

## Permeability a dynamic property of barrier materials

Stephan A. Jefferis<sup>1</sup>

**Abstract:** Permeability of barrier materials is often regarded as a fixed property such as strength, which can be varied only by a change in the effective stress or chemical damage. Furthermore chemical attack, if it occurs, tends to be treated as a ‘once-off’ phenomenon i.e. once it has occurred the process is finished. In fact a barrier material such as clay or cement-bentonite is a chemical reactor with a dynamic permeability. Flow through this reactor is controlled by the overall permeability of all the reaction zones that exist within it. Each reaction zone may have a different permeability, be of time-varying length and involve some local volume change. Recognition of a barrier as chemical reactor offers possibilities for maintenance and repair as well as the development of new reactive systems for specific chemical control. The existence of reaction fronts means that the permeability may vary within a barrier and, for materials that reduce in permeability with time, reaction path length can be important. Volume change on reaction also is important and requires more research.

**Rate of movement of a reaction front:** There is a substantial literature on the effects of sorption on the rate of migration of chemical species and a standard result with a linear sorption isotherm is a retardation of  $(1 + \rho K_d/n)$  relative to interstitial flow velocity of the fluid (where  $\rho$  is the density of the material,  $K_d$  the partition coefficient and  $n$  the porosity). For chemical reaction there is a very limited literature but a basic form of the retardation relationship for a species,  $r$  is:

$$R = 1 + (C_{rS}/C_{rL} n) \quad (1)$$

Where  $C_{rS}$  is the concentration of species  $r$  in the solid phase and  $C_{rL}$  is the concentration in the liquid phase of a species that reacts with  $r$  (both concentrations in equivalents per unit volume). Equation 1 is the most basic relationship. When considering actual reaction processes, it may be necessary to consider volume changes of both the solid and liquid phases on reaction. For species  $r$ , the ratio  $C_{rS} / C_{rL}$  gives the volume of the solid phase that will react with one cubic meter of liquid phase in a simple laboratory beaker or a stirred reactor. The extra volume ‘ $n$ ’ is required to deliver the reactive species to the reaction front. Equation 1 gives the retardation for species  $r$  but there may be many different reacting species as well as mineral dissolution and so there may be many different reaction fronts. Computer modeling will be required to describe the complex and interacting chemistry of all but the simplest situations.

The rate of movement of reactions fronts will be a function of the overall permeability of the system (see Jefferis, 1992 for a procedure for a single reaction front). It follows that if permeability reduces with time (for example as cement hydrates) reaction fronts may move relatively faster in young materials (see Jefferis and Fernandez, 2000 where it is shown that inclusion of a geomembrane by lengthening a critical flow path greatly extended the design life of a barrier). Another effect of the movement of reaction fronts is that a sample cored from a within a barrier may show a quite different permeability to a sample from the edge if reaction is occurring with the surroundings. Samples cored from the bulk of a young cement-bentonite barrier can be poor indicators of the overall permeability as reaction with groundwater typically leads to a substantial reduction in permeability at the boundaries.

---

<sup>1</sup> Professor in Civil Engineering, School of Engineering in the Environment, University of Surrey, Guildford, Surrey, GU2 7XH, England, S.Jefferis@Surrey.ac.uk

In an investigation of the effects of chemical reaction a sample of cement-bentonite was permeated first by water, then saturated lime solution and finally magnesium sulfate solution. The sample was prepared by mixing a sodium activated bentonite with water, allowing some time for hydration and then adding ordinary Portland cement and blastfurnace slag. The mix was designed to have a high initial permeability to promote rapid movement of reaction fronts.

