

NEAR FIELD TRANSPORT PROCESSES

Ivars Neretnieks

*Dep. of Chemical Engineering, Royal Institute of Technology,
S-100 44 Stockholm, Sweden*

ABSTRACT

In repositories for nuclear waste there are many processes which will be instrumental in corroding the canisters and releasing the nuclides. Based on experiences from studies on the performance of repositories and on an actual design the major mechanisms influencing the integrity and performance of a repository are described and discussed. The paper addresses only conditions in crystalline rock repositories. The low water flow rate in fractures and channels plays a dominant role in limiting the interaction between water and waste. Molecular diffusion in the backfill and rock matrix as well as in the mobile water is an important transport process but actually limits the exchange rate because diffusive transport is slow. Solubility limits of both waste matrix and of individual nuclides are also important. Complicating processes include gas generation by iron corrosion and alpha-radiolysis.

INTRODUCTION

The author has participated in the Swedish work on high level waste repository studies KBS-3 (1983) and earlier studies, The WP Cave design and the SFR repository for Low and Intermediate waste (Neretnieks 1989) as well as the Swiss Gewähr study (Nagra 1985), all in crystalline rock. The experience gathered is thus limited to crystalline rock repositories. Although many of the mechanisms which are active in this setting will be of importance in other repository designs and rock types such as clay and salt, this paper is limited to repositories in crystalline rocks.

OVERVIEW OF REPOSITORY TYPES

In high level waste and spent fuel repositories the radioactive waste will be emplaced in canisters. The canisters are deposited in holes or tunnels in crystalline rock at large depths, 500 m or more, and are surrounded by a backfill, often bentonite clay, with or without an admixture of sand or crushed rock to economize on the clay. Although the repository designs in Canada, Sweden (KBS-Type) and Switzerland differ in some important respects, the general long term performance and the mechanisms which are active are essentially the same. The Swedish alternative repository type, the WP-Cave concept, is based on a different idea. In the WP-Cave repository the fuels in their canisters is not individually imbedded in the clay but many hundred canisters are emplaced in tunnels in a large (hundreds of meters) egg shaped rock body. The whole rock body is surrounded by a thick (several meters) layer of bentonite-sand mixture. The individual canisters are surrounded by crushed rock. In this design a few mechanisms which are of no concern in the earlier repository types become important.

The low and intermediate level waste repository, SFR, at Forsmark started operating in 1988 and is also located in crystalline rock but at a depth between 50 and 100 m below the bottom of the Baltic. Many of the mechanisms of importance in the High Level Waste (HLW) repositories are active in this setting also. In addition some specific mechanisms related to the presence of concrete and large amounts of iron become important.

This paper first outlines some repository environments and materials and then proceeds to discuss the various transport and release mechanisms. Also some mechanisms of importance for the degradation of canisters are discussed. Some models and aspects of modelling the mechanisms are also discussed.

REPOSITORY DESIGNS AND ENVIRONMENT

Waste form

Spent fuel consists of about 95-98 % of crystalline uranium oxide. Other actinides and fission products are imbedded in the crystals with a few notable exceptions. Some noble gases, Iodide and Cesium have migrated out from the crystals to some small but important extent and are found at crystal boundaries and outside the fuel pellets. These nuclides can escape more readily than those inside the crystals.

Vitrified waste consists essentially of a glass structure in which the nuclides have been incorporated. Release and transport processes from HLW and Vitrified waste are the same to a large extent although there are some important differences related among others to the redox chemical behaviour of uranium.

Canisters and canister materials

Three types of canister materials will be treated. Copper is the candidate material in the KBS-3 concept. Copper will not corrode by reaction with water alone to any appreciable extent (KBS-3 1983). Corrosive agents dissolved in water must be present for corrosion to take place. Dissolved oxygen would corrode copper but at the depths considered for HLW repositories oxygen is not present. Any infiltrating oxygen with rainwater is consumed by reaction with reducing agents in the rock. Sulphide is another agent which can corrode copper. The corrosive agent must be transported to the surface of the canister. The corrosion rate will be limited by the transport rate of corrosive agents. The transport mechanisms are the same as those for transporting the dissolved constituents from the canister and HLW.

