

## Development of an accurate pH measurement methodology for the pore fluids of low pH cementitious materials

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# Preface

This report is a summary of the “Development of an accurate pH measurement methodology for the pore fluids of low pH cementitious materials” project, which was conducted from June 2008 until May 2011. The project was initiated through the network of people that participated in the three “low pH cement for a geological repository” workshops (October 2003, June 2005 and June 2007) and the participants of the Engineering Studies and Demonstrations of Repository Designs (ESDRED) project (February 2004–January 2009).

The work for this report has been performed as a joint international project with the following waste management organisations:

- 1) Empresa Nacional de Residuos Radiactivos (ENRESA), Madrid, Spain.
- 2) Japan Atomic Energy Agency (JAEA), Ibaraki, Japan.
- 3) Nationale Genossenschaft für die Lagerung radioaktiver Abfälle (NAGRA), Wettingen, Switzerland.
- 4) Nuclear Waste Management Organization of Japan (NUMO), Tokyo, Japan.
- 5) Posiva Oy, Eurajoki, Finland.
- 6) Svensk Kärnbränslehantering AB, (SKB), Stockholm, Sweden.

The Nuclear Decommissioning Authority (NDA), UK, also participated during the initial phase of the project, but chose to opt out. A consortium agreement was signed between the above listed participating organisations before the start of the experimental test phase, with SKB adopting the role of project coordinator.

During the initial stage of the project, CSIC (Consejo Superior de Investigaciones Científicas) conducted a literature review and planned, tested and designed the experimental phase of the project. CSIC has also developed the protocols for the reference (Pore Fluid Expression, PFE) method and the routine (*Ex Situ* Leaching, ESL) methods and have collated, evaluated and reported the results from the other national laboratories.

The national laboratories participating in the experimental phase of the project were:

- 1) EMPA, Laboratory for Concrete and Construction Chemistry, Duebendorf, Switzerland.
- 2) RAWRA/NRI, Waste Disposal Department, Nuclear Research Institute, Czech Republic.
- 3) TFB, Technische Forschung und Beratung für Zement und Beton, Wildegg, Switzerland.
- 4) CSIC, The Spanish National Research Council, Madrid, Spain.
- 5) VTT Technical Research Centre of Finland, Espoo, Finland.
- 6) CEA, Commissariat à l’Energie Atomique, Laboratoire d’Etude de l’Enrobage des Déchets, Bagnols-sur-Cèze cedex, France.
- 7) Taiheiyo Cement, Chiba, Japan.
- 8) CRIEPI, Central Research Institute of Electric Power Industry, Japan.
- 9) AECL, Whiteshell Laboratories, Pinawa, Canada.

The different national laboratories are hereafter referred to by their number as shown in the above list, e.g. Lab 1, Lab 2, Lab 3, etc.

## Summary

The main objective of this project has been the development of an agreed set of protocols for the pH measurement of the pore fluid of a low pH cementitious material. Three protocols have been developed (Chapter 2), a reference method, based on pore fluid expression (PFE), and two routine methods with and without filtering, based on *Ex Situ* Leaching (ESL) procedures. Templates have been designed on which to record details of the pH measurement for the reference (PFE) method (Appendix C) and the routine (ESL) methods without and with filtering (Appendix D).

Preliminary protocols were based on a broad review of the literature (Appendix A) and refined through a series of test experiments of the more critical parameters (Appendix B).

After definition of the preliminary protocols, two phases of interlaboratory tests were performed. The first phase (Chapter 3) used the same low pH cement paste and enabled the nine participating laboratories to use, become familiar with and to identify any problems/uncertainties in the preliminary protocols. The reported pH values were subjected to a statistical analysis of the (within-laboratory) repeatability and (between-laboratory) reproducibility and so provided a reliability test of the preliminary protocols. The second phase (Chapter 4) of interlaboratory tests used four different candidate low pH cementitious materials in the same nine laboratories, which allowed testing, validation and comparison of the reported pH values, which were obtained using the final protocols for the reference (PFE) and routine (ESL) methods by statistical analysis.

The proposed final protocols (Chapter 2) have resulted in the reported pH values having low deviation and high reproducibility and repeatability. This will allow confidence in the pH value when selecting a candidate low pH cementitious material to be used in the engineered component of a high-level nuclear waste repository.

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# 1 Introduction

## 1.1 Background

Cementitious materials are likely to be used for the construction of an underground repository for the geological disposal of high level radioactive waste. The long-term integrity of the repository is managed by selecting engineered component materials that not only meet their specified functional requirements, but that are also chemically compatible with each other and with the host rock of the chosen site. Conventional Ordinary Portland Cement (OPC) cementitious materials are not suitable because of the potential to release a high pH (= 12.5–13.8) plume into groundwater. Such a high pH is detrimental to the performance of the intended bentonite buffer, used to envelop the waste canisters, and will affect the hydrological characteristics of the host rock through poorly characterised dissolution/precipitation reactions. Instead, low pH cementitious materials are being developed by replacing a portion of the OPC with other siliceous pozzolans. It is intended that these newly developed materials will have a maximum pore fluid pH = 11 to mitigate these detrimental effects.

A fundamental aspect of the development of low pH cementitious materials is the accurate and reliable measurement of the pore fluid pH in order to qualify and help quantify mix designs to achieve a target  $\text{pH} \leq 11$ . Proper qualification criteria are required in order to select candidate low pH cementitious materials that can be used in an underground repository for high level waste.

The lack of an internationally accepted method for the pH measurement of the pore fluid of cementitious materials has been a problem for some time. The need for a pH measurement project was discussed at the first international low pH workshop in Stockholm (15<sup>th</sup>–16<sup>th</sup> October 2003). Discussions of pH measurement continued at the following low pH workshops in Madrid (15<sup>th</sup>–16<sup>th</sup> June 2005) and in Paris (13<sup>th</sup>–14<sup>th</sup> June 2007); arranged within the 6<sup>th</sup> Euratom Framework Programme for Nuclear Research and Training of the European Union 6<sup>th</sup> Framework Programme as a part of the ‘Engineering Studies and Demonstrations of Repository Designs’ (ESDRED) project (1<sup>st</sup> February 2004–31<sup>st</sup> January 2009). Different alternatives to start a project for standardisation of pH measurements were discussed during these workshops, but no definitive decision was taken.

As a consequence of these discussions it was decided to start a project with the objective of the development of an agreed set of protocols for the accurate pH measurement for the pore fluid of low pH cementitious materials.

## 1.2 Aims of the project

The main aim of this project has been that the developed protocols will be implemented in the research programs of the participating organisations by helping to make an informed decision over which low pH cementitious material to use in the underground repository for the geological disposal of high level radioactive waste. Eventually, the developed protocols could be recognized as basic recommendations to develop international standards for pH measurements of cementitious materials.

## 1.3 Report overview

A literature review of pH measurement methods of cementitious (and other) materials was conducted and is attached to this report as Appendix A. From this literature review, two methods were selected for further development:

- A reference method based on Pore Fluid Expression (PFE).
- A routine method based on *Ex Situ* Leaching (ESL), with two variant cases, without and with filtering.

These two methods were tested and revised through a series of experiments at the CSIC laboratories, described in Appendix B, which were used to draft the preliminary pH measurement protocols (Chapter 3).

Testing of the preliminary pH measurement protocols was undertaken by nine different national laboratories working on the same hardened low pH cement paste (Chapter 3). From a statistical evaluation of the reported pH values, it was concluded that following some minor revisions, the two methods were suitable for use as protocols for the measurement of the pore fluid pH of a low pH cementitious material.

To test the revised and final protocols, the same nine laboratories worked on four different candidate low pH cementitious materials (Chapter 4). From a statistical evaluation of the reported pH values, it was concluded that the two methods were suitable for use as final protocols for the measurement of the pore fluid pH of a low pH cementitious material.

The final protocols for each method are described in Chapter 2 of this report. Recommended templates, as used by the different laboratories to record and report the pH measurements are attached as Appendix C and D to this report.

The results of the project have also been presented at two international congresses:

- 1) **Alonso M C, García Calvo J L, Petterson S, Cuñado Peralta M A, Vuorio M, Weber H, Ueda H, Naito M, Walker C, 2011a.** Development of an accurate methodology for measure the pore fluid pH of low pH cementitious, materials. XIII International Congress on the Chemistry of Cement, Madrid, Spain, 3–8 July 2011.
- 2) **Alonso M C, García Calvo J L, Petterson S, Puigdomenech I, Cuñado Peralta M A, Vuorio M, Weber H, Ueda H, Naito M, Walker C, Takeshi Y, Cau Dit Coumes C, 2011b.** Round robin test analysis for accurate protocol definition of low pH cementitious materials. In Proceedings of the 1st International Symposium on Cement-based Materials for Nuclear Wastes (NUWCEM 2011), Avignon, France, 11–14 October 2011.



## 2 Final protocols for pH measurement of the pore fluid of low pH cementitious materials

### 2.1 Protocol for the reference (PFE) method

#### 2.1.1 Scope of the method

The method is widely known as ‘pore pressing’ or, as adopted in the current report, ‘pore fluid expression’ (PFE). The objective of this test is to extract the pore fluid of the hardened low pH cement material under pressure and to measure its pH either by a pH meter with a combination pH electrode and/or OH<sup>-</sup> titration.

#### 2.1.2 Apparatus and auxiliary equipments

- Press and extraction apparatus. The press must be similar to that described by Longuet et al. (1973), Barneyback and Diamond (1981) or Yonezawa et al. (1988).
- pH meter with temperature compensation and a combination pH electrode specifically designed to measure in the pH range of 7–14.
- Analytical balance capable of weighing to an accuracy of 0.1 g.
- Coverable/sealable glass and sealable plastic beaker/flask.
- Argon or N<sub>2</sub> gas.
- Hammer and chisel.
- Filtration apparatus using a filter pore size = 0.45 μm. Filters made of Nylon, PolyVinylidene DiFluoride (PVDF) or Hydrophile PolyTetraFluoroEthylene (PTFE) should be used.

#### 2.1.3 Reagents

Buffer solutions for calibration of the pH electrode: a minimum of three standard buffer solutions must be used to bracket the expected pH range = 10.5–12.5 for low pH cementitious materials. Ideally, the standard buffer solutions should be at least 3 pH units apart so that the lowest buffer solution should be pH = 7, an intermediate pH = 10 ±0.8 and the highest pH = 13 or 14. Temperature correction must also be included in the calibration and all buffer solutions, as well as the pore fluid samples must be at the same temperature prior to use.

#### 2.1.4 Sample preparation

If the low pH cementitious material must be transported to the laboratory where pressing and pH measurements will be made, they must be sealed in plastic bags to prevent drying and CO<sub>2</sub> contamination. Covering the low pH cementitious material with a damp clean cloth/wipe before placing them in the sealed plastic bags is also recommended to prevent sample drying.

The low pH cementitious material must be cured in a chamber with 100% RH at 21 ±2°C for 90 days until the pH measurements are made.

The external surface (5–10 mm depth) of the low pH cementitious material must be removed by a hammer and chisel or other appropriate tools. This is to exclude any material that may have been exposed to the atmosphere during handling and curing. The low pH cementitious material must be crushed manually to a maximum particle size of 5 mm using a hammer and a chisel (Figure 2-1). Note that mechanical grinders might overheat the samples and result in particles being too small. Sieving should not be used to obtain this particle size. All of the resulting crushed low pH cementitious material then forms the sample in the reference (PFE) method.

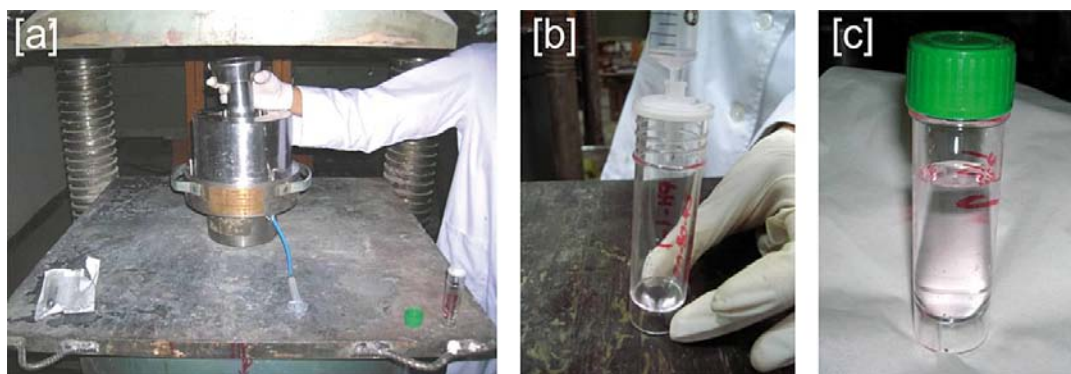


**Figure 2-1.** Particle size required in the reference (PFE) method. The black-and-white scale is five mm.

### 2.1.5 Procedure

Approximately 125 g of the sample is weighed and placed into the cavity of the pore pressing apparatus; the exact amount of sample will vary depending on the cavity size of the apparatus used. Pressure is then applied to the piston according to:

- A maximum pressure of 400–500 MPa is used for paste based samples; up to 650 MPa may be necessary for concrete samples.
- Pressure is increased gradually with a mean rate increase of 50 MPa/min. If the pore fluid flow is noticeably high, pressing should wait until the flow becomes noticeably slower before resuming the pressure increase. To avoid gas interference during pressing, it is recommended to withdraw the plunger of the syringe a short distance and to temporarily disconnect the syringe and vent the accumulated gas several times during each expression. After the maximum pressure is reached wait until no more pore fluid is obtained. The volume of pore fluid so obtained will vary as a function of the moisture content of sample and the amount of sample contained in the cavity of the press apparatus. A minimum volume of 5 ml is necessary to carry out all pH measurements with a pH meter and combination pH electrode and/or OH<sup>-</sup> titration.
- The pore fluid is collected in a syringe, which is connected to the hole of the bottom plate via a short flexible plastic tube (Figure 2-2a). The pore fluid cannot be extracted with the aid of a peristaltic pump because this can cause deviations in the measured pH values due to the introduction of atmospheric CO<sub>2</sub>. After collection, the pore fluid is immediately filtered through a 0.45 μm filter made of Nylon, PVDF or PTFE (Figure 2-2b) and stored in a sealed plastic container protected from atmospheric CO<sub>2</sub> (under Argon or N<sub>2</sub> gas) until further analysis (Figure 2-2c).



**Figure 2-2.** Obtaining the sample in the reference (PFE) method. (a) Press apparatus and syringe used to collect the pore fluid sample, (b) filtration and (c) storage in a plastic container protected from atmospheric CO<sub>2</sub>.



**Figure 2-3.** Pore fluid pH measured with a pH electrode under inert atmosphere.

Two methods can be used to make the pH measurement, direct measurement with a pH meter and combination pH electrode and/or indirect determination by  $\text{OH}^-$  titration. These should be done as soon as possible after pressing.

- *Direct pH measurement:* The pH electrode system must be calibrated by a minimum of three standard buffer solutions (see Section 2.1.3). Calibration should be in accordance with the instructions supplied by the manufacturers of the pH meter and the combination pH electrode. It is recommended that a calibration slope of  $\geq 0.97$  is used to ensure accuracy of the results. As temperature fluctuations will cause measurement errors, especially at high pH, a temperature sensor for automatic temperature compensation is necessary and furthermore, that all solutions (buffer and sample solutions) should be the same (room) temperature prior to use. The calibration of the pH electrode should be checked regularly by measuring the pH (ideally within  $\pm 0.05$  pH units) of the buffer solutions.

The calibrated pH electrode is inserted in the pore solution, protected from atmospheric  $\text{CO}_2$  contamination by passing Argon or  $\text{N}_2$  gas through the head space of the plastic container, and left without stirring until the pH value is stable (Figure 2-3).

- *Indirect pH measurement:* The pH value can also be obtained by  $\text{OH}^-$  titration following the procedure described in is ASTM D 1067-92 “Standard test methods for acidity or alkalinity of water”. In this case, if the crushed sample is pre-conditioned, the  $\text{OH}^-$  titration must be corrected for the initial moisture content of the material, the amount of sample tested and the amount of  $\text{CO}_2$  free deionised water added. The following steps describe the procedure of pH determination by  $\text{OH}^-$  titration. As many steps as possible should be made under Argon or  $\text{N}_2$  gas to protect the solutions from atmospheric  $\text{CO}_2$  contamination:
  - a) Transfer 0.5–5 ml of the pore fluid into a conical (Erlenmeyer) flask. The exact volume,  $V$  (ml), of the pore solution has to be known accurately.
  - b) Add one drop of Phenolphthalein indicator to the pore fluid sample. The colour will change to violet. The Phenolphthalein indicator is made by mixing 0.5 g of Phenolphthalein in ethanol to obtain 50 ml of solution.
  - c) Add 0.01 M HCl solution to a burette (manual or automatic equipment). Carefully add the HCl solution to the Erlenmeyer flask containing the pore fluid sample until the Phenolphthalein indicator turns from violet to colourless. The added volume of the HCl solution,  $V_{PN}$  (ml), has to be known accurately.
  - d) Add one drop of Methyl orange indicator to the solution in the Erlenmeyer flask. The colour will change to yellow. The Methyl orange indicator is made by mixing 0.1 g of Methyl orange in ethanol to obtain 100 ml of solution. Filtration of the resulting indicator solution may be necessary.
  - e) Continue to carefully add the 0.01 M HCl solution from the burette to the Erlenmeyer flask until the Methyl orange indicator turns from yellow to orange. The additional total volume of HCl solution,  $V_T$  (ml), has to be known accurately.

f) The OH<sup>-</sup> concentration, [OH<sup>-</sup>] (moles/L), is then calculated from:

$$[\text{OH}^-] = \frac{0.01 \cdot (2V_{PN} - V_T)}{V}$$

The pH can then be determined from the following approximation at room temperature (25°C):

$$\text{pH} \approx 14 + \log [\text{OH}^-]$$

### 2.1.6 Recording the results

The results should be recorded on the templates provided (Appendix C). The information recorded for each pH measurement should be as detailed as possible for future reference and must include:

- Sample identification: Label, material, distinguishable features.
- Key dates: Sample fabrication, curing, sent/received, and/or pH measured.
- Curing time and conditions.
- Time taken for each part of the protocol: Sample preparation, pore fluid expression, pH measurement, and/or OH<sup>-</sup> titration (see Section 2.1.7).
- Measured pH value to 2 decimal places and the method by which it was determined, either directly or indirectly. Note that for a given cementitious material, the expected repeatability and reproducibility of the pH measurement (within 95% probability) is close to or even lower than the ±0.1 error that can be assigned to the pH electrode.

### 2.1.7 Time schedule

An outline of the time schedule for each part of the reference (PFE) method is given below:

- Sample preparation (crushing): < 20 min.
- Pore fluid expression: pressing, extracting and filtering: 15–30 min. Note that the actual time needed for pressing depends on the material, which tends to be longer for concretes and shorter for cement pastes.
- pH measurements, as soon as possible after pore fluid expression: < 5 min.

## 2.2 Protocol for the routine (ESL) methods

### 2.2.1 Scope of the method

This method is based on *Ex Situ* Leaching (ESL) procedures whereby a powdered portion of the sample is mixed with an equivalent mass of deionised CO<sub>2</sub>-free water. Measurement of the pH is undertaken for either the resulting suspension without filtering or of the filtered solution.

### 2.2.2 Apparatus and auxiliary equipment

- pH meter with temperature compensation and a combination pH electrode specifically designed for measuring suspensions in the pH range of 7–14.
- Analytical balance – capable of weighing to an accuracy of 0.1 g.
- Magnetic stirrer.
- Coverable/sealable glass and plastic flasks/beakers.
- Grinding equipment (e.g. automatic grinder or mortar and pestle).
- Argon or N<sub>2</sub> gas
- Filtration apparatus using a filter pore size = 0.45 μm. Filters made of Nylon, PolyVinylidene DiFluoride (PVDF) or Hydrophile PolyTetraFluoroEthylene (PTFE) should be used.

### 2.2.3 Reagents

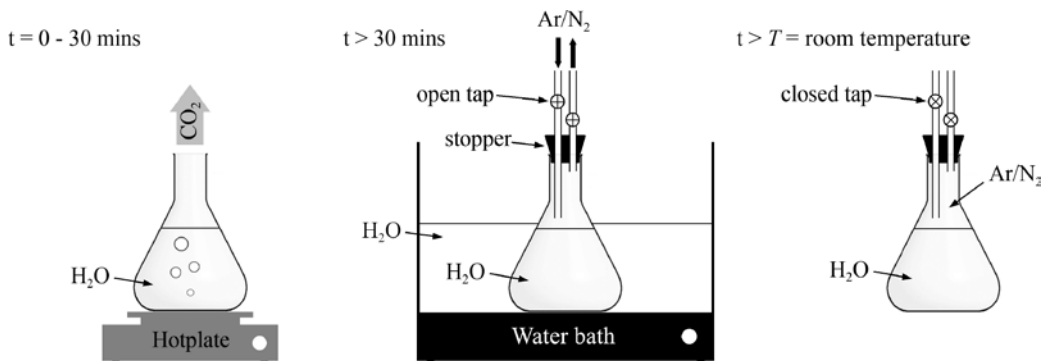
- CO<sub>2</sub>-free deionised water needs to be freshly prepared for each test. Boil 100 ml of deionised water in a glass beaker/flask for 30 min. After this time, the glass beaker/flask must be placed in a water bath to facilitate rapid cooling. To prevent atmospheric CO<sub>2</sub> contamination during cooling, argon or N<sub>2</sub> gas is passed through the head space of the beaker/flask. The CO<sub>2</sub>-free deionised water should only be used after cooling to room temperature. It is recommended to isolate the water from the atmosphere until it is used (Figure 2-4).
- A minimum of three standard buffer solutions must be used to calibrate the combination pH electrode, which should bracket the expected pH range (= 10.5–12.5) of low pH cementitious materials. Ideally, the standard buffer solutions should be at least 3 pH units apart, e.g. pH = 7, 10 ±0.8 and 13–14.

### 2.2.4 Sample preparation

If the samples must be transported to the laboratory where the pH measurements will be made, they must be sealed in plastic bags to prevent drying and CO<sub>2</sub> contamination. Covering the samples with a damp clean cloth/wipe before placing them in the sealed plastic bags is also recommended.

The samples must be cured in a chamber with 100% RH at 21 ±2°C for 90 days until the pH measurements are made.

The external surface (5–10 mm depth) of the low pH cementitious material must be removed by a hammer and chisel or other appropriate tools. This is to exclude any material that may have been exposed to the atmosphere during handling and curing. The low pH cementitious material is ground with an automatic grinder or mortar and pestle, taking care not to heat and subsequently dry the sample. The sample has to be ground to allow approximately 80% of the particles to pass through an 80 µm sieve, see Figure 2-5, noting that a sieve cannot be used during this process and that grinding should be performed as quickly as possible.



**Figure 2-4.** Idealised schematic representation of the preparation of CO<sub>2</sub>-free deionised water. *t* = 0–30 mins: Deionised water is boiled. *t* > 30 mins: Water is cooled under N<sub>2</sub> or Argon gas and submerged in cold water to assist cooling. *t* > *T* = room temperature: Vessel is sealed to prevent atmospheric CO<sub>2</sub> contamination.



**Figure 2-5.** Powdered particle size required in both routine (ESL) methods. (a) The sample is ground with a pestle and mortar to obtain (b) a particle size diameter,  $\phi \approx 80 \mu\text{m}$ .

## 2.2.5 Procedure

- *Calibration of the pH electrode:* The pH electrode system must be calibrated by a minimum of three standard buffer solutions before performing the pH measurements. Calibration should be in accordance with the instructions supplied by the manufacturers of the pH meter and the pH electrode. It is recommended that a calibration slope of  $\geq 0.97$  is used to ensure accuracy of the results. As temperature fluctuations will cause measurement errors, especially at high pH, a temperature sensor for automatic compensation is necessary and furthermore, that all solutions (buffer and sample solutions) should be the same (room) temperature prior to use. The calibration of the pH electrode can be checked between the pH measurements by measuring the pH (ideally be within  $\pm 0.05$  pH units) of the buffer solutions.
- Mix 10 g of powdered sample and 10 ml of the CO<sub>2</sub> free deionised water (water/solid ratio = 1) in a plastic beaker and stir vigorously and continuously for 5 minutes using a magnetic stirrer (Figure 2-6). Argon or N<sub>2</sub> gas should be passed through the head space of the beaker to prevent CO<sub>2</sub> contamination.
- *pH measurement:* The following steps describe the procedure of pH measurement in the two variant routine (ESL) methods, either a) without or b) with filtering.
  - a) *pH measurement without filtering:* Continue stirring and insert the calibrated combination pH electrode into the suspension, while still being protected from atmospheric CO<sub>2</sub> contamination by passing argon or N<sub>2</sub> gas through the head space of the beaker (Figure 2-7). Leave the apparatus until the pH value is stable.
  - b) *pH measurement with filtering:* Stop stirring and pass the suspension through a 0.45  $\mu\text{m}$  Nylon, PVDF or PTFE filter while passing argon or N<sub>2</sub> gas through the head space of the filtering device (Figure 2-8). Transfer the filtered solution into a small plastic beaker. Insert the calibrated combination pH electrode into the filtered solution, again while passing N<sub>2</sub> or Argon gas through the head space of the beaker (Figure 2-8), and start stirring. Leave the apparatus until the pH value is stable.

Repeat the procedure for two more powdered samples of the same low pH cementitious material, giving a total of three measured pH values.

Acceptably recorded pH values for the same low pH cementitious material should consistently be within the  $\pm 0.1$  error that can be assigned to the pH electrode. If higher differences are found, the pH electrode should be recalibrated and the measurement repeated. If the difference remains, use larger volumes of samples to lessen heterogeneity effects (heterogeneous distribution of components) in the sample, while maintaining the same water/solid ratio = 1.

It is recommended that the laboratory temperature, during the pH measurement period, is near constant and within a range of 20–25°C.



**Figure 2-6.** Initial stirring procedure used in both routine (ESL) methods. The suspension is stirred while N<sub>2</sub> (optionally Argon) gas is passed through the head space of the beaker.



**Figure 2-7.** pH measurement procedure for the routine (ESL) method without filtering. (a)  $N_2$  (optionally Argon) gas is passed through the head space above the stirred suspension. (b) Detailed view of gas passed through head space and the temperature sensor and combination pH electrode in the suspension.



**Figure 2-8.** Filtering and pH measurement procedure in the routine (ESL) method with filtering. (a)  $N_2$  (optionally Argon) gas is passed through the head space of the filtering apparatus. A peristaltic pump is used to assist filtration with the pore water sample collected in the bottom flask. (b)  $N_2$  (optionally Argon) gas is passed through the head space of the vessel with a temperature sensor and combination pH electrode in the stirred pore fluid sample.

## 2.2.6 Recording the results

The results should be recorded on the templates provided (Appendix D). The information recorded for each pH measurement should be as detailed as possible for future reference and must include:

- Sample identification: Label, material, observed features.
- Key dates: Sample fabrication, curing, sent/received, and/or pH measured.
- Curing time and conditions.
- Time taken for each part of the protocol: Sample preparation, suspension preparation, filtering (if used) and pH measurement (see 2.2.7 Time schedule).
- Sample mass and water volume.
- The measured pH value must be reported as the mean value of the three measurements and their standard deviation (SD).
- Measured pH values to 2 decimal places, as well as the mean and SD of the three pH measurements. Note that for a given cementitious material, the expected repeatability of the pH measurement (within 95% probability) is close to or even lower than the  $\pm 0.1$  error that can be assigned to the pH electrode. The expected reproducibility of the pH measurement (within 95% probability) is  $\pm 0.29$  pH units (according to the results shown in this report).

### **2.2.7 Time schedule**

An outline of the time requirements involved in each step of the routine (ESL) methods is given below:

- Sample preparation (powdering): < 15 min (or less if the samples is powdered using an automatic grinder).
- Preparation of the suspension: < 5 min.
- Stirring: = 5 min.
- Filtering (if used): < 5 min.
- pH measurements: < 5 min.



## 3 Preliminary protocol investigation

### 3.1 Introduction

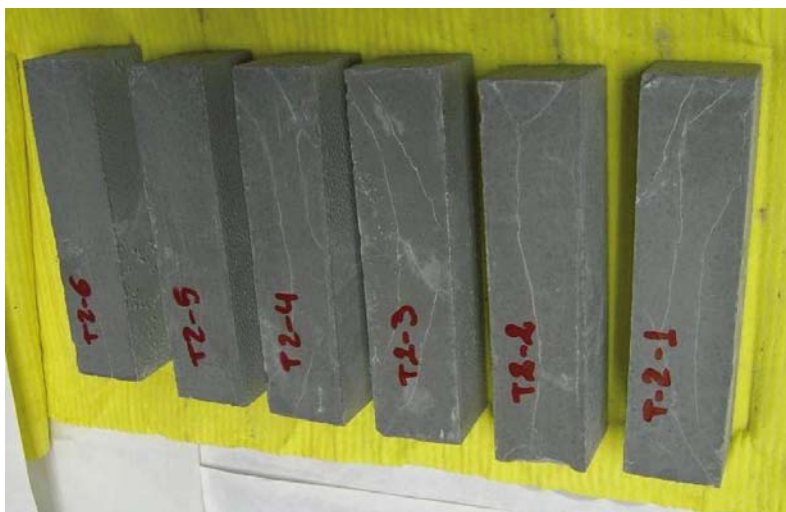
The initial literature review (Appendix A) and experimental investigation of more critical parameters identified therein (Appendix B), were used to draft the preliminary pH measurement protocols. The protocols were based on the selection of two different measuring methods: Pore Fluid Expression (PFE) as the reference method and *Ex Situ* Leaching (ESL) as the routine method, the latter consisting of two variant cases, without or with filtering.

Testing of the preliminary pH measurement protocols was undertaken on the same hardened low pH cement paste by the nine different national laboratories participating in the project. Low pH cement paste samples were fabricated on 11 November 2009 at the CBI laboratory as 4×4×16 cm bricks (Figure 3-1) with the composition specified in Table 3-1, as requested by SKB.

All samples were stored in a chamber with 100% RH at 21 ±2°C before three samples were shipped to each of the participating laboratories in sealed plastic bags to minimize drying and CO<sub>2</sub> contamination during transit. Once received, the laboratories stored the three samples in a chamber of the same relative humidity and temperature range (100% RH and 21 ±2°C) for a total of 90 ±5 days since fabrication before measuring the pH of the pore fluid. Table 3-2 shows the laboratories that carried out the pH measurements and the number of measurements made and those expected in each case; noting that not all the participating laboratories made the proposed measurements so there were fewer results than expected. It should be noted that Lab-9 made the pH measurements at longer ages (120 and 160 days) using both ESL methods.

**Table 3-1. The composition of the low pH cement paste samples fabricated by CBI Laboratory.**

Material	kg/m <sup>3</sup>
CEM I 42.5 MH/SR/LA	321.6
Silica fume (SF) (densified)	214.4
Water	434.16
Limestone filler L25	989.0
Glenium 51	6.38
Water/cement	1.35
Water/(cement+SF)	0.81



**Figure 3-1.** Photo of the low pH cement paste samples received by CSIC. Each of the 6 samples has dimensions 4×4×16 cm.

**Table 3-2. Laboratories involved in the preliminary investigation and number of pH measurements expected and made in each case.**

Organisation	Laboratory	Lab number	Routine (ESL) method					
			Reference (PFE) Method		Without filtering		With filtering	
			Expected	Made	Expected	Made	Expected	Made
Nagra	EMPA	Lab-1	3	3	–	–	–	–
RAWRA/NRI	NRI	Lab-2	3	–	9	9	9	9
Nagra	TFB	Lab-3	–	–	9	3	9	3
Enresa	CSIC	Lab-4	3	3	9	9	9	9
Posiva	VTT	Lab-5	–	–	9	9	9	9
CEA	CEA	Lab-6	3	3	9	9	9	9
JAEA	Taiheiyo Cement	Lab-7	3	3	9	9	9	9
NUMO	Criepi	Lab-8	3	3	9	3	9	3
AECL	AECL	Lab-9	–	–	9	9	9	9
Total measurements at 90 days			18	15	63	51	63	51
Total measurements			18	15	72	60	72	60

The pH measurements reported from each laboratory were collated and subject to a statistical analysis to evaluate the repeatability and the reproducibility of both methods, and the accuracy of the routine (ESL) methods without and with filtering compared to the reference (PFE) method.

In accordance with ISO 5725 standard (“Accuracy (trueness and precision) of measurement methods and results”) (ISO 5725:1994), repeatability is defined as “the closeness of agreement between the results of successive measurements of the same value and carried out subject to all of the following conditions: the same measurement procedure, the same observer, the same measuring instrument used under the same conditions, the same location and repetition over a short period of time”. Reproducibility is defined as “the closeness of agreement between the results of measurements of the same measurand, where the measurements are carried out under changed conditions such as: different principles or methods of measurement, different observers, different measuring instruments, different locations, different conditions of use or different periods of time”. Thus reproducibility is not just related to a method but rather to a measurand, while repeatability is estimated for a single method (Feinberg 1995).

In the present work, the requirements to carry out a statistical analysis of the reference (PFE) and the two variant routine (ESL) methods were:

- The pH measurements of all the samples had to be done immediately after the same  $90 \pm 5$  days of curing. This extended timeframe was to allow for an increase in the extent of the pozzolanic reaction between the OPC and the densified SF (Table 3-1).
- The pH measurements had to be conducted by strict adherence to the preliminary protocols.
- According to ISO 5725 standard, the use of statistics to validate the method being analyzed can only be considered reliable with at least eight participants that make replicate determinations.

## 3.2 Preliminary protocol for the reference (PFE) method

### 3.2.1 Scope of the method

The protocol was based on pore fluid expression procedure whereby the actual pore fluid of a hardened low pH cement paste/concrete is extracted under pressure and the pH of the expressed pore fluid is measured directly with a pH meter and combination pH electrode and/or determined indirectly by  $\text{OH}^-$  titration.

### 3.2.2 Apparatus and auxiliary equipments

- Press and extraction device.
- pH meter with the ability to compensate for variations in temperature and a pH electrode for measuring pH in solutions.
- Analytical balance capable of weighing 0.1 g.
- Oven capable of heating to 105°C.
- Glass beaker.
- N<sub>2</sub> gas (optionally Argon).
- Hammer and chisel.
- Filter (pore size 0.45 µm) according to the minimum sample size.

### 3.2.3 Reagents

CO<sub>2</sub>-free deionised water: 100 ml of deionised water were boiled in a glass beaker for 30 min. The glass beaker, after boiling the water, must be covered with a watch glass until the water is cooled down to room temperature. Nitrogen or argon should be bubbled through the water during cooling to avoid contamination from atmospheric CO<sub>2</sub> (Figure 3-2). The CO<sub>2</sub> free deionised water cannot be used until the water has cooled down to room temperature and should be freshly prepared for each test.

Buffer solutions for calibration of the pH-electrode: a minimum of three buffer solutions were used, one in the neutral pH = 7 range, another in the alkaline region pH = 13 or 14 and the third with an intermediate value, e.g. pH = 10 ± 1. Primary standard buffers were used for accuracy of the pH measurements. Temperature correction was included in the calibration and all solutions were the same (room) temperature prior to use.



**Figure 3-2.** Cooling procedure for CO<sub>2</sub>-free deionised water. The glass beaker is partially covered by a watch glass and N<sub>2</sub> (optionally Argon) gas is bubbled through the solution using a plastic tube.

### 3.2.4 Sample preparation

Low pH cement paste samples were prepared on 11 November 2009 at the CBI laboratory as bricks (4×4×16 cm) with the composition shown in Table 3-1. All samples were stored in a chamber with 100% RH at 21 ±2°C before shipping 3 samples to each of the different laboratories in sealed plastic bags to minimize drying and CO<sub>2</sub> contamination during transit.

Once received, the three low pH cement paste samples were kept in a chamber at 100% relative humidity and 21 ±2°C and cured since fabrication for a total time of 90 ±5 days (4–14 February 2010).

After curing, the low pH cement paste sample was manually crushed down to a maximum particle size of 5 mm using a hammer and a chisel without using a sieve, but using the entire resulting crushed sample in the PFE method. Figure 2-1 shows an example of the prepared sample.

Approximately 15 grams (g) of the crushed sample was taken and used to determine the initial moisture content in the pore space. The determination of the initial moisture content in the pore space was given as follows:

- Weigh a glass beaker,  $W_0$  (g).
- Put ≈ 15 g of the sample in the glass beaker and record the exact weight of sample + glass beaker,  $W_1$  (g).
- Dry the sample in the glass beaker in an oven at 105°C for 24 hours.
- After this time, the dry sample was weighed with the glass beaker,  $W_2$  (g).

Assuming that the density of the pore fluid is approximately 1 g/ml at room temperature, the moisture in the pore space can therefore be calculated from:

- Sample weight (g) =  $W_1 - W_0$
- Moisture in the pore space (ml) =  $W_1 - W_2$
- Moisture in the pore space/sample weight (ml/g) =  $(W_1 - W_2) / (W_1 - W_0)$

For the PFE method itself, approximately 125 g of sample were weighed and recorded. The exact mass can vary depending on the cavity of the cylinder (or die body) size of the press apparatus used.

#### Sample pre-conditioning

Sample pre-conditioning may be necessary if and **only if** the low pH cementitious material is seen to be very dry. A small volume of CO<sub>2</sub>-free deionised water must be sprayed on the crushed sample surface just before pressing. The amount of water added will vary depending on the initial moisture content of the sample and has to be enough to give a wet surface, but with no excess free water remaining either on the surface of the crushed sample or in the container. The volume of water added has to be known gravimetrically by weighing the sample before and after the addition of the CO<sub>2</sub>-free deionised water. Figure 3-3 illustrates the procedure for sample pre-conditioning.



**Figure 3-3.** Sample pre-conditioning procedure (CO<sub>2</sub>-free deionised water addition). (a) Initial surface of dry sample, (b) water spraying, (c) surface of wet sample.

### 3.2.5 Procedure

The prepared crushed sample was placed into the cavity of the cylinder (or die body) of the press apparatus. Pressure was then applied to the piston according to the following:

- *Maximum pressure value:* between 400–500 MPa. CSIC, for example, used a maximum pressure value of 480 MPa in pressing the samples.
- *Rate of pressure application:* should be gradual, with a mean rate increase of 50 MPa/min. If the pore water flow is noticeably high, it is recommended to pause pressing and wait until the flow of pore water becomes noticeably slower before increasing the pressure again. To avoid gas interference during the expression, it was found to be helpful to withdraw the plunger of the syringe a short distance to maintain a negative pressure, and also to temporarily disconnect the syringe and vent the accumulated gas from it several times during each expression. After the maximum pressure is reached, wait for 5 minutes until no more pore water is obtained.

Figure 2-2 shows the collection and storage of the pore water sample. The pore water was collected in a syringe, which was connected to the hole of the bottom plate of the press apparatus by a short rubber tube, and filtered ( $\leq 0.45 \mu\text{m}$ ) and stored in a plastic container until analysis under a  $\text{N}_2$  gas atmosphere to protect the pore water sample from atmospheric  $\text{CO}_2$  contamination.

