will then remain in place except very near the hole.

To illustrate this, assume that there is a hole in the canister which allows water with a zero concentration of uranium to be in contact with the broken fuel rod. The uranium diffusing out along the gap between the pellets and the zircaloy (assumed to be intact except where broken) has a driving concentration gradient equal to the solubility of the uranium divided by the distance it has to diffuse. Assume that the distance is very short, 1 cm. This will give a conservatively high transport rate. The solubility at oxidizing conditions is taken to be $3 \cdot 10^{-4}$ mol/l or about 70 ppm (Karlsson, 1990). The cross section area of the gap, A2 in figure 3, through which diffusion takes place is $A=8.6 \cdot 10^{-4}$ m^2. The effective diffusivity of the dissolved uranium species in the corrosion products is taken to be 10^{-10} m^2/s. The rate of transport then is:

$$N = - D_e A \frac{dc}{dx} \tag{4}$$

This is equal to $8 \cdot 10^{-5}$ mol/year uranium diffusing out. In 1 million years 80 mol or 19 kg will have escaped. This obviously is very small and considering that this is conservative, the loss of uranium will be very small.

The transport distance dx has been chosen to be very short, 1 cm. Any portion of the fuel at a larger distance will have an even lower transport rate.

It is clear that the longitudinal rate of transport of dissolved uranium along the gap is very small and will prevent most of the uranium to escape. Thus, the radiolysis products will essentially remain in place and fill up the gap which will decrease the radiolysis considerably as discussed earlier.

The reason for this very small rate of transport is that the cross section for diffusion along the gap in all the fuel rods together is so very small: $8.6 \cdot 10^{-4}$ m^2. This is equivalent to a hole of 30 mm squared. Thus even a very short transport distance of 1 cm together with the low uranium solubility even at oxidizing conditions will result in a very low transport rate. Figure 2 illustrates the geometry of the degraded canister in a simplified way, and Figure 3 the concentration profile in the gap and the corrosion products inside the copper canister.

These simple calculations illustrate that the transport rate in the gap is very small. As long as the copper canister only has a hole of limited extent, and the transport path inside the canister must go along the fuel rods, the dissolution rate will be very small.

Only when large portions of canister are degraded and transport can take place through a large part of the then degraded copper canister, will the resistance to transport become smaller and comparable to the diffusional resistance in the backfill and the resistance due to transport out into the slowly passing water in the fractures in the rock. The corroded hole in the canister must be larger than about 0.01 m^2 in order to have a resistance comparable to that of the resistances in the clay and in the water flowing in the fractures.

We will briefly investigate the possible size of a hole in the canister produced by corrosion. The corrosion of the copper canister is proportional to the rate of transport to the canister of sulfides from the water. The concentration of sulfides has been estimated to be on the order of 1 ppm (KBS-3 1983) and the rate of transport to the canister surface to be equivalent to the transport capacity of 1 l/year of water. In one million years then 1 kg of sulfides would be carried to the canister. As every molecule of sulfide will react with 2 molecules of copper and the ratio of copper to sulfide molecular weights is 3.97 the amount of copper corroded would be 8 kg or 0.88 liters (density 8.92 kg/l). A 10 cm thick copper wall would have a hole of 147 cm^2 (0.015 m^2) if all the corrosion is located at one spot.

The copper canister, even after being corroded through, will make up a very large resistance to the transport of nuclides by diffusion. The transport of dissolved uranium by diffusion through the corrosion products in the hole is obtained from Equation (4), and will be $22 \cdot 10^{-5}$ mol/year, using the same data for diffusion as above. This is about the same rate as was obtained for transport in the gap. Thus also a corroded hole in the canister will constitute a large obstacle for the diffusive transport of the nuclides.

Corrosive attack on the copper by the oxidizing species formed by the radiolysis is of course possible. A larger hole could then form. This is not very probable because the uranium is readily oxidized and is in a much closer reach for the oxidizing species. We conclude that nearly all the corrosion products will stay in place and thus reduce the radiolysis by two or more orders of magnitude.