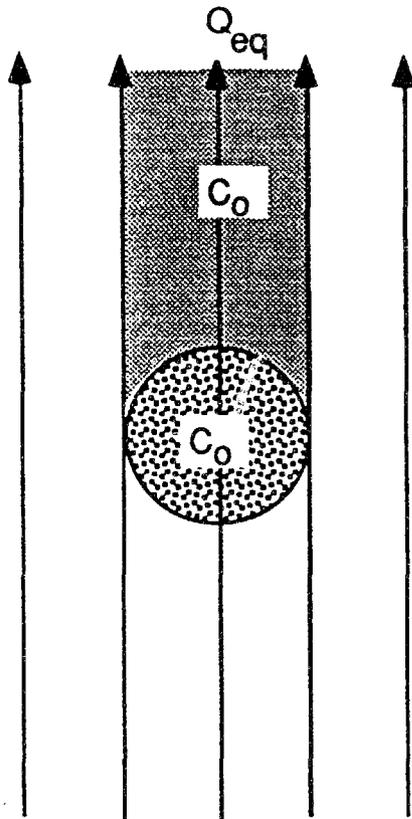
In contrast, iron canisters can corrode by reaction with water without the need to have other corrosive agents. The process is essentially governed by chemical reaction kinetics and will not be further treated here.

Concrete in concrete boxes or larger constructions containing and isolating the waste displays a very complex corrosion behaviour in comparison copper and iron. It may degrade by both dissolution of some readily soluble constituents such as sodium and potassium hydroxides, some less soluble compounds such as calcium hydroxide and silica but also by reactions with intruding species such as magnesium or sulphate which under some circumstances may form expanding precipitates which crack the concrete from within. Similar dissolution-precipitation processes in the concrete could possibly be active in the transport and retardation of escaping radionuclides.

Backfill

The backfill considered in all the mentioned repositories is bentonite clay. This clay is made up of very small particles with a very large specific surface, on the order of 1000 m²/g. The surface is chemically active and will adsorb water molecules strongly which makes the bentonite swell very strongly. Compacted bentonite has very low hydraulic conductivity and water flow under normal repository gradients is practically negligible. Ions dissolved in water will, however, move in the voids between the clay particles by molecular diffusion. All cations will adsorb or ion exchange on the clay particle surfaces because these are negatively charged. Many neutral species will also sorb on the clay, whereas negatively charged species will be hindered from entering the smallest passages due to electric repulsive forces.

FLOW THROUGH CASE



FLOW PAST AND OUT DIFFUSION

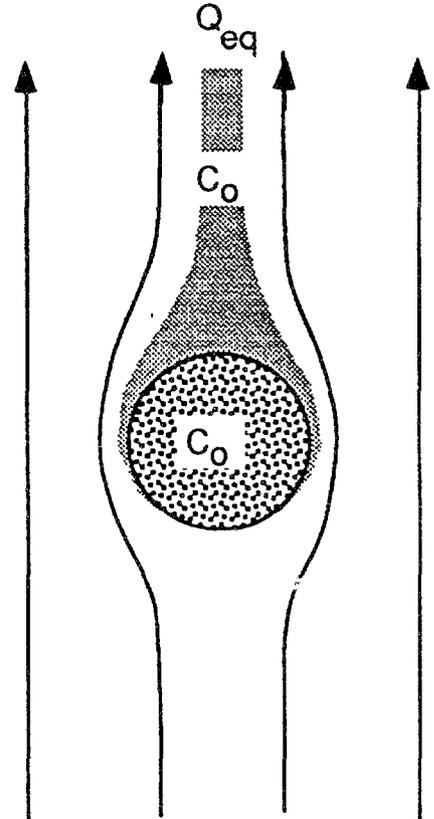


Figure 1. Contamination of water by advective transport (left) and diffusive transport (right)

Near-field rock

Crystalline rocks such as granites and gneisses are fractured and practically all the water flows in the fractures. The rock matrix is porous but the hydraulic conductivity is so low that practically no water flow takes place through the rock matrix. The porosity is connected over large distances (Skagius and Neretnieks, 1986, Birgersson and Neretnieks, 1990) and species of molecular size can move by molecular diffusion in the matrix. The frequency of conducting fractures is small and varies between 1 per a few meters and 1 per nearly 100 meters (Palmqvist 1987, Abelin et al., 1987, Neretnieks et al., 1987). Fractures are not open over their whole surface. Only small parts of a fracture conducts water in what is often called channels (Moreno et al., 1988, Abelin et al., 1990). The channel transmissivities vary within a wide range. This means that not all waste canisters need be located near a channel and only a few will have a channel with a high flowrate nearby.

