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# **Recycled Materials In Concrete Barriers**

by

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Synopsis: This paper reports results from a research programme into the use of concrete in the construction of barriers to contain leachate from waste in landfills. The barriers are of composite multi-layer construction with layers of concrete above and below a clay core. This work is intended to provide a financially attractive alternative to current technologies such as bentonite and high-density polyethylene membranes. A wide range of different materials have been tested for use in the concrete including different slags, ashes, and other industrial by-products. Many of the mixtures do not contain any constituents, which have commercial value. The results indicate that the barriers are durable but the concept of durability must be carefully understood in this context.

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## **INTRODUCTION**

Despite major initiatives for waste minimisation, disposal of large volumes of waste in landfills will continue for the foreseeable future. The landfill industry is now based on facilities which are engineered to minimise pollution of the local environment. The containment of leachate arising from waste which has been disposed of in a landfill is normally achieved with clay-based systems supplemented with high-density polyethylene (HDPE) membranes. This paper describes a project which investigated a totally new barrier concept. The programme started in 1998 and is being carried out in the UK by Imperial College and Coventry University.

## **EXPERIENCE FROM THE NUCLEAR INDUSTRY**

A 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. However, 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 by dissolving alkalis in the groundwater. The alkalis are free sodium, potassium, and lime and subsequently the calcium silicate hydrate which forms the structure of the hardened cement.

## **Physical containment**

Physical containment with concrete is well understood and documented (1). The degree of containment depends primarily on the permeability and diffusion coefficient of the barrier.

## **Chemical containment**

Chemical containment has been studied in detail for nuclear waste (2). In the type of repository for which a chemical barrier could be used, the main mechanism of loss of radionuclides is caused by flowing groundwater (3). 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.

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 electrochemical potential (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 cementitious matrix carbonates and reacts with sulphates and other materials to an extent, which would indicate inadequate durability in a conventional structure.

## **OBJECTIVES FOR WASTE CONTAINMENT**

In order to select concrete mixtures for non-nuclear waste containment, it is important to establish clear objectives for the system. These may be divided into short-term and long-term objectives.

### **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 to degrade 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 organic reactions but controls the leachate head on the liner.

## **Long-term**

In the very long-term the contents of a landfill will disperse by processes such as diffusion and pressure driven flow back into the environment from which they came. For nuclear waste the objective is to contain the waste until the activity has substantially decayed. For non-nuclear waste, however, once the organic degradation is complete, there is no further reduction in toxicity. The long-term objective for non-nuclear waste containment may therefore be to provide an environmentally acceptable transition between the aim of an 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, gives a different meaning to the concept of durability than that which applies to normal structures. The liner may be defined as having good durability even at the stage when the waste inventory is being dispersed to the environment in the manner which has been envisaged by the design. It is of note that some waste materials (e.g. fly ash) have a sufficiently low permeability that in normal deposition they do not generate leachate for about 30 years (4), therefore short-term containment is irrelevant.

## **THE MULTI-LAYER BARRIER CONCEPT**

Fig. 1 illustrates the type of multi-layer barrier which was used for the work described in this paper. Each layer has a specific function and enhances the performance of the others. The clay provides a physical seal and is protected from mechanical damage and extrusion by the concrete above and below. The upper concrete provides a hard working surface for vehicles to use during waste emplacement and eliminates the need to use selected waste near the liner (as required when an HDPE liner is used). The lower layer provides long-term physical and chemical containment. Once the waste has been placed (normally to depths of about 20m) the barrier will be subject to compression and the clay is expected to extrude into any cracks that form in the concrete. The possibility of light mesh reinforcement in the lower concrete layer has been considered for conditions where foundation conditions may lead to uneven settlement.

## **Requirements of the barrier concrete**

The following requirements for the barrier concrete arise from the above considerations:

1. A cube strength of 5 N/mm<sup>2</sup> is adequate.
2. The strength requirement is only for emplacement. After 2 years little strength is required.
3. Expansion of the barrier is harmless so the dimensional stability of the mixtures is not important. In operation it will be subject to triaxial compression. Thus sulphate attack or unsound cements should be harmless.
4. The leachate permeability through the barrier must remain low.
5. Cracking is inevitable. What must be avoided are large cracks with large "boulders" between them. Small cracks will close due to the compression and

- will seal from mineral deposition (autogenous healing) or clay intrusion from the middle layer.
6. Alkaline buffering is essential but this must only be available to the leachate permeating through the barrier. There can never be sufficient buffering for the entire waste load.

