

PERFORMANCE OF ENGINEERED BARRIERS FOR INTERMEDIATE AND LOW LEVEL WASTE DISPOSAL

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ABSTRACT

This paper describes research in progress to estimate how steel and concrete are likely to perform as barriers to radionuclide release from a repository. For both carbon and stainless steel this covers localised and uniform corrosion and, for carbon steel, the production of hydrogen gas. For cementitious materials the research addresses transport properties (dissolved radionuclides and gases), the durability of concrete (especially in sulphate-bearing groundwaters) and the ability of cement to control pH in the repository.

The research is indicating that such engineered barriers can provide useful physical containment of radionuclides for periods of a few hundred years and make an effective contribution to chemical containment for hundreds of thousands of years.

INTRODUCTION

In the UK it is planned that UK Nirex Ltd (Nirex) will build and operate a deep repository for the burial of low and intermediate level radioactive wastes (LLW and ILW). For the wet conditions of the UK the dominant release pathway for radionuclides is by dissolution and transport in groundwater. The repository will include a number of engineered barriers to the movement of radionuclides into the geosphere. These barriers are the wasteform itself (usually cement-based), metallic containers (eg. steel drums and boxes), structural concrete items (eg. floors, walls and boxes), and a cement-based backfill.

The engineered barriers contain the radionuclides by mainly physical means in the short term, and mainly chemical means in the long term. Over the long timescales involved, total containment is clearly not possible; nor is it necessarily desirable, since, for example, gases generated within the repository must be allowed to dissipate in order not to pressurise the repository. The research is indicating that in the short term, a few hundred years, physical containment will be provided by the concrete and steel components. This is useful in that the shorter lived radionuclides (those with half lives of up to about 30 years, which includes important fission products) will be largely contained by these barriers. In order to evaluate their physical performance, it is necessary to understand the corrosion behaviour of the steel, and the durability and mass transport properties of the concrete, over this timescale.

The chemical containment provided by the engineered barriers resides in the reducing conditions generated by the steel and the alkalinity and high surface area of the concrete. These properties do not depend on the physical integrity of the steel and concrete and they persist for very long times. They assist in containing the radionuclides by creating predictable chemical conditions which maintain low concentrations of radionuclides in aqueous solution either through imposing a low solubility

limit, or through encouraging adsorption onto solid surfaces.

The research described in this paper is carried out by the Harwell Laboratory for a range of organisations (Nirex, the European Commission and the Department of the Environment). It is concerned with the following specific issues, illustrated schematically in Figure 1:

- Localised corrosion of carbon and stainless steels in oxygenated (aerobic) conditions.
- General corrosion of the steels in oxygen-free (anaerobic) conditions.
- The transport of gases and dissolved radionuclides through concrete.
- The durability of concrete.
- The ability of concrete to control repository chemistry.

Since the timescale for repository performance is so long, these topics cannot be addressed by direct experimental evaluation alone. Therefore the approach which has been adopted in the research programme[1] is to identify the key processes, develop mechanistic models of these processes, and confirm the predictions of the models over practical experimental timescales.

AEROBIC CORROSION OF STEEL CONTAINERS

The Aerobic Period

In the wet, aerobic and alkaline conditions of a repository soon after backfilling and closure the steel will be protected from rapid corrosion by a passivating film of hydrated oxide on the steel surface. Nevertheless, more rapid corrosion can occur locally if the film is broken down by aggressive ions (eg Cl⁻), or local acidity. Such localised corrosion is no longer a risk when the supply of oxygen is insufficient to maintain the passive film overall and thus the duration of this risk is to be equated with the duration of the aerobic period.

Oxygen will be consumed in the repository by the corrosion reaction itself, which is controlled by the dissolution rate of the passive film or the rate of oxygen diffusion to the steel surface (whichever is the slower). The aerobic period therefore depends on the type of steel, the

geometrical distribution of components in the repository and the degree of saturation by water. The process of oxygen consumption has been modelled for a variety of likely conditions and known ranges for the passive film dissolution rate[2]. The results are summarised in Table I. The maximum periods occur in unsaturated conditions and the minimum periods in saturated conditions. The estimates are more uncertain for stainless steel (eg 18% Cr austenitic steel) than for carbon steel since the passive film dissolution rate is not well established for the more corrosion resistant material.

