

Long term leachate evolution during flow-through leaching of a vault backfill (NRVB)

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ABSTRACT

Some of the illustrative concepts for the disposal of intermediate-level waste in a geological disposal facility in the UK employ a cementitious backfill around the waste packages. The concept for higher strength rocks would use a highly alkaline backfill composed of Portland cement (now known as CEM I), hydrated lime and limestone flour, referred to as Nirex reference vault backfill (NRVB).

This paper reports a study of the extensive leaching of cured NRVB in a range of generic leachant compositions (deionized water, 0.1 M and 1 M NaCl solutions) under flow-through conditions using a flexible wall permeameter. The experiments were designed to run for up to two years and to pass at least 1000 volumes of leachant (defined as the cumulative leachate volume produced/NRVB solid specimen volume) through the NRVB samples. Results for the pH evolution profiles of the leachates and the microstructural analysis of the unleached and leached samples are presented.

KEYWORDS: buffering capacity, leaching, NRVB, flow-through, geological disposal facility, repository, pH evolution, near field.

Introduction

SOME of the illustrative concepts for the disposal of intermediate-level waste (ILW) in a geological disposal facility (GDF) in the UK employ a cementitious backfill around the waste packages. The concept for higher strength rocks would utilize a highly alkaline backfill composed of Portland cement (CEM I), hydrated lime and limestone flour. This is known as the Nirex reference vault backfill (NRVB) and is designed to have physical and chemical properties that reduce radionuclide migration from the near field of a GDF. The NRVB is designed to be a highly porous, relatively low strength cementitious material that will promote homogeneous chemical conditions within a GDF, and allow gas migration

and retrievability of backfilled waste packages if required. (Nirex, 2001)

One of the functions of the NRVB is to maintain alkaline conditions in the near field environment over an extended period after the resaturation of the repository as the backfill is progressively leached. However, experimental data are not available to demonstrate the evolution of the leachate pH during extensive leaching of the NRVB. The principal components in the NRVB that will contribute to buffering the pH in the highly alkaline range (pH >10) will be the hydrated lime and the Portland cement hydration products.

This study on the long-term leaching of NRVB under flow through conditions has been performed to provide data on the evolution of pH during extensive leaching of the NRVB. In the current absence of a possible site for a GDF in the UK, three generic leachants (deionized water, 0.1 M and 1 M NaCl solutions) have been used. The

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experiments were designed to run for up to two years and to pass at least 1000 volumes of leachant (defined as the cumulative leachate volume produced/NRVB solid specimen volume) through the NRVB under flow through conditions, using a flexible wall permeameter.

Testing method selection

A wide range of leach testing methods have been developed to assess the leaching of contaminants and cementitious components from both waste-forms and cementitious materials (Conner, 1990). In order to achieve accelerated leaching, one method generally used is to reduce the sample particle size to increase the surface area available for leaching and to agitate the solution to decrease the time to achieve chemical equilibrium. A number of these batch type methods have been developed, with the simplest being a 'once-only' method, with more extensive multiple batch methods also being available that allow the same sample of solid cementitious materials to be exposed sequentially to multiple volumes of leachant. In this latter approach solid samples are agitated with a volume of leachant for a fixed period of time, then separated (usually by filtration) and then agitated with a new batch of leachant. This is repeated for the required number of leaching cycles and provides leaching profiles of the solid versus a cumulative volume of leachate. However, although the method is relatively fast and straightforward, it can overestimate the rate at which leaching occurs and the proportion of the cement that is available for leaching in an intact sample because of the size reduction and agitation steps used to accelerate the process. This overestimation occurs because under near-field conditions in which groundwater flows through cement based grouts, the leachable proportion of the cementitious components will be limited to surfaces which can be contacted by the leachant. As a result, within the porous matrix of a cementitious system, as leaching proceeds and preferential channels develop, volumes of high alkalinity may be bypassed and be unable to contribute to buffering of the leachate produced.