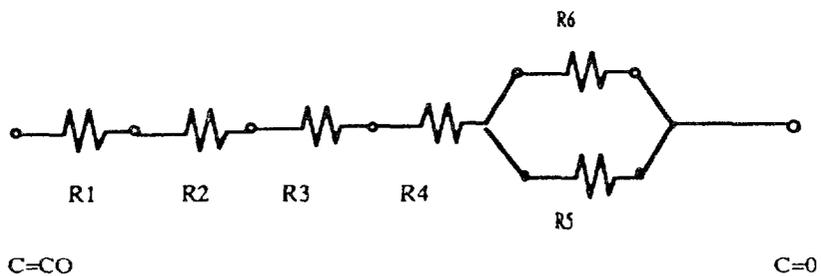
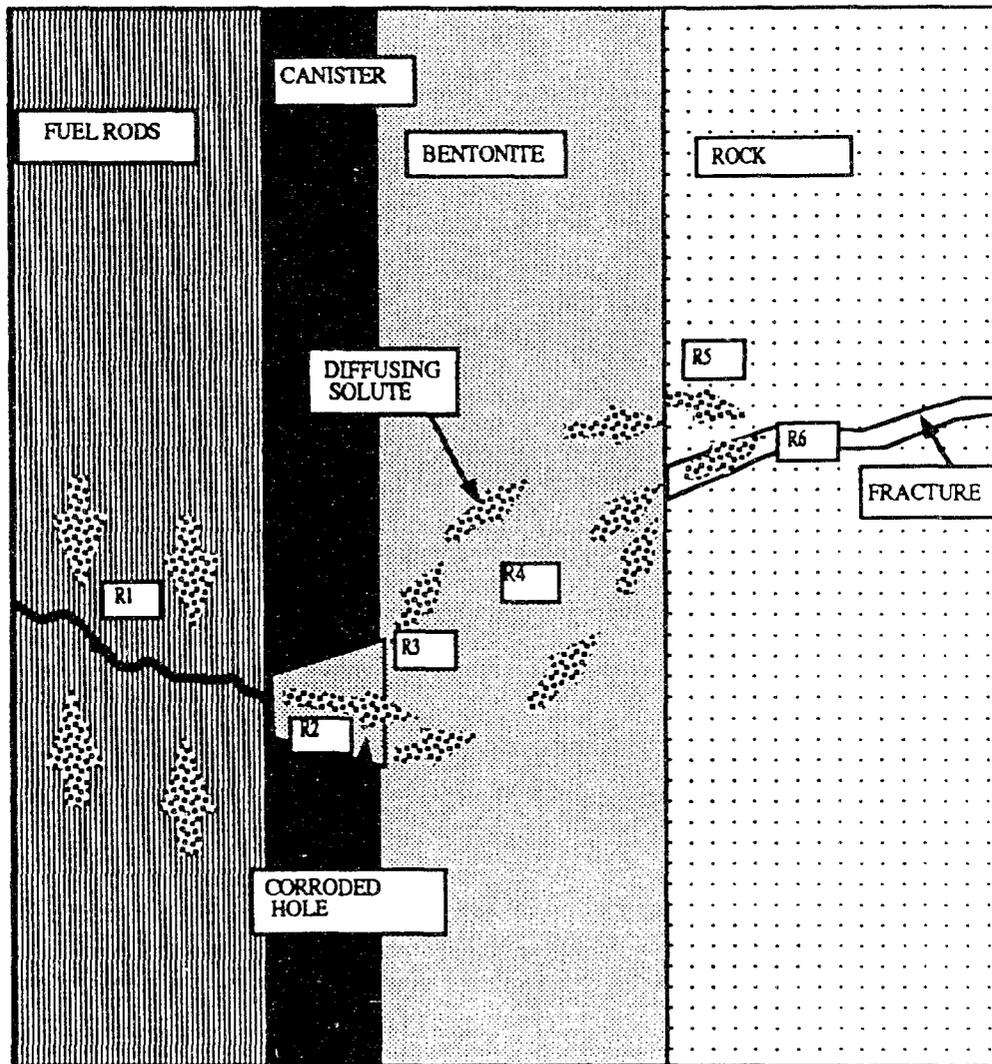


