A MECHANISTIC STUDY OF THE UNIFORM CORROSION OF COPPER IN COMPACTED Na-MONTMORILLONITE/SAND MIXTURES

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Abstract—The uniform corrosion behaviour of copper has been studied in environments similar to those expected in a Canadian nuclear fuel waste disposal vault. Under the experimental conditions used, the rate of corrosion is limited by the diffusion of copper through the compacted clay–sand buffer material that will surround the nuclear waste containers. The extent of the copper diffusion process was determined at the end of each test by measuring the copper concentration profile in the buffer material. In the presence of γ-radiation, the copper diffused further than in the unirradiated tests, but the corrosion rate was lower. Rate control by copper diffusion can account for both of these effects, with the effect of γ-radiation being to reduce the extent of sorption of copper by the clay. The results are consistent with a mass transport controlled corrosion reaction dominated by pore-water diffusion in the presence of γ-radiation and surface-water diffusion in the absence of radiation.

INTRODUCTION

THE prediction of the corrosion behaviour of materials over periods of hundreds, thousands and even tens of thousands of years is a problem unique to the disposal of nuclear fuel waste. Such predictions should only be attempted, and certainly can only be justified, on the basis of a sound mechanistic understanding of the various processes taking place. In this paper the results of a mechanistic study of the uniform corrosion behaviour of copper under conditions similar to those expected in a Canadian disposal vault are presented.

The Canadian concept,[1] like many others around the world, is based on the disposal of nuclear fuel waste in metallic containers emplaced in a vault in a stable geological formation. In Canada, the concept calls for the construction of a vault at a depth of 500–1000 m in the plutonic rock of the Canadian Shield. The containers would be surrounded by a compacted mixture of Na-bentonite and silica sand, known as buffer material. Groundwaters at these depths tend to be saline,[2] with Cl$^-$ concentrations up to ~1 mol dm^{-3}. Radioactive decay of the waste will produce elevated temperatures within the vault and a significant γ-radiation field near the container surface.[3] The maximum container-skin temperature is expected to be ~100°C, although the exact distribution of temperatures will depend on the age and nature of the waste fuel and the design of the vault. The variation of the container surface temperature and γ-radiation dose rate with time leads to two target lifetimes: (1) 300–500 y to cover the period of high γ-radiation activity and temperature, and (2) ~20,000 y after which the temperature in the vault will be close to ambient.

The various alloys proposed as possible container materials can be broadly classified as being either corrosion-resistant or corrosion-allowance materials.[3,4]

One material from each category has been studied in Canada: titanium is the selected corrosion-resistant material[4] and oxygen-free copper (UNS C10100) is the candidate corrosion-allowance material. Copper is the container material of choice in Sweden,[5] where disposal conditions similar to those in Canada are expected. In both countries the containers will be surrounded by a compacted clay-based material that is expected to influence the rate of uniform corrosion of the container. In the Swedish program, where the thick-walled container design results in insignificant γ-radiation fields, the rate of uniform corrosion is assumed to be limited by the transport of oxidants through the compacted buffer material to the container surface. Deep groundwaters contain little dissolved oxygen, so the amount of available oxidants is limited. Consequently, 20 cm thick copper containers are predicted[5] to last for hundreds of thousands of years. A subsequent analysis[6] of a 10 cm thick container produced similar lifetimes.

In contrast, the use of thinner-walled copper containers (possibly ~2.5 cm) in the Canadian concept would result in a significant γ-radiation field at the container surface. This field may produce oxidizing radiolysis products at the metal/ environment interface,[3,7] making oxidant transport control less likely than for a thicker container design. Furthermore, the chloride concentrations are higher in Canadian groundwaters, and it is known[8,9] that the dissolution rate of copper rotating-disc electrodes in aerated NaCl solutions is controlled by the anodic transport process, not by the rate of supply of oxygen. Therefore, a study of the uniform corrosion of copper under simulated disposal conditions has been carried out aimed at establishing whether the rate of transport of dissolved copper through the compacted buffer material controls the overall rate of corrosion.

PROPERTIES OF COMPACTED CLAY—SAND BUFFER

Most common clay minerals are composed of sheets of silica tetrahedra and alumina octahedra. The various clay minerals result from different combinations of these two sheets and from different amounts of substitution of Al and Si by elements of lower valency.[10] Smectite refers to a group of clays with two silica sheets sandwiched around an alumina sheet and a net layer charge of 0.2–0.6 per formula unit. Montmorillonite is the most common member of the smectite group and the charge results predominantly from the substitution of Al^{3+} by Mg^{2+}. If Na^+ is the charge-balancing cation, the unit cell formula is $Na_x(Al_{2-x}Mg_x)Si_4O_{10}(OH)_2$ (Fig. 1). Bentonite, the clay component of the compacted buffer material, is a naturally occurring material composed mainly of montmorillonite, but also containing other clay minerals and quantities of gypsum ($CaSO_4 \cdot 2H_2O$) and calcite ($CaCO_3$).[11] For the present purposes, the sand component of the buffer material can be considered as an inert filler, although the inclusion of sand in the mixture improves its engineering properties.[12]

The water in a saturated sample of compacted clay (or clay/sand mixture) can be classified as either surface-water or pore-water.[13] Surface-water, with a thickness of perhaps two layers (~0.6 nm),[14] is closely associated with the clay surfaces by hydrogen bonding and, consequently, has a higher viscosity than bulk water.[15] Pore-water occupies the larger pores of the soil and those regions at a distance of several layers from the clay surfaces, and has properties similar to those of bulk water. At the same time the clay can sorb cations,[10,15] either by adsorption at specific sites or by exchange with the charge-balancing cations of the mineral (e.g. Na^+ in
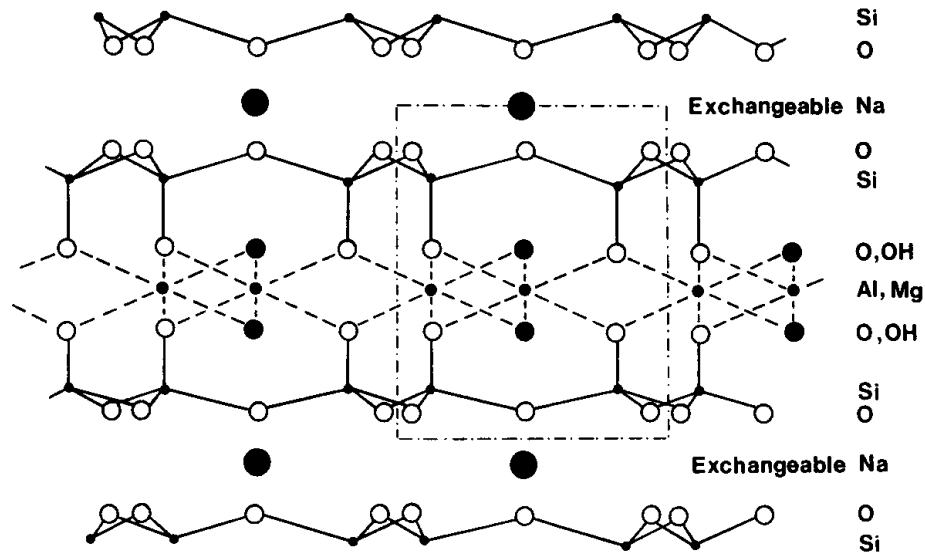
FIG. 1.   Structure of Na-montmorillonite illustrating $Na_x(Al_{2-x})Si_4O_{10}(OH)_2$ unit cell (Adapted with permission from *Chemistry of the Soil*, F. E. Bear (ed), 2nd edition, ACS Monograph Series No. 160, p. 96. Copyright 1964 American Chemical Society.)