## LITERATURE REVIEW

An initial study on cementitious barriers of this type has been reported by Claisse and Unsworth (5). However, the vast majority of commercial applications of and hence research efforts into landfill liners focuses on HDPE based systems; yet interest in mineral barriers continues to grow, especially overseas (6). Current research is concentrated in three subject areas: geotechnical investigations into the composite sand-clay-geotextile system, leak detection studies undertaken on behalf of both the regulators and operators (7) and research into waste leaching (8,9). The latter has resulted in the formation of an European Community (EC) thematic network on leach testing procedures (10), which has direct relevance to this project. Similar work in construction materials has generated a wealth of knowledge in the leaching of cements and concretes, which has also resulted in an EC thematic network being established (11). The European Standards Commission (CEN) have drawn on these initiatives along with those of the national standards authorities in Europe and North America (12) to produce draft standard procedures for waste characterisation and testing of wastes and construction materials.

## SELECTION OF MATERIALS.

### Cementitious components.

Portland cement (OPC) was used as a minor component in some mixtures but was kept to a minimum to reduce cost. Numerous other materials were tested having been selected primarily for their ability to provide alkalinity to the mixture. All of these other materials are by-products that are wasted and many of them currently present an expensive disposal problem.

**Soda Slag.** -- This material was obtained from the pyrometallurgical refining of lead. It contains mixed heavy metals both as oxides and sulphides in addition to sodium carbonate.

**Borax slag** -- This is a zinc oxide-containing sodium tetraborate slag, which is a by-product of silver refining. The material was ground before use and found to have hydraulic properties similar to cement.

**Ashes** -- The ashes were derived from coal combustion for power generation. The "run of station" ash was from an unclassified source and contained a relatively high-carbon content. The "lagoon ash" contained less carbon but was obtained from the discharge lagoon without any processing. The classified pulverised-coal fly-ash (CFA) was a selected material suitable for use in structural concrete.

**Cement Kiln Dust (CKD)** -- The CKD was obtained from a cement production plant. This material is collected from the stack by electrostatic precipitation and contains cement minerals and a considerable quantity of finely divided calcite. It is of note that predictions of the disappearance of this material from the industry due to plant improvements have consistently failed to materialise and it continues to present a disposal problem to cement producers in the UK and probably in other parts of the world.

**Blast-furnace slags.** -- Blast-furnace slag was obtained from steel production and ground (GBFS). The Ground Granulated Blast-furnace Slag (GGBFS) was suitable for structural concrete.

**Ground Glass.** -- This material was from used fluorescent lighting and contained too much mercury for conventional recycling within normal environmental constraints.

**Limex 70** -- This is a trade name for a fine limestone by-product from sugar refining. It contains numerous organics.

**Gypsum Waste** -- The gypsum was “red gypsum” which is a waste from titanium oxide pigment production and is heavily contaminated with iron oxides. Some of this material was used as supplied and some was calcined to hemi-hydrate.

### **Mixture liquids.**

Many of the mixtures were made with water but for some of them sodium sulphate waste was used from the recycling of lead-acid batteries. After recovery of the lead and some of the plastics the remaining acid currently presents a disposal problem. The acid is neutralised with sodium hydroxide to give sodium sulphate which is then diluted before being discharged into the environment. For this project the material was taken from the tanks prior to dilution.

### **Aggregate materials**

**Foundry sands** -- These are pure quartz sands with a coating of a binder in order to permit their use in forming shapes for casting. They are repeatedly sieved and recycled but after several uses the adhesive properties are lost because the binder is degraded by the molten metal. Greensand is coated with glauconite or other clay minerals and Shell sand is coated with a synthetic binder such as phenolic resin.

#### **Ferrosilicate slag**

This slag is a ubiquitous product of pyrometallurgy and is available in very large quantities in a variety of sizes. The larger sizes are very hard to crush and present challenges for mixing with conventional plant.

