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SCM PASTE SAMPLES EXPOSED TO AGGRESSIVE SOLUTIONS

Cementitious Barriers Partnership

December 2014

CBP-TR-2015-007, Rev. 0

CEMENTITIOUS BARRIERS PARTNERSHIP
TASK 12 – EXPERIMENTAL STUDY

SCM Paste Samples Exposed to Aggressive Solutions

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and

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CBP website: http://cementbarriers.org/
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FOREWORD

The Cementitious Barriers Partnership (CBP) Project is a multi-disciplinary, multi-institutional collaboration supported by the United States Department of Energy (US DOE) Office of Waste Processing. The objective of the CBP project is to develop a set of tools to improve understanding and prediction of the long-term structural, hydraulic, and chemical performance of cementitious barriers used in nuclear applications.

A multi-disciplinary partnership of federal, academic, private sector, and international expertise has been formed to accomplish the project objective. In addition to the US DOE, the CBP partners are the Savannah River National Laboratory (SRNL), Vanderbilt University (VU) / Consortium for Risk Evaluation with Stakeholder Participation (CRESP), Energy Research Center of the Netherlands (ECN), and SIMCO Technologies, Inc. The Nuclear Regulatory Commission (NRC) is providing support under a Memorandum of Understanding. The National Institute of Standards and Technology (NIST) is providing research under an Interagency Agreement. Neither the NRC nor NIST are signatories to the CRADA.

The periods of cementitious performance being evaluated are >100 years for operating facilities and > 1000 years for waste management. The set of simulation tools and data developed under this project will be used to evaluate and predict the behavior of cementitious barriers used in near-surface engineered waste disposal systems, e.g., waste forms, containment structures, entombments, and environmental remediation, including decontamination and decommissioning analysis of structural concrete components of nuclear facilities (spent-fuel pools, dry spent-fuel storage units, and recycling facilities such as fuel fabrication, separations processes). Simulation parameters will be obtained from prior literature and will be experimentally measured under this project, as necessary, to demonstrate application of the simulation tools for three prototype applications (waste form in concrete vault, high-level waste tank grouting, and spent-fuel pool). Test methods and data needs to support use of the simulation tools for future applications will be defined.

The CBP project is a five-year effort focused on reducing the uncertainties of current methodologies for assessing cementitious barrier performance and increasing the consistency and transparency of the assessment process. The results of this project will enable improved risk-informed, performance-based decision-making and support several of the strategic initiatives in the DOE Office of Environmental Management Engineering & Technology Roadmap. Those strategic initiatives include 1) enhanced tank closure processes; 2) enhanced stabilization technologies; 3) advanced predictive capabilities; 4) enhanced remediation methods; 5) adapted technologies for site-specific and complex-wide D&D applications; 6) improved SNF storage, stabilization and disposal preparation; 7) enhanced storage, monitoring and stabilization systems; and 8) enhanced long-term performance evaluation and monitoring.

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EXECUTIVE SUMMARY

This report summarizes experimental work performed by SIMCO Technologies Inc. (SIMCO) as part of the Cementitious Barriers Partnership (CBP) project. The test series followed an experimental program (Protière 2014) dedicated to the study of ordinary Portland cement (OPC) hydrated cement pastes exposed to aggressive solutions. In the present study, the scope is extended to hydrated cement pastes incorporating supplementary cementitious materials (SCM) such as fly ash and ground granulated blast furnace slag (GGBFS). Also, the range of aggressive contact solutions was expanded.

The experimental program aimed at testing aggressive contact solutions that more closely mimic the chemical composition of saltstone pore solution. Five different solutions, some of which incorporated high levels of carbonate and nitrate, were placed in contact four different hydrated cement paste mixes. In all solutions, 150 mmol/L of SO_4^{2-} (14 400 ppm) were present. The solutions included different pH conditions and different sodium content.

Two paste mixes were equivalent to Vault 1/4 and Vault 2 concrete mixes uses at SRS in storage structures. Two additional paste mixes, cast at the same water-to-cement ratio and using the same cements but without SCMs, were also tested.

The damage evolution in samples was monitored using ultrasonic pulse velocity (UPV) and mass measurements. After three and twelve months of exposure conditions, samples were taken out of solution containers and analyzed to perform migration tests and porosity measurements.

Globally, results were in line with the previous study and confirmed that high-pH may limit the formation of some deleterious phases like gypsum. In this case, ettringite may form but is not necessarily associated with damage. However, the high concentration of sodium may be associated with the formation of an AFm-like mineral called U-phase.

The most significant evidences of damage were all associated with the Vault 2 paste analog. This material proved very sensitive to high-pH. All measurement techniques used to monitor and evaluate damage to samples indicated significant alterations to this mix when immersed in contact solutions containing sodium hydroxide. It was hypothesized that the low cement content, combined with high silica content coming from silica fume, fly ash and GGBFS led to the presence unreacted silica. It is possible that the pozzolanic reaction of these SCMs could not be activated due to the low alkali content, a direct consequence of low cement content. In this scenario, the material end up having a lot of silica available to react upon contact with sodium hydroxide, possibly forming a gel that may be similar to the gel formed in alkali-silica reactions. This scenario needs further experimental confirmation but it may well explain the poor behavior of mix PV2 in presence of NaOH.

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1.0 INTRODUCTION

This report summarizes experimental work performed by SIMCO Technologies Inc. (SIMCO) as part of the Cementitious Barriers Partnership (CBP) project. The test series followed an experimental program (Protière 2014) dedicated to the study of ordinary Portland cement (OPC) hydrated cement pastes exposed to aggressive solutions. In the present study, the scope is extended to hydrated cement pastes incorporating supplementary cementitious materials (SCM) such as fly ash and ground granulated blast furnace slag (GGBFS). Also, the range of aggressive contact solutions was expanded.

Concrete barriers are viewed as a potential solution to store contaminated wasteform[1] resulting from nuclear material production processes. In this context, concrete is expected to act as a contaminant barrier for extended period of time. Wasteform in direct contact with concrete can compromise the integrity of the barrier due to the high concentration of potentially deleterious ionic species it contains.

The initial phase of the study presented in (Protière 2014) focused on the potential deleterious effect of wasteform containing a high pH pore solution with an important level of sulfate, placed in contact with concrete. The purpose of the study was to improve understanding of the complex concrete/wasteform reactive transport problem, in particular the role of pH in sulfate attack. This study indicated that the high sulfate content found in the wasteform pore solution will not necessarily lead to severe damage to concrete. Good quality mixtures could prove durable over the long term and act as an effective barrier to prevent radionuclides from reaching the environment. As stated previously, only OPC hydrated cement pastes were tested at the time.

The second phase of the experimental program aimed at testing aggressive contact solutions that more closely mimic the chemical composition of saltstone pore solution. Five different solutions, some of which incorporate high levels of carbonate and nitrate, were placed in contact four different hydrated cement paste mixes. Two paste mixes were equivalent to Vault 1/4 and Vault 2 concrete mixes uses at SRS in storage structures. Two additional paste mixes, cast at the same water-to-cement ratio and using the same cements but without SCMs, were also tested.

The following sections summarize the paste mixtures prepared for the study, their conditioning, the contact solution experiments and all test methods that were used to characterize materials.

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[1] The wasteform mentioned in the report is the Savannah River Site's saltstone.

2.0 RAW MATERIALS

This section presents the characteristics of the cements and supplementary cementing materials used in the preparation of four hardened cement pastes mixtures. All materials were provided to SIMCO by Savannah River National Laboratory (SRNL). Relative densities and Blaine surfaces of binders are given in Table 1.

Table 1 – Relative density and fineness of binders

	Type I/II cement Lafarge	Type V cement Lehigh	GGBFS Holcim	Force 10000 SF Grace	Class F Fly Ash SEFA
Relative density (g/cm3)	3.182	3.224	2.924	2.259	2.432
Blaine surface (cm2/g)	4340	3765	5990	2055	4055

The chemical composition of binders is in Table 2. They were evaluated using the X-ray fluorescence technique.

Table 2 – Chemical composition of binders (%)

Oxides	Type I/II cement Lafarge	Type V cement Lehigh	GGBFS Holcim	Force 10000 SF Grace	Class F Fly Ash SEFA
CaO	64.8	63.8	37.8	0.60	1.32
SiO_2	20.9	21.0	39.6	95.0	54.5
Al_2O_3	4.80	3.82	7.61	0.18	28.1
Fe_2O_3	3.43	4.75	0.47	0.07	8.65
SO_3	1.75	1.15	1.05	0.18	<0.1
MgO	1.05	2.60	12.2	0.22	1.19
K_2O	0.54	0.61	0.47	0.48	2.82
Na_2O	0.22	0.15	0.28	0.18	0.41
LOI	1.13	0.84	-0.45	3.32	1.41

Type I Portland cement is known as common or general purpose cement. Type V cement is commonly used in sulfate-rich aggressive environments. It has a very low aluminate (C_3A) content and is thus less prone to formation of expansive mineral phases upon sulfate ingress.

3.0 HYDRATED PASTE MIXTURES

Although laboratory concrete is a more realistic material to test the impact of aggressive solutions on durability, the presence of aggregates makes the characterization of degradation difficult to achieve. Accordingly, a series of neat cement pastes (identified as PV1 and PV2) corresponding to Vault concrete mixtures 1/4 and 2 was prepared in December 2011. A series of reference mixtures without SCMs (identified as PV1b and PV2b) was also prepared in order to have simpler systems to analyze and highlight effects that could be caused by SCMs.

A 2-liter mixer was used to mix pastes. Following *ASTM Standard C305 - Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency* procedure, 1.35L batch volumes were realized to prepare at least twenty Ø100x70mm samples per mixture. To limit bleeding, samples were cast in short plastic cylindrical molds of 80 mm in height and 100 mm in diameter (cf. Figure 1).

The mixture proportions of reference pastes (PV1b and PV2b) and pastes based on Vault 1/4 and Vault 2 concretes (PV1 and PV2) are presented in Table 3. All materials were prepared at a water-to-binder (w/b) ratio of 0.4. No chemical admixtures such as superplasticizer were used in the preparation of the paste mixes.

Table 3 – Mixture proportions of materials

Description	**Density**	**w/b = 0.40**			
		PV1b	**PV2b**	**PV1**	**PV2**
	(g/cm3)	***Q(kg)*** *(% of total binders)*			
Type I/II (Lafarge)	*3.18*	**1331.9** *(100%)*	0.0 *(0%)*	**788.8** *(60%)*	0.0 *(0%)*
Type V (le High)	*3.22*	0.0 *(0%)*	**1339.6** *(100%)*	0.0 *(0%)*	**376.3** *(30%)*
GGBFS (Holcim)	*2.92*	0.0 *(0%)*	0.0 *(0%)*	**522.7** *(40%)*	**503.7** *(40%)*
Force SF (Grace)	*2.26*	0.0 *(0%)*	0.0 *(0%)*	0.0 *(0%)*	**84.0** *(7%)*
Class F Fly ash (SEFA)	*2.43*	0.0 *(0%)*	0.0 *(0%)*	0.0 *(0%)*	**295.4** *(23%)*
Water	*1.00*	**532.7**	**535.8**	**524.6**	**503.7**

Samples were demolded between 24 and 28 hours after casting. Paste specimens were then placed in saturated limewater solution for curing until being tested. Mixture preparation is illustrated on Figure 2.

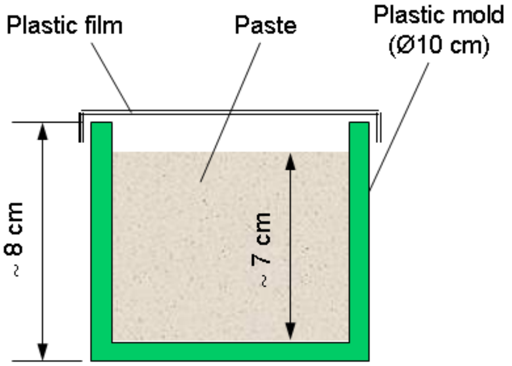
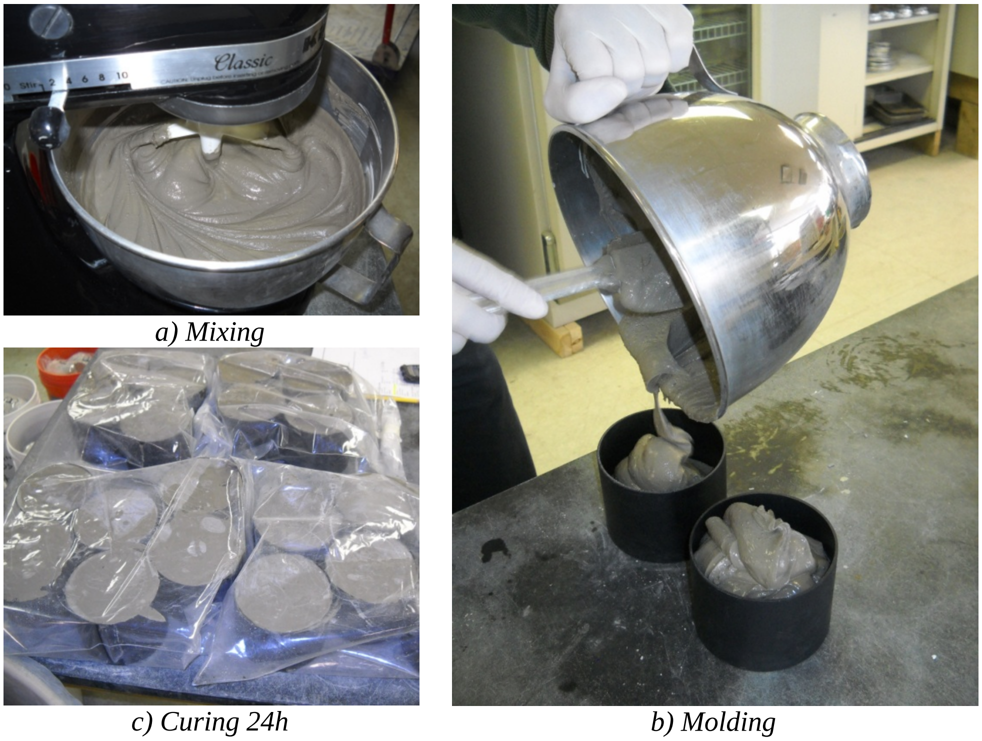


Figure 1 – Pastes casted into cylindrical mold approximately 70 mm in height



a) Mixing

c) Curing 24h

b) Molding

Figure 2 – Mixture preparation

4.0 EXPERIMENTAL PROGRAM

The main objective of the study was to expose paste samples to aggressive contact solutions and characterize resulting damage. The experimental program is detailed in the present section.