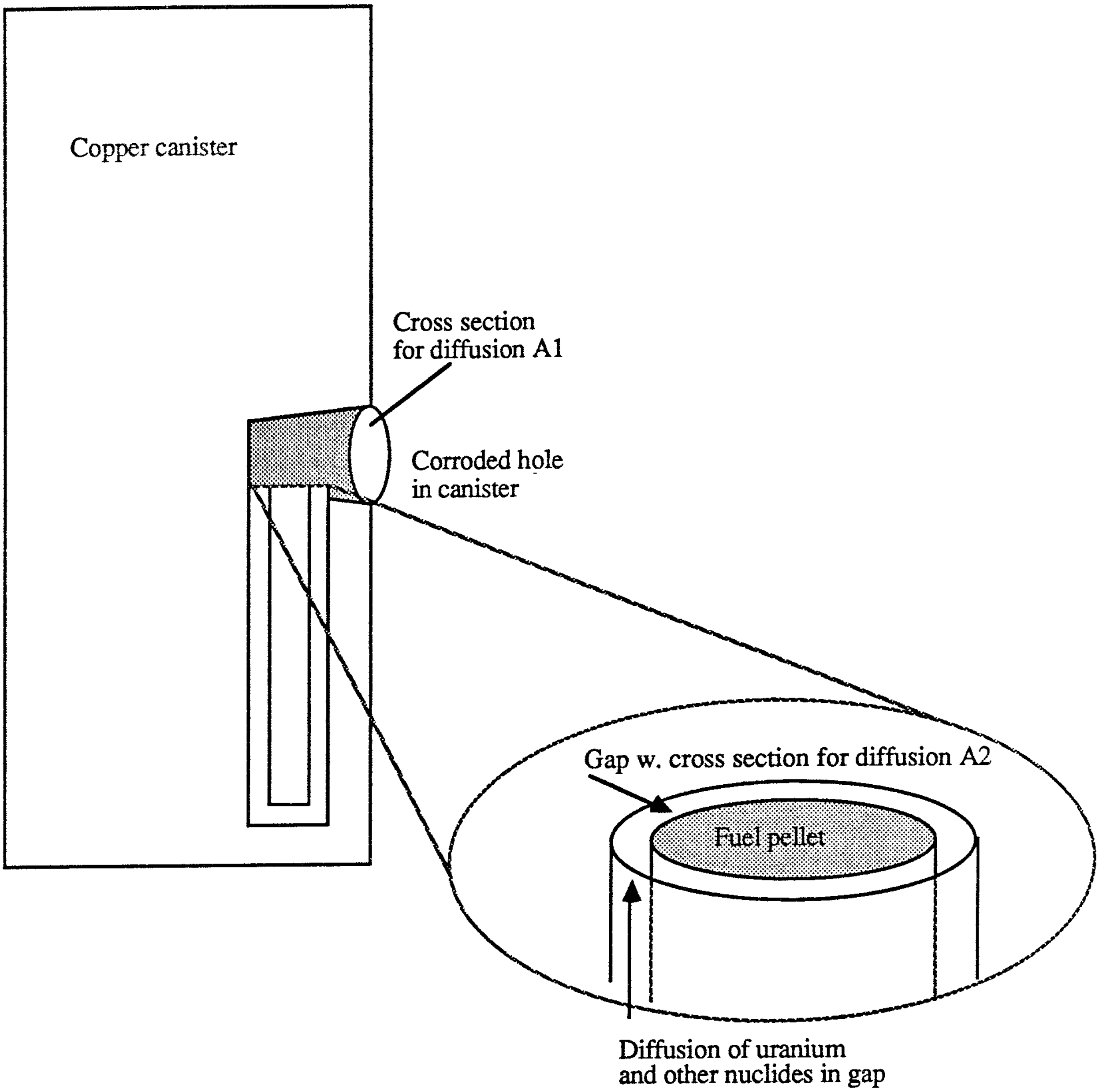

Figure 2 Illustrates the geometry of the degraded canister in a simplified way

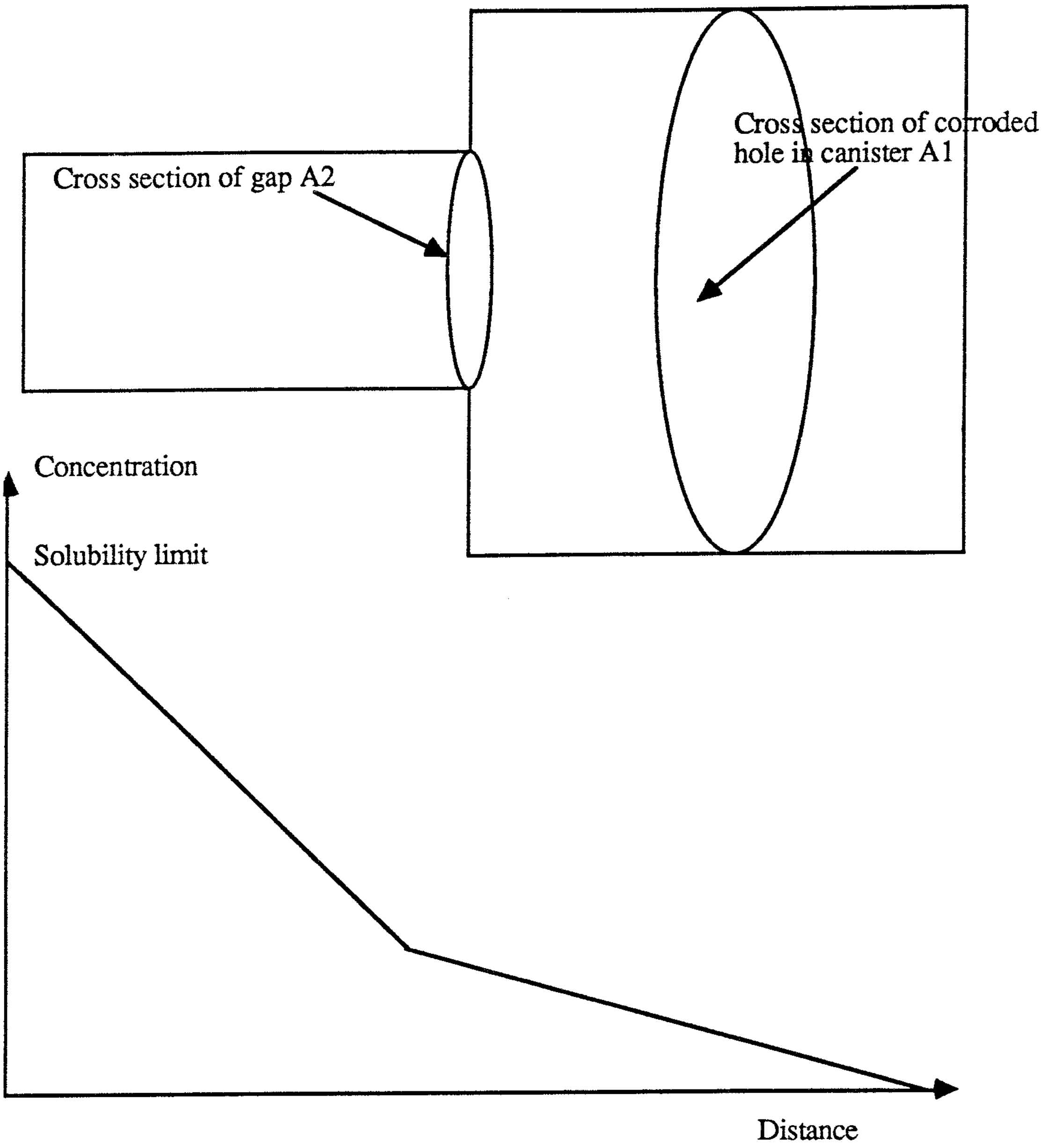

Figure 3 Illustrates the concentration profile in the gap and in the corrosion products in the copper canister.

2.3 Gas transport through the compacted bentonite

Concerning the hydrogen gas production by radiolysis of water, two stages can be considered. When there is no gas production and no gas over pressure, the groundwater may flow through the pores of highly compacted bentonite and into the degraded copper canister. If the zircaloy tubes containing the fuel pellets also are degraded, the water will eventually come in contact with the radioactive materials and become radiolyzed by alpha radiation.

As a result, a certain amount of hydrogen and an equal amount of hydrogen peroxide will be produced. The hydrogen and the peroxide will at first dissolve in the water. The dissolved components will diffuse out through the water in the gap to the corroded hole in the canister.

Then the diffusion proceeds through the corrosion products in the hole in the copper canister, and further out through the clay backfill and the rock. If and when transport by diffusion is not fast enough, the hydrogen gas cannot stay dissolved and gas bubbles form. At this stage the gas pressure starts to rise, and will expand outward towards the copper-clay interface. The presence of the gas bubbles will decrease the amount of water which can be radiolyzed. In the corrosion products water can, in principle, if released by the bentonite, intrude by capillary flow in the fine pores at a rate sufficient to maintain the rate of production of the escaping gas.

The bentonite clay, however, has a very fine pore structure, very probably much finer than the corrosion products and thus may prevent water coming in. With sufficiently high pressure the gas can overcome the capillary forces and flow through the larger pores of the bentonite. Also it may overcome the capillary forces and expel water from some small pores in order to open required paths to gas flow. Even the larger pores of the bentonite are small (discussed later) and require a considerable pressure to open and let gas flow start.