**Chrome alumina** -- This is a by-product of chromium manufacture and contains 90%  $Al_2O_3$ . It consists of very hard fused lumps.

**Furnace bricks** -- These came from a rotary furnace and a kettle. They were produced during routine re-lining. They were crushed before use.

## **MIXTURE PROPORTIONS**

With a large number of different materials to work with, it is clearly not practical to attempt a study of all possible combinations. Mixtures were, therefore, proportioned using as many as possible of the different materials while aiming to meet the objectives. The mixtures from the laboratory program are shown in Table 1. The mixtures had up to three different cementitious components (identified in the columns headed as Cem1, Cem2 and Cem3) and three aggregates (identified in the columns headed Fine agg, Agg2 and Agg3). The percentage by weight of the whole mixture is given in the adjacent columns to each component. The mixtures selected for the field trials are in Table 2. These mixtures were chosen from the results of the laboratory trials and also on the basis of cost. Due to the high cost of disposal in landfill in the UK (including a landfill tax) the savings in disposal costs would exceed the production costs for most of these mixtures so they may be defined as “negative cost” concretes.

## **LABORATORY TESTING**

### **Test apparatus**

Cylindrical samples approximately 30 mm long with diameters of 55 mm or 100 mm were subjected to liquid pressures up to 14 MPa on one of their flat surfaces. The test was carried out in a modified Hoek cell (12) (see Fig. 2), as used in rock testing. In this cell the sample is contained in a membrane through which a confining oil pressure is applied on the curved surface. The confining pressure is kept above the applied liquid pressure. Measurements were made after one sample (barrier) volume of liquid had passed through the concrete. Assuming an average permeability of  $10^{-9}$  m/s and a maximum leachate head of 1m above the liner (as required in UK landfills) one barrier volume would flow through a barrier in 16 years of exposure in service.

### **Test liquids**

Tests were carried out with water and also with a simulated leachate (see Table 3). Different concrete/mortar samples were used for each test.

### **Permeability**

The coefficient of permeability was measured by collecting a small volume of liquid from the outflow and measuring the volume and the time of the outflow.

### **Through pH**



The pH of the liquid from the outflow was measured. The pH of the simulated leachate before testing was 5.

## FIELD TRIALS

Three field trials were constructed. These consisted of miniature waste cells in the shape of inverted pyramids which contained waste to a depth of one metre and had sides at 30 degrees of slope, giving a total width of 8 m. Each cell contained a total of 22 m<sup>3</sup> of concrete in the two layers. Fig. 3 shows Cell 1 during construction. It is of note that the concrete in this picture contained only spent borax as its cementitious component – a material with no calcium or silica. Initial trials were carried out to determine a suitable workability to place the sloped sides and from these a slump of 30 - 50 mm was selected. This proved to be satisfactory on site. After construction, the cells were filled with shredded waste and leachate and kept covered to prevent rain ingress.

## RESULTS AND DISCUSSION

The results from the high-pressure tests are shown in Table 1a, b and c. In these tables the 7 and 28 day strengths are shown in MPa. In the next two columns the permeability to water and leachate in m/s is given (headed Water perm and Leachate perm). In the final two columns the pH of the eluted liquid from the high pressure test is given both for experiments with water and simulated leachate.

The results are plotted and identified by their main cementitious component in Fig. 4. Fig. 4a shows the mixtures generally performing as would be expected with the clear exception of two GGBFS mixtures with a liquid/cementitious ratio of 1.5 but still a strength above 10MPa. This performance is explained by the replacement of the water with waste sodium sulphate solution which reacts with the GGBFS to increase the strength. Fig. 4b shows the relationship between the permeability to water and simulated leachate. This relationship was of concern during the design process and the deviation of two borax mixtures from the trend indicated problems with these particular mixtures. Fig. 4c shows the ability of the mixtures to buffer the leachate and it is essential that the barrier performs this function both for water and leachate. Many of the mixtures show excellent performance by buffering the leachate from 5 up to as high as 13. There were, however, some that perform far worse. Fig. 4d is the final graph from which the candidate mixtures were selected. The selected mixtures were intended to have a permeability below 10<sup>-9</sup> m/s and a strength below 10 MPa. It is important to note that higher strengths can degrade barrier performance because they may promote the formation of rigid “boulders” which promote flow around them and create volumes which do not contribute to the buffering. It may be seen that relatively few mixtures lie in the required range for both strength and permeability.

