

THE ENGINEERING OF A CEMENTITIOUS BARRIER

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ABSTRACT: When cementitious materials are used for the containment of waste they act in two different and sometimes conflicting ways. The first is physical containment in which the waste is physically isolated from the environment. The second is chemical containment in which the water passing through the barrier is buffered to high pH thereby very substantially reducing the solubility of many harmful species and promoting sorption onto the cement matrix. Chemical barriers have been extensively researched for nuclear waste containment and this paper explores the possibility of using them for non-nuclear waste.

Initial results are presented which show that cementitious barriers containing cement replacement materials may be well suited to barrier construction. It is, however, concluded that cementitious barriers would have to be used as part of a composite system in order to comply with current legislation.

INTRODUCTION

The cementitious chemical barrier is one of the main engineering features of the current plans for a UK repository for medium and low level nuclear waste. The concept has been developed in response to a requirement for a barrier which will have a predictable performance in a deep saturated geological environment over a timescale of up to a million years. The barrier is built out of conventional engineering materials but its method of operation is far from conventional for an engineering structure because it is essentially sacrificial. The main function of the barrier is to condition the chemistry of the repository to high pH and to do this the free lime and subsequently the calcium silicate hydrate which forms the structure of the hardened cement dissolve in the groundwater.

This paper outlines the main features of a cementitious chemical barrier and explores the possibility of applying this technology to non-nuclear waste. Figure 1 shows schematic a representations of a repository for nuclear waste. The grout is a soft material with a strength of about 4 MPa containing cement, lime, bentonite and other components and is the main chemical barrier. Figure 2 shows a typical arrangement of a landfill for non-nuclear waste. The waste may have been solidified using cement or some other alkaline material but this is not normally the case and the chemical barrier could work by establishing a local alkaline region while the bulk of the waste remained acidic.

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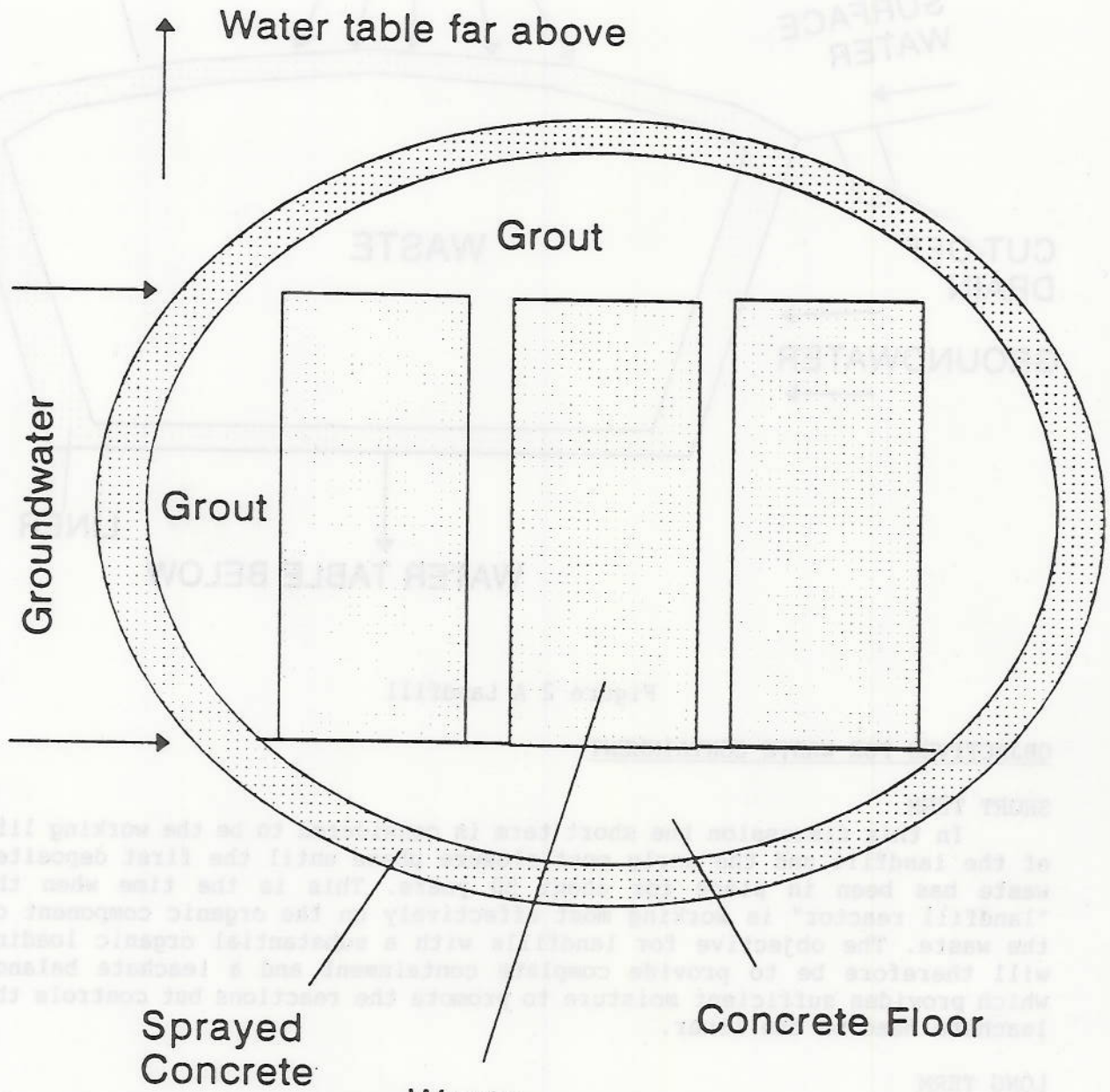


