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MASS TRANSFER IN A SALT REPOSITORY

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Abstract

To meet regulatory requirements for radioactive waste in a salt repository it is necessary to predict the rates of corrosion of the waste container, the release rates of radionuclides from the waste package, and the cumulative release of radionuclides into the accessible environment. The mechanisms that may control these rates and an approach to predicting these rates from mass-transfer theory are described. This new mechanistic approach is suggested by three premises: (a) a brine inclusion originally in a salt crystal moves along grain boundaries after thermal-induced migration out of the crystal, (b) brine moves along a grain boundary under the influence of a pressure gradient, and (c) salt surrounding a heat-generating waste package will soon creep and consolidate as a monolithic medium surrounding and in contact with the waste package. After consolidation there may be very little migration of intergranular and intragranular brine to the waste package. The corrosion rate of the waste container may then be limited by the rate at which brine reaches the container and may be calculable from mass-transfer theory, and the rate at which dissolved radionuclides leave the waste package may be limited by molecular diffusion in intragranular brine and may be calculable from mass-transfer theory. If porous nonsalt interbeds intersect the waste-package borehole, the release rate of dissolved radionuclides to interbed brine may also be calculable from mass-transfer theory. The logic of these conclusions is described, as an aid in formulating the calculations that are to be made.

1. Motion of Brine in Heated Polycrystalline Salt

Radioactive decay of high-level radioactive waste emplaced in natural salt heats the salt, and the resulting temperature gradients can induce motion of brine liquids initially present in the salt. Natural polycrystalline salt contains brine in grain boundaries and brine inclusions in crystals. A liquid inclusion in a salt crystal migrates up the temperature gradient to the grain boundary because of temperature-dependent solubility, at a rate determined by the rate of molecular and thermal diffusion of dissolved salt from the hot face to the cold face of the inclusion and by the kinetics of dissolution and crystallization [1-6]. Earlier studies [7] predicted thermally driven

transport of brine towards the waste package, assuming that a brine inclusion in a crystal moves across the grain boundary into the adjacent crystal and finally reaches the waste package.

Later experiments [8] indicated that brine reaching a grain boundary remains within the grain boundary rather than moving into adjacent crystals, and subsequent analyses [9-11] assumed that the grain-boundary brine moves along the grain boundary at a velocity proportional to the pressure gradient. Although the law of pressure-induced motion of grain-boundary brine is not known, it is assumed here that the motion of grain-boundary brine increases with pressure gradient and depends only on the pressure gradient. Because the pressure gradient is not necessarily in the same direction as the temperature gradient, as illustrated below, it is not necessary that brine move towards the waste package.

2. Flow Into a Low-Pressure Cavity Surrounding the Waste Package

To explain the pressure-induced motion of grain-boundary brine, assume for simplicity that all inclusion brine has reached the grain boundaries, that brine transports along grain boundaries as through interconnected pores, and that the salt and pore liquid behave as a thermoelastic medium. Pressure gradients to cause the transport of intergranular brine can be developed by the existence of a low-pressure boundary, as would occur if a cavity exists between the waste package and salt and by a temperature gradient within the salt. Brine in regions of higher temperature will be at a higher pressure than the liquid in cooler salt, because the liquid brine has a higher coefficient of thermal expansion than does the surrounding salt.

If the waste package is within a cavity such that the annular space between the waste container and salt is at near-atmospheric pressure, some of the intragranular brine will flow into the waste cavity and other intergranular brine will flow outward into cooler salt. Figure 1 illustrates the pressure profile that will result with no intragranular flow and the profiles that will result after pressure-induced flow, assuming a low-pressure cavity surrounding the waste package and assuming a steady temperature profile. In Figure 1 and in subsequent illustrations it is assumed that salt creep results in a stationary fluid pressure of intergranular brine that is near or equal to the lithostatic pressure, rather than the hydrostatic pressure of pore liquid that would occur if the rock behaves as an unyielding porous skeleton.