Na-montmorillonite). The net negative surface charge of montmorillonite also has the effect of excluding anions from the surface-water layers.

The reference buffer material[16] is a 1:1 mixture (by dry mass) of Na-bentonite and sand, compacted to a dry density (ρ_d) of about 1.65 g cm^{-3}, with an initial moisture content of 17–19%. The hydraulic conductivity of the buffer is so low[16] ($\sim 10^{-10}$ cm s^{-1}) that mass transport is primarily by diffusion. Cations will tend to diffuse mainly through the surface-water layers, whereas anions will diffuse through the pore-water because of anion exclusion from the surface-water layers. The distribution of dissolved copper between the sorbed and pore-water states, and hence the relative importance of the surface and pore-water diffusion pathways, is determined by its speciation, which is a function of the composition of the pore-water. Oxygen can diffuse through both the liquid phase and, in an unsaturated soil, through the gas or vapour phase. The effective diffusion coefficient of oxygen in a 70%-saturated soil is of the order of 10^{-3} cm^2 s^{-1} because transport occurs predominantly through the gas phase.[17] The variation of the oxygen diffusivity with moisture content is of interest in this study because the degree of saturation varied during the tests. In a disposal vault, however, saturated conditions will prevail.

The one-dimensional mass-balance equation for copper diffusion in a clay-based soil is[13,18]

$$\frac{\partial c}{\partial t} = \frac{D_i}{r} \frac{\partial^2 c}{\partial x^2} \tag{1}$$

where c is the copper pore-water concentration, D_i is the total intrinsic diffusion coefficient and r is the capacity factor. In equation (1), it is assumed that D_i is not a function of concentration (c), distance (x) or time (t), and that the ratio of sorbed to pore-water copper concentrations is constant. The total intrinsic diffusion coefficient includes terms for both surface and pore-water diffusion[18]

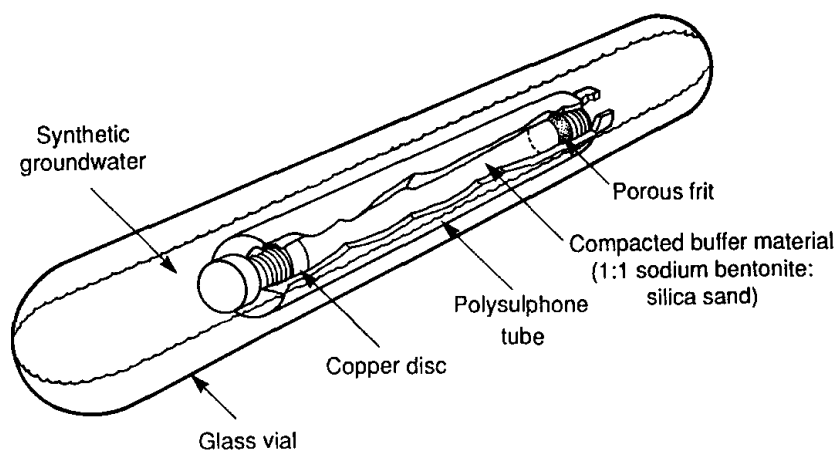$$D_i = D_{iw} + \rho_d K_d D_s \tag{2}$$

FIG. 2.   A schematic diagram of the experimental apparatus for copper corrosion tests in compacted buffer material.

where D_{iw} is the intrinsic diffusion coefficient in the pore-water, D_s is the surface diffusion coefficient and K_d is the distribution coefficient of copper between sorbed and pore-water phases ($K_d = [Cu]_{sorbed}/[Cu]_{pore-water}$). The capacity factor can be thought of as the capacity of the buffer to sorb copper and is given by[18]

$$r = \phi_e + \rho_d K_d \tag{3}$$

where ϕ_e is the porosity for pore-water diffusion.

EXPERIMENTAL METHOD

The experimental arrangement is illustrated in Fig. 2. A disc of oxygen-free electronic grade copper (UNS C10100, min. 99.99 wt% Cu) was placed at the closed end of a polysulphone tube with an internal diameter of 1.25 cm. Polysulphone (Union Carbide) is a radiation-resistant polymer suitable for use at temperatures ≤140°C. Five individual plugs of compacted buffer material, each ~2 cm long, were then placed end to end in the bore of the tube, followed by a porous frit made from carborundum and finally a hollow polysulphone end-plug. The uncompacted buffer material was moistened with a synthetic groundwater solution, standard Canadian Shield saline solution (SCSSS) (Table 1), so that the compacted plugs were about 80% saturated initially. The buffer consisted of a 1:1 mixture (by dry weight) of Avonlea bentonite and graded silica sand. The entire polysulphone tube assembly was sealed in a glass vial

TABLE 1.   COMPOSITION OF THE SYNTHETIC
GROUNDWATER   STANDARD   CANADIAN
SHIELD SALINE SOLUTION (SCSSS)