Figure 1. A Scheme for a Radwaste Repository

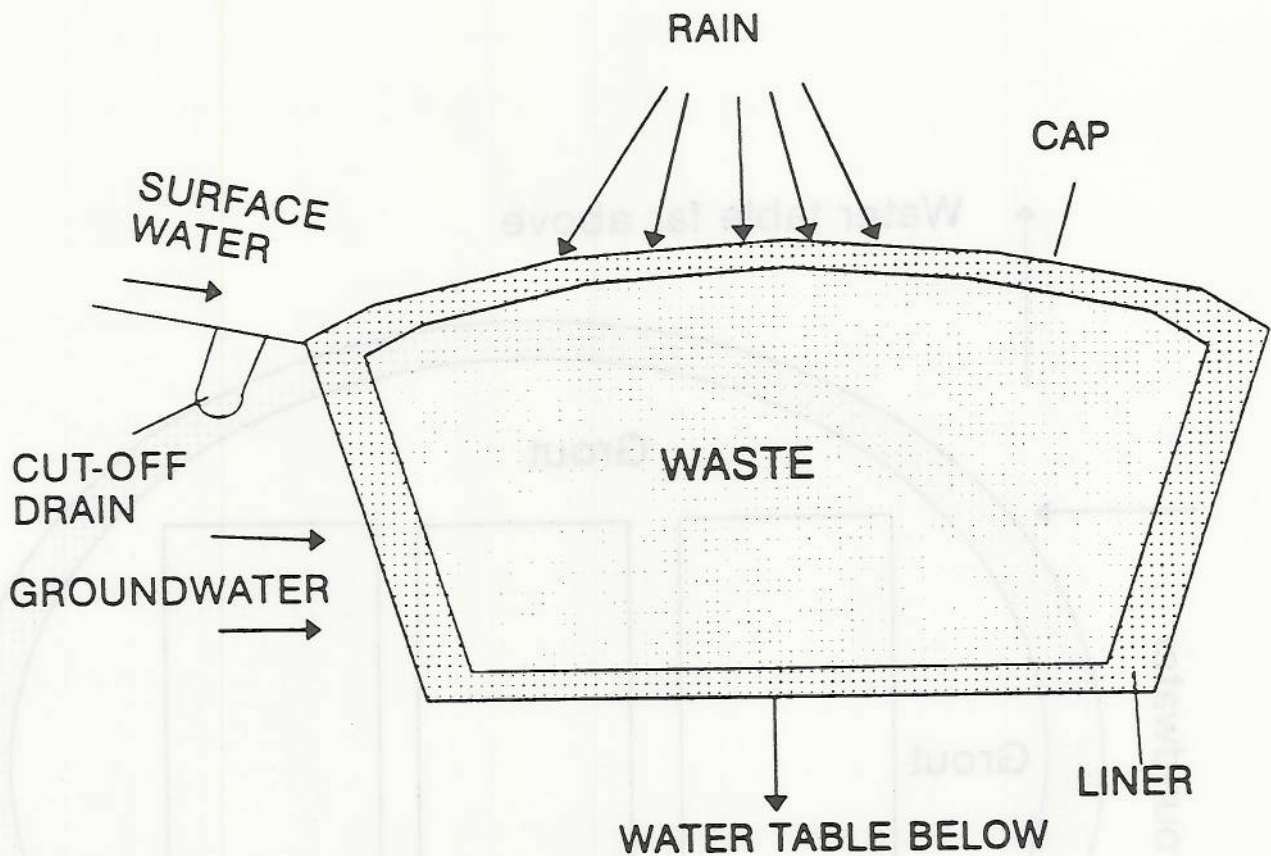


Figure 2 A Landfill

OBJECTIVES FOR WASTE CONTAINMENT

SHORT TERM

In this discussion the short term is considered to be the working life of the landfill and the early post closure phase until the first deposited waste has been in place for about 50 years. This is the time when the "landfill reactor" is working most effectively on the organic component of the waste. The objective for landfills with a substantial organic loading will therefore be to provide complete containment and a leachate balance which provides sufficient moisture to promote the reactions but controls the leachate head on the liner.

LONG TERM

In the very long term the contents of a landfill will disperse into the environment from which they came. For nuclear waste the objective is to contain the waste until the activity has substantially decayed but, once the organic degradation is complete, there is no further reduction in toxicity for non-nuclear waste. The long term objective for non-nuclear waste containment may therefore be to provide an environmentally acceptable transition between the aim of absolute containment in the short term and the certainty of dispersion in the very long term. The absolute physical certainty that all landfills will eventually have to dilute and disperse their inventory of heavy metals and other stable toxins does not appear to be recognised by current legislation. It is of note that some waste materials (e.g. Pulverized Fuel Ash) have a sufficiently low permeability that in

normal deposition they do not generate leachate for about 30 years so short term containment is irrelevant.

PROPERTIES OF CEMENTITIOUS MATERIALS IN BARRIERS

PHYSICAL CONTAINMENT

Physical containment with concrete is well understood and documented. The degree of containment will depend on the permeability of the barrier. The permeability of concrete is relatively easy to measure and this has been achieved in a wide variety of different ways. One of the better methods is the use of a modified Hoek cell.