The pH measurements must be done as soon as possible after the pore water has been collected and can be measured directly using a pH meter and combination pH electrode or determined indirectly by  $\text{OH}^-$  titration; it is, in fact, preferable if the laboratories can undertake both direct and indirect measurements:

- Direct pH measurement (Figure 3-4): A combination pH electrode was determined to be needed. The sensor used was designed to measure in the pH = 7–14 range. Calibration of the electrode was made using three standard buffers of pH = 7,  $10 \pm 1$  and 13, which will bracket the expected pH range of the pore water samples and which are approximately three pH units or more apart. Recalibrating the electrode may be necessary if repeated pH measurements are not within 0.1 pH units of the three buffer solutions. Calibration should be in accordance with the instructions supplied by the manufacturers of the pH meter and the pH electrode. For the actual pH measurement, the pH electrode is inserted in the pore water sample and left until the pH value becomes stable. As temperature fluctuations will cause measurement errors, a temperature sensor for automatic compensation is strongly recommended.
- Indirect pH determination under  $\text{N}_2$  gas protected from  $\text{CO}_2$ : the pH value can also be obtained by  $\text{OH}^-$  titration following the procedure described in is ASTM D 1067-92 “Standard test methods for acidity or alkalinity of water”. In this case, if the crushed sample is pre-conditioned, the  $\text{OH}^-$  titration must be corrected for the initial moisture content of the material, the amount of sample tested and the amount of  $\text{CO}_2$  free deionised water added. The conversion from  $\text{OH}^-$  into pH can be determined from the following approximation at room temperature ( $25^\circ\text{C}$ ):

$$\log K_w \approx -14 = \log [\text{H}^+] + \log [\text{OH}^-] \quad (\text{Eq. 1})$$

where  $K_w$  is the ionization constant of water and square brackets denote activities of the ions in solution. Given that  $\text{pH} = -\log [\text{H}^+]$  and assuming the solution behaves ideally, rearrangement of Equation (1) gives:

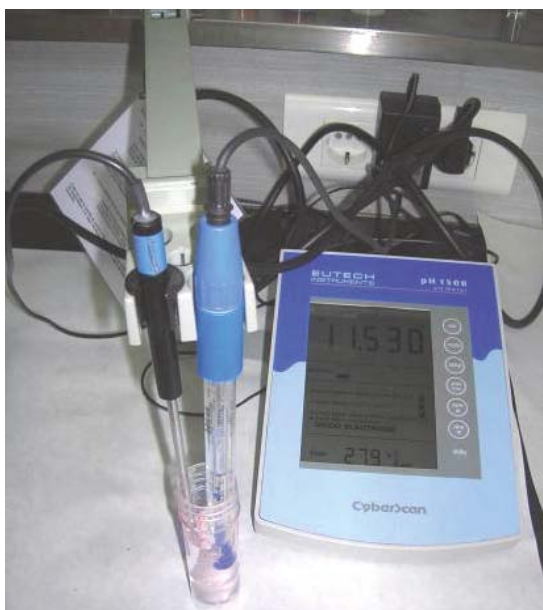
$$\text{pH} \approx 14 + \log [\text{OH}^-]$$

where square brackets denote molar concentration.

### 3.2.6 Recording the results

The result was expressed as the pH value with reference to:

- The pH result obtained by direct measurement with a combination pH electrode.
- The pH result determined indirectly by  $\text{OH}^-$  titration.



**Figure 3-4.** Pore water pH measured with a combination pH electrode and temperature corrected under an  $N_2$  (optionally Argon) gas atmosphere.

### 3.2.7 Time schedule

To assess the similarity of test conditions in all the laboratories, it was recommended that all the laboratories follow the procedure over a similar timeframe. To simplify this issue, in the following times are guidelines for each part of the procedure:

- Sample preparation (crushing): < 20 min.
- Sample pre-conditioning ( $CO_2$ -free water addition): < 5 min.
- Pore fluid expression including filtering: 15–20 min.
- pH measurements under  $N_2$  gas: just after pore fluid expression (< 5 min).

## 3.3 Preliminary protocol for the routine (ESL) methods

### 3.3.1 Scope of the method

This protocol was based on the *ex situ* leaching procedures whereby a powdered portion of the sample is mixed with deionised free  $CO_2$  water, and the pH is either measured directly in the suspension without filtering or in the solution obtained with filtering.

### 3.3.2 Apparatus and auxiliary equipment

- pH meter with the ability of temperature compensation.
- A specific combination pH electrode to measure the pH of a suspension in the range of pH = 7 to 14.
- Analytical balance capable of weighing 0.1 g.
- Magnetic stirrer.
- Small beaker.
- Grinding equipment.
- $N_2$  gas.
- Filtering device (with a filter < 0.45  $\mu m$ ).

### 3.3.3 Reagents

- *CO<sub>2</sub>-free deionised water*: 100 ml of deionised water was boiled in a glass beaker for 30 min. After boiling, the glass beaker was covered until the water has cooled down to room temperature. Nitrogen or argon were bubbled through the water during cooling in order to minimize contamination from atmospheric CO<sub>2</sub>. The CO<sub>2</sub> free deionised water cannot be used until the water has cooled down to room temperature and should be freshly prepared for each test.

*Buffers solutions for calibration of the pH electrode*: a minimum of three buffer solutions were used, one in the neutral range pH = 7, another in the alkaline region pH = 13 or 14 and the third with an intermediate value, e.g. pH = 10 ± 1. Primary standard buffers were used for accuracy. Temperature correction was also included in the calibration and all solutions should be the same (room) temperature prior to use.

### 3.3.4 Sample preparation

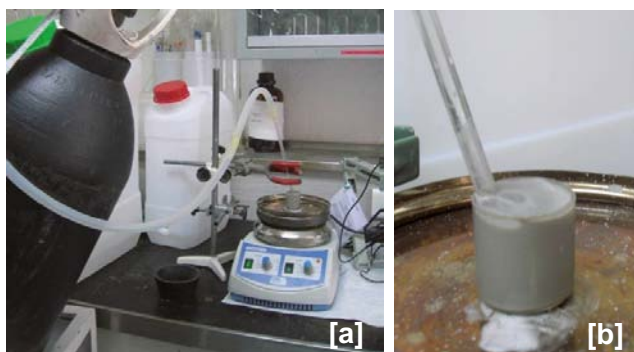
- *Sample preparation* (see Figure 2-5): crushed powder ≈ 100 grams of the low pH cementitious material with a particle diameter of around 80 μm (powder size), but without using a sieve. For this procedure an automatic grinder can be used or the sample can be manually ground with a pestle and mortar, taking care not to heat and subsequently dry the sample. Crushing of the samples has to be performed as quickly as possible.

### 3.3.5 Procedure

- *Calibration of the combination pH electrode*: The instrument/electrode system was calibrated by a minimum of three pH buffer solutions that bracket the expected pH of the samples and are ideally three pH units or more apart. Recalibrating the electrode may be necessary if repeated pH measurements are not within 0.1 pH units of the three buffer solutions. Calibration should be in accordance with the instructions supplied by the manufacturers of the pH meter and the combination pH electrode. As temperature fluctuations will cause measurement errors, a temperature sensor for automatic temperature compensation was required. Temperature correction was, therefore, also included in the calibration and all solutions should be the same (room) temperature prior to use.
- *pH measurement (the whole procedure under N<sub>2</sub> gas protected from CO<sub>2</sub>)*: Mix 10 g of powdered sample in a beaker with 10 ml of the CO<sub>2</sub>-free deionised water and continuously and vigorously stir the suspension for 5 minutes (Figure 3-5).

After stirring, two procedures must be followed:

- To measure the pH of the suspension directly with the combination pH electrode, stirring continuously during the measurement until the pH value is stable and record the value obtained, see Figure 3-6. The measure must be made under N<sub>2</sub> gas.
- To pass the suspension through a 0.45 μm filter and measure the pH of the filtered solution. The filtration of the suspension and the pH measurement must also be made under an inert atmosphere by bubbling/flushing with N<sub>2</sub> gas, see Figure 3-7.



**Figure 3-5.** Stirring procedure followed in the routine (ESL) methods. (a) Suspension stirred for 5 minutes with a magnetic stirrer and (b) (detailed view) N<sub>2</sub> (optionally Argon) gas continuously bubbled through the suspension to minimize atmospheric CO<sub>2</sub> contamination.



**Figure 3-6.** Pore water pH measurement for the routine (ESL) method without filtering under  $N_2$  (optionally Argon) gas with the combination pH electrode and temperature sensor inserted directly in the suspension.



**Figure 3-7.** Stirring and filtration procedures followed in the routine (ESL) method with filtering. Filtering the suspension is conducted under  $N_2$  (optionally Argon) gas.

Repeat each procedure with two more powdered samples in order to obtain three pH values measured directly in the suspension and three pH values measured for the filtered solution for the same low pH cementitious sample.

### 3.3.6 Recording the results

The measured pH must be expressed as the mean and SD of the three pH measurements. The acceptance criterion of the measured pH values is that the difference between two values is less than the  $\pm 0.1$  error, which can be assigned to the electrode. If greater differences are found, the combination pH electrode should be recalibrated and the pH measurements repeated. If a significant difference remains then evaluate the homogeneity of the powdered material.

For each sample two pH values must be reported:

- The pH value measured directly in the suspension.
- The pH value measured in the solution after filtering the suspension.



### 3.3.7 Time schedule

To assess the similarity of test conditions in all the laboratories, it is recommended that all the laboratories follow the procedure over a similar time frame. The following times are guidelines for each step of the procedure:

- Sample preparation (powdering) < 15 min (or less if the samples are powdered using an automatic grinder).
- Preparation of the suspension < 5 min.
- Stirring = 5 min.
- Filtering (when it is made) < 5 min.
- pH measurements, just after stirring or filtration, depending on the procedure followed.

## 3.4 Results of the preliminary protocol investigation

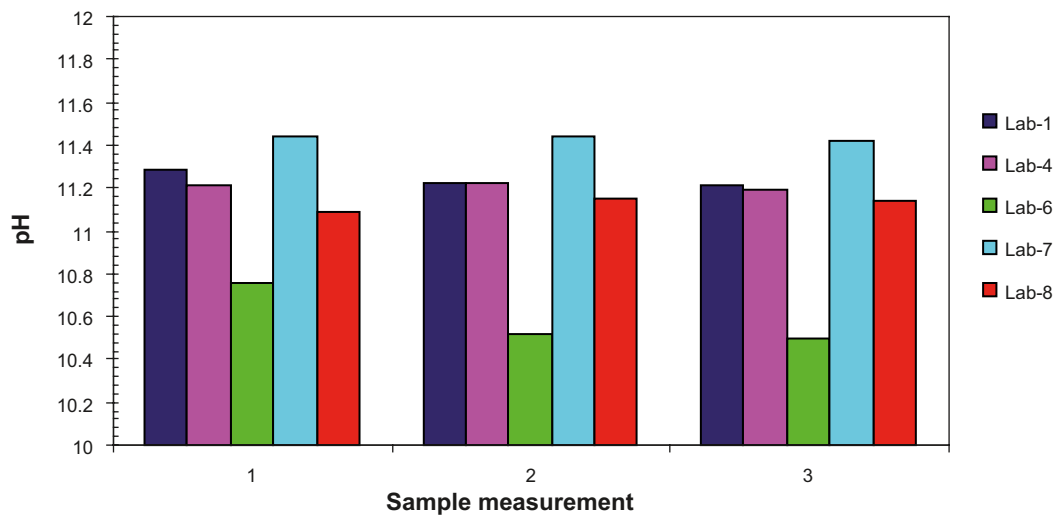
### 3.4.1 Reference (PFE) method results

#### *PFE results: pH measured with a pH electrode*

Figure 3-8 shows the recorded pH values obtained using the reference (PFE) method that were measured directly with a pH electrode, and Table 3-3 presents the mean pH values and  $\pm$ SD, but which have also been calculated with the exclusion of Lab-6 and Lab-7 that consistently recorded lower and higher pH values, respectively.

**Table 3-3. Mean pH values and SD obtained using the reference (PFE) method and measured directly with a combination pH electrode.**

Laboratories included	Mean pH $\pm$ SD
All laboratories	11.12 $\pm$ 0.30
All laboratories except Lab-6	11.25 $\pm$ 0.12
All laboratories except Lab-7	11.04 $\pm$ 0.28
All laboratories except Lab-6 and Lab-7	11.19 $\pm$ 0.06



**Figure 3-8.** Pore water pH values obtained using the reference (PFE) method measured with a combination pH electrode.

It can be seen Lab- 1, Lab-4 and Lab-8 have obtained very similar results by following the same recommended procedures; and was partly expected given that this method is commonly used in these laboratories. However, the pH values obtained by Lab-6 are consistently lower, by approximately  $-0.7$  pH units, and those from Lab-7 are consistently higher, by approximately  $+0.2$  pH units. Excluding Lab-6 and Lab-7, the  $SD = \pm 0.06$  is lower than the measurement error that can be assigned to the combination pH electrode. The pH measured using the reference (PFE) method with a combination pH electrode is, therefore, satisfactory in terms of both repeatability and reproducibility.

The consistently lower and higher pH values obtained by Lab-6 and Lab-7, respectively, can be explained by both laboratories not following the recommended procedures and the effect this had on the extent of pozzolanic reaction between the OPC and the densified SF (Table 3-1). Lab-7 reported that the samples were kept sealed after their reception and not in a chamber at 100% RH as recommended in the procedure. This would affect the degree of hydration, lessen the extent of pozzolanic reaction and cause the pH values reported by Lab-7 to be higher.

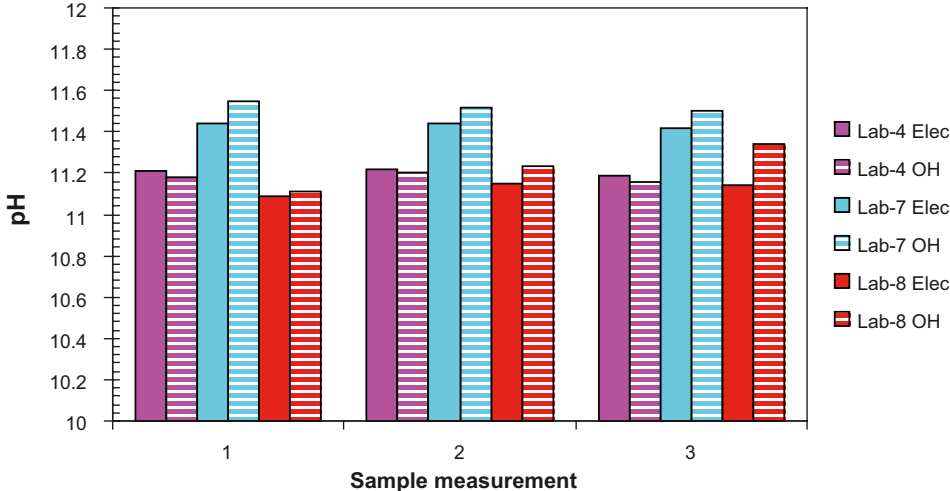
Another aspect of the reference (PFE) method, not easily tested in one laboratory alone, was that each laboratory used different sample masses, constrained by the size of the cavity in the press apparatus they each used, but that the moisture contents ( $= 0.17-0.20$  ml/g after 90 days of curing) were similar. Using different masses of sample had, therefore, seemingly no effect on the pH value of the pore water.

**PFE results: pH determined by OH<sup>-</sup> titration**

Figure 3-9 shows the pH results as determined by OH<sup>-</sup> titration, and are compared with those measured by a combination pH electrode. Table 3-4 shows the mean pH values from the OH<sup>-</sup> titration and  $\pm SD$ , again, taking into account different subpopulations of the participating laboratories. No results were reported by Lab-1 and Lab-6 because they did not conduct the OH<sup>-</sup> titration. In general, similar results are obtained when the pH is either measured by a combination pH electrode

**Table 3-4. Mean pH values and SD from the reference (PFE) method as measured directly with a combination pH electrode and as determined indirectly by OH<sup>-</sup> titration.**

Laboratories included	Mean pH $\pm$ SD	
	pH electrode	OH <sup>-</sup> titration
All laboratories (Lab-4, Lab-7 and Lab-8)	11.25 $\pm$ 0.14	11.31 $\pm$ 0.17
Lab-4 and Lab-8	11.17 $\pm$ 0.05	11.20 $\pm$ 0.08



**Figure 3-9. Pore water pH values obtained using the reference (PFE) method as measured directly with a combination pH electrode (Elec) and as determined indirectly by OH<sup>-</sup> titration (OH).**

or determined by OH<sup>-</sup> titration. The differences are in fact less than the pH = ±0.1 error assigned to the electrode. Both the pH measured directly with a combination pH electrode or determined indirectly by OH<sup>-</sup> titration are, therefore, valid in obtaining an accurate pH value for the reference (PFE) method.

In accordance with ISO 5725 standard /2-1/, the use of statistical methods to validate the analyzed method can only be done with at least eight participants that make replicate determinations. Thus in the case of the reference (PFE) method, the repeatability and reproducibility cannot be accurately determined. In a qualitative sense, however, both repeatability and reproducibility are quite good because the three replicates made in each laboratory are very similar and the differences between different laboratory results are quite low, respectively. The differences observed between the pH values reported by Lab-6 and Lab-7 and the ones reported by the other laboratories are due to the protocol not being followed and are not through a problem in the protocol itself.

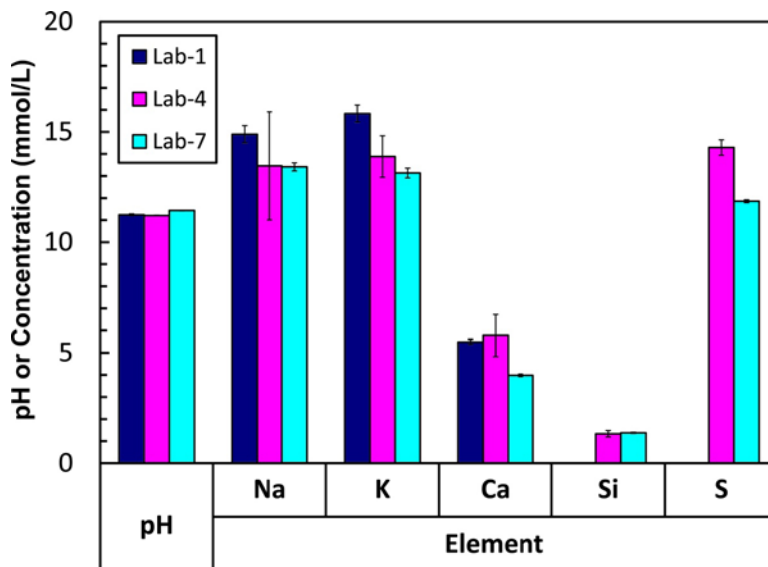
**PFE results: Chemical composition of the pore water**

Further to the pH measurements, Lab-1, Lab-4 and Lab-7 analyzed the chemical composition of the pore water for concentrations of Na, K, Ca (all), Si, Al, Fe, Mg, and S (Lab-4 and Lab-7) (Figure 3-10). These data are reported here for reference.

Concentrations of Fe were ≤ 0.02 mmol/L and of Al and Mg were mostly below the limit of detection and so are not shown in Figure 3-10.

Although the results only come from 3 laboratories, both the repeatability and the reproducibility of the chemical analyses are overall quite good, but are not as consistent as the measured pH values; noting that pH is on the log scale of [H<sup>+</sup>] activity. With the exception of Na and K in Lab-4, the concentrations of each element from each laboratory are quite similar with low SD showing good repeatability. Reproducibility of the results is also good, with the same general trends in concentrations being reported by each laboratory and the greatest concentration differences being of the order 10–31%.

Overall, both the measured pH values, as determined by pH electrode and OH<sup>-</sup> titration, and solution composition are acceptably reproducible and repeatable in the different laboratories. The reference (PFE) method that has been developed as part of this work therefore provides a satisfactory means of measuring the pH value of the pore water of low pH cementitious materials.



**Figure 3-10.** Mean chemical composition of the pore water from Lab-1, Lab-4 and Lab-7 using the reference (PFE) method. Error bars are SD.

### 3.4.2 Routine (ESL) methods results

Figure 3-11 shows the results obtained using the routine (ESL) method without filtering and Figure 3-12 those obtained using the routine (ESL) method with filtering the suspension. In both cases the pH was measured directly with a combination pH electrode under a N<sub>2</sub> atmosphere. Table 3-5 presents the mean values and the SD of the pH measurements, but which have also been calculated with the exclusion of laboratories that consistently recorded lower (Lab-6) or higher (Lab-7) pH values. These two laboratories reported similar differences in using the reference (PFE) method (see Section 3.4.1).

There are more deviations for the routine (ESL) methods than in case of the reference (PFE) method. This was partly expected because this was the first time most of the laboratories have used these ESL protocols, whereas the reference (PFE) method is commonly used.

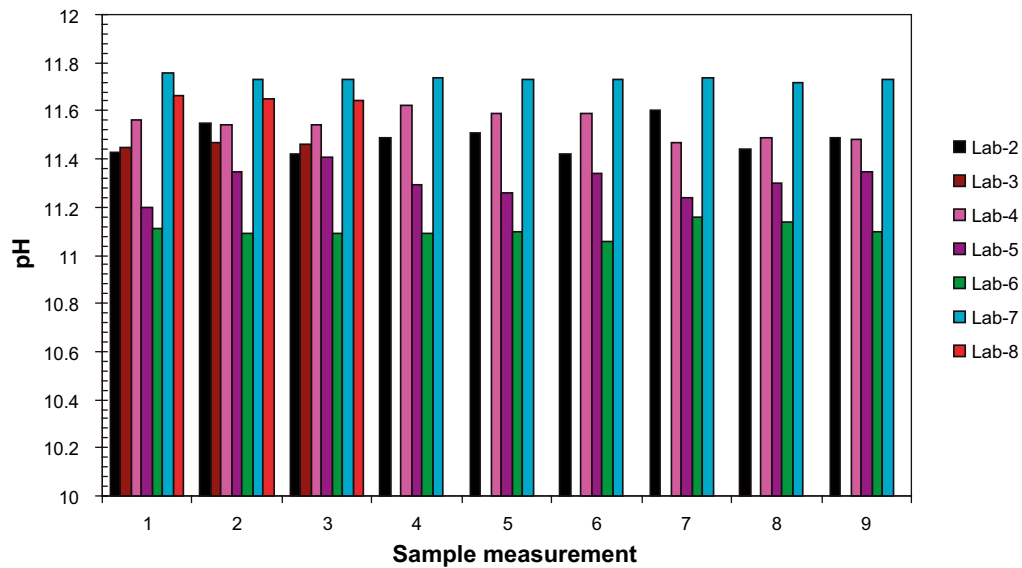


Figure 3-11. pH values measured with a pH-electrode using the routine (ESL) method without filtering the suspension.

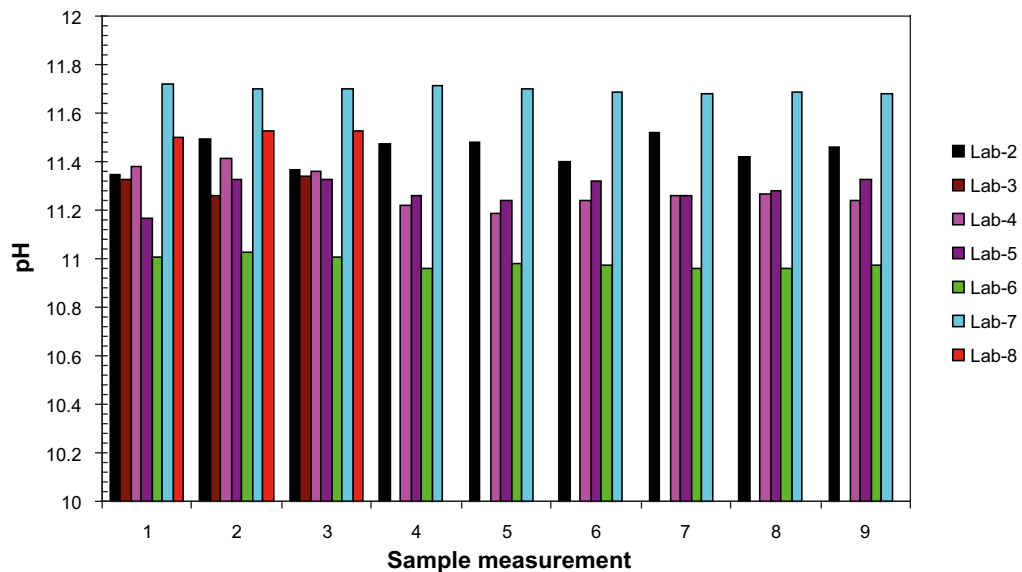


Figure 3-12. pH values measured with a pH electrode using the routine (ESL) method with filtering the suspension.

**Table 3-5. Mean pH values and SD from the routine (ESL) methods without and with filtering.**

Laboratories taken into account	Mean pH $\pm$ SD without filtering	Mean pH $\pm$ SD with filtering
All laboratories	11.45 $\pm$ 0.21	11.35 $\pm$ 0.23
All laboratories except Lab-6	11.52 $\pm$ 0.16	11.42 $\pm$ 0.17
All laboratories except Lab-7	11.39 $\pm$ 0.18	11.27 $\pm$ 0.18
All laboratories except Lab-6 and Lab-7	11.46 $\pm$ 0.12	11.35 $\pm$ 0.10

The pH values obtained using the “filtering protocol” are generally lower by  $-0.1$  pH units than those measured directly in the suspension. This pH lowering effect was also observed in the preliminary experiments (Appendix B), has been observed in other cementitious systems (Räsänen and Penttala 2004) and is well known in the chemical literature where it is referred to as the suspension effect, e.g. Oman et al. (2007) (and references therein).

Again, it can be seen that most of the laboratories have obtained similar results, with the same lower pH values (approximately  $-0.3$  pH units) obtained by Lab-6 and higher pH values (approximately  $+0.4$  pH units) obtained by Lab-7 for the routine (ESL) methods without and with filtering. The lowest SD, and, therefore, the best case, is obtained when the results from these two laboratories are not included. In the case of Lab-6, the protocol was not followed in that they manually ground the sample residues on a  $80\ \mu\text{m}$  sieve to get a particle size below  $80\ \mu\text{m}$ , which lasted 2 hours. Preparing the sample in this way would likely cause a significant increase in the carbonation of the powdered sample. Furthermore, Lab-6 reported some problems with the electrode, which was not really appropriate for measuring in suspensions. Moreover, Lab-6 also reported that only a small volume of solution was obtained from filtering and so may have been problematic in making reliable pH measurements. All these factors could contribute to the pH measurements made by Lab-6 being consistently lower. The pH values reported by Lab-6 cannot, therefore, be reliably compared with those of the other laboratories. In the case of Lab-7, the samples were left sealed after their receipt and not properly cured under 100% RH at room temperature, as was the case for the reference (PFE) method. The samples would therefore not have reached the same degree of hydration and so too, therefore, the same extent of pozzolanic reaction as those samples correctly cured in the other laboratories, which would contribute to the pH measurements made by Lab-7 being consistently higher.

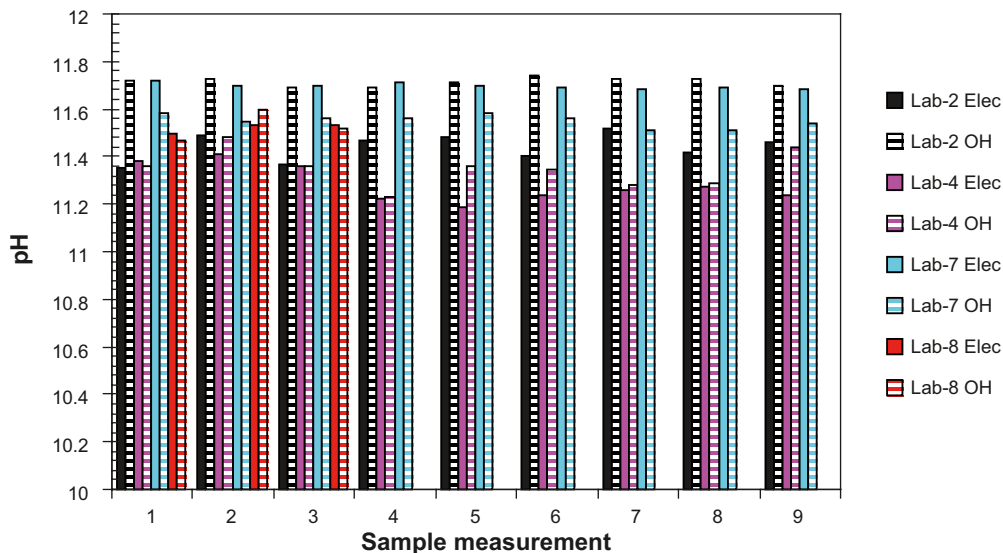
An aspect of the routine (ESL) methods was that Lab-3, without and with filtering, and Lab-2, with filtering, used a higher mass and volume of 30 g of sample and 30 ml of  $\text{CO}_2$ -free deionised water, respectively. The liquid:solid ratio (1:1) specified in the protocol was therefore maintained. This change to the protocol does not seem to have influenced the pH measurements and indicates that the most important thing is to maintain a constant liquid:solid ratio = 1:1 to prepare the suspension.

Another aspect of the protocol was that Lab-2 and Lab-5 used a centrifuge to facilitate the filtering procedure. The total time taken for the filtration procedure in both laboratories was similar to the time requirement of the protocol, and so this additional procedure did not seem to have influenced the pH measurements.

Figure 3-13 shows the pH values of the routine (ESL) method with filtering as determined by  $\text{OH}^-$  titration and for comparison, are shown with those measured by a combination pH electrode. Table 3-6 shows the mean pH values and SD of the routine (ESL) method with filtering as measured by a combination pH electrode and as determined by  $\text{OH}^-$  titration. Only Lab-2, Lab-4, Lab-7 and Lab-8 undertook  $\text{OH}^-$  titrations and so are the only laboratories considered in Figure 3-13 and Table 3-6.

**Table 3-6. Routine (ESL) method with filtering mean pH values  $\pm$ SD as measured by a combination pH electrode and as determined by  $\text{OH}^-$  titration.**

Laboratories included	Mean pH $\pm$ SD pH electrode	Mean pH $\pm$ SD $\text{OH}^-$ titration
All laboratories (Lab-2, Lab-4, Lab-7, and Lab-8)	11.48 $\pm$ 0.17	11.54 $\pm$ 0.15



**Figure 3-13.** Comparison of pH values for the routine (ESL) method with filtering as measured by a combination pH electrode (Elec) and as determined by OH<sup>-</sup> titration (OH).

In this case, although the mean values measured with the pH electrode and those determined by OH<sup>-</sup> titration are similar (Table 3-6), there are more differences between the individual determinations than in the reference (PFE) method (cf. Figure 3-9 and Figure 3-13). This was also seen in the preliminary experimental investigation made at CSIC (Appendix B), where it was concluded that for the routine (ESL) method with filtering, pH measurements made with a combination pH electrode give more reliable results than those determined by OH<sup>-</sup> titration.

### 3.5 Factors affecting results

#### 3.5.1 Pore water extraction method in the reference (PFE) method (Lab-6)

Lab-6 performed additional tests on the method they used to extract the pore water in the reference (PFE) method in May 2010 (sample age = 180 days). The pressing device was the same as used in the previous test of the preliminary protocol investigation after 90 days. In the previous tests, however, the pore solution was collected in a plastic tube placed in a flask under a slight vacuum provided by a peristaltic pump. After the pore water had been collected, the sampling tube was transferred to a N<sub>2</sub> filled glovebox and the collected pore water was passed through a 0.2 μm before pH measurements were made following the protocol; noting that other laboratories used the recommended 0.45 μm filter. In the new method, the flask and pump were dispensed with and the pore water was instead collected in a 40 ml glass flask connected directly to a valve on the side of the chamber of the pressing device. The flask was closed except for a septum plug to allow gas evacuation from the flask with a syringe during liquid collection. The pH measurements taken using the previous and new extraction methods are shown in Table 3-7.

**Table 3-7.** Lab-6 pH measurements using previous and new pore water extraction methods in the reference (PFE) method. Pressures (MPa) are shown for reference.

Previous pore water extraction method Curing time = 90 days. Temperature = 20°C			New pore water extraction method Curing time = 180 days. Temperature = 18°C		
Sample	pH electrode	Pressure* (MPa)	Sample <sup>§</sup>	pH electrode	Pressure <sup>†</sup> (MPa)
PA-1	10.50 <sup>‡</sup>	275	No. 1	10.51	350
PA-2	10.52	250	No. 2	10.72	650
PA-3a	10.76	240	—	—	—

\*at which pore water extraction began. †final pressure of pore water extraction. ‡pH measurements delayed by 1 hour.  
<sup>§</sup>Samples No. 1 and No. 2 were prepared from the same material as samples PA-1, PA-2, and PA-3a, except cured for different times.

The pH values appear not to have changed significantly (Table 3-7). The low pH cementitious material samples used for the new pore water extraction method have been cured for 180 days instead of 90 days and so their pore solution pH might be expected, all things being equal, to be lower from the continued pozzolanic reaction of the low pH cement paste. The new pore water extraction method might therefore, have had the desired effect of increasing the consistently lower pH values obtained by Lab-6. However, the pH values measured using the new pore water extraction method are still significantly lower than those inferred from the routine method on the same samples (Table 3-8), which may indicate that there is still an unidentified bias in this new pore water extraction method.

### 3.5.2 Changing the pH electrode in the routine (ESL) methods (Lab-6)

As part of the investigation into their consistently lower pH values, Lab-6 also changed the combination pH electrode used to measure the pH of the pore water sample for the routine (ESL) methods. The replacement combination pH electrode was specifically for use in suspensions, as recommended in the defined protocol. The pH values obtained using the old pH electrode after 90 days and the new pH electrode after 150 and 180 days are shown in Table 3-8.

**Table 3-8. Results from Lab-6 following the routine (ESL) methods after 90 days using the old pH electrode and after 150 days and 180 days using the new pH electrode.**

Routine (ESL) method	Old pH electrode (90 days)		New electrode		
	Without filtering	With filtering	(150 days)		(180 days)
			Without filtering	With filtering	Without filtering
Temperature at which pH was measured (°C)	24	24	28	28	23.5
Measured pH values	11.10 11.08 11.13	11.02 10.97 10.96	11.27 11.28 11.29	11.08 11.06 11.13	11.39 11.40
Mean value ±SD (Difference)	11.10 ±0.03 (-)	10.98 ±0.03 (-)	11.28 ±0.01 (+0.18)	11.09 ±0.04 (+0.11)	11.40 ±0.01 (+0.30)

Instead of the 150 day curing time resulting in a lower pH from the continuation of the pozzolanic reaction, the mean pH values measured with the new electrode was increased by  $\approx 0.15$  pH units. Despite this increase, the pH values after 150 days are still lower than the values measured by other laboratories at 90 days, where the mean pH excluding outliers =  $11.46 \pm 0.12$  for the routine (ESL) method without filtering and =  $11.35 \pm 0.10$  for the routine (ESL) method with filtering (Table 3-5). It should be noted however that the temperature in the glove box used to perform the pH measurements was 28°C. The deviation between the results may thus have resulted from a temperature effect.

To check this assumption, the chemical compositions of two filtrates were determined using ICP-AES and ionic chromatography after acidification with nitric acid (200  $\mu$ L of HNO<sub>3</sub> 34% for 10 ml of solution). The pH was assessed from the measured concentrations to get the electrical balance. The geochemical software JCHESS (van der Lee 1998) was used for the calculations (activity correction model = truncated Davies, default data base, precipitation disabled). The calculated pH values at 28°C are in good agreement with the experimental data obtained with the Mettler electrode ( $11.09 \pm 0.04$ ). Moreover, calculating the pH evolution of such solutions with temperature (Table 3-9) shows that a pH of 11.1 at 28°C corresponds to a pH of 11.35 at 20°C, which is consistent with the results obtained by the other laboratories.

**Table 3-9. Influence of temperature on the pH of the filtrates collected from the 150 day old samples (calculated).**

Temperature (°C)	18	20	22	24	26	28	30
Filtrate 1	11.45	11.39	11.33	11.26	11.20	11.14	11.08
Filtrate 2	11.41	11.35	11.29	11.22	11.16	11.10	11.04

Lab-6 repeated the pH measurements with the new pH electrode following the routine (ESL) method without filtering after 180 days curing (Table 3-8). The measured pH values of 11.39 and 11.40 are still in good agreement with the mean pH excluding outliers = 11.46 ± 0.12 reported by the other laboratories for the routine (ESL) method without filtering after 90 days curing (Table 3-5).

### 3.5.3 Carbonation in the reference (PFE) method (Lab-6)

Further to Lab-6 reporting consistently lower pH values, the pore water samples obtained after 90 days curing were analysed for their composition, including total inorganic carbon (TIC) concentrations, to assess if carbonation of their samples had been significant (cf. Appendix B). The chemical composition of the three pore water samples are shown in Table 3-10.

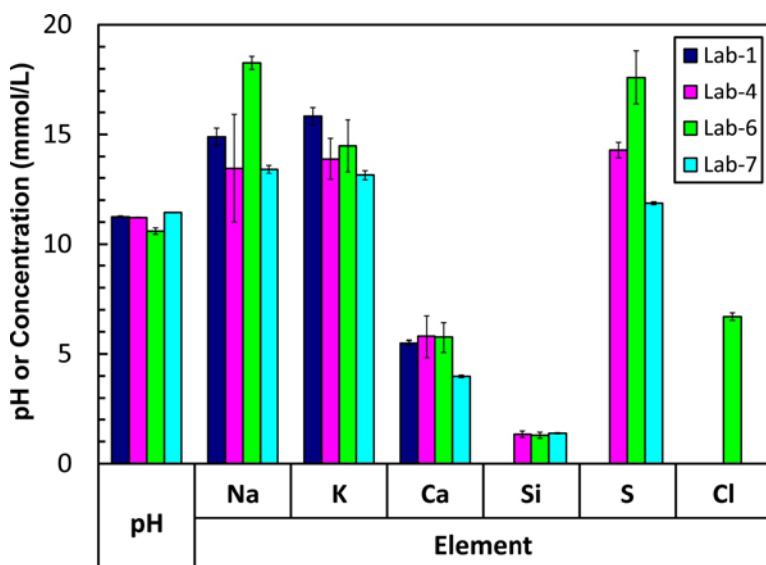
The repeatability of the chemical analyses are very good, with a mean difference, if Al is excluded, of 11.25% (S.D. = 6.63); Al is prone to significant errors with concentrations being on the order of µm. The pore water sample compositions are also in good agreement with those analysed in the other laboratories showing good reproducibility (Figure 3-14).

The mean pH and element concentrations shown in Figure 3-14 are typical of a low pH cement having undergone some degree of pozzolanic reaction. Na and K concentrations are significantly lower than the 100's of mmol/L typical of hydrated OPC by their uptake into the calcium silicate hydrate gel (e.g. Hong and Glasser 1999, Lothenbach and Winnefeld 2006), Ca and S are increased by the destabilization and dissolution of ettringite and, if formed, monosulfate, and Si is saturated with respect to amorphous silica.

**Table 3-10. Composition of Lab-6 pore water samples after 90 days using the reference (PFE) method. Concentrations in mmol/L, except for Al in µmol/L.**

Sample	Measured pH (18°C)	K	Na	Ca	Si	Al (µmol/L)	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	TIC*
PA-1	10.50	15.55	18.03	6.14	1.13	–	18.63	6.53	0.34 <sup>†</sup>
PA-2	10.52	14.68	18.60	6.12	1.38	16.57	17.92	6.87	0.35
PA-3a	10.76	13.22	18.18	4.96	1.35	2.32	16.26	6.67	0.33

\*TIC = Total Inorganic Carbon. <sup>†</sup>Estimated value by analogy with PA-2 and PA-3a.