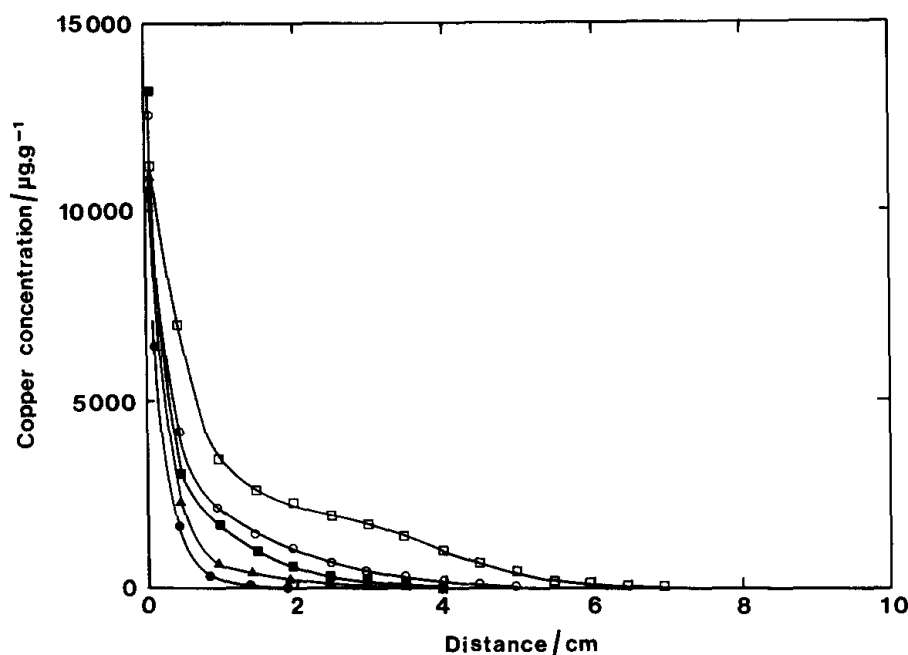| Species	Concentration	
	$\mu g\ g^{-1}$	$mol\ dm^{-3}$
Na^+	5050	0.22
K^+	50	0.0013
Mg^{2+}	200	0.0082
Ca^{2+}	15,000	0.37
Sr^{2+}	20	0.00023
Si	15	0.00054
HCO_3^-	10	0.00016
Cl^-	34,260	0.97
SO_4^{2-}	790	0.0082
NO_3^-	50	0.00081

Fig. 3. Copper concentration profiles in compacted buffer material determined after exposure at 100°C for times between 33 days and 362 days (buffer dry density 1.65 g cm^{-3}). ● 33 days, ▲ 61 days, ■ 89 days, ○ 180 days, □ 362 days.

containing ~250 cm^3 aerated SCSSS. During the course of the experiment the buffer absorbed moisture from the bulk solution and the five individual buffer plugs coalesced into one continuous sausage of buffer material. No attempts were made to vary the amount of oxygen contained in the vial, although post-test gas analyses were performed using mass spectrometry after several of the tests.

Tests were performed at temperatures of 50 and 100°C for periods of between 1 month and 2 y. Three buffer dry densities (ρ_d = 1.45, 1.65 and 1.79 g cm^{-3}) were used in order to vary the rate of copper diffusion through the buffer. Twelve tests were irradiated (absorbed dose rate ~5 Gy h^{-1} ≡ ~500 rad h^{-1}) using a used CANDU* fuel bundle as the source of γ-radiation. The irradiated tests were performed at 100 and 135°C using a slightly modified set-up in which three tests shared a common bulk solution phase in a Ti autoclave, rather than being placed in individual glass vials. In the six irradiated tests at 100°C the copper coupon was situated in the centre of a 15 cm long column of buffer material rather than at one end.

At the end of each test the buffer material was extruded from the polysulphone tube in one piece and sectioned for copper analysis. The first 2 mm slice, designated as slice 1A, was taken from the end of the buffer in direct contact with the copper disc. The remaining buffer material was sectioned into 5 mm slices. After drying, the total copper concentration in each slice was determined by X-ray fluorescence. The total amount of copper in each slice comprises both the sorbed and pore-water copper in the pre-dried sample.

Corrosion rates were estimated from the weight loss of the coupon (after stripping corrosion products by dissolution in 1:1 concentrated HCl:water) using the surface area of the coupon in contact with the buffer. Although some of the coupons were wrapped in PTFE tape on the edge and back face of the samples, some corrosion inevitably occurred in these regions, resulting in overestimation of the corrosion rate.

EXPERIMENTAL RESULTS AND DISCUSSION

Copper concentration profiles

Figure 3 shows the development of the copper concentration profiles in the buffer with time for five unirradiated tests at 100°C and ρ_d = 1.65 g cm^{-3}, for periods of between 33 and 362 days. The origin on the x-axis represents the interface between the copper disc and the column of buffer material. The mean total copper concen-

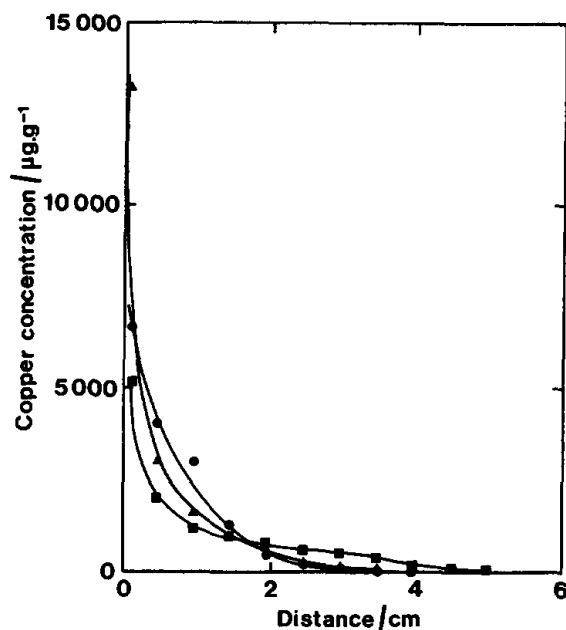*CANadian Deuterium Uranium, registered trademark of AECL.

FIG. 4. The effect of buffer dry density on the copper concentration profiles in compacted buffer material after 3 months exposure at 100°C. ● 1.45 g cm^{-3}, ▲ 1.65 g cm^{-3}, ■ 1.79 g cm^{-3}.

trations in each slice are plotted at a distance corresponding to the centres of the slices. The profiles suggest that copper diffusion is a slow process since, even after 12 months, copper has barely penetrated more than half-way along the column of buffer material. A crude analysis of the profiles suggests that it could take of the order of 10 y to establish steady-state diffusion conditions, i.e. a constant concentration gradient. This period contrasts with the time of less than 1 s to establish steady-state mass transport conditions at a rotating disc electrode in aqueous solution, and illustrates the low permeability of the compacted buffer material.

At the interface, the concentration of copper in the 1A slice (the 2 mm slice adjacent to the copper disc) appears to reach a constant value of between 10,000 and 15,000 μg g^{-1}. In subsequent tests,[13] this concentration was found to vary between 2000 and 20,000 μg g^{-1}, and there was no obvious trend with exposure time, buffer density or temperature. The nature of the diffusing copper species is unknown. Before analysis for copper, some of the 1A slices were analysed by X-ray diffraction, even though the maximum copper concentration observed (1–2 wt%) is barely above the detection limit. The only copper species identified in the buffer were[13] $CuSO_4 \cdot 3H_2O$ and $CuCl_2 \cdot 2H_2O$. On the copper disc itself basic cupric chloride, $CuCl_2 \cdot 3Cu(OH)_2$, was often found as discrete crystals lying on top of an oxide layer[13] (possibly Cu_2O). Although the SCSSS is essentially a Ca/Na-based chloride solution, cupric species seem to form in preference to the cuprous species produced in aerated NaCl solution[8,9] (e.g. $CuCl_2^-$, $CuCl_3^{2-}$).