TABLE I

The Duration of the Aerobic Period (in years)
For Steel Corrosion

	Minimum	Maximum
Carbon Steel		65
Stainless Steel	3	108

Pitting Corrosion of Carbon Steel

For carbon steel during this period (maximum duration of 65 years) the localised corrosion risk is pitting corrosion (Fig. 1). Pitting corrosion has an initiation phase and a propagation phase. The approach taken in this research has been to consider only the propagation phase (which is thus pessimistic). The research comprises both theoretical models and experimental studies of pit growth[3,4].

In the experiments steel coupons are partially embedded within blocks of cementitious materials of the type anticipated in the repository (see later). The specimens are then stored either in wet (saturated) or humid conditions and are contaminated with chloride to initiate pitting. These conditions simulate a worst case situation, such as an air pocket in the backfilling process. Specimens are examined destructively at intervals to develop statistical data for pit growth. An example is shown in Fig. 2, and illustrates that pits grow to a depth of about 1 mm in 1.5 years, but at a rate which decreases with time.

The theoretical model[5,6], which has been developed to describe pit growth, includes transport processes, electrochemical reactions and precipitation of corrosion products as shown schematically in Fig. 3. The model has been validated against extensive experimental

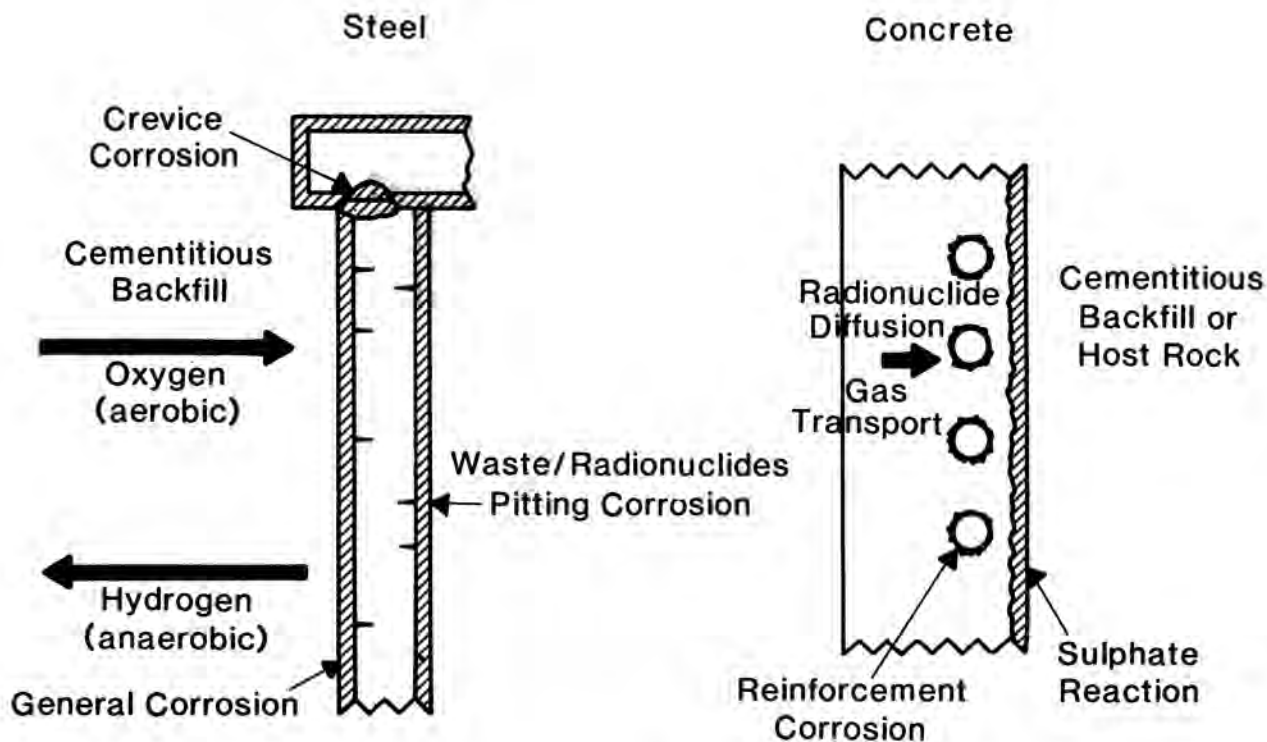


Fig. 1. The Engineered Barriers are Steel and Concrete. Some of the Key Research Issues are Illustrated Schematically.

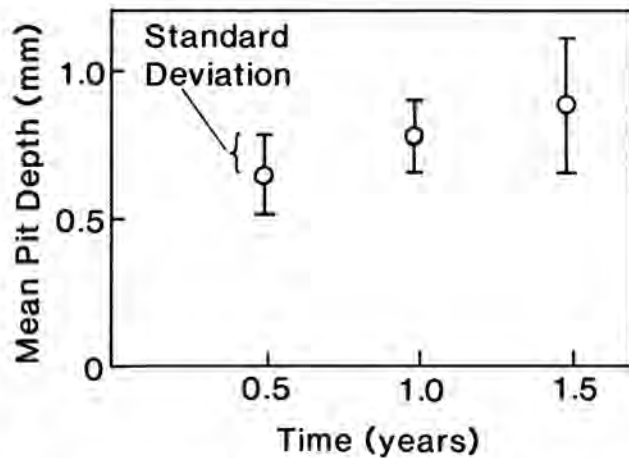


Fig. 2. Pit Growth Kinetics Measured on Carbon Steel Coupons in Cement Blocks Stored in Humid Aerobic Conditions (3).

therefore experiments are in progress to obtain more reliable data for this parameter.

ANAEROBIC CORROSION OF STEEL CONTAINERS