Figure 2. Nuclides from fuel rods in a degraded canister diffuse out to the water seeping in the fractures in the rock.

PROCESSES AND MODELLING

Generally speaking there are only a few basic processes which govern the release and transport of radionuclides in the near field. They are reaction rate, advection (flow) and molecular diffusion. In addition sorption processes may modify the rate of movement, radiolysis will change the chemical environment and may produce gas which will influence the transport processes. Chemical reactions such as precipitation will influence the release rate.

Some of the processes may dominate over others in one repository design whereas it may be different in other designs. In the following it will be attempted to illustrate both qualitatively and quantitatively some of the main mechanisms which have been addressed and modelled in the repositories discussed initially.

Some basic concepts

Corrosion of copper and concrete as well as the release and transport of the radionuclides strongly depends on the flowrate of water that carries the corrosive agents to the canister/waste and the dissolved nuclides from the fuel surface. In some cases when water actually can flow through a degraded canister and come in direct contact with the waste this flowrate will be the flowrate which contacts the waste and picks up the nuclide with its solubility concentration C_0 . In most situations of interest, however, backfill, corrosion products or more or less stagnant water volumes will act as diffusion barriers decreasing the flowrate which actually comes in contact with the waste. The transport of corrosive agents into the system can be described in the same way. For the quantitative description of the transport processes it has been found convenient to introduce the concept of *Equivalent Flowrate* Q_{eq} . The rate of transport of a nuclide from, or a corrodant to the canister is the product of the concentration C_0 and the equivalent flowrate Q_{eq} . Figure 1 below shows the concept.

In the advection case it is in principle straightforward to assess the flowrate which flows through a degraded canister. When there are diffusive barriers involved the process of diffusion and the geometry for diffusion must be accounted for. Figure 2 below illustrates a case where there are fuel rods within a corroded canister. The transport of dissolving nuclides will first be in the gaps between the fuel pellets and the tubes surrounding them (zircaloy in the Swedish case). The nuclides must find their way to the corroded hole in the canister, out through the backfill and to the water flowing in fractures in the rock. The figure illustrates the different paths the nuclides must take. Some paths have larger diffusion resistances than others because they may exhibit a smaller cross section for diffusion, a longer travel distance or a lower diffusivity. Conceptually it is illustrative to think of the various paths as having resistances which can be added like an electrical network. This is illustrated at the bottom of Figure 2. The over all resistance can be obtained from the individual resistances. The equivalent flowrate Q_{eq} is inversely proportional to the overall resistance.

In the KBS-3 (1983) and SFR Safety analysis it was found that one of the dominating resistances was that due to diffusion in the slowly seeping water in the fractures in the rock. The diffusion and uptake in the passing water in the fractures in the rock is essentially an unsteady state diffusion (Neretnieks, 1980, Pigford et al., 1990) in the sense that the water that approaches the canister is devoid of nuclide but as it passes the vicinity of the canister nuclides diffuse out into the water and contaminate it. The amount of nuclides which have passed to the water will depend on the residence time of the water, in a nonlinear fashion, as it passes the canister (or backfill outside). This transport process was found to make up the largest resistance by far in the central cases in the above studies both for the corrosion and for the contaminant release.

Corrosion

The corrosion of copper and of concrete will be governed by the rate of transport of corrosive agents. This is governed mainly by the diffusive processes discussed above. In the Swedish KBS-3 study (1983) it was found that the equivalent flowrate Q_{eq} which can carry corrosive agents to the copper was less than 1 liter per year for one canister. The main corrosive agent was found to be sulphide which is present in the deep groundwaters in concentrations less than 1 mg/l. This means that a canister would receive less than 1 mg of corrosive sulphide per year. It is evident that this corrosion would not have any serious impact on the integrity of a copper canister, weighing many tonnes, for many millions of years.