Unexpectedly, there is no obvious effect of buffer dry density on the copper concentration profiles. Generally, D_i decreases with increasing ρ_d, because the tortuosity is greater at higher ρ_d.[19] Figure 4 shows a series of profiles from 3 month unirradiated tests at 100°C with the three different buffer densities. The greatest penetration of the copper is between 4 and 5 cm for all densities. The copper
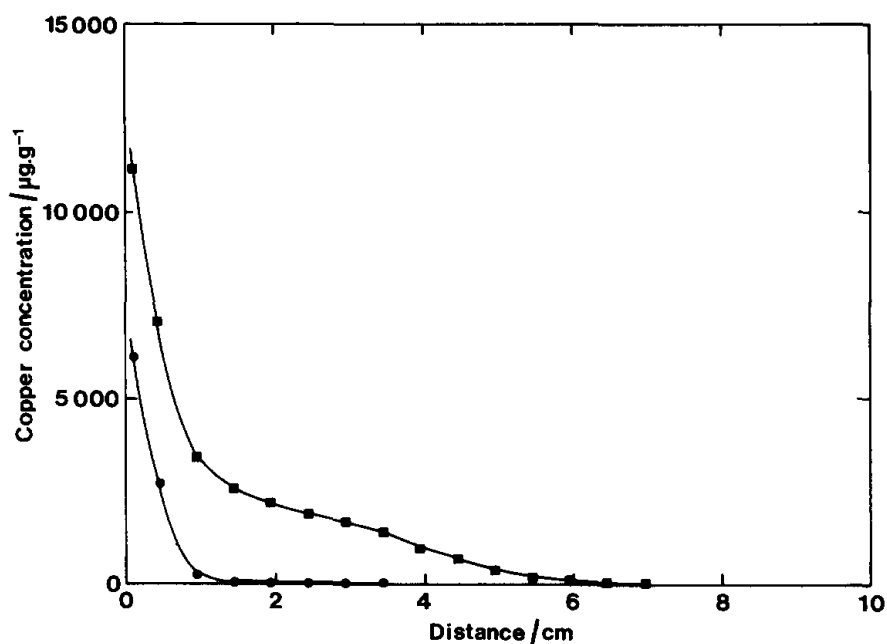
Fig. 5.   The effect of temperature on the diffusion of copper in compacted buffer material in contact with a corroding copper coupon (1 y exposure, buffer density 1.65 g cm^{-3}). ● 50°C, ■ 100°C.
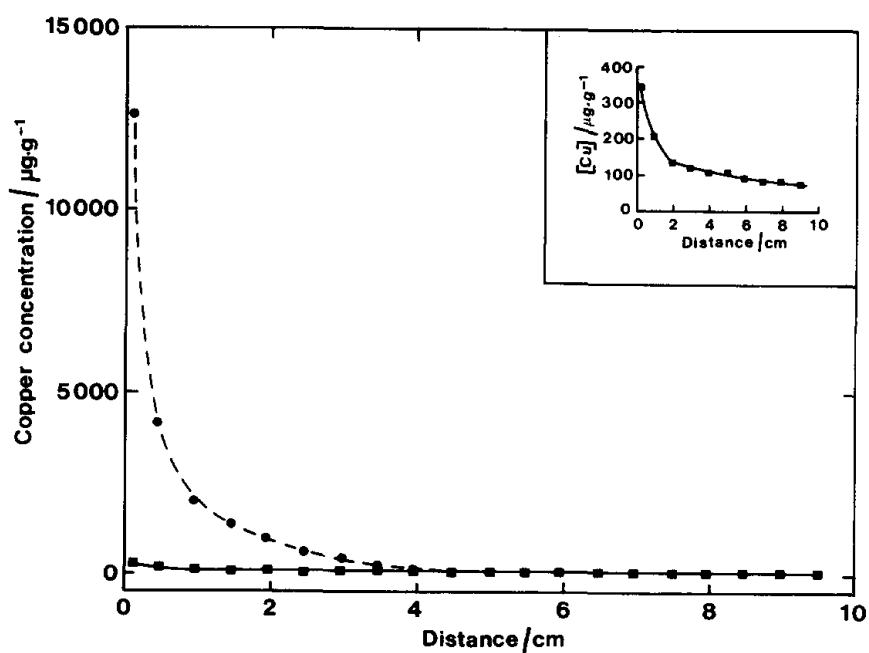

Fig. 6.   The effect of γ-radiation on the copper concentration profiles in compacted buffer material (buffer density 1.65 g cm^{-3}) after 6 months exposure. —●— unirradiated at 100°C, —■— irradiated (absorbed dose rate ~5 Gy h^{-1}) at 135°C (also shown on expanded scale in inset).
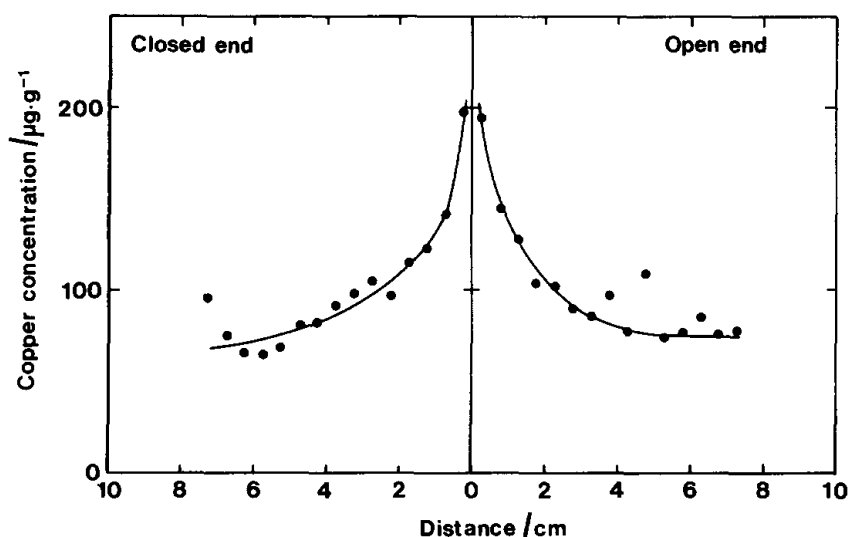
FIG. 7. Copper concentration profiles measured in the presence of γ-radiation at 100°C for 407 days for a copper coupon situated in the centre of a 15 cm long column of compacted buffer material (buffer density 1.65 g cm^{-3}).

concentration profiles were affected by the temperature, with copper diffusing further at 100°C than at 50°C (Fig. 5).