CHEMICAL CONTAINMENT

Chemical containment has been studied in detail for nuclear waste. In the type of repository for which a chemical barrier would be used the main mechanism of loss of radionuclides is caused by flowing groundwater. This flow may be present in the area before the repository is built or it may be caused by the heat generated in the repository. In order to operate for a long time a chemical barrier depends on other barriers to limit the flow of groundwater through it. This is normally achieved by positioning the repository in a geology with a very low permeability. In this situation the permeability of the repository itself can be shown not to have a significant effect on the flow of water through it.

Thus water will enter the repository very slowly and the chemical barrier works by conditioning it before it reaches the waste and also after it leaves the waste but before it leaves the repository. Before it reaches the waste the barrier will raise the Ph of the water, reduce the Eh, and remove many dissolved ions such as sulphates. In this way the barrier will ensure that the solubility of the radionuclides in the waste is as low as possible. For example raising the Ph from 8 to 12.5 will reduce the solubility of Uranium by an order of magnitude, Plutonium and Protactinium by one and a half and Americium by three and a half. After the water leaves the waste the barrier will provide a high capacity for sorption to remove radionuclides from it.

It may be seen that, unlike a conventional engineering structure, the method of operation of a chemical barrier is sacrificial. As it operates the cement matrix carbonates and reacts with sulphates and other materials to an extent which would indicate failure in a conventional structure.