In the anaerobic period (after a maximum of about 65 years for carbon steel) there is insufficient oxygen to maintain the passive film and steel corrodes at a slow uniform rate with the evolution of hydrogen from water (Fig. 1). An initial estimate for this corrosion rate, based on published data, was about $13 \mu\text{m}$ per year under alkaline conditions[1]. Experiments are being carried out at Harwell Laboratory to improve these estimates using cemented samples prepared totally in an anaerobic environment. Additional experiments are in progress to examine what effect an overpressure of hydrogen will have on the corrosion rate (if the hydrogen gas cannot escape sufficiently quickly from the repository). The preliminary results indicate corrosion rates of no more than $5 \mu\text{m}$ per year, which decrease still further as the hydrogen pressure increases.

In the case of stainless steel the course of anaerobic corrosion is less certain, but similar studies are generating evidence that the passive film will break down under anaerobic conditions. Preliminary conservative estimates[1] of the rate of anaerobic corrosion suggested a maximum of about $17 \mu\text{m}$ per year. More recent experiments have shown that this is more likely to be about $5 \mu\text{m}$ per year or less. An overpressure of hydrogen is likely to reduce this rate in a similar manner to that for carbon steel.

PHYSICAL PROPERTIES OF CEMENT AND CONCRETE

It is likely that two classes of cementitious material will be deployed in the repository; a structural concrete (high strength and low mass transport) and a backfilling material (lower strength and higher mass transport). Typical structural concretes that have been studied in this research are based on Portland cement, and cements modified with pulverised fuel ash (pfa) or blast furnace slag (bfs), with a cementitious content in the region of 400 kg m^{-3} . The backfilling material is still under development, but some experiments have been carried out on lime-Portland cement mixtures of high water/solids ratio (approximately 0.8 - 0.9 by weight).