**Figure 3-14.** Mean chemical composition of the pore water from Lab-1, Lab-4, Lab-6, and Lab-7 using the reference (PFE) method. Error bars are SD. TIC reported by Lab-6 are not shown because of their low concentration = 0.33–0.35 mmol/L (cf. Table 3-10).



All pore water sample compositions from Lab-1, Lab-4, Lab-6, and Lab-7 were the subject of speciation calculations with the assistance of the computer program PHREEQC (for Windows) v2.17 (Parkhurst and Appelo 1999) and the tried and tested CEMDATA07v2 thermodynamic database (Babushkin et al. 1985, Hummel et al. 2002, Lothenbach et al. 2008, Lothenbach and Winnefeld 2006, Matschei et al. 2007, Möschner et al. 2008, 2009) (Table 3-11). The inclusion of Cl and TIC in the analyses of Lab-6 gives a seemingly complete analysis of the pore water samples with a mean percent error =  $+0.29 \pm 0.60$ ; positive percent errors indicate an excess of cations and negative values an excess of anions in the analysis.

By only analysing the concentrations of Na, K and Ca, predominantly cationic aqueous species of  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Ca}^{2+}$ , respectively, the solution compositions of Lab-1 show the largest positive mean percent error =  $+93.82 \pm 0.67$ . Consequently, by charge balancing the Lab-1 pore water samples on pH, to account for the absence of anions in the analysis, gives the largest pH =  $12.71 \pm 0.01$  (Table 3-11). Including concentrations of Si and S, predominantly anionic aqueous species of  $\text{H}_3\text{SiO}_4^-$  and  $\text{SO}_4^{2-}$ , respectively, the solution compositions of Lab-4 and Lab-7 show lower percent errors, but the calculated mean pH =  $11.99 \pm 0.15$  and  $12.04 \pm 0.01$ , respectively, are still too high (Table 3-11).

With an acceptably low percent error from a seemingly complete analysis, calculating charge balance on pH for Lab-6 has a relatively low effect on the pH values with the largest difference of  $+0.44$  pH units seen for the largest percent error of  $+0.89$  for pore water sample PA-2 (Table 3-11). If the measured C concentrations of  $0.33\text{--}0.35$  mM are excluded, the calculated charge balance on pH increases further, with the largest difference of  $+0.69$  pH units again seen for pore water sample PA-2. The calculated mean pH without carbonation =  $11.09 \pm 0.11$  (Table 3-11) would make the results of Lab-6 comparable with the mean pH =  $11.19$  (S.D.  $\pm 0.06$ ) reported by the other laboratories excluding outliers (Table 3-3).

Furthermore, if the C concentrations were solely buffered by calcite, as would be expected from the limestone component of the cement (Table 3-1), the so calculated C concentrations would be one order of magnitude lower than those measured in Lab-6 (Table 3-12). Conversely, if the pore water samples from Lab-6 were equilibrated with atmospheric  $\text{CO}_2$ , the so calculated C concentrations would be one order of magnitude higher than those measured with a corresponding decrease in the pH of over 2 pH units (Table 3-12). It is reasonable to infer, therefore, that the pore water samples from Lab-6 had undergone some carbonation from atmospheric  $\text{CO}_2$ , which contributed to their consistently lower measured pH values.

**Table 3-11. Measured pH, percent error and calculated charge balance on pH for Lab-1, Lab-4, Lab-6, and Lab-7 pore water samples.**

Lab, Sample/Mean	Measured pH (18°C)	Percent error*	Calculated pH charge balance (18°C)	
			as provided (with carbonation)	without carbonation
Lab-6, PA-1	10.50	+0.29	10.69	11.06
Lab-6, PA-2	10.52	+0.89	10.96	11.21
Lab-6, PA-3a	10.76	-0.30	10.60	10.99
Lab-6, Mean $\pm$ S.D.	$10.59 \pm 0.14$	$+0.29 \pm 0.60$	$10.75 \pm 0.18$	$11.09 \pm 0.11$
Lab-1, Mean $\pm$ S.D.	$11.24 \pm 0.04$	$+93.82 \pm 0.67$	NR	$12.71 \pm 0.01$
Lab-4, Mean $\pm$ S.D.	$11.21 \pm 0.02$	$+12.25 \pm 4.23$	NR	$11.99 \pm 0.15$
Lab-7, Mean $\pm$ S.D.	$11.43 \pm 0.01$	$+12.67 \pm 0.33$	NR	$12.04 \pm 0.01$

\*100 (Cations–Anions)/(Cations+Anions). NR = carbon concentrations Not Reported.

**Table 3-12. Measured and calculated pH values and C concentrations for Lab-6 pore water samples.**

Sample	Measured		Calculated		
	pH (18°C)	TIC conc. (mM)	Calcite buffered C conc.* (µM)	Atmospheric CO <sub>2</sub> buffered	
				pH	C conc. (mM)
PA-1	10.50	0.34 <sup>†</sup>	12.77	8.23	1.20
PA-2	10.52	0.35	12.61	8.31	1.41
PA-3a	10.76	0.33	12.99	8.38	1.66
Mean pH ±S.D.	10.59 ±0.14	0.34 ±0.01	12.79 ±0.19	8.30 ±0.08	1.42 ±0.23

\*pH as measured. <sup>†</sup>Estimated value by analogy with PA-2 and PA-3a.

### 3.5.4 Curing time in the routine (ESL) methods (Lab-6 and Lab-9)

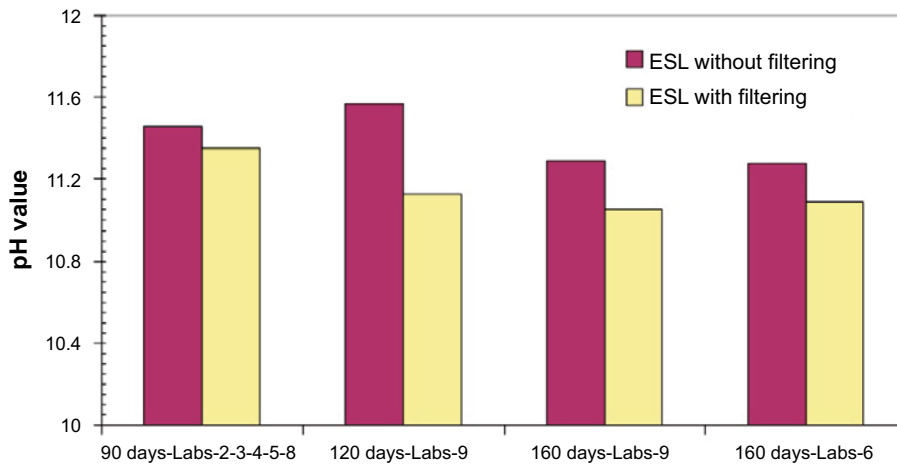
Both Lab-6 and Lab-9 made pH measurements after prolonged curing times using the routine (ESL) methods without and with filtering. For this reason they cannot be included in the statistical analysis of the results because the use of standard used (ISO 5725) requires that all the samples are of the same age. They are nevertheless useful to assess the reproducibility of the routine (ESL) methods after extended curing times and also to assess the extent of pozzolanic reaction in the low pH cement.

The extended curing of 160 and 180 days in Lab-6 was, however, used to assess the reliability of the pore water sample extraction method and a replacement pH electrode described in Section 3.5.1 and 3.5.2, respectively. With these changes, Lab-6 measured pH increases with curing time, which is not a true reflection of the extent of pozzolanic reaction, which should result in a decrease in the measured pH value with increasing curing time.

The pH values obtained by Lab-9 are shown in Table 3-13. In general, assuming that longer curing result in lower pH values from the continuation of the pozzolanic reaction, the measured pH values are in good agreement (±0.2 pH units) with those obtained by the other laboratories after 90 days. The repeatability of the routine (ESL) methods is excellent with SD generally being lower than the ±0.1 error that can be assigned to the pH electrode. The only exceptions to this arise from the consistently lower 1<sup>st</sup> pH measurement using the routine (ESL) method with filtering (Table 3-13). Reasons for this lower 1<sup>st</sup> pH measurement are believed to result from carbonation related to the vacuum pump used to pass the sample through the filter. If these measurements are excluded then the repeatability of the routine (ESL) method with filtering is also excellent after extended curing in Lab-9.

**Table 3-13. pH values measured by Lab-9 using the routine (ESL) methods.**

Laboratory, Sample/Mean	Curing (days)	Without filtering	With filtering	Comment
All laboratories, Mean pH ±SD	90 ±5	11.46 ±0.12	11.35 ±0.10	Excluding Lab-6 and Lab-7 (Table 3-5)
Lab-9, Sample-1	120	11.52	11.00	Lower 1 <sup>st</sup> measurement with filtering
		11.58	11.12	
		11.60	11.14	
Lab-9, Sample-1, Mean pH ±SD	120	11.57 ±0.04	11.09 ±0.08	Excluding 1 <sup>st</sup> measurement
		–	11.13 ±0.01	
Lab-9, Sample-2	160	11.25	10.56	Much lower 1 <sup>st</sup> measurement with filtering
		11.26	11.03	
		11.27	11.06	
Lab-9, Sample-2, Mean pH ±SD	160	11.26 ±0.01	10.88 ±0.28	Excluding 1 <sup>st</sup> measurement
		–	11.05 ±0.02	
Sample-3	160	11.34	10.89	Lower 1 <sup>st</sup> measurement with filtering
		11.33	11.02	
		11.31	11.08	
Lab-9, Sample-3, Mean pH ±SD	160	11.33 ±0.02	11.00 ±0.10	Excluding 1 <sup>st</sup> measurement
		–	11.05 ±0.04	



**Figure 3-15.** Comparison of the mean pore water pH values obtained by different laboratories after different curing times using the routine (ESL) methods.

The mean pH values measured using the routine (ESL) methods without and with filtering by the different laboratories after different curing times are shown in Figure 3-15. This figure provides a visual assessment of the reproducibility of the routine (ESL) methods for different curing times and also of the extent of pozzolanic reaction. This figure illustrates that the mean pH values obtained using the routine (ESL) methods by Lab-6 and Lab-9 after 160 days are very similar and so both laboratories made the tests in a reproducible way. A general decrease of the mean pH value with age can also be observed, which can be attributed to the continued pozzolanic reaction of the low pH cement.

### 3.6 Statistical analysis of the repeatability and the reproducibility of the routine (ESL) methods

(Within-laboratory) repeatability and (between-laboratory) reproducibility are defined as the closeness of agreement between two measurements obtained under repeatable or reproducible conditions, respectively. It is possible to compute the variances of these differences between two measurements ( $2S_r^2$  and  $2S_R^2$ ) and SD  $\sqrt{2}S_r$  or  $\sqrt{2}S_R$ , where  $S_r^2$  is the variance of repeatability and  $S_R^2$  the variance of reproducibility. The uncertainty is equal to the confidence interval of differences (with a confidence limit of  $1-\alpha$ ). By convention, the confidence limit is taken to be 95% and the Student's variable to be equal to 2 (also known as the 'coverage factor') (Feinberg 1995). While  $2\sqrt{2} = 2.83$ , the practical definitions of repeatability ( $r$ ) and reproducibility ( $R$ ) are:

$$r = 2.83S_r$$

$$R = 2.83S_R$$

Under these premises, the repeatability,  $r$ , can be defined as the value below which the absolute difference between two different individual results obtained under the same conditions (e.g. same operator, same device, same laboratory, same period of time, etc) is obtained with a probability of 95%. In the same way, the reproducibility,  $R$ , is the value below which the absolute difference between two different individual results, but obtained under different conditions (e.g. different operators, different device, different laboratories, etc) is obtained with a probability of 95% (Castellote and Andrade 2001).

In the evaluation of the repeatability and the reproducibility of the routine (ESL) methods without and with filtering, several assumptions have to be made in order to use the statistical tests proposed in the ISO 5725 standard:

- All laboratories have made the same number of nine replicate analyses, even though Lab-3 and Lab-8 only made three (Table 3-2).
- Lab-1 has not been included because they only made pH measurements following the reference (PFE) method protocol (Table 3-2).

- It has been assumed that the data distribution follows a normal distribution; Figure 3-16 shows the histogram of the pH values obtained by all the laboratories using the routine (ESL) method without filtering and Figure 3-17 shows the histogram of the pH values obtained using the routine (ESL) method with filtering.
- As the determination of the pH from the OH<sup>-</sup> titration has only been made by four laboratories, this procedure has not been subjected to a statistical test.

The repeatability and the reproducibility tests have been made using the same three laboratory subpopulations for which the *w* ratio was calculated:

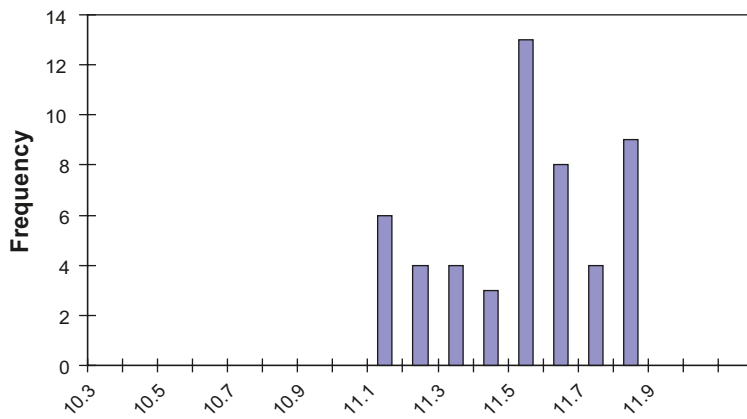
- All laboratories, except Lab-9.
- Excluding the consistently lower pH values reported by Lab-6.
- Excluding both Lab-6 and Lab-7, the latter reporting consistently higher pH values.

The main equations used the statistical study of the repeatability and the reproducibility of the routine methods are given by:

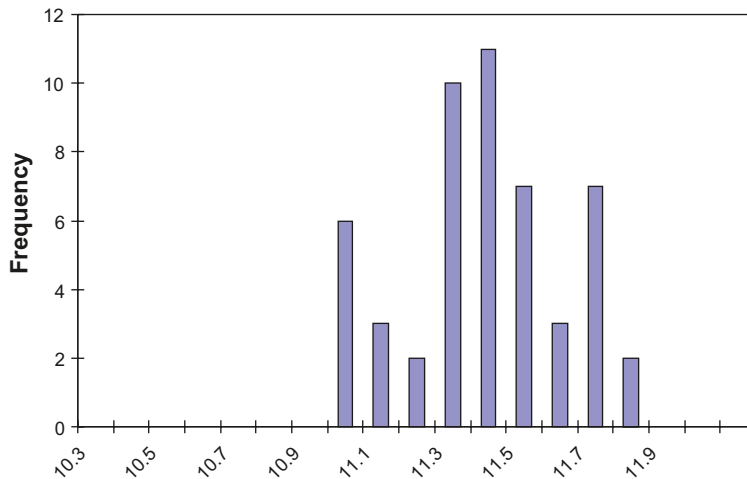
- *Estimation of the repeatability variance ( $S_r^2$ ):*

$$S_r = \sqrt{\frac{SS_r}{N-p}}$$

where  $SS_r$  is the residual, i.e. the within-laboratory sum of squares,  $N$  is the total number of data and  $p$  is the number of laboratories.



**Figure 3-16.** Histogram of the pH values obtained using the routine (ESL) method without filtering.



**Figure 3-17.** Histogram of the pH values obtained using the routine (ESL) method with filtering.

- *Value of repeatability:*

$$r = 2.83 S_r$$

- *Percentage of variation or repeatability variability:*

$$V_r = 100 S_r/m$$

where  $m$  is the gross average value.

- *Estimation of between-laboratory variance ( $S_L^2$ ):*

$$S_L = \sqrt{\frac{(p-1)\left(\frac{SS_L}{p-1}\right) - S_r^2}{N'}}$$

where  $SS_L$  is the factorial, i.e. between-laboratory sum of squares and  $N'$  is the total number of data.

- *Estimation of reproducibility variance ( $S_R^2$ ):*

$$S_R^2 = S_L^2 + S_r^2$$

- *Value of reproducibility:*

$$R = 2.83 S_R$$

- *Percentage of variation or reproducibility variability:*

$$V_r = 100 S_R/m$$

Table 3-14 and Table 3-15 show the statistical parameters obtained for the different laboratory subpopulations using the routine (ESL) methods without and with filtering, respectively.

**Table 3-14. Statistical parameters corresponding to the routine (ESL) method without filtering for different laboratory subpopulations.**

Statistical Parameters	All laboratories	Excluding Lab-6	Excluding Lab-6 and Lab-7
$S_r$	0.047	0.050	0.056
$r$	<b>0.132</b>	<b>0.141</b>	<b>0.159</b>
$V_r(\%)$	0.41%	0.43%	0.49%
$S_R$	0.231	0.170	0.125
$R$	<b>0.654</b>	<b>0.482</b>	<b>0.355</b>
$V_R(\%)$	2.02%	1.48%	1.10%

**Table 3-15. Statistical parameters corresponding to the routine (ESL) method with filtering for different laboratory subpopulations.**

Statistical Parameters	All laboratories	Excluding Lab-6	Excluding Lab-6 and Lab-7
$S_r$	0.050	0.053	0.061
$r$	<b>0.142</b>	<b>0.153</b>	<b>0.172</b>
$V_r(\%)$	0.44%	0.47%	0.53%
$S_R$	0.248	0.187	0.114
$R$	<b>0.702</b>	<b>0.528</b>	<b>0.321</b>
$V_R(\%)$	2.19%	1.63%	1.00%

Several conclusions can be drawn from the statistical parameters shown in Table 3-14 and Table 3-15:

- The routine (ESL) methods without and with filtering show similar repeatability ( $r$ ) and reproducibility ( $R$ ) values and so their accuracy is quite similar.
- The repeatability ( $r$ ) of the routine (ESL) methods without and with filtering is very good, with the values obtained being close to the  $\pm 0.1$  error that can be assigned to the pH electrode. These repeatability values show that with a probability of 95%, the difference between two different individual results obtained under the same conditions in the same laboratory will be below 0.16 without filtering and below 0.17 with filtering. This indicates that all the laboratories involved in the project were able to measure the pH in a repeatable way and so the developed routine (ESL) methods without and with filtering are suitable protocols for measuring the pH of the pore water of low pH cementitious materials.

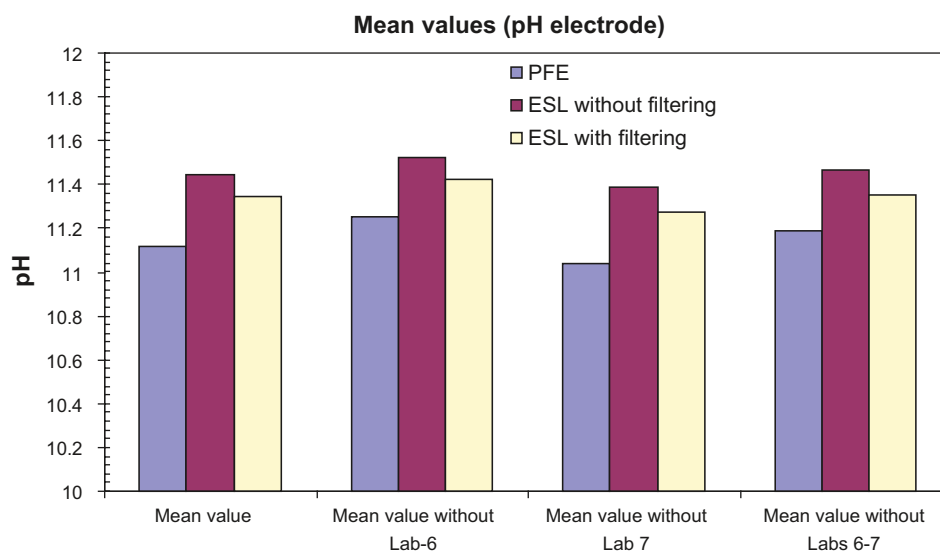
The increase in the  $r$  value by excluding Lab-6 and Lab-7 is a statistical artefact resulting from a smaller subpopulation.

- The reproducibility ( $R$ ) of the routine (ESL) methods without and with filtering only becomes acceptable using the subpopulation that excludes Lab-6 and Lab-7. These reproducibility values show that with a probability of 95%, the difference between two different individual results obtained under the same conditions in different laboratories will be below 0.36 without filtering and below 0.32 with filtering. Taking into account that most of the laboratories have used the routine (ESL) methods for the first time, the reproducibility values so obtained are acceptable.

### 3.7 Comparison of the reference (PFE) and routine (ESL) methods

Figure 3-18 shows the mean pH values obtained using the reference (PFE) and routine (ESL) methods without and with filtering, but which have also been calculated with the exclusion of the consistently lower or higher pH values reported by Lab-6 or Lab-7, respectively.

Overall, similar results are obtained using the reference (PFE) and routine (ESL) methods without and with filtering. The largest difference in terms of mean pH = 0.32 when the reference (PFE) method is compared to the routine (ESL) method without filtering and all laboratories are included.



**Figure 3-18.** Comparison between the mean pH measurements obtained using the reference (PFE) and routine (ESL) methods without and with filtering.

The lowest difference in mean pH = 0.1 when the reference (PFE) method is compared to the routine (ESL) method with filtering and the results from Lab-6 and Lab-7 are excluded. These results are consistent with those obtained during the preliminary experimental investigation at CSIC (Appendix B), where the pH values obtained using the routine (ESL) method with filtering were in good agreement with those obtained using the reference (PFE) method.

A statistical analysis has been made of the trueness of the measured pH values using the routine (ESL) methods without and with filtering compared to those using the reference (PFE) method. This was undertaken as a part of the main objective of the current project, which was to address the following points:

- The development of a pH measurement method that is simple and suitable for laboratory use.
- A method that can be used in different laboratories using different low pH cementitious materials.
- A rapid evaluation of the suitability of a candidate low pH cementitious material to be used in a HLW repository.

An extension of the ISO 5725 standard is the use of repeatability and reproducibility to quantify the trueness of the pH values obtained by the routine (ESL) methods without and with filtering compared to the reference (PFE) method. Simple statistical tests are available to perform verifications for trueness. This trueness comparison is performed statistically by calculating the  $w$  ratio which represents the trueness of the ESL method as compared to the PFE:

$$w = \frac{|\bar{x}_M - \bar{x}_A|}{\delta}$$

where  $\bar{x}_M$  is the gross average of the reference (PFE) method,  $\bar{x}_A$  is the gross average of the alternative method (the routine (ESL) methods in this case) and the SD,  $\delta$ , is calculated from:

$$\delta = 2 \sqrt{\frac{S_{LA}^2 + S_{rA}^2}{p_A}}$$

where  $S_{LA}$  is the within-laboratory variance,  $S_{rA}$  is the between-laboratory variance and  $p_A$  is the number of laboratories included in the test. To decide if the routine (ESL) methods are a true reflection of the reference (PFE) method, the ratio  $w$  must be less than or equal to unity ( $w \leq 1$ ). Furthermore, the accuracy of the routine (ESL) methods can be assessed from the closeness of the  $w$  ratio to unity.

This statistical test has been made using three laboratory subpopulations:

- All laboratories, except Lab-9.
- Excluding the consistently lower pH values reported by Lab-6.
- Excluding both Lab-6 and Lab-7, the latter reporting consistently higher pH values.

Table 3-16 shows the calculated  $w$  ratios from the three laboratory subpopulations from the routine (ESL) methods without and with filtering.

**Table 3-16.  $w$  ratios corresponding to the routine (ESL) methods without and with filtering for different laboratory subpopulations.**

Routine (ESL) method	w ratio		
	All laboratories, except Lab-9	Excluding Lab-6	Excluding Lab-6 and Lab-7
Without filtering	1.88	1.94	1.55
With filtering	1.20	1.13	0.98

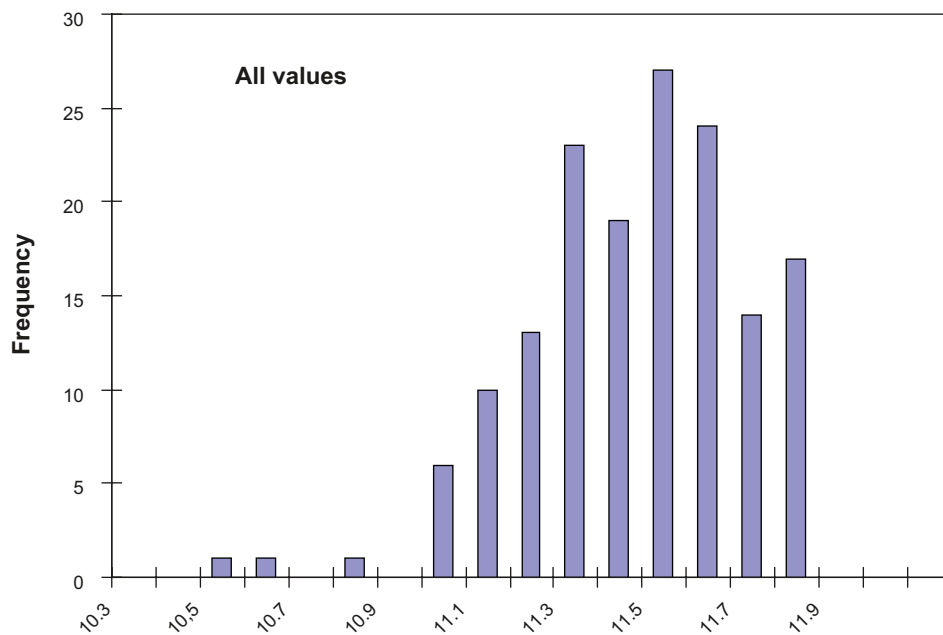
Several conclusions can be drawn from the calculated  $w$  ratios shown in Table 3-7:

- When the outlier results from Lab-6 and Lab-7 are excluded, the  $w$  ratios obtained in the routine (ESL) methods without and with filtering are acceptable.
- In all subpopulation tests, the routine (ESL) method with filtering is in better agreement with the reference (PFE) method results, as the  $w$  ratios are always smaller. Moreover, when the outlier results are excluded, according to the ISO 5725 standard, the  $w$  ratio being close to unity is indicative of the routine (ESL) method with filtering having the same trueness as those measured using the reference (PFE) method.
- In all subpopulation tests, the  $w$  ratio decreases when the outlier results are discarded. From a statistical point of view this confirms that these results are inconsistent with those obtained by the other laboratories.

Given that most of the laboratories have used these protocols for the first time, it can be expected that through continued use more accurate pH results will be obtained.

Other qualitative confirmation of the trueness of the developed routine (ESL) methods is by plotting all the pH measurement results in a histogram, together with the results obtained from the reference (PFE) method (Figure 3-19).

Excluding the data between 10.5 and 10.8, corresponding to the consistently lower pH measurements made by Lab-6, the data distribution approximates a normal distribution, which is indicative of all the data belonging to the same statistical population. Moreover, this implies that the pH measurements are reasonably similar and so the developed routine (ESL) methods are sufficiently accurate.



**Figure 3-19.** Histogram of all pH measurements reported by all laboratories using the routine (ESL) methods.



### 3.8 Conclusions from the preliminary protocols

The main conclusions drawn from the investigation of the preliminary protocols can be summarized as follows:

1. The repeatability of the pH measurement protocols evaluated, the reference (PFE) method and routine (ESL) methods without and with filtering, is very good. The pH measurements are close to the  $\pm 0.1$  pH unit error that can be assigned to the pH electrode when measuring high pH ( $> 10$ ) solutions. This means that all the laboratories involved in the project made the pH measurement in a very repeatable way which has allowed a critical and accurate evaluation of the methods.
2. Some notable differences have been found in the pH measurements made, but these were restricted to two laboratories which did not follow the recommended protocols as opposed to problems with the protocols themselves.
3. The reference (PFE) method ensures the acquisition of accurate pH values and chemical composition of the pore water taken from low-pH cementitious materials. There are no differences, within error, in measuring the pH directly with a pH electrode or in its determination by  $\text{OH}^-$  titration.
4. Taking into account that most of the laboratories have used the routine (ESL) methods for the first time, the results are quite promising in showing satisfactory repeatability and reproducibility values. When the outlier results are discarded the trueness obtained in the routine (ESL) methods is acceptable when compared to the reference (PFE) method. This trueness is better for the routine (ESL) method with filtering, which, according to ISO 5725, is as accurate as the reference (PFE) method. Therefore, major modifications to the developed protocols are unnecessary, although minor improvements could be considered.
5. For this low pH cementitious material, the expected reproducibility of the pH measurement, with a probability of 95%, is  $\pm 0.12$  pH units using the reference (PFE) method (based on 2 times the calculated SD) and  $\pm 0.3$  pH units using the routine (ESL) methods without and with filtering from the reproducibility values.
6. From the results and statistical analyses, the routine (ESL) method with filtering protocol and measuring the pH with a combination pH electrode is recommended to measure the pH of the pore water of a low pH cementitious material. This protocol fulfils the requirements of a method that is reproducible in different laboratories, is fast, simple and suitable for laboratory use, and that allows an accurate pH measurement the pore water of a low pH cementitious material. To minimize errors, the protocols must be followed carefully. As found in this instance, the samples must be subject to the same curing conditions and the maximum time periods allowed for each procedure must not be exceeded.
7. It is very important to use a pH meter which can compensate for fluctuations in temperature and a combination pH electrode specifically designed for measuring high pH solutions. Temperature correction must also be included as a part of the calibration and all solutions should be the same temperature prior to use. It is recommended that the laboratory temperature, during the pH measurement period, is within the range of 20–25°C. Furthermore, if the routine (ESL) method without filtering is used then the combination pH electrode should be suitable for pH measurements in suspensions.

## 4 Final protocol investigation

### 4.1 Introduction

The pH measurement of the pore water of a low pH cementitious material was assured by the preliminary protocol investigation of the reference (PFE) method and routine (ESL) methods without and with filtering in the low pH cement pastes fabricated by SKB (Chapter 3). It was further considered necessary to validate the developed protocols for different low pH cementitious materials.

Four low pH cementitious materials, two concretes and two cement pastes, were prepared by four participating organisations/laboratories (Lab-4, Lab-5, Lab-7, and Lab-8) and samples were distributed amongst Labs 2-9. The pH measurement of the pore water of each low pH cementitious material was undertaken following the revised protocols after development and testing of the preliminary protocols detailed in Chapter 3.

Table 4-1 shows the laboratories involved in the final protocol investigation and the number of pore water pH measurements taken for each low pH cementitious material after  $90 \pm 5$  days of curing. The number of measurements designated to each laboratory was the same as used in the preliminary protocol investigation (cf. Table 3-2).

**Table 4-1. Laboratories involved in the final protocol investigation and the number of pore water pH measurements carried out for each low pH cement material after  $90 \pm 5$  days curing.**

Organisation	Lab	Lab number	PFE	ESL Without filtering	ESL With filtering
RAWRA/NRI	NRI	Lab-2	–	9	9
Nagra	TFB	Lab-3	–	3	3
Enresa	CSIC	Lab-4	3*	9	9
SKB/Posiva	VTT	Lab-5	–	9	9
CEA	CEA	Lab-6	–	3	3
JAEA	TCL	Lab-7	–	9	9
NUMO	CRIEPI	Lab-8	3*	3	3
AECL	AECL	Lab-9	–	9	9
<b>Total measurements</b>			<b>6*</b>	<b>54</b>	<b>54</b>

\* In the cement pastes, but not in the concretes. Lab-8 also used the reference (PFE) method for the concrete samples, but in this case they could not make the necessary three measurements to be included in the statistical analysis.

It should be noted that Lab-9 analyzed the concretes from SKB/Posiva after 90 days, the samples from Enresa and NUMO after 140 days, and the samples from JAEA after 160 days. Consequently, with the exception of the correctly timed SKB/Posiva samples, all other data provided by this laboratory are not included in the statistical analysis, but are meaningful to assess the continuation and/or extent of the pozzolanic reaction.

### 4.2 Sample preparation

The mixture proportions and appearance of the four low pH cementitious material samples are described in the following sections.

#### 4.2.1 CM-1: SKB/Posiva low pH concrete sample

The concrete samples from SKB/Posiva were a low pH concrete developed for the emplacement room plugs (Vogt et al. 2009) and were prepared by CBI, Stockholm, on 15<sup>th</sup> June 2010. The nominal concrete composition is shown in Table 4-2. Figure 4-1 shows the concrete samples (10×10×10 cm) from SKB/Posiva as received by CSIC.

**Table 4-2. Composition of the low pH concrete from SKB/Posiva.**

Material	kg/m <sup>3</sup>
CEM I 42.5 MH/SR/LA	120
Silica fume (densified)	80
Water	165
Limestone filler L25	369
Sand 0–8 mm	1,037
Gravel 8–16 mm	558
Glenium 51 (Superplasticizer)	6.38
Water/cement	1.375
Water/binder	0.825
Water/powder	0.29

#### 4.2.2 CM-2: Enresa low pH concrete sample

The concrete samples from Enresa were similar to the low pH concrete developed for the long plug in the ESDRED project, but in this case using Spanish aggregates. Cylindrical samples (15Ø×10 cm, Figure 4-2) of the composition shown in Table 4-3 were prepared in the CSIC laboratory on 29<sup>th</sup> June 2010.

**Table 4-3. Composition of the low pH concrete from Enresa.**

Material	kg/m <sup>3</sup>
CEM I 42.5 MH/SR/LA	165
Silica fume (densified)	110
Water	230
Limestone filler L25	70
Sand 0–3 mm	1,066
Gravel 3–6 mm	593
Superplasticizer	5.1
Water/cement	1.39
Water/binder	0.84

#### 4.2.3 CM-3: JAEA low pH cement pastes

The low pH cement paste samples from JAEA were developed as a grouting material. Samples (10×10×10 cm, Figure 4-3) were prepared by Taiheiyō Consultants Ltd. (TCL) on 18<sup>th</sup> June 2010 using the mixture proportions given in Table 4-4.

**Table 4-4. Mixture proportions (by mass) of the low pH cement paste from JAEA.**

Material	Per 100 g binder
Superfine OPC	50
Silica fume	50
Superplasticizer	5.5
Water	125
Superplasticizer/Binder ratio	0.055
Water/Binder ratio	1.25



*Figure 4-1. Concrete samples from SKB/Posiva as received by CSIC.*



*Figure 4-2. Concrete samples from Enresa.*



*Figure 4-3. Hardened low pH cement paste samples from JAEA as received by CSIC.*



*Figure 4-4. Cement paste samples from NUMO. Images from Lab-4 as received by CSIC.*

#### 4.2.4 CM-4: NUMO low pH cement pastes

Prismatic low pH cement paste samples (4×4×16 cm, Figure 4-4) from NUMO were prepared by CRIEPI on 1<sup>st</sup> July 2010 using the mixture proportions shown in Table 4-5.

**Table 4-5. Mixture proportions (by mass) of the low pH cement paste from NUMO.**

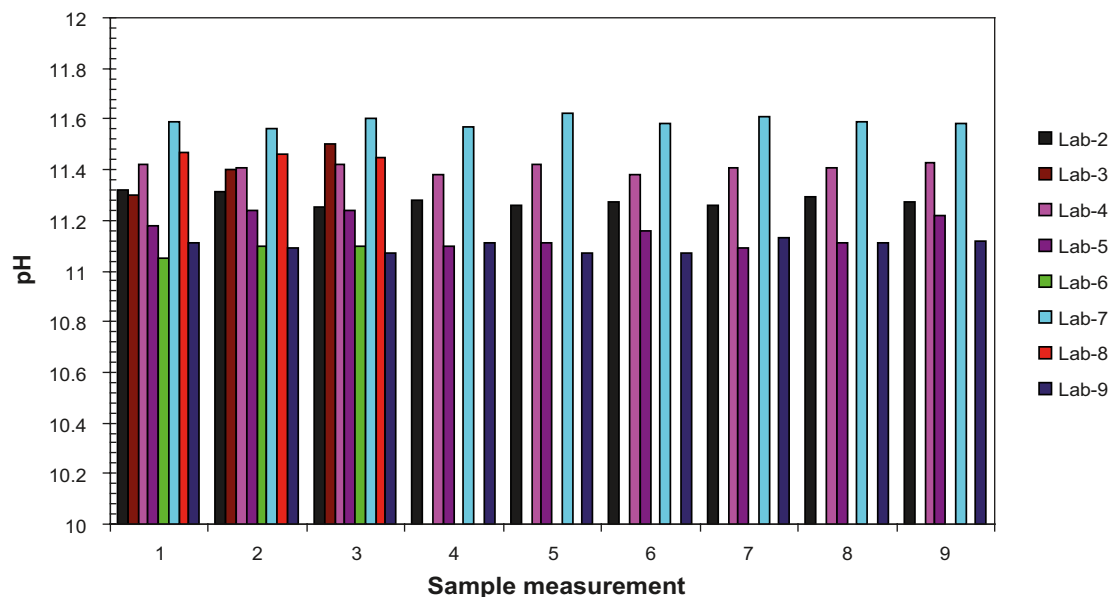
Material	Per 100 g binder
OPC	60
Fly ash	40
Water	35
Water/Binder ratio	0.35

### 4.3 Results

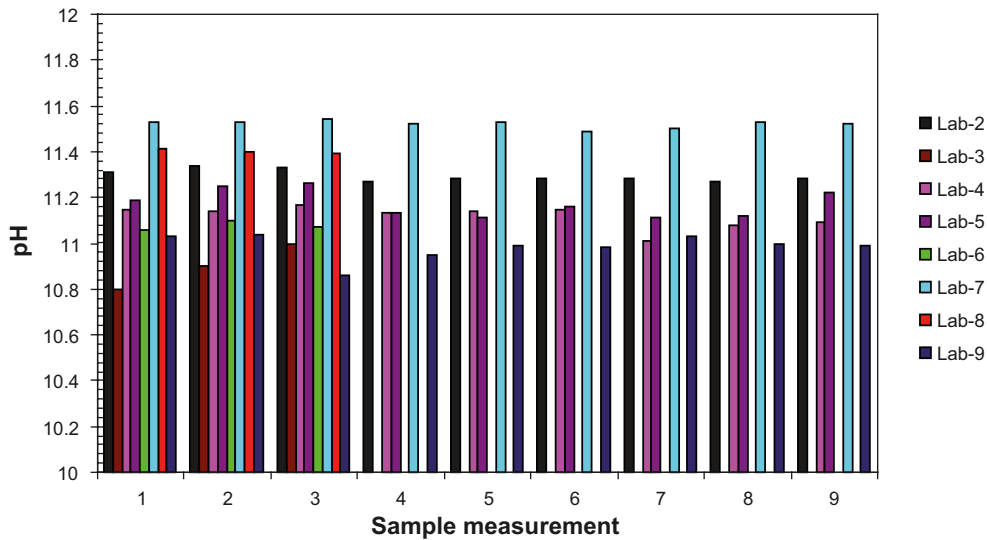
#### 4.3.1 Routine (ESL) methods results for the SKB/Posiva concrete

Figure 4-5 and Figure 4-6 show the results obtained from replicate pH measurements of the SKB/Posiva concrete sample using the routine (ESL) methods without and with filtering, respectively. In all cases, the pore water pH was measured with a pH and temperature calibrated combination pH electrode under a controlled N<sub>2</sub> atmosphere.