Therefore in this series of tests of the leaching and pH evolution of the NRVB, the selection of a flow-through method of leach testing was designed to simulate the conditions which may occur after resaturation of a GDF with groundwater flowing through connected porosity of the NRVB. During this process, dissolution (or

leaching) of alkaline components of the NRVB will occur causing an increase in the pH of the resulting leachate solutions. Leaching of the cementitious components will occur preferentially based on solubility, with the most soluble components (particularly those accessible through the NRVB porosity) being dissolved initially, with progressive leaching of the remaining components through either congruent dissolution of components such as calcium hydroxide or the incongruent dissolution of cement components such as calcium-silicate-hydrate (C-S-H).

Although any form of leach testing will introduce some artificiality into the rate of leaching in order to produce data over an experimental timeframe, this flow-through method was judged as being a reasonable compromise to produce data on the pH evolution of leachate from NRVB under flow-through conditions over relatively short testing periods of a couple of years.

Samples and experimental procedure

Cementitious powders

The following cementitious powders were used in the preparation of the NRVB samples for testing: (1) ordinary Portland cement supplied by Hanson Cement in accordance with Sellafeld Ltd. specification, fineness 364 m²/kg. test certificate number 62 (Hanson Lab reference number 11868); (2) limestone flour supplied by Tendley Quarries; and (3) lime supplied by Limbux Ltd, Buxton, in accordance with Sellafeld Ltd specification.

Nirex reference vault backfill formulation

The composition of the NRVB formulation is listed in Table 1.

TABLE 1. Nirex reference vault backfill composition.

Component	Mass (g)
Lime	300
Limestone flour	990
Portland cement	900
Water	1230

Water:solids ratio 0.55:1.

Preparation and curing of NRVB samples

All samples were produced at a laboratory scale using a Hobart low shear mixer initially followed by a Silverson high shear mix as per the National Nuclear Laboratory (NNL) standard acceptance mix methodology for the production of cementitious samples. The NRVB samples were cast into 70 mm diameter, 20 mm height cylindrical sample moulds and then cured in sealed conditions for 32 days. The samples were cured under controlled conditions ($20\pm 2^\circ\text{C}$ and greater than 95% relative humidity) for a further 34 days prior to the start of the flow through leaching trials. Six samples of NRVB were tested in total, with replicate pairs tested for each of the three leachants.

*Leachant samples components and preparation**Materials*

Deionized water from the NNL Workington Laboratory was used as the deionized water leachant and to produce the 0.1 and 1.0 M NaCl leachants. Sodium chloride (Technical grade) was supplied by Fisher Scientific Ltd, Loughborough, Leicestershire. All leachant samples were de-aerated by boiling, and stored under an argon atmosphere prior to use.

Leach testing apparatus

All flow-through leaching trials were performed using standard design flexible wall water permeameters, all of which were fabricated from stainless steel, in order to minimize the corrosion of the components during the extended duration of the test. The design of the equipment consists of a central sample plinth (diameter 70 mm, height 20 mm). The NRVB samples to be tested were placed between two porous stones which had coarse hardened (Whatman 540 grade) filter papers placed between the sample and the porous stone. One of the experimental systems is shown in Fig. 1.

Samples under test are isolated from the confining fluid in the permeameter by a latex membrane to which water pressure, greater than that applied to produce flow of the leachant, is applied. Leachant is passed through the samples from an external reservoir, under upward flow conditions and then collected as leachate in a pre-weighed 3 l vessel which was fitted with a 30 ml sub vessel. Leachant initially flowed into the 30 ml sub vessel which then overflowed into the 3 l vessel. The rate of flow was controlled by adjusting the air pressure applied to the air side of the external leachant reservoir. The pressure applied initially was 2 bar g with the lowest pressure achievable being 0.01 bar g.