Transport of Soluble Radionuclides

In intact structural concrete the main transport mechanism for aqueous radionuclides will be diffusion through water-saturated pores, modified by adsorption onto solid surfaces. These processes may be characterised[8,9] by an intrinsic diffusion coefficient, D_i (which describes diffusion in the absence of sorption), and a capacity factor, a , equal to the average radionuclide concentration in the saturated porous material divided by the concentration in the aqueous phase alone. Thus for strongly sorbed species $a \gg 1$. The combination D_i/a gives an effective diffusion coefficient, D_{eff} , which can be used to estimate mass transfer by diffusion. Experimental

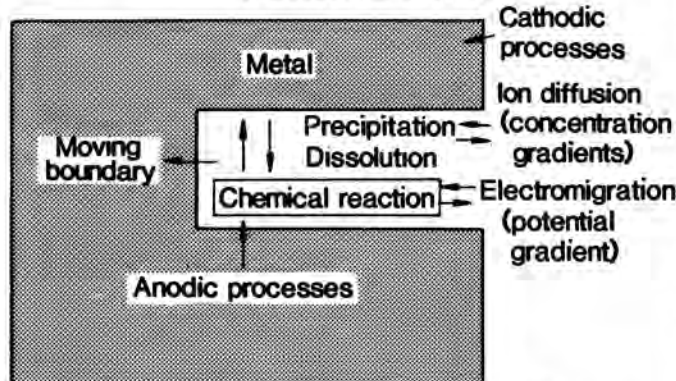


Fig. 3. Coupled Physical and Chemical Processes Included in the Model for Localised Corrosion.

data obtained in other programs for pit growth under conditions relevant to high level waste disposal and the agreement between model and experiment is within a factor of three (the model being the lower) for times up to 2 years. Such a model gives confidence in extrapolating the experimental data to the maximum limits envisaged for the aerobic period and is also used to explore the consequences of changes in conditions.

Crevice Corrosion of Stainless Steel

Stainless steels are more resistant to pitting corrosion than are carbon steels and the main concern during the aerobic period is localised corrosion at crevices (Fig. 1). A similar model to that described in the previous section has been developed to estimate the changing chemical conditions within a passive crevice and to determine whether they are likely to initiate enhanced corrosion within the crevice[7]. The model has been validated against published experimental data for chemical conditions within crevices. The model has indicated that the development of aggressive conditions within a crevice is particularly sensitive to the passive dissolution rate and

values[1] for sulphate resisting Portland cement (SRPC) are given in Table II and these are also typical of structural concretes[9], although diffusivity in cements containing substantial replacement by bfs is about an order of magnitude lower.

TABLE II

Diffusion Parameters for Ions at Low Concentrations ($< 10^{-4}$ mole l^{-1}) in Water-Saturated SRPC Paste (Water/Cement ratio = 0.40)

C_s^+	Sr^{2+}	3H_2O	
$D_i/10^{-12} m^2 s^{-1}$	2(± 1)	3(± 2)	7(± 3)
$\alpha (= \epsilon + \rho K_d)$	0.5(± 0.2)	9(± 3)	0.16(± 0.02)

Transport of Gases Through Cement

Hydrogen will be generated by the corrosion of steel and, although the rate is slow, the total volume of gas is substantial over long periods. The transport of gas through 'dry' cement and concrete (ie. material containing no liquid water) is relatively easy and we have measured permeability coefficients of the order of $10^{-17} m^2$ in typical structural concretes.

As the pores fill with water they effectively block direct transport in the gas phase and the gas can only bypass these blockages either by displacing water, or by dissolving in and diffusing through the water. Experiments using structural concretes equilibrated at 75% relative humidity have shown that the effective permeability is reduced by about three orders of magnitude by the water. Research is indicating that the backfilling grouts have much higher permeabilities in the wet condition (about the same as dry structural concretes).

Durability of Concrete

There are many potential causes for the deterioration of concrete structures; inappropriate selection of materials and poor workmanship amongst them. For an underground repository the most likely have been identified[11] as sulphate attack and corrosion of reinforcement. A survey of available data (from historical examination and accelerated laboratory studies) concluded that the degradation rates should be no greater

than 1 mm per year under likely repository conditions[1,11].