In connection with this, the successive expelling may cause high gas permeability, a large gas flow rate, and consequently possible partial drying of clay. The pressure will then decrease below the critical pressure at which the channels close. When the pressure is increased again the gas may open some channels and a cyclic process could conceivably develop.

This process could in turn also cause a cyclic water flow. But a cyclic flow is not probable for large volumes of bentonite, because there will be a multitude of possible pathways with somewhat different opening pressures. Instead a sufficient number of paths will always be open according to the existing pressure. This process may cause a more steady over pressure to develop.

When the pressure has reached a certain 'critical' value, the gas will start to flow through the larger pores, leaving the smaller pores water filled. As long as there is a higher gas pressure, larger than the hydrostatic pressure, inside the bentonite, water can not flow from the fine pores of the bentonite into the larger pores in the copper corrosion products and into the gap around the pellets (Figure. 4).

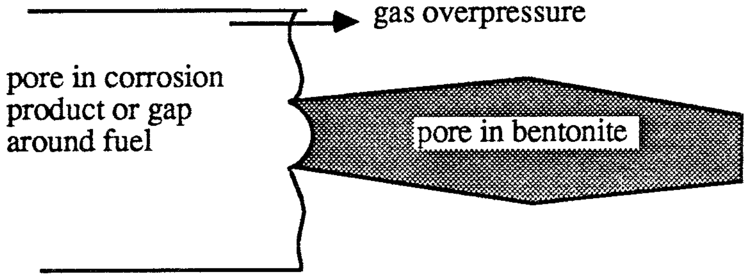

Figure 4 Schematic diagram showing the condition at the interface between the corrosion products and the bentonite with pores in the corrosion products larger than the pores in the bentonite.

Therefore, water can, only by diffusive processes, be transported to the surface of the fuel pellets. In the gas phase water vapor will be able to diffuse and through surface diffusion a thin mobile film of adsorbed water may be formed on the surface of the pellets. We will discuss this process in more detail later.

A situation will develop where the gas escapes by flow through the larger pores, the smaller pores are water filled but cannot release the water against the gas over pressure. Water will be transported inwards into the canister by diffusional processes to replenish the water which is split by radiolysis. In this case with gas filled pores the overall rate will be determined by the rate at which water can diffuse in.

In earlier investigations, it was projected that gas bubbles would start to form when the rate of production of hydrogen is larger than the escape rate by diffusion in the water filled capillaries (Pusch and Forsberg, 1983). The pressure at which this occurs is the hydrostatic pressure which is equal to 5 MPa at 500 m depth. For flow to take place the pressure must be raised by the critical opening pressure in addition.

The experimental measurements on gas conductivity have verified that there is a critical pressure for the gas penetration through highly compacted bentonite (Pusch et al, 1985). In Table 2 the pressures are given at which the gas break-through for different bulk densities of bentonite occur.

From the investigation it is concluded that, at gas break-through, a small part of the pore water will be expelled, because the pressurized gas will initially pass through the larger passages. As it penetrates the saturated high bulk density clay, the gas will displace the closely located aggregates to make its path.

The critical pressure for gas break through is related to the swelling pressure. The last column in the table presents the estimated pore radii corresponding to the opening pressures.

Table 2. Measured critical gas pressure.

Test no	Bulk density t/m^3	Swelling pressure MPa	Critical pressure MPa	Equivalent radius Å
1	2.08	26	5	280
2	2.02	18	5	280
3	1.88	1.8	1.6	875
4	1.92	2.7	2.4	583
5	1.70	0.1-0.2	0.3-0.4	4700-3500
6	2.14 (2.20)	34-45	21	70
7	2.10	25-30	11	127
8	2.12	30-40	19 (H2 gas)	74

We illustrate the principle of gas flow out in the larger capillaries of the clay while the smaller capillaries of the clay, although filled with water, do not allow the water to flow into the "large" pores of the corrosion products in the following way.

Gas has formed inside the corroded canister (Figure 5). The gas pressure has risen to the critical pressure of the larger capillaries, $\Delta P=14$ MPa, and gas starts to flow out through the larger pores of the clay. The smaller pores are filled with water. The pressure inside the clay is 14 MPa plus the hydrostatic pressure outside the clay, in this case taken to be 5 MPa. As in our assumptions (nearly) all the pores of the corrosion products are larger than the small pores of the clay, water cannot be released from the bentonite and migrate in through the corrosion products and further into the gap.

Thus as long as there is gas with a pressure inside the clay exceeding the hydrostatic pressure outside the clay, water cannot flow in through the clay by flow. When the water that intruded when there was no internal gas has been consumed by radiolysis radiolysis would slow down considerably. As it does the gas would eventually escape by diffusion and water would again intrude. The process would start all over again.

The process would of course not be so clear cut in practice. Water vapor will diffuse into the gas filled pores. Liquid water films would form on the outside of the corrosion product particles. Hydrogen dissolved in the water will constantly escape by molecular diffusion. The process will stabilize at a hydrogen production rate which is at most so high that gas just forms in the corrosion products inside the bentonite. Were it higher, the gas would prevent water from entering.

At a lower hydrogen production rate, the concentration of dissolved hydrogen in water will stabilize at a level just high enough to allow the hydrogen to diffuse out through the water filled pores of the bentonite.

The rate of escape by diffusion will be explored below.

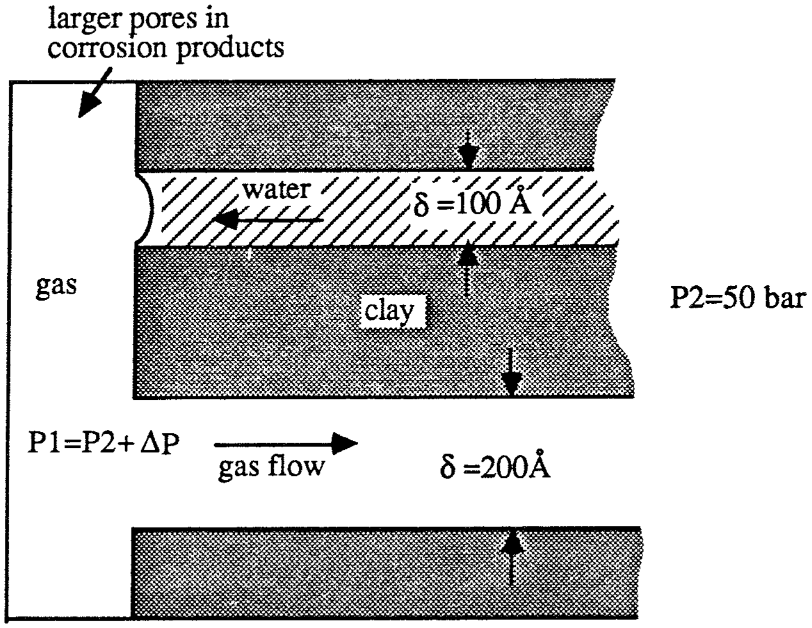

Figure 5. The conceptual condition for the gas migration through the capillaries of the highly compacted bentonite.