In the SFR repository for low and intermediate level waste (Neretnieks 1989), most of the intermediate level waste will be emplaced in a concrete silo surrounded by a bentonite and sand mixture. The silo is 50 m high, 30 m in diameter and has 0.8 m thick reinforced concrete walls. Also, in this case the diffusive resistance in the slowly seeping water in the rock will dominate over the diffusion resistance in the backfill and the concrete itself. The exchange of corrosive agents with the water in the rock will not be important in this case. There are other processes which will influence the integrity of the concrete and bentonite backfill which are more important than the exchange with the water into the rock. The bentonite acts as a source for sulphate and a sink for calcium and hydroxyl ions. Intruding sulphate from the bentonite will potentially form expanding solids, such as ettringite, and the depletion of calcium and hydroxyl ions will eventually weaken the concrete. The bentonite in turn will react with the hydroxyl ions and be degraded. In the time scale of a few thousand years these processes will at most have influenced a few tens of centimeters of the concrete and buffer.

Dissolution of waste and release of nuclides

Spent fuel and vitrified waste will dissolve and release its nuclides by several independent mechanisms. Dissolution of the matrix will take place when there is passing water which can pick up and carry away the dissolved matrix components such as uranium, in the case of spent fuel or silica, alumina, borates or other constituents of the glass matrix. The notion of the equivalent flowrate Q_{eq} can be used to conceptualize this process. In addition there will be diffusive processes which will allow readily mobile nuclides in the waste/fuel to move out independently of the dissolution of the matrix. The solubility of the matrix components C_0 will together with the flowrate determine the rate at which the matrix dissolves.

The solubility of uranium in the spent fuel is strongly influenced by the redox conditions at the fuels surface. Mainly alpha-radiolysis will strongly influence the redox potential. The radiolysis splits water into a reducing fraction, mostly hydrogen, and an oxidizing fraction containing oxygen, hydrogen peroxide and other components. The hydrogen is a small readily mobile molecule which may diffuse out of the system before it has re-reacted. There will then locally develop an oxidizing environment in which the uranium has a solubility of the order of milligrams per liter instead of micrograms per liter or less under reducing conditions. The oxidizing species will oxidize the uranium from U(IV) to U(VI) which can dissolve at the higher solubility limit. There will then be a situation when either the rate of radiolysis limits the supply of U(VI) and it cannot be released to the passing at a larger rate, or if the rate radiolysis is large, the release is limited by the equivalent flowrate. In the KBS-3 study (1983) the maximum rate of radiolysis was estimated to be comparable to the maximum carrying capacity of the water. Even so, with an equivalent flowrate of less than a liter per canister per year and a solubility of a few milligrams per liter, the dissolution rate is extremely small.

When the rate of radiolysis and the resulting formation of U(VI) are larger than what can be carried away by the water, there will form new crystalline phases. The re-crystallized uranium will not necessarily re-incorporate the other radionuclides which originally were located inside the UO₂ matrix. The release rate of these will be determined by their own solubility and the equivalent flowrate. The latter is, with a good approximation, the same for all dissolved species with a small molecular weight. If the water flow rate does not have the capacity to carry away all of a dissolved nuclide, this will precipitate at the fuels surface as the surface dissolves away.

In recent work Neretnieks and Faghihi (1990) it has been found that the rate of radiolysis may be considerably lower than assumed in KBS-3 because the hydrogen gas and corrosion products formed during the radiolysis will strongly limit the amount of water which is present at the fuels surface.