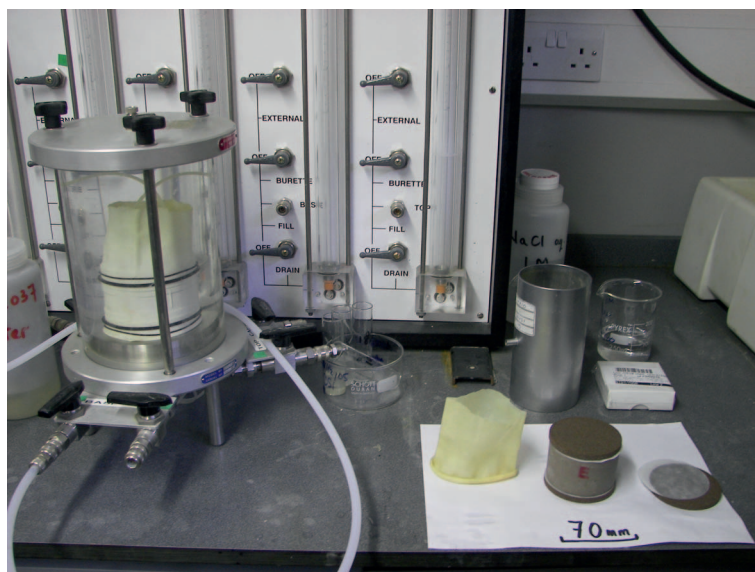


FIG. 1. Flexible wall permeameter main vessel and control panel showing fully assembled equipment (left) and sample, porous stones and latex membrane (right).

The 3 l scale vessel was sealed, with a perforated bag of Carbosorb attached to the inner lid to absorb the carbon dioxide present in the ullage space within the vessel. The 30 ml subsamples were collected and stored prior to measurement of pH. Determination of leachate was performed using an Orion Model 250 pH meter connected to a Fisher Brand FB68800 electrode. The pH meter and electrode were calibrated using pH 7.00 and 10.00 certified buffer solutions prior to use.

All experimental trials were performed in a temperature-controlled cell at 35°C to simulate the possible long term temperature in a GDF (Nirex, 2005).

Results and discussion

Profiles of the leachate pH vs. cumulative volume of leachate passed through the replicate solid samples for the deionized water leachant, 0.1 M NaCl and 1 M NaCl leachants, respectively, are shown in Fig. 2 to Fig. 4 respectively. The volume of leachate collected is expressed in specimen volumes (the cumulative volume of leachate collected divided by the volume of the solid NRVB samples).

Leaching with deionized water: samples 1 and 4 Initial leaching

The first pass of deionized water (equivalent to 0.25 and 0.35 specimen volumes, respectively) produced leachates that although highly alkaline, were not the highest pH samples recorded, with values of 12.8 and 12.9. The next leachate samples in the cumulative sequence, with pH values of 13.1 were the most alkaline leachates generated. It is expected that these leachate samples will contain a combination of sodium and potassium hydroxides, with some calcium hydroxide from the dissolution of portlandite. The lower pH of the first leachate samples produced is attributed to dilution of the highly alkaline pore solution by interstitial water present in the porous stones at the start of the experiments that were wetted with deionized water prior to use to remove any air. The porous stones (designed to allow the flow of leachant through the samples to be spread across their entire surface area) are approximately 5 mm in thickness and therefore in combination represent 50% of the volume of an NRVB sample.

After the initial peak pH, leachate samples showed a general steady pH of 12.5 to 12.7 up to