The rate of diffusion of the dissolved hydrogen under a steady state condition is estimated by using Fick's law:

$$N = - D_{H_2} \cdot A \cdot \frac{dc}{dz} \tag{5}$$

A in Equation (5) is the transport area, c the concentration of the dissolved gas, and dz the thickness of the bentonite. The diffusivity D_{H_2} in bentonite was found in different investigations. It is determined as the product of the pore diffusivity D_p and the porosity ε_p i. e. the fraction of the geometric area which consists of water. It is between 4–$40 \cdot 10^{-12}$ m^2/s (Neretnieks, 1982). In the calculations below we use $D_{H_2}=22 \cdot 10^{-12}$ m^2/s.

The concentration c of hydrogen at the clay interface can be determined using Henry's law:

$$p = H \cdot x = H \cdot c / c_0 \tag{6}$$

where p is the pressure, x is the mole fraction of hydrogen in solution, H is the proportionality constant ($6.8 \cdot 10^4$ bar at 20°C) (Perry, 1973), and c_0 the molar concentration of the mixture which is mostly water. At 50 bar c_0=40.8 mol/m^3. We first explore a case where all the copper canister is corroded or where at least all the outer surface of the canister has the same concentration, see Figure 6.

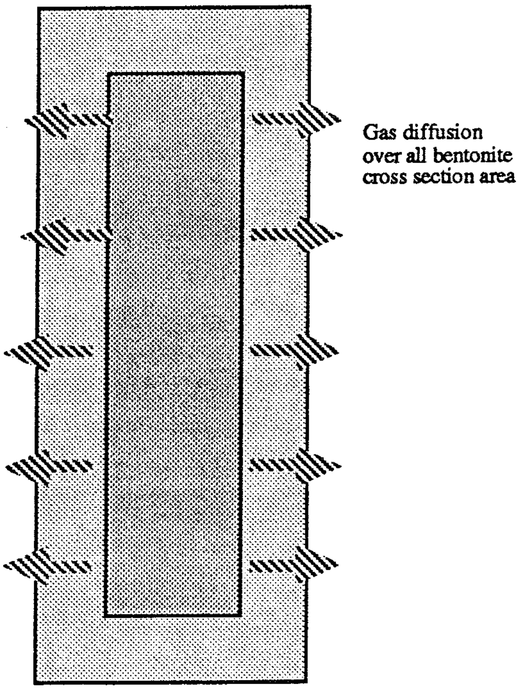

Figure 6. Gas can escape from all the outer surface of the canister.

For p=50 bar and the area A=12 m^2 (the outer surface of the copper canister) with the thickness of the bentonite $\Delta z = 0.4$ m, the rate of transport of hydrogen N=0.8 mol/y.

The hydrogen production, due to the alpha radiolysis of water at the exposed fuel surface in a copper canister has been calculated (Christensen and Bjergbakke, 1982). Two conditions are considered regarding the partial recombination of the produced radiolysis products.

Table 3 below summarizes the rate of production and the integrated amount produced for the two cases. The exposed pellet surface is 144 m^2 and the whole 0.03 mm gap is filled with water (Christensen and Bjergbakke, 1982).

Comparison of the computed production rates with the estimated diffusion rates indicate that when there is recombination after radiolysis, all the gas which is produced is dissolved in the water and is transported out by diffusion. In this case case gas bubbles would never form.

In the case where there is no recombination, the hydrogen gas is carried away by both flow and diffusion. The diffusion rate is of the same order of magnitude as or larger than the radiolysis rates up to some thousand years of storage time. If the diffusivity is at the lower end of the range then the diffusive transport is about 5 times smaller and the time would extend into the ten thousand years range.

Before this time gas may form and limit the radiolysis by preventing water to enter. After this time the radiolysis can proceed at the rate in Table 3, because the hydrogen gas can escape by diffusion and the whole gap may be filled by water. The presence of corrosion products would decrease the rate of radiolysis given in Table 3 by several orders of magnitude as discussed earlier.

It may be noted that the rate of diffusion is proportional to the gas pressure. An increase of pressure by a factor 2, gives rise to an increased diffusion rate by the same factor. However, the production rates and the integrated production of the hydrogen gas in the the case where there is no recombination indicate that with storage time of less than some 1000 years the gas escapes by both diffusion and flow. As the production rate diminishes, pressure decreases below the critical pressure, and the transport is by diffusion of dissolved gas only.

Table 3. Rate of production of hydrogen in one canister with 144 m^2 exposed pellet surface and 0.03 mm water filled gap.

Storage time years	Production rate moles/year	Integrated production moles
I. Recombination of some radiolysis products		
100	$8.3\ 10^{-4}$	0.054
300	$6.7\ 10^{-4}$	0.20
1000	$4.6\ 10^{-4}$	0.60
10^4	$2.5\ 10^{-4}$	3.84
10^5	$1.8\ 10^{-4}$	23
10^6	$0.9\ 10^{-4}$	144
II. No recombination		
100	3.6	260
300	2.5	860
1000	1.17	2100
10^4	0.25	8600
10^5	0.012	20600
10^6	0.006	29000

Below we consider a case when the copper canister is not degraded except for a cylindrical hole 0.1 m in diameter.

Figure 7 below shows a case where a hole has formed in the copper canister. The hole has a diameter d. If the hole is small in relation to the thickness of the clay the clay can be taken to be infinite from the diffusional transport point of view. All the resistance to transport is then equivalent to a cylindrical clay plug outside the hole with thickness d/4 (Bird et al 1960). The rate of transport by diffusion is $N = k \cdot A \cdot \Delta c$, where A_{hole} area of the hole, $A = \pi d^2/4$, k is the mass transfer coefficient $k = 2 D_e/d$ if the corrosion products form a half sphere on the surface of which there is a constant concentration (Bird et al 1960), and Δc is the concentration difference from the mouth of the hole to infinity (outer limit of clay)