To make a bounding calculation of the maximum rate of release of radionuclides from the waste package, the Salt Repository Project, which is developing a DOE repository for high-level commercial radioactive waste in natural salt, calculates the rate of accumulation of brine in the cavity and multiplies this brine accumulation rate by the solubility of each radioelement to obtain a conservatively high estimate of the release rate [12]. The calculation is simple and bounding, but it requires a reliable calculation of the rate at which brine migrates to the cavity. To estimate container life the Project relies on corrosion tests of container samples immersed in liquid brine, again conservatively assuming that liquid brine will accumulate in the

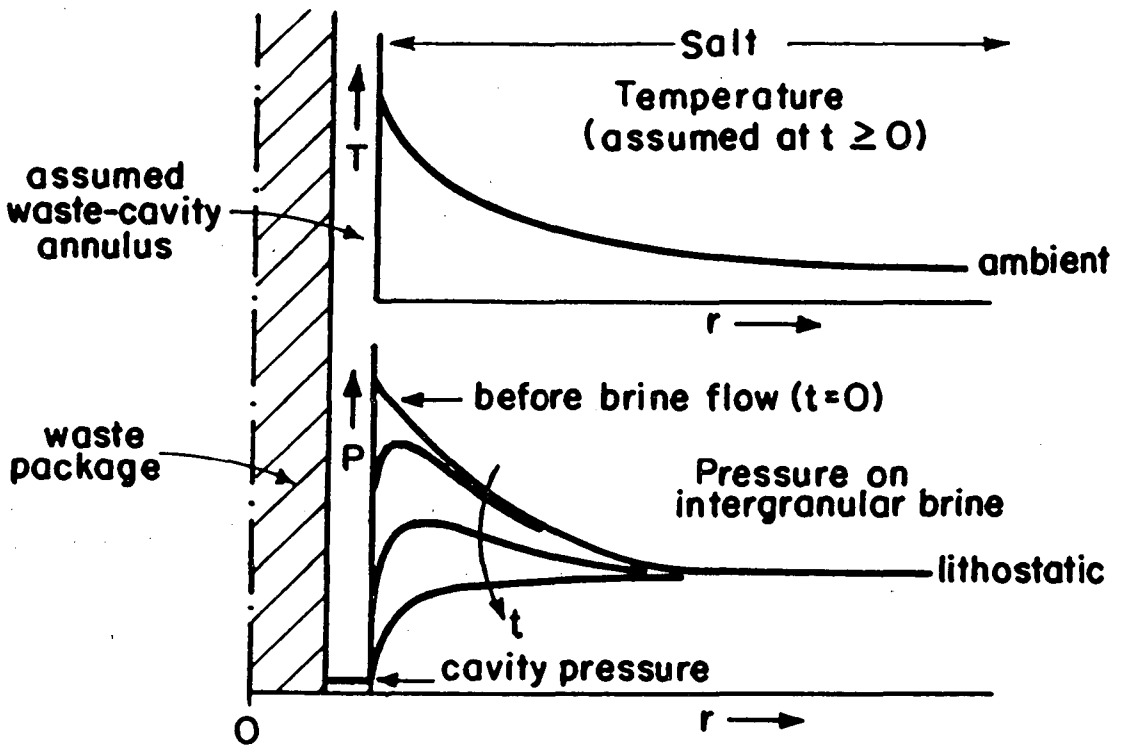

Figure 1. Profiles of pressure on intergranular brine neglecting salt creep (steady temperature profile assumed for illustration)

waste cavity. Here the chemical composition of the accumulated brine is the principal brine property affecting corrosion rate.

A more realistic calculation by Ratigan [13] considers the effect of salt creep and suggests that the cavity surrounding the waste package will not exist during the time period of interest. If so, the boundary condition affecting brine migration is considerably changed, and there may be a simpler method of estimating rates of radionuclide release and container corrosion. This idea is developed in the following section.