It can be seen that in the routine (ESL) methods without and with filtering, the 9 or 3 replicate pore water pH measurements in each laboratory were of low variability, which is a reflection of the protocol having good (within-laboratory) repeatability. In the routine (ESL) method without filtering, most of the pH values so obtained were between 11.15 and 11.40, whereas in the routine (ESL) method with filtering the pH values were between 11 and 11.25. Lowering the pH by approximately 0.25 pH units by filtering the solution was broadly seen in all laboratories. This effect was also observed in the preliminary protocol investigation (Table 3-5), the preliminary experiments (Appendix B), is known for other cement systems (Räsänen and Penttala 2004) and is well known in the chemical literature where it is referred to as the suspension effect (Oman et al. 2007) and references therein.



**Figure 4-5.** pH values measured with a pH electrode using the routine (ESL) method without filtering the suspension for the SKB/Posiva sample.

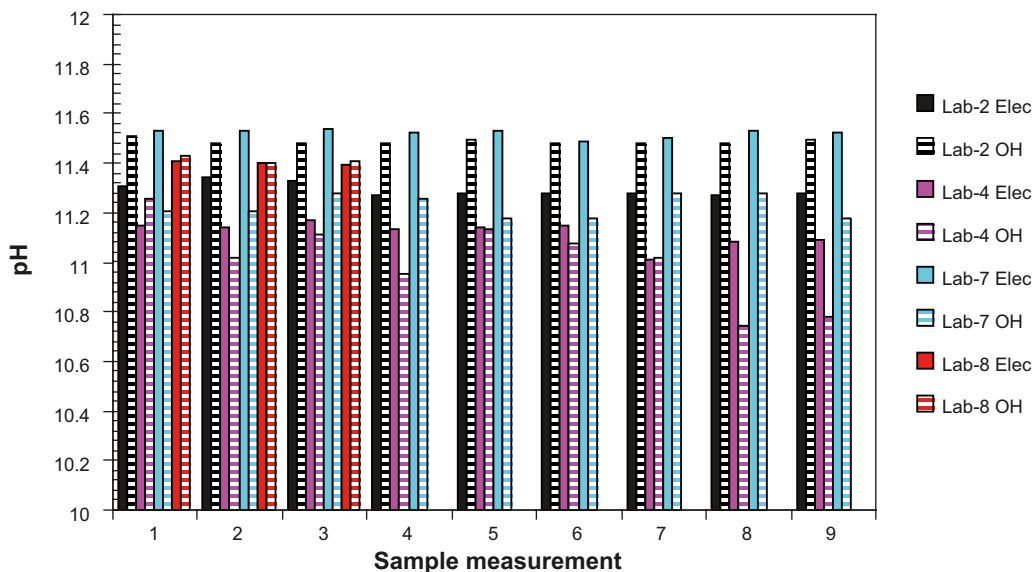


**Figure 4-6.** pH values measured with a pH electrode using the routine (ESL) method with filtering for the SKB/Posiva sample.

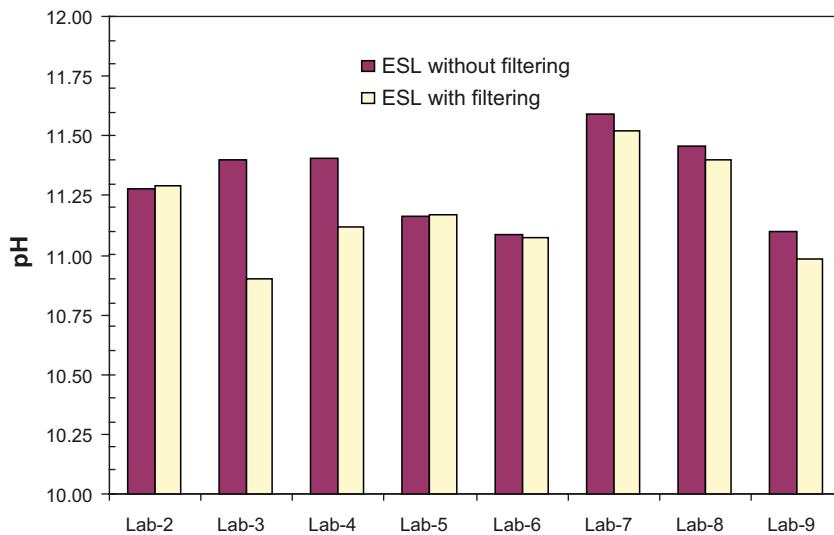
Lab-7 again reported that the samples were kept sealed after their reception, affecting the pozzolanic reaction and resulting in the measured pH values of the routine (ESL) methods being consistently higher than in the other laboratories.

Laboratories 2, 4, 7, and 8 also determined the pH by OH<sup>-</sup> titration (Figure 4-7). In general, although the pH results were not enormously different, the variability within and between laboratories was increased. As already described in Chapter 3 and Appendix B, this confirms that the pH measurement in the routine (ESL) method with filtering should only be made directly with a combination pH electrode.

Table 4-6 shows the mean pH and ±SD for the SKB/Posiva concrete sample reported from all laboratories and excluding Lab-7. Figure 4-8 shows a comparison of the mean pH values obtained from the same samples using the routine (ESL) methods without and with filtering in each laboratory.



**Figure 4-7.** Comparison of pH values obtained by pH electrode (Elec) and OH<sup>-</sup> titration (OH) using the routine (ESL) method with filtering for the SKB/Posiva sample.



**Figure 4-8.** Comparison between the pH values obtained from the routine (ESL) methods without and with filtering for the SKB/Posiva sample.

**Table 4-6.** Mean pH values and  $\pm$ SD from the routine (ESL) methods for the SKB/Posiva sample.

Laboratories included	Without filtering	With filtering	
	pH electrode	pH electrode	OH <sup>-</sup> titration
All laboratories	11.31 $\pm$ 0.18	11.20 $\pm$ 0.20	11.26 $\pm$ 0.22
All laboratories except Lab-7	11.25 $\pm$ 0.14	11.14 $\pm$ 0.15	11.27 $\pm$ 0.26

It can be clearly observed from Figure 4-8 that the mean pH values obtained for the SKB/Posiva concrete are quite similar in most of the laboratories, with differences typically lower than 0.25 pH units. Moreover, when the pH values from Lab-7 are not taken into account, the decrease in SD becomes close to the  $\pm$ 0.1 error assigned to the pH electrode (Table 4-6). The reverse tendency is seen in the pH values determined by OH<sup>-</sup> titration, where the SD increases by excluding Lab-7, but which is against the recommended protocol of using a pH electrode for the routine (ESL) method with filtering and so can be reasonably ignored.

### 4.3.2 Routine (ESL) methods results for the Enresa concrete

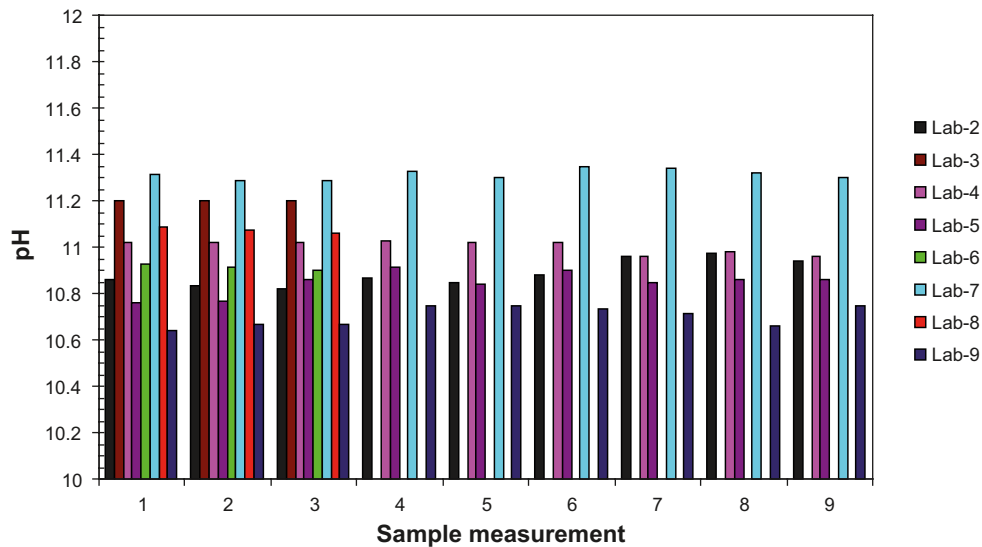
Figure 4-9 shows the replicate pH measurements of the Enresa concrete sample from each laboratory using the routine (ESL) method without filtering. Figure 4-10 and Figure 4-11 show those obtained from a pH electrode and pH electrode vs. OH<sup>-</sup> titration, respectively, using the routine (ESL) method with filtering.

As seen for the SKB/Posiva concrete samples, each laboratory obtained near identical pH values for each replicate measurement, demonstrating excellent (within-laboratory) repeatability of the routine (ESL) methods without and with filtering. Most of the pH values obtained without filtering were between 10.85 and 11.15, (Figure 4-9), whereas the pH values obtained with filtering were slightly lower, ranging from 10.65 to 10.90 (Figure 4-10). Again, the effect of filtering on lowering the pH has been seen in all previous tests (Table 3-5, Table 4-6 and Appendix B) and is referred to as the suspension effect (Oman et al. 2007) (and references therein).

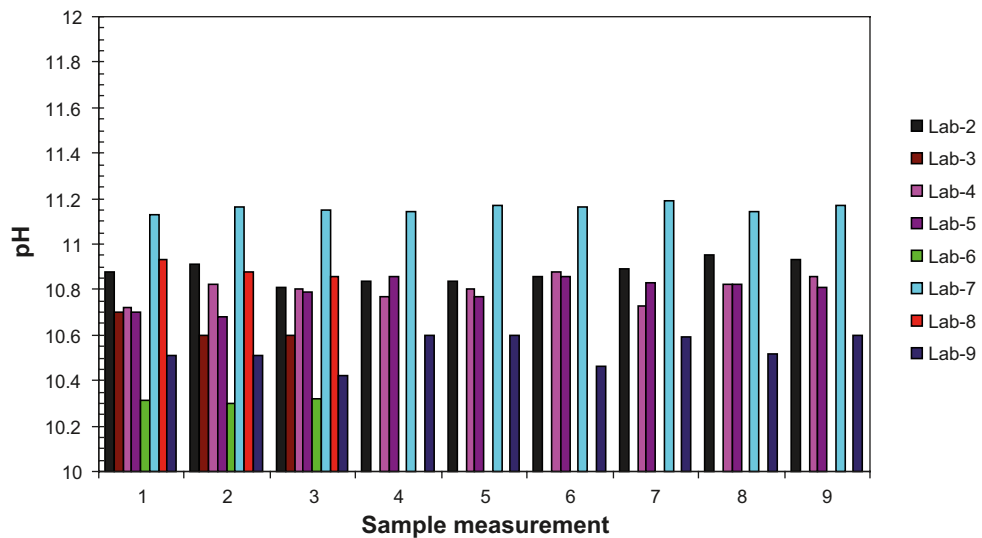
Lab-6 again reported consistently lower pH values using the routine (ESL) method with filtering (Figure 4-10) and Lab-7 again consistently higher pH values using the routine (ESL) methods without and with filtering (Figure 4-9 and Figure 4-10). In the case of Lab-6, the lower pH values

were only observed after filtering. Comparing the pH measurements made without (Figure 4-9) and with filtering (Figure 4-10), it can be seen that Lab-6 also recorded the largest drop in pH of approximately 0.6 pH units as a result of the suspension effect. The higher pH values reported by Lab-7 were again a consequence of keeping the samples sealed after their reception affecting the extent of pozzolanic reaction (described in Chapter 3). The measured pH values in Lab-9 are also consistently lower for the routine (ESL) methods without and with filtering. The lower pH values measured in Lab-9 can be attributed to the measurements being made after 140 days, thereby increasing the extent of pozzolanic reaction.

The pH determined by OH<sup>-</sup> titration reported by Lab-2, Lab-4, Lab-7, and Lab-8 shows a wider variability (Figure 4-11), which again confirms the recommended use of a combination pH electrode for the pH measurements in the routine (ESL) method with filtering protocol.



**Figure 4-9.** Pore water pH measured with a combination pH electrode using the routine (ESL) method without filtering for the Enresa sample.



**Figure 4-10.** Pore water pH measured with a combination pH electrode using the routine (ESL) method with filtering for the Enresa sample.



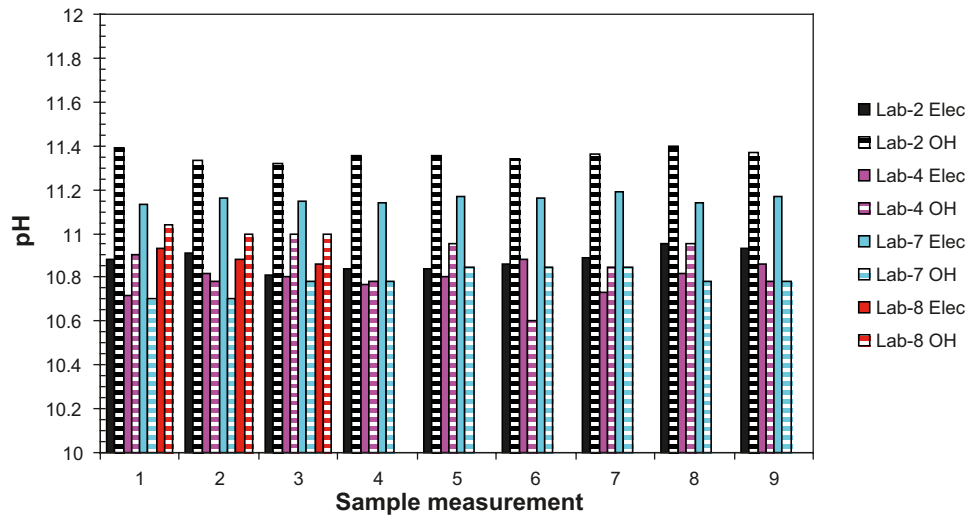


Figure 4-11. Comparison of pore water pH measured directly with a pH electrode (Elec) and determined indirectly by OH<sup>-</sup> titration (OH) using the routine (ESL) method with filtering for the Enresa sample.

Table 4-7 shows the mean pH values and  $\pm$ SD taking into account all laboratories and different subpopulations thereof, excluding Lab-6, Lab-7 and Lab-9 individually and excluding all these outlying laboratories, and Figure 4-12 presents the mean pH values obtained for the Enresa concrete sample from each laboratory using the routine (ESL) methods without and with filtering.

Table 4-7. Mean pore water pH values and  $\pm$ SD from the routine (ESL) methods without and with filtering for the Enresa sample.

Laboratories included	Without filtering	With filtering	
	pH electrode	pH electrode	OH <sup>-</sup> titration
All laboratories	10.97 $\pm$ 0.20	10.80 $\pm$ 0.23	11.00 $\pm$ 0.26
All laboratories except Lab-6	–	10.82 $\pm$ 0.20	–
All laboratories except Lab-7	10.90 $\pm$ 0.14	10.72 $\pm$ 0.18	11.09 $\pm$ 0.26
All laboratories except Lab-9	11.02 $\pm$ 0.18	10.85 $\pm$ 0.21	11.09 $\pm$ 0.26
Discarding all outliers	10.95 $\pm$ 0.11	10.81 $\pm$ 0.09	11.09 $\pm$ 0.26

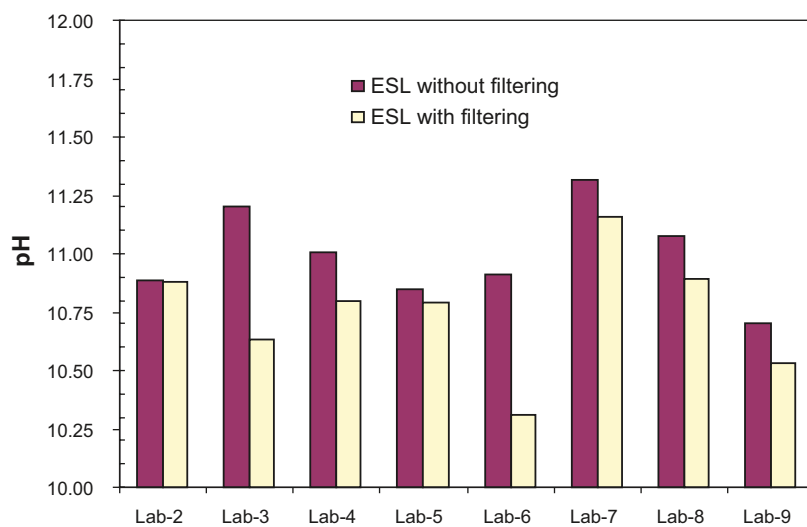


Figure 4-12. Comparison between the pore water pH values for the Enresa sample using the routine (ESL) methods without and with filtering.

It can be observed from Figure 4-12 that the majority of mean pH values were similar for the Enresa concrete sample. Again, by discarding the outliers (Table 4-7), the SD becomes close to or even within the  $\pm 0.1$  error that can be assigned to the pH electrode.

An indicator of the good reproducibility of the developed routine (ESL) methods without and with filtering protocols is that for two similar, but not identical low pH concretes (SKB/Posiva and Enresa), the mean pH values obtained are within  $\pm 0.3$  pH units for both types of concretes (Table 4-6 and Table 4-7).

#### 4.3.3 Reference (PFE) and routine (ESL) methods results for the JAEA low pH cement paste

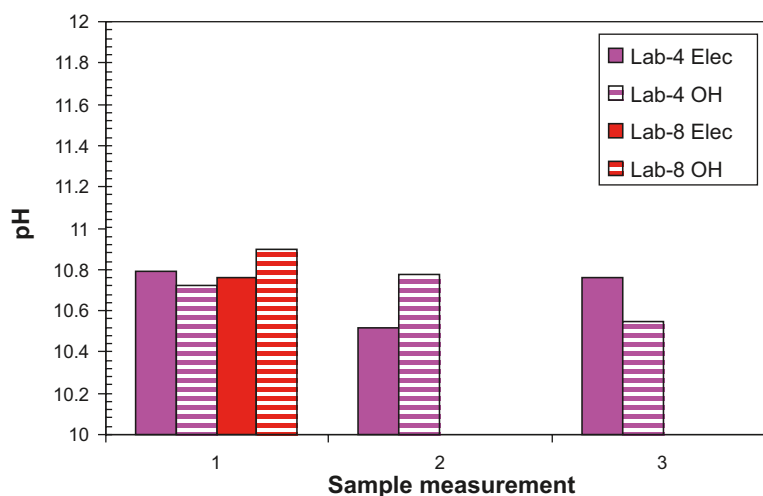
Figure 4-13 shows the replicate pH values measured with a combination pH electrode and determined by  $\text{OH}^-$  titration for the JAEA low pH cement paste sample using the reference (PFE) method.

Very similar pH values were obtained by both Lab-4 and Lab-8 and moreover, by both methods of obtaining the pH value. The mean pH value measured with a combination pH electrode was  $10.71 \pm 0.13$  and as determined by  $\text{OH}^-$  titration was  $10.74 \pm 0.15$ . The difference in mean pH values is less than the  $\pm 0.1$  error that can be assigned to the pH electrode. As noted in Chapter 3, using a pH electrode or  $\text{OH}^-$  titration are both suitable to determine a reliable pH value in the reference (PFE) method. Reasons for the suitability of  $\text{OH}^-$  titration in the reference (PFE) method, but its inefficiency in the routine (ESL) method with filtering were not subject to further investigation.

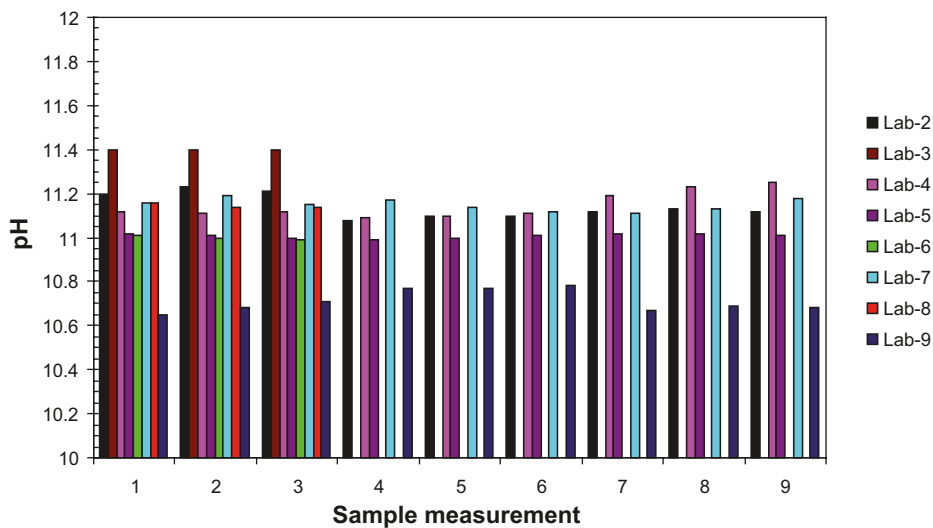
Figure 4-14 shows the replicate pH measurements of the JAEA low pH cement paste sample from each laboratory using the routine (ESL) method without filtering. Figure 4-15 and Figure 4-16 show those obtained by a pH electrode and pH electrode vs.  $\text{OH}^-$  titration, respectively, using the routine (ESL) method with filtering.

The repeatability of the pH measurements made in each laboratory was very good. In this case, however, the reproducibility is higher in the routine (ESL) method without filtering than with filtering, even without taking into account the consistently lower pH values reported by Lab-9. Most reported pH values in the routine (ESL) method without filtering, were between 11.00 and 11.20, whereas the pH values in the routine (ESL) method with filtering were generally lower and between 10.50 and 11.00.

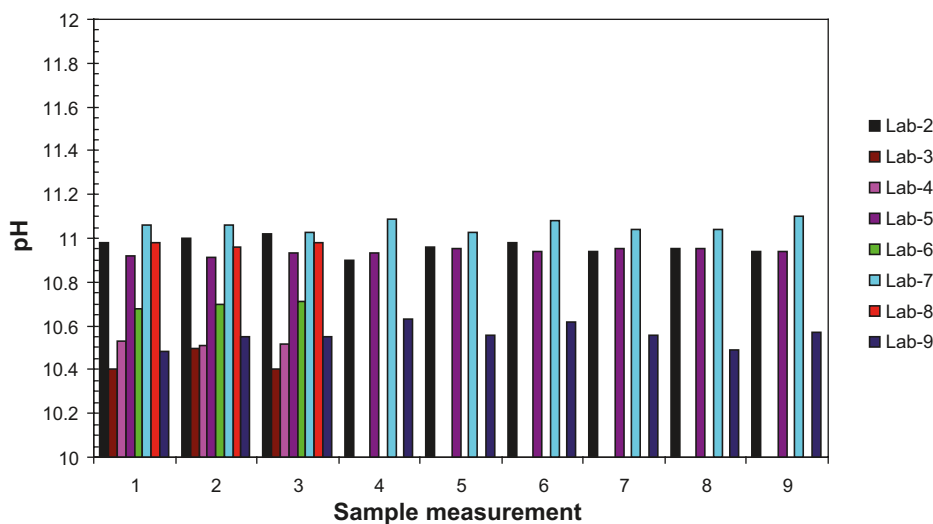
Large disparities were observed between the pH values measured by a combination pH electrode and determined by  $\text{OH}^-$  titration within each laboratory and furthermore, that the pH values determined by  $\text{OH}^-$  titration between laboratories were very variable using the routine (ESL) method with filtering (Figure 4-16). These results again confirm that pH determination by  $\text{OH}^-$  titration is unsuitable in the routine (ESL) method with filtering and that the pH should be measured directly using a combination pH electrode.



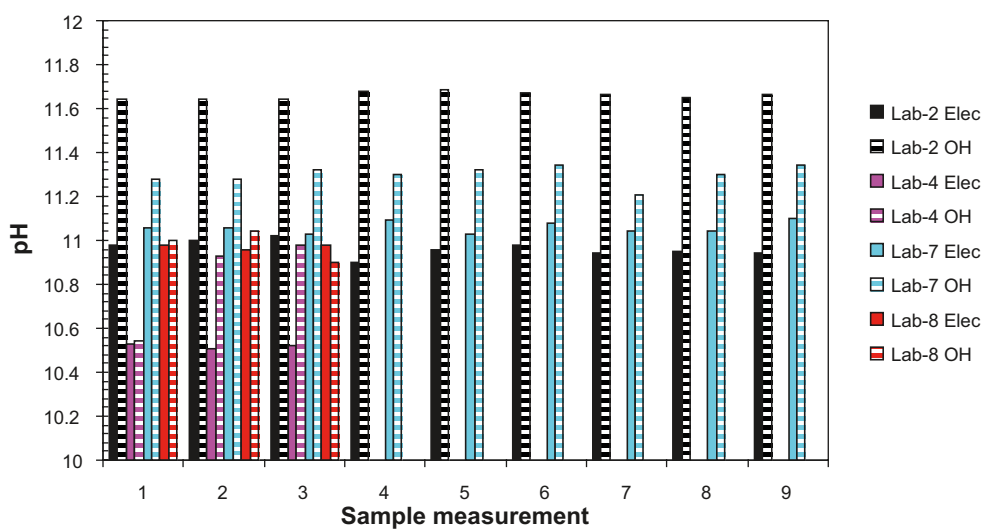
**Figure 4-13.** Comparison of the pore water pH values measured by pH electrode (Elec) and determined by  $\text{OH}^-$  titration (OH) using the reference (PFE) method for the JAEA sample.



**Figure 4-14.** Pore water pH values measured with a combination pH electrode using the routine (ESL) method without filtering for the JAEA sample.



**Figure 4-15.** Pore water pH values measured with a combination pH electrode using the routine (ESL) method with filtering for the JAEA sample.



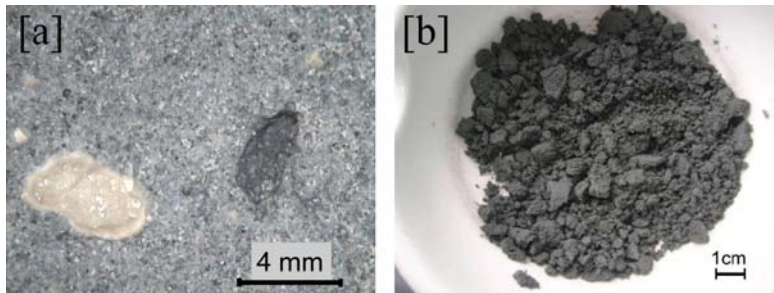
**Figure 4-16.** Comparison of pore water pH values measured with a combination pH electrode and determined by  $\text{OH}^-$  titration using the routine (ESL) method with filtering for the JAEA sample.

In measuring the pore water pH of the JAEA low pH cement paste, Lab-4 observed coarse ( $\varnothing = 0.5\text{--}5\text{ mm}$ ) particles (Figure 4-17a) in the samples. Consequently, these pastes were difficult to grind to a powder  $\approx 80\ \mu\text{m}$  as defined in the protocol (Figure 4-17b), and so did not disperse well when mixed with  $\text{CO}_2$  free deionised water, which necessitated repeating the routine (ESL) methods a number of times to obtain representative pH values. This sample heterogeneity is believed to be the main contributory factor to the large drop of  $\approx 0.6\text{ pH}$  units reported by Lab-4 and the  $\approx 1.0\text{ pH}$  unit drop reported by Lab-3 (Figure 4-15 and Figure 4-16).

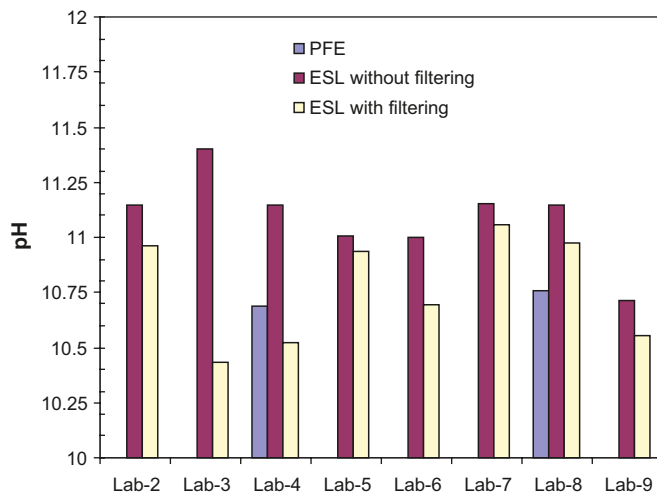
Table 4-8 shows the mean pH values and the  $\pm\text{SD}$  taken from all and subpopulations of the different laboratories and Figure 4-18 presents the mean pH values reported by each laboratory for the JAEA low pH cement paste, using the reference (PFE) and the routine (ESL) methods without and with filtering. Overall, similar results were obtained by the reference (PFE) and routine (ESL) methods and confirm the recommendation in Section 3.5 that the pH values obtained by pH electrode using the routine (ESL) method with filtering are in close agreement with those obtained using the reference (PFE) method. In this case, the higher SD of the routine (ESL) method with filtering can be assigned to the problems in grinding the sample.

**Table 4-8. Mean pH values and  $\pm\text{SD}$  from reference (PFE) and routine (ESL) methods without and with filtering for the JAEA sample.**

Laboratories included	PFE		ESL		
	pH electrode	$\text{OH}^-$ titration	Without filtering	With filtering	
			pH electrode	pH electrode	$\text{OH}^-$ titration
Lab-4 and Lab-8	10.71 $\pm$ 0.13	10.74 $\pm$ 0.15	–	–	–
All laboratories	–	–	11.06 $\pm$ 0.18	10.76 $\pm$ 0.29	11.16 $\pm$ 0.46
All laboratories except Lab-9	–	–	11.13 $\pm$ 0.10	10.80 $\pm$ 0.30	11.16 $\pm$ 0.46



**Figure 4-17.** (a) Coarse particles observed in JAEA low pH cement paste which (b) made it difficult to grind to a  $80\ \mu\text{m}$   $\varnothing$  powder as defined in the routine (ESL) methods protocol.



**Figure 4-18.** Comparison between pore water pH values obtained using the reference (PFE) and the routine (ESL) methods without and with filtering for the JAEA sample.

#### 4.3.4 Reference (PFE) and routine (ESL) methods results from NUMO low pH cement paste

Figure 4-19 shows the replicate pH values measured with a combination pH electrode and determined by OH<sup>-</sup> titration for the NUMO low pH cement paste sample using the reference (PFE) method.

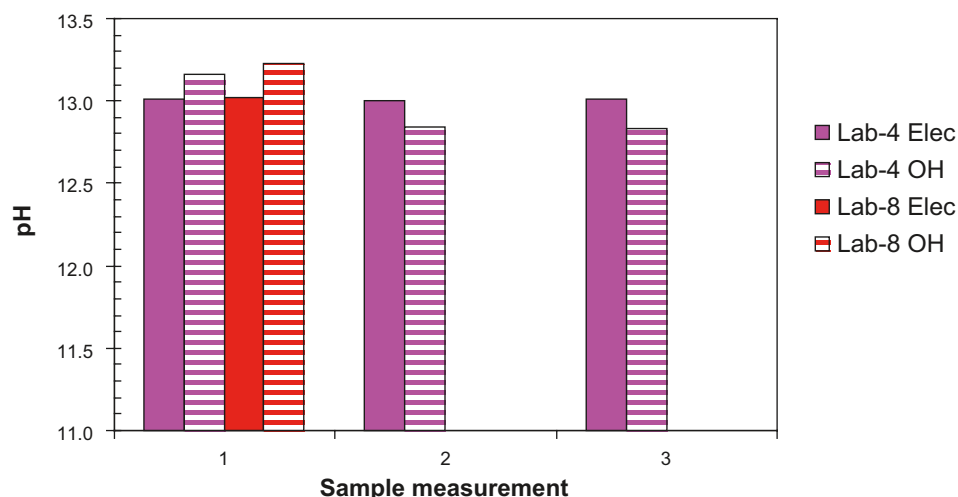
Both Lab-4 and Lab-8 obtained near identical pH values as measured with a combination pH electrode and as determined by OH<sup>-</sup> titration for the reference (PFE) method. The mean pH value measured with a combination pH electrode was 13.01 ±0.01 and determined by OH<sup>-</sup> titration was 13.02 ±0.21. Despite these pH values being too high for the NUMO cement paste to be considered a candidate low pH cement material, the similarity of the reported pH values again confirms a reliable pH value can be obtained for the reference (PFE) method by measuring the pH with a combination pH electrode and determined by OH<sup>-</sup> titration. Furthermore, that both procedures can tentatively be used for conventional high pH cementitious materials and are not only limited for use with low pH cementitious materials.

The high pH of the NUMO cement paste pore water can be attributed to the use of fly ash as a pozzolanic additive, which is well known to have a pozzolanic reaction on the order of years as opposed to days and weeks for silica fume (Atkins and Glasser 1992, Massazza 1998). Consequently, in the relatively short 90 ±5 day curing time recommended in the protocols, the NUMO low pH cement paste has a pH ≈ 13 as would be expected in hydrated OPC.

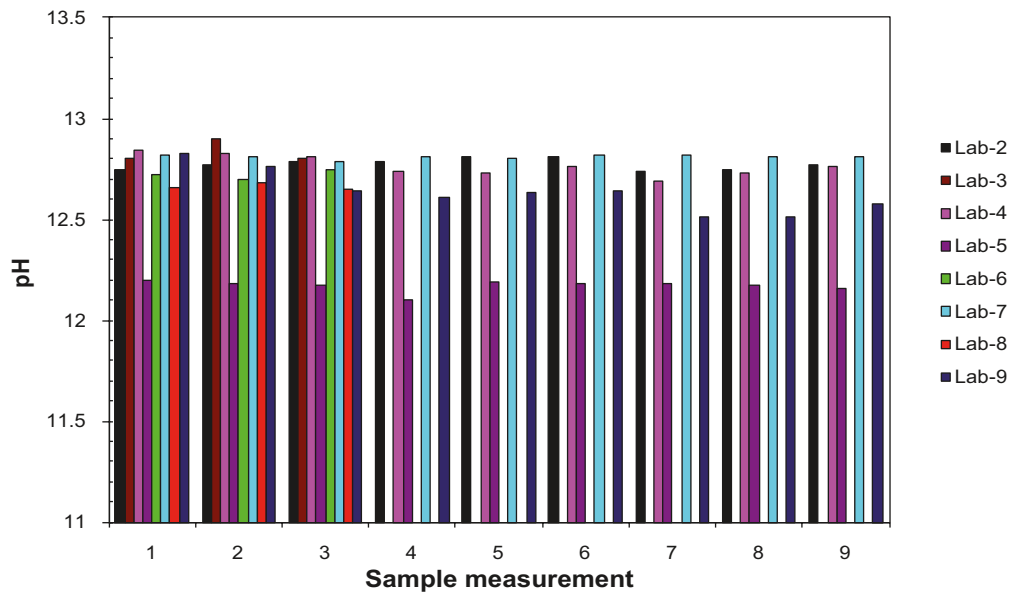
Figure 4-20 shows the replicate pH measurements of the NUMO low pH cement paste sample from each laboratory using the routine (ESL) method without filtering. Figure 4-21 and Figure 4-22 show those obtained by a pH electrode and pH electrode vs. OH<sup>-</sup> titration, respectively, using the routine (ESL) method with filtering.

Although the pH values ≈ 12.6–12.8 were again considerably higher and more in keeping with a conventional OPC pore water, the (within-laboratory) repeatability was very good. With the exception of Lab-5 reporting consistently lower pH values than all other laboratories by approximately 0.5 pH units (Figure 4-20 and Figure 4-21), the (between-laboratory) reproducibility was also very good as the values obtained were very similar.

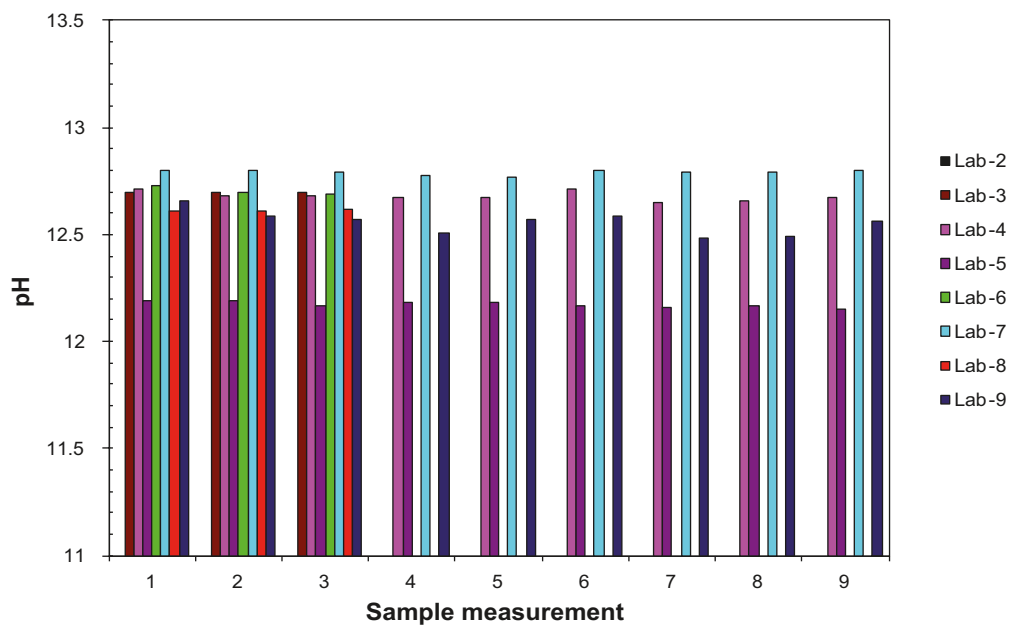
The extended curing time of 140 days in Lab-9 had little effect on the measured pH values using the routine (ESL) methods because the pozzolanic reaction of fly ash is very slow.



**Figure 4-19.** Comparison of pH values measured with a combination pH electrode (Elec) and determined by OH<sup>-</sup> titration (OH) for the NUMO sample using the reference (PFE) method.

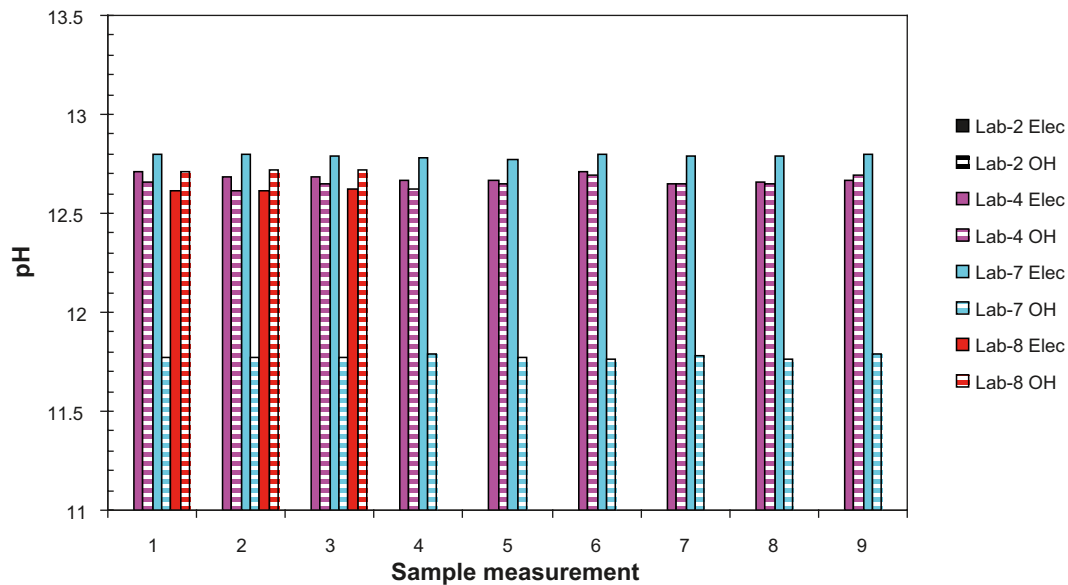


**Figure 4-20.** Pore water pH values measured with a combination pH electrode using the routine (ESL) method without filtering for the NUMO sample.