Diffusion and sorption in backfill

The bentonite in the backfill has a low hydraulic conductivity but a high porosity even when compacted. Dissolved ions, such as radionuclides, migrate by diffusion through the water filled pores. Positively charged and many neutral species will sorb on the clay surfaces and accumulate there. Negatively charged species such as iodide may partly be excluded from the water by repulsive electric forces. Before the sites are saturated (equilibrated) with the sorbing species little of the substance will pass the empty sites. The sorbing nuclides will be retarded in relation to the non sorbing species. Many short lived nuclides with high sorption may be retarded to such an extent that they will decay to insignificant concentrations. Once the sites are saturated (equilibrated) the diffusion of the species will proceed without retardation with a rate similar to non sorbing species. A very simple criterion for when a nuclide would go through essentially without decay and when it would decay to insignificance in a backfill barrier. It can be expressed in the following way (Neretnieks 1985).

When the group of variables $H = Z_0(\lambda D_a)^{0.5}$ is less than 0.1 there is no significant decay in the buffer. For values of H larger than 30 the nuclide will have decayed to insignificance i.e. less than 10^{-10} of its original concentration. Z_0 is the buffer thickness, λ is the decay constant and D_a is the apparent diffusivity which includes the retardation due to sorption.

Diffusion to and transport in the adjacent rock

It has been found that the rock matrices of crystalline rocks such as granites and gneisses have connected porosities in which small molecules move by molecular diffusion (Skagius and Neretnieks 1986, Birgersson and Neretnieks 1990). The hydraulic conductivity of the matrix is so low that water flow is extremely slow and over short distances, at least, the dissolved species will move faster by diffusion than by flow.

The dissolved species will thus have access to the interior of the the rock matrix, given time. Non sorbing species may reach very far into the rock matrix, 10's of meters, but strongly sorbing species will be retarded and reach only 10's of centimeters over periods of hundreds of thousands of years. The escape from the near field by molecular diffusion through the rock matrix is thus ruled out. Matrix diffusion may, however, play a very important role in the near field by allowing the oxidizing species generated by radiolysis to reach reducing iron minerals in the rock in contact with the backfill. Also sorbing nuclides will diffuse into the matrix, be sorbed and given more time to decay.

To a small extent, also, the diffusion in the matrix may form a transport path from the backfill to the flowing water in the fractures. This is illustrated by the path denoted R5 in Figure 2.

Fractures play a dominant role in transporting the nuclides from, and corrodants to, the canisters. Due to the low diffusivity of the matrix, only channels with flowing water which actually intersect the rock very near a canister will transport any nuclides. Channels which pass at more than a meter from the repository drift or hole will in practice be isolated from the dissolved species in the canister.

Gas evolution and transport

Corrosion of iron canisters or iron reinforcement in concrete constructions in the repository may generate considerable amounts of hydrogen gas. Alpha-radiolysis will also generate gas but to a smaller extent. The gas must escape by flow or diffusion. Otherwise overpressures may develop which may disrupt the rock. At the SFR repository the lid of the large silo will be designed with vents to let the gas escape from the silo to the surrounding backfill. Backfill with small pores, such as bentonite, exerts strong capillary pressures and an overpressure is needed in excess of the hydrostatic pressure to allow the gas to expel the water from the small pores in the buffer. For the sand-bentonite mixture used at SFR the over pressures needed are small, less than an atmosphere, but in the Swiss repository design with compacted bentonite surrounding the steel canisters, the opening pressure can reach many tens to hundreds of atmospheres (Nagra 1985). Once the pores have been freed from water, the gas permeability increases to high values and the gas escapes readily.

SUMMARY DISCUSSION AND CONCLUSIONS

The processes which govern the potential escape of nuclide from repositories in crystalline rock center around the transport capacity of the mobile water in the fractures in the rock. In repositories where a tight backfill such as bentonite is used water flow through the buffer will not act as an important transport process. Molecular diffusion will be faster. The rate of escape of the nuclides will depend on the diffusion paths and resistances. The diffusion in the mobile water in the very narrow channels in the rock often is the largest resistance. The low solubility of the waste matrix and of many nuclides will be an important limiting factor. Alpha-radiolysis may potentially increase the solubility of the spent fuel which consists of more than 95% uranium but there are several mechanisms which strongly counteract and limit radiolysis. A canister of a material such as copper will corrode only by reaction with corrosive agents transported by the water to the copper surface and because the equivalent (or effective) water flowrate is very small and because the water contains very low concentrations of the corrosive agents, the corrosion rate is extremely small. Gas which evolves due to corrosion of iron may build up considerable pressures before the capillary forces in the buffer let it escape.