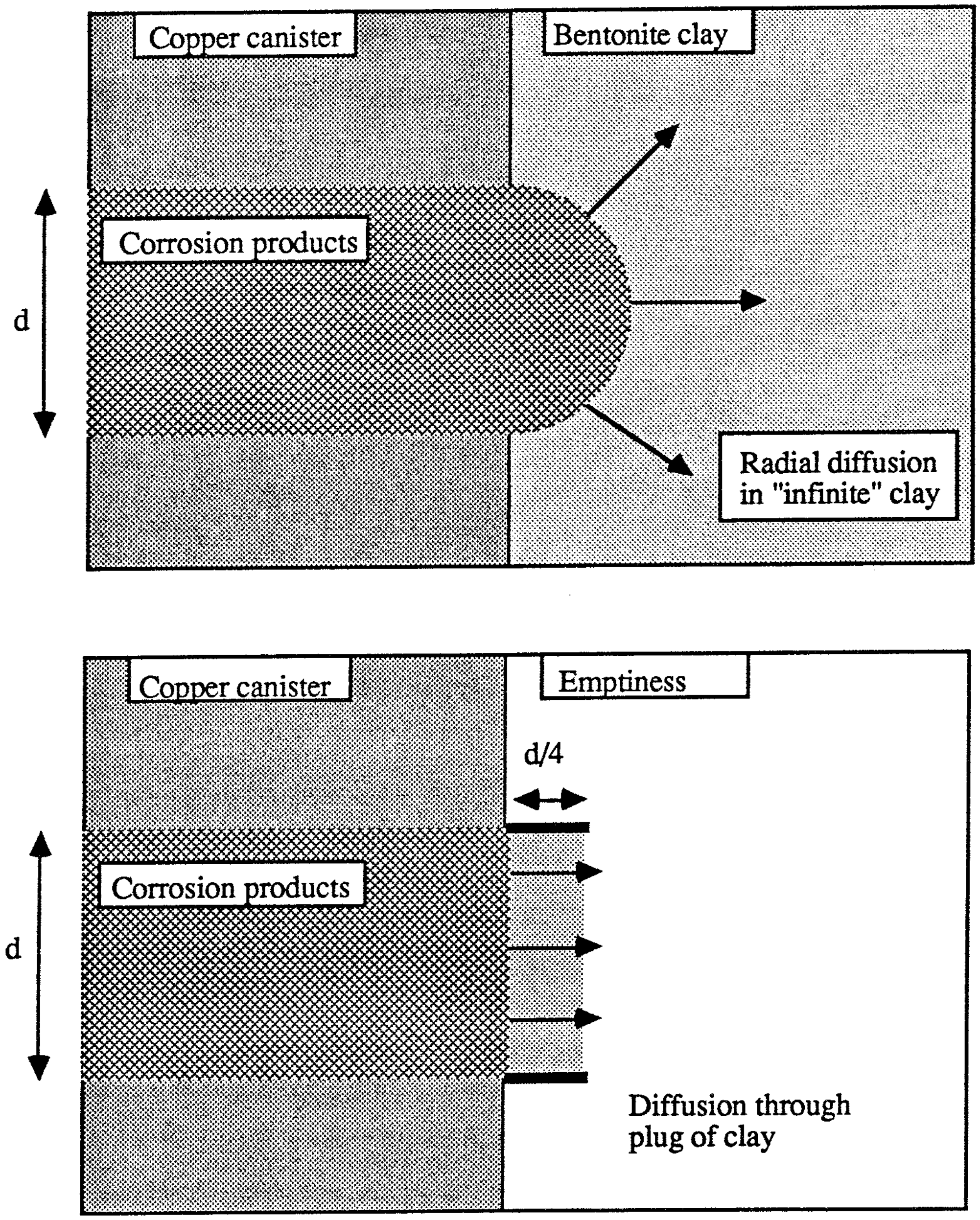

Figure 7. For diffusion into an infinite medium (the clay) from a sphere (the corrosion products), the resistance to diffusion is equivalent to that through a clay plug with thickness d/4

The rate of transport of hydrogen becomes:

$$N = \pi \frac{d^2}{4} D_e \frac{\Delta c}{d/4} = A_{hole} D_e \frac{\Delta c}{d/4} = \pi D_e d \Delta c \qquad (7)$$

For a pressure of 50 bar where the solubility of hydrogen is 40.8 moles/m^3, the diameter of the hole in the canister is 0.1 m, and using the hydrogen diffusivity $D_e = 22 \cdot 10^{-12}$ m^2/s, we obtain a diffusion rate of hydrogen equal to $0.9 \cdot 10^{-2}$ mol/y.

It is seen that when the gas has to escape through a hole 0.1 m in diameter the rate of transport by diffusion is about two orders of magnitude less than when all the canister is degraded and accessible to transport.

The production rate of hydrogen by radiolysis in the case where there is no recombination will decrease considerably, order to orders of magnitude, when the hydrogen must escape through a small hole in the copper canister.

As discussed earlier the corrosion of the copper canister by known mechanisms i.e. sulfide corrosion, will not permit a large hole to develop. The rate of radiolysis will then always be less than or equal to the maximum rate of escape of hydrogen by diffusion. Otherwise gas will form and prevent water from entering as discussed earlier.

There are additional resistances to transport in the corrosion products of the copper canister and through the rock beyond the clay. This is explored below.

With gradual corrosion of the copper canister, a hole filled with copper corrosion products will form. To estimate the rate of diffusion, it is assumed that the area of the hole A=0.01 m^2, and the thickness of the canister to be 0.06 m. With the diffusivity in water ($D_{H_2} = 1.4.10^{-8}$ m^2/s) through the corrosion products ($\varepsilon=0.1$) and assuming that all the concentration difference is over the corrosion products, the rate of diffusion N=0.09 mol/y at p=5 MPa. The resistance to transport is lower by one order of magnitude than in the bentonite clay outside.

When the hydrogen has migrated out of the canister, through the clay and reached the rock it must either diffuse out through the rock matrix or be transported away by the flowing water in the fractures. For the gas transport through the rock matrix, the mass transfer coefficient around a sphere of diameter d with an infinite region around it, is used. Setting the area (33 m^2) of the cylindrical clay around the waste canister equal to the area of the hypothetical surrounding sphere, with the same procedure as for the hole around the hole in the canister, the diffusion rate is found to be $N=6\cdot10^{-4}$ mol/y. An effective diffusion coefficient into the rock of $D_{er}=5\cdot10^{-14}$ m^2/s was then used

(Skagius and Neretnieks, 1982). This shows that the gas can not be transported outward through the rock matrix by diffusion alone. The excess must be transported by convection.

When the hydrogen gas has penetrated the clay barrier and reached the fractured rock, it can be transported further in the rock matrix by the water flowing in the fractures. Transport to the flowing water can be expressed in the form of an equivalent water flow of about 1 l/canister and year (KBS 3, 1983). With a concentration of 41 mol/m^3 at the interface of clay-rock (solubility at 50 bar), the rate of transport 0.041 mol/year corresponds to the radiolysis rate at more than 10 000 years storage time. With smaller production rates the hydrogen can escape through the rock without forming a gas phase. At higher production rates gas would form.