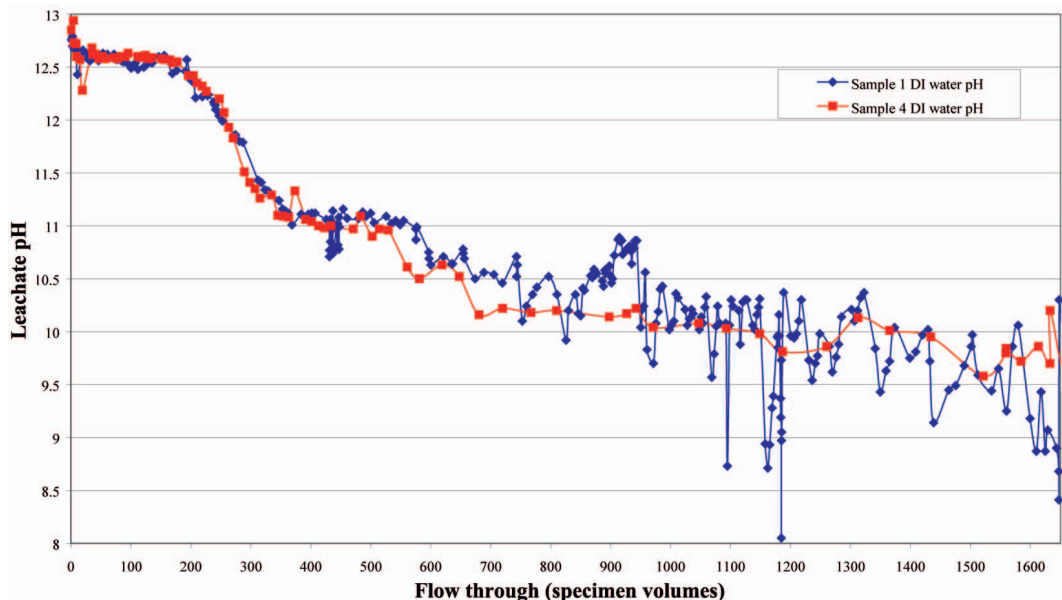


FIG. 2. Leachate pH vs. cumulative leachate volume for samples 1 and 4 leached with deionized water.

LEACHING OF CURED NRVB

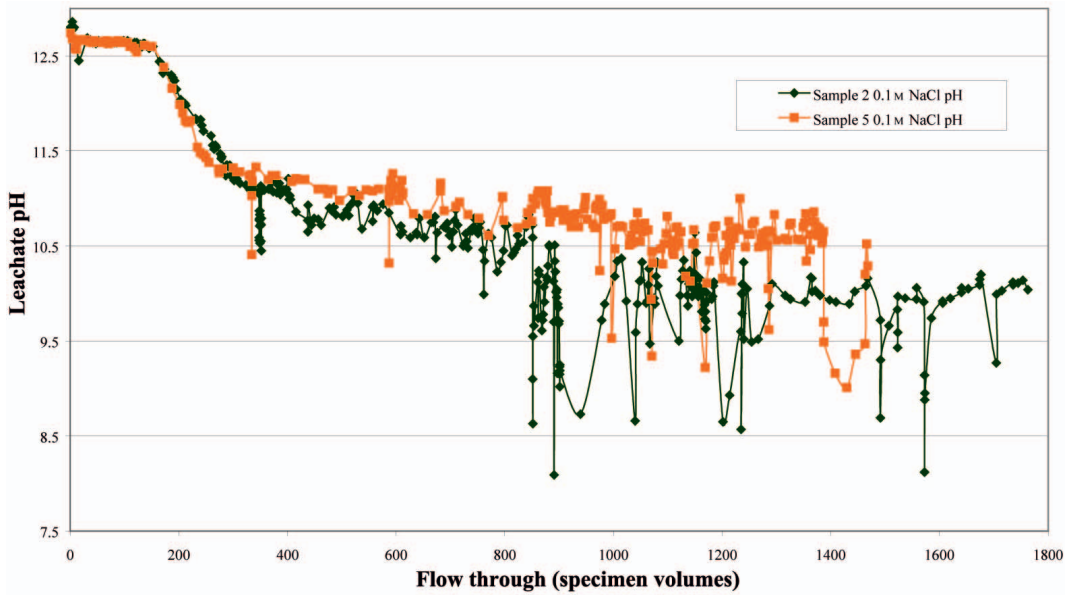


FIG. 3. Leachate pH vs. cumulative leachate volume for samples 2 and 5 leached with 0.1 m NaCl solution.

approximately 175 to 195 cumulative specimen volumes. This is expected to be due to the leaching of portlandite, releasing hydroxide during congruent dissolution, although the

values are slightly higher than the expected value of about 12.5 from dissolution of calcium hydroxide at 25°C. As calcium hydroxide solubility decreases with increasing solution