**Figure 4-21.** Pore water pH values measured with a combination pH electrode using the routine (ESL) method with filtering for the NUMO sample.

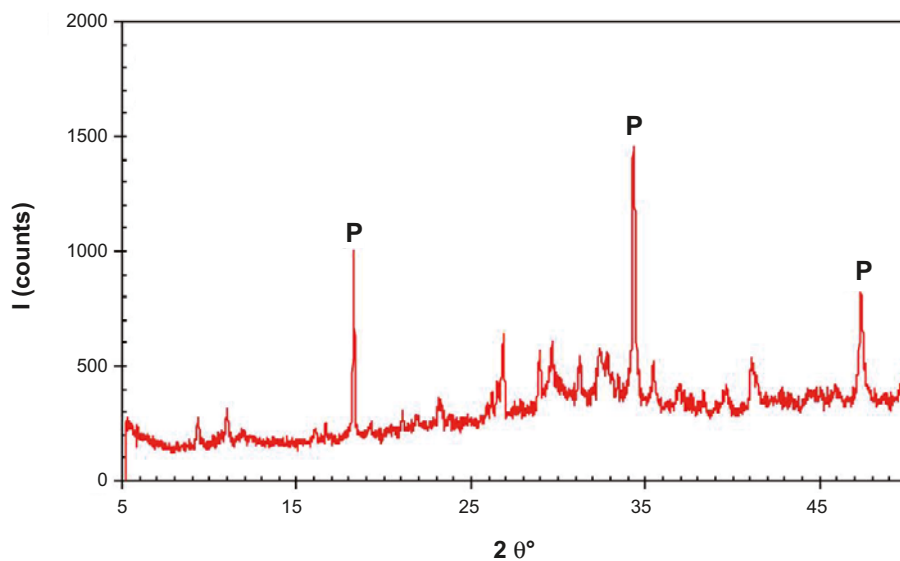
Excluding Lab-5, the routine (ESL) methods without and with filtering can be deemed acceptable in providing a reliable measure of pH values  $\geq 12.5$ , given the similarity of the pH values shown in Figure 4-20 and Figure 4-21. As in the other three low pH cementitious samples, the determination of the pH by  $\text{OH}^-$  titration was repeatable within each laboratory, but not reproducible between laboratories (Figure 4-22) and again confirms that  $\text{OH}^-$  titration should not be used with the routine (ESL) method with filtering.



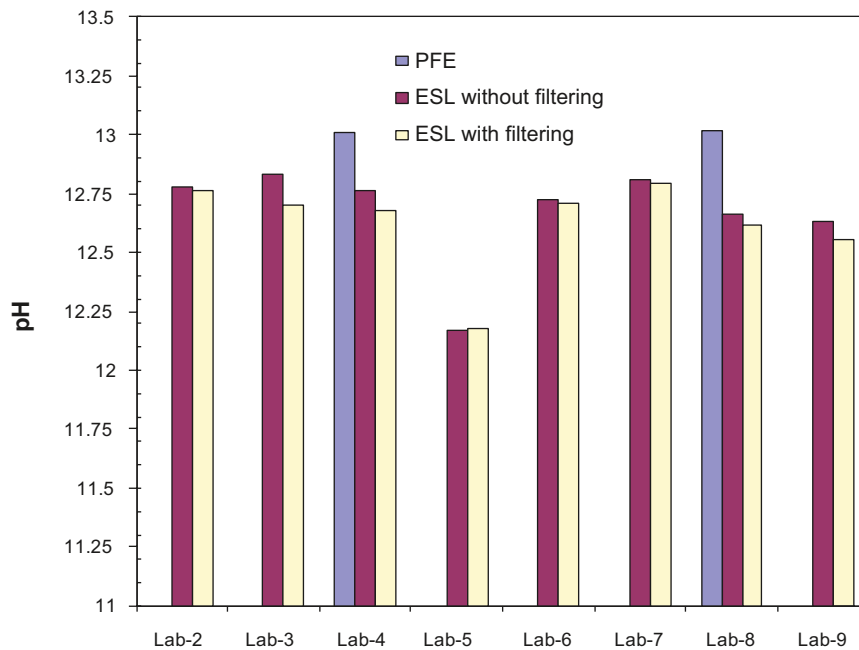
**Figure 4-22.** Comparison of pore water pH values measured by a combination pH electrode (Elec) and determined by OH titration (OH) using the routine (ESL) method with filtering for the NUMO sample.

XRD patterns of the NUMO low-pH cement sample confirmed the presence of portlandite, see Figure 4-23, which explains the high pH reported by all the laboratories; except for Lab-5. Portlandite buffers the pH of a solution to values  $\approx 12.5$ – $12.6$ , with the ‘as measured’ pH values  $\approx 12.6$ – $12.8$  no doubt including contributions from the alkali metals K and Na.

Table 4-9 shows the mean pH values and  $\pm$ SD taken from all and different subpopulations of the laboratories and Figure 4-24 shows a comparison of the mean pH values reported by each laboratory for the NUMO low pH cement paste, using the reference (PFE) and the routine (ESL) methods without and with filtering. Again, similar results were obtained by the different methods and by excluding Lab-5, the pH measurements from the routine (ESL) methods using a combination pH electrode were within the  $\pm 0.1$  error assigned to the pH electrode.



**Figure 4-23.** XRD pattern of NUMO low-pH cement paste after 90 days curing. Peaks assigned to portlandite are marked with the letter P.



**Figure 4-24.** Comparison between pH values using the reference (PFE) and both routine (ESL) methods for the NUMO samples.

**Table 4-9.** Mean pH values and  $\pm$ SD from the reference (PFE) and routine (ESL) methods for the NUMO samples.

	PFE		ESL		
	pH electrode	OH <sup>-</sup> titration	Without filtering	With filtering	
pH electrode			pH electrode	OH <sup>-</sup> titration	
Lab-4 and Lab-8	13.01 $\pm$ 0.01	13.02 $\pm$ 0.21	–	–	–
All laboratories	–	–	12.65 $\pm$ 0.23	12.61 $\pm$ 0.21	12.43 $\pm$ 0.44
All laboratories except Lab-5	–	–	12.75 $\pm$ 0.09	12.69 $\pm$ 0.09	–

#### 4.4 Summary of the pH values obtained for each cementitious material

Table 4-10 shows the mean pH values and  $\pm$ SD obtained for each cementitious material excluding the outliers (identified as exceptions in Table 4-6 to Table 4-9). Except when the pH is determined by OH<sup>-</sup> titration using the routine (ESL) method with filtering, similar results are obtained by the different methods for each cementitious material after the 90  $\pm$ 5 days curing period. It is important to note that, in general, the SD is very close to or within the  $\pm$ 0.1 error that can be assigned to the pH electrode. Moreover, the methods used allow a rapid test of a candidate low pH cementitious material and the closeness of the pore water to a target pH  $\leq$  11. This was not seen at all in the NUMO low pH cement paste, but which can be interpreted as being a consequence of the slow pozzolanic reaction of the fly ash component.



**Table 4-10. Summary of mean pH values and  $\pm$ SD obtained from the reference (PFE) and routine (ESL) methods without and with filtering for the four candidate low pH cementitious materials.**

	PFE		ESL		
	pH electrode	OH <sup>-</sup> titration	Without filtering	With filtering	
pH electrode			pH electrode	OH <sup>-</sup> titration	
SKB/Posiva	–	–	11.25 $\pm$ 0.14	11.14 $\pm$ 0.15	11.27 $\pm$ 0.26
Enresa	–	–	10.95 $\pm$ 0.11	10.81 $\pm$ 0.09	11.09 $\pm$ 0.26
JAEA	10.71 $\pm$ 0.13	10.74 $\pm$ 0.15	11.13 $\pm$ 0.10	10.80 $\pm$ 0.30	11.16 $\pm$ 0.46
NUMO	13.01 $\pm$ 0.01	13.02 $\pm$ 0.21	12.77 $\pm$ 0.05	12.73 $\pm$ 0.06	12.43 $\pm$ 0.44

## 4.5 Factors affecting results

### 4.5.1 Reference (PFE) method filtering (Lab-4)

In the reference (PFE) method protocol, the expressed pore water is filtered before the pH measurement. This is recommended to eliminate any influence on the pH measurement by particles that may be suspended in the pore water sample, but which may cause differences in the measured pH value. In order to test this hypothesis, the pH of the pore water of the CBI fabricated low pH cement described in Chapter 3, with curing at 100% RH and 21°C for 500 days, has been measured using the reference (PFE) method without and with filtering the expressed pore water. The filter used was made of hydrophilic nylon with a pore size = 0.45  $\mu$ m.

The mean pH value  $\pm$ SD of the pore water without filtering was 11.00  $\pm$ 0.06 and of the pore water with filtering was 10.93  $\pm$ 0.06. The obtained difference and associated  $\pm$ SD is lower than the error that can be assigned to the combination pH electrode and so it seems that filtration in the reference (PFE) method has little effect on the measured pH value.

### 4.5.2 Routine (ESL) method with filtering (Lab-4)

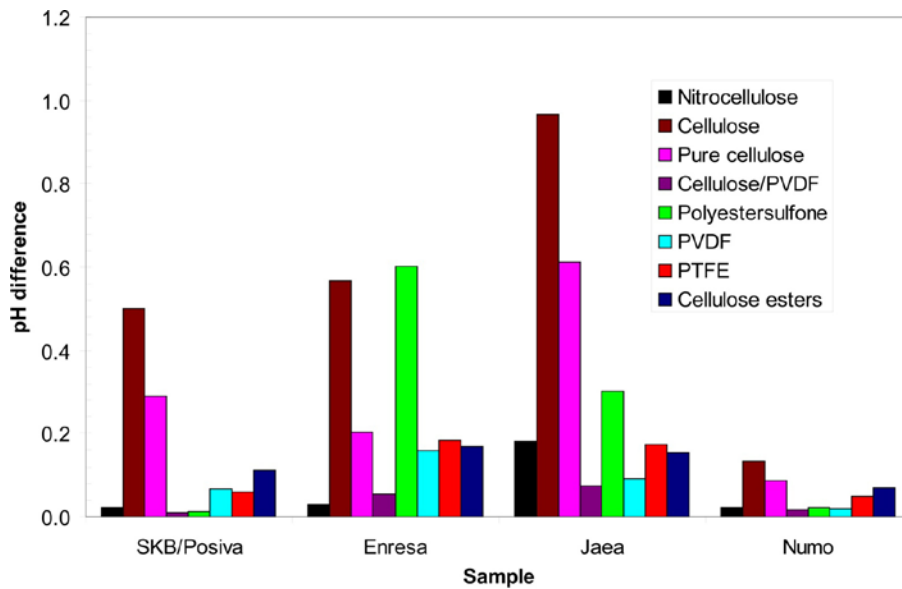
The suspension effect seen for all cementitious samples using the routine (ESL) method with filtering has been subject to further experimental investigation by Lab-4. The decrease in pH attributed to the suspension effect was found to vary between laboratories for the same cementitious material and so might be influenced by the filter type used. Figure 4-25 shows the differences observed between the measured pH using the routine (ESL) methods without or with filtering the suspension with an indication of the filter material used.

Using either PVDF or PTFE filter types can be recommended because using these filter types results in the lowest difference between the measured pH values using the routine (ESL) methods without and with filtering. Conversely, filters made of cellulose are best avoided because they seem to generate higher differences between the routine (ESL) methods without and with filtering.

Consequently, the cellulose filters were subjected to further experimental investigation. The cement used in these further tests was the CBI fabricated low pH cement described in Chapter 3, with curing at 100% RH and 21°C for 500 days. The filter used in these tests was a 0.45  $\mu$ m filter paper made of pure cellulose manufactured by FILTER-LAB.

Four different tests have been performed in triplicate with the pH value measured after each filtration:

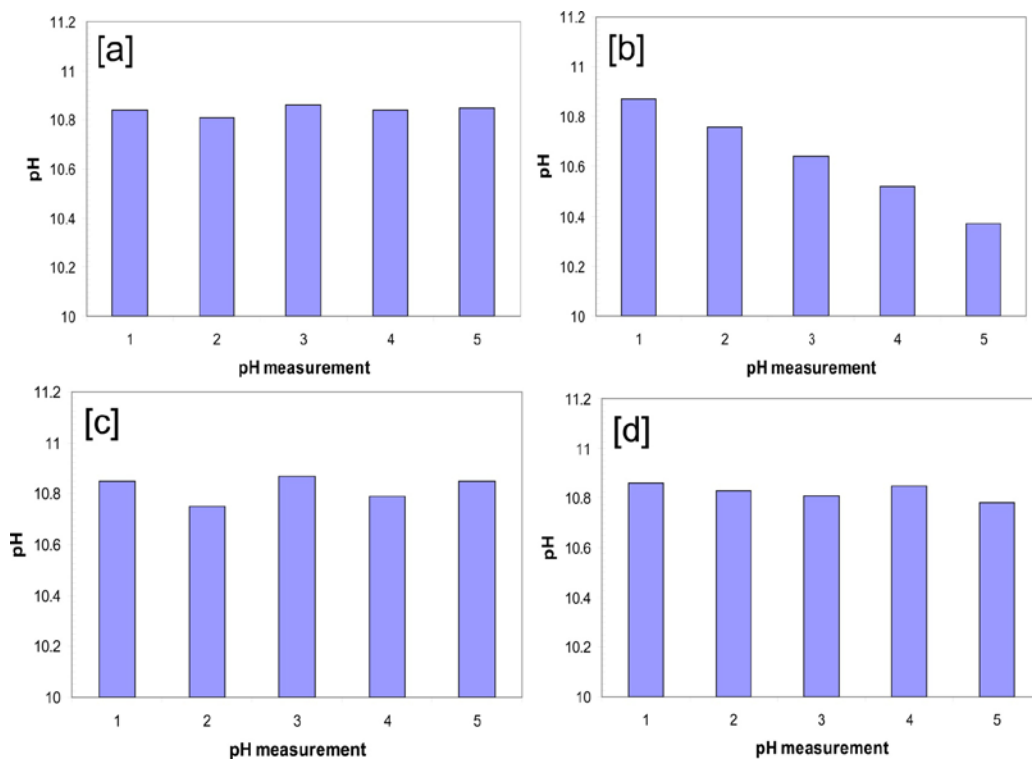
- Filter the same 10 g sample in 10 ml CO<sub>2</sub>-free deionised water suspension through the same filter 5 times.
- Filter the same 10 g sample in 10 ml CO<sub>2</sub>-free deionised water suspension 5 times using a fresh filter each time.
- Five different portions of the same 50 g sample in 50 ml CO<sub>2</sub>-free deionised water suspension were filtered using the same filter.
- Five different 10 g sample in 10 ml CO<sub>2</sub>-free deionised water suspensions were made from the same cement paste and filtered using the same filter.



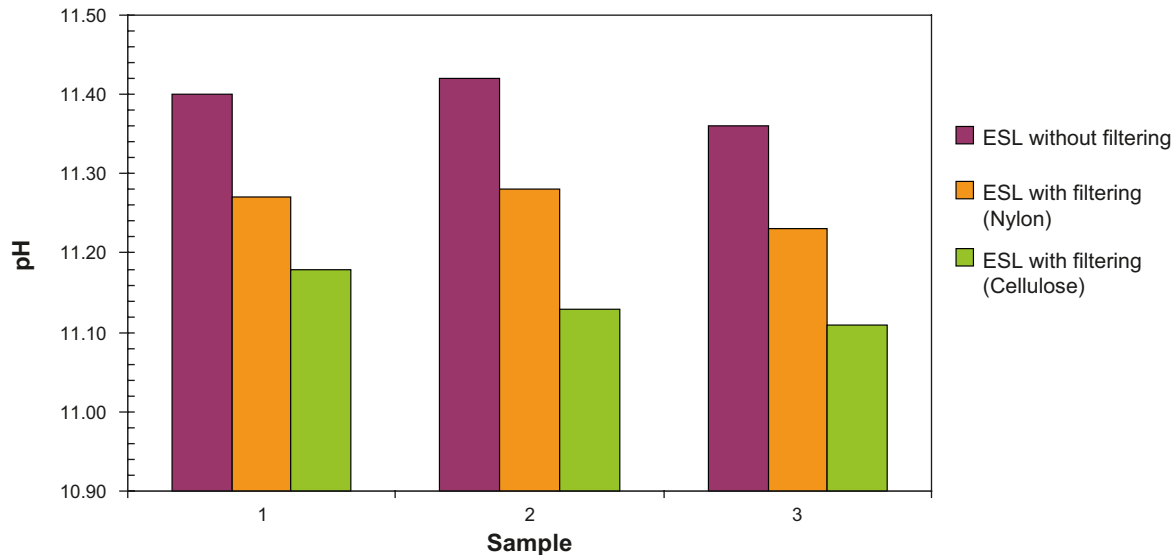
**Figure 4-25.** Influence of filter type and the differences obtained for each sample using the routine (ESL) methods without or with filtering. PVDF: PolyVinylideneDiFluoride; PTFE: PolyTetraFluoroEthylene.

The results obtained from each test are shown in Figure 4-26. It seems that the measured pH values remain within the  $\pm 0.1$  error assigned to the combination pH electrode when using the same filter, regardless of whether the same solution, different suspensions of the same sample or different portions of the same suspensions are filtered. In using a fresh filter for each filtration, a continuous decrease in the pH values was measured, with a total decrease of 0.5 pH units after filtering 5 times (Figure 4-26b).

It can therefore be inferred that using a new filter decreases the measured pH value, but is thereafter unaffected.



**Figure 4-26.** Influence of cellulose filter on the pH value measured using the routine (ESL) method with filtering. (a) Same suspension/same filter. (b) Same suspension/different filter. (c) Different portions of the same suspension/same filter. (d) Different suspensions of same sample/same filter.



**Figure 4-27.** Influence of filter type on the pH value measured using the routine (ESL) method with filtering.

In order to corroborate that the decrease in the pH value is influenced by the filter material, the routine (ESL) method with filtering was tested in Lab-4 using filters of cellulose and of nylon. The samples used in this test were the SKB/Posiva concrete described in Section 4.2.1. The resulting measured pH values are shown in Figure 4-27, which confirms that the pH decrease due to the suspension effect is lower when a filter made of nylon is used as opposed to cellulose.

Considering the results obtained in this filter type investigation, it seems clear that the filter material influences the measured pH value. Furthermore, that Nylon, PVDF or PTFE filter types are strongly recommended to use in the routine (ESL) method with filtering and that cellulose filter types are best avoided.

#### 4.5.3 Statistical analysis of the repeatability and the reproducibility of both routine (ESL) methods

To evaluate the repeatability and the reproducibility of the two routine (ESL) methods and in order to use the statistical studies proposed in the ISO 5725 standard, it was assumed that the data follows a normal distribution. Figure 4-28 and Figure 4-29 shows the histograms of the pH values of each of the four low pH cement materials reported by all the laboratories using the routine (ESL) methods without and with filtering the suspension, respectively.

The repeatability and the reproducibility have been analyzed for each low pH cement material individually. According to the ISO 5725:1994 standard, it is necessary to critically examine individual values in order to find entries that are considered irreconcilable with the other data, which have been identified as outliers in previous subsections of this Chapter. According to this standard, the data reported from such an outlying laboratory can be reasonably discarded. Consequently, both the repeatability and the reproducibility of the pH measurements have been calculated for each low pH cement material by including and excluding the outliers.

The main equations used (according to ISO 5725) in the statistical study of the repeatability ( $r$ ) and the reproducibility ( $R$ ) of the routine (ESL) methods are given by the equations in Section 3.6.

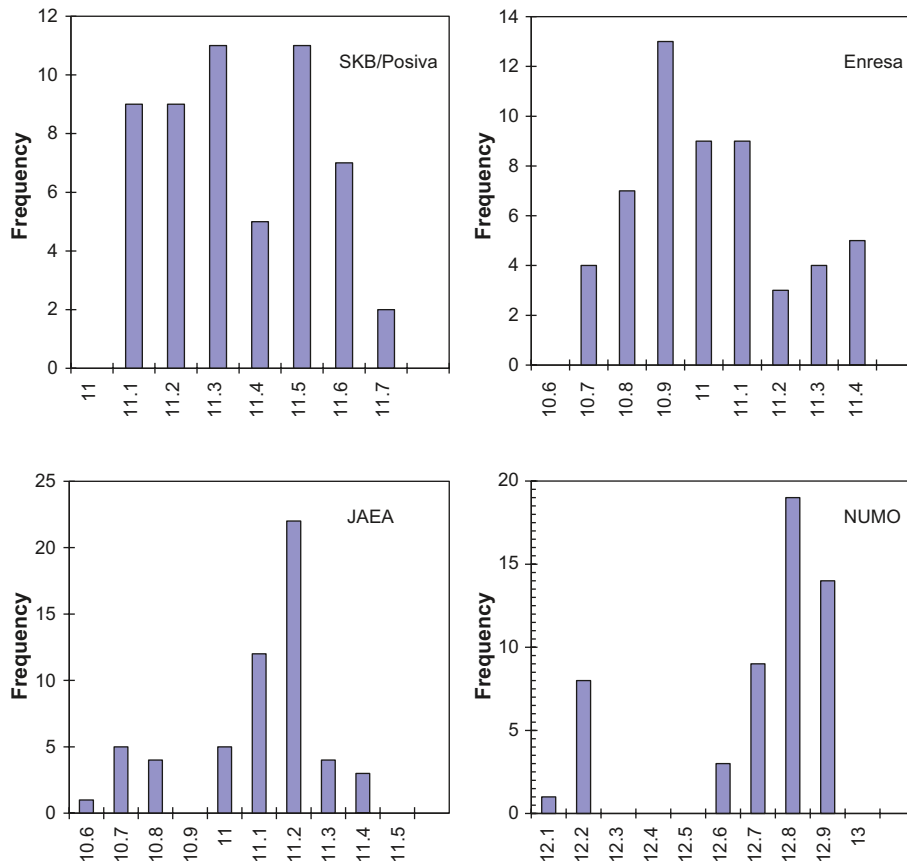


Figure 4-28. Histograms of the pore water pH of the four low pH cementitious materials obtained using the routine (ESL) method without filtering.

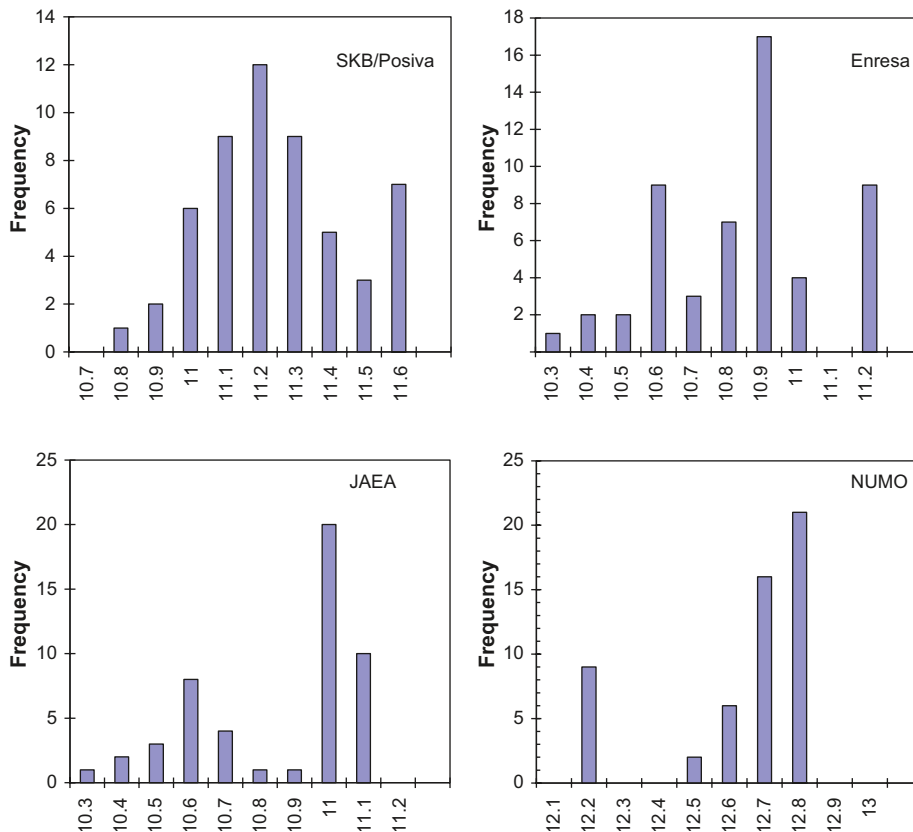


Figure 4-29. Histograms of the pore water pH of the four low pH cementitious materials obtained using the routine (ESL) method with filtering.

Table 4-11 and Table 4-12 show the statistical parameters determined for the four low pH cement materials using the routine (ESL) method without filtering including all results from all laboratories and excluding the outliers, respectively. The corresponding statistical parameters determined for the routine (ESL) method with filtering are shown in Table 4-13 and Table 4-14. All four tables include the statistical parameters obtained for the SKB hardened low pH cement paste shown in Chapter 3.

**Table 4-11. Statistical parameters for the routine (ESL) method without filtering.**

Statistical Parameters	Low pH cementitious materials				SKB (Chapter 3)
	SKB/Posiva	Enresa	JAEA	NUMO	
$S_r$	0.040	0.040	0.042	0.053	0.047
$r$	<b>0.107</b>	<b>0.112</b>	<b>0.118</b>	<b>0.151</b>	<b>0.132</b>
$V_r(\%)$	0.34%	0.36%	0.38%	0.42%	0.41%
$S_R$	0.192	0.218	0.196	0.247	0.231
$R$	<b>0.544</b>	<b>0.616</b>	<b>0.555</b>	<b>0.698</b>	<b>0.654</b>
$V_R(\%)$	1.70%	1.98%	1.77%	1.95%	2.02%

**Table 4-12. Statistical parameters for the routine (ESL) method without filtering, excluding the outliers.**

Statistical Parameters	Low pH cementitious materials				SKB (Chapter 3)
	SKB/Posiva	Enresa	JAEA	NUMO	
$S_r$	0.041	0.042	0.041	0.034	0.056
$r$	<b>0.116</b>	<b>0.119</b>	<b>0.116</b>	<b>0.096</b>	<b>0.159</b>
$V_r(\%)$	0.36%	0.38%	0.37%	0.26%	0.49%
$S_R$	0.142	0.124	0.080	0.057	0.125
$R$	<b>0.402</b>	<b>0.351</b>	<b>0.226</b>	<b>0.163</b>	<b>0.355</b>
$V_R(\%)$	1.25%	1.13%	0.72%	0.45%	1.10%

**Table 4-13. Statistical parameters for the routine (ESL) method with filtering.**

Statistical Parameters	Low pH cementitious materials				SKB (Chapter 3)
	SKB/Posiva	Enresa	JAEA	NUMO	
$S_r$	0.047	0.051	0.033	0.027	0.050
$r$	<b>0.132</b>	<b>0.145</b>	<b>0.095</b>	<b>0.076</b>	<b>0.142</b>
$V_r(\%)$	0.42%	0.47%	0.31%	0.21%	0.44%
$S_R$	0.209	0.245	0.239	0.227	0.248
$R$	<b>0.591</b>	<b>0.694</b>	<b>0.676</b>	<b>0.641</b>	<b>0.702</b>
$V_R(\%)$	1.87%	2.27%	2.21%	1.88%	2.19%

**Table 4-14. Statistical parameters for the routine (ESL) method with filtering, excluding the outliers.**

Statistical Parameters	Low pH cementitious materials				SKB (Chapter 3)
	SKB/Posiva	Enresa	JAEA	NUMO	
$S_r$	0.051	0.054	0.025	0.014	0.061
$r$	<b>0.145</b>	<b>0.153</b>	<b>0.072</b>	<b>0.040</b>	<b>0.172</b>
$V_r(\%)$	0.46%	0.51%	0.23%	0.11%	0.53%
$S_R$	0.144	0.094	0.112	0.064	0.114
$R$	<b>0.409</b>	<b>0.266</b>	<b>0.317</b>	<b>0.181</b>	<b>0.321</b>
$V_R(\%)$	1.30%	0.87%	1.02%	0.50%	1.00%

Several conclusions can be drawn from analyzing the statistical parameters shown in Table 4-11 to Table 4-14:

- Both routine (ESL) methods without and with filtering show similar repeatability ( $r$ ) and reproducibility ( $R$ ) values and so both can be considered reliable.
- The calculated  $r$  values for both routine (ESL) methods are very good and are quite close to or even lower than the  $\pm 0.1$  error that can be assigned to the pH electrode. These repeatability values show that with a probability of 95%, the difference between two different individual results obtained under the same conditions in the same laboratory will be below 0.15, which indicates that the developed protocols are quite accurate. A pH unit difference of 0.15 also represents less than 0.5% of the pH values measured.
- Calculated values of  $r$  are lower and so significantly better for the low pH cement pastes (JAEA and NUMO) than for the low pH concretes (SKB/Posiva and Enresa) in using the routine (ESL) method with filtering. This can simply be attributed to a paste being more homogeneous than a concrete; notwithstanding the coarse particles found in the JAEA low pH cement paste (Figure 4-17). Moreover, the  $r$  values calculated for the JAEA and NUMO low pH cement pastes imply that the differences observed between the pH measurements made in the same laboratory can be assigned to the  $\pm 0.1$  error of the pH electrode used.
- The number of laboratories taken into account,  $p$ , influences the calculation of the  $R$  values for both routine (ESL) methods. When all the laboratories are considered, the absolute maximum differences in  $R$  values = 0.69 between two individual results measured in different laboratories for both routine (ESL) methods. This difference in  $R$  values is very similar to those presented in Chapter 3 of 0.65 without filtering and 0.70 with filtering. If however, the outliers are excluded, the maximum differences between two individual results measured in different laboratories will be  $\leq 0.3$  pH units with a probability of 95%. In three of the low pH cement materials, the reproducibility is better (closer to 0) than that obtained in the material evaluated in Chapter 3, which indicates that the protocols have improved from their preliminary to final versions.

In summary, this statistical study demonstrates that the developed routine (ESL) methods without and with filtering show satisfactory repeatability ( $r$ ) and reproducibility ( $R$ ) values when they are used for different low pH cementitious materials, even with high pH values as measured for the NUMO ‘low’ pH cement paste.

#### 4.7 Comparison of the reference (PFE) and routine (ESL) methods

A critical evaluation of the accuracy of the routine (ESL) methods without and with filtering with respect to the measured pH values using the reference (PFE) method can only be made for the two low pH cement paste materials of JAEA and NUMO.

The calculation of the  $w$  ratio, as described in Chapter 3, has been made considering the routine (ESL) methods without and with filtering for each low pH cement paste material individually, from which the outliers (Lab-6 and Lab-7) have been excluded (Table 4-15).

**Table 4-15.  $w$  ratios corresponding to the routine (ESL) methods.**

Routine (ESL) method	$w$ ratio	
	JAEA sample	NUMO sample
Without filtering	1.78	1.71
With filtering	0.53	1.93

Several conclusions can be drawn from the  $w$  ratios shown in Table 4-15:

- In the JAEA low pH cement paste material, the pH measurements using the routine (ESL) method with filtering are in better agreement ( $w \leq 1$ ) with respect to the pH measurements using the reference (PFE) method. This high trueness indicates that the routine (ESL) method with filtering is as accurate as the reference (PFE) method in this case.
- The  $w$  ratios obtained for the NUMO 'low' pH cement paste are similar in both routine (ESL) methods. Although the calculated  $w$  ratios are not less than unity, they are still acceptable. However, it is evident that the routine (ESL) methods developed in this project, mainly with filtering, are more accurate when they are used in materials that can be demonstrated as being a low pH cement after  $90 \pm 5$  days of curing.
- The decrease in the measured pH value for the routine (ESL) method with filtering can be explained by the suspension effect. It is considered that this gives the more representative pH value of the low pH cement pore water without being artificially elevated by the suspended particles.

## 5 Conclusions and recommended protocols

The main conclusions drawn from the results obtained in this work:

- Protocols for measuring the pH of the pore fluid of low pH cementitious materials have been developed and tested. The final protocols are presented in Chapter 2 of this report.
- The interlaboratory tests carried out have allowed the validation of the developed methods for different candidate low pH cementitious materials.
- The repeatability of the reference (PFE) and routine (ESL) methods without and with filtering is very good as the resulting pH values are close or even lower than the  $\pm 0.1$  error that can be assigned to the pH electrode when measuring high pH ( $> 10$ ) solutions.
- For a given low pH cementitious material, the expected reproducibility of the pH measurement is  $\pm 0.12$  pH units within 95% probability using the reference (PFE) method and  $\leq \pm 0.3$  pH units using the routine (ESL) methods without and with filtering.
- The reference (PFE) method is excellent to assure the acquisition of accurate pH values and chemical composition of pore waters derived from low pH cementitious materials. There are no differences within error in measuring the pH directly with a pH electrode or in its determination by  $\text{OH}^-$  titration.
- Furthermore, in the case of the NUMO 'low' pH cement paste, the reference (PFE) method has been demonstrated to be applicable to pH values  $\geq 12$ . 5 expected of more conventional Portland cement materials.
- The developed routine (ESL) methods without and with filtering fulfils the requirements of a method that is fast, simple, inexpensive, reproducible, laboratory based, and allows the accurate determination of the pH of a low pH cementitious material pore water.
- Some deviations have been found in the reported pH measurements, but these deviations are restricted to very specific cases, such as consistently lower or higher measurements in a particular laboratory, and do not reflect inherent problems with the methods that have been developed as part of this project.
- Although the reference (PFE) method was not used in all the low pH cementitious materials tested, the trueness of the pH measured from the routine (ESL) method with filtering is excellent when compared with the pH measured from the reference (PFE) method for low pH cementitious materials. Furthermore, the same trueness comparison for the routine (ESL) method without filtering and for conventional cementitious materials is still acceptable.
- The routine (ESL) method with filtering and measuring the pH with a pH electrode seems to give more comparable results to the reference (PFE) method.
- The decrease in the measured pH value for the routine (ESL) method with filtering is due to the suspension effect. It is considered that this gives the more representative pH value of the low pH cement pore water without being artificially elevated by the particles forming the suspension. The higher pH value measured using the routine (ESL) method without filtering, however, allows the safety case to be considered in a more conservative sense.
- The pH values obtained in two similar low pH concretes (SKB/Posiva and Enresa) were similar, which demonstrates the high reproducibility of the developed methods.
- The low pH cementitious materials must be subjected to the same curing conditions if the reported pH values are to be comparable.
- In most cases, the calculated reproducibility ( $R$ ) values became better (closer to 0) in the final protocol tests (Chapter 4) as compared with those calculated from the results in the preliminary protocol tests (Chapter 3). It can therefore be concluded that the developed methods have been improved through the duration of the project.
- In the filtration procedures described Nylon, PVDF or PTFE filter types should be used and cellulose based filters are best avoided



## List of acronyms

AECL	Atomic Energy of Canada Limited (Canada)
ASTM	American Society for Testing and Materials
CBI	The Swedish Cement and Concrete Research Institute (Sweden)
CEA	French Atomic Energy and Alternative Energies Commission (France)
CRIEPI	Central Research Institute of Electric Power Industry (Japan)
CSIC	Spanish National Research Council (Spain)
DTA/TG	Differential thermal analysis/Thermogravimetric analysis
EMPA	Swiss Federal Laboratories for Materials Science and Technology (Switzerland)
ENRESA	Spanish National Waste Management Company (Spain)
ESL	<i>Ex situ</i> leaching
JAEA	Japan Atomic Energy Agency (Japan)
NAGRA	National Cooperative for the Disposal of Radioactive Waste (Switzerland)
NRI	Nuclear Research Institute (Czech Republic)
NUMO	The Nuclear Waste Management Organization of Japan (Japan)
OPC	Ordinary Portland Cement
PFE	Pore Fluid Expression
POSIVA	Posiva Oy Nuclear Waste Management (Finland)
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene Difluoride
RAWRA	The Radioactive Waste Repository Authority's (Czech Republic)
RH	Relative Humidity
SD	Standard Deviation
SKB	Swedish Nuclear Fuel and Waste Management Co (Sweden)
TFB	Technische Forschung und Beratung für Zement und Beton (Switzerland)
VTT	Technical Research Centre of Finland (Finland)

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## Literature review on pH measurement methods

### A1 Background

This appendix describes the background information and the basic methodology taken from the literature for an agreed pore water pH measurement procedure for low pH cementitious materials. This procedure, if accepted, is planned to be used by the agencies involved as the definitive method for determining the pH value of low pH cementitious materials. In order to achieve this goal several steps have been undertaken:

1. A literature review of the different methods employed for measuring the pore water pH of cementitious or analogue materials.
2. Based on the literature review, the selection of the most reliable pore water pH measurement methods that are suitable for achieving the expected aim. If none of the existing methods can be adopted for the specific case of low pH cementitious materials, a new method will be defined or it will be a composite of several methods.
3. The selected pH methodology will be refined in different laboratories using the same low pH cementitious material (Chapter 3).
4. The final method selected must comply with the following requirements:
  - It must be a method agreed on by the nuclear agencies involved in the experimental study of candidate low pH cementitious materials.
  - It must be reproducible in different laboratories and in different samples (Chapter 4).
  - It must permit the identification and accurate classification of a candidate low pH cementitious material.
  - The method should be simple to use, suitable for laboratory use and the influencing parameters should be known.
  - Apart from the methodology for measuring the pore water pH, the curing conditions (including age) and the pre-conditioning procedure of the materials have to be determined.

### A2 Generalities about cementitious materials

Concrete is the most widely used material in the world, used in a variety of civil engineering applications and environmental conditions. Concrete can be generally defined as a composite of three components (Neville 1995):

- 1) Cement: the binding phase, which can include mineral admixtures
- 2) Aggregate
- 3) Water

When the three components are mixed, the water reacts with the anhydrous cement phases to produce a new hydrated solid phase assemblage that forms a rigid, but porous material.

The wide use of concrete is due to its technological properties:

- Shortly after mixing, the concrete can be shaped to any specific form, which allows for a variety of applications.
- As the hydration proceeds, the cement hardens and binds the aggregates to produce the composite material with variable, though predictable mechanical properties.