Calculating the rate of loss of radionuclides from the repository is made relatively simple by assuming that the chemical barrier is in complete equilibrium. Thus if the sectional area of the repository perpendicular to the direction of groundwater flow is A (m^2), the Darcy velocity of the flow is V (m/s) and the solubility of the radionuclide in the pore solution of the barrier is C (mol/m^3) the loss rate is CAV (mol/s). It should be noted that only a small fraction of the radionuclides in a cementitious barrier can be lost by this mechanism since most of them are sorbed onto the matrix. The ratio of those in solution to the total inventory in the barrier is P/a where P is the porosity and a is the capacity factor and typical values for this are 3×10^{-5} (Uranium) and 6×10^{-6} (Plutonium).

Measurements of the buffering and sorption capacity of concrete have been carried out using "batch" experiments in which a solution with a fixed contaminant loading is mixed with ground concrete and permitted to come to equilibrium. The solution is then filtered off and analyzed for pH and loss of contaminants. An alternative system is to use a "through flow" cell in

which the solution is pumped through an intact sample of concrete. The requirements of the apparatus are similar to those for permeability measurements and a modified Hoek cell is again very suitable for this.

INITIAL EXPERIMENTAL OBSERVATIONS

When a barrier material is tested it will act both physically and chemically as it would in service. Both types of containment are therefore measured in the same experiment. In the experiments which are reported here samples of cementitious materials approximately 20mm thick were exposed to water pressures up to 10MPa in a 100mm diameter modified Hoek cell. To measure the physical containment the flow rate was measured and this was used to calculate a coefficient of permeability. To measure the ability of the barrier to buffer the leachate the buffering capacity of the water flowing from the cell was measured by titration. The theoretical buffering capacity of the sample was calculated and the proportion of this that was remaining was plotted against the number of sample volumes that had flowed through the cell. A typical plot is shown in fig.3. The results from the initial observations are summarised in Table 1, these show the effect of permeating a volume of water equal to 30 times the sample volumes.

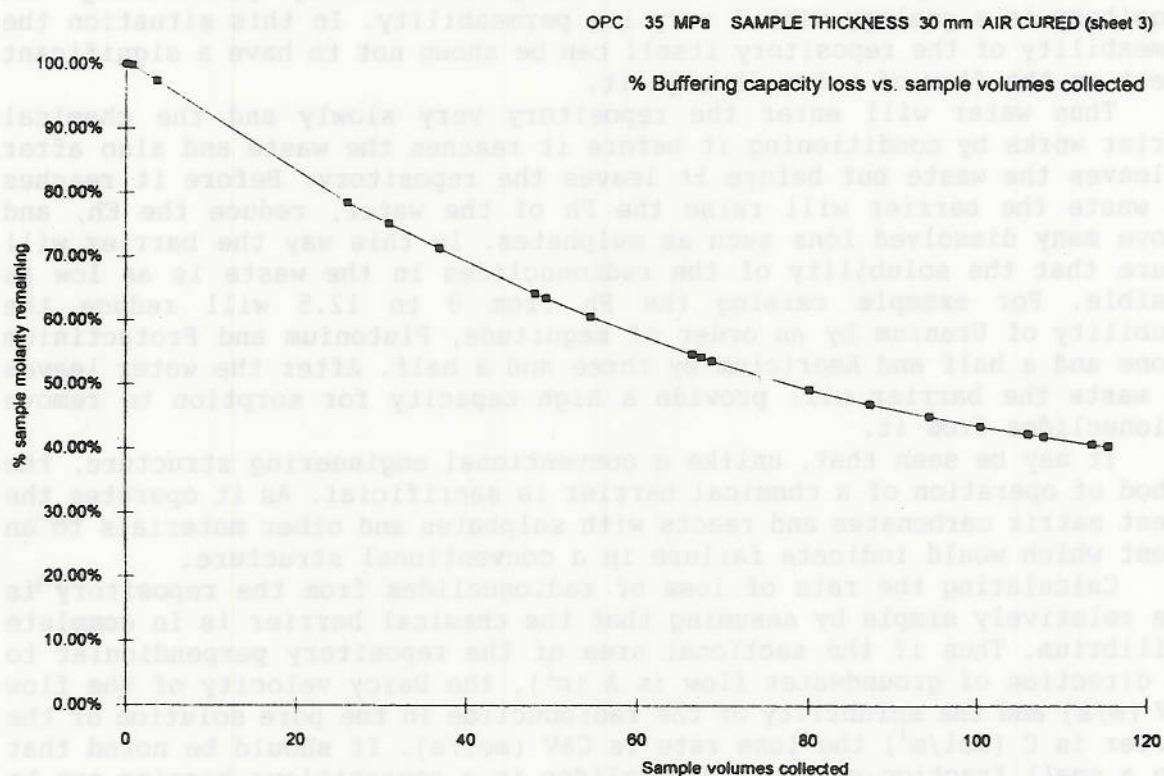


Figure 3 Typical result from Initial Experiments

Table 1. Initial Experimental Results.