CHEMICAL PROPERTIES OF CEMENT AND CONCRETE

The beneficial high pH environment established by the cementitious materials is due to the preferential dissolution of calcium ions from the hydrated calcium silicates (which are the principal binding constituents of cured Portland cements) to give $Ca(OH)_2$ in aqueous solution. The basic chemistry of this dissolution is well established and has been used to estimate how pH is likely to vary with time and initial composition for a typical cementitious repository[13]. Such estimates indicate that pH will tend to fall with time as soluble calcium is removed by leaching in groundwater, by reaction with certain groundwater constituents (eg. bicarbonate) or by reaction with solids of high silica content within the repository (eg. pfa).

For the first two of these processes the timescale for the reduction in pH is determined by the time required for a given volume of water to pass through unit mass of cement in the cementitious materials. In the real repository this depends on the groundwater flux density (typically $10^{-10} ms^{-1}$), the dimension of the repository in the direction of water flow (typically 10 m) and the average cement content of the repository (typically $200 kg m^{-3}$). This relationship enables the timescale to be accelerated so that it can be investigated in the laboratory. This has been done for a variety of cement types using demineralised water and a simulated groundwater[14,15]. The example in Fig. 4 shows experimental results for SRPC cement leached by a simulated groundwater (containing $6 \times 10^{-3} M$ bicarbonate). The estimated timescale for the repository is based on the parameters given above. Both the experimental results and the predictions, using basic solubility data, demonstrate that the cement should have sufficient buffering capacity to maintain pH above 10.5 for a time of the order of 3×10^5 years in this typical case.

PERFORMANCE OF THE ENGINEERED BARRIERS

The research described in this paper has not been specific to a design of repository, container or backfill. The objective of the research has been to establish the basic principles, methods and fundamental data that are required to address most specific cases as they are presently envisaged. Nevertheless, it is possible to draw some general conclusions from the research concerning the barrier performance.

The physical short term containment is mainly associated with the steel containers. For carbon steel containers a corrosion allowance design can be adopted (ie. reliance on sufficiently thick-walled containers). If the repository saturates quickly and anaerobic conditions are established after one year then a thickness of 5 mm should give a period of about 300 years during which the container will not be penetrated using the best available (but probably pessimistic) corrosion data. If the