The field trial served to show that the concrete mixtures could be made and placed in large quantities. Some particular problems were identified, such as crystallisation of the sodium sulphate on a cold day and difficulties with mixing large ferrosilicate aggregate. It became clear, however, that mixing the recycled materials on a large scale was both possible and practical. All of the difficulties that were encountered could be solved more easily when moving up from field trial to industrial

scale. Leachate sampling lines have been placed in the trial cells and they will be analysed further when they are dismantled.

## **CONCLUSIONS**

1. The concept of durability must be defined relative to the intended purpose of a concrete mixture. For example, in a landfill liner long-term dimensional stability is not relevant to durability.
2. There is a wide range of industrial by-product materials available which are suitable for the production of concrete for particular applications, which do not require the same properties as structural concrete.
3. For landfill liners, it is possible to make concretes that perform well but have negative cost.

## **Acknowledgement**

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	Cell 1 lower layer	Cell 1 upper layer	Cell 2 lower layer	Cell 2 upper layer	Cell 3 lower layer	Cell 3 upper layer
<b>Spent borax</b>		450				
<b>GGBFS</b>	180					
<b>Portland cement</b>	20				25	
<b>Cement kiln dust</b>			290	500	335	370
<b>Run of station ash</b>			195			
<b>Lagoon ash</b>				330	120	245
<b>water</b>		210		250	240	170
<b>Sodium sulphate solution</b>	295		195			
<b>Ferrosilicate sand</b>		895				615
<b>Green sand</b>	645		100		110	
<b>20mm limestone</b>		1085				
<b>Chrome alumina slag (5mm)</b>			720		720	
<b>Chrome alumina slag (40mm)</b>	1515		1175		1175	
<b>Ferrosilicate slag</b>				1245		1230
<b>28-day strength, MPa</b>	13	4.5	6.9	1.7	6	1.3
<b>Permeability to water, m/s</b>	nil	1E-8	2E-9	4E-9	1E-8	1E-8
<b>Permeability to leachate, m/s</b>	2E-12	4E-8	4E-9	5E-9	6E-9	7E-9
<b>Through pH water</b>		10	10.1	11.8	8.5	12.2
<b>Through pH leachate</b>	8.5		9.9	12.3	7.6	12.1

Table 2. Properties and mixture proportions in kg/m<sup>3</sup> as designed for site trials

Concentrated sulphuric acid	2.043 g/l
Acetic acid	4.48 g/l
Potassium chloride	1.897 g/l
Calcium acetate	7.755 g/l
Ammonium chloride	1.186 g/l
Sodium chloride	0.91 g/l
Sodium hydroxide	2.59 g/l

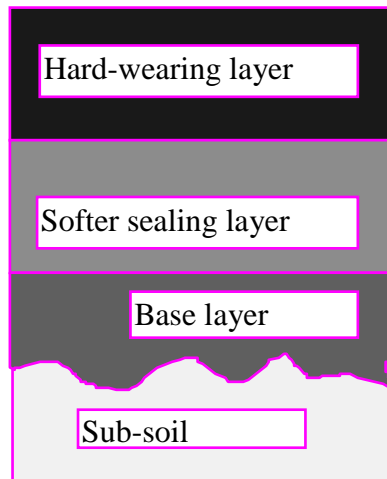
Table 3. Artificial leachate composition

**Composition**

Concrete or mortar 0.2m thick with good mechanical properties during the operating phase

Non-swelling clay 0.5m thick

Concrete or mortar 0.3m thick with high alkaline buffering and low leaching



**Main Physical Function**

Mechanical support of vehicles during operational phase

Physical containment of leachate and crack sealing.