3. The Effect of Salt Creep

In a salt repository for high-level radioactive waste the maximum salt temperature occurs within a decade after waste emplacement and slowly relaxes for the next few hundred years. The waste container is required to withstand corrosion by incoming brine for 300 years or longer [14], and release of radionuclides from the waste package into surrounding brine or salt must be predicted to at least 10,000 years. On this time scale creep of salt is appreciable, even at ambient temperature.

Ratigan [13] predicts that salt surrounding a waste package will creep and consolidate as a monolithic structure surrounding the waste package within a few years after emplacement. Here consolidation refers to the filling of voids and gaps by salt creep. For any natural salt the actual consolidation time will depend on the rate of heat generation, the amount of salt backfill (if any), dimensions of the emplacement hole and waste container, repository depth, and creep properties of the salt. For such early consolidation we should analyze brine transport without assuming a low-pressure cavity for brine to flow into.

If brine were continuously driven towards the waste package by thermally induced force, as assumed in earlier analyses of brine migration [7], the lack of a low-pressure cavity need not affect the brine inflow. Brine thermally driven to the waste package could displace the surrounding salt and create its own cavity, if not first consumed by chemical reaction with the container. However, with pressure-driven transport of intergranular brine the direction of flow depends on the boundary condition at the container-salt interface. The salt tends to consolidate so that the interface pressure rises to the lithostatic pressure. If the salt is heated more rapidly than it can relieve thermal stress by creep, the salt adjacent to the container will be under additional compression because of thermal expansion of the hot salt. Fluid within the grain boundaries expands more when heated than does the salt, so heating generates a pressure on confined fluid that is greater than the lithostatic pressure. Therefore, neglecting the effect of brine-container chemical reaction, the fluid pressure at the interface of the container and consolidated salt will equal or exceed the lithostatic pressure, the main driving force for creep and consolidation.

For simplicity, assume that creep has consolidated the salt. A steady nonuniform temperature profile is assumed to be applied at $t = 0$, and the

effect of chemical reaction between brine and the container is neglected. Heating puts the hot salt under further compression, increasing the contact pressure between waste package and salt. The resulting profiles of fluid pressure before and after flow and creep are shown in Figure 2. Salt creep and outward motion of the brine provide fluid expansion and reduce the fluid motion to zero. The brine flows outward into the cooler salt until a zero gradient of fluid pressure is reached. Surface tension can result in a brine film between the salt and waste package. The local fluid pressure of this liquid film can temporarily exceed the local compressive stress on the salt until outward flow of brine through grain-boundary pores relaxes the fluid pressure to lithostatic. Thereafter there is no mechanism for brine to flow across the package-salt interface, other than consumption of brine components by chemical reaction or radiolysis.

The sequence of heating, salt creep, and brine flow, after consolidation of salt around the waste package, need not be the simplified sequence assumed here for illustration. Gradients in fluid pressure caused by heating and cooling are relieved by fluid displacement and by creep, relaxing the fluid pressure to the constant lithostatic pressure.

These local adjustments in stress, strain, and density of the hot salt and intergranular brine near the waste package are likely to follow the temperature changes without significant time delay. However, this should be verified by calculation. Later, when the salt near the waste package begins to cool, some brine must move from the outer salt into the inner cooling salt where the brine density is now increasing, but no net brine transport at the package-salt interface is expected, other than that required by chemical and radiolysis reactions.

4. Effect of Chemical Reaction of Brine with the Container

Now the imaginary salt-like waste package considered above is replaced with a real waste package whose container can react with brine. The solid products of the brine-metal reaction are of lower density than the original metal, so the salt-container reaction must generate a higher pressure against the surrounding salt and must cause outward elastic and plastic strain. This results in a locally higher fluid pressure that moves fluid outward, away from the waste package. However, brine can still reach the container surface, though it may be impeded by the mass-transfer resistance of the corrosion product on the surface as well as by the diffusional resistance in the grain-boundary pores.