2.4 Summary and overview of the hydrogen generation and transport calculations

Originally there is a void of 4.3 l between the fuel pellets and the zircaloy rods. The gap is about 0.03 mm. This is the range of alpha particles in water. If and when the copper canister is breached water will enter the gap and radiolysis starts. The rate of radiolysis has been estimated for two different cases, one being about two hundred times larger than the other.

Several possible cases are explored. In one case the radiolysis will cause oxidation of the uranium oxide which will fill up the gap with a less dense U_3O_8. If the corrosion products have a porosity of 5 % the radiolysis will decrease by 100 times below that which takes place in unconfined water in the gap. This case is deemed to be quite probable. The reduction of radiolysis by more than a factor of 100 is also deemed to be probable.

In another case we explored the formation of hydrogen gas inside the canister based on the assumption that the production of hydrogen by radiolysis is larger than what can escape by diffusion of dissolved hydrogen in the water. It was shown that in such a case the bentonite clay which has very small pores and exerts strong capillary forces will not permit any water to enter the gap by flow.

The rate of radiolysis will stabilize at a rate which is about that at which the hydrogen may escape by diffusion through the clay. If all the canister has corroded away this rate is high and this mechanism will only be effective at very early times. This is of course contradictory because at short times the canister will not have had a chance to corrode fully.

A more probable case is that there is a local small hole in the canister through which the water must enter and through which the gas must escape. In the sample calculation where a hole 0.1 m in diameter has penetrated the canister, the rate of radiolysis would be limited to less than 0.01 moles per year at most. The limitation would be caused by the formation of hydrogen gas inside the canister.

A smaller hole would limit the rate proportionally. Considering that the known mechanism for copper corrosion will not even permit a hole this size to form in one million years, the reduction of radiolysis by this mechanism seems to be feasible and probable.

Calculations of the further transport of the hydrogen through the rock shows that purely diffusive transport is not sufficient even for the limited radiolysis. The transport away by flowing water in the fractures can however carry away the hydrogen if the equivalent flowrate of water is on the order of 1 l/canister and year, which is near the figure estimated for (KBS-3, 1983).

It is thus deemed probable that radiolysis will decrease considerably by filling up the gap with corrosion products as well as due to capillary forces not permitting water to enter.

When there is a gas phase inside the canister and this prohibits the water from being released by the capillaries in the clay some water will migrate in by surface and gas phase diffusion. Below we explore some mechanisms which may cause water to enter although there are capillary forces hindering the transport of water against a higher gas pressure.

3 ADSORPTION AND CAPILLARY CONDENSATION IN THE CORROSION PRODUCTS

3.1 Adsorption in the corroded gap

If a wetting fluid is confined within the fine pores of a porous solid, then the equilibrium vapor pressure of the liquid in the pores is less than the vapor pressure over a large body of unconfined fluid. An interaction between the porous medium and the fluid takes place.

The finer pores will be filled by the fluid even at a lower vapor pressure than the condensation pressure. This also means that if there is a medium with a pore size distribution of fine pores which is contacted with an unsaturated vapor, the vapor will "condensate" in the finer pores because these have a lower equilibrium vapor pressure. This mechanism is called capillary condensation. With an increasing vapor pressure larger and larger pores can fill up.

In our situation the water in the coarser pores of the bentonite has a higher vapor pressure and water evaporates there. This water vapor diffuses in through the corrosion products in to the uranium pellets and their corrosion products and condenses in the finer pores there. Some liquid water may thus always be present even in a more coarse grained porous medium as long as there are at least some small pores or capillaries.

In addition, plane surfaces can also adsorb vapors onto the surfaces. The adsorbed molecules can form a sparse layer where only a fraction of the surface is covered by the vapor molecules or at higher vapor pressures a mono molecular layer may form. Multilayer adsorption is also not uncommon.

For a particular fluid and porous solid, one can experimentally determine the relationship between vapor pressure and fluid concentration at a given temperature inside the porous medium. Such curves are referred to as adsorption isotherms.

In the earlier computations of the effect of alpha radiation from spent fuel on water, which has penetrated into the fuel rods in one copper canister, it was assumed that all the voids between the fuel pellets and the zircaloy cladding is evenly filled with water (4.3 l). Furthermore, it was assumed that the water film with a thickness of 30 μm forms on the outer surface of the pellets.

Oxidizing conditions at the fuel surface could be produced by the radiolysis of water, which may form corrosion products. They will then expand into the voids between the fuel pellets and the zircaloy cladding. Therefore, it is expected that a porous medium with fine pores is formed. Some exploratory calculations of the possible water content of this medium are done below by assuming spherical solid bodies with pores of equal size to have formed.

The hydrogen which has evolved as the result of the radiolysis of the water, provided that the hydrogen production rate is higher than the rate of escape, will exert a high gas pressure throughout the porous medium. The fine pores may then be occupied by non wetting gas phase. In addition, there may exist adsorbed and condensated water in capillaries, which may cover the surface and form a wetting phase.

There are two main mechanisms by which the water can be transported to the surface of the pellets. From the clay surface water evaporates and diffuses in the form of vapor through the hole in the canister wall. The difference in water vapor pressure at the saturated clay surface (20^0 C) and at the interior of the canister where the water is consumed by radiolysis is the driving force for diffusion.

Assuming a hole ($A=0.01$ m^2), with $D_v=2.2 \cdot 10^{-5}$ m^2/s (Perry, 1973), 0.1 porosity, in the canister as a reference case for water vapor diffusion, it is found that 1.2 mol/y water can be transported in by vapor phase diffusion. This value corresponds to the radiolysis rate of around 1000 years of storage time and gas phase diffusion could thus easily replenish all the water that is radiolyzed. For smaller holes in the canister the diffusion rate is smaller and may limit the radiolysis.

The existence of a pressure difference between water in the pores of the bentonite and the high pressure gas give rise to a curved interface at the interface between the clay and canister corrosion products. This interfacial pressure difference is also related to the vapor pressure with which the curved surface is in equilibrium. For a concave meniscus the equilibrium vapor pressure decreases with increase in curvature. This relationship is expressed by Kelvin's equation:

$$\Delta P = \frac{RT}{M} \ln \frac{P_0}{P_1} \qquad (8)$$

where ΔP is the difference in pressure across the interface. This will be determined by the capillary size. It can be obtained from Equation (1). M is the molecular weight of water, P_0 the vapor pressure of a free water surface and P_1 the vapor pressure of the curved interface.

In the pores which contain gas and are smaller than those in the bentonite, the water vapor forms a liquid phase in the capillaries. The mechanism, by which this phase is formed, is closely related to the curvature of the water in the pores of the bentonite.