Base for sealing layer

Fig 1 Schematic arrangement of the Barrier

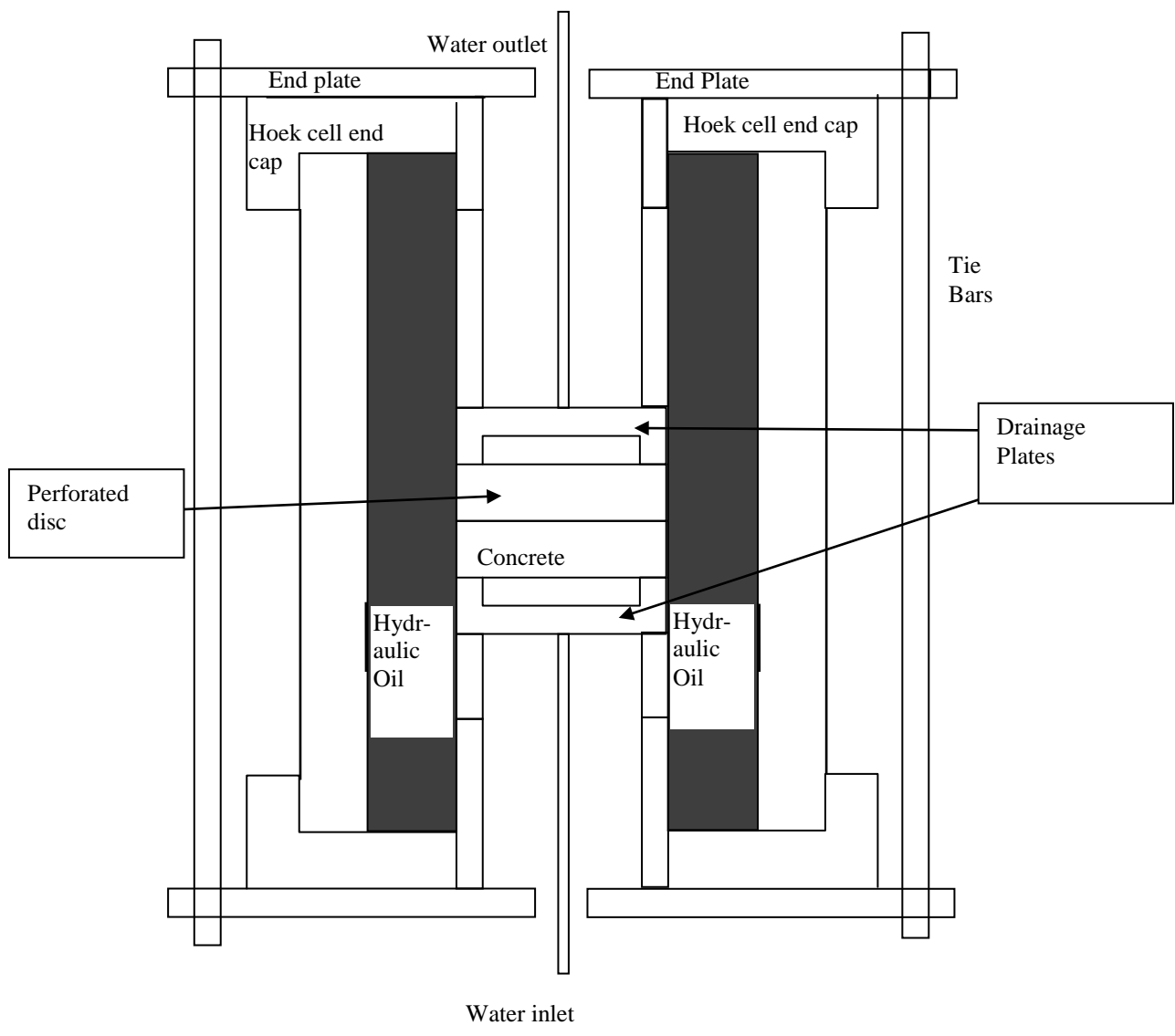


Fig. 2. High Pressure Through Flow Cell



Fig. 3. Placing concrete in the field trial



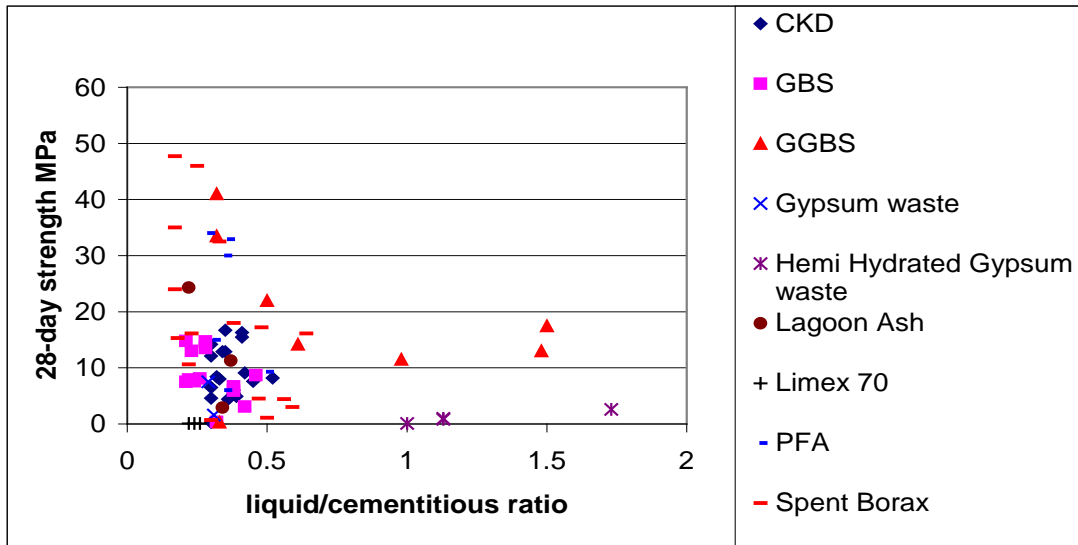