4.1. Overview

When the paste cylinders reached 56 days of hydration in limewater, the samples were prepared and conditioned for testing. Tests were performed at 56 days to characterize materials before immersion in aggressive solution. After that, the samples were immersed in contact solutions. Samples were periodically monitored (once per month) to measure their mass. Also, ultrasonic pulse velocity (UPV) measurements were performed to assess damage level in samples. After 3 and 12 months of exposure to solutions, some samples were removed from solutions and tested to obtain a more in-depth characterization of their evolution. The overall testing program is illustrated on Figure 3.

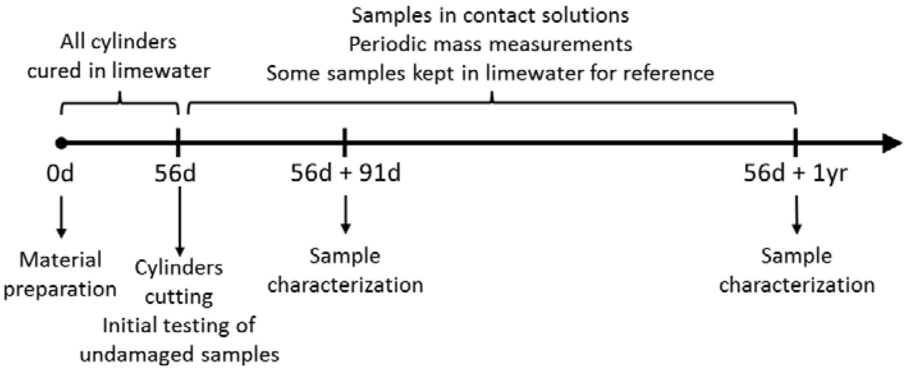


Figure 3 – Timeline of experimental program

The following tests were performed after the 56-day curing period, to characterize the initial state of samples prior to immersion in contact solutions:

- Pore solution: extraction of solution by applied pressure.
- Pore size distribution: evaluated from Mercury Intrusion Porosimetry (MIP) measurements.
- Porosity[2]: based on *ASTM Standard C642 - Standard Test Method for Density, Absorption, and Voids in Hardened Concrete* procedure. The standard procedure has been modified and applied to hardened cement pastes.
- Electrical current values: measured on the basis of migration tests, a modified version of the ASTM C1202 procedure: Standard Test Method for Electrical Indication of material’s Ability to Resist Chloride Ion Penetration. The test gives information on the resistivity of samples. It is used in this

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[2] The use of porosity in the report refers to the volume of permeable voids, as measured with the ASTM C642 procedure.

study to see how the exposure to contact solutions can alter resistivity and provide information on the extent of damage.

- Ultrasonic pulse velocity values.

Since the microstructure of cementitious materials evolves with time due to the hydration process, a series of samples was kept in limewater after 56 days. The previous tests were performed on those samples at 56 + 91 days and 56 + 365 days to provide baseline values for undamaged samples.

During immersion in contact solutions, the following measurements were performed once per month:

- Mass measurements,
- Ultrasonic pulse velocity measurements.

The samples were removed from solutions, tested, and replaced in solutions. These simple measurements allowed monitoring the evolution of samples.

After initial characterization, samples were immersed in different contact solutions (section 4.3). After 91 days and 1 year in solutions, samples were removed and characterized on the basis of the following tests:

- Porosity: based on *ASTM Standard C642 - Standard Test Method for Density, Absorption, and Voids in Hardened Concrete* procedure.
- Electrical current values: measured on the basis of migration tests, a modified version of the ASTM C1202 procedure: Standard Test Method for Electrical Indication of material’s Ability to Resist Chloride Ion Penetration.

In addition to this, photographs of the contact surface were taken to visually document degradation sustained by samples.

4.2. Sample preparation

After 56 days of hydration, cylinders were prepared for immersions and material characterizations. The following preparation stages were performed:

- Three disks (Ø100mm x 12mm) were cut from one cured cylinder. Two disks were used to perform porosity measurements. From the remaining disk, prisms were prepared to perform Mercury Intrusion Porosimetry (MIP) measurements. The remainder of the disk was used as material for pore solution extraction.
- Two disks (Ø100mm x 25mm) were cut from another cylinder. Those disks were used to perform migration measurements.
- Thirty-four disks (Ø100mm x 25mm) were cut from seventeen cured cylinders. Thirty disks were used for immersion in aggressive solutions. As schematized on Figure 4, those disks were sealed on the side surface with epoxy, and immersed in the contact solutions having two exposed surfaces. Four disks were kept in cured condition (i.e. limewater).

- One back-up cylinder was kept in limewater.

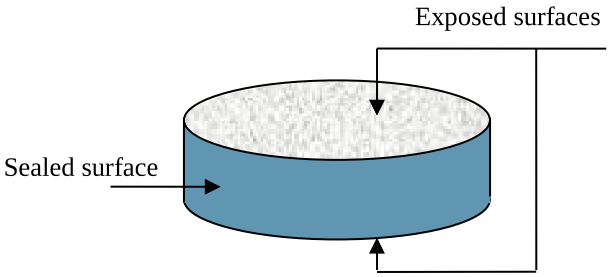


Figure 4 – Representation of an immersed sample

Considering all the mixtures and contact solutions, over 140 samples was prepared.

4.3. Contact solutions

Paste samples were exposed to five highly concentrated sulfate solutions. Those solutions were inspired from wasteform pore solution composition and are presented in Table 4. These different exposure conditions allowed studying the effect of the main components of a typical wasteform solution on cementitious materials. In all solutions, 150 mmol/L of SO_4^{2-} (14 400 ppm) were present. The solutions included different pH conditions to attempt to replicate behavior observed on OPC samples, as tested in a previous study (Protière, 2014). In this past study, high pH prevented damage to samples even though sulfate was present in solutions.

Table 4 – Contact solution compositions

	Concentrations (mmol/L)				
Salts	**Sol.1**	**Sol.2**	**Sol.3**	**Sol.4**	**Sol.5**
Na_2SO_4	150	150	150	150	150
NaOH	0	500	0	500	0
$NaNO_3$	0	0	3000	3000	0
Na_2CO_3	0	0	0	0	150

Immersion started once pastes were 56 days ± two weeks old. The beginning of immersion in contact solutions was spread over time to allow sufficient time for testing after 3 months and 1 year of exposure.

Samples were placed in 25-liters containers. In order to get a significant *volume of solution / exposed surface* ratio, a maximum of eight samples were placed in a single container. Figure 5 presents the disposition of the samples in one container. During the exposure period, the solution was renewed on a monthly basis in order to maintain uniform conditions.

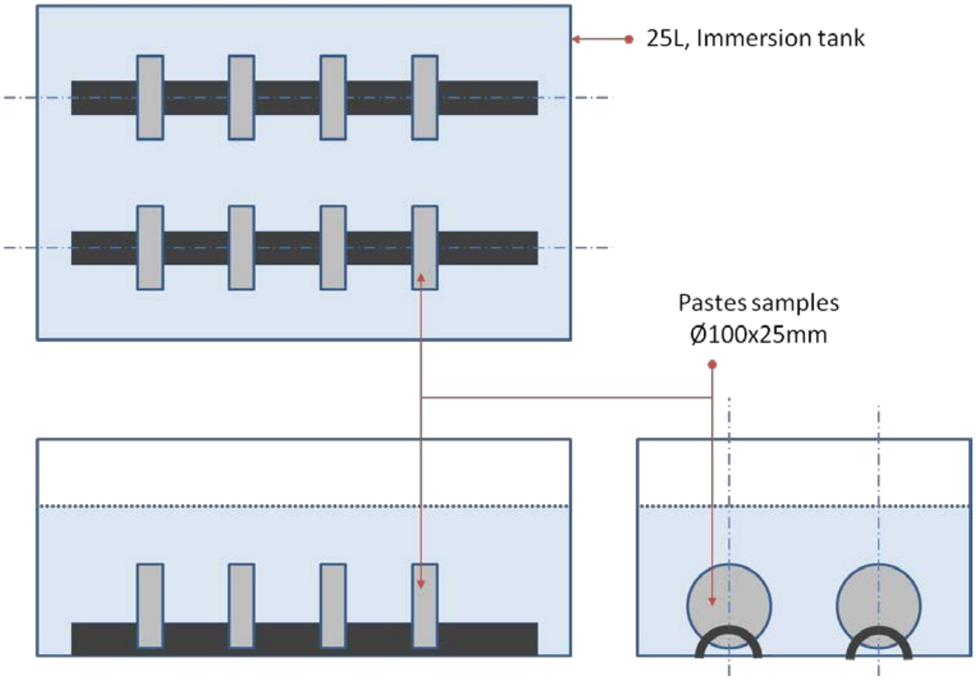


Figure 5 – Disposition and number of samples in a 25L solution container

Ultrasonic Pulse Velocity (UPV) was measured every month on each sample with PUNDIT apparatus, providing data on the damage state evolution for every paste mixture and immersion case. During the immersion time, five samples were kept in limewater in order to consider the hydration effect in the analysis.

Six samples were initially used for each hardened cement paste mix and immersion case, for a total of 140 samples. After an exposure of three months, three samples were removed from each immersion case. Migration and porosity measurements were performed on two samples each. An additional sample was set aside and kept in a freezer, in case further analyses are needed. Figure 6 summarizes scheduled experiments at 3 and 12 months of immersion exposures.

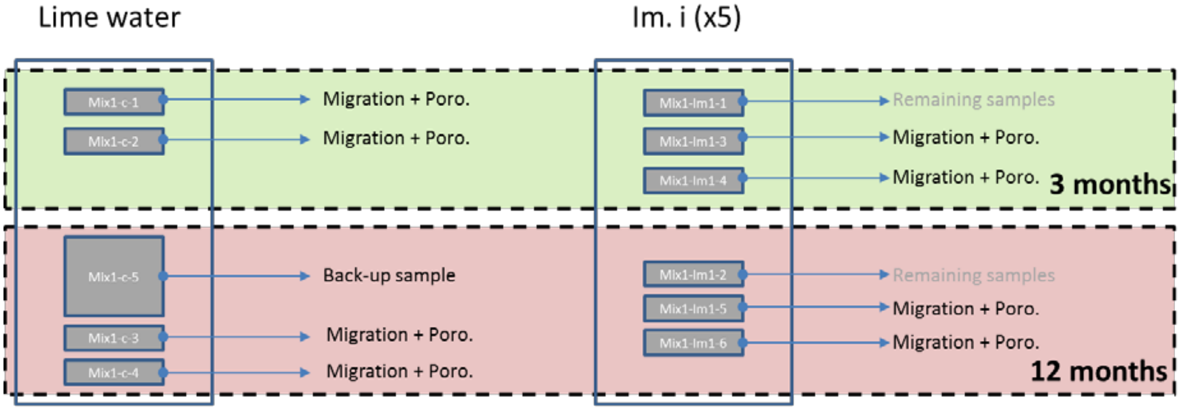


Figure 6 – Measurements scheduled after 3 and 12 months of exposure

5.0 CHARACTERIZATION OF UNDAMAGED SAMPLES

As mentioned in section 4.1, the following tests were performed on undamaged samples after 56 days of curing in limewater:

- Porosity: based on *ASTM Standard C642 - Standard Test Method for Density, Absorption, and Voids in Hardened Concrete* procedure. The standard procedure has been modified and applied to hardened cement pastes.
- Electrical current values: measured on the basis of migration tests, a modified version of the ASTM C1202 procedure: Standard Test Method for Electrical Indication of material's Ability to Resist Chloride Ion Penetration. The test provides an indication of alteration to the tortuosity of samples.
- Pore solution: extraction of solution by applied pressure.
- Pore size distribution: evaluated from Mercury Intrusion Porosimetry (MIP) measurements.