Mix Type	% buffering remaining after 30 volumes	Initial permeability m^2	Permeability after 30 volumes m^2
OPC 35 MPa	94	2E-16	9E-17
OPC 20 MPa	70	9E-16	4E-16
60/40 OPC/PFA	90	9E-18	4E-18
55/45 OPC/PFA	98	8E-17	1E-17
45/55 OPC/GGBS	98	7E-19	5E-17

OPC: Ordinary Portland Cement

PFA: Pulverized Fuel Ash

GGBS: Ground Granulated Blastfurnace Slag

The results showed considerable variations between samples but it is clear that the blended cements release their buffering more slowly and would therefore appear to be more suitable for barriers.

MODES OF FAILURE

EXHAUSTION OF BUFFERING

The principal mode of chemical failure of the barrier is the exhaustion of its buffering and sorption capacity. Fortunately it is possible to carry out accurate calculations of the design life of the barrier to this mode of failure. The relationship between groundwater flow rates and the volume of material in the barrier indicate a life in excess of a million years for current design concepts for nuclear waste.

CRACKING

This is the obvious mode of physical failure which has been the reason why concrete barriers have not been common in the past. Cracking could be caused by drying or thermal effects or the imposed stresses on the barrier. The problem is overcome by using composite barriers which are discussed in the last section of this paper (Fig. 5).

HIGH PH "BOULDER" FORMATION

A possible cause of premature chemical failure which is the subject of a research programme is the formation of impermeable "boulder-like" pieces with preferential flow paths for water around them. These boulders could develop impermeable surface layers through the formation of carbonates, chloroaluminates or magnesium compounds in a similar manner to that observed at the surface of existing concrete structures in hostile environments. If this occurred the alkaline buffering and sorption capacity of the interior of the boulders would be lost. In this way the total buffering and sorption capacity of the repository would be substantially reduced.

In current plans for nuclear waste it is currently envisaged that

almost all of the cementitious material will be in the form of a soft grout. This material has been chosen to comply with various operational criteria including being readily pumpable into small spaces between the packages and having a low strength. These requirements have the effect that the formation of hard impermeable boulders will be strongly inhibited.

ACTION OF SULPHATES.

Sulphates react with hardened concrete and cause expansion of the matrix which leads to significant loss of strength. This effect may be prevented by the use of sulphate resisting cement or Blastfurnace Slag cement. It is of note, however, that in a deep nuclear repository the effect is harmless because the expansion is contained by the surrounding rock. For non-nuclear applications where the containment pressures are insufficient it would be necessary to use sulphate resisting cement but the aluminate phases of the cement which are omitted in order to give it sulphate resistance have substantial capacity for sorption so this method should not be used if it is avoidable. Cement replacement with blastfurnace slag probably represents a better option.

GAS TRANSMISSION THROUGH THE BARRIER

GAS GENERATION

Gas is generated in significant quantities in most forms of waste. Organic materials are responsible for a number of gases including methane and hydrogen and this will be the main source of gas in a normal near surface landfill. In deep nuclear waste disposal the main source of gas is hydrogen from the anaerobic corrosion of steel.