The condensation in the corrosion products can be explained by considering the small pores between the idealized spheres as conical capillaries. The vapor will begin to condense at the bottom of the pore, which will start to fill with liquid.

As long as the radius of the liquid meniscus is small compared to the meniscus at the bentonite, and the vapor pressure above it is less than that above the curved interface, the pore will continue to fill. When the pore has filled to the point where the equilibrium vapor pressure is equal to that in the pore in the bentonite, condensation will cease and a state of equilibrium has been reached.

Using the available volume which may fill with water (4.3 l), and assuming that the particles of the corrosion products with the radius of 500 Å fill the gap, the amount of water condensated may be computed. Figure 8 shows the principle of capillary condensation between the spheres. At this radius the amount of water which can be held would be 0.054 kg. The variation of the amount of water with different size of the particles in the corroded gap is shown in Figure 9.

In the calculations the porosity is assumed to be 0.3, which reduces the total water capacity to 1.3 kg if all the porosity was filled with water. As it can be seen from the figure, the adsorption of water increases with decreasing particle size. With the above assumptions a reduction of the particle size to 20 Å is needed to adsorb 1.3 kg water i.e. fill all the pore space.

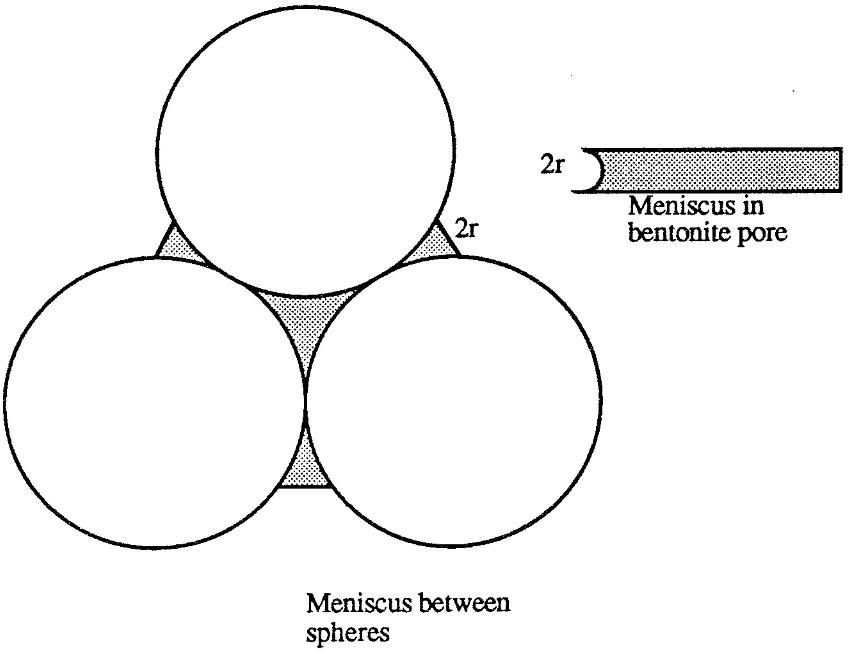

Figure 8. Capillary condensation between spheres. Meniscus between spheres has same radius as in bentonite pore.

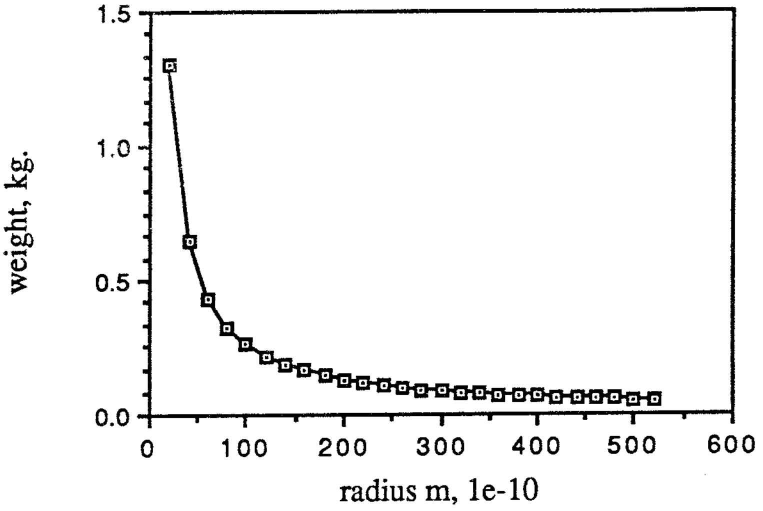

Figure 9. The curve showing the amount of water held versus the size of the particle in the porous medium.

However, the degree of the reduction of the water volume depends on the population and size of the particles. In the course of time, the gradual increase of corrosion and release of the other products as a result of water contact with the materials will necessarily reduce the size of the gap, and consequently the amount of water which can be present.

In order to establish a correlation between particle size and pore size of a consolidated porous medium, an information about the packing of the particles as well as about their shape is necessary. Since it is difficult if not impossible to determine these properties on purely theoretical grounds, models based on spheres are used for studying the phenomenon in such media. As the particles are of unequal sizes and they are not spherical more theorizing does not lead anywhere. Experiments are needed to determine the extent of capillary condensation in the real corrosion products.

In addition to the water which condenses in the finer capillaries the surfaces of the particles may hold adsorbed water. The thickness of the adsorbed distilled water film on a solid surface has been measured experimentally (Eriksson and Manev, 1990) on mica and its value is estimated to be of the order of 1000 Å. Distilled water is expected to form thicker films than waters which contain dissolved salts because the electrical forces reach further out in distilled water than in water with dissolved charged ions.

As a first approximation the maximum thickness of adsorbed water can be taken to be proportional to the thickness of the electrical double layer. For ground water an ionic strength of 1-5 mmol/l is assumed, and the double layer thickness is estimated. The thickness of the groundwater film which is adsorbed on the free surfaces in the gap is estimated to be between 10-20Å.

Taking the cross section area of a water molecule, 8-10 $Å^2$, the thickness of the adsorbed film is 5-10 molecular layers,which results in an amount of water between 0.18-0.35 kg on particles with a radius of 500Å. Comparing the monolayer water film adsorbed (0.054 kg) with the multilayer film, the amount of water which may be adsorbed in the latter case increases by about 3-6 times.

The above simplified exploratory calculations indicate that the porosity and the size of the corrosion products strongly can influence the amount of water that can be present in the corrosion products in the gap. The amount of water is sufficient to maintain a certain degree of radiolysis. The transport of the water into the gap to replenish the water radiolyzed can easily be maintained by gas phase diffusion. As the calculations are based on a series of simplifying assumptions the numerical results are approximate at best. To obtain more reliable results experiments must be performed on real corrosion products.