Also, samples were kept in limewater and characterized after 56 + 91 days and 56 + 365 days in limewater to quantify the impact of hydration over time. The results of those tests are presented in the following sections.

5.1. Porosity measurements

The porosity measurements were performed on the basis of ASTM C642 standard procedure: *Standard Test Method for Density, Absorption and Voids in Hardened Concrete*. The samples used were first tested in migration before the ASTM C642 procedure was applied**.** The migration test does not alter the pore structure and thus does not affect porosity measurement results.

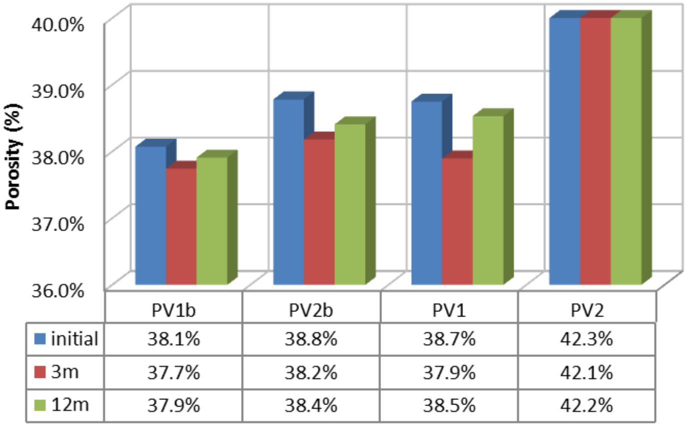
For this study, porosity measurements procedure has been slightly modified from the original ASTM C642 methodology. The ASTM procedure recommends stopping the test when mass changes on consecutive days for both the absorption and drying phases are under 0.5% mass variation. Using this criterion tends to underestimate porosity values for good quality mixtures. In the present case, a criterion of 0.1% was used instead. Also, the drying and boiling phases included in the procedure can open up additional pore space, especially for paste samples which were already weakened by sulfate attack. To calculate porosity, the following mass measurements were performed:

- After the migration tests, samples were immersed in lime water during a week. After that, mass was measured and identified as saturated mass **C**.
- The associated immersed mass **D** was also measured to calculate the sample volume, $V_s = \frac{C-D}{\rho_l}$, ρ_l being the water density.
- After that, the sample was dried at 105°C until mass stabilized, which yield dry mass **A**.
- The porous volume V_p was then calculated, assuming that it corresponds to the volume occupied by the evaporable water, as: $V_p = \frac{C-A}{\rho_l}$.

The porosity value was then calculated using the following expression: $\phi = \frac{V_p}{V_s} = \frac{C-A}{C-D}$

Porosity values at different maturities are presented in Figure 7**.**

Values presented in Figure 7 show very little variation of porosity over time for each separate mixture. Similar observations were made by SIMCO on different concrete mixtures. Porosity values are higher for the PV2 mixture. Similar observations were made on the Vault 2 concrete mix compared to the Vault 1/4, as reported in (Protière 2014b).



	PV1b	PV2b	PV1	PV2
🟦 initial	38.1%	38.8%	38.7%	42.3%
🟥 3m	37.7%	38.2%	37.9%	42.1%
🟩 12m	37.9%	38.4%	38.5%	42.2%

Figure 7 – Porosity values measured at 56 days (initial), and after an additional 3 and 12 months of curing for pastes PV1b, PV2b, PV1 and PV2

5.2. Migration test measurements

The objective of the migration test is to determine the tortuosity and diffusion coefficients of paste mixture. The test is a modified version of the ASTM C1202 procedure: *Standard test method for electrical indication of concrete's ability to resist chloride ion penetration*.

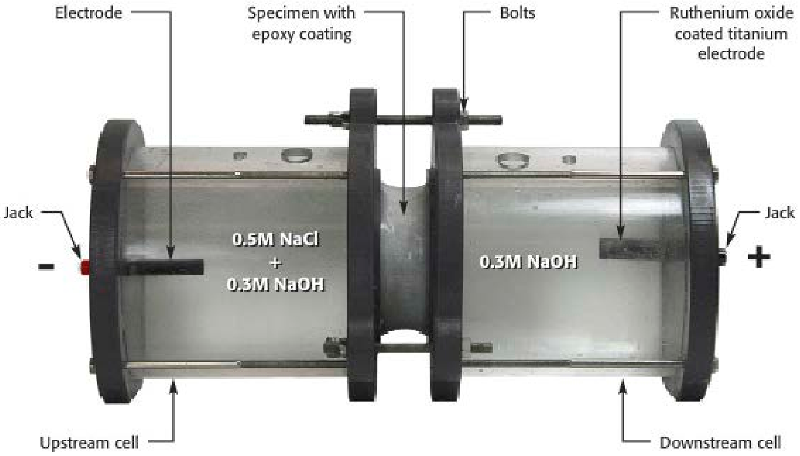
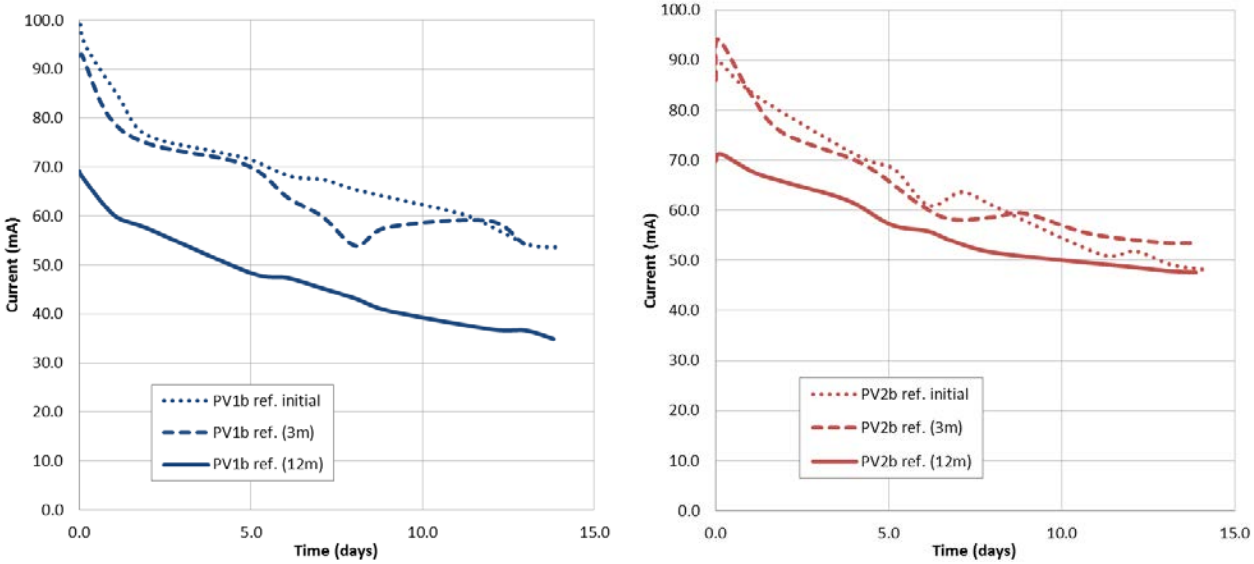


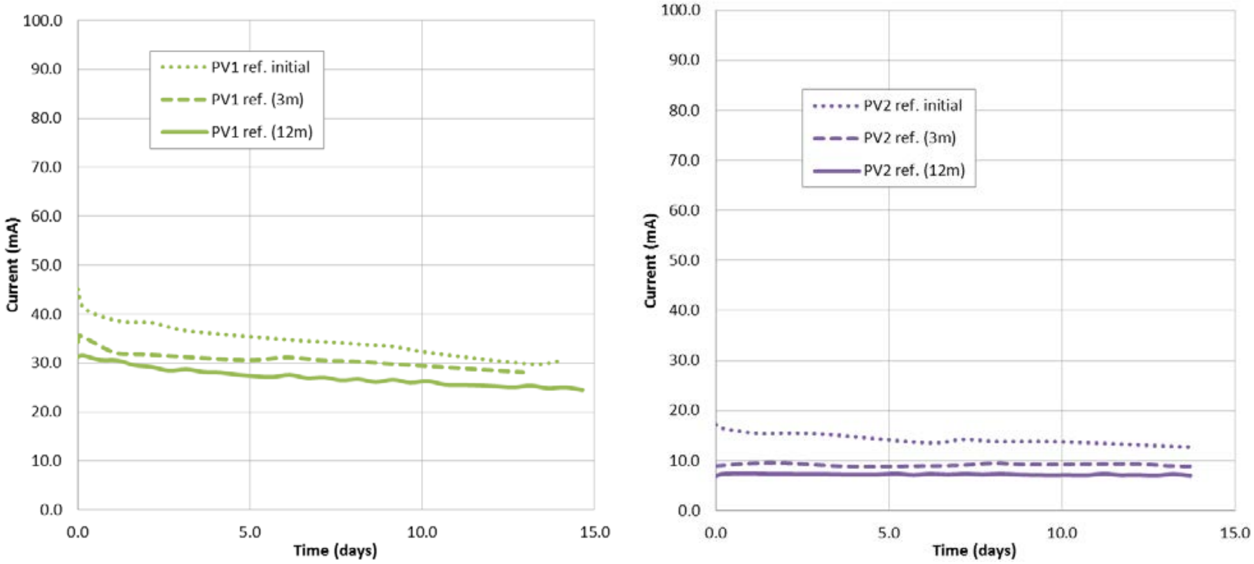
Figure 8 – Migration test set up

The method developed by SIMCO consists in accelerating the ions under an external potential and measuring the electrical current across the sample over a 10 to 15-day period. The setup is illustrated on Figure 8. In the present study, the measured current curves are used to quantify the impact of chemical degradation on paste samples by comparing current measurements.

The test was performed on samples 100 mm in diameter and 25 mm in thickness. For each test condition, two disks were tested. Discs were mounted between cells filled with 2.7 L of 0.3M NaOH solution. The upstream cell solution also contained 0.5M dissolved NaCl salt. The applied voltage was set to 5 V and measured regularly to make sure it was constant over the testing duration.



a) Paste PV1b b) Paste PV2b



c) Paste PV1 d) Paste PV2

Figure 9 – Average current values of undamaged paste samples after 56 days, 56 + 91 days and 56 + 365 days of curing in limewater

The measured currents are presented on Figure 9 for all four undamaged mixtures. The average of current values measured on two disks is plotted. The measured current amplitude gradually decreased as a function of the curing duration, which indicates a reduction of the transport properties as the hydration process continues in the materials. These experimental data also show that the current values are lower for PV1 and PV2 mixture compared to their OPC PV1b and PV2b counterparts, which indicates lower diffusion coefficients and is a consequence of the presence of fly ash and slag in the mixes. It is also interesting to note that despite having a higher porosity, PV2 mix exhibits lower currents, which emphasizes its capacity to resist chemical species transport.

5.3. Chemical composition of expressed pore fluids

The pore solution extraction procedure consists in applying sufficient pressure on a paste sample to extract the solution from the material. Pore solution was extracted by squeezing crushed samples under compressive loading using the device shown in Figure 10. Solution was delivered through a drain ring and channel and recovered with a syringe in order to limit the exposure to the atmosphere. Pore solution analyses were carried out shortly after the extraction tests.

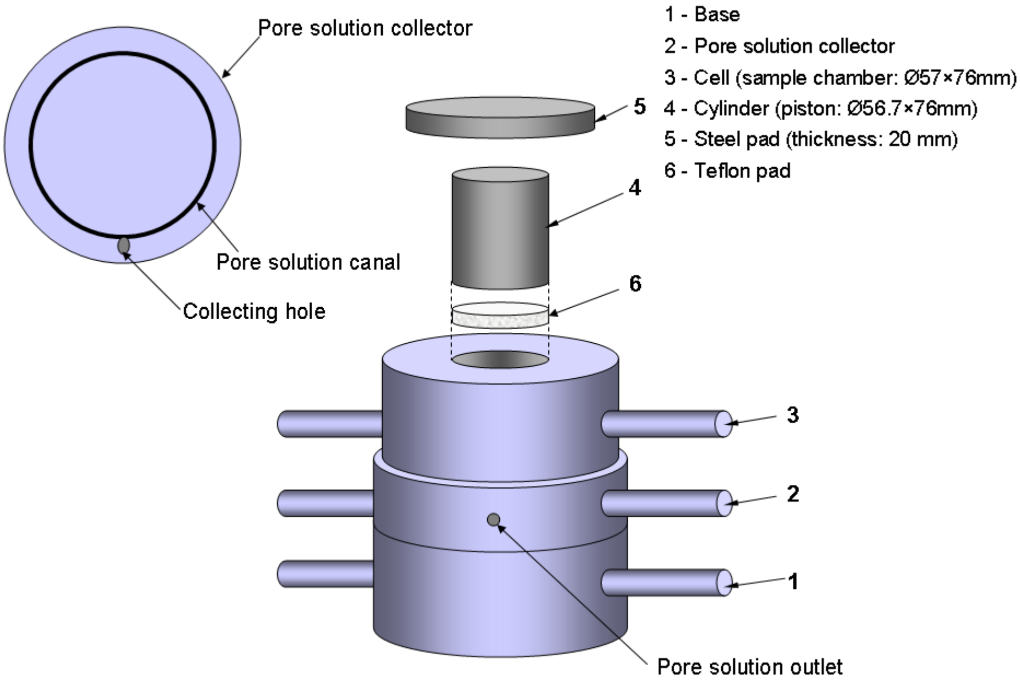


Figure 10 – Experimental setup for pore solution extraction

Pore solution extractions were made on the hardened cement pastes prior to the present test series, after 56 days of curing. The specimens for pore solution extraction were sawn from cylinders. Samples were broken in small pieces, placed in the cell, and crushed at a high pressure. Pore solution analyses were carried out using an Atomic Absorption Analyzer and Ion Chromatography as well as pH titration to obtain the contents of the main ions in the pore solution: OH^-, Na^+, K^+, SO_4^{2-}, Ca^{2+}, Cl^-. Table 5 presents the results of the chemical composition of expressed pore fluids.