REFERENCES

Abelin H., Birgersson L., Widen H., Ågren T., Neretnieks I., Moreno L. Channeling Experiment, Stripa Project, Technical report, July 1990, In print.

Abelin H., Birgersson L., Gidlund J., Moreno L., Neretnieks I., Widén H., Ågren T. 3-D migration experiment-Report 3, Part I, Performed experiments, Results and Evaluation. Stripa Project Technical Report 87-21, Stockholm, Nov. 1987.

Birgersson L., Neretnieks I. Diffusion in the Matrix of Granitic Rock. Field Test in the Stripa Mine. Water Resources Res. In print 1990.

Bolvede P., Christiansson R. SKB Forsmarksarbetena SFR. Vattenförande Sprickor inom Lagerområdet. VIAK Co, Stockholm, Jan 1987. (Water bearing fractures in the repository area) (In Swedish).

KBS-3, Final Storage of Spent Nuclear Fuel, SKBF/KBS, 1983.

Moreno, L., Tsang Y.W., Tsang C.F., Hale F.V., and Neretnieks I. Flow and tracer transport in a single fracture. A stochastic model and its relation to some field observations. Water Resources Research, 24, p 2033-3048, 1988.

NAGRA Project Gewähr. Endlager Für Hochaktive Abfälle: Das System der Sicherheitsbarrieren. Nagra, Baden, Switzerland, Jan 1985.

Neretnieks I. Transport Mechanisms and Rates of Transport of Radionuclides in the Geosphere as related to the Swedish KBS Concept. Underground disposal of Radioactive Wastes, 2, IAEA-SM-243/108, p 315-339, 1980.

Neretnieks I. Diffusion in the Rock Matrix: An Important Factor in Radionuclide Retardation? J. Geophys. Res. 85, 1980, p 4379-4397.

Neretnieks I. Diffusivities of some Constituents in Compacted Wet Bentonite Clay and the Impact on Radionuclide Migration in the Buffer. Nuclear Technology, 71, p 458-470, 1985.

Neretnieks, I. The Swedish repository for low and intermediate level reactor waste-SFR. Radioactivity release and transport calculations. Symposium on scientific basis for nuclear waste management. Berlin Oct 10-13, 1988.

Neretnieks I. Channeling in crystalline rocks. Its possible impact on transport of radionuclides from a repository, Colloque international, Impact de la physico-chimie sur l'étude, la conception et l'optimisation des procédés en milieu poreux naturel, Nancy, 10-12 Juin 1987.

Neretnieks I., Abelin H., and Birgersson L. Some recent observations of channeling in fractured rocks. Its potential impact on radionuclide migration. In DOE/AECL conference, Sept 15-17, 1987, San Francisco, Proceedings.

Neretnieks, I. The Swedish Repository for Low and Intermediate Reactor Waste-SFR. Radioactivity Release and Transport Calculations. Scientific Basis for Nuclear Waste Management, Materials Res. Soc. 1989, p 537-544.

Neretnieks L., Faghihi M. Some mechanisms which may reduce radiolysis. SKB Technical Report, TR 91-46, Stockholm, Aug. 1991. Dep. Chemical Engineering, Royal Institute of Technology, Stockholm, Sweden.

Palmqvist K., Stanfors R. The Kymmen power station TBM tunnel. Hydrogeological mapping and analysis. SKB Technical Report, TR 87-26, Stockholm, Dec. 1987.

Pigford, T.H., Chambré P.L., Lee W.W. A review of Near-Field Mass Transfer in Geologic Disposal Systems, Lawrence Berkeley Laboratory, LBL-27045, Feb 1990.

Pusch R., Ranhagen L., Nilsson K. Gas Migration through MX-80 Bentonite, Swedish Geological, Lund, Sweden., TR 36, 1985.

Skagius K., and Neretnieks I. Porosities and diffusivities of some nonsorbing species in crystalline rocks. Water Resources Res. vol 22, p. 389, 1986.
WP Cave Assessment of feasibility, safety and development potential, SKB Technical Report, TR 89-20, Stockholm, September 1989.