Water in brine reacts with a ferritic container to generate hydrogen. The hydrogen must move outward from the surface, through the intergranular passages that contain brine, so a mixture of brine and hydrogen must exist within the grain-boundary salt pores near the container-salt interface. If hydrogen dissolves in the brine, the concentration of water in the liquid near the container surface is less than that in brine not containing hydrogen, so water can transport toward the container by molecular diffusion while dissolved hydrogen diffuses away. If the partial volume of dissolved hydrogen

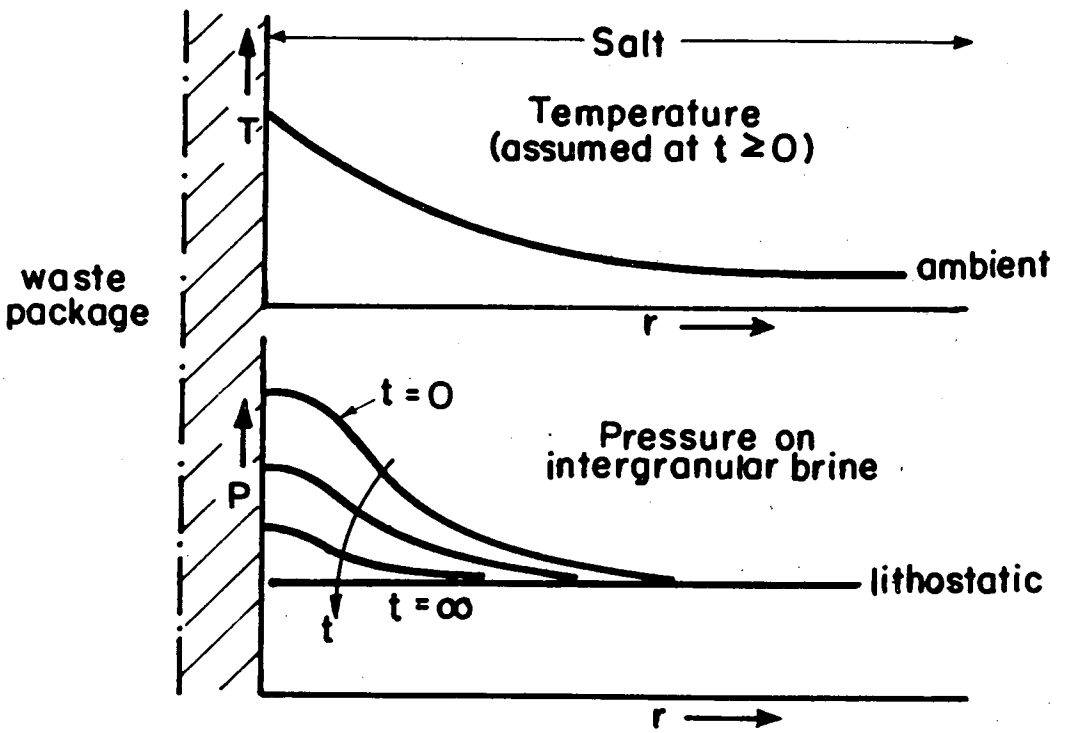

Figure 2. Profiles of pressure on intergranular brine if creep has consolidated salt against the waste package (for illustration, we assume that creep has initially consolidated the salt and a steady temperature profile is then imposed at t = 0)

is less than that of the reacted water, and if not offset by the volume expansion of the solid corrosion products, the container-water reaction can also result in a slight positive pressure gradient that may contribute to some inward flow of brine, as illustrated in Figure 3.

Conservatively assuming an infinite reaction rate of container with water and neglecting the diffusional resistance of the solid reaction products, we can calculate from mass-transfer theory a uniform-corrosion life of the container. Because molecular diffusion through the intergranular passages is likely to be very slow, this calculated corrosion life can be less than that extrapolated from laboratory corrosion experiments, where a metallic sample is immersed in excess liquid.