It should be noted that the results listed in Table 5 are not strictly neutral (charge-balanced). This is a result of experimental errors associated with the procedure.

Table 5 – Chemical analyses of pore fluids extracted after 56 days of curing, [mmol/L]

Mixtures	OH^-	Cl^-	Ca^{2+}	K^+	Na^+	$SO4^{2-}$
	(mmol/L)					
PV1b	358.2	9.6	0.2	278.1	92.3	5.9
PV2b	191.9	8.5	0.4	117.7	52.2	2.2
PV1	339.9	<0.1	0.4	306.9	38.3	2.9
PV2	65.3	<0.1	1.5	22.3	14.8	<0.1

The chemical composition of the solution extracted from PV2 exhibits much lower concentrations than those of the other mixes. The pH of the PV2 solution is at 12.7, whereas it is 13.2 and higher for the other mixes. This can be attributed to the presence of slag in the PV2 mix.

5.4. Mercury Intrusion Porosimetry (MIP)

The determination of the pore size distribution is commonly performed using mercury intrusion porosimetry (MIP). The MIP experiment is based on the physical principle that a non-reactive, non-wetting liquid, such as mercury, will not penetrate the pores until sufficient pressure is applied to force its entrance (Nagy 2005). The porosimeter measures the mercury volume, which penetrates into the samples as the applied pressure increases. The applied pressure P_s is directly related to the pore radius r into which the mercury is intruded. The relationship between the pressure P_s [Pa] and the pore radius r [m] is given by the Washburn equation, (Washburn, 1921):

$$P_s = \frac{2\gamma}{r}\cos\theta$$

where γ [N/m] is the surface tension of the liquid and θ is the angle of contact. Figure 11 shows the Mercury Porosimeter Micromeritics Autopore IV apparatus that was used for this study.

Figure 12 shows measured mercury differential intrusion dV/dlog(r) for hardened cement pastes after 56 days of limewater curing. Results are presented in milliliter per gram of dried samples. The results emphasize the impact of SCMs (fly ash and slag) on the pore size distribution. For the OPC pastes (PV1b and PV2b), the largest porous volume is centered around pores in the 40-60 nm radius range. With the addition of SCMs, the bulk of the pore volume is formed of pores with a radius below 10 nm. So even though the overall pore volume is approximately the same for all mixes (Figure 7), mixtures PV1 and PV2, prepared with SCM’s, have a much finer pore network, which translates into lower diffusive properties and explains why these two mixes exhibited lower current values during migration tests (Figure 9).

It should be mentioned that MIP is known to underestimate the total porous volume available (Abell, 1999); the finer gel (C-S-H) pores are outside the range of the pore radius measurement (r < 5nm). In this present analysis, it is particularly difficult to use MIP to study the total pore space volume, especially for PV1 and PV2 pastes exhibiting a finer pore structure. Nevertheless, these MIP measurements clearly show that pore sizes are more important for basic OPC mixtures, without any SCMs.

Figure 11 – Mercury Porosimeter Micromeritics Autopore IV,

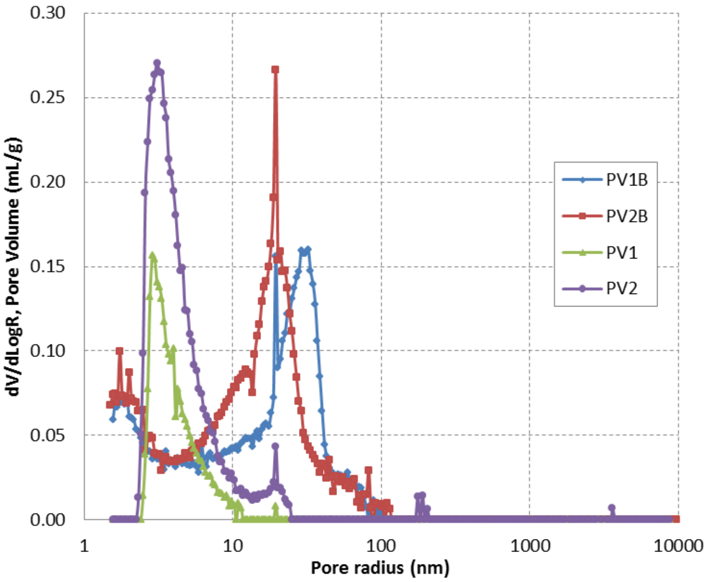


Figure 12 – MIP measurements for hardened cement pastes after 56 days of curing

6.0 CHARACTERIZATION OF DAMAGED SAMPLES

This section summarizes test results obtained on samples exposed to the different contact solutions. As mentioned previously, the following measurements were performed once per month on samples pulled out of contact solutions:

- Mass measurements.
- Ultrasonic pulse velocity measurements.

In addition to this, samples were taken out of containers after three and twelve months of exposure to aggressive solutions and tested for porosity and migration current flow. To complement test results, visual observations were made on immersed samples in solutions. These observations are reported in the next section.

6.1 Visual observations

Visual observations after 3, 8 months[3] of immersion are presented in this section. Selected pictures showing damage on samples are presented in this section. All pictures are presented in the appendix.

a. Three-month exposure

After three months exposure, some hardened cement pastes started to show physical degradation.

Contact solution 1: 0.15M Na_2SO_4
Samples showed very limited surface defects.

Contact solution 2: 0.15M Na_2SO_4 + 0.5M NaOH
Samples showed no significant visual damage, except for the PV2 mix which presented limited spalling on the surface. Surface defects around air bubbles were also observed on PV2b sample.

Contact solution 3: 0.15M Na_2SO_4 + 3M $NaNO_3$
PV1 and PV1b samples presented some spalling on the surface, while PV2 and PV2b samples (mixes prepared with type V cement) seemed intact.

Contact solution 4: 0.15M Na_2SO_4 + 3M $NaNO_3$ + 0.5M NaOH
Samples showed no significant damage, except for the PV2 mix which presented important spalling on its surface.

Contact solution 5: 0.15M Na_2SO_4 + 0.15M Na_2CO_3
PV1b and PV2b samples presented a very limited surface microcracking, while PV1 and PV2 samples (mixes prepared with SCMs) seemed to present no damage. Slight discoloration was also observed on PV2 sample.

A summary of observations after three months of exposure is presented in Table 6.

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[3] Some observations were delayed to 10 months due to schedule constraints.

Table 6 – Visual degradation on pastes after 3 months exposure

	PV1b	**PV1**	**PV2b**	**PV2**
Reference (limewater)	No significant damage	No significant damage	No significant damage	No significant damage
Sol.1	Limited surface defects	Very limited surface defects	Very limited surface defects	Very limited surface defects
Sol.2	No significant damage	No significant damage	Slight surface defects around air bubbles	**Slight surface spalling**
Sol.3	Slight surface defects	**Slight spalling surface**	No significant damage	No significant damage
Sol.4	No significant damage	No significant damage	No significant damage	**Surface spalling**
Sol.5	very slight surface microcracking	very slight surface microcracking	No significant damage	Slight discoloration

Solution 1 (0.15mol/L Na_2SO_4) seemed to have a very limited impact on all mixtures. The same can be said of solutions 2 and 4, except for mixture PV2, which seems particularly sensitive to the presence of NaOH. On the other hand, only mixes PV1 and PV1b seemed affected by solution 3.

b. Eight-month exposure

Pictures taken after eight months immersion are presented in the appendix. Some of those pictures were selected and presented here to emphasized key observations.

Contact solution 1: 0.15M Na_2SO_4
No significant bulk damage was observed on samples exposed to solution 1. Still, slight cracking and formation of salt crystals was nevertheless observed on sample surfaces.

Contact solution 2: 0.15M Na_2SO_4 + 0.5M NaOH
No significant surface alteration was observed on PV1 and PV1b samples exposed to solution 2. However, Figure 13 shows that PV2 sample exhibited an important surface crack network. The cracks are evenly distributed on the material surface. A portion of PV2b's surface was spalled but it is difficult to conclude this can be attributed to chemical damage or sample manipulation in the lab.

Figure 13 – Surface cracking on PV2 after 8 months of exposure in Sol. 2.

The damage observed on PV2 samples had an important impact on UPV measurements. After 10 months of exposure, the velocity could no longer be measured.

Contact solution 3: 0.15M Na_2SO_4 + 3M $NaNO_3$

This exposition was particularly severe for all mixtures. Pictures presented in the appendix show that PV1b, PV1, PV2b and PV2 samples all had their surfaces altered. The type of alteration seems to vary from one mixture to another. Type I/II cement mixtures PV1b (Figure 14) and PV1 (Figure 15) samples were more affected. Important spalling on their surface and deep cracks (cf. PV1 picture in appendix) were observed. A slight spalling surface was observed on Type V cement (PV2b and PV2) mixtures.

Figure 14 shows several types of alterations observed in the PV1b material. (a) Important spalling occurred on the surface. (b) Air bubbles seemed to play a role in the degradation observed. (c) Cracks in the periphery of the sample were also observed, seemingly the result of an expansion of the material.

Similarly, several types of alterations were observed on the PV1 material (Figure 15). The sample color is darker than samples removed from other contact solutions. An important amount of small-size particles were found on the surface. This limited spalling weakened the surface, revealing a network of cracks. Deep cracks in the periphery of the sample were also observed. They are more important than those observed on PV1b samples. They may be the result of an expansion of the material.

Figure 14 – Apparent damage on PV1b after 10 months of exposure in Sol.3.

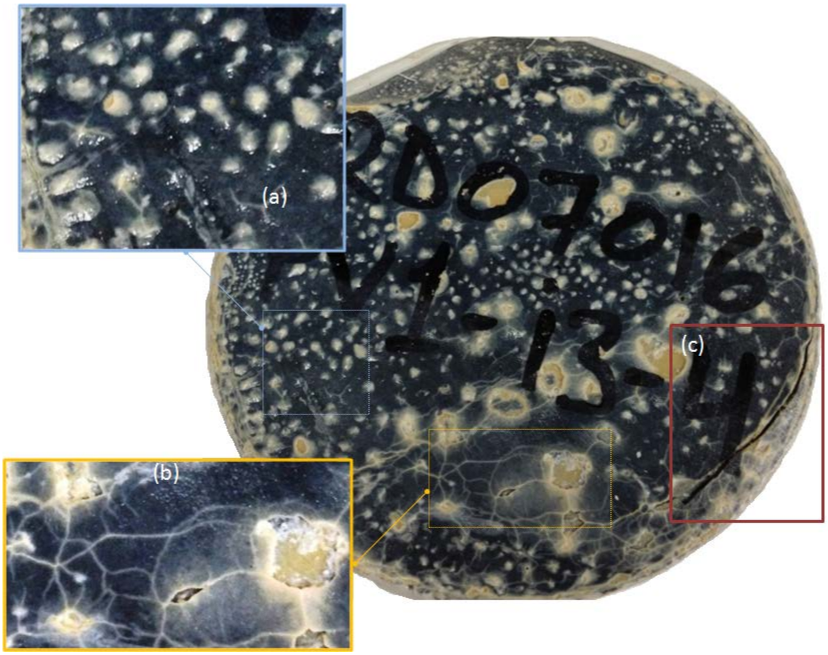


Figure 15 – Apparent damage on PV1 after 10 months of exposure in Sol.3.

Contact solution 4: 0.15M Na_2SO_4 + 3M $NaNO_3$ + 0.5M NaOH
No significant damage was observed on PV1b, PV1 and PV2b samples, even though PV2b sample exhibited slight defects on surface.

As shown on Figure 16, PV2 mixture was particularly affected by solution 4. It is likely that the same reaction observed in the solution 2 case takes place in solution 4.