The most marked effect on the concentration profiles was observed when the tests were irradiated. Unfortunately, there are no exactly equivalent tests with and without γ-radiation, but Fig. 6 shows a comparison betwen copper profiles from two 6-month experiments with a buffer dry density of 1.65 g cm^{-3}, one at 135°C in the presence of radiation (also see inset) and one unirradiated at 100°C. In the irradiated test, the copper has diffused the full length of the buffer material, and the interfacial concentration is a factor of ~40 lower than in the unirradiated experiment (350 μg g^{-1} compared with 12,500 μg g^{-1}). Figure 7 shows typical profiles from the irradiated tests at 100°C in which the coupon was centred in the middle of the column of buffer material. The profiles are the same regardless of whether the copper is diffusing towards the open or closed end of the tube. In all, 18 copper concentration profiles were determined in the presence of γ-radiation, all showing the same effects of low copper concentration and of diffusion the full length of the buffer.[13]

Corrosion rates

The weight-loss corrosion rates for the unirradiated tests at 50 and 100°C for the three buffer densities are shown as a function of exposure time in Fig. 8. In the log–log form, the data can be fitted[13] to a straight line with a slope of −0.7, close to the value of −0.5 that would be expected for a transport-limited corrosion reaction. For exposure times of 1 y or greater, the corrosion rate is independent of temperature and buffer density. At shorter times, the corrosion rates are more scattered, but there is also no systematic variation of the rate with temperature or buffer density. The scatter in the data at short times is believed to be caused by variations in the time required to fully saturate the buffer with moisture, an effect that seems to be unimportant after ~1 y.

In the presence of γ-radiation, the corrosion rates are much lower than in the unirradiated tests, and there is some dependence on both temperature and buffer density (Table 2). After 407 days (1.12 y) exposure at 100°C and an absorbed dose
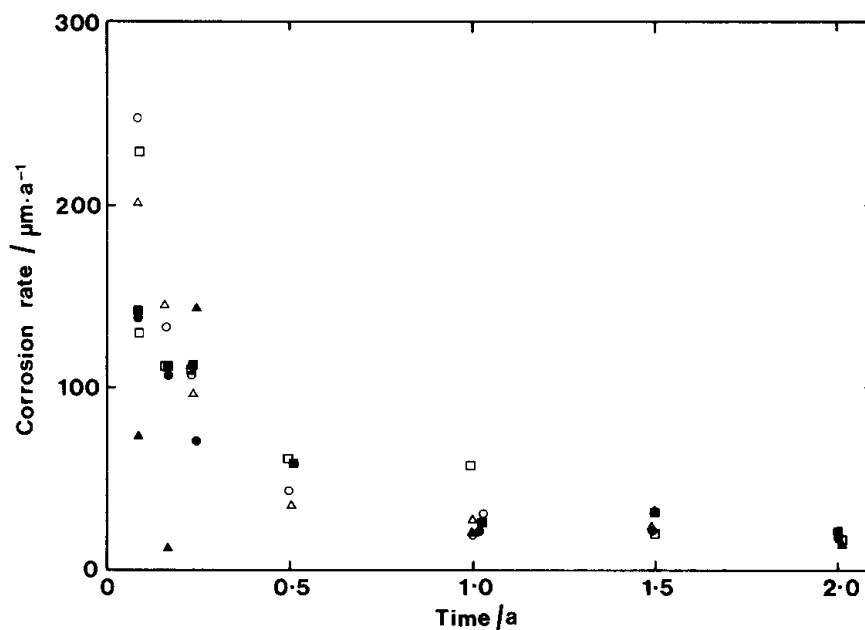
Fig. 8.   Copper corrosion rates determined from weight loss of coupon in contact with compacted buffer material in absence of γ-radiation. ● 50°C, 1.45 g cm^{-3} buffer density; ■ 50°C, 1.65 g cm^{-3}; ▲ 50°C, 1.79 g cm^{-3}; ○ 100°C, 1.45 g cm^{-3}; □ 100°C, 1.65 g cm^{-3}; △ 100°C, 1.79 g cm^{-3}.

rate of 5 Gy h^{-1}, the mean corrosion rate for all three buffer densities was 2.5 μm y^{-1} (number of points, $n = 6$; standard deviation, $\sigma = 0.5\,\mu$m y^{-1}). By comparison, the mean of the unirradiated corrosion rates at 100°C after 1 y exposure was 31 μm y^{-1} ($n = 6$, $\sigma = 13\,\mu$m y^{-1}). At 135°C, if the small buffer density effect is ignored, the mean corrosion rate from a 6 month (187 day) irradiated test was 7.4 μm y^{-1} ($n = 6$, $\sigma = 1.8\,\mu$m y^{-1}). After 6 months at 100°C in the absence of radiation, the rate was 49 μm y^{-1} ($n = 4$, $\sigma = 12\,\mu$m y^{-1}). Thus, the irradiated rates are up to a factor of 12

TABLE 2.   CORROSION RATES OF COPPER IN CONTACT WITH COMPACTED BUFFER MATERIAL IN THE PRESENCE OF γ-RADIATION (ABSORBED DOSE RATE 5 Gy h^{-1})

Test	Time (d)	Temp. (°C)	ρ_d (g cm^{-3})	Rate (μm y^{-1})
I1	407	100	1.45	2.9
			1.65	2.9
			1.79	2.1
I2	407	100	1.45	2.4
			1.65	2.8
			1.79	1.7
I3	187	135	1.45	8.0
			1.65	8.7
			1.79	5.7
I4	187	135	1.45	9.7
			1.65	7.5
			1.79	4.8

times lower than those determined in the absence of a γ-radiation field. If a $t^{-1/2}$ dependence for the irradiated corrosion rates is assumed, the rate at 135°C is approximately twice that at 100°C, for a similar exposure period. Furthermore, the irradiated data show a dependency on the buffer density, with the rates at $\rho_d = 1.79$ g cm^{-3} consistently lower than those at $\rho_d = 1.45$ and 1.65 g cm^{-3} at both 100 and 135°C (Table 2).

The mechanism of copper corrosion in compacted buffer material

In these tests, an attempt was made to establish a link between the rate of diffusion of copper and the corrosion rate by varying the buffer dry density and, by doing so, to demonstrate that copper transport is the rate-controlling process. However, neither the observed copper concentration profiles nor the corrosion rate (in the absence of γ-radiation) show any dependence on ρ_d. Instead, this link was established by irradiating the tests. In the presence of γ-radiation copper diffuses further, but, paradoxically, the corrosion rate is lower. The interpretation of these observations is that copper transport is rate-controlling and that the effect of radiation is to reduce the extent to which the diffusing copper species are sorbed by the clay fraction of the compacted buffer material. Less strongly sorbed copper is more mobile and will diffuse further. At the same time, since copper sorption acts like a sink for dissolved copper species, driving the dissolution process, the corrosion rate is lower because the copper is less-strongly sorbed.