The most widely used cement in concrete is Ordinary Portland Cement (OPC), which consists largely of four anhydrous phases: Alite ( $C_3S$ ), Belite ( $C_2S$ ), Aluminate ( $C_3A$ ) and Ferrite ( $C_4AF$ ). Cement chemistry shorthand notation is often used to represent the stoichiometries of these phase by their component oxides, where C = CaO, S = SiO<sub>2</sub>, A = Al<sub>2</sub>O<sub>3</sub>, F = Fe<sub>2</sub>O<sub>3</sub>,  $\underline{s}$  = SO<sub>3</sub>,  $\underline{c}$  = CO<sub>2</sub>, N = Na<sub>2</sub>O, K = K<sub>2</sub>O, M = MgO, and H = H<sub>2</sub>O. Accessory phases include gypsum ( $C\bar{s}H_2$ ), calcite ( $C\bar{c}$ ) and N, K and M either dissolved in the four main anhydrous phases and/or present as distinct phases

of thenardite ( $\text{Ns}$ ), arcanite ( $\text{Ks}$ ) and perclase ( $\text{M}$ ). The hydrated OPC solid phase assemblage is composed primarily of a calcium silicate hydrate (C-S-H) gel, portlandite (CH), and aluminoferrite bearing AFt and AFm phases of ettringite ( $\text{C}_6(\text{A},\text{F})_3\text{H}_3\text{S}_2$ ), monosulfate ( $\text{C}_4(\text{A},\text{F})_2\text{H}_1\text{S}_2$ ) and/or monocarbonate ( $\text{C}_4(\text{A},\text{F})_2\text{H}_1\text{C}$ ) (Taylor 1990, Lothenbach and Winnefeld 2006). These hydrated solid phases all contain water in their structure, but excess free water is also present in the pore space (Figure A2-1) which originates from the excess water used during mixing to achieve the necessary consistency for its intended application (Mehta 1986).

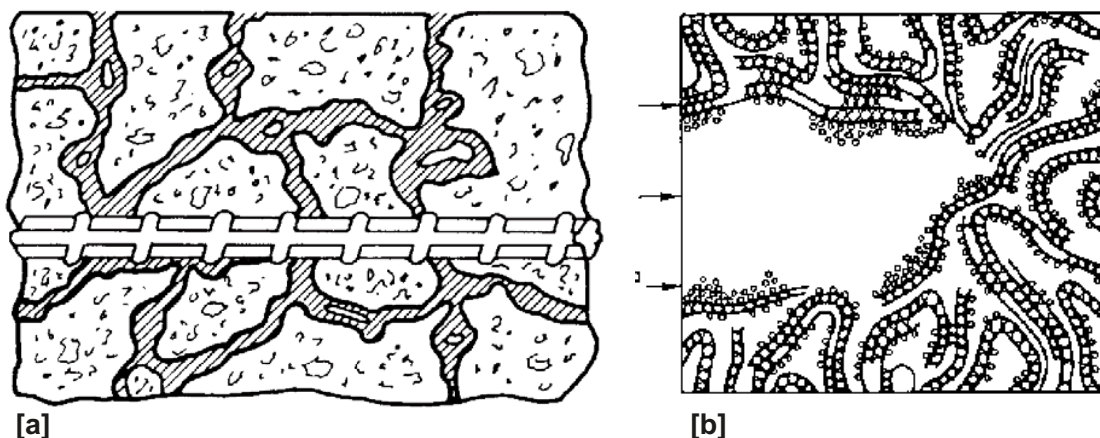
The consumption of protons from the dissolution of the completely soluble alkalis (K and N) and of CH contribute to the characteristic high  $\text{pH} \geq 12.5$ –13.7 pore water of hydrated OPC (Taylor 1987). Hydrated OPC is known to react with percolating groundwaters affected by:

- Flow rate of groundwater.
- Chemical composition of the groundwater.
- Chemical stability of the hydrated solid phase assemblage.

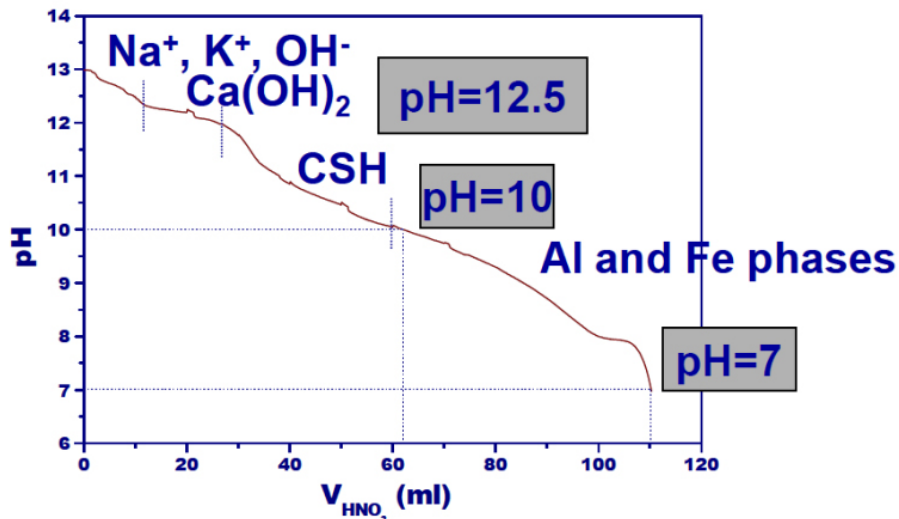
In principle, the expected processes, described by Taylor (1987), Adenot and Buil (1992), Glasser and Atkins (1994) and Hidalgo et al. (2005a), partially illustrated in Figure A2-2 (Hidalgo et al. 2005a), follow a sequence:

- Diffusion and loss of soluble ions  $\text{Na}^+$  and  $\text{K}^+$ . Initial  $\text{pH}$  decreases.
- Dissolution and loss of CH. Buffered  $\text{pH} \approx 12.5$ .
- Increase in porosity.
- Dissolution of C-S-H gel and hydrated (AFt and AFm) aluminoferrite phases. C-S-H gel dissolution approaches congruency. Buffered  $10 \leq \text{pH} < 12.5$ .
- Loss of mechanical strength.
- Loss of cement.  $\text{pH}$  returns to ambient groundwater  $\text{pH}$ .

The addition of fly ash, silica fume or other pozzolanic materials removes this relatively well known sequence by consuming CH to form more C-S-H gel and overall lower the molar Ca/Si ratio of the C-S-H. Additionally, lowering the Ca/Si ratio of the C-S-H gel allows the uptake of a greater proportion of other cationic species into its structure, most notably  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Al}^{3+}$  in cementitious systems (Hong and Glasser 1999). A sequence of processes to describe the degradation of a hydrated low  $\text{pH}$  cement, which includes these changes, has not yet knowingly been published.



**Figure A2-1.** Pore structure and alkaline liquid phase of concrete. (a) (Andrade and Feliu 1989). (b) Types of water associated with C-S-H gel based on the model by Feldman and Sereda (1970) and basic pore water ionic composition.



**Figure A2-2.** Decrease of pH in pores of OPC cement paste during degradation in nitric acid (Hidalgo et al. 2005a).

### A3 Role of cementitious materials in a HLW repository

Concretes play an important role as part of the engineered barrier system (EBS) of the repositories for low and intermediate level waste, where the limitation of accessibility of groundwater is one requirement, because of its influence on the chemical stability of the repository. Concrete is also used in the repositories of spent fuel in crystalline rock, e.g. as plugs or as mortar in rock bolts. Grouts also play an important role in the construction of the repository to limit the ingress of groundwater, and thus the intrusion of surface waters and up-coming of saline waters into the repository.

Hyper-alkaline cementitious materials have been demonstrated to play a key role in the alteration of the bentonite buffer employed in the EBS of high level radioactive waste (HLW). For this reason, an important aspect of the construction of a HLW repository is the use of low pH cementitious materials, in order to avoid the formation of an alkaline plume from the cementitious materials in contact with groundwater that might perturb the barriers of the repository.

One approach to ensure bentonite stability is the development and use of cementitious materials with a targeted pore water pH  $\leq 11$ . Below this critical pH, the swelling ability of bentonite is not compromised (Ramírez et al. 2002) or, according to the report by (Savage and Benbow 2007), the degradation rate of bentonite is significantly decreased below pH = 10.

A requirement of the formulation of OPC based low pH cementitious materials is that the formation of free CH and its associated pH  $\approx 12.5$  buffer is avoided. This can be achieved in cementitious systems by silica based mineral additions to consume CH during hydration via pozzolanic reaction (Lagerblad et al. 2007, Cau Dit Coumes et al. 2006, Alonso et al. 2007). Silica based materials (silica fume or fly ash, etc) allow the production of low pH cementitious material, either using one mineral addition (binary mixes) or using several mineral blends (ternary or higher blended cements). In the case of low pH cementitious materials production, it has been demonstrated that if OPC is used as basic cement of the low pH blend, at least 55 wt% of SiO<sub>2</sub> must be present in the binder, or pozzolan blended additions above 40 wt% have to be employed (Alonso et al. 2007, Cau Dit Coumes et al. 2006).

The production of low pH blended cements must be based on the physical requirements of the cementitious material developed (fluid properties, mechanical generation properties, permeability, pH requirement, etc). Hence, the development of low pH cementitious materials requires an accurate measurement of the pH of the pore water in order to be able to qualify mix designs and select candidate low pH cements for repository use.



## A4 pH testing methods for cementitious materials in the literature

The different methods described in the literature for characterizing the pore water of cementitious materials (cement pastes, mortars, grouts, and concretes) can be classified into five broad categories:

1. Pore fluid expression.
2. *Ex situ* leaching methods.
3. *In situ* leaching methods.
4. Percolation methods.
5. Embedded pH sensors.

Methods 1-4 are used for extracting the pore solution of the concrete before the pH is determined, while the fifth using the embedded pH sensors, takes direct measurement of pore fluid pH value *in situ*. Apart from these general techniques, the influence of those factors affecting the pH value or expression by different methods must be determined to understand how they influence the final pH value.

A detailed description of the above categories from the literature has been made and their critical parameters and limitations have been assessed.

### A4.1 Pore fluid expression (PFE)

Table A4-1 provides a summary of the literature references describing this method.

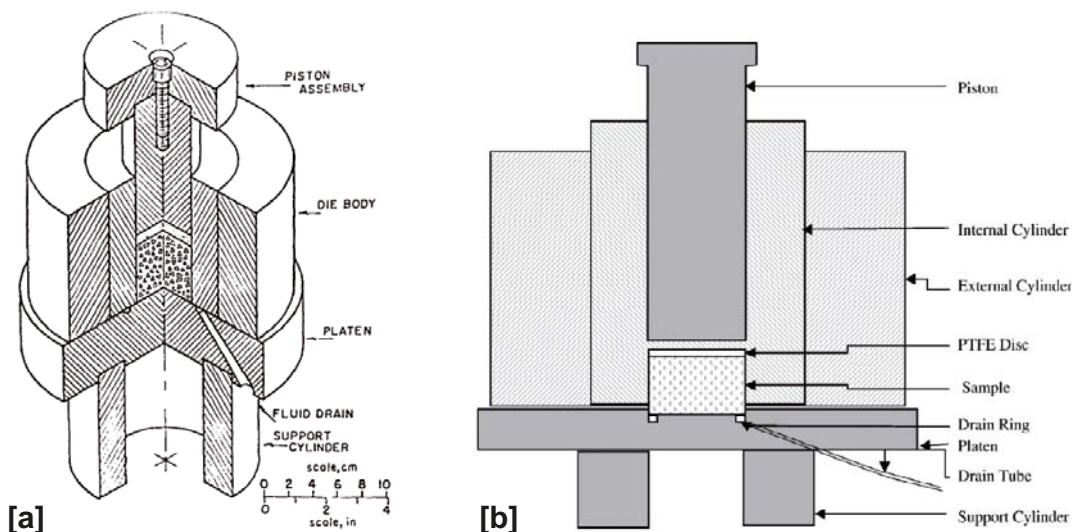
#### A4.1.1 Scope of the method

The basic objective of this procedure is to extract the actual pore fluid of hardened cementitious materials using specialized high pressure equipment that permit squeezing of set cement/concrete (Longuet et al. 1973, Barneyback and Diamond 1981) and analyze its chemical composition. Although there are several differences between the pore fluid expression procedures described in the literature, the basic principle is described here.

#### A4.1.2 Apparatus and auxiliary equipment

This procedure requires a specific and expensive device, initially developed by Longuet et al. (1973). Figure A4-1 and Figure A4-2 show two schemes and a picture of this device, respectively.

Although there is no company that specifically fabricates the pieces of the device needed for the pore fluid expression, some authors specify their properties and their size parameters.



**Figure A4-1.** (a) Isometric half-section scheme of pore fluid expression device. (Barneyback and Diamond 1981). (b) Schematic diagram of pore solution expression apparatus (Yonezawa et al. 1988).



Therefore, the equipment developed for this purpose consists of:

- 1 A cylinder or die body: which is designed as a jacketed cylinder because it has a cavity in the middle where the sample to be tested is placed. The diameter of this cavity usually ranges between 30 and 40 mm.
- 2 A piston: that is inserted in the cavity of the cylinder during the test.
- 3 A bottom plate: that contains a channel and a hole for collection of the pore solution.
- 4 A support Cylinder.

*Figure A4-2. Pore fluid expression device. CSIC equipment (Hidalgo et al. 2005b).*

This assembly is placed between the plates of a mechanical press with the sample of cement, mortar or concrete placed inside the cylinder (Figure A4-3). This press has to be sufficiently strong to achieve maximum pressures between 200 and 600 MPa (Longuet et al. 1973, Barneyback and Diamond 1981, Diamond 1981, Page and Vennesland 1983, Byfors et al. 1986, Tritthart 1989, Duchsene and Bérubé 1993, Kayyali and Haque 1995, Sagüés et al. 1997, Li et al. 1999, 2005, Räsänen and Penttala 2004, Hidalgo et al. 2005b).

Barneyback and Diamond (1981) recommend the use of SAE 4340 alloy steel for the fabrication of all the components of the apparatus as fatigue resistance is important during expression.

This method is more useful for pastes and mortars since expression yields for concrete, particularly high performance ones, are difficult (Byfors et al. 1986).



*Figure A4-3. Pore expression device placed between the plates of a mechanical press. Photo of CSIC equipment.*

### A4.1.3 Sample preparation

Pore water pH of cement pastes, mortars or concretes of undefined size can be analyzed using this method:

- *Curing conditions*: the samples are stored in different conditions related with the reaction to be studied and according to the adequate standards. The curing conditions reported by different authors are: in a sealed recipe or plastic devices at 20–22°C (Longuet et al. 1973, Byfors et al. 1986, Tritthart 1989), at laboratory temperature ( $\approx 23^\circ\text{C}$ ) (Diamond 1981), in plastic bottles or without plastic at 100% RH (Duchsene and Bérubé 1993, Sagüés et al. 1997, Hidalgo et al. 2005b), etc. The curing times defined by the authors also vary from days to months or even years.
- *Sample amount and preparation*: after the curing time is complete, a prefixed amount of sample is weighed. This amount of sample and the size of the crushed pieces clearly differ between authors (mass = 125–600 g and  $\varnothing = 5\text{--}41$  mm).

The method usually yields good results, but sometimes only a small amount of liquid can be expressed from aged concrete specimens or partially dry cores, meaning not enough solution is recovered for analysis. In these cases, if the pH value is the only parameter to be determined, a micro-pH electrode can be used, but even this may not be possible in some cases. Furthermore, in these cases it is impossible to extract a sufficient amount of liquid phase to perform a complete chemical composition characterization if one is required.

### Sample pre-conditioning

A procedure for solving the problem of low pore water yields consists of increasing the water content by rewetting the concrete until mass equilibrium is achieved (Kagimoto et al. 2000). Other authors proposed spraying a small amount of deionised water just before the expression of the sample (Sagüés et al. 1997, Hidalgo et al. 2005b). There is no standard in the literature for the volume of water sprayed; it can be fixed or can vary depending on the initial moisture content of the sample.

When adding extra deionised water, two samples are taken from the material and both samples are weighed (simultaneously and just prior to the start of the test); one is used to determine the moisture content of the sample and the other for extracting the pore water and measuring its pH value.

To determine the initial volume of the pore water contained in the sample, part of the sample must be dried at  $105^\circ\text{C}$  for 24 hours. The remaining part of the sample is pre-conditioned by spraying extra-deionised water. The pore fluid expression should be done as soon as possible to avoid potential errors in the pH measurements, and to avoid extra dissolution of solid phases (Hidalgo et al. 2005b). Therefore, the ion concentrations obtained are corrected by taking into account the initial moisture content of the sample and the water added during the pre-conditioning phase.

### A4.1.4 Procedure

After the sample has been crushed, and the ‘if necessary’ preconditioning procedure applied, the crushed sample is placed into the cavity of the cylinder (or die body) of the pore pressing device. Pressure is then applied to the piston and the pore solution is collected in a syringe inserted into the hole of the bottom plate (see Figure A4-2), and stored in plastic containers for analysis. The most common differences in approaches to this procedure are in the maximum pressure that can be applied and the rate of pressure application (Byfors et al. 1986):

- *Maximum pressure value*: ranges between 170 and 650 MPa. The lower values are recommended for cement pastes and the higher ones for concrete samples.
- *Rate of pressure application*: should be gradual but not usually defined by the authors. Regarding this matter, an error can occur if the pressure is increased too rapidly (Tritthart 1989) and it has also been shown to be highly beneficial to adopt the recommendations of Gunkel (1983) and not press continually but increase pressure in steps until the flow of pore-water becomes noticeably slower, after which the pressure is increased again. Steps of approximately 5 to 10 MPa were recommended up to a pressure where all pore water has been expunged.

As the pressure increases, not only is the pore solution collected in the syringe but also gas. Therefore it is helpful to withdraw the plunger of the syringe a short distance, to put a slight negative pressure on the pore fluid drainage system. It is also helpful to temporarily disconnect the syringe and vent the accumulated gas from it several times during each expression (Barneyback and Diamond 1981).

After the expression of the sample the pore fluid solution is filtered and the pH is measured directly with a combined pH electrode or determined indirectly by  $\text{OH}^-$  titration.

#### **A4.1.5 Measurement**

If the pH is measured with a combination pH electrode, it gives the pH value directly, usually with an accuracy of  $\pm 0.1$  for high pH solutions. For values obtained by  $\text{OH}^-$  titration, the pH value has to be calculated.

#### **A4.1.6 Special considerations**

The main limitations of this method are the requirement of a special and relatively expensive device. Quite a large amount of sample is required to ensure sufficient pore water can be extracted and is quite a time consuming method. Apart from these limitations there are many parameters involved in the procedure that have to be considered and specific standards or protocols that take into account all of these have not yet been developed.

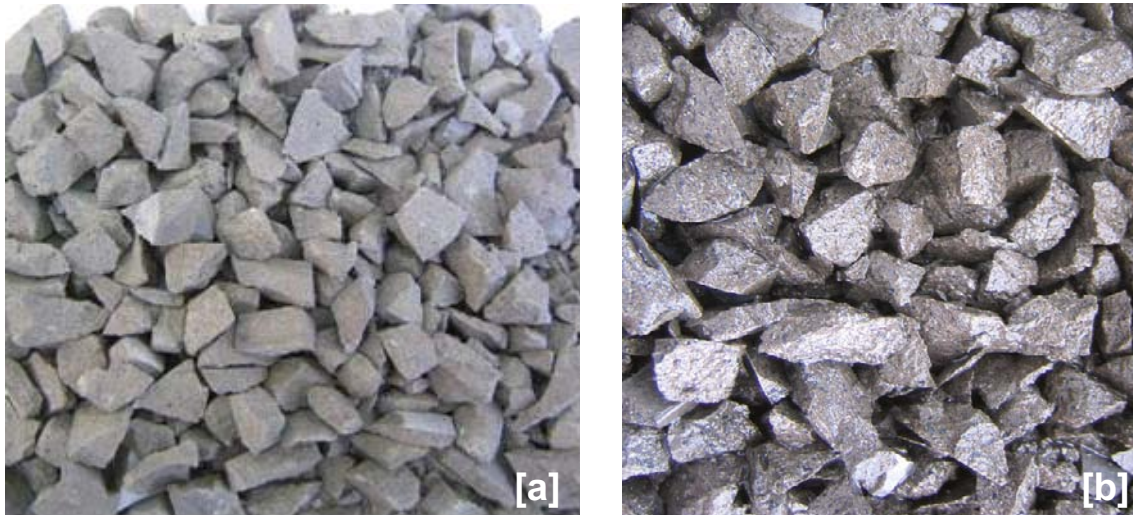
The main considerations specifically related to the pore fluid expression method can be summarized as:

- *Curing conditions*: it is recommended measuring the pore water pH in water saturated samples in order to obtain the most reliable value. For this reason, before the measurements of the pH of the samples, it should be guaranteed that the pores of the material are water saturated. Hence, when working under typical laboratory conditions, the fabricated samples must be cured in a humidity chamber (100% RH and  $21 \pm 2^\circ\text{C}$  temperature) before the pore fluid expression is carried out.
- *Pre-conditioning of the sample*: the addition of extra water is often necessary, due to the difficulties in extracting a sufficient amount of pore water. This method for quick saturation of samples has been proved to be a reliable procedure that does not vary the pore water pH significantly (Hidalgo et al. 2005b). It is not recommended to spray a fixed volume of deionised water but an amount depending on the moisture level of the sample. When an extra addition of deionised water is needed for saturation, Hidalgo et al. (2005b) suggest: To spray a small amount of deionised water on the surface of the sample and wait for absorption of the water by the material, then repeat the process. No excess of liquid water should remain on the surface which indicates oversaturation, the final aspect of the sample is as that shown in Figure A4-4.
- *Pressure considerations*: as described, the maximum pressure used differs between the different papers published. Chatterji (1991) proposed that ions use different channels to those of an expressed pore water and are more concentrated and more strongly bound in overlapping water layers adjacent to the solid particles than in the pore space. Duchesne and Bérubé (1994) demonstrated that the pressure load under which the samples are expressed has no influence on the alkali concentration measured in the pore solution sample, obtaining similar results in the pore fluid composition using pressure intervals of 0–200 MPa and 200–560 MPa. The maximum pressure level seems, therefore, to be only dependent on the type of sample: near 600 MPa for concretes and between 300–500 MPa for mortars and even lower for cement pastes. When concretes are expressed, there is an important limitation due to the damage that can be caused to the pore expression device by the aggregates present in the material. Regarding the rate of pressure application the previously highlighted recommendations of Gunkel (1983) should be carried out.

- *Influence of high pressures on precipitation phenomena:* an increase in CO<sub>2</sub> partial pressure (PCO<sub>2</sub>) during pressing may generate an increase in cation concentrations in some cases. The product of (H<sup>+</sup>)(HCO<sub>3</sub><sup>-</sup>) increases directly with PCO<sub>2</sub>, leading to increases in concentrations of base cations from exchange sites and higher alkalinities.
- *Special considerations for low pH cementitious materials:* in the case of the low pH cementitious materials, the curing time and the curing conditions needed to obtain the most reliable pore water pH are very important. The pH of low pH cementitious materials based on OPC varies with the curing time, especially at short ages of less than 28 days as demonstrated in the ESDRED project (Alonso et al. 2009). In general, the greater the curing time then the lower the pH value, until stabilisation. Therefore, it can be concluded that to obtain the representative pH value of a candidate low pH cementitious material long curing ages, such as 90 days, are recommended (Hidalgo et al. 2005b, Alonso et al. 2009). This pore fluid pH decrease is a consequence of the kinetics of the pozzolanic reaction being on the order of days and weeks (Saeki and Monteiro 2005, Lagerblad et al. 2007, Cau Dit Coumes et al. 2006, Alonso et al. 2007).
- *Control of carbonation:* authors do not specify any special CO<sub>2</sub> protection during the sample preparation or the pressing procedure. The main recommendation on this matter is to maintain the pore fluid expressed in a sealed plastic or glass tube until pH measurements or chemical analyses are made. The pH measurements should occur as soon as possible, preferably within minutes of the pore water being expressed.

Despite the limitations of this method, it is believed that the pH and the chemical compositions of the pore water obtained using the pore water expression technique are representative of that of the bulk of the pore solution within the cementitious material from which the solutions have been obtained (Barneyback and Diamond 1981).

The pore water expression method is the most commonly employed technique and is considered to be the most reliable in the literature. It is also frequently used in the literature as the reference method with which to compare the results obtained from other methodologies.



**Figure A4-4.** (a) Non-saturated sample. (b) Saturated sample.

**Table A4-1. Shows the conditions given by the authors for the pore fluid expression method.**

Author	Equipment	Applied pressure	Pressure rate	pH measurement	Material	Curing/Preservation	Sample amount	Sample size
Longuet et al. (1973)	Detailed in the paper.	343 MPa	–	Electrode and OH <sup>-</sup> titration	Paste	Sealed container at 20°C	–	–
Barneyback and Diamond (1981)	(Longuet et al. 1973). Cavity size: 53 mm.	550 MPa 2.8 MPa/sec (non critical parameter)	–	OH <sup>-</sup> titration	Paste and mortar	–	250 g	–
Diamond (1981)	(Longuet et al. 1973).	170 MPa	–	OH <sup>-</sup> titration	Paste	Laboratory temperature (≈ 23°C)	–	–
Page and Vennesland (1983)	(Longuet et al. 1973, Barneyback and Diamond 1981)	375 MPa Gradual increment	Gradual	OH <sup>-</sup> titration	Paste	Sealed container at 22 ±2°C	–	–
Byfors et al. (1986)	(Barneyback and Diamond 1981). Cylinder cavity: 30 mmØ×80 mm; other cylinders: 50 mmØ×50 mm and 70 mmØ×200 mm	–	–	Electrode and OH <sup>-</sup> titration	Paste	Wrapped in plastic and stored at 20°C for 3 months	–	–
Trithart (1989)	(Longuet et al. 1973, Barneyback and Diamond 1981). Dimensions given.	343 MPa	10 bar/s or Gunkel (1983) recommendations	Electrode and OH <sup>-</sup> titration	Paste	In plastic bags at 20°C	400–600 g	< 10 mm
Duchsene and Bérubé (1993)	–	0–200 MPa 200–560 MPa	–	K <sup>+</sup> y Na <sup>+</sup> titration	Paste and mortar	In plastic bottles at 38°C and 100% RH	–	–
Kayyali and Haque (1995)	(Longuet et al. 1973, Barneyback and Diamond 1981).	600 MPa	–	OH <sup>-</sup> titration	Concrete	–	–	Ø = 41 mm h = 100 mm
Sagúés et al. (1997)	(Longuet et al. 1973, Barneyback and Diamond 1981).	–	–	–	–	8 weeks at 100%HR or adding a fix amount of deionised water	–	Ø < 3.5 mm
Li L et al. (1999, 2005), Li Q et al. (2000)	(Longuet et al. 1973, Barneyback and Diamond 1981).	650 MPa/200 MPa	Gradual increase every 20 min	–	–	–	–	–
Räsänen and Penttala (2004)	(Barneyback and Diamond 1981, Diamond 1981)	500 MPa	–	–	Mortar and concrete	–	–	–
Hidalgo et al. (2005b)	(Longuet et al. 1973, Barneyback and Diamond 1981).	483 MPa	Gradual following Gunkel (1983) recommendations	Electrode and OH <sup>-</sup> titration	Paste and mortar	100% HR/adding deionised water if necessary	125 g	Ø < 5 mm

## A4.2 *Ex situ* leaching method

Table A4-2 provides a summary of the literature references describing this method.

### A4.2.1 Scope of the Method

*Ex situ* leaching relies on mixing a small and known amount of cementitious material with a known volume/mass of de-ionized water and to measure the pH of the resulting suspension or of the solution after filtration (Haque and Kayyali 1995, Thangavel and Rengaswamy 1998, Pavlík 2000, Castellote et al. 2002, Räsänen and Penttala 2004, Hidalgo et al. 2005b, Vuorinen et al. 2005, Li et al. 2005, Cau Dit Coumes et al. 2006).

In the literature, various potentially suitable *ex situ* leaching methods have been described for determining the chloride concentration of the pore water in hardened cementitious materials; some of them in connection with the determination of chloride-induced corrosion of reinforcing steel. These leaching methods can also be used to determine the pH and chemical composition of the pore water.

### A4.2.2 Apparatus and auxiliary equipment

Unlike the pore fluid expression technique, the *ex situ* leaching methods can be performed using standard laboratory equipment. The equipment consists of a balance, a stirrer (usually magnetic) and a beaker where the suspension of water and cementitious material sample is mixed. The actual pH of the solution can be measured directly with a pH meter and combination electrode or determined indirectly by OH<sup>-</sup> titration. Figure A4-5 shows the equipment necessary for measuring the pore water pH in the *ex situ* leaching method used by Hidalgo et al. (2005b).

However, there are some more sophisticated devices described in the literature (e.g. Castellote et al. 2002) (Figure A4-6). In this case, the samples are placed in a glass device that consists of a cylindrical body with a tube and a valve in its bottom to obtain the leached liquid. It has a porous glass in which the sample to be leached is placed. The apparatus has a hermetic cap, as well as three inlets (for inert gas (N<sub>2</sub>), leaching solution and aeration). A filter must be placed between the sample and the porous glass.

The insertion of the sample/solvent suspension in a capsule with N<sub>2</sub> atmosphere while stirring is also used in other *ex situ* leaching methods described in the literature, which is carried out to avoid the possible carbonation of the sample during the stirring time.

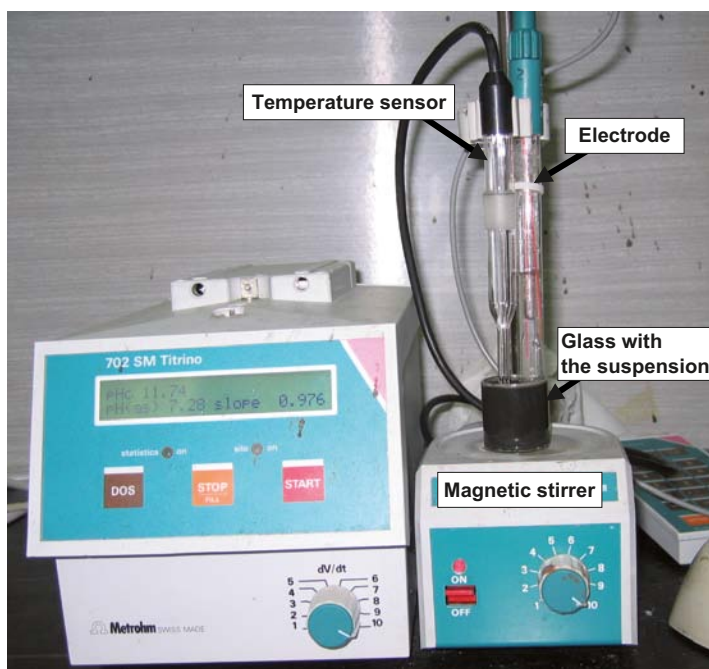


Figure A4-5. Equipment used in the CSIC *ex situ* leaching method (Hidalgo et al. 2005b).

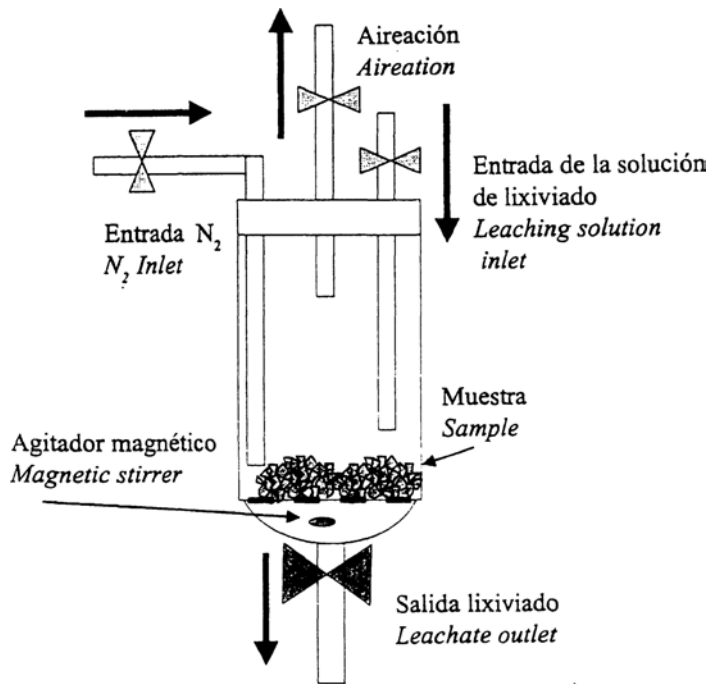


Figure A4-6. Device used in the *ex situ* leaching method, by Castellote et al. (2002).

#### A4.2.3 Sample preparation

These methods can be used with cement pastes, mortars or concretes. As the sample is powdered and a selection of the sample analyzed there is no set sample size required.

- *Curing conditions*: the samples can be sealed in plastic at different temperatures (depending on the evaluated process) or stored at 100% RH. The curing times used by the authors also vary, usually from a few days to 28, although pH measurements at longer ages have been considered for pH evolution determination.
- *Sample amount and preparation*: after the curing time is complete, a predetermined amount of sample is weighed. The sample weight ranges between 3 and 100 grams. The weighed sample can be crushed or milled, so the diameter size of the obtained pieces or particles clearly differs between authors, with diameters used ranging from 0.075 to 16 mm.

#### Sample pre-conditioning

Prior water saturation of samples is not required for these *ex situ* leaching procedures because the sample is immersed in water as a part of the method. Therefore there are no pre-conditioning procedures reported in the literature.

#### A4.2.4 Procedure

The procedure followed in the *ex situ* leaching methods can be divided into the following steps:

- *Preparation of the suspension*: a known mass of granulated or powdered sample is mixed with a known quantity of liquid solvent (usually deionised water). The solid/solvent mass ratio is one of the more variable parameters and ranges from 2:1 to 1:50, but 1:1 is the most used.
- *Extraction or leaching period*: the time that the solvent and the crushed or powdered sample are in contact. The leaching periods tested in the literature range from 3 minutes to 30 days. In many cases, an initial displacing of the air with N<sub>2</sub> gas is performed.
- *Stirring time*: this process is included in the leaching period. Once the suspension is made, it is stirred for a specific time. The stirring time varies between different authors and, in some cases the suspension is not stirred constantly until the pH measurement, but there are periods between two stirring times where the suspension is left to rest.



- *Pore fluid pH measurement*: after the stirring procedure, if the leached liquid is filtered, the pH can be measured either with an electrode or by titration. Otherwise, the pH is measured directly in the suspension with an appropriate electrode.

#### A4.2.5 Recording the results

It is recommended that at least three complete procedures (with the subsequent three pH measures) are undertaken for any one cementitious material (Hidalgo et al. 2005b). The acceptance of the obtained pH values requires that the difference between the values is less than that could be associated to the error of the electrode (typically 0.1). If higher differences in pH between identical samples are measured a recalibration of the electrode should be performed or the homogeneity of the materials should be evaluated.

#### A4.2.6 Special considerations

The *ex situ* leaching procedures are reasonably suitable for measuring the pore water pH of cementitious materials, as the majority of them give good results when compared to the pH values obtained using the pore fluid expression method. Furthermore, it is important to note that some of these methods have been tested in low pH cementitious materials (Hidalgo et al. 2005b, Vuorinen et al. 2005, Cau Dit Coumes et al. 2006).

However, in evaluating the *ex situ* leaching methods the following parameters should be considered:

##### Parameters related to the material preparation:

- *Solvent*: deionised water or even CO<sub>2</sub> free deionised water is normally used, but others solvents have also been tried (Castellote et al. 2002), e.g. 0.3 M NaOH solution because it is assumed to provide a mean pH of the pore water in hardened OPC or a filtered CH saturated solution to avoid CH dissolution.
- *Sample amount*: this parameter varies significantly from 3 to 100 g, but it does not seem to be a critical parameter (as long as the sample is representative of the material being sampled).
- *Fineness of particles*: some studies indicate that with increasing fineness of sample particles the pH of the suspension increases; the larger surface area in contact with the solvent allows more OH<sup>-</sup> ions to be released (Räsänen and Penttala 2004). However, this parameter is closely linked with the extraction time. In the works published in the literature, longer stirring period usually correlates with a larger particle size. Therefore, for shorter stirring times a powdered sample is recommended (around 0.8 µm particle size are used in Hidalgo et al. (2005b) showing good correlation with the pH measured for the same sample using the pore fluid expression technique).
- *Solid/solvent ratio*: it has been shown that an important dilution effect exists when the ratio of solvent to solid increases, resulting in a decrease in the pH value as compared with the results obtained using the pore fluid expression technique (Hidalgo et al. 2005b). In fact, with the addition of high amounts of water, the concentration of ions in the solution is generally low, especially for the unbuffered concentrations of Na and K. For this reason, low solid/solvent ratios are recommended (usually ≤1:1).
- *Temperature of powder sample*: when crushing a cementitious material its temperature can easily increase and facilitate carbonation. However, it does not seem to be a critical parameter, as some authors demonstrate that although the increase in temperature of concrete or mortars during powdering could decrease the obtainable pH value, the detected changes are very small (Räsänen and Penttala 2004).
- *Control of carbonation*: most authors do not specify any special procedures for avoiding the possible carbonation of the sample during the whole test period, including the sample preparation. Some of the protective measures described for avoiding carbonation are:
  - constant displacement of the air with N<sub>2</sub> gas while stirring the sample (Castellote et al. 2002, Hidalgo et al. 2005b),
  - transferring the crushed material into small sealed glass bottles and sealing the suspension in a Teflon vessel while stirring (Pavlik 2000),
  - removing the external surface of the intact monolithic sample just before crushing (Räsänen and Penttala 2004, Li et al. 2005).

### Parameters related to the pore water extraction:

- *Extraction time*: there is a great variability between authors in the time taken to extract. Some studies have reported that the pore solution pH value increases continuously over the whole test period (Räsänen and Penttala 2004), because when leaching using deionised water, the concentration of OH<sup>-</sup> ions can be overestimated as the precipitated phases of a cementitious material (mainly CH in OPC) are dissolved (Castellote et al. 2002, Li et al. 2005). The longer the sample is in contact with the solvent the greater the expected leaching and thus lack of precision in the pH measurement. Some authors suggest that correction factors are required to calculate the real OH<sup>-</sup> concentration in the pore solution, taking into account the Ca concentration and also both evaporable and non-evaporable water of the sample (these determinations can be undertaken in an oven and a furnace kept at 105°C and 1,050°C, respectively). Castellote et al. (2002) propose that the concentration of OH<sup>-</sup> in the pore solution can be calculated by means of the following equation:

$$[\text{OH}^-]_{\text{pores}} = 0.49 \left[ \frac{W + 2}{W} \right] ([\text{OH}^-]_{\text{leach}} - 2[\text{Ca}]_{\text{leach}})$$

where  $[\text{OH}^-]_{\text{pores}}$  is the concentration of OH<sup>-</sup> in the pore solution (mol/L),  $[\text{OH}^-]_{\text{leach}}$  is the concentration of OH<sup>-</sup> in the leaching solution (mol/L),  $[\text{Ca}]_{\text{leach}}$  is the concentration of Ca in the leaching solution (mol/L), and  $W$  is the evaporable water in the sample (ml).

Li et al. (2005) suggest a similar expression:

$$[\text{OH}^-]_{\text{pores}} = ([\text{OH}^-]_{\text{leach}} - 2[\text{Ca}]_{\text{leach}}) \cdot \frac{V_{\text{leach}}}{V_{\text{pores}}}$$

where  $V_{\text{leach}}$  is the total volume of leaching water plus the volume of pre-existing pore water in the sample (L) and  $V_{\text{pores}}$  is the total capillary pore volume of the water saturated sample (L).