TRANSMISSION IN SATURATED BARRIERS

If concrete is dry it will transmit gas very easily. This will often be the situation with a concrete cap on a landfill and represents a major advantage for concrete barriers. If the concrete is saturated, however, the permeability will be very low. A major study has been carried out in this area for nuclear waste disposal (Harris et al, 1992) and the results of this are summarised in Fig.4. In this study four different cementitious formulations were tested and for each there is a horizontal line on the graph drawn at a stress level corresponding to its tensile strength. The four mixes were "PFA", a Pulverized Fuel Ash concrete, "BFS" a Blastfurnace Slag concrete, "LIMESTONE" a grout with limestone dust in it and "LIME" a grout with lime in it. The saturated and dry coefficients of permeability of each mix were measured and are represented on the graph. Numerical modelling of the effect of releasing gas at the estimated generation rate for the repository into voids of different radii was carried out. These voids were assumed to be present above the vents which will be placed in the top of each drum of waste and the resulting stresses generated by the gas are shown by the curves on the graph for three different radii. The solid line is for a radius of 0.1m which will be the radius of the vents. It may be seen from the graph that the calculations indicated that the grouts would survive but the concretes would fail. The backfill in the UK repository will be a soft grout so the results are satisfactory.

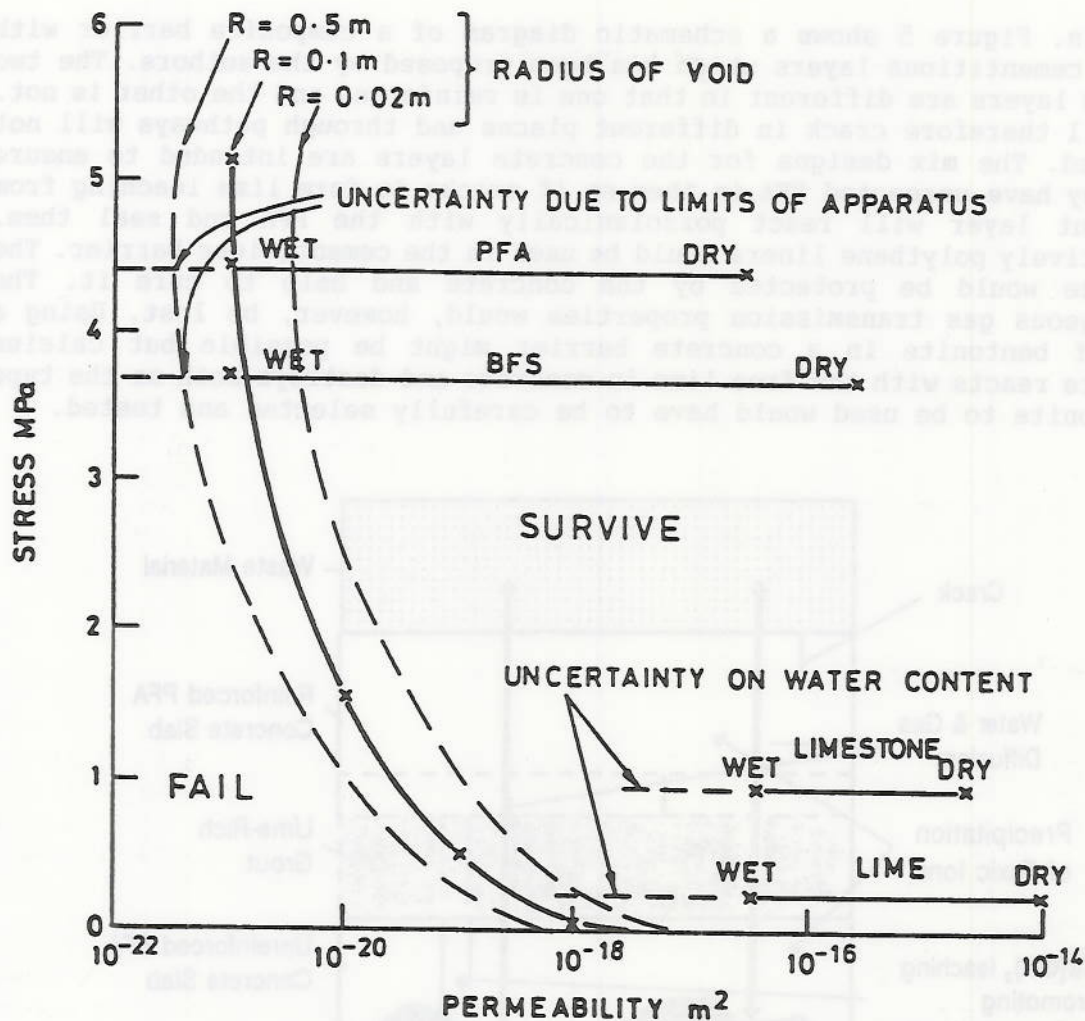


Figure 4. Gas Transport in a repository

PORE WATER EXPULSION.