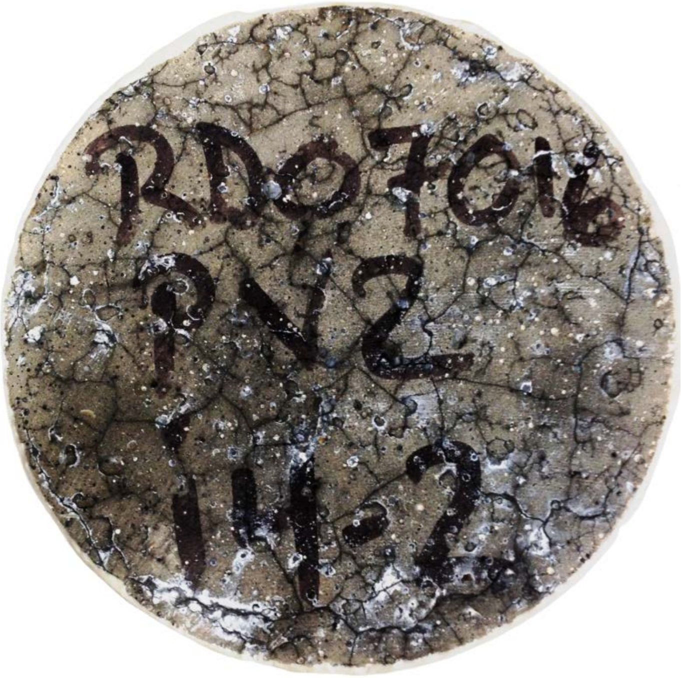


Figure 16 – Apparent damage on PV2 after 8 months of exposure in Sol.4.

Contact solution 5: 0.15M Na_2SO_4 + 0.15M Na_2CO_3

No major damage was observed for this exposure case. However, PV1 sample showed a darker surface. PV2 sample presents white streaks probably due to a partial surface carbonation.

A summary of observed damage after eight months of exposure is presented in Table 7.

Table 7 – Visual degradation on pastes after 8 months exposure

	PV1b	PV1	PV2b	PV2
Reference (limewater)	No significant damage	No significant damage	No significant damage	No significant damage
Sol.1	Slight surface alterations	Slight surface cracking	Very slight surface cracking	Slight surface cracking
Sol.2	No significant damage	No significant damage	No significant damage	**Important crack network**
Sol.3	**Important surface spalling + cracking**	**Important surface spalling + cracking**	**Surface spalling**	**Surface spalling**
Sol.4	No significant damage	No significant damage	No significant damage	**Important crack network**
Sol.5	No significant damage	No significant damage	No significant damage	Slight discoloration

Solution 3 (0.15M Na_2SO_4 + 3M $NaNO_3$) had a significant impact on all mixtures. Surface spalling was observed on all samples. Comparatively, solution 1 (0.15M Na_2SO_4) exposition was less severe than solution 3, suggesting that the presence of $NaNO_3$ plays a role in the chemical degradation.

The presence of NaOH in solutions 2 and 4 limits the degradation in the case of pastes PV1b, PV1b and PV1. This observation is in line with observations made in the previous study on OPC paste samples (Protière, 2014). In this past study, it was hypothesized that the presence of sodium hydroxide increases gypsum solubility, thus preventing precipitation of this mineral in the cementitious matrix. The hypothesis still seems valid here.

However, this explanation does not comply with PV2 mixture. This complex paste, which otherwise exhibits low diffusive properties (see Figure 9d), is particularly sensitive to the NaOH exposure in solution 2 and 4.

Finally, the presence of carbonate in solution 5 did not seem to have a major impact on paste degradation.

6.2 Damage level evaluation

The paste samples were monitored monthly to get data on damage time evolution. Ultrasonic pulse velocity (UPV) and mass measurements were performed and are presented in this section.

a. UPV measurements

The pulse velocity measurements were performed on saturated sample taken out of solutions with the PUNDIT apparatus presented in Figure 17. The velocity was used to estimate the damage level d_i of the material, on the basis of the following equation:

$$d_i = 1 - \frac{v_i}{v_0}$$

where v_i [m/s] is the pulse velocity in the sample and v_0 [m/s] is the reference velocity value of the undamaged sample maintained in limewater.

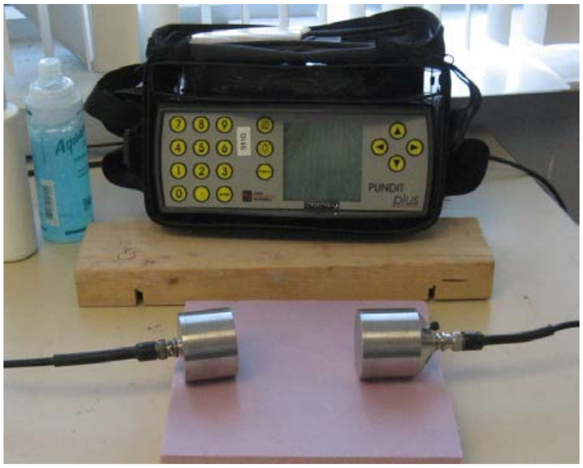


Figure 17 – Dynamic Testing Apparatus - PUNDIT

Velocity is deduced by dividing the sample thickness h_i (distance traveled by the wave) by the transmission time t_i of the ultrasonic wave (see Figure 18):

$$v_i = \frac{h_i}{t_i}$$

t_i and h_i were measured each time a sample was removed from the exposure solution. Since pulse velocity measurements were always compared to a reference value from samples in limewater, the hydration process was accounted for in the analysis and the results thus represent the actual alteration caused by aggressive solutions.

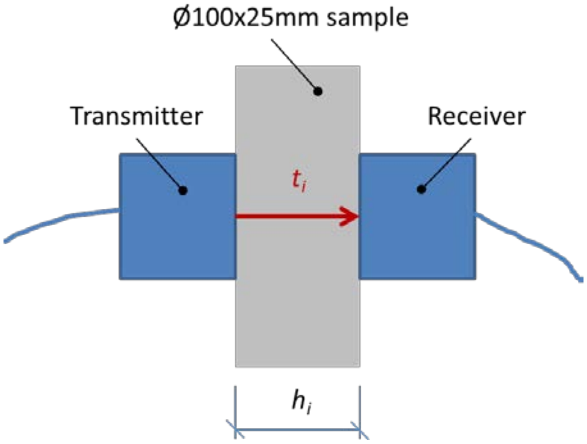
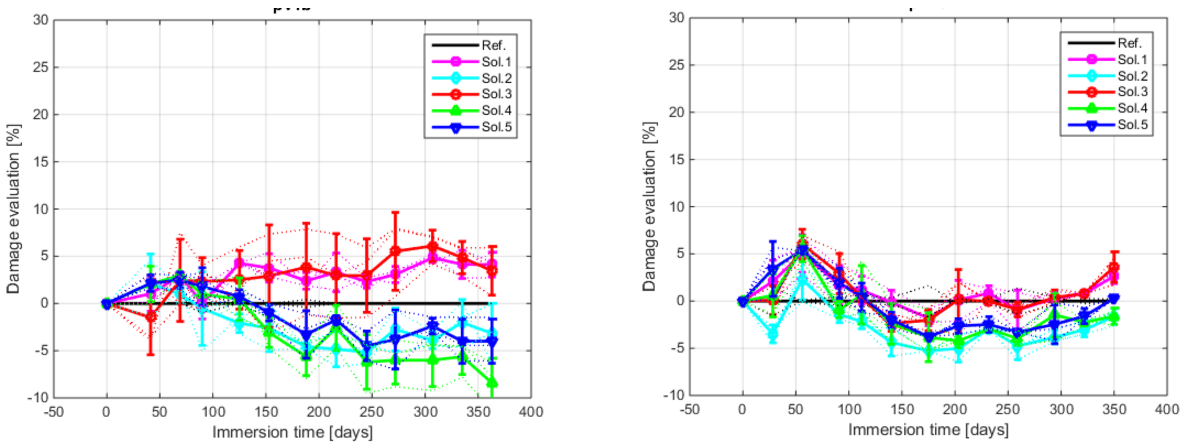


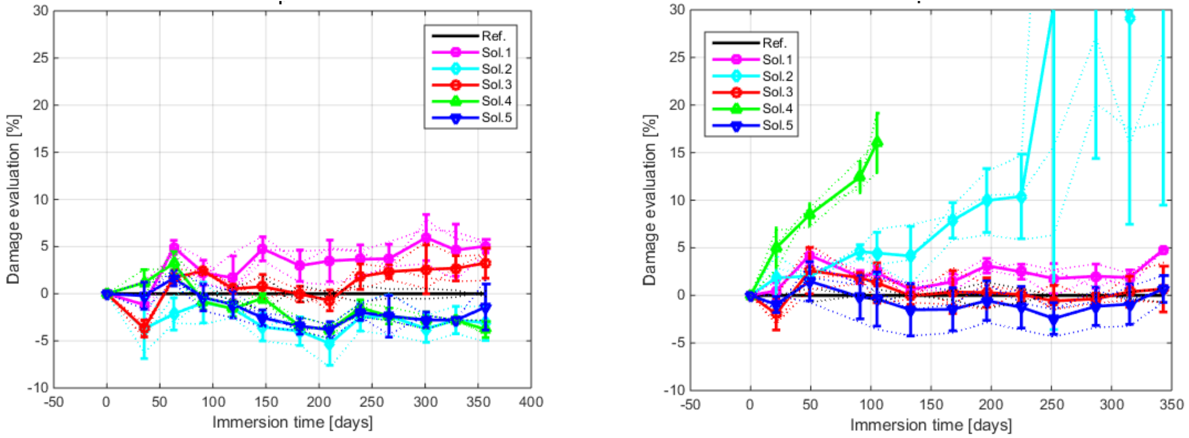
Figure 18 – PUNDIT (UPV) measurement

Measurements were performed on at least three samples. For each mixture PV1b, PV1, PV2b and PV2, the damage level evolution is presented in Figure 19. Each sample measurement is plotted in dotted lines, and the average value in solid line. Associated standard deviations (SD) bars are also included on the next figures.



a) Paste PV1b

b) Paste PV2b



c) Paste PV1

d) Paste PV2

Figure 19 – UPV damage level during the 12-month exposure period

Several observations can be made from Figure 19 results:

- For mixes PV1, PV1b and PV2b, the exposure to solutions 2, 4 and 5 yields negative damage levels. This can be attributed to formation of phases in the pore space of the materials that block pores without actually creating cracks. In the case of solution 2 and 4, a sulfate-bearing mineral such as ettringite may have formed but the presence of NaOH prevented formation of gypsum. In the case of solution 5, it is possible that the presence of carbonates led to formation of calcite but again prevented formation of more aggressive sulfate minerals like gypsum. XRD analyses could be used to validate these speculations.
- For mixes PV1 and PV1b, the exposure to solutions 1 and 3 (sulfate solutions without NaOH or carbonates) led to limited damage levels in the samples. The surface of these samples showed visual sign of damage.

- Contrary to PV1 and PV1b, material PV2b, did not exhibit the same damage measurements in solutions 1 and 3. This may be due to the use of Type V cement for this mix, compared to Type I/II cement used for mixtures PV1 and PV1b. The lower C_3A content apparently provided the expected protection against sulfate exposure.
- The results that stand out the most are again associated to mix PV2. Degradations of PV2 pastes immersed in high sodium hydroxide concentration solutions (Sol.2 and Sol.4) are clearly confirmed by the UPV measurements. In the case of solution 4 (0.15M Na2SO4 + 3M NaNO3 + 0.5M NaOH) damage was so important that it was no longer possible to receive sound waves transmitted through the sample after only 4 months of exposure. In the case of solution 2 (0.15M Na2SO4 + 0.5M NaOH), damage reached a similar level after 8 months of exposure. It was nevertheless still possible to measure the transmission times t_i from UPV measurements. However, these last transmission times were particularly variable.

b. Mass measurements during the immersion period

Mass measurements were performed on a regular basis on immersed samples, at the same time UPV measurements were made. Mass increase can indicate several alterations to the material:

- Mass increase can be attributed to the ongoing hydration process. Water is consumed by unhydrated cement and SCMs particles to form hydration products.
- The penetration of salts such as sulfate leads to the formation of new minerals in the pore structure, which continuously adds to the mass of material.
- Finally, the formation of microcracks can open up pores that fill with solution, which can also contribute to the mass increase of samples.

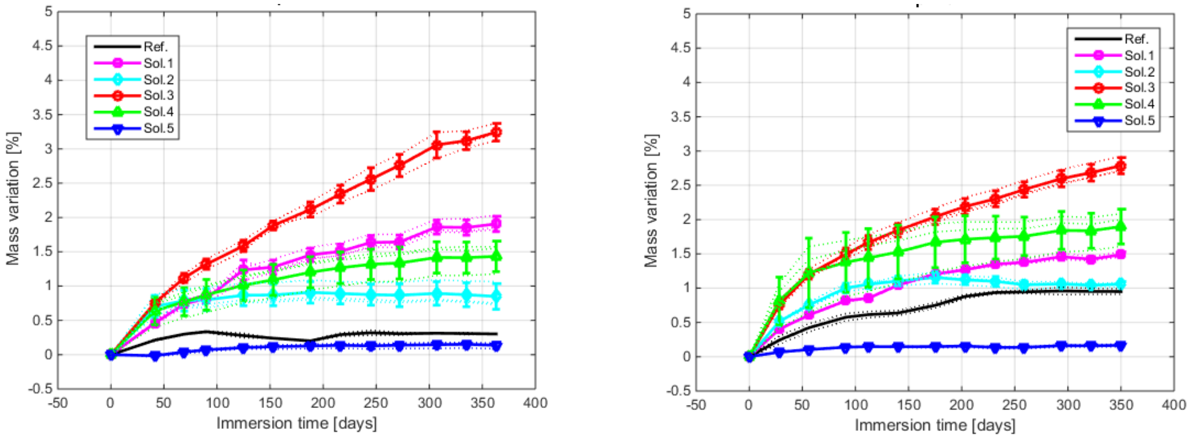
Figure 20 presents the mass variations versus time for each sample, in dotted lines. Average values are presented in solid lines. On all graphs, the thick black line indicates mass measurements on samples kept in limewater. This baseline shows the portion of mass uptake that can be attributed to hydration.