The two effects of radiation can be seen quantitatively by solving equation (1) subject to appropriate initial and boundary conditions. If it is assumed that the buffer material is semi-infinite and initially free of copper, and that the copper pore-water concentration at $x = 0$ (c_o) is constant, then the initial and boundary conditions for one-dimensional diffusive mass transport are

$$c(x,0) = 0 \qquad \text{for } 0 < x < \infty$$

$$c(0,t) = c_o \qquad \text{for } t > 0$$

$$c(\infty,t) = 0 \qquad \text{for } t > 0.$$

The solution to equation (1) given these conditions is[13]

$$\frac{c}{c_o} = 1 - \text{erf}\left[\frac{x}{2t^{1/2}}\left(\frac{r}{D_i}\right)^{1/2}\right]. \tag{4}$$

Equation (4) gives the variation of the copper pore-water concentration as a function of x and t, i.e the copper pore-water concentration profiles. For species obeying a linear sorption isotherm in compacted buffer material, the total copper concentration in each slice is proportional to the pore-water concentration. Equation (4) also describes the total copper concentration profiles determined in the tests described here. At the copper/buffer interface, the flux of copper ($J_{x=0}$) is given by Fick's law

$$J_{x=0} = -D_i\left(\frac{\partial c}{\partial x}\right)_{x=0}. \tag{5}$$

Differentiating equation (4) and substituting in equation (5) gives an expression for the interfacial flux of copper which is proportional to the corrosion rate[13]

$$J_{x=0} = \frac{(D_i r)^{1/2} c_0}{(\pi t)^{1/2}}.$$

(6)

From equation (3), it can be seen that if irradiation reduces the extent of copper sorption by the clay (i.e. smaller K_d) then r is smaller. A smaller value of r in equation (4) results in a larger value of c/c_0 at a given time and distance, reflecting the behaviour of a more mobile diffusing copper species. At the interface, the flux (equation 6) is smaller for a smaller value of r because the driving force for copper dissolution is diminished. Thus, both of the apparently contradictory effects of γ-radiation can be explained in terms of a reduction in the extent of copper sorption and a copper transport rate-determining step.

The exact mechanism by which irradiation reduces the extent of copper sorption remains, as yet, unknown. No evidence for an irreversible radiation-induced alteration of the clay, e.g. alteration of the montmorillonite to a less-sorbing illitic clay, was found from X-ray diffraction studies of the irradiated buffer.[13] It is possible that irradiation causes a decrease in the pore-water pH, reducing the extent of copper sorption. Alternatively, the speciation of the diffusing copper species may change in the presence of γ-radiation. An interesting possibility is that the Cu(II) species that seem to predominate in the absence of radiation are reduced to Cu(I) species in the presence of radiation. Cuprous ions would be less strongly sorbed than Cu(II), especially if the Cu(I) were in the form of anionic chloro-complexes such as $CuCl_2^-$ and $CuCl_3^{2-}$. This mechanism is shown schematically in Fig. 9.

Reduction of Cu(II) to Cu(I) by e^-(aq), $H^{\cdot}$ and O_2^-, all products of the γ-radiolysis of water, has been reported.[20,21] Photochemical studies of clay systems containing Cu(II) show that copper quenches the luminescence of adsorbed Ru(II) and organic complexes excited by UV-radiation.[22,23] The significance of these studies is that the quenching mechanism involves either energy transfer by a photochemical process, or, especially if the copper is incorporated in the clay lattice,[23] electron transfer resulting in the reduction of Cu(II) to Cu(I). Further evidence for redox reactions involving metal ions in clays can be found in the field of clay-modified electrodes.[24,25] One study,[26] involving a zeolite-modified electrode incorporating Cu(II), suggests that Cu(II) can be reduced to Cu(I) and even Cu(0).
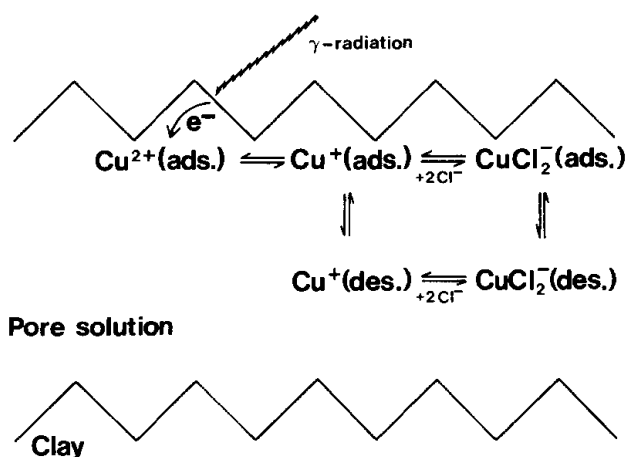

Fig. 9.   The proposed mechanism for the radiation-induced reduction in the extent of copper adsorption/cation exchange by Na-montmorillonite.

At present, however, there is no direct evidence for the speciation of the copper in the pore-water, with or without γ-radiation.

Irradiation produces equal amounts of oxidizing and reducing species. Indeed, some water radiolysis products, such as HO_2^- and O_2^-, can act as both oxidants and reductants under different conditions.[20] Others, such as O_2, $OH^{\cdot}$ and H_2O_2, will be oxidants.[20,21] Before this study started, it was believed that the major effect of γ-radiation would be to increase the corrosion rate by the production of oxidants.[7] That the corrosion rate is actually lower in the presence of γ-radiation, possibly because of the greater reactivity of reducing radiolysis products, shows that the understanding of the effect of γ-radiation on corrosion processes in such environments is incomplete.[27]

This explanation for the effect of γ-radiation and of the mechanism of the corrosion reaction can help rationalize the dependence (or lack of dependence) of the corrosion rate on ρ_d and temperature, under both irradiated and unirradiated conditions. Firstly, in the absence of radiation, the corrosion rate did not vary with either ρ_d or temperature. The proposed mechanism suggests that copper diffusion is rate-limiting and that the dominant transport process is surface diffusion, i.e diffusion through the surface-water layers. Increasing the dry density of the buffer reduces the amount of pore-water whilst the amount of surface-water per unit volume of wet buffer remains relatively constant.[13] Since the copper is diffusing through the surface-water rather than the pore-water, changing ρ_d does not change the rate of copper diffusion, and hence does not affect the corrosion rate.