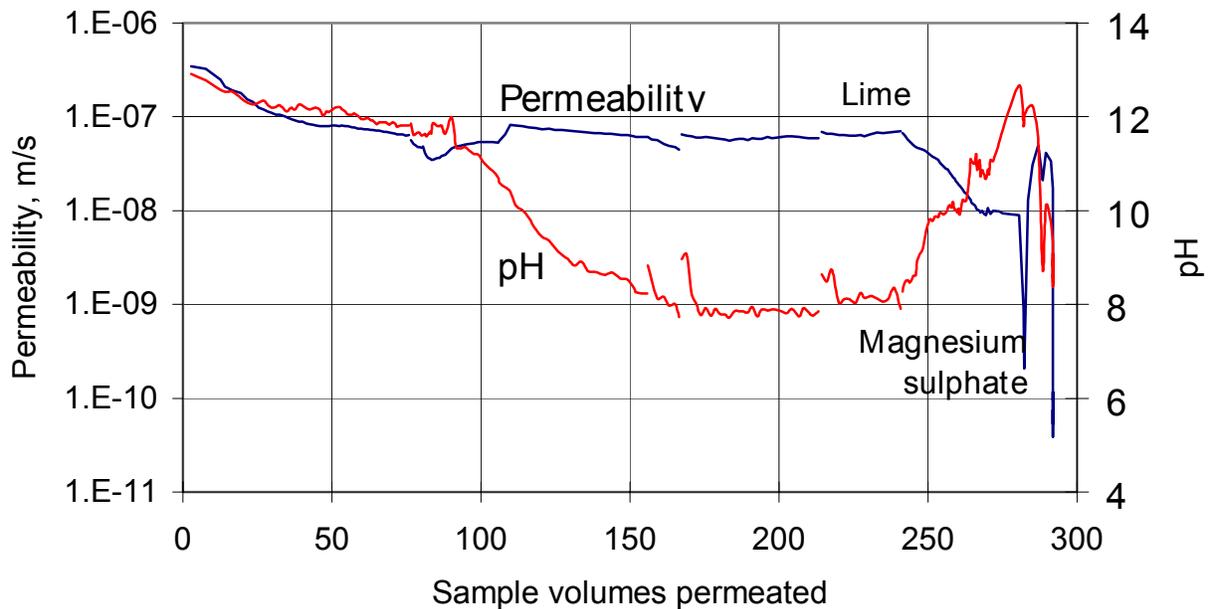


Figure 1 - Permeability and effluent pH for a sample cement-bentonite

At age seven days the sample had developed sufficient strength to be mounted in a triaxial cell. It was then permeated with tap water for about 240 sample volumes over a period of three years. Figure 1 shows a plot of permeability of the sample and the pH of the effluent as a function of the number of sample volumes of water passed through it. Sample volume is a convenient non-dimensional measure of the leaching and more relevant to chemical reaction than ‘pore volume’ which although often used in the literature is convenient only for physical phenomena such as change of dielectric constant. The permeation was interrupted on a few occasions and on the re-establishment of flow the initial effluent was of slightly higher pH as can be seen from the ‘spikes’ on the pH curve. The sample showed a continuing reduction in permeability up to about 80 sample volumes of water. At this point the pH started to decline more rapidly – possibly corresponding to the onset of degradation of the calcium silicate hydrates. The associated slight increase in permeability is therefore not surprising. By 150 sample volumes the pH had reached a plateau at about 8 and the permeability was effectively constant. The reduction in permeability of cement-bentonites on water leaching is well established and the behavior shown in this part of Figure 1 is as expected. However, the figure denies a thesis implied by some of the current literature that the permeability of cement-bentonite continues to decrease without limit.

Water leaching beneficially reduces the permeability of cement-bentonites but does cause some volume reduction and could also permit the release of any heavy metals trapped in a barrier as hydroxides. To see if the pH of a leached sample could be re-established, the sample (after 280 sample volumes of water) was permeated with saturated calcium hydroxide (lime) solution. It

took 40 sample volumes of lime permeation to establish an effluent pH equal to the influent the pH showing that a considerable quantity of calcium was taken up by the leached mass. It may be noted that lime permeation caused a further reduction in the sample permeability and this reached a plateau after about 30 volumes of lime (permeability is not an indicator of equilibrium, effluent chemistry must be monitored). The combined effect of sample ageing, water leaching and lime permeation was a reduction of some 30 times on the initial permeability.

After the lime permeation, to assess the effect of a potentially damaging ions the sample was permeated with a 12.5 g/liter magnesium sulfate solution (10 g/liter sulfate ion) a concentration sufficient to destroy structural concrete and unconfined samples of cement-bentonite materials). From Figure 1 it can be seen that there was an immediate reduction in permeability – presumably from the precipitation of gypsum. However, the effect was short-lived and the permeability increased again to about five times that at the end of lime permeation, indicating that there was some damage. After some 10 sample volumes of solution had passed, the permeability dropped again, possibly due to further precipitation. In other tests magnesium sulfate was found to reduce the permeability of a fully water leached sample (without re-introduction of lime) by over two orders of magnitude and the effect appeared to be sustained showing that magnesium sulfate is beneficial in the absence of alkali when there is no potential for the formation of expansive phases. For an unleached sample the permeability increased by a factor of a few times.

Volume Change: A feature of chemical reaction within barrier materials which has received rather little attention is the associated volume change. In the field expansive reactions are likely to be resisted by the passive resistance of the surrounding soil. Shrinkage may be more significant especially if it occurs parallel rather than perpendicular to the barrier as it may lead to the opening of cracks at intervals along the barrier. Unfortunately small scale laboratory tests are poor indicators of the effects of cracking. Further work is needed in this area, preferable at field scale. However, something that can be done at laboratory scale is the investigation of the length of reaction zones. If a reaction has kinetics which are slow compared with the flow process or reaction/sorption is weak then a long and diffuse reaction front is to be expected. In contrast, rapid or strong reactions are likely to produce a sharp front, a discontinuity in the sample possibly sufficient to cause localized cracking. It would seem that a diffuse front is to be preferred for control of cracking. Materials design to avoid sharp reaction fronts and promote diffuse fronts presents an important challenge.

Summary: Permeability is a dynamic property sensitive to the chemical history. This can be exploited to extend the life of barriers, protect them from damage and modify their chemical activity. Permeation history is crucial and can totally change the impact of some chemical species. Cracking induced by volume change may limit to barrier performance against aggressive chemicals. Research is needed on the shape of reaction zones and associated cracking.

#### References

- Jefferis, S.A. and Fernandez, A. Spanish dyke failure leads to developments in cut-off wall design, International Conference on Geotechnical and Geological Engineering, Melbourne, Australia, November 2000.
- Jefferis, S.A. Contaminant - grout interaction, ASCE Specialty conference, Grouting, Soil improvement and Geosynthetics, New Orleans, February 1992.