The main conclusions of mass measurements are summarized in the following paragraphs.

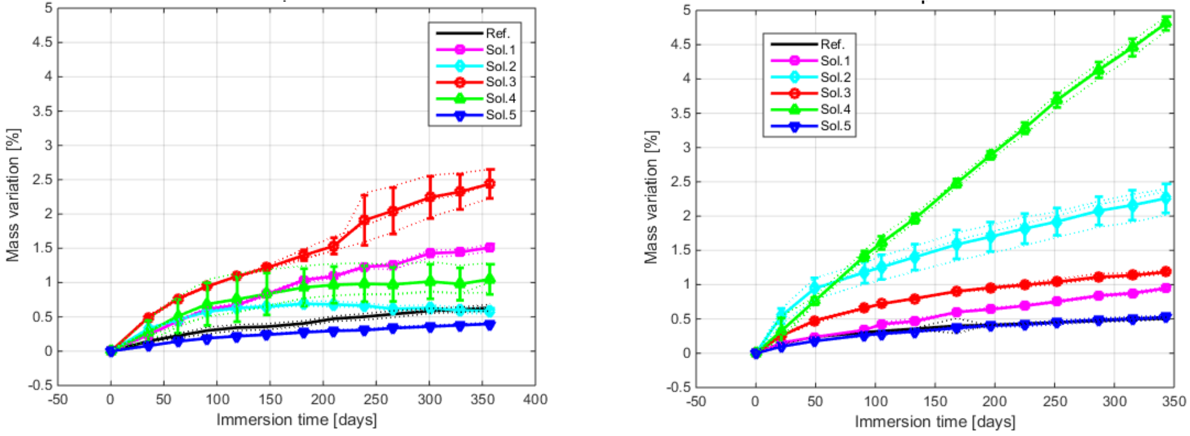
- In all cases, except pastes in solution 5 (carbonate solution), all materials exhibited mass gain higher than the reference (hydration process) curve. This means that new minerals formed in the immersed samples as a result of chemical precipitation, and that the total mass of newly formed phases outweighed the possible dissolution reactions that may have occurred at the same time.
- As for solution 5 (0.15M Na_2SO_4 + 0.15M Na_2CO_3), the presence of carbonate in solution in combination with sulfate possibly resulted in the formation calcite, monocarboaluminate (CO_3^{2-}-AFm, Matschei 2007) and thaumasite, a silica/carbonate/sulfur compound known to form in concrete in sulfate and carbonate-rich environments (Scholtzova 2014). The newly-formed phases seem to occupy the same space as the minerals they replaced, but are much less dense. UPV measurements for samples in this solution (Figure 19) did not show damage but a densification of the samples. These two series of observation possibly indicate that minerals were formed and blocked the pores, but without creating enough pressure to create cracks.
- For mixes PV1, PV1b and PV2b, the exposure to solution 3 (0.15M Na2SO4 + 3M NaNO3) caused a mass gain that is significantly higher than for the other solutions. The results of UPV measurements on those mixes led to the conclusion that mineral phases were formed, but likely not gypsum. There is

obviously another phase that precipitated in significant amount. One potential candidate is the U-phase (Li 1996, Li 1996b, Li 1997), an AFm-like layered mineral that incorporates sulfate and sodium. Additional testing like XRD is needed to confirm this assumption.

- Comparing pastes PV1b and PV2b show that mass uptakes for PV2b are usually equal or lower. It is likely that the Type V cement played its role and that the lesser C_3A content contributed to limit the formation of minerals associated with sulfate ingress, compared to Type I/II cement. However, this conclusion is not valid for the solution 4 (Na_2SO_4/NaOH/$NaNO_3$) case.
- But the most unusual results are again associated to PV2 samples in solution 2 (Na_2SO_4/NaOH) and solution 4 (Na_2SO_4/NaOH/$NaNO_3$). The mass gain rate for these two cases is clearly higher than what was measured for the other cases for this paste, which is in line with UPV measurements and visual observations. The combination of all previous measurements emphasizes a problem with mix PV2 in presence of high OH^- concentration levels.



a) Paste PV1b b) Paste PV2b



c) Paste PV1 d) Paste PV2

Figure 20 – Mass uptake during the 12-month exposure period

6.3 Migration test measurements

After three and twelve months of exposure in contact solutions, samples were taken out of aggressive solution containers to perform migration and porosity measurements.

As previously mentioned in section 4, migration tests were used in this study to see how contact solutions would affect the resistivity of samples and provide information on damage sustained by materials. As illustrated on Figure 21, samples were exposed on both sides and two layers of altered resistivity had an impact on measured currents. All measurements were made with an external applied voltage of 5V.

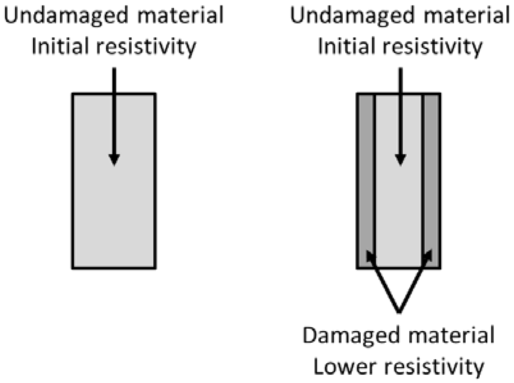


Figure 21 – Illustration of the effect of chemical alteration on resistivity

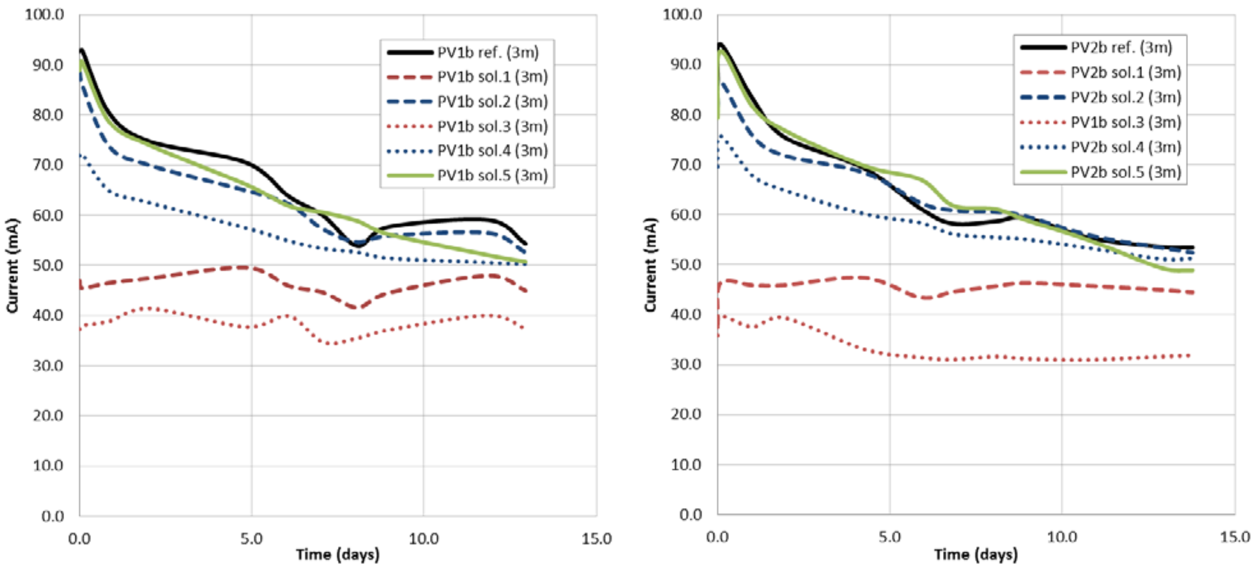
By creating microcracks on both surfaces of samples, it was expected to see an increase in measured currents for damaged materials. It must be noted that the materials were in contact with highly concentrated solutions, which may also have affected the intrinsic conductivity of samples. This is especially the case for the contact solutions with NaOH, the hydroxide ions carrying a significant fraction of total current.

Figure 22 and Figure 23 present current measurements after three and twelve months of exposure. One graphic is presented per mixture. Red lines correspond to lower-pH, and blue lines to higher-pH exposures. Green lines are associated to the carbonate-based solution. Black solid lines correspond to the reference material kept in limewater.

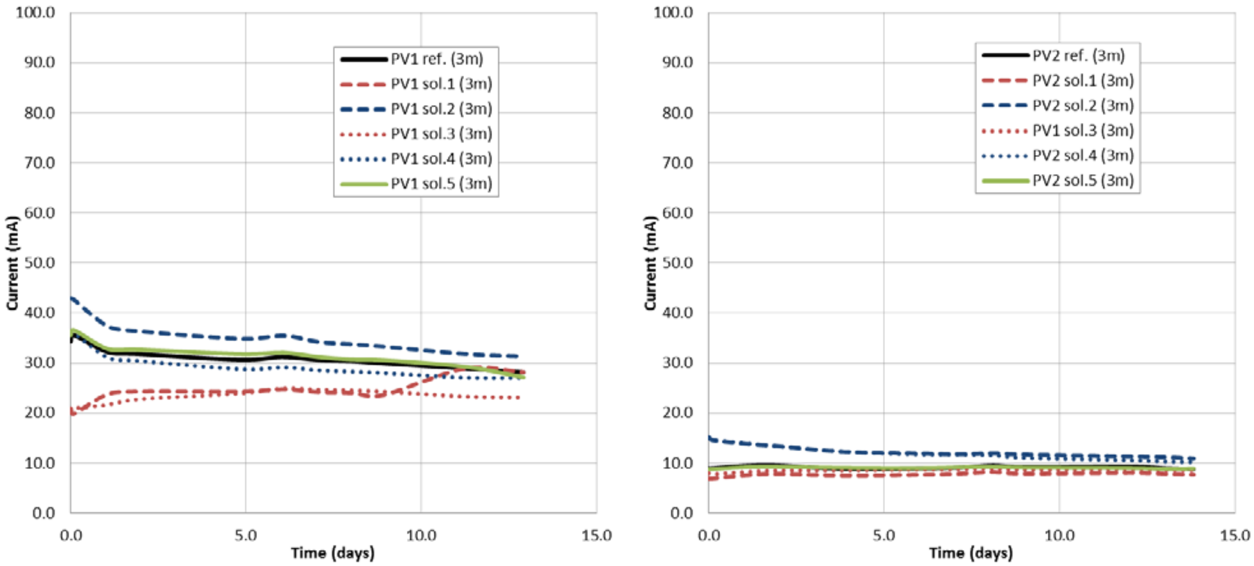
a. <u>Three-month exposure</u>

Currents measured from migration tests after three months of exposure conditions are presented in Figure 22. For most cases, the measured currents from samples in aggressive solutions were equal or lower, compared to the reference measurement. This can be explained by the formation of layers of pore-filling sulfate minerals, possibly ettringite, which decreased locally the electrical conductivity of the material and then the current measured. As shown in Samson (2007), ettringite tend to penetrate rapidly in materials, compared to gypsum. It is thus possible that pores were filled by ettringite first, before other deleterious phases were formed. This would explain the current drop after three months.