The lack of temperature dependence of the corrosion rate in the absence of irradiation can be thought of as the consequence of two opposing temperature-dependent processes. It is assumed that sorbed copper tends to desorb as the temperature is increased, resulting in the lower capacity factor. Then, if D_i increases with temperature as is usually the case, these two temperature dependences act in different directions, and the term $D_i r$, and hence the corrosion rate (equation 6), will be relatively insensitive to changes in the temperature. The temperature dependences of D_i and r have not been determined separately to confirm this explanation, but measurements[28] of D_i/r from copper diffusion experiments exhibit a very large temperature dependence: between room temperature and 95°C, D_i/r varies from $\sim 1 \times 10^{-10}$ cm^2 s^{-1} to 2×10^{-7} cm^2 s^{-1}. A variation of over three orders of magnitude in a temperature range of 70°C is not possible in terms of the temperature dependence of D_i alone, and suggests that both D_i and r vary with temperature, but in opposite directions.

The irradiated corrosion rates showed dependence on both temperature and ρ_d (Table 2). In the presence of γ-radiation, copper diffusion in the pore-water is thought to be the rate-controlling process, since the copper is not strongly sorbed. Increasing ρ_d reduces the amount of pore-water and, indeed, the corrosion rates for $\rho_d = 1.79$ g cm^{-3} are significantly lower than those at the other two densities at both 100 and 135°C (Table 2). After correcting for the different exposure times, the irradiated rates are also seen to be temperature-dependent, with the rate approximately doubling between 100 and 135°C. For pore-water diffusion, D_i would be expected to increase with temperature as the viscosity decreases.[29] At the same time, since the diffusing species is predominantly in the pore-water, an increase in temperature is unlikely to result in a significant decrease in r because of copper desorption from the clay surface. Consequently, for pore-water diffusion, the

temperature dependences of D_i and r will not cancel, and the dominant effect of temperature on D_i will lead to an increase in the corrosion rate with temperature.
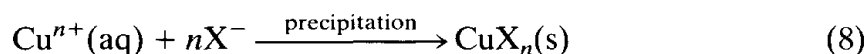
Although the effect of γ-radiation provides good evidence that copper diffusion is the rate-controlling process, there are two aspects of these results that require further study: the possibility of O_2 transport limitation, and the influence of the precipitation of dissolved copper. As previously stated, the oxygen concentration was neither maintained during the course of the experiments nor varied from test to test. After 180 days exposure at 100°C, the atmosphere inside one of the unirradiated glass vials contained 15.5 vol% O_2 compared to the original 21 vol%. In the presence of γ-radiation, duplicate tests were performed for 407 days at 100°C (tests I1 and I2 in Table 2) and for 187 days at 135°C (tests I3 and I4). In one of each of the duplicate sets of tests (tests I2 and I4), post-test gas analysis by mass spectrometry revealed that all of the oxygen had been consumed. In the other duplicate test in each set (tests I1 and I3), less than half of the available oxygen was consumed; this is an effect that cannot presently be explained. Regardless of the reason for this difference, the rate of supply of oxygen to the copper coupon must have been different in the duplicate tests. The corrosion rate data in Table 2 show that the rates in each of the sets of duplicate tests were very similar and do not reflect this difference in the rate of oxygen supply, suggesting that O_2 transport was not rate-limiting in these tests.

Further evidence that O_2 transport was not rate-limiting comes from the 1, 2 and 3 month unirradiated tests at 50 and 100°C. Measurement of the moisture content of each slice of buffer at the end of the test showed[13] that the rate of moisture uptake is slower at 50°C than at 100°C. Since O_2 diffuses faster in unsaturated soils than in fully saturated ones,[17] the corrosion rate at 50°C would be expected to be higher than at 100°C in these short-term tests, if O_2 transport was rate-controlling. However, there was no significant difference in the corrosion rate at the two temperatures (Fig. 8), again suggesting that O_2 transport was not rate-controlling in these tests. Further work is planned in which the oxygen concentration will be varied from test to test in order to establish under what conditions O_2 diffusion is rate-controllling.

Precipitation, like sorption, is a process that can drive the dissolution of copper by removing copper ions from solution. For the reaction

$$Cu(s) \rightleftharpoons Cu^{n+}(aq) + ne^- \tag{7}$$

either of the following processes will drive the reaction to the right:

$$Cu^{n+}(aq) + nX^- \xrightarrow{\text{precipitation}} CuX_n(s) \tag{8}$$

$$Cu^{n+}(aq) + nNa\text{-}Y \xrightarrow{\text{sorption}} CuY_n(ads) + nNa^+ \tag{9}$$

where X^- represents an anionic species with which the dissolved copper precipitates and Na–Y represents a sorption site on the Na-montmorillonite. Precipitation of copper inevitably occurred in all of the tests, with usually more than half of the total copper corroded being in the form of precipitate rather than being sorbed on the clay. Precipitation accounts for the fact that the areas under the copper concentration profiles at 50 and 100°C in Fig. 5 are different, even though the corrosion rates determined from the weight loss are similar. If corrosion rates are to be predicted on

the basis of slow copper diffusion, it will be necessary to demonstrate that only a limited amount of copper is immobilized in the form of precipitate.

Notwithstanding these uncertainties, equation (6) can be used to calculate theoretical corrosion rates for comparison with the experimental data. Equation (6) was derived for a constant copper pore-water concentration (c_0) at the copper/buffer interface. As an estimate of this concentration, the total copper concentration (m_{1A}) in the 2 mm slice of buffer (slice 1A) closest to the copper disc will be used. The total and pore-water copper concentrations are related by the capacity factor according to[13]

$$c_0 = \frac{m_{1A}\rho_d}{r} \tag{10}$$

where m_{1A} is in units of mol g^{-1} and c_0 is in units of mol cm^{-3}. m_{1A} will be taken as 2.0×10^{-4} mol g^{-1}, which is equivalent to 12,500 μg g^{-1} (cf. Fig. 3). Equation (6) predicts the instantaneous interfacial flux (or corrosion rate) and, for comparison with the mean corrosion rates derived from weight-loss measurements, must be averaged over the exposure period of the test. After carrying out this averaging, converting the flux to a corrosion rate and substituting equation (10) into equation (6), one obtains the theoretical expression for the mean corrosion rate, R_t:

$$R_t = \frac{2m_{1A}\rho_d A_{Cu}}{(\pi t)^{1/2}\rho_{Cu}}\left(\frac{D_i}{r}\right)^{1/2} \tag{11}$$

where A_{Cu} is the atomic mass of copper, ρ_{Cu} is the density of copper and (D_i/r) is the apparent diffusion coefficient, which has been measured independently[28] and has a value of 2×10^{-7} cm^2 s^{-1} at 95°C. The factor of 2 in the numerator arises from the averaging procedure.