Sweden's KBS project [15-17] utilizes a similar approach towards predicting the corrosion life of a thick copper container, limited by the calculable rate of diffusion of sulfide in groundwater through bentonite backfill. Several independent reviews have found the KBS approach to be acceptable.

5. Estimating Radionuclide Release Rate

A simple and bounding estimate of the rate of radionuclide release from the waste package into surrounding consolidated salt can be made by assuming that the container is not there, assuming saturation concentrations of radioelements in grain-boundary brine adjacent to the waste surface, and calculating the rate of molecular diffusion of the dissolved radioelements and their isotopes through the grain-boundary brine. Although there may be some finite influx of brine into the waste-package interstices when the container fails, we can conservatively assume that the interstices are immediately filled with brine and that the reaction of brine with the waste form quickly brings all of this liquid to saturation concentration. Further flow of liquid into the interstices is unlikely because the solid reaction products are of lower density and because of the expected (and required) very low rate of dissolution of the waste material. If the pressure-induced brine flow is very small, brine necessary to continue the small but finite dissolution reactions is more likely to be supplied by molecular diffusion, with a mechanism similar to but slower than that described above for container corrosion. Therefore, the problem of release rate from the waste package can be reduced conservatively to that of calculating the rate of molecular diffusion of dissolved species through grain-boundary brine, beginning at the package/salt interface and extending into the salt.

This is the same mass-transfer analysis [18,19] that has been presented for the dissolution of radioelements from a waste package immediately surrounded by saturated porous rock, with negligible convective transport. The steady-state mass-transfer rate can be predicted for known waste-package geometry. For each long-lived radioelement two additional parameters are required: (a) the saturation concentration of the radioelement in brine and (b) the coefficient for molecular diffusion of the element in grain-boundary brine. Each of these parameters can be measured separately.

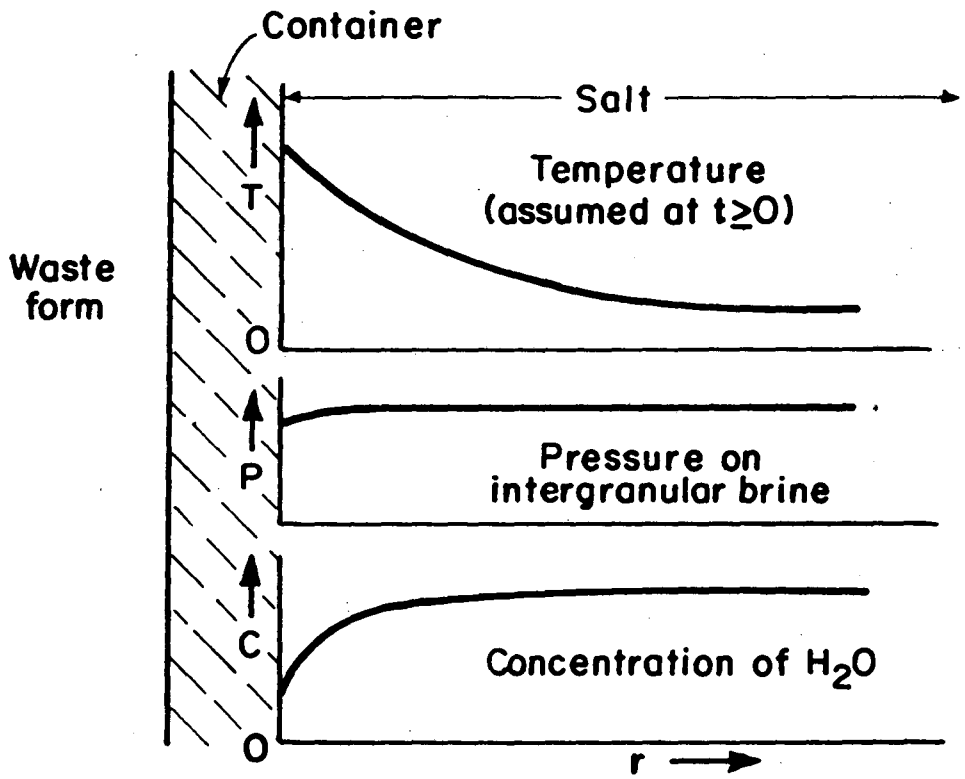

Figure 3. Profiles of fluid pressure and water concentration, with container-water reaction (steady temperature profile assumed for illustration).