For pastes PV1 and PV2, samples immersed in solution 2 (Na_2SO_4 + NaOH) showed a slight increase in current values. However, this cannot necessarily be associated with damage at this point. The addition of NaOH to the paste pore solutions can increase their conductivity. This is especially the case for paste PV2, for which pore solution extraction (Table 5) showed low level of hydroxide and alkalis.



a) Paste PV1b b) Paste PV2b



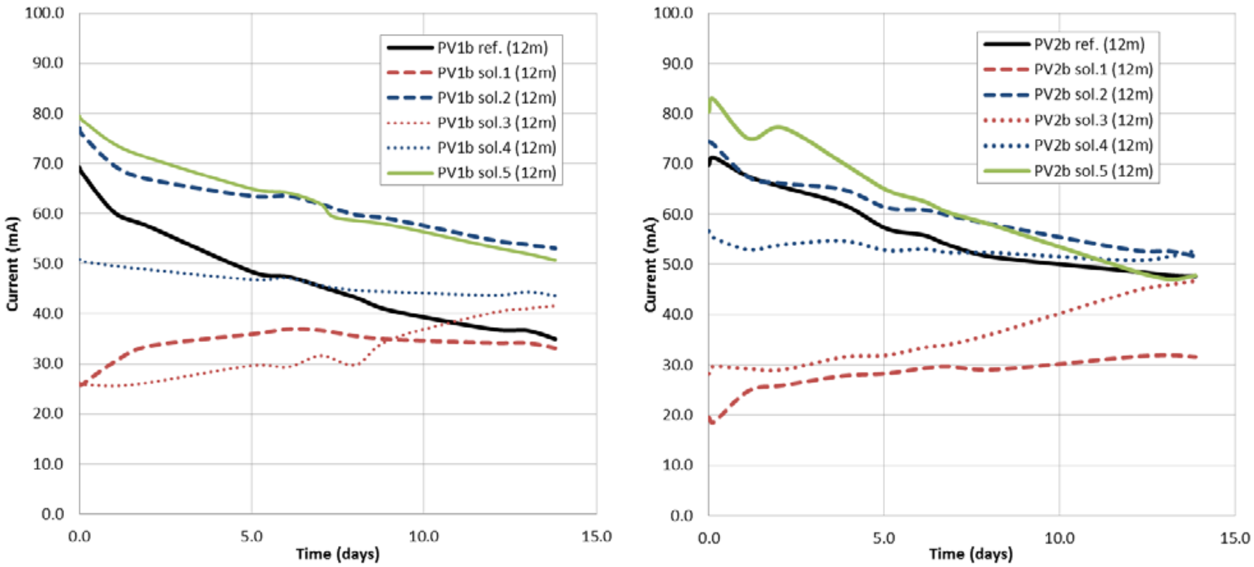
c) Paste PV1 d) Paste PV2

Figure 22 – Average current values measured after 3 months of solution expositions

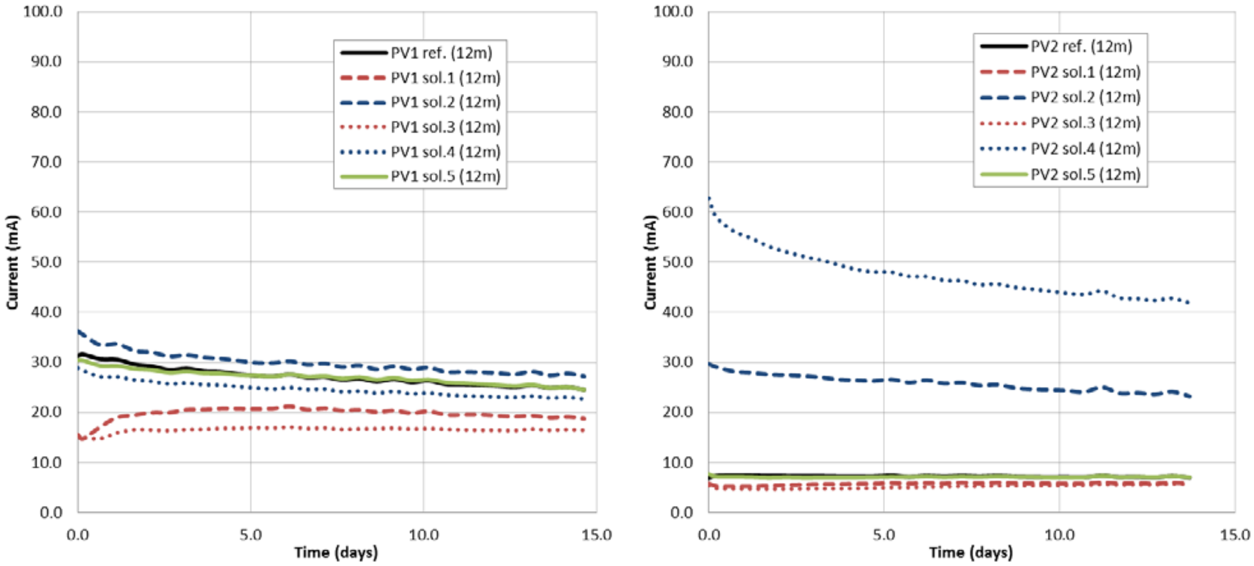
b. Twelve-month exposure

Currents measured from migration tests after twelve months of exposure conditions are presented in Figure 23.

Lower current values are still measured for every pastes immersed in lower-pH conditions (Sol.1 and Sol.3). Higher currents were expected due to damage sustained by the materials, especially for solution 1 where the absence of NaOH tends to promote the formation of both ettringite and gypsum (Samson 2007). These observations do not correlate with UPV and mass uptake measurements.



a) Paste PV1b b) Paste PV2b



c) Paste PV1 d) Paste PV2

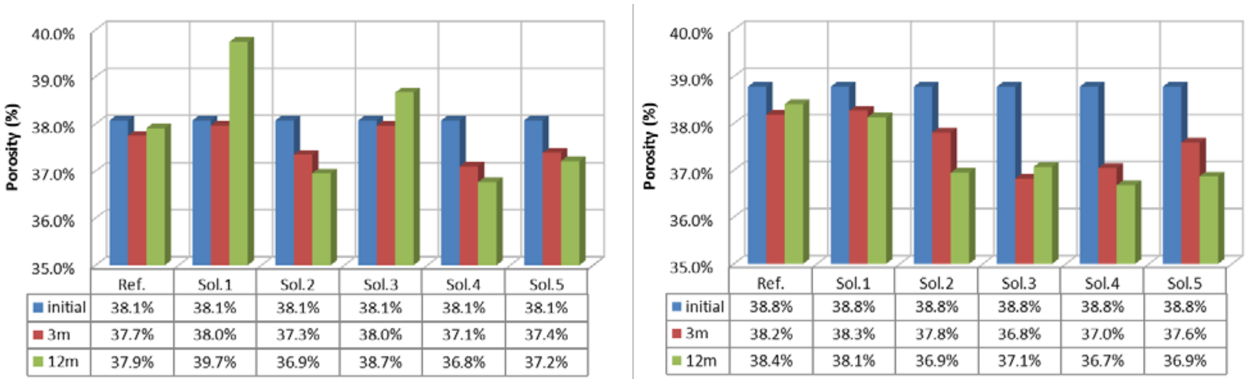
Figure 23 – Average current values measured after 12 months of solution expositions

On the contrary, currents for solutions 2 and 5 tend to be above the reference curve, especially for PV1b and PV2b. This is again in opposition with UPV and mass uptake curves, for which solutions 2 and 5 suggested lesser damage, if any. At this point, it is not possible to tell if this is indicative of any alteration sustained by the materials, simply an effect of conductivity change of the pore solution, or simply that the migration test is not a good test to evaluate damage level in altered samples.

The exception to all these observations is, again, paste PV2. In this case, migration test results clearly exhibited a current increase for high-pH solutions 2 and 4. This corresponds to previous results obtained with UPV and mass uptake measurements. Moreover, the apparent damage to PV2 is more important in solution 4, which all three techniques confirm. Clearly, the presence of NaOH plays a role, but $NaNO_3$ also significantly contributes to alter this specific mixture. At this point, additional investigation is needed to understand what is happening with this mix, and if these observations can also be applied to the corresponding Vault 2 concrete mix. One key aspect of the mix is the low cement content and the high silica content. Silica is obviously present in silica fume, but also in large amount in fly ash and GGBFS. It is possible that the latter SCMs contain a lot of unreacted silica, for which the pozzolanic reaction could not be activated due to the correspondingly low alkali content, a direct consequence of low cement content. This may have led to the unwanted consequence of having a lot of silica available to react upon contact with sodium hydroxide, possibly forming a gel that may be similar to the gel formed in alkali-silica reactions. This scenario needs further experimental confirmation but it may well explain the poor behavior of mix PV2 in presence of NaOH.

6.4 Porosity measurements

After three and twelve months of exposure conditions, samples used in migration tests were used to perform porosity measurements. Porosity values after 3 and 12 months of exposure for each paste mixture are presented in Figure 24.

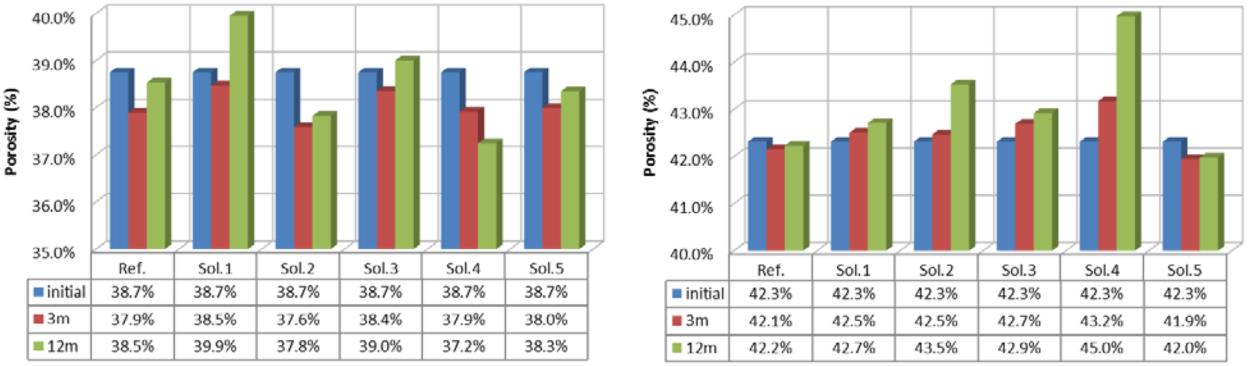


	Ref.	Sol.1	Sol.2	Sol.3	Sol.4	Sol.5
■ initial	38.1%	38.1%	38.1%	38.1%	38.1%	38.1%
■ 3m	37.7%	38.0%	37.3%	38.0%	37.1%	37.4%
■ 12m	37.9%	39.7%	36.9%	38.7%	36.8%	37.2%

	Ref.	Sol.1	Sol.2	Sol.3	Sol.4	Sol.5
■ initial	38.8%	38.8%	38.8%	38.8%	38.8%	38.8%
■ 3m	38.2%	38.3%	37.8%	36.8%	37.0%	37.6%
■ 12m	38.4%	38.1%	36.9%	37.1%	36.7%	36.9%

a) Paste PV1b

b) Paste PV2b



	Ref.	Sol.1	Sol.2	Sol.3	Sol.4	Sol.5
■ initial	38.7%	38.7%	38.7%	38.7%	38.7%	38.7%
■ 3m	37.9%	38.5%	37.6%	38.4%	37.9%	38.0%
■ 12m	38.5%	39.9%	37.8%	39.0%	37.2%	38.3%

	Ref.	Sol.1	Sol.2	Sol.3	Sol.4	Sol.5
■ initial	42.3%	42.3%	42.3%	42.3%	42.3%	42.3%
■ 3m	42.1%	42.5%	42.5%	42.7%	43.2%	41.9%
■ 12m	42.2%	42.7%	43.5%	42.9%	45.0%	42.0%

c) Paste PV1

d) Paste PV2

Figure 24 – Pastes Porosity before, and after 3 and 12 months exposure

Overall, changes in porosity are relatively low. Some trends can nevertheless be noted in these small variations. Porosities of Type I/II cement mixtures (PV1b and PV1) exposed to lower-pH solutions (solution 1 and 3) are more important after 12 months of exposure conditions, confirming a physical degradation of these materials. Porosities of Type V PV2b paste decreased with time for all immersion cases except solution1.

Higher porosity values were measured for PV2 samples immersed in high-alkali solutions. Porosity value from sample exposed to solution 4 (0.15M Na_2SO_4 + 3M $NaNO_3$ + 0.5M NaOH) is also higher than porosity values from sample exposed to solution 2 (0.15M Na_2SO_4 + 0.5M NaOH), emphasizing the role of alkalis on this type of degradation. These results correlate with all previous observation on PV2 and confirm the mixture sensitivity to high-pH contact solutions.

7.0 CONCLUSIONS

The study presented in this report focused on a chemical degradation of four paste mixtures exposed to aggressive environments. Two mixtures correspond to concrete mixes Vault 1/4 and Vault 2, used at SRS is saltstone disposal structures. Two other paste mixes, based on the previous two but prepared without supplementary cementitious materials, were also tested.

The main objective was to gather data that would help improve understanding of damage on cementitious materials transport properties exposed to saltstone pore solution, such as nitrates, sulfates and carbonates at different pH conditions. The study follows a previous experimental program (Protière 2014) where ordinary Portland cement samples, were exposed two different sulfate-laden solutions.

Pastes were cured 56 days in limewater before being exposed to five highly concentrated sulfate solutions designed from saltstone pore solution composition. The damage evolution was monitored using ultrasonic pulse velocity (UPV) and mass measurements. After three and twelve months of exposure conditions, samples were taken out of containers and analyzed to perform migration and porosity measurements.

Globally, results were in line with the previous study and confirmed that high-pH may limit the formation of some deleterious phases like gypsum. In this case, ettringite may form but is not necessarily associated with damage. However, the high concentration of sodium may be associated with the formation of an AFm-like mineral called U-phase.

The most significant evidences of damage were all associated with the Vault 2 paste analog. This material proved very sensitive to high-pH. All measurement techniques used to monitor and evaluate damage to samples indicated significant alterations to this mix when immersed in contact solutions containing sodium hydroxide. It was hypothesized that the low cement content, combined with high silica content coming from silica fume, fly ash and GGBFS led to the presence unreacted silica. It is possible that the pozzolanic reaction of these SCMs could not be activated due to the low alkali content, a direct consequence of low cement content. In this scenario, the material end up having a lot of silica available to react upon contact with sodium hydroxide, possibly forming a gel that may be similar to the gel formed in alkali-silica reactions. This scenario needs further experimental confirmation but it may well explain the poor behavior of mix PV2 in presence of NaOH.