Theoretical rates from equation (11) are directly comparable with weight-loss corrosion rates, and the comparison with the unirradiated experimental rates measured at 100°C is shown in Fig. 10, where the theoretical rates have been calculated for each of the three buffer densities. The agreement between the theoretical and experimental corrosion rates is reasonable, given the assumptions and uncertainties in the calculations and measurements. Since equation (11) tends to overestimate the experimental rate for exposure periods of more than 1 y, it appears that the exclusion of precipitation processes from the theoretical calculations does not represent a serious flaw in our ability to predict the corrosion rate. Furthermore, because these predictions will form part of a safety assessment, it is gratifying that the theoretical expression overestimates, rather than underestimates, the experimental rates.

At this stage, not all of the observed phenomena can be predicted with equation (11). For example, the equation explicitly states that the rate is proportional to ρ_d, whereas no such dependency was observed experimentally. The variation of R_t with ρ_d is small, as can be seen from Fig. 10, and is not significant in comparison with the scatter in the experimental data. Secondly, the unirradiated rates showed no dependence on the temperature. Although there is no known value of D_i/r at 50°C, it will probably be much less than the value of 2×10^{-7} cm^2 s^{-1} determined at 95°C, for reasons stated previously. Consequently, in order for R_t to be independent of temperature, the value of m_{1A} would have to be higher at 50°C than at 100°C. In the
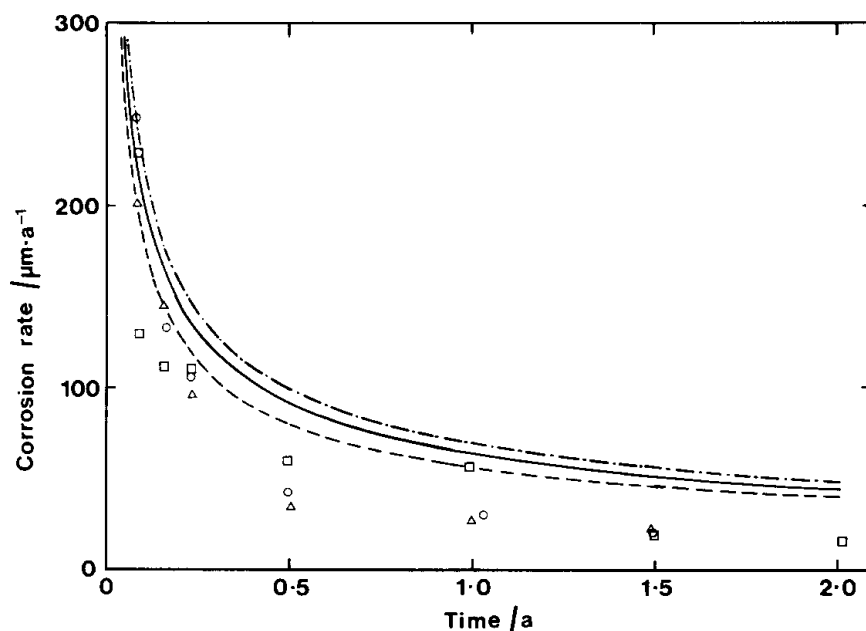
Fig. 10.   A comparison of theoretical and experimental copper corrosion rates at 100°C. Experimental rates for buffer dry densities of: $\bigcirc$ 1.45 g cm^{-3}, $\square$ 1.65 g cm^{-3}, $\triangle$ 1.79 g cm^{-3}. Theoretical rates for buffer dry densities of: – – – – 1.45 g cm^{-3}, —— 1.65 g cm^{-3}, – · – · – 1.79 g cm^{-3}.

present tests, the m_{1A} values were widely scattered but showed no obvious dependence on temperature. Neither is it possible to calculate theoretical rates in the presence of γ-radiation because of the lack of irradiated (D_i/r) data. The observed rates were ~12 times lower and the m_{1A} values ~40 times smaller in the presence of γ-radiation. Consequently, an increase in (D_i/r) by a factor of ~11 under irradiated conditions would account for the observed effect of radiation. Such an increase in (D_i/r) is qualitatively consistent with the proposed mechanism, which involves a more mobile copper species in the presence of γ-radiation.

The results of this study will be used to predict the rate of uniform corrosion of copper nuclear waste containers under Canadian disposal conditions.[30] There are several benefits of basing these predictions on the mechanism, of the corrosion process.[4] Firstly, the predictions will be more justifiable if it can be shown that they are based on a sound understanding of the process being modelled. It would be far more difficult to justify predictions based on a simple linear extrapolation of corrosion rates. For this particular application, such rates could only be measured over periods far shorter than the time-scale of the predictions. Secondly, the effect on the corrosion rate of changes in the environment can be predicted if the mechanism is well understood. For example, if copper transport is rate-controlling, any process that increases the rate of transport is likely to lead to an increase in the corrosion rate. Thus, one would not choose to put a disposal vault in a region of highly fractured rock, where the groundwater flow rate could be high. Finally, provided the chosen rate-determining process is correctly modelled, it is impossible to underestimate the rate of corrosion. In a disposal vault it is quite likely that, at some stage, the rate-controlling process for the corrosion of a copper container will become the rate of supply of oxidants. If the corrosion rate is calculated on the basis of the copper transport step, however, the predicted rate can only be higher than the

actual rate. Consequently, the predicted container lifetimes will be conservative, which, for a safety assessment, is not an undesirable situation.

CONCLUSIONS

Evidence has been presented that suggests the rate of copper corrosion in clay/ sand buffer material is limited by the diffusion of dissolved copper away from the corroding surface. The most important property of the clay is its ability to adsorb and exchange diffusing cationic species. In the presence of γ-radiation, the copper was found to diffuse faster in the buffer material but the corrosion rate was lower. This effect of γ-radiation is the primary evidence that copper diffusion is rate-controlling and can be explained in terms of a radiation-induced decrease in the extent of copper sorption by the clay. As a consequence, the copper is more mobile in the γ-radiation field because it is not retarded by the adsorption and cation exchange processes. Simultaneously, because these sorption processes drive the copper dissolution reaction, the corrosion rate is lower. A mechanism for the radiation effect has been proposed involving the reduction of sorbed cupric species to non-sorbed anionic cuprous-chloro complex ions in the presence of γ-radiation.

In the absence of radiation, the corrosion rate was found to be independent of both the temperature and the density of the compacted buffer material. Conversely, the corrosion rate increased with temperature and was inversely related to the buffer density under irradiated conditions. These observations are consistent with the proposed mechanism and suggest that surface-water diffusion is the dominant diffusive pathway in the absence of radiation, but pore-water diffusion dominates in the presence of γ-radiation.

Reasonable agreement is found between experimental corrosion rates and theoretical rates calculated on the basis of a slow copper transport step. Since the theoretical rate tends to be higher than the experimental rate, it is believed that the assumptions underlying the calculated values do not lead to serious underestimation of the corrosion rate. It is suggested that the rate of uniform corrosion of copper nuclear waste containers be calculated on the basis of slow copper transport.

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