3.2 Summary of results

Figure 10 below shows the rate of radiolysis when there is no recombination for the case of unlimited supply of water and all the gap available for liquid water "Unlimited rate", when the gap is gas filled and the copper canister has turned into a porous mass "H2 diffusion large" and when there is a 0.1 m diameter corroded hole in the canister "H2 diffusion small". It is seen that in the more probable case of a limited hole the radiolysis is much smaller than in the case where there is unlimited access of water. The integrated mass of radiolyzed water during the first 100 000 years would be 800 mol when limited instead of 20 600 mol when unlimited.

In the described cases there is no limitation of the available water due to the presence of porous corrosion products in the gap around the uranium oxide pellets.

When there are corrosion products which fill the gap the rate of radiolysis is strongly reduced. With 5% porosity the reduction is one hundred fold. This is also shown in the same figure "5% pores". It is seen that up to about 1000 years a hole in the canister would be the limiting mechanism and after this time the decrease of the available water due to filling of the gap by corrosion products will limit the rate. The integrated amount of radiolyzed water in 100 000 years will be less than 200 mol in this case

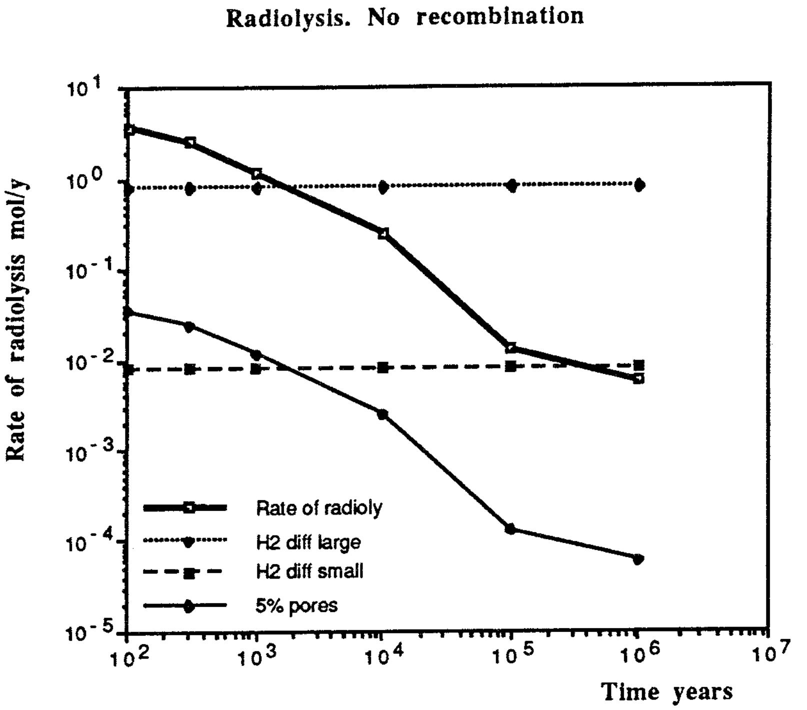

Figure 10 Rate of radiolysis in the case of no recombination. Unlimited by a gas phase, limited by hydrogen escape through totally degraded canister, through hole in canister and due to the presence of corrosion products in the gap.

4 DISCUSSION AND CONCLUSIONS

The present study is based on the previous assessments of the rate of radiolysis of the free water intrusion which forms a film around the uranium oxide pellets. Simplified models and geometries are used for the calculations in the examples. This may be justified by the fact that experiments are still lacking which could furnish the data to confirm the validity of the assumptions and the estimated results.

The conditions that prevail in the near field are considered to depend on the alpha radiolysis of the water film formed on the outer surface of pellets. The results which are obtained indicate that the rate of radiolysis depends on both the water intrusion rate and the water content in the gap inside of the copper canister. Also porosity and pore size distribution of the corrosion products, to a great extent, determine the amount of water present and accessed by the alpha particles which in turn determines the rate of radiolysis.

If a gas phase forms and liquid water cannot intrude by flow it still can intrude by vapor diffusion and surface diffusion to fill out the finer pores of the corrosion products and to adsorb on the surfaces of the corrosion products. With a porosity of 0.3 and particle size of 500 Å, the amount of water which can be adsorbed in a mono molecular layer is reduced to 1.3 % of the total volume of the gap. The estimated water film thickness which forms (multilayer approximation) on the free surface indicates that the content would be 4 to 8 % of the gap volume. These water masses are comparable to the water content in the corrosion products with 5% porosity which is deemed to be a reasonable value considering the lack of experimental data. At these water contents the rate of radiolysis decrease by about a factor of 100.

The above results and conclusions are based on a series of assumptions. Although they seem reasonable the projected results must be tesTed by experiments. One of the crucial assumptions is that corrosion products will fill the gaps. Another effect which must be tested experimentally is that the bentonite clay will not permit liquid water to fill up all the pores of the corrosion products.

5 PROPOSED FURTHER WORK

The following data should be gathered by realistic experiments

1 Porosities of corrosion products
2 Porosities of pellets
3 Pore size distribution of corrosion products
4 Water adsorption isotherm on corrosion products

Further experiments should be conducted to show that the pellets are oxidized and that corrosion products grow on their surfaces and do not dissolve and diffuse away.

An experiment should be designed to demonstrate that gas that evolves inside the gap results in an over pressure which does not permit water to intrude and replenish the water in the gap. This latter could probably be made using electrolysis instead of radiolysis.

5.1 Other points of interest

It was found in the above deliberations that the canister is probably not fully degraded even after one million years, but if at all corroded through, there will be only a hole of limited size. Such a small hole exerts a quite large resistance not only to gas escape but also to the escape of radionuclides. A 0.1 m diameter hole filled with copper corrosion products would have a transport resistance comparable to an equivalent water flowrate of less than 1 liter per year. A smaller hole would have a proportionally larger resistance. A hole would in addition force the diffusion to take place in a small section of the clay, further decreasing the rate of transport.

A calculation sequence as follows suggests itself.

For any given canister with a known water flowrate in the near field, the corrosion rate is determined. The corrosion is assumed to take place at one location on the canister. Some assumptions on the form of the hole are made and the time to breakthrough is calculated. After this time the hole is allowed to grow and the diffusional resistance in the corrosion products, the clay barrier and the fractured rock is calculated. At early times when the hole is small, the hole and adjacent clay will exert the largest resistance to transport.

In addition the rate of radiolysis, which will be very much smaller than that assumed in (KBS-3, 1983) will be used to determine the rate of oxidation of the fuel and the associated release of radionuclides.

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[1]MBT Tecnologia Ambiental, CENT, Cerdanyola, Spain
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