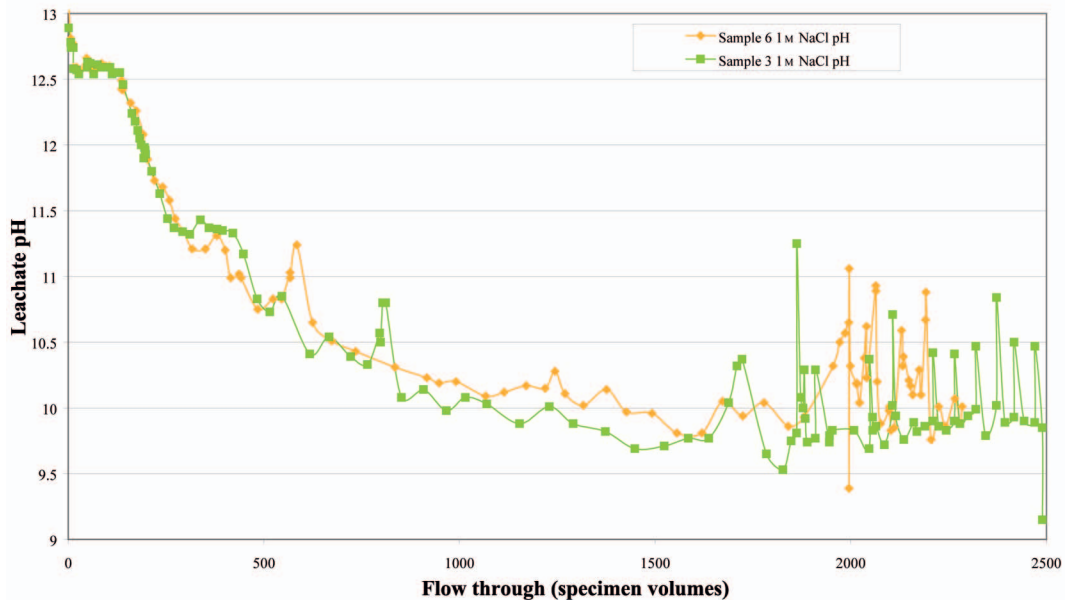


FIG. 4. Leachate pH vs. cumulative leachate volume for samples 3 and 6 leached with 1 m NaCl solution.

temperature, with an expected pH of 12.13 at the 35°C temperature at which this series of trials was performed (National Lime Association, 2007), it is most likely that this may represent a slight systematic uncertainty in the pH determinations although alternative hypotheses, such as a slow contribution from less accessible sodium and potassium oxides not removed in the initial leachate volumes, are possible.

pH 12.5 to ~ 10 region

In the range of approximately 200 to 350 specimen leachate volumes the pH data showed the behaviour expected from previous work on leaching of calcium from C-S-H gel, with hydroxide at lower concentrations than those for saturated calcium hydroxide solutions (Zamorani *et al.*, 1986; Atkinson *et al.*, 1987; Berner, 1992; Krupka and Serne, 1998) and the pH falling from about 12.6 to 11.1.

Comparison of data from samples 1 and 4 shows the same trend during this period, with good agreement between the leachate pH values observed. It was noted that even at this early stage of leaching the flow rates through these replicate samples was significantly different with sample 4 giving approximately twice the leachate flow rate at the same applied pressure compared to sample 1. This indicates that the leachate pH is relatively insensitive to flow rate during this period of the test although reducing the leachant pressure for sample 1 from 2 to 0.5 bar g between 430 to 445 cumulative volumes, reduced the flow rate from ~20 to ~7 ml h⁻¹. However, the samples collected during this period showed greater pH scatter. The lower pH values seem to be associated with relatively small volumes (20–35 ml) of collected leachate. It is possible that these lower pH values are due to the absorption of carbon dioxide from the air within the larger collection vessel, despite the presence of Carbosorb, leading to a reduction in pH. Such an effect would be more noticeable as the volume of leachate decreased relative to the capacity of the collection vessel.