The time to reach steady state mass transfer is likely to be very long, so the transient rate of mass transfer into the salt must also be considered, requiring as an additional parameter the retardation coefficient of the radioelement due to sorption on the salt [19].

6. Summary of Brine Transport in Salt

If there is early consolidation of salt around the waste package, it seems likely that brine transport may never be appreciable or will have long since ceased over most of the several-hundred-year period of container life and by the time radioelement release can be important. The resulting release-rate estimates from mass-transfer analysis seem likely to be more realistic and smaller than those calculated from the estimated rate of brine accumulation in a hypothesized waste cavity. They do not require knowledge of the rate of brine transport along grain boundaries. They rely on the mass-transfer theory that has already been extensively studied.

The foregoing discussion of expected mechanisms of consolidation and brine migration suggest different kinds of experiments and analyses than have been carried out heretofore to characterize brine migration in a salt repository. In fact, to characterize brine migration quantitatively, including the effect of salt expansion and creep, would require an ambitious program of experiment and analysis. Ignoring these mechanisms and ignoring the effect of salt consolidation can lead to a highly unrealistic and artificial picture of brine migration in a salt repository.

However, quantitative prediction of brine migration may not be needed to predict release rates from a buried waste package if the boundary across which release rates are to be calculated is identified as the inner surface of consolidated salt surrounding the package. Bounding values of the release rates across that surface can be calculated by analysis of solubility-limited mass-transfer rates [18,19].

7. Effect of Flow in Interbeds Intersecting Bore Holes

Another source of brine in a salt repository is flow through nonsalt sedimentary layers that may be present in thin seams surrounded by salt. Here it is assumed that such interbeds occur over horizontal distances encompassing many waste packages and that the interbed flow is driven by some overall pressure gradient. The interbed brine is likely to be saturated because of its contact with adjacent salt layers, although its composition will not necessarily be the same as that of brine in inclusions and grain boundaries. It seems unlikely that a waste package will be knowingly placed in a bore hole known to be intersected by an interbed, but if interbeds intersecting boreholes are frequent or not easily detected, it may be necessary to consider the effect of interbed flow on container corrosion and radionuclide release rate.