It may be seen from Fig.4 that there was some uncertainty with the measured saturated permeability of the grouts because they may not have been fully saturated. The samples were kept under water after casting and held in sealed containers over a flat water surface during testing but they still lost some weight. These grouts have substantial porosity with maximum radii in the $1\mu\text{m}$ range. Classical calculations indicate that a pore with this radius should remain full at an RH of 99.9% and have a capillary height of 14m and should thus have been full. As expected pore water expulsion at pressures over about 150 kPa was observed. The observation that the pores tended to empty at pressures below this indicates, however, that barriers made with materials of this type might drain into gas filled areas beneath them permitting easy escape of the gas.

DESIGN OF CEMENTITIOUS BARRIERS

It is clear that a single cementitious barrier will not provide sufficient short term containment to satisfy current regulations. In order to take advantage of this type of barrier it will be necessary to use a composite system with several cementitious layers or layers of other

materials. Figure 5 shows a schematic diagram of a composite barrier with several cementitious layers which has been proposed by the authors. The two concrete layers are different in that one is reinforced and the other is not. They will therefore crack in different places and through pathways will not be formed. The mix designs for the concrete layers are intended to ensure that they have unreacted PFA in them so if cracks do form lime leaching from the grout layer will react pozzolanically with the PFA and seal them. Alternatively polythene liners could be used in the cementitious barrier. The polythene would be protected by the concrete and help to cure it. The advantageous gas transmission properties would, however, be lost. Using a layer of bentonite in a concrete barrier might be possible but calcium bentonite reacts with the free lime in concrete and destroys both so the type of bentonite to be used would have to be carefully selected and tested.

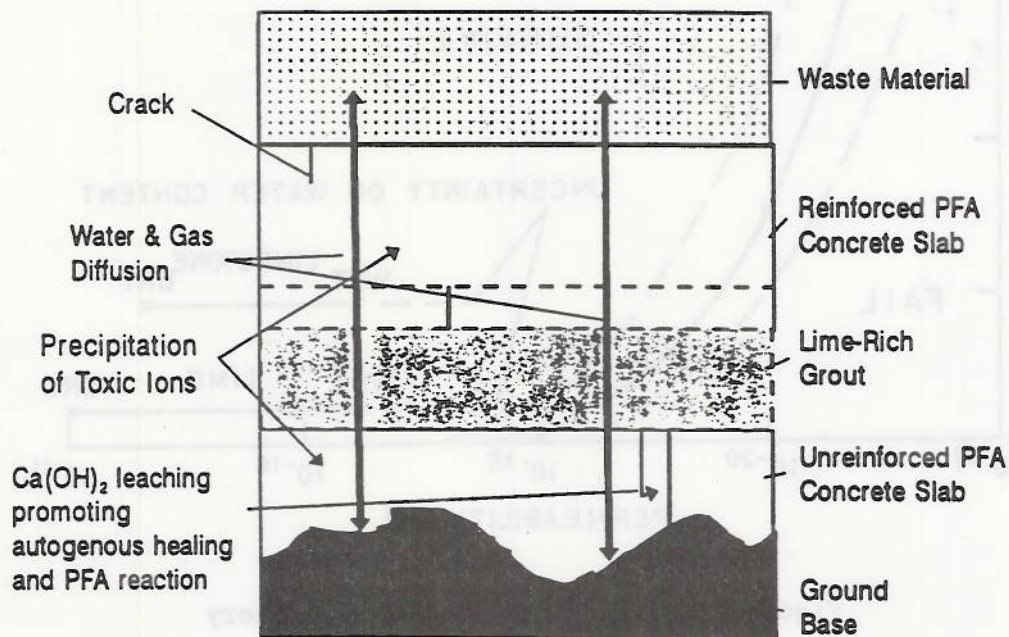


Figure 5. A Composite Cementitious Barrier

REFERENCE

Harris A W, Atkinson A and Claisse P A. Transport of gases in concrete barriers, Waste Management, Vol 12 pp.155-178, 1992.