However, taking into account that the CH content of low pH cementitious materials based on OPC is quite low or even non-existent, the dissolution of the precipitated phases during the leaching process is less significant than in conventional cementitious materials. Nevertheless, short extraction times are highly recommended.

- *Stirring time*: as has been previously described, some authors do not stir the suspension constantly, rather incorporate rest periods, but others stir the mix continuously. It seems that an increase in stirring time increases the pH of the cementitious materials although the detected changes are moderate and the obtained increase can be explained by the effect of the extraction time that has more of an effect on the pH value.

### Parameters related to the pH measurement procedure:

- *Filtration*: it seems that filtration of the leachate after the extraction time slightly decreases pH values (Räsänen and Penttala 2004). For this reason, a direct pH measurement of the suspension using a pH electrode is suggested, but only if an electrode specially designed for measuring in suspensions is used. If, after the extraction, the chemical composition of the pore water is to be analyzed then it must be filtered. Authors do not specify the filter size used as it would depend on the particle fineness of the sample used for testing.

### Comparison between pH values obtained using *ex situ* leaching methods and those obtained from pore fluid expression:

- Most of the authors contrast the pH values obtained using their suggested *ex situ* leaching methods with those determined by the pore fluid expression technique. Most authors state that the results are good and do not specify the difference between the measured values using both methods. In those cases where specific values are given (Räsänen and Penttala 2004, Hidalgo et al. 2005b, Li et al. 2005) the differences between methods are usually lower than 0.2 pH units and correction procedures are proposed, such as giving a correcting factor for OPC cementitious materials (Castellote et al. 2002).

**Table A4-2. Shows the conditions given by the authors for the *ex situ* leaching method.**

Author	Equipment	Material	Curing or Pre-conditioning	Sample: amount and size	Solid/water	Leaching time	Filtration	pH measurement	Considerations
Haque and Kayyali (1995)	No special	Concrete		∅: 600 mm	1:3.5 to 1:4	24 hours	Yes	Electrode	–
Thangavel and Rengaswamy (1998)	No special	Concrete	De-moulded at 24 h and cured in distilled water for 7 days	100 g (powder)	1:2	1 hour	Yes	Electrode	–
Pavlík (2000)	No special	Paste	Sealed for 35 days	3 ranges ∅: 0–05 mm, 0.5–1 mm, 1–2 mm	1:2, 1:5 and 1:50	1, 6 or 24 h. Several stirring times.	Yes	OH <sup>-</sup> titration	Ca <sup>2+</sup> , Cl <sup>-</sup> and K <sup>+</sup> measured
Castellote et al. (2002)	Special device with N <sub>2</sub> inlet	Mortar	100% RH	3 g. Crushed. ∅ = 2.5 and 3.5 mm	1:0.67	30 s stirring, resting for 24 h and stirring again	Yes	OH <sup>-</sup> titration considering Ca <sup>2+</sup> and pore fluid volume	Test 3 different solvents
Räsänen and Penttala (2004)	No special	Mortar and concrete	In plastic at 45% RH at 20°C.	30 g/powder 16 > ∅ > 0.075 mm	Between 1:1.5 and 1:0.67	15 min	No	Electrode	–
Li et al. (2005)	No special	Concrete	–	50 g/powder	1:0.7–1:1–1:2–1:4	1, 3, 10, 30 days. Stirring periodically.	Yes	OH <sup>-</sup> titration considering cement content and % alkalis.	Ca <sup>2+</sup> .measured
Hidalgo et al. (2005b)	No special (CO <sub>2</sub> protection)	Paste, mortar and concrete	100% RH	10 g/powder ∅ ≈ 0.075 mm	1 :1	3 minutes continuously stirring	No	Electrode	–
Cau Dit Coumes et al. (2006)	In N <sub>2</sub> atm	Paste and mortar	–	5 g/powder	1:9	Slow stirring. Monitoring pH value until stabilization.	No	Electrode	–

#### **A4.2.7 Special *ex situ* leaching method (Vuorinen et al. 2005)**

Although this is not a method developed for measuring the pore fluid pH of cementitious materials, but for characterizing their leaching behaviour commonly used for testing in radioactive waste research, it is nevertheless interesting due to its similarities with the *ex situ* leaching methods described above. The authors of this work developed two leaching methods: one for assessing the maximum equilibrium pH deep in the geosphere with slow turnover of groundwater (equilibrium (EQ) test), and another test (diffusion (DIFF) controlled release) which facilitates the assessment of long-term safety by derivation of leach rates. Tests were run inside an anaerobic glove-box (nitrogen atmosphere with low ( $\leq 0.01$  ppm)  $\text{CO}_2$ ) in order to avoid carbonation.

In the EQ test part of the leached solution is extracted and replaced periodically with the same amount of fresh leaching water, whereas in the DIFF tests the entire leachate volume is replaced at each exchange point. The duration of the entire testing period ranges from 70 to 180 days depending on the composition of the evaluated sample (grout mixes were used).

The grout mixes are cast in plastic pipes and after an adequate curing period at 20°C or 50°C suitable disks are sawn (diamond blade) for leach testing. In each sample vessel, two 1 cm thick slices ( $\text{Ø} = 2.84$  cm, total volume of the samples was 12.7 cm<sup>3</sup>) are placed in 30 ml of leachate to give a liquid/solid ratio  $\approx 2:1$ . The leach tests are performed in tightly closed polyethylene vessels inside the anaerobic glove-box. The leaching solutions used in the study are simulated ground-waters. The leach specimens are kept immersed in the leachates without stirring until each sampling point, and the system is stirred only before extracting any solution sample. All solution samples extracted are filtered (0.2  $\mu\text{m}$ ) in order to remove possible fragments or larger colloidal particles present in the leachates and in the filtered solution the pH is measured with a pH electrode.

##### *Critical parameters and considerations for the Vuorinen et al. (2005) ex situ leaching method*

Problems with this special method include:

- This test potentially requires long time periods to perform, as it is necessary to reach equilibrium between the pore solution of the material and the water added.
- Errors introduced by carbonation of the sample can also occur.

#### **A4.3 *In situ* leaching method**

##### **A4.3.1 Scope of the method**

In addition to the *ex situ* leaching methods, there is also an *in situ* leaching method described in the literature. This method basically consists of making small cavities in the surface of the cementitious material, adding a few drops of water to each cavity and measuring the pH of the water after a pre-determined length of time. This method is used to minimize the dilution effects that may be a source of error in the *ex situ* leaching method, but requires preconditioning procedures (adding water) that can last two weeks or more. As with the *ex situ* methods, pore water expressions were performed for comparison and calibration of the measured pH value, giving acceptable results with the difference between both values usually lower than 0.2 pH units (Sagüés et al. 1997, Li et al. 1999).

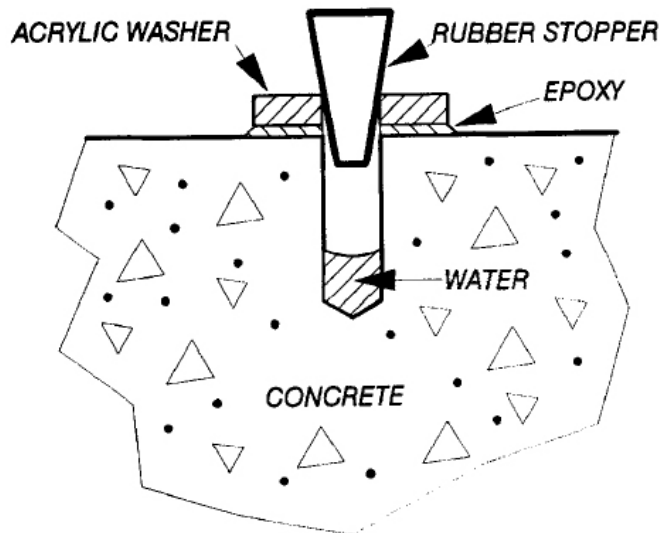
##### **A4.3.2 Apparatus and auxiliary equipment**

The *in situ* leaching method mainly uses standard laboratory equipment, apart from the requirements of a masonry drill bit to make the small cavities and a micro electrode to measure the pore water pH in the cavities.

##### **A4.3.3 Sample preparation**

In the trials published in the literature concrete and mortar samples of variable size have been tested.

The cementitious materials have to be initially saturated with water. For this reason, these methods have a preconditioning procedure that typically takes two or more weeks, where the hardened concrete samples are allowed to achieve constant weight at  $22 \pm 2^\circ\text{C}$  inside a closed 100% RH chamber. Periodic mist-spraying of distilled water is also used to prevent the sample from drying out and to ensure that there is always some water present in the cavities.



**Figure A4-7.** Schematic of the arrangement for the *in situ* leaching method developed by Sagüés *et al.* (1997).

#### A4.3.4 Procedure

The *in situ* leaching procedure can be divided into the following steps:

1. Two or three holes of approximately 5 mm in diameter and 25 mm deep are drilled using a masonry drill bit on the upper surface of the sample.
2. Dust and debris is removed from the holes, and 0.2–0.4 ml of distilled water is pipetted into each hole. An acrylic washer is affixed around the mouth of the hole with fast-setting epoxy adhesive, and a tapered rubber stopper is pressed firmly into the washer (see Figure A4-7).
3. The sample is then returned to the humidity chamber and kept there for subsequent monitoring.
4. The pH of the water in each hole is monitored periodically by means of a pH micro electrode. Authors suggest that after approximately a week the pH in cavities of the specified size with the defined water content may be approaching the pH of the pore water.

#### A4.3.5 Recording the results

Two or three cavities are made in the same concrete sample and the results are given as the mean pH value of the measurements from each cavity. As in the case of the *ex situ* leaching methods, the difference between the obtained pH values should be less than the  $\pm 0.1$  error which can be micro electrode used.

#### A4.3.6 Special considerations

One of the limitations associated with the *in situ* leaching method is that, in some instances, despite the  $> 2$  week exposure of the samples to the 100% RH chamber environment, water inside the hole tended to be slowly absorbed into the cementitious material. This was reported as being particularly problematic during the initial stages of the curing and in concrete mixes of high water-to-cementitious (w/c) ratios. In these cases, the solution inside the holes had to be periodically replenished by pipetting 0.2 ml of distilled water as needed, but the authors state that this procedure does not represent the recommencement of the pre-conditioning period.

Another limitation when using these procedures is that the pH of the water in the cavity is assumed to have approached that of the concrete pore water, but deviations between the pH in the cavity and in the pores of the surrounding cementitious material could occur for a number of reasons:

- Likely carbonation of such a small volume of water from the atmosphere.
- Slow equilibration and dilution from repeated additions of the water in the cavity.
- Loss of cavity water into the surrounding concrete.
- Possible heterogeneities in macroscopic samples and in the pore network.

Excessively slow equilibration of the cavity with the surrounding concrete may lead to underestimation of the final pH, and may aggravate errors introduced by carbonation (Sagüés et al. 1997). Giving consideration to all these potential sources of error, the *in situ* leaching method seems not to be particularly useful when the pH measurements must be made under specific, repeatable and reproducible conditions.

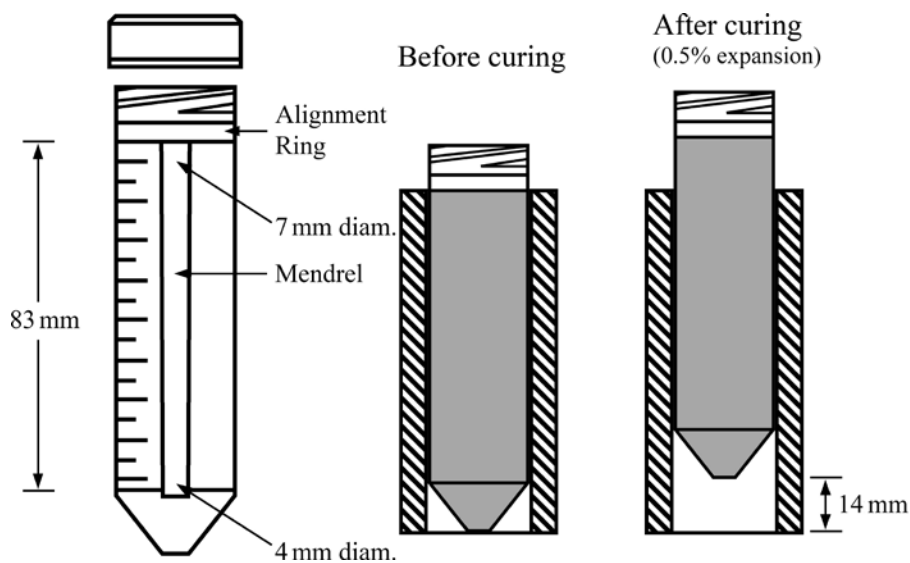
#### A4.3.7 Special *in situ* leaching method (Goguel et al. 2000)

The *in situ* method described by Goguel et al. (2000), is similar to those already described, but with some important differences. Samples are cast as mortars in a standard 50 ml polypropylene centrifuge tube around a carefully machined mandrel of 4 mm diameter at the bottom tapering to 7 mm diameter at the top. The mandrel is centrally positioned with a centring ring that contains a vent hole to allow excess mortar to escape. The centrifuge tube is then vibrated the mandrel removed after hardening, replaced with water, sealed, and allowed to cure for approximately 6 weeks. The final aspect of the sample is shown in Figure A4-8. This set up allows only a thin 10 mm wall of mortar to equilibrate with the added water. By having the sample and water contained in a sealed polypropylene tube, no water is lost so that the w/c ratio of the sample can be accurately defined and maintained.

After curing, the water can be extracted and the pH measurement made using a pH meter and combination pH electrode.

##### *Critical parameters and considerations for Goguel et al. (2000) in situ leaching method*

- Small size of the centrifuge tube does not allow for testing concretes with coarse aggregates.
- In addition to the recommended 90 days curing, a further 6 weeks is necessary to achieve equilibrium between the pore solution of the cementitious material and the water inside the cavity, which makes the pH measurement rather time consuming.
- Risk of carbonation inside the cavity during measurement that can lead to underestimation of the pore water pH value.



**Figure A4-8.** Centrifuge tube and die for obtaining pore solution analyses (Goguel et al. 2000).

## **A4.4 Percolation methods**

### **A4.4.1 Scope of the method**

Percolation methods also involve the extraction of the pore solution, in this case by miscible displacement using a high pressure permeameter enabling the eluted water to be analysed for chemical composition. The objective of this testing method is to study the evolution of chemical and microstructural changes occurring when cementitious materials are subjected to a continuous flow of groundwater. The method is also employed to determine the hydraulic permeability factor of cementitious materials.

This leaching method has not been used for measuring the pore water pH of cementitious materials, but for characterizing their potential leaching behaviour in the context of their use in radioactive waste repositories and for measuring the liquid conductivity of porous construction materials.

### **A4.4.2 Percolation leaching test I (Hidalgo et al. 2005a)**

#### **Sample preparation**

Concrete or mortar samples are cast as cylindrical monoliths of  $\varnothing = 50$  mm and length = 50 mm.

#### **Leaching test procedure**

Concrete or mortar samples are placed between two cylinders of metacrylate containing holes for water inlet and outlet. The block is sealed with an epoxy-resin to ensure that water passes only through the sample and that the measured fluxes are correct. Once the samples are placed in contact with the water, a sample dependent water head between 0.5 and 5 bars pressure is maintained and the test is allowed to continue for at least 1 month. The permeability of the samples and the applied head pressure regulate the water flow rate. Percolating water is collected for analysis of the chemical composition. The equipment used is showed in Figure A4-9.

#### *Characteristics for Hidalgo et al. (2005a) percolation tests*

- The need of a high pressure permeameter.
- Column leaching test (open system).
- Unidirectional flow.
- Control of the inflow and outflow solutions.
- Material shape: monolithic (cylinders 50 mm diameter and 50 mm length).
- Samples are saturated for 24 hours, before the starting of the test.
- Water head of 0.5–5 bars.

#### *Critical parameters and considerations for Hidalgo et al. (2005a) percolation tests*

- The need of a high pressure permeameter.
- Only initial leached water is useful for pH determination.
- Samples with low porosity, low w/c ratio, etc, are too impermeable to allow measurable water flow in a short time, and if not enough leaching solution is extracted in an acceptable time, it is not possible to measure the pH of the pore solution.

### **A4.4.3 Percolation leaching test II (Buckley et al. 2007)**

Buckley et al. (2007) developed a water percolation method in which the pore solution is also removed by miscible displacement, but with water in a high pressure Hassler cell permeameter described by Green et al. (1999) (Figure A4-10). The Hassler cell permeameter is a high pressure axial-flow permeameter designed to accommodate a cylindrical core of  $\varnothing = 25$  length = 75 mm.

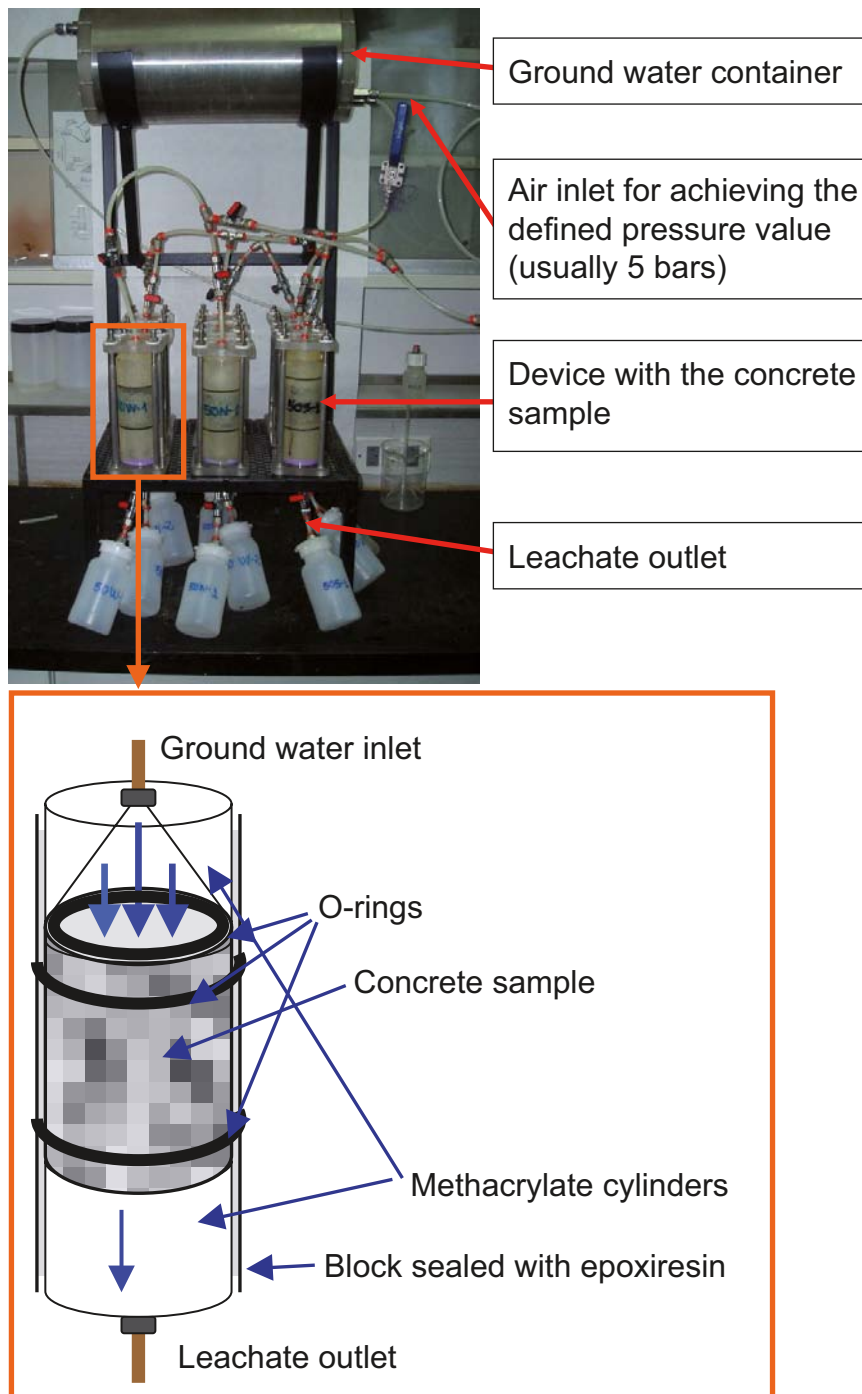


Figure A4-9. Equipment used in percolation tests (Hidalgo et al. 2005a).

Before being loaded into the Hassler cell, the sample must be saturated with water. The core is encased in a nitrile rubber sleeve to which a containing pressure is applied that exceeds the pressure of the deionised water flowing through the sample. The containing pressure seals the circumferential face of the sample and ensures axial-flow. A chromatography pump provides a pulse-free constant flow rate of liquid through the sample and the pressure necessary to maintain this flow is recovered. A flow rate of 1 ml/min was used for each test case, resulting in fluid pressures ranging between 0.1 and 1 MPa. The containing pressure is held constant at 4 MPa. The eluent is collected over the first 400 s and subsequently over 200 s intervals for a total of 30 minutes. Both containing and fluid pressures are measured using pressure transducers. If the pumped and saturated liquids are completely miscible the latter is completely displaced. The eluted pore solution was collected and analysed for its chloride concentration, but could be analysed for pH and concentrations of other elements.



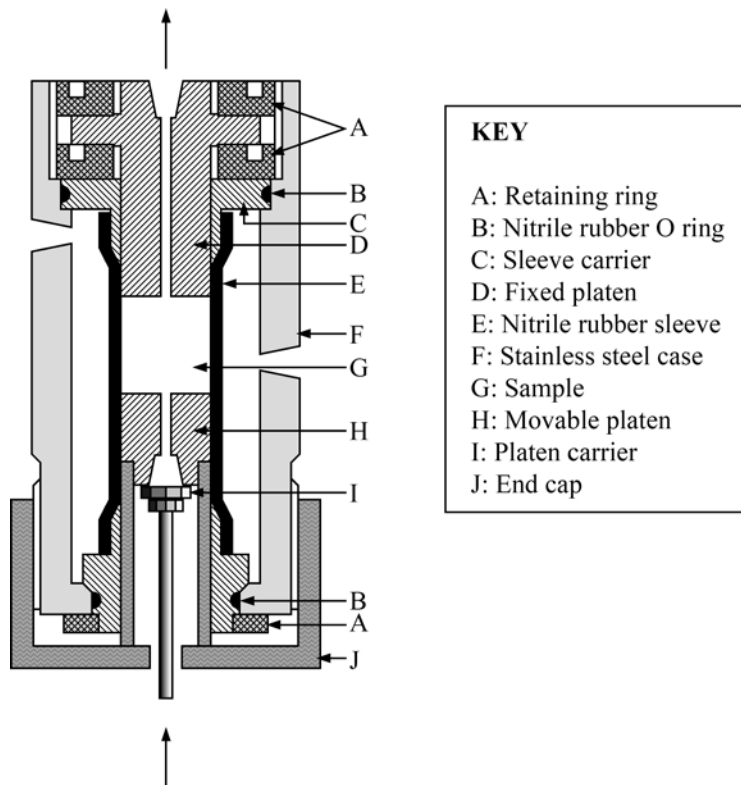


Figure A4-10. Hassler cell permeameter (Green et al. 1999).

*Critical parameters and considerations for Buckley et al. (2007) percolation tests*

- The need of a high pressure permeameter.
- There is a decrease in chloride ion concentration as the test continues. In the case of pH only the initial eluted water could be used to obtain a representative pH measurement.
- Samples with low porosity, low w/c ratio, etc, are too impermeable to allow measurable water flow in a short time, and if not enough leaching solution is extracted in an acceptable time, it is not possible to measure the pH of the pore solution.

## A4.5 Embedded pH sensors

### A4.5.1 Scope of the method

Sensors that detect changes in the pH of cementitious materials have also been evaluated for measuring the *in situ* pore water pH. In the majority of cases an ionic sensor and a reference electrode are used. In the wider literature, several embedded pH sensors have been described, but the majority have not been used in cementitious materials. Embedding sensors in cementitious materials, however, requires that the sensors can withstand the harsh conditions of a high alkaline environment for a prolonged length of time (Blumentritt et al. 2008).

In recent years, much attention has been paid to metal/metal oxide electrodes with a pH dependent equilibrium potential to be used as pH sensors because they are robust in structure, small in size and have a quick response time (Zhou et al. 1994, Kriksunov et al. 1994, Kreider et al. 1995, Castro et al. 1996, Li et al. 2000, Du et al. 2006, Tan 2007). The majority of these kind of sensors have been developed to measure the advance of the carbonation front in reinforced concretes, in order to assess the corrosion velocity of the reinforcement. Moreover, several of these sensors have been used in combination with chloride measurements.

The basis for metal oxide electrodes serving as hydrogen ion-selective electrodes is that the redox reaction for metal/metal oxide (M-MO) is reversible in aqueous solutions. Before the sensors are embedded in the cementitious materials, they have to be calibrated using solutions of known pH.

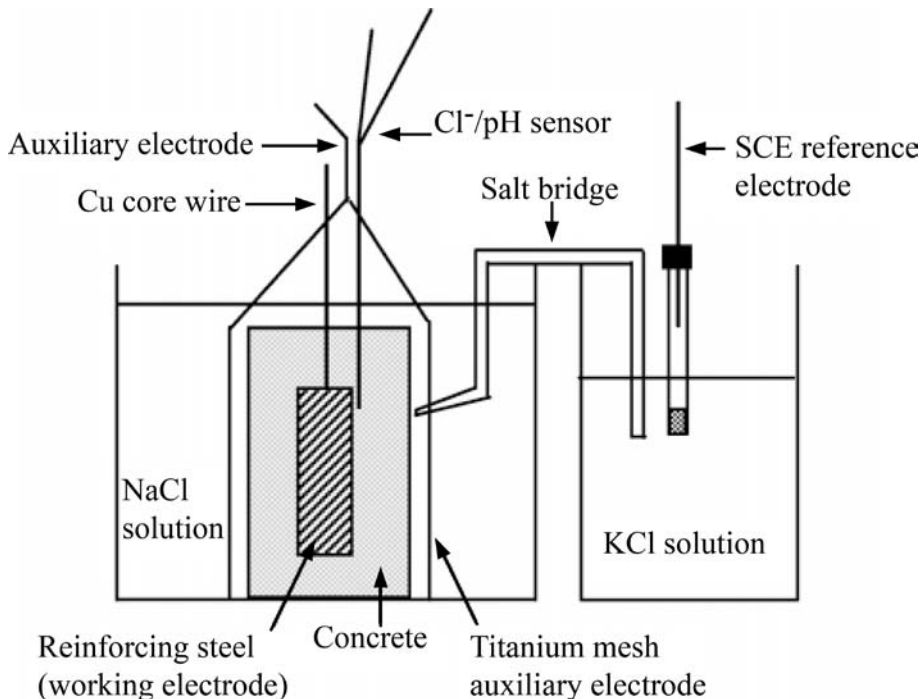
The metal oxide electrodes developed for this purpose include oxides of Ir, Pt, Pd, Rh, Ti, Sn, Al, Ru, Os, Ta, Mo, W, and Co. Compared with other metal oxide electrodes, iridium oxide electrodes exhibit better stability over a wide pH range, higher resolution, and quicker response at high temperatures, high-pressures and in aggressive media. Castro et al. (1996) clearly documented the dependence of the potential of M-MO activated titanium on the pH value.

#### A4.5.2 Apparatus and auxiliary equipment

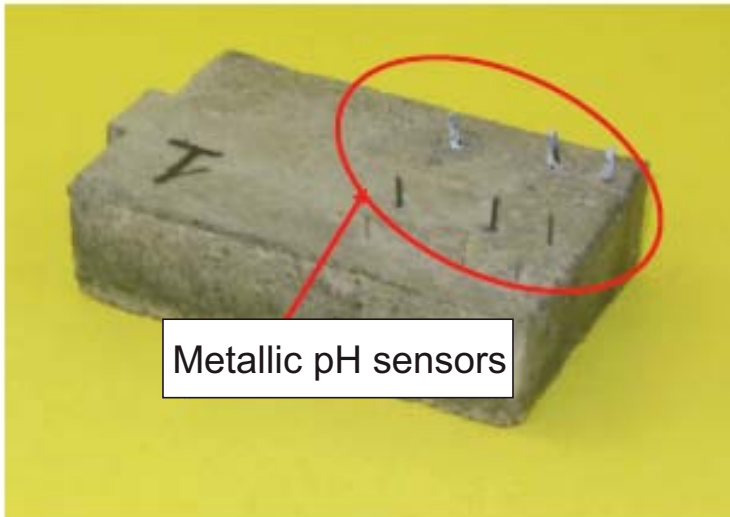
A great diversity of methods for preparing a metal/metal oxide electrode have been developed including electrochemical oxidation (Hitchman and Ramanathan 1988), electrochemical deposition (Baur and Spaine 1998), thermal oxidation in a carbonate bath (Du et al. 2006) and sputtering (Kreider et al. 1995). A schematic diagram of a “Combination  $\text{Cl}^-/\text{pH}$  Sensor” for *in situ* measurement of  $\text{Cl}^-$  concentrations and pH at the steel/concrete interface is shown in Figure A4-11 (Du et al. 2006). In this case the sensor consisted of an Ag/AgCl electrode and an iridium/iridium oxide electrode. They are aligned in parallel with a distance of  $\approx 1.5$  mm between the two tips and fixed in place with epoxy resin. Caution must be taken to avoid a short circuit occurring between the two electrodes.

A similar but simpler procedure for measuring the pore water pH of cementitious materials has been developed by Sánchez and Alonso (2007) as a preventative method for measuring the advance of the carbonation front in concrete. This method is based on the possibility of using small metallic pH sensors ( $\text{Ø} = 1.6$  mm and length = 15 mm). The authors tested four types of metallic sensors ( $\text{Ø} = 1.6$  mm and length = 15 mm). The trials were carried out in different pH solutions, simulating the pore solutions of concretes, and also in OPC based mortar specimens including low pH cement mortar (Figure A4-12).

The stability of the sensors was evaluated by means of periodical potential measurements, obtaining the calibration line E-pH. The evaluated sensors were quite stable in the solutions considered, giving detectable changes in the potential values when the pH of the solution was modified.



**Figure A4-11.** Schematic diagram for *in situ* measuring  $\text{Cl}^-$  concentrations and pH at the reinforcing steel/concrete interface and electrochemical parameters of the steel in concrete (Du et al. 2006).



**Figure A4-12.** Small metallic pH sensors embedded in mortar samples as tested by Sánchez and Alonso (2007).

#### A4.5.3 Sample preparation

Most of the studies took place in simulated concrete pore solutions, but some were conducted in small (reinforced) concrete or mortar samples. Furthermore, authors state that the *in situ* measurement of the pore water pH of cementitious materials using these sensors is also suitable for real applications, but this has yet to be proven.

The measurement of the electrode potential of the sensor is similar to the steel half-cell potential (corrosion potential) measurement, which has been widely used for reinforced concrete structures in real environments (Broomfield et al. 2002, Montemor et al. 2003, McCarter and Vennesland 2004). The pH sensors or Cl<sup>-</sup>/pH sensors can be embedded in reinforced concrete structures. An electrode of Ag/AgCl or Cu/CuSO<sub>4</sub> can be used as the reference electrode contacting the concrete through a piece of filter paper or foam plastics with an electrolyte solution, such as KNO<sub>3</sub>, on the concrete surface near the metallic pH sensors in the concrete. Lastly, the electrode potentials of the sensors can be measured periodically using a high impedance digital voltmeter or a potentiostat.

**Pre-conditioning of the samples.** Due to these methods having only been developed in recent years, they are in a preliminary research phase and no pre-conditioning procedures have yet been reported, because the main interest is that they are used for *in situ* measurements.

#### A4.5.4 Procedure

In these *in situ* methods, pH is determined by measuring the potential difference between a pH electrode and a reference electrode in solutions of known pH; the potential difference can therefore be used to determine pH in the cementitious material. All these metal/metal oxide electrodes methods are based on the same procedure and some of them were developed for monitoring not only the pH values but also Cl<sup>-</sup> concentrations. In these electrodes, the pore water pH and Cl<sup>-</sup> concentration of the concrete are obtained through the calibration curve of the potentiometric response of the sensors and measuring the potentials of the sensors, respectively. The tests are carried out at room temperature (25 ± 2°C). The principle of a metal/metal oxide electrode as a pH sensor can be interpreted using different equations described by Kinoshita and Madou (1984). According to these equations, at a given temperature, the equilibrium potential of a metal/metal oxide electrode depends only on pH in the solution. By measuring the metal/metal oxide potential, the pH value of the test solution can be calculated.

#### A4.5.5 Critical parameters and considerations

The main advantages of the use of metal/metal oxide electrodes for measuring the pore water pH of cementitious materials are that they are non-destructive and they seem to be sufficiently robust and sensitive. However, their application has been mainly focussed on the study of corrosion and protection of steel reinforcements in concrete. So, although the measurement of pH values and of  $\text{Cl}^-$  concentration gives good results, they are not yet fully developed for analyzing the concentrations of other elements/species in the pore water of cementitious materials. Furthermore, their application in real cementitious materials and environmental conditions has yet to be evaluated.

A lot of these sensors have also been developed to analyse the advance of the carbonation front in cementitious materials, which is reasonably well defined, but requirements for the accuracy of the pH sensors are not necessarily high (Bertolini et al. 1998). Their possible application to the accurate determination of the pore water pH of low pH cementitious materials is, therefore, not yet known.

#### A4.5.6 Fibre-optic transmission sensors

Fibre-optical planar transmission sensors have been recently developed for monitoring pH in concrete structures (Blumentritt et al. 2008). The fibre-optic planar transmission sensor setup uses a wafer saw for cutting the sensitive zone, which can monitor *in situ* pH in concrete. The sensitive zone of the fibre-optic sensor setup is filled with a sensing material, the colour of which varies reversibly upon change of pH. The sensing material is an azo-dye, which acts as a weak acid with a protonated and deprotonated form. The deprotonated form exhibits a bathochrome shift of absorption compared to the protonated one, resulting in a colour change of the dye from yellow to red. Therefore the colour of the sensing material depends upon the ratio of concentrations of the protonated and deprotonated form of the dye, which in turn is dependent upon the pH of the surrounding medium.

A calibration of the sensing material has been done with five planar transmission sensors, placed in a dilute KOH solution with a pH = 10.40. The pH of the solution was incrementally increased every five minutes by the addition of more KOH. During the experiment the pH was determined with a pH-meter. The absorption of all five fiber-optical sensors was measured every 30 s. Figure A4-13 shows the absorption spectra of one of these sensors. The spectra were measured shortly before the pH of the KOH solution was increased.

Although this novel technique appears promising, thorough testing and evaluation are required prior to application in low pH cementitious materials.

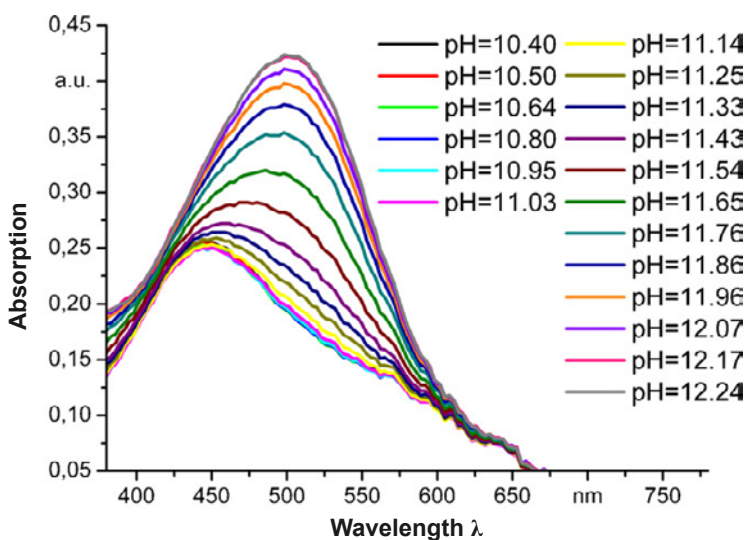


Figure A4-13. Absorption spectra of a pH sensor in different pH solutions (Blumentritt et al. 2008).

#### A4.6 pH testing methods for other materials

As well as the pH measurement procedures described above, there are several standard pH measurement methods that have been mainly developed for soils and wastes. Some of these methods include:

- Method EPA 9045 D, “Soil and waste pH”: An *ex situ* leaching method using a solid:water (s:w) ratio = 1:1.
- University of Oregon. WCC 103 Publication: An *ex situ* leaching method using s:w ratios of 1:1 and 1:2.
- ASTM Standard D4972-89 “Test Method for pH of soils”: An *ex situ* leaching method using a s:w ratio of 2.5:1.
- ASTM D4542-07 “Test method for pore water extraction and determination of the soluble salt content of soils by refractometer”.

The information that can be extracted from these methods indicates that the *ex situ* leaching methods of low S:L ratios are preferred in other research fields and can be assumed to give tried and tested pH values that are reliable given their acceptance use by the scientific community. All these methods agree on using low s:w ratios, as well as the majority of the *ex situ* leaching methods used for cementitious materials described above.

#### A4.7 pH measurement

In addition to the procedures used for extracting the pore water, the methods used to actually measure the pH value must also be considered. The method used to measure the pH may affect the value depending on whether a direct measurement of the pH is made with an electrode or is determined by titration of OH<sup>-</sup> ions (Diamond 1981, Byfors et al. 1986). Discrepancies between the pH values measured with the electrode and those determined by titration may be primarily due to the fact that the electrode does not measure the hydroxyl ion concentration but the lower proton activity (Trithart 1989).

Even if the pH is measured directly with an electrode, several considerations have to be taken into account:

- Samples with very low or very high pH may give incorrect readings on the meter. For samples with an expected pH > 10 as is the case for all hydrated OPC based cementitious materials, the measured pH may be incorrectly low. This error can be minimized by using a low sodium-error electrode. Strong acid solutions, with a pH < 1, may also give incorrectly high pH measurements, but which is not considered important in the case of cementitious systems.
- Combination electrodes incorporating both measuring and reference functions are convenient to use.
- Temperature fluctuations will cause measurement errors, particularly at high pH. Therefore, a thermometer and/or a temperature sensor for automatic compensation are recommended.
- Electrodes have to be maintained and cleaned regularly to avoid slow responses and errors arising from electrodes that are not clean. Electrodes can be cleaned (1) with an ultrasonic bath, (2) with a detergent, rinsed several times with water, placed in 1:10 HCl acid so that the lower third of the electrode is submerged, and then thoroughly rinsed with water, or (3) following the manufacturer's instructions.

Furthermore, as already described, an electrode specially designed for measuring in suspensions must be used if a direct pH measurement of the suspension is made using an *ex situ* leaching procedure.

A detailed operating procedure of a pH meter and electrode setup system cannot be incorporated into this report due to the wide variety of commercially available pH meters, electrodes and accessories. It is important, however, that each analyst is fully acquainted with the operation of their pH measurement system and familiar with all instrument functions. The pH electrode must be calibrated by a

minimum of two pH buffers (three buffers is strongly recommended) that bracket the expected pH of the samples and are approximately three pH units or more apart. Repeat adjustments on successive portions of the two or three buffer solutions until readings are within  $\pm 0.05$  pH units of the buffer solution value.

pH indicators can also be used to give a bracket range of pH values (e.g. between 8.4 and 10.0 if using Phenolphthalein; a pH indicator commonly used in the evaluation of the concrete carbonation). However, although these pH indicators are very simple to use, they do not provide a specific pore water pH of a cementitious material and so cannot be used in the current project.