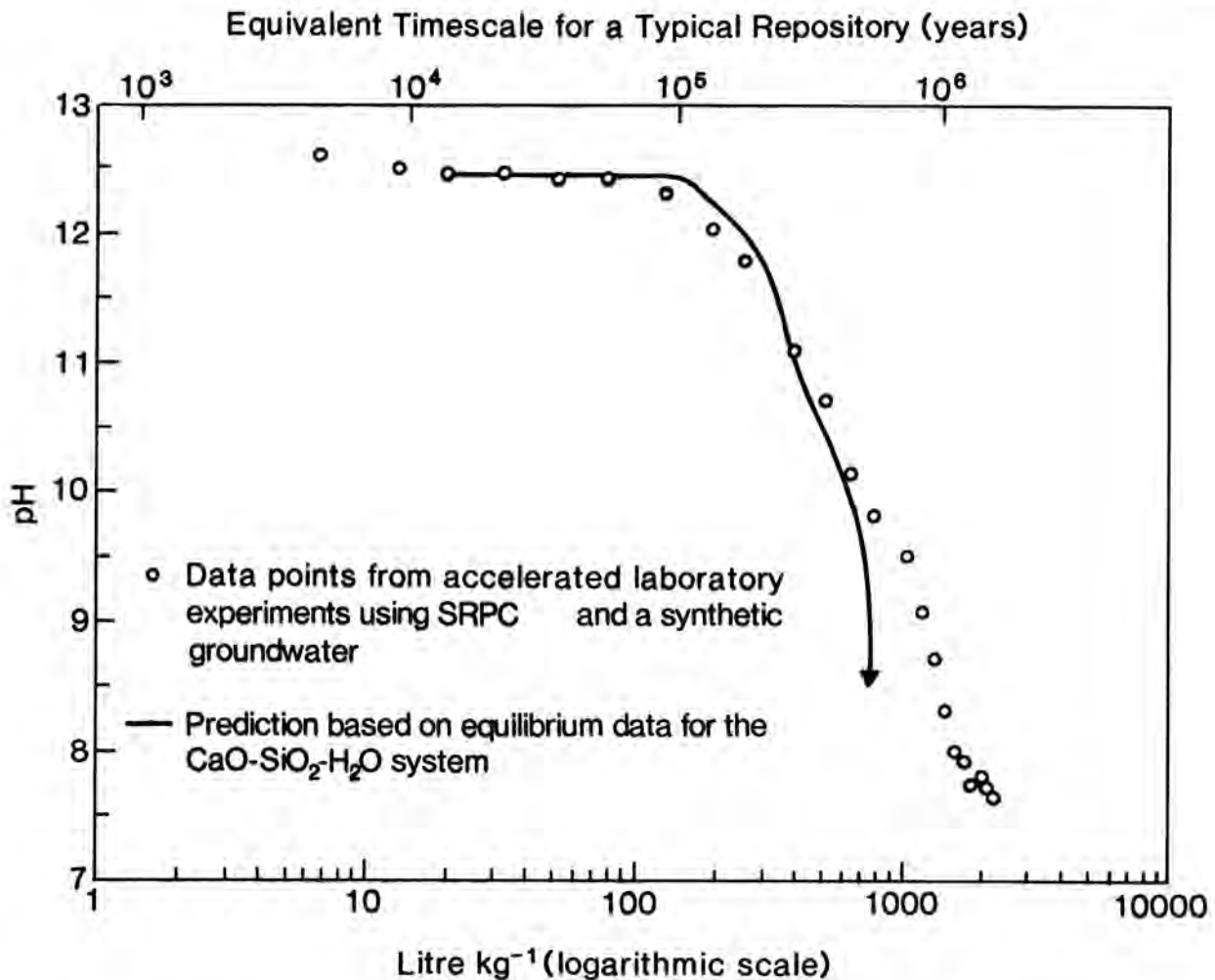


Fig. 4. Time Dependence of pH as Cement Hydrates Dissolve in, and React with, Groundwater. The Repository Timescale (Upper Scale) has been Estimated Using the Parameters Given in the Text.

repository is aerobic for its maximum period then penetration by pitting cannot be dismissed on the data obtained thus far, unless the wall thickness is increased. Nevertheless, there are other constraints (such as the total supply of oxygen) on the possible number of penetrations per unit area. Stainless steel is usually used in thin sections because of its good corrosion resistance in aerobic conditions. Using a value of 5 lm per year for the uniform corrosion rate in anaerobic conditions (again probably pessimistic) it is concluded that a 2 mm section should last for at least 200 years. However, the resistance of stainless steel to crevice corrosion requires more detailed consideration, especially in view of the possibility of a longer aerobic period for stainless steel.

Good quality structural concrete is anticipated to have sufficient durability for 300 mm thick sections to have useful engineering properties for several hundred years. During this period concrete walls could make an additional contribution to physical containment. The diffusion parameters indicate that a 300 mm section would

be an effective barrier to contain caesium and strontium for over 100 years[1].

Stable alkaline chemical conditions in the repository should be achievable by a suitable choice of cementitious backfill (in addition to the structural concretes and waste packaging grouts). In a typical repository the average pH is likely to be maintained above 10.5 for longer than 10⁵ years and thus provide long term chemical containment for many radionuclides.

Transport of gases (such as hydrogen) through intact structural concrete under saturated conditions may be difficult. However, cementitious backfills of relatively high permeability should be capable of allowing gases to escape without disrupting the structure of the near field.

Such backfills would also assist the attainment of uniform chemical conditions in the repository.

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