Fig. 4a Relationship between 28 day strength and liquid/cementitious ratio

Fig. 4. Results from the high pressure test (all graphs use the same legend)

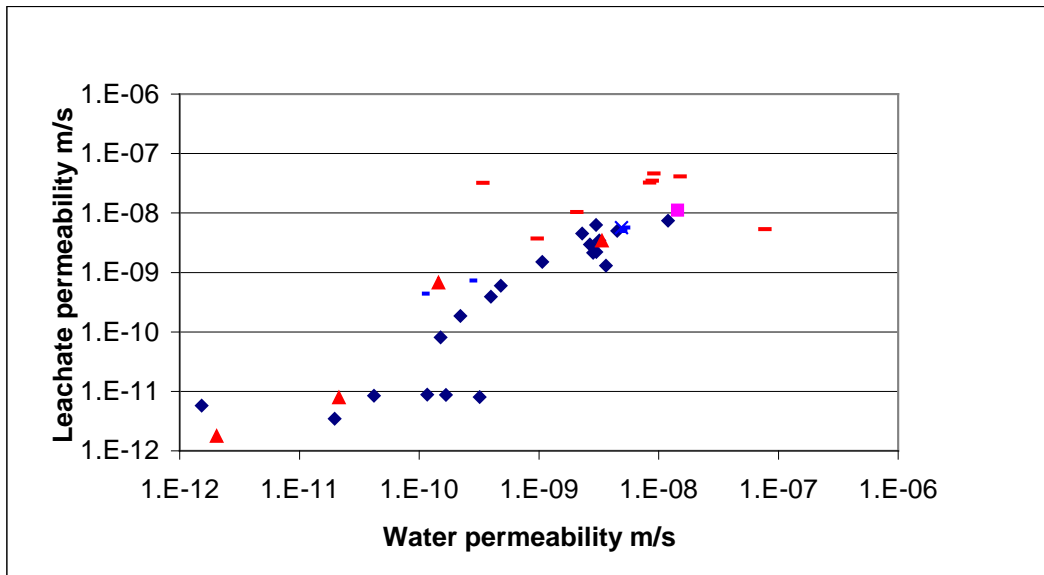


Fig. 4b Comparison of Permeabilities from the High Pressure test (for legend see fig. 4a)