#### A4.8 Evaluation of pH measurement methods

Considering the pH measurement methods described in the literature and the initial requirements demanded of the selected method for measuring the pore fluid pH of low pH cementitious materials, a critical evaluation of all identified methods is provided.

It is recommended that “Pore fluid expression” is selected as the reference method for pH determination of the pore fluid of cementitious materials, as it is usually considered as being the reference case in the literature.

Due to the limitations of this method, however, such as the requirement for a special and expensive press apparatus, the need for a fairly large amount of sample and careful pre-conditioning of the samples to extract a sufficient amount of pore fluid, the pore expression technique is not practical enough to be recommended as a routine method. The selection of a simpler and faster method is, therefore, necessary.

In order to choose the most reliable method for a routine pH measurement method for low pH cementitious materials, a critical evaluation of the advantages and disadvantages has been performed between those pH measurement methods reviewed from the literature and those more widely employed, summarized in Table A4-3.

**Table A4-3. Comparison of pH measurement methods from the literature.**

Considerations	pH measurement method		
	<i>Ex situ</i> leaching methods	<i>In situ</i> leaching methods	Embedded sensors
Has the method been calibrated with pore expression procedure?	Yes	Yes	No
Is it a faster and simple method that can be used as routine?	It depends on the extraction time used.	No, it requires a long period of pre-conditioning.	It could be, after the calibration of the developed electrode.
Equipment requirements.	No special device.	No special device.	It needs the fabrication of a specific M-MO electrode.
Sample requirements.	It needs small amount of sample to be extracted from the tested material.	It can be used <i>in situ</i> in real structures.	It can be used <i>in situ</i> in real structures.
Errors in pH measurement.	pH value mainly affected by dilution from very low solid/solvent ratios and carbonation. May also be affected by differences in dissolution rates of hydrated phases.	Deviations may occur due to carbonation, slow equilibration and dilution from excessive cavity/ water volume.	The electrode calibration must be accurate.
Has the method been used by many authors?	Yes	No	No
Has the method been tested in many cementitious materials?	Yes	No	No
Has the method been tested in low-pH cementitious materials?	Yes	No	No

According to Table A4-3, among the procedures described in this report the *ex situ* leaching methods are the more suitable to be developed as a routine method for the stated objective. This conclusion is based on the following considerations:

- The majority of the *ex situ* leaching methods are reasonably fast and easy to use, because the procedures are simple and do not require any special or expensive equipment.
- Pre-conditioning of the samples is not required as is the case with the *in situ* leaching methods that demand a long pre-conditioning time. Using *ex situ* leaching methods, the pore fluid pH of the materials can therefore be analyzed at any specific age of hydration.
- The majority of authors that used *ex situ* leaching methods also compared the obtained pH values with those obtained using pore fluid expression technique, giving credibility and validity to this kind of procedure.
- The *ex situ* leaching methods are more commonly used than any other pH measurement methods described in the literature and so their critical parameters are better known.
- No limitation exists in the type of material, either paste, mortar or concrete, that can be used with the *ex situ* leaching method, and the volume of sample is limited by the volume of the beaker used.
- *Ex situ* leaching methods have been already tested in low pH cementitious materials giving good results.

The main disadvantage of the *ex situ* leaching methods is the possible error caused by dilution and/or dissolution of the different phases in cementitious materials. However, this is less problematic than conventional OPC with its concentrations of Na and K in the pore water and Ca buffered by CH.

In order to select a suitable protocol for a pH measurement method based on *ex situ* leaching, the following considerations should be taken into account:

- *Solvent*: the recommended solvent by all authors in the literature is deionised water or CO<sub>2</sub> free deionised water. For the proposed method the recommended solvent is CO<sub>2</sub> free deionised water and its preservation in either an argon or nitrogen atmosphere should be evaluated.
- *Sample amount*: a sample between 5 and 30 grams is sufficient for a representative sample and is an easily obtainable/manageable quantity.
- *Fineness of particles*: influences the time for the cementitious material to equilibrate with any liquid it comes into contact with and so for shorter extraction times a powdered sample of  $\phi = 80 \mu\text{m}$  is recommended.
- *Water:solid ratio*: the more commonly used ratios range between 1:1 and 5:1.
- *Extraction time*: given that one of the objectives of the present report is to obtain a fast method, short extraction times are preferred, on the order of a few minutes in the case of powdered samples.
- *Stirring time*: in using short extraction times, it is recommended that the suspension is stirred vigorously.
- *Filtration*: is not needed if a direct measurement of the pH suspension is taken with an appropriate electrode. If determination of the pH by OH<sup>-</sup> titration or the chemical composition of the pore fluid is required, however, the suspension must be filtered. In which case both procedures, without and with filtering the suspension, would have to be compared due to the identification in the literature of a pH decrease due to filtering e.g. Räsänen and Penttala (2004).
- *Curing time*: in the case of the low pH cementitious materials, the curing time and the curing conditions are crucial factors in obtaining a reliable pH measurement for low pH cementitious materials. This is due to the expected pozzolanic reaction and associated decrease in pH being on the order of days and weeks. To obtain the representative pH value of a low pH cementitious material, a curing time of 90 days is recommended.
- *Control of carbonation*: in order to prevent the carbonation of the cementitious material samples, the use of an argon or nitrogen atmosphere during the whole test must be evaluated.

## Preliminary experimental investigation of factors influencing pH

Following the literature review and the selection of pore fluid expression (PFE) as the reference method and *Ex Situ* Leaching (ESL) methods as the routine method, CSIC conducted different tests in order to define the preliminary protocols (Chapter 3). The tests were conducted to evaluate the critical parameters identified in the literature review that may affect the measured pH values using the reference (PFE) and routine (ESL) methods.

The cement paste used for the tests had the same composition as the cement paste samples fabricated by the CBI Laboratory (Chapter 3, Table 3-1), but in this case the samples were fabricated by the CSIC laboratory. After fabrication, all samples were stored in a chamber with 100% RH at  $21 \pm 2^\circ\text{C}$ . The curing time defined for the majority of the tests was 28 days with some being conducted after the recommended 90 days based on the literature review (Appendix A).

### Critical parameters for the reference (PFE) method

The matrix of critical parameter tests for the reference (PFE) method is summarized in Table B-1. Each test was repeated in duplicate and the pH value obtained directly with a pH electrode and determined indirectly by  $\text{OH}^-$  titration.

Table B-2 shows the pore fluid pH values obtained from the critical parameter tests. The mean value from each test method is shown in Figure B-1.

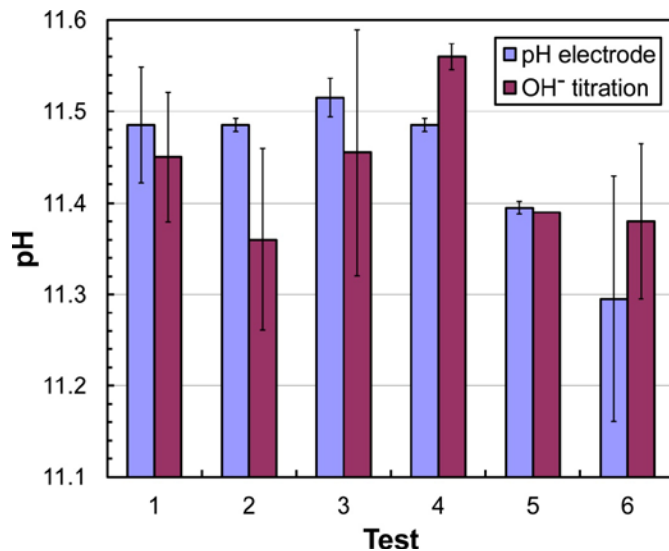
**Table B-1. Critical parameter tests for the reference (PFE) method.**

Test	Particle size			$\text{N}_2$ protection against carbonation			
				$\text{CO}_2$ -free water used		During pH measurement	
	5 mm	10 mm	20 mm	Yes	No	Yes	No
1	○				○		○
2	○			○			○
3	○				○	○	
4	○			○		○	
5		○			○		○
6			○		○		○

**Table B-2. Pore fluid pH values obtained directly with a pH electrode and determined by  $\text{OH}^-$  titration for the reference (PFE) method after 28 days curing.**

Test	pH electrode			$\text{OH}^-$ titration		
	1 st measure	2 nd measure	Mean pH $\pm$ SD	1 st measure	2 nd measure	Mean pH $\pm$ SD
1	11.44	11.53	11.49 $\pm$ 0.06	11.40	11.50	11.45 $\pm$ 0.07
2	11.49	11.48	11.49 $\pm$ 0.01	11.29	11.43	11.36 $\pm$ 0.10
3	11.50	11.53	11.52 $\pm$ 0.02	11.36	11.55	11.46 $\pm$ 0.13
4	11.49	11.48	11.49 $\pm$ 0.01	11.55	11.57	11.56 $\pm$ 0.01
5	11.39	11.40	11.40 $\pm$ 0.01	11.39	11.39	11.39 $\pm$ 0.00
6	11.39	11.20	11.30 $\pm$ 0.13	11.44	11.32	11.38 $\pm$ 0.08
Mean pH $\pm$ SD			11.44 $\pm$ 0.09			11.43 $\pm$ 0.09
Mean pH $\pm$ SD (Tests 1–4)			11.49 $\pm$ 0.03			11.46 $\pm$ 0.10





**Figure B-1.** Mean pore fluid pH values obtained by direct measurement with a pH electrode and determined by OH<sup>-</sup> titration for the reference (PFE) method critical parameter tests after 28 days curing. Error bars are ±SD.

Several conclusions can be drawn from analyzing the test results shown in Table B-2 and Figure B-1:

- Overall, a similar mean pH value was obtained for each test and demonstrates good reproducibility of the reference (PFE) method.
- In general, the pH values obtained either by direct measurement with a pH electrode or as determined by OH<sup>-</sup> titration are quite similar for each test and so both procedures are valid for use in the reference (PFE) method. The ±SD, however, tends to be smaller when the pH is obtained with a pH electrode as opposed to determination by OH<sup>-</sup> titration.
- If each step of the protocol is made over the timeframe of minutes (cf. Section 3.2.7), carbonation does not appear to affect the pH values obtained; similar pH values are obtained without and with atmospheric protection of N<sub>2</sub> gas (Figure B-1, Tests 1–4).
- The particle size seems to affect the pH value, with coarser particle sizes (Figure B-1, Test 5 and 6) resulting in a slightly lower pH. It is evident that the SD shown in Table B-2 is lower when the pH is measured with a pH electrode and only the tests using a crushed particle size Ø = 5 mm (Tests 1–4) are considered.

In addition to the pore fluid pH values, the chemical composition of all the expressed pore solutions was analyzed (Figure B-2).

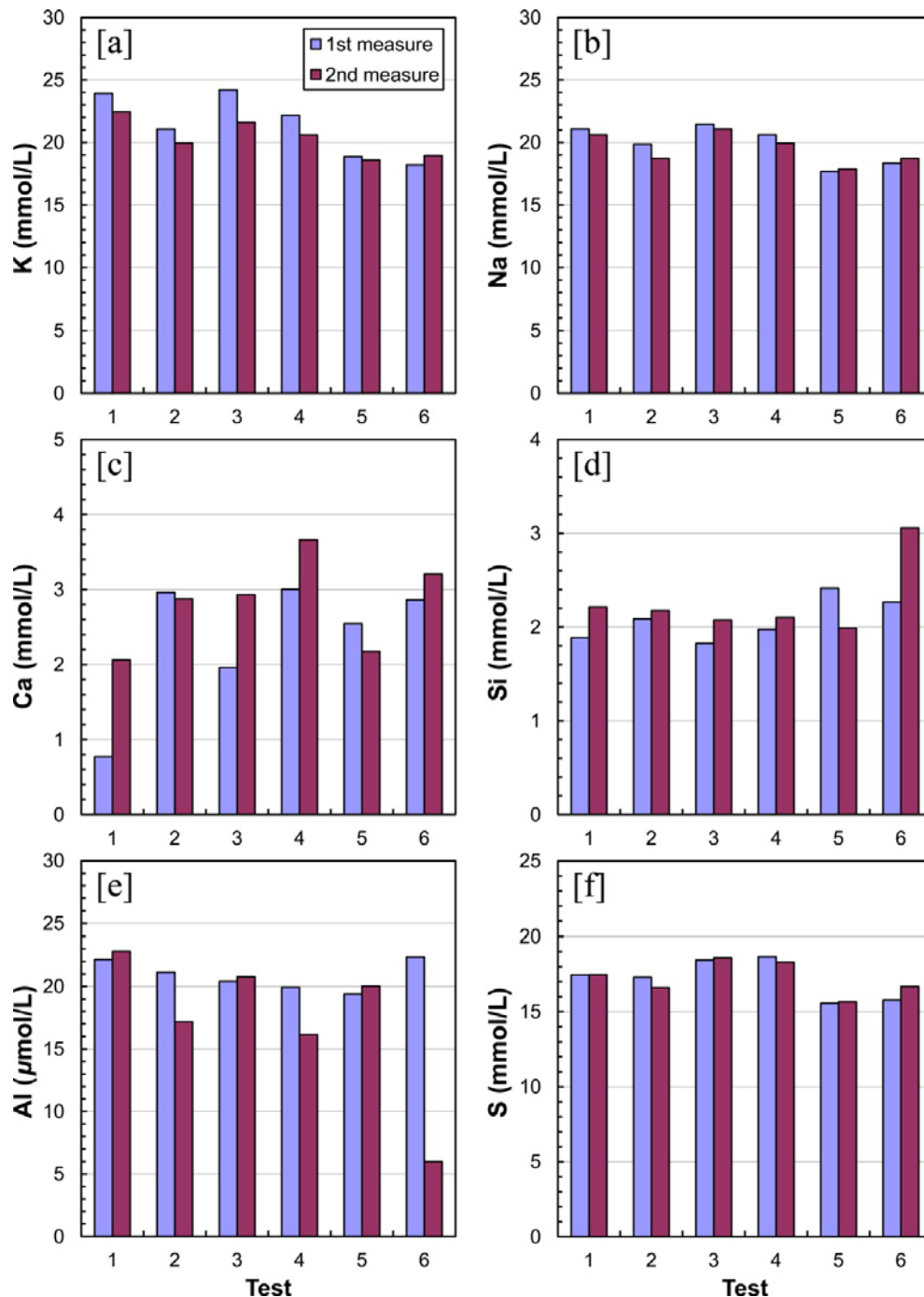
The lower pH values obtained for the coarsely crushed particle size of 10 and 20 mm in tests 5 and 6, respectively (Figure B-1), is a likely consequence of the lower K and Na concentrations in solution (Figure B-2a and b). The differences in the increased Si concentration (Figure B-2d) and decreased S concentrations (Figure B-2f) would have relatively little effect on the pH.

### Sample pre-conditioning for the reference (PFE) method

Further to tests 1–6 described in the previous section, consideration was also given to the addition of sprayed water in the sample pre-conditioning for the reference (PFE) method. Using the same composition low pH cement pastes (Table 3-1) the addition of the CO<sub>2</sub>-free deionised water for pre-conditioning was evaluated in terms of the possible effects on:

- The pH value and the chemical composition of the pore water.
- The dilution of the pore water and of the dissolution of the hydrated solid phases.

Little effect was seen on the pH value by the addition of water with the pH = 11.50 with no spraying and pH = 11.48 with spraying, giving a negligible difference of 0.02 pH units.

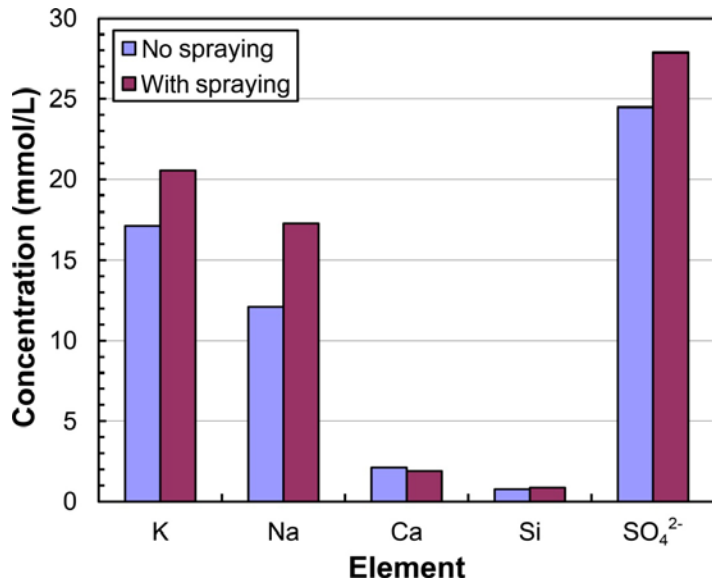


**Figure B-2.** Chemical composition of pore waters for the reference (PFE) method after 28 days curing. All concentrations are shown in mmol/L except for Al shown in  $\mu\text{mol/L}$ . (a) K, (b) Na, (c) Ca, (d) Si, (e) Al, (f) S.

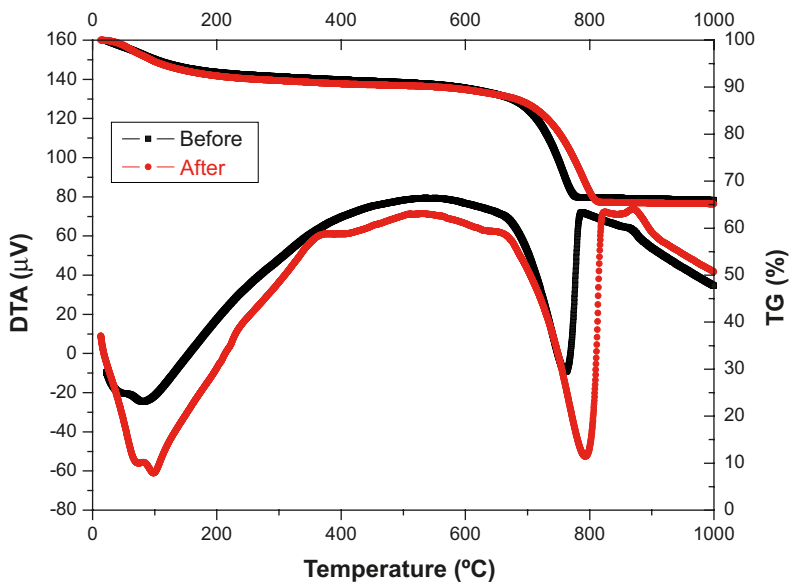
The major element chemical composition of the pore waters with no spraying and with spraying are shown in Figure B-3.

According with Figure B-3, the addition of  $\text{CO}_2$ -free deionised water does not significantly affect the chemical composition of the pore water, but there are some differences. Instead, it is recommended that if, and only if, the low pH cementitious material is seen to be very dry that water can be sprayed onto the surface to assist in obtaining sufficient pore water for subsequent analysis.

With respect to the possible influence of the addition of  $\text{CO}_2$ -free deionised water in the dilution of hydrated solid phases, DTA/TG analysis were done before and after pore fluid expression (Figure B-4).



**Figure B-3.** Chemical compositions of pore water from the reference (PFE) method after 28 days curing with no spraying and with spraying CO<sub>2</sub>-free deionised water to pre-condition the sample.



**Figure B-4.** Combined DTA/TG before and after pore fluid expression of the low pH cement pastes following 28 days curing.

Only an acceptably slight deviation can be seen between the DTA/TG before and after the pore fluid expression (Figure B-4) and can be interpreted as representing the same hydrated solid phases. Consequently, the addition of water and the reference (PFE) method itself seem to have no effect on the hydrated solid phases in the low pH cementitious materials. Furthermore, no CH could be identified by the absence of an endothermic peak between 400–500°C, which is an expected consequence of the pozzolanic reaction and is consistent with the measured pH being below 12.5.

### Conclusions and recommendations from the critical parameter tests on the reference (PFE) method

Several conclusions can be drawn from these critical parameter tests and their potential effects on the reference (PFE) method:

- Although carbonation does not seem to influence the measured pore water pH significantly, it is nevertheless recommended that each step of the procedure is undertaken as quickly as possible and an inert gas, either N<sub>2</sub> or argon, should be used to protect the pore water sample from carbonation.
- The most suitable crushed particle size is 5 mm.
- The CO<sub>2</sub>-free deionised water addition must only be done when the low pH cementitious sample is seen to be dry, especially if the chemical composition of the pore water is going to be analyzed.

### Critical parameters for the routine (ESL) method

The matrix of critical parameter tests for the routine (ESL) method is summarized in Table B-3. Each test was repeated in triplicate and the pH value obtained directly with a pH electrode and also determined by OH<sup>-</sup> titration, but only for the filtered pore waters.

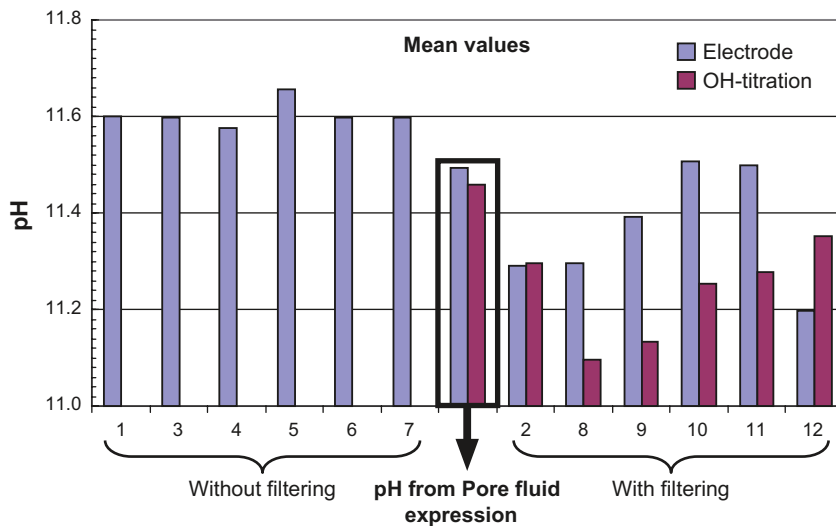
Table B-4 shows the pore water pH values obtained from the critical parameter tests of the routine (ESL) method. The mean value from each test method is shown in Figure B-5.

**Table B-3. Critical parameter tests for the routine (ESL) method.**

Test	Particle size Ø		CO <sub>2</sub> protected stirring?		Filtered?		CO <sub>2</sub> protected filtration?		CO <sub>2</sub> protected CO <sub>2</sub> -free deionised water?		CO <sub>2</sub> protected pH measurement?		Stirred pH measurement?	
	80 µm	2.5 mm	Yes	No	Yes	No	Yes	No	Yes	No	Yes	No	Yes	No
1	○			○		○		–		○		○	○	
2	○			○	○			○		○		○	○	
3		○		○		○		–		○		○	○	
4	○			○		○		–		○		○		○
5	○			○		○		–	○			○	○	
6	○		○			○		–		○	○		○	
7	○		○			○		–	○		○		○	
8	○		○		○		○			○		○	○	
9	○		○		○		○		○			○	○	
10	○		○		○		○			○		○	○	
11	○		○		○		○		○		○		○	
12		○		○	○			○		○		○	○	

**Table B-4. Pore water pH values measured using the routine (ESL) method tests.**

Test	pH electrode				OH <sup>-</sup> titration			
	1 st measure	2 nd measure	3 rd measure	Mean pH ±SD	1 st measure	2 nd measure	3 rd measure	Mean pH ±SD
1	11.60	11.60	11.60	11.60 ±0.00	–	–	–	–
2	11.32	11.28	11.27	11.29 ±0.03	11.38	11.20	11.30	11.29 ±0.09
3	11.62	11.59	11.58	11.60 ±0.02	–	–	–	–
4	11.57	11.60	11.56	11.58 ±0.02	–	–	–	–
5	11.66	11.65	11.66	11.66 ±0.01	–	–	–	–
6	11.62	11.58	11.59	11.60 ±0.02	–	–	–	–
7	11.57	11.61	11.61	11.60 ±0.02	–	–	–	–
8	11.25	11.33	11.31	11.30 ±0.04	11.15	11.04	11.10	11.09 ±0.05
9	11.38	11.41	11.39	11.39 ±0.02	11.00	11.11	11.29	11.13 ±0.15
10	11.54	11.48	11.50	11.51 ±0.03	11.41	11.23	11.11	11.25 ±0.15
11	11.49	11.48	11.52/11.50	11.50 ±0.02	11.15	11.28	11.41/11.36	11.28 ±0.13
12	11.37	10.95	11.27	11.20 ±0.22	11.43	11.30	11.32	11.35 ±0.07
Mean pH ±SD				11.48 ±0.16				11.24 ±0.13



**Figure B-5.** Mean pH values obtained after 28 days curing measured with a pH electrode and determined by OH<sup>-</sup> titration from the 12 tests of the routine (ESL) method. Also shown for reference are the mean pH values from the reference (PFE) method.

Several conclusions can be drawn from the pH values obtained from the critical parameter tests of the routine (ESL) method shown in Table B-4 and Figure B-5:

- As seen for the reference (PFE) method, a similar pH value is obtained for each of the triplicate measurements for each test. The repeatability of the routine (ESL) method is therefore satisfactory with low SD. The only exception to this was seen in test 12, which used a coarse crushed particle size (2.5 mm) and no protection against carbonation.
- In the case of the unfiltered suspensions, the pH values obtained are very consistent regardless of the test conditions, mean pH = 11.60, SD = 0.03. Differences arising from particle size and/or carbonation are, therefore, seemingly insignificant if measuring the pH of a low pH cementitious material suspension.
- In comparison with the unfiltered suspensions, the pH values of the filtered solutions are very variable with the largest decrease seen in the tests that used no protection against CO<sub>2</sub> contamination (Tests 2, 8, 9, and 12). The use of N<sub>2</sub> gas to protect the pore water sample from CO<sub>2</sub> contamination is therefore necessary if filtering is used.
- The pH values determined by OH<sup>-</sup> titration are not consistent with the pH measured with a pH electrode and are much lower than the mean pH value(s) for the reference (PFE) method. Determining the pH by OH<sup>-</sup> titration is therefore not recommended for the routine (ESL) method.
- The best match to the mean pH value using the reference (PFE) method is made with filtering, and protecting the pore water sample from atmospheric CO<sub>2</sub> contamination. It is therefore recommended that this approach forms the basis of the preliminary routine (ESL) method protocol.
- Using a crushed particle size Ø = 2.5 mm particle size gives a consistently lower pH value and furthermore, takes longer for the actual pH measurement to stabilize.

#### Further testing of the critical parameters affecting the routine (ESL) method

From the results shown in Table B-4 and Figure B-5, another batch of the low pH cement paste was made and after curing for 28 days, a new set of critical parameter tests were conducted to assess:

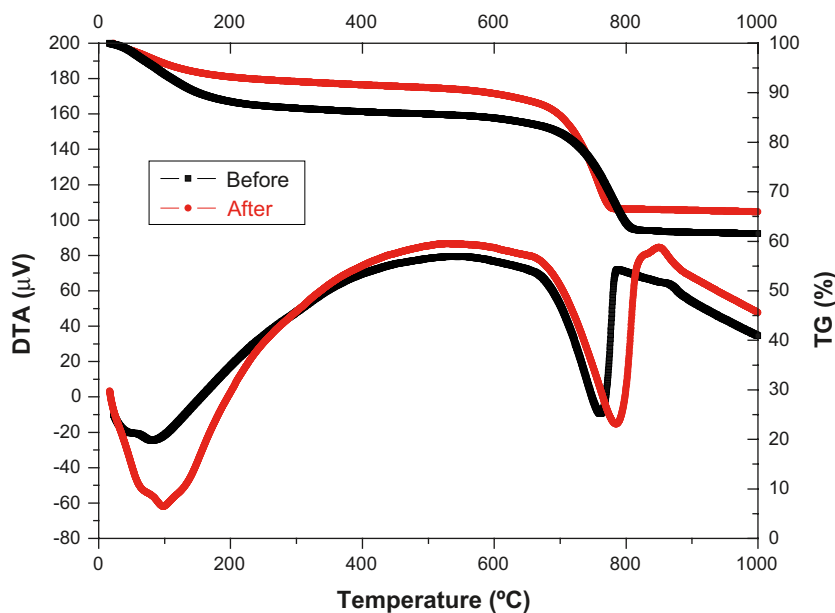
- The possible influence of the CO<sub>2</sub>-free deionised water added during the preparation of the suspension had on the dilution of the hydrated solid phases.
- The possible influence of carbonation when a particle size Ø = 2.5 mm is used.
- The increase in temperature as a result of the powdering process and the effect this may have on facilitating carbonation of the sample. Given the difficulty in powdering a concrete manually, this part of the study was also conducted using an automatic grinder and after 90 days curing.

The possible dilution of the hydrated solid phases was investigated with DTA/TG on the low pH cementitious material before the suspension was prepared and after the pH measurement of the pore water (Figure B-6). As in the case of the reference (PFE) method, the before and after DTA/TG were acceptably similar and could be interpreted as the same hydrated phases being present and so any dilution effects can be reasonably assumed to be negligible.

The possible influence of carbonation when the particle size  $\varnothing = 2.5$  mm was assessed through 10 tests to assess the difference with the mean pH value obtained from the reference (PFE) method (Table B-5).

**Table B-5. Differences between pore fluid pH values measured using the *ex situ* leaching technique ( $\varnothing = 2.5$  mm) 2.5. 28 days curing.**

Test	Parameters	Difference with reference (PFE) method
1	No CO <sub>2</sub> protection	-0.28
2	CO <sub>2</sub> -free water under an N <sub>2</sub> atm.	-0.27
3	Stirring and pH measured under an N <sub>2</sub> atm.	-0.12
4	CO <sub>2</sub> -free water under an N <sub>2</sub> atm. Stirring and pH measured under an N <sub>2</sub> atm.	-0.09
5	Filtering	-0.38
6	Filtering Stirring and filtering under an N <sub>2</sub> atm.	-0.35
7	Filtering pH measured under an N <sub>2</sub> atm. Stirring and filtering under an N <sub>2</sub> atm.	-0.50
8	Filtering CO <sub>2</sub> -free water under an N <sub>2</sub> atm. Stirring and filtering under an N <sub>2</sub> atm.	-0.48
9	Filtering CO <sub>2</sub> -free water under an N <sub>2</sub> atm. pH measured under an N <sub>2</sub> atm. Stirring and filtering under an N <sub>2</sub> atm.	-0.42
10	Filtering pH measured under an N <sub>2</sub> atm.	-0.52



**Figure B-6.** DTA/TG of the low pH cement pastes before preparing the suspension and after filtration and the pH measurement had been made.

The use of a particle size  $\varnothing = 2.5 \text{ mm}$  in the routine (ESL) method gives consistently lower pore water pH values in comparison to the mean pH value obtained using the reference (PFE) method. Furthermore, the closest values are obtained when the pH is measured directly in the suspension with a pH electrode and the stirring and the pH measurement are made under a  $\text{CO}_2$  protected  $\text{N}_2$  atmosphere.

Figure B-7 shows thermographic images taken before and after manually powdering the low pH cement pastes and it can be seen that the temperature does not increase significantly ( $+3.5^\circ\text{C}$ ) during this procedure.

Figure B-8 shows the thermographic images taken before and after the low pH cement pastes were powdered with an automatic grinder and the same temperature increase ( $+3.5^\circ\text{C}$ ) is, again, not significant. Furthermore, using an automatic grinder had no effect on the pore water pH = 11.43 in comparison with the pore water pH = 11.38 from manually grinding the low pH cement paste.

### Conclusions and recommendations from the critical parameter tests on the routine (ESL) method

Taking into account the results obtained during this evaluation of the routine (ESL) method, several conclusions and recommendations can be made:

- When the pH is measured directly in the suspension with a pH electrode, carbonation effects do not seem to be a problem. However, the protection against carbonation is mandatory if the suspension is filtered and the pH is measured in the filtered solution.
- The more suitable particle size for use in the routine (ESL) method is a fine powder of  $\varnothing \leq 80 \mu\text{m}$ .
- Using a pH electrode and sufficient  $\text{CO}_2$  protection, the routine (ESL) method with filtering gives a pH value that is comparable with that obtained using the reference (PFE) method.
- The method used to powder the low pH cementitious material does not seem to influence the pH value of the pore water.

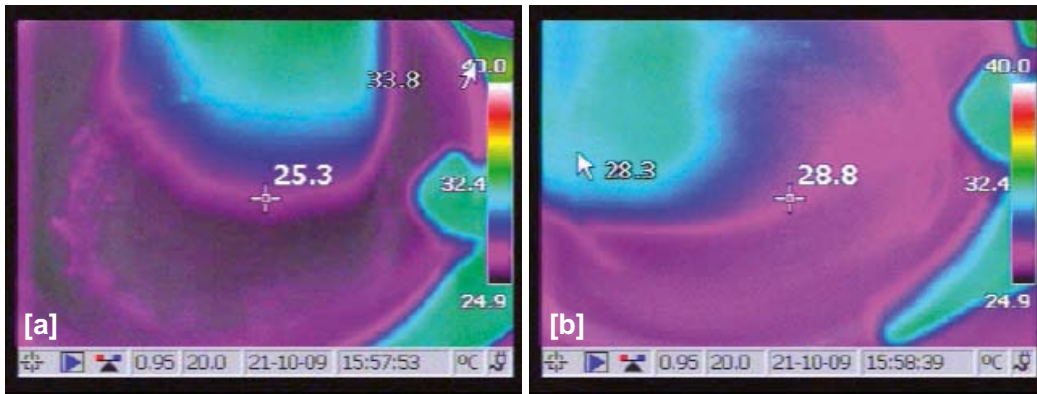


Figure B-7. Thermographic images taken (a) before and (b) after manually powdering the low pH cement pastes.

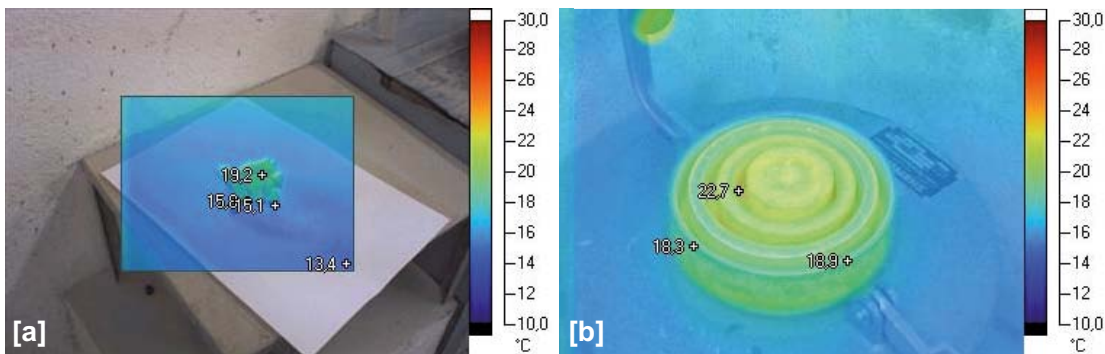


Figure B-8. Thermographic images taken (a) before and (b) after powdering the low pH cement pastes with an automatic grinder.

## Template – Reference method – To be used for each sample

## REFERENCE METHOD: TEMPLATE FOR EACH SAMPLE

Laboratory:

Sample identification:

Date of receipt of sample:

Visual inspection of sample at receipt, comments (dry, wet, colour, other observations):

Storage of sample (RH, Temperature etc):

Storage time (days):

Date for measurement of pH of the sample:

	Time involved (min)	Protocol problems detected or comments					
Sample preparation							
Sample pre-conditioning							
Pore fluid expression							
Direct pH measurement after filtering with 0.45 µm filter.							
[OH <sup>-</sup> ] titration after filtering with 0.45 µm filter.							
Moisture content (ml/g)	Sample Weight (g)	CO <sub>2</sub> -free deionised water added	Dilution factor	Direct pH (measured with electrode)	[OH <sup>-</sup> ] (mg/L)	[OH <sup>-</sup> ] corrected considering dilution factor	pH from [OH <sup>-</sup> ]



**TEMPLATE FOR REFERENCE METHOD RESULTS**

	Moisture content (ml/g)	Sample Weight	CO <sub>2</sub> -free deionised water added	Dilution factor	Direct pH (measured with electrode)	[OH <sup>-</sup> ] (mg/L)	[OH <sup>-</sup> ] corrected considering dilution factor	pH from [OH <sup>-</sup> ]
Sample-1								
Sample-2								
Sample-3								
Mean value ± SD								
Comments	Electrode buffers used:							

## Templates – Routine method – To be used for each sample

SKB R-12-02

ROUTINE METHOD (measuring the pH directly in the suspension): TEMPLATE FOR EACH SAMPLE						
Laboratory:						
Sample identification: Moisture content (ml/g):						
Date of receipt of sample:						
Visual inspection of sample at receipt, comments (dry, wet, colour, other observations):						
Storage of sample (RH, Temperature etc):						
Storage time (days):						
Date for measurement of pH of the sample:						
	Time involved (min)			Protocol problems detected or comments		
	1 <sup>st</sup> meas.	2 <sup>nd</sup> meas.	3 <sup>rd</sup> meas.			
Sample preparation (Powdering)				Manually or using an automatic grinder:		
Suspension preparation						
pH measured directly in the suspension						
Powdered sample weight (g) and CO <sub>2</sub> -free deionised water added (ml)						
1 <sup>st</sup> powdered sample			2 <sup>nd</sup> powdered sample		3 <sup>rd</sup> powdered sample	
g	ml		g	ml	g	ml
Direct pH measured with electrode in the suspension						
1 <sup>st</sup> measurement		2 <sup>nd</sup> measurement		3 <sup>rd</sup> measurement		Mean value ± SD

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**ROUTINE METHOD (measuring the pH in the filtered solution): TEMPLATE FOR EACH SAMPLE**

Laboratory:

Sample identification:Moisture content (ml/g):

Date of receipt of sample:

Visual inspection of sample at receipt, comments (dry, wet, colour, other observations):

Storage of sample (RH, Temperature etc):

Storage time (days):

Date for measurement of pH of the sample:

	Time involved (min)			Protocol problems detected or comments	
	1 <sup>st</sup> meas.	2 <sup>nd</sup> meas.	3 <sup>rd</sup> meas.		
Sample preparation (Powdering)				Manually or using an automatic grinder:	
Suspension preparation					
Filtering 0.45 µm					
pH measured in the suspension after filtering					
[OH <sup>-</sup> ] titration after filtering with 0.45 µm filter.					
Powdered sample weight (g) and CO <sub>2</sub> -free deionised water added (ml)					
1 <sup>st</sup> powdered sample		2 <sup>nd</sup> powdered sample		3 <sup>rd</sup> powdered sample	
g	ml	g	ml	g	ml
pH measured with electrode in the filtered suspension					
1 <sup>st</sup> measurement		2 <sup>nd</sup> measurement		3 <sup>rd</sup> measurement	
				Mean value ± SD	

<b>TEMPLATE FOR ROUTINE METHOD RESULTS</b>						
	Moisture content (ml/g)	pH measured directly in the suspension	pH measured in the suspension after filtering	pH from [OH <sup>-</sup> ] after filtering	pH measured with electrode using the reference method	pH from [OH <sup>-</sup> ] using the reference method after filtering
Sample-1						
Sample-2						
Sample-3						
Mean value $\pm$ SD						
Comments	Electrode buffers used:					