The pH then showed a shallower rate of reduction over the next period of leaching (350 to 1000 cumulative specimen volumes), falling from pH ~11.0 to 11.3 after the passage of 350 cumulative volumes, to pH ~10 at 1000 cumulative specimen volumes. The pH values observed were less than 10 in the period beyond ~1200 cumulative volumes for sample 1 and were generally in the region 9.5–10 up to 1600 cumulative volumes for sample 4. Increased scatter was observed in the

data, especially for sample 1, at these extended cumulative leachate volumes.

In total samples 1 and 4 were run for approximately 1650 and 3200 cumulative volumes, respectively. The differences in the cumulative volumes achieved reflect the differences in evolved permeabilities and hence increasing difficulty in controlling leachate flow rates through the extensively leached solids during the later stages of the experiments.

Leaching with 0.1 M and 1 M NaCl solutions

Data from leaching with 0.1M and 1M NaCl solutions are shown in Figs 3 and 4, respectively.

0.1 M NaCl leachant

Unlike the first samples collected for deionized water leachate, the initial samples for the 0.1 M NaCl solution showed the highest pH (12.8) of all of the samples collected for this leachant. The leachate pH then held a fairly consistent value of ~12.6 to 12.7 until approximately 165 cumulative specimen volumes had passed through the NRVB. At this point the pH began to steadily fall to about 11.2 after about 300 specimen volumes and then decreased more slowly until ~800 cumulative volumes, at which point the flow rate through sample 2 increased appreciably. The data for this sample became widely scattered due to the increased flow rate and the difficulty in controlling this despite progressively reducing the applied pressure as low as 0.01 bar g. However, as shown in Fig. 3 the leachate pH recorded for sample 5 was more stable, with most of the data in the region of 10.7–10.5 for the leaching period between 1000 and 1400 cumulative sample volumes, when the trial was terminated.

1 M NaCl Solution

The first leachate samples collected for the 1 M NaCl leachant showed the highest pH of all of the samples collected in the trial set, with values of 12.9 to 13.1. After this, the leachate pH fell to a fairly consistent value of ~12.6 to 12.7 and remained there until approximately 130 cumulative specimen volumes had passed through the NRVB as shown in Fig. 4. The pH then decreased, falling to about pH 10 at 1000 cumulative specimen volumes, and continued to decrease slowly thereafter. Good agreement is observed between the leachate pH values up until this point, although greater variability was observed beyond 1500 sample volumes.

The pH variability is attributed to the greater observed variability in flow as the samples underwent progressive leaching. In the region until ~500 cumulative sample volumes flow rates were low (both samples were being operated at a leachant pressure of 2 bar g). However, as the cumulative specimen volume leached increased beyond this point a large increase in the flow rate at the 2 bar g leachant driving pressure was observed. To reduce the flow rate, the leachant pressure was reduced to 0.5 bar g at 800 and 970 cumulative specimen volumes for samples 3 and 6, respectively, and then further reduced progressively to 0.05 and 0.01 bar g. However, despite the relatively high and extremely variable flow rates obtained, it can be observed from Fig. 4 that the leachate pH was relatively insensitive to the flow conditions for much of the leaching regime. Cumulative leachate specimen volumes of 2200 and 2500 were achieved for samples 6 and 3, respectively.

Comparison of leaching behaviour

To illustrate the effect of differing leachants on the early leachate cumulative pH evolution, the data for all the samples up to 500 specimen volumes are plotted in Fig. 5. This shows a clear trend of a reducing volume of leachant required to

give leachate pH values below pH 12.5 from deionized water to 0.1 M NaCl solution to 1 M NaCl solution. This decrease in cumulative volume compared to the deionized water experiments may be indicative of the faster leaching of the cement hydration products by chloride-containing solutions as reported by Hill *et al.* (2006) and the greater solubility of calcium chloride compared to calcium hydroxide. Clearly, the increased chloride concentration increased the rate of leaching of the calcium.

Reduction in NRVB sample permeability (as calculated from flow rates and pressures applied to the leachant) due to collapse of the structure resulting from the loss of the strength providing (C-S-H and portlandite) cement phases from the NRVB due to long term leaching was not observed.