If the inner cored surface of the porous interbed connects with the

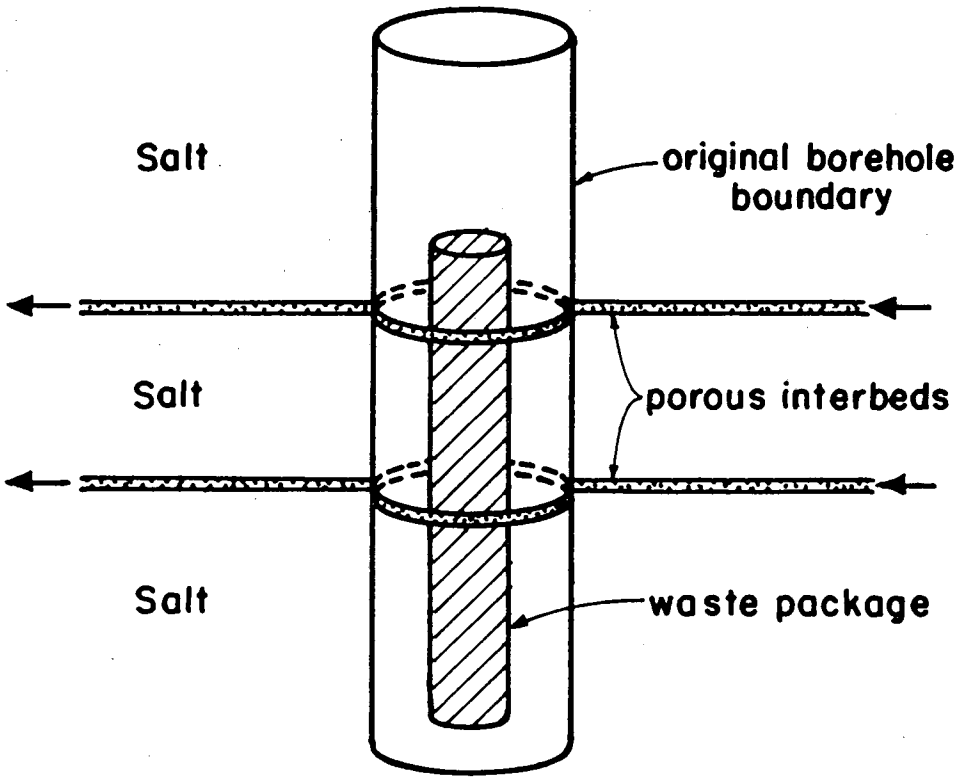

Figure 4. Flow in porous interbeds intersecting borehole

surface of the waste package, as illustrated in Figure 4, we have a pathway for mass transfer of brine water from the flow through the porous interbed to the waste container surface for chemical reaction and for mass transfer of reaction-generated hydrogen from the container to the interbed brine. Later, assuming that the container is not present, there is mass transfer of dissolved radionuclides from the cored edge of the interbed into the interbed flow stream. This problem of diffusive-convective mass transfer for flow in a porous medium surrounding a cylinder, conservatively assuming saturation concentration in the liquid at the cylinder surface, has already been analyzed by Chambre' [18-20].

If the annular bore hole space is backfilled with salt, creep consolidation should transform the backfill into a monolithic structure connecting the outer salt, and it will separate the cored edge of the interbed from the waste package. Interbed brine can diffuse through this consolidated backfill to corrode the container. Later, released radionuclides can diffuse through the consolidated backfill to reach the interbed water. This is a mass-transfer problem analogous to the problem analyzed by KBS [15-17], wherein groundwater flowing through a horizontal fracture in granite supplies sulfide oxidant that diffuses through a compressed bentonite backfill to reach the copper container. Later, dissolved radionuclides, assumed to be at saturation concentrations in liquid at the waste surface, diffuse through the backfill into the moving fracture-flow water. A similar approach is suggested for analyzing the mass transfer from and to interbeds intersecting the bore holes in a salt repository.

8. Recommendations

Main premises of this discussion are that a brine inclusion remains in grain boundaries after its thermally induced migration from the crystal in which it originally resided, that brine in grain boundaries moves principally under the influence of a pressure gradient, and that the only important effect of a nonuniform temperature profile on intergranular brine is to generate thermally a induced pressure gradient. These may need confirmation by further experiment. Also, the kinetics of salt consolidation and creep under the influence of lithostatic and thermally induced stresses should be estimated, as well as the kinetics of pressure-induced fluid motion near the salt-container interface, to establish the time period at which the motion of intergranular brine becomes negligible.

The analyses of time-dependent mass transfer described above should be applied to estimate the mass-transfer-limited corrosion rate of the waste container and the release rate of radioelements and radionuclides.

9. References

1. T. R. Anthony and H. E. Cline, "Thermal Migration of Liquid Droplets Through Solids," J. Appl. Phys., 42, 3380 (1971).

2. G. H. Jenks, "Effects of Temperature, Temperature Gradients, Stress, and Irradiation on Migration of Brine Inclusions in a Salt Repository," ORNL-5526, July 1979.