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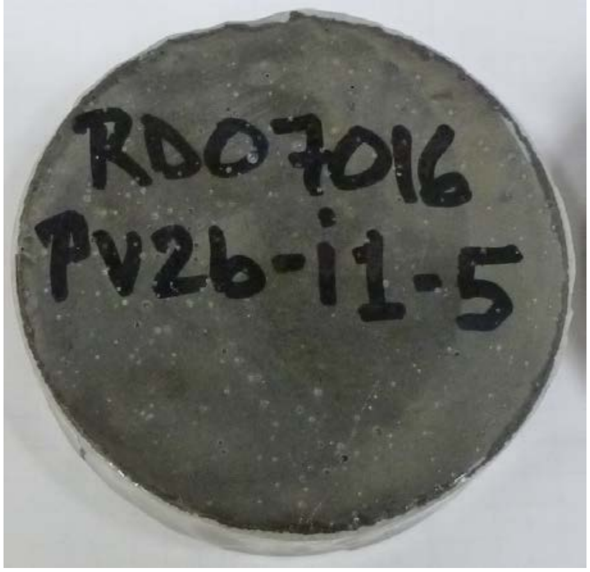
APPENDIX – PICTURES OF CEMENT PASTES AFTER IMMERSION IN CONTACT SOLUTIONS

Pictures after 3 months exposure

After 3 months in Sol.1: 0.15M Na_2SO_4

a) Paste PV1b



b) Paste PV2b

c) Paste PV1

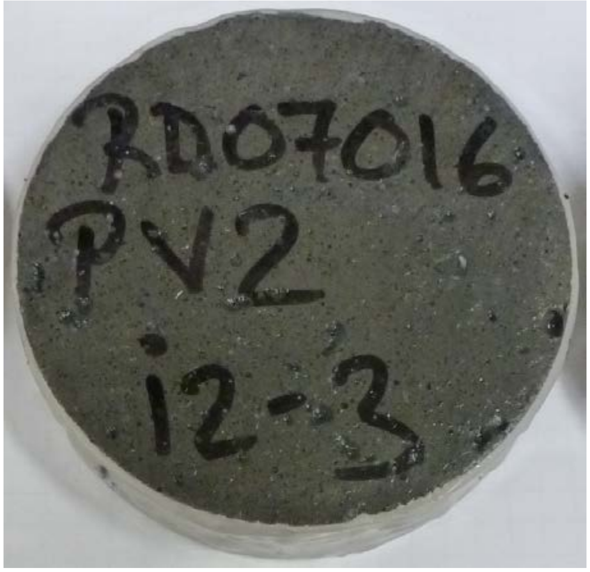
d) Paste PV2

After 3 months in Sol.2: 0.15M Na_2SO_4 + 0.5M NaOH

a) Paste PV1b

b) Paste PV2b

c) Paste PV1



d) Paste PV2

After 3 months in Sol.3: 0.15M Na_2SO_4 + 3M $NaNO_3$

a) Paste PV1b b) Paste PV2b

c) Paste PV1 d) Paste PV2

After 3 months in Sol.4: $0.15M\ Na_2SO_4 + 0.5M\ NaOH + 3M\ NaNO_3$

a) Paste PV1b

b) Paste PV2b

c) Paste PV1

d) Paste PV2

After 3 months in Sol.5: $0.15M\ Na_2SO_4 + 0.15M\ Na_2CO_3$

a) Paste PV1b

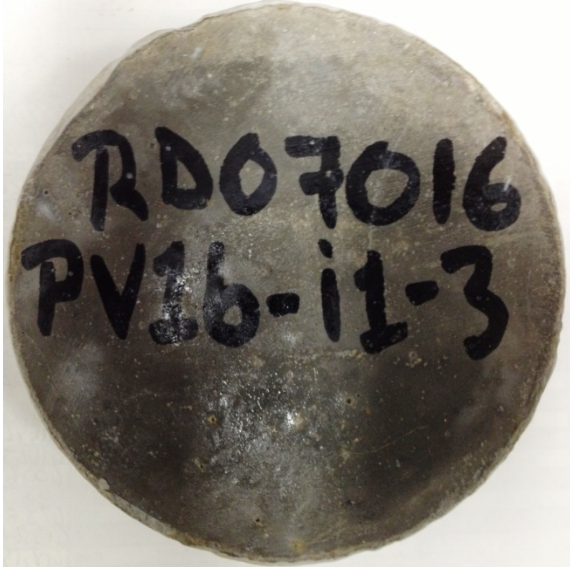
b) Paste PV2b

c) Paste PV1

d) Paste PV2

Pictures after 8 months exposure

After 8 months in Sol.1: 0.15M Na_2SO_4



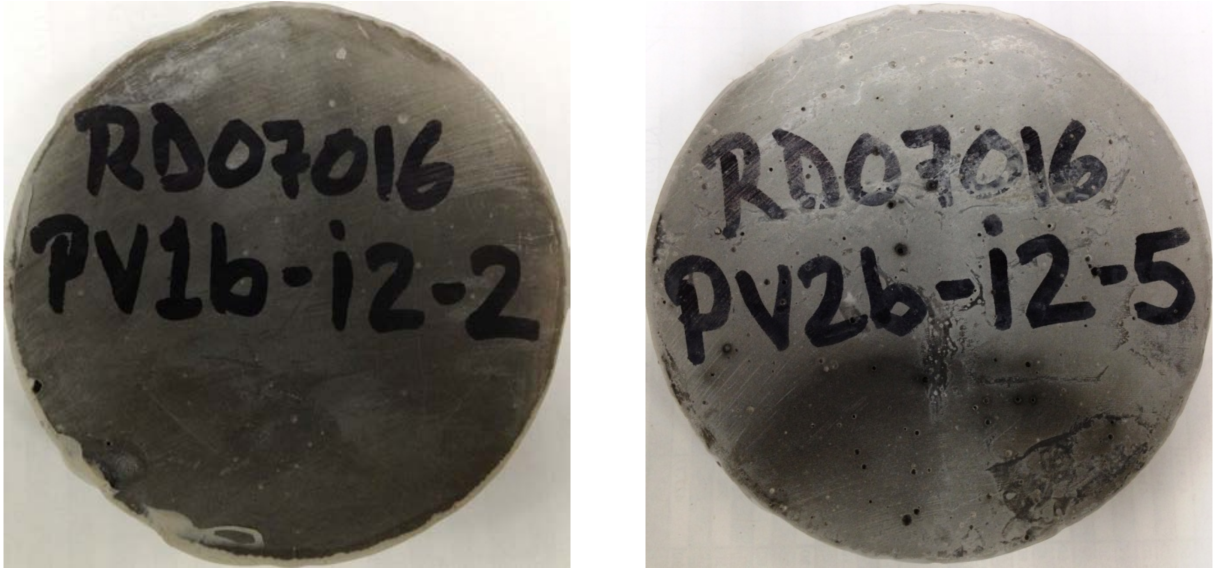
a) Paste PV1b

b) Paste PV2b

c) Paste PV1

d) Paste PV2

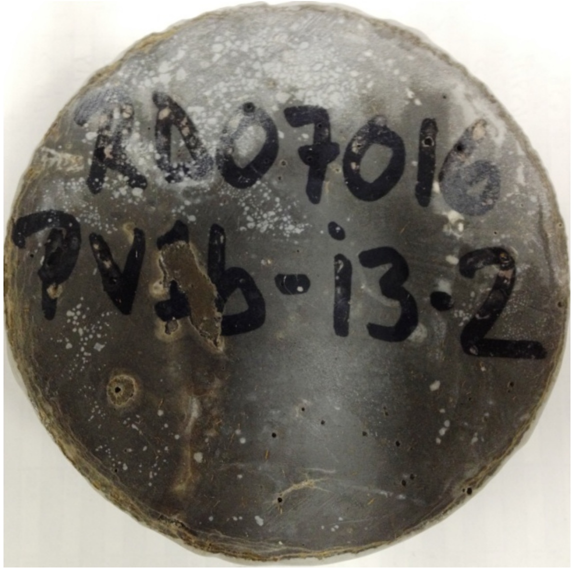
After 8 months in Sol.2: 0.15M Na_2SO_4 + 0.5M NaOH



a) Paste PV1b b) Paste PV2b

c) Paste PV1 d) Paste PV2

After 8 months in Sol.3: 0.15M Na_2SO_4 + 3M $NaNO_3$



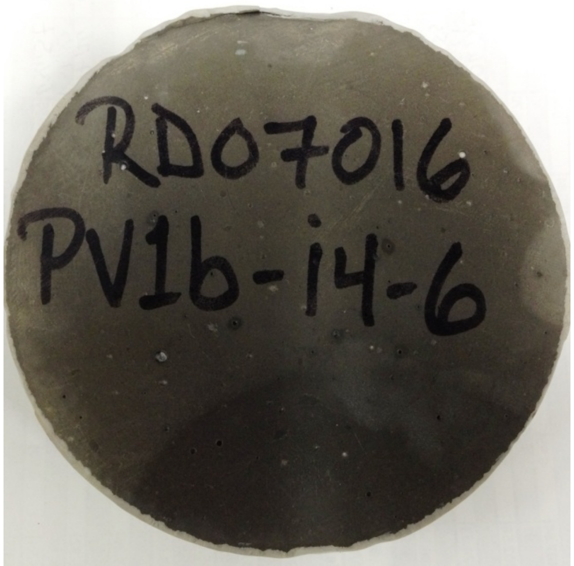
a) Paste PV1b

b) Paste PV2b

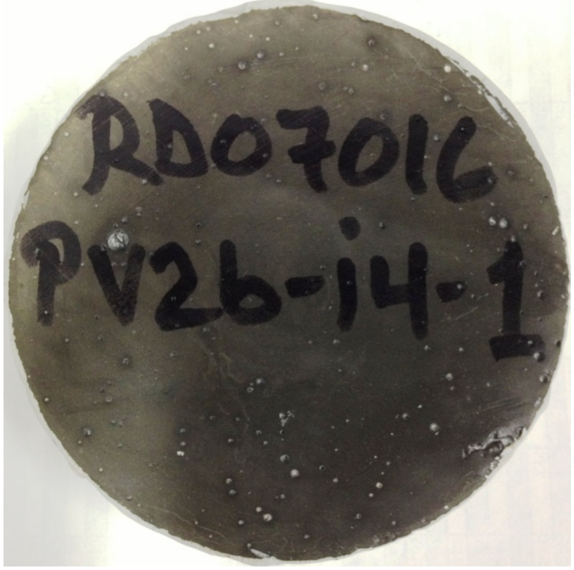
c) Paste PV1

d) Paste PV2

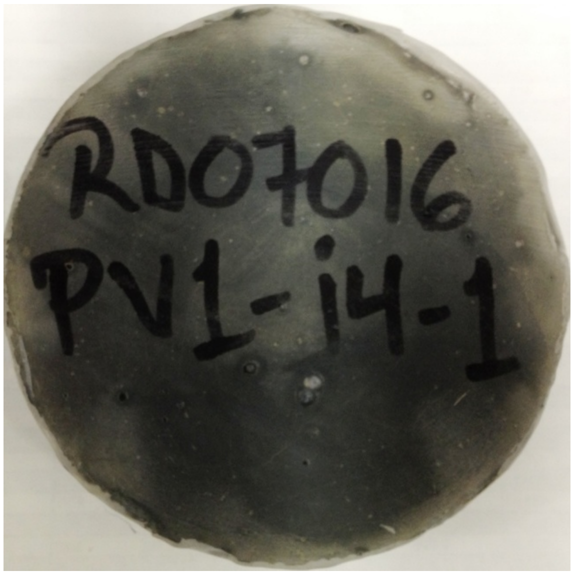
After 8 months in Sol.4: 0.15M Na_2SO_4 + 0.5M NaOH + 3M $NaNO_3$



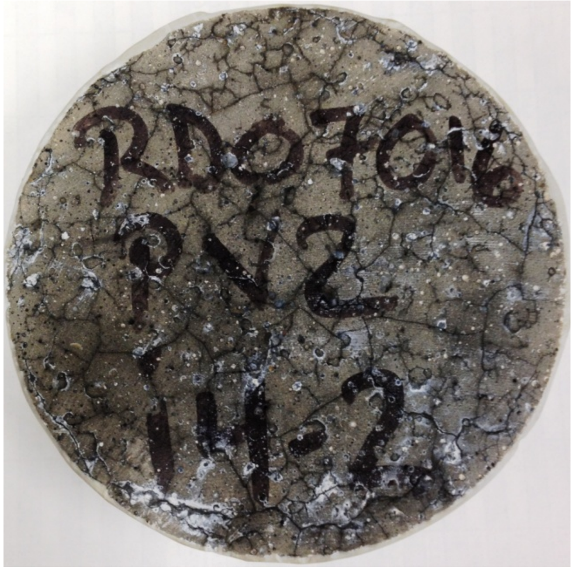
a) Paste PV1b



b) Paste PV2b



c) Paste PV1



d) Paste PV2

After 8 months in Sol.5: 0.15M Na_2SO_4 + 0.15M Na_2CO_3

a) Paste PV1b

b) Paste PV2b

c) Paste PV1

d) Paste PV2

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