Scanning electron microscopy and energy-dispersive X-ray analysis

Microstructural analysis of unleached NRVB samples and subsamples of the samples leached with deionized water, 0.1 M NaCl and 1 M NaCl were undertaken, following the leach tests. All scanning electron microscopy (SEM) analysis was performed in backscattered-electron imaging

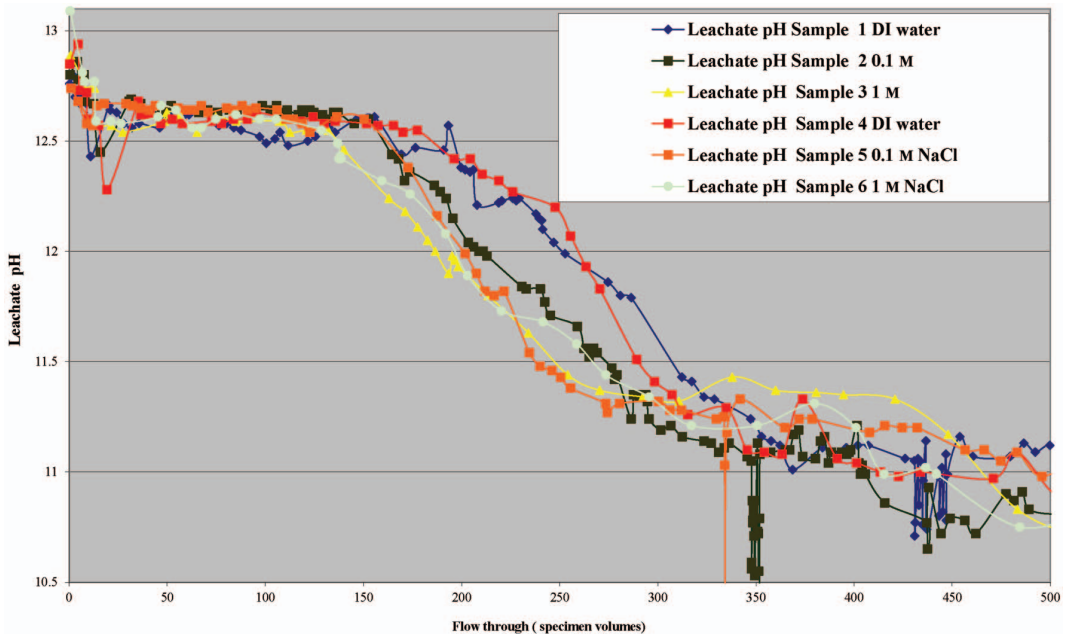


FIG. 5. Comparison of leachate pH evolution for initial 500 specimen flow through volumes.

(BEI) mode using a BSED (backscattered electron detector) or a GAD (gaseous analytical detector) detector. As the microscope was able to operate without the need for high vacuum within the analysis chamber, the samples did not require coating; charging was reduced by using adhesive aluminium tape. Analysis was performed using a FEI Quanta 200 Mark 2 Field Emission Gun environmental scanning electron microscope, fitted with an Oxford Instruments Inca 250 energy dispersive X-ray spectrometer. This equipment is capable of imaging and analysing moist and non-conducting samples without coating or other pre-treatment.

Attention was focussed mostly on possible differences between the microstructure and composition at the leachant inflow face, the centre of the samples and the leachant outflow face. A sample of the unleached hardened NRVB paste, previously cured in the same manner as the leached samples, was analysed in the same manner to provide comparative data.

Comparison of 1.0 M NaCl leached samples with unleached samples

The major elements detected in all areas studied of both leached and unleached samples were calcium, silicon, aluminium, carbon and oxygen. Sodium and chlorine from the leachant were detected in the leached samples, and minor amounts of magnesium, iron, sulfur and potassium were detected in all samples. Apart from the absence of portlandite in the leached sample, there was no difference in elemental composition between the leached and unleached samples, or in the leached samples between material at the leachant inflow face, at the centre of the sample and at the leachant outflow face. The EDX and XRD data for the leached samples suggests that the main phases detected at all positions analysed were calcium carbonate and calcium/silicon-rich areas, probably C-S-H, possibly substituted with aluminium.