3. Ya. E. Geguzin, A. S. Dzyuba, and V. S. Korzhanov, Sov. Phys. Crystallogr. 20, 234 (1975).

4. D. R. Olander, A. J. Machiels, M. Balooch, and S. K. Yagnik, "Thermal Gradient Migration Inclusions in Synthetic Alkali Halide Single Crystals," J. Appl. Phys., 53, 669 (1982).

5. T. H. Pigford, "Migration of Brine Inclusions in Salt," Nuclear Technology, 56, 93 (1982).

6. T. H. Pigford, "Reply to 'Remarks on Migration of Brine Inclusions in Salt'," Nuclear Technology, 63, 509 (1983).

7. G. H. Jenks and H. C. Claiborne, "Brine Migration in Salt And Its Implication in the Geologic Disposal of Nuclear Waste," ORNL-5818, 1981.

8. E. Roedder and H. E. Belkin, "Migration of Fluid Inclusions in Polycrystalline Salt Under Thermal Gradients in the Laboratory and in Salt Block II," Proc. 1980 National Waste Terminal Storage Program Information Mtg., ONWI-212, p. 361, Office of Nuclear Waste Isolation (1980).

9. D. R. Olander, "A Model of Brine Migration and Water Transport in Rock Salt Supporting a Temperature Gradient," Nuclear Technology, 58, 256 (1982).

10. J. L. Ratigan, "A Finite element Formulation for Brine Transport in Rock Salt," International Journal for Numerical and Analytical Methods in Geomechanics, 8, 225 (1984).

11. D. F. McTigue, "Salt as a Porous Thermoelastic Material: Laboratory and Field Applications," SRP Brine Migration Workshop, Berkeley, Ca., April 17-19, 1985.

12. J. A. Lieberman, S. N. Davis, D. R. F. Harleman, R. L. Keeney, D. Langmuir, R. B. Lyon, W. W. Owens, T. H. Pigford, W. W.-L. Lee, "Performance Assessment National Review Group," Weston Report RFW-CRWM-85-01, February 1985.

13. J. L. Ratigan, SRP Brine Migration Workshop, Berkeley, Ca., April 17-19, 1985.

14. U.S. Nuclear Regulatory Commission, "Disposal of High Level Radioactive Waste in Geologic Repositories - Technical Criteria," Title 10, Code of Federal Regulations, Part 60 (1981).

15. G. Andersson, A. Rasmusson, I. Neretnieks, "Migration Model for the Near Field," Royal Institute of Technology, KBS TR 82-24, November 1982.

16. I. Neretnieks, "Leach Rates of High Level Waste and Spent Fuel - Limiting Rates as Determined by Backfill and Bedrock Conditions," Proceedings of the Fifth International Symposium on the Scientific Basis for Nuclear Waste Management, Berlin, 1982, 559, North-Holland (1982).

17. Swedish Nuclear Fuel Supply Co/Division KBS, "Final Storage of Spent Nuclear Fuel - KBS-3, III Barriers," 1983.

18. Pigford, T. H., J. O. Blomeke, T. L. Brekke, G. A. Cowan, W. E. Falconer, N. J. Grant, J. R. Johnson, J. M. Matusek, R. R. Parizek, R. L. Pigford, D. E. White, "A Study of the Isolation System for Geologic Disposal of Radioactive Wastes," National Academy Press, Washington, D.C., April, 1983.

19. P. L. Chambre′ and T. H. Pigford, "Prediction of Waste Performance in a Geologic Repository," Proceedings of the Materials Research Society, The Scientific Basis for Nuclear Waste Management, Boston, 1983.

20. P. L. Chambre′, T. H. Pigford, A. Fujita, T. Kanki, A. Kobayashi, H. Lung, D. Ting, Y. Sato, S. J. Zavoshy, "Analytical Performance Models for Geologic Repositories," Report LBL-14842, Vol. II, Chapter 7, October 1982.

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