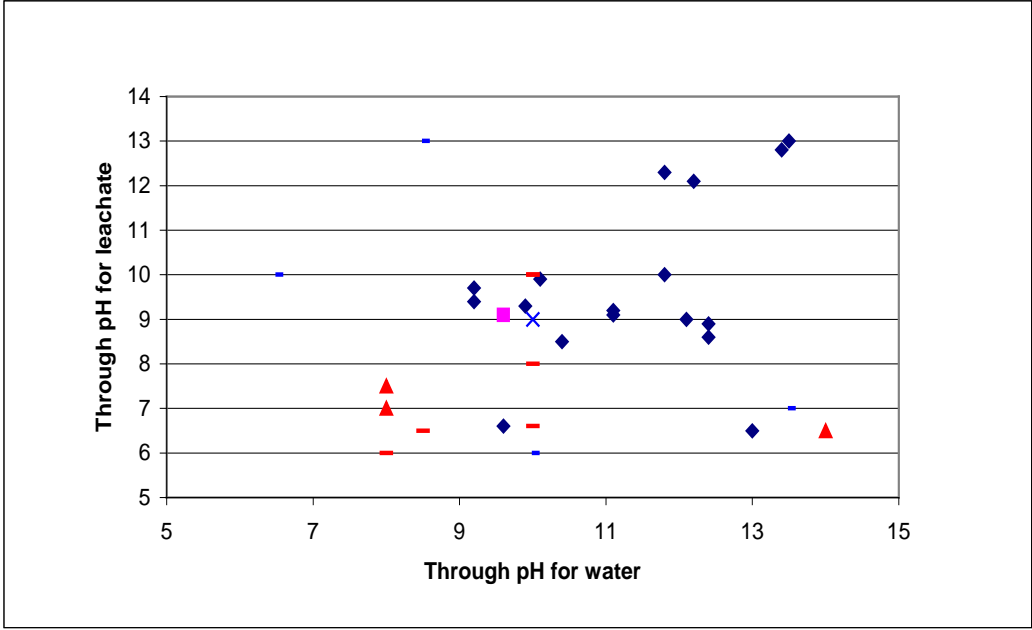


Fig. 4c Comparison of pH for outflow from High Pressure Test (for legend see fig. 4a)

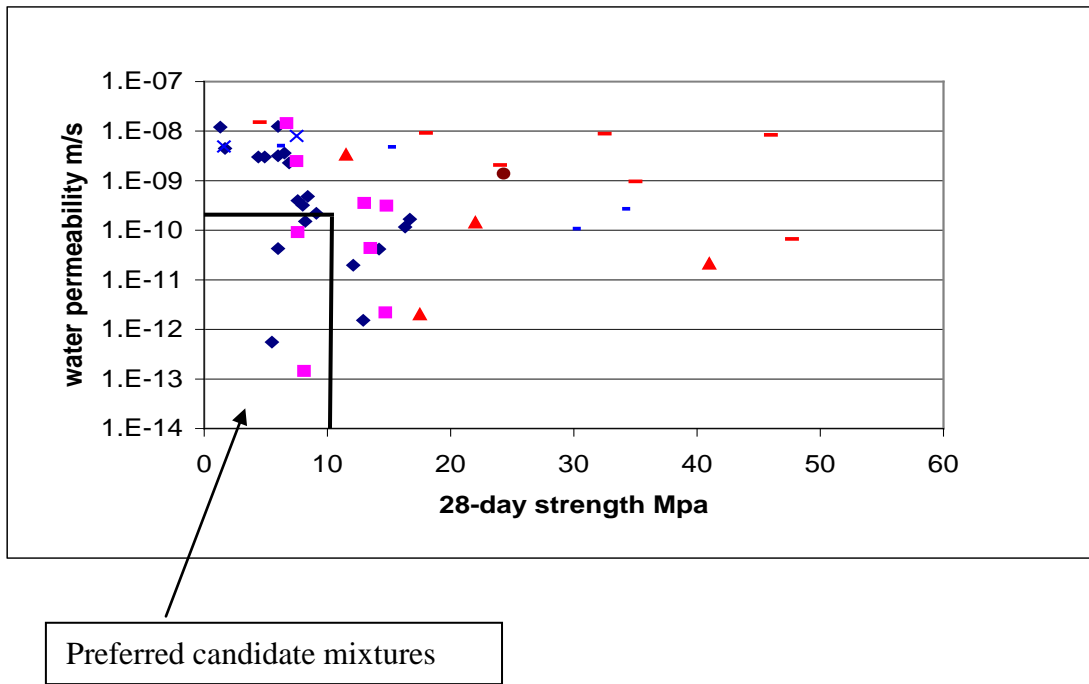


Fig. 4d Effect of strength on permeability (for legend see fig. 4a)