The microstructure of both leached samples appeared to be homogenous and little or no difference in porosity was apparent at any of the areas investigated. Differences in the porosity of the leached and unleached samples were difficult to determine because of the difficulties associated with low sample strength and resin impregnation.

Portlandite, C-S-H and calcite were identified in the unleached samples as expected. However unlike previous studies (Harris and Nickerson, 2002), ettringite and hydrotalcite were not found.

Comparison of 0.1 M NaCl and deionized water leached samples with unleached samples

The major elements detected in all the areas analysed of both the leached and unleached samples were calcium, silicon, aluminium, carbon and oxygen. Minor elements detected include magnesium, iron, sulfur, potassium, sodium and chlorine, with the concentration of the latter two elements being slightly higher in the samples leached with 0.1 M NaCl than in those leached with deionized water. The EDX and XRD data suggests that the main phases detected at all positions analysed in the leached samples were calcite and phases containing calcium and silicon (probably C-S-H which may have possibly been substituted with aluminium), whereas the unleached sample also contained portlandite. No other crystalline phases were detected. As in the 1 M NaCl samples, the leaching process appears to have removed all portlandite from these samples.

The microstructures of all the leached samples appeared to be homogenous and little or no difference in porosity was observed, although this was difficult to confirm because of the difficulties associated with low sample strength and resin impregnation.

These results, with those for the 1 M NaCl leached samples, suggest that a homogeneous leaching front has moved vertically through the NRVB samples, resulting in consistent leaching of the cementitious phases, without leaving relics of unleached material, in all cases. No difference was observed between the samples leached with 0.1 and 1 M NaCl solution, respectively.

Conclusions

Extensive leaching of NRVB under flow-through leaching conditions has been performed using three generic leachants: deionized water; 0.1 M NaCl solution; and 1 M NaCl solution. The results show that there is sufficient alkaline buffering capacity present to maintain the leachate above pH 10 for 1000 cumulative specimen volumes (i.e. up to 1000 multiples of the solid NRVB volume of leachate volume passed through the NRVB sample) for all three leachants. The pH leachate profiles are as expected from observations by previous researchers with the leaching of cements occurring in the following order: (1) leaching of soluble alkalis (sodium and potassium oxides) initially to give pH values greater than 12.7; (2) portlandite (calcium

hydroxide) leaching to provide a leachate pH buffer at pH 12.4–12.7; and (3) incongruent leaching of C-S-H giving decreasing pH from 12.4 to ~10.

The trend of the reduction in pH from the pH 12.5–12.6 plateau in the order of 1 M NaCl > 0.1 M NaCl > deionized water can be observed. This is in agreement with work performed by other researchers who have produced data which indicates that chloride will increase the rate of leaching of the calcium within cementitious materials.

As noted by previous researchers (Hooton, 1998), who have assessed the permeability of cementitious materials, large variations between the permeabilities of duplicate samples produced at the same time and cured under identical conditions is observed (in this case as the experiments progressed). However, reduction in NRVB sample permeability due to collapse of the structure resulting from the loss of the strength providing (C-S-H and portlandite) cement phases from the NRVB due to long term leaching was not observed. The permeability of the NRVB increased more rapidly in the samples leached with 1 M NaCl solution.

Analysis of the unleached NRVB identified portlandite, C-S-H and calcite as being present in the samples. All leached samples were observed to have the same elemental composition as the unleached samples, with some phases which were probably C-S-H remaining. Portlandite was absent from the leached samples as expected, with the only remaining crystalline phase identified being calcite. The microstructure of all leached samples appeared to be homogenous and little or no difference in porosity was apparent at any of the areas investigated although differences in the porosity of the leached and unleached samples were difficult to determine. No significant differences were observed in the microstructure between any of the leached samples, regardless of the leachants that had been used.

Acknowledgements

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