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## ER-0985 Variables impacting sorption of Pu to the CILVA-immobilization matrix

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# Variables impacting sorption of Pu to the CILVA-immobilization matrix

## Results of screening for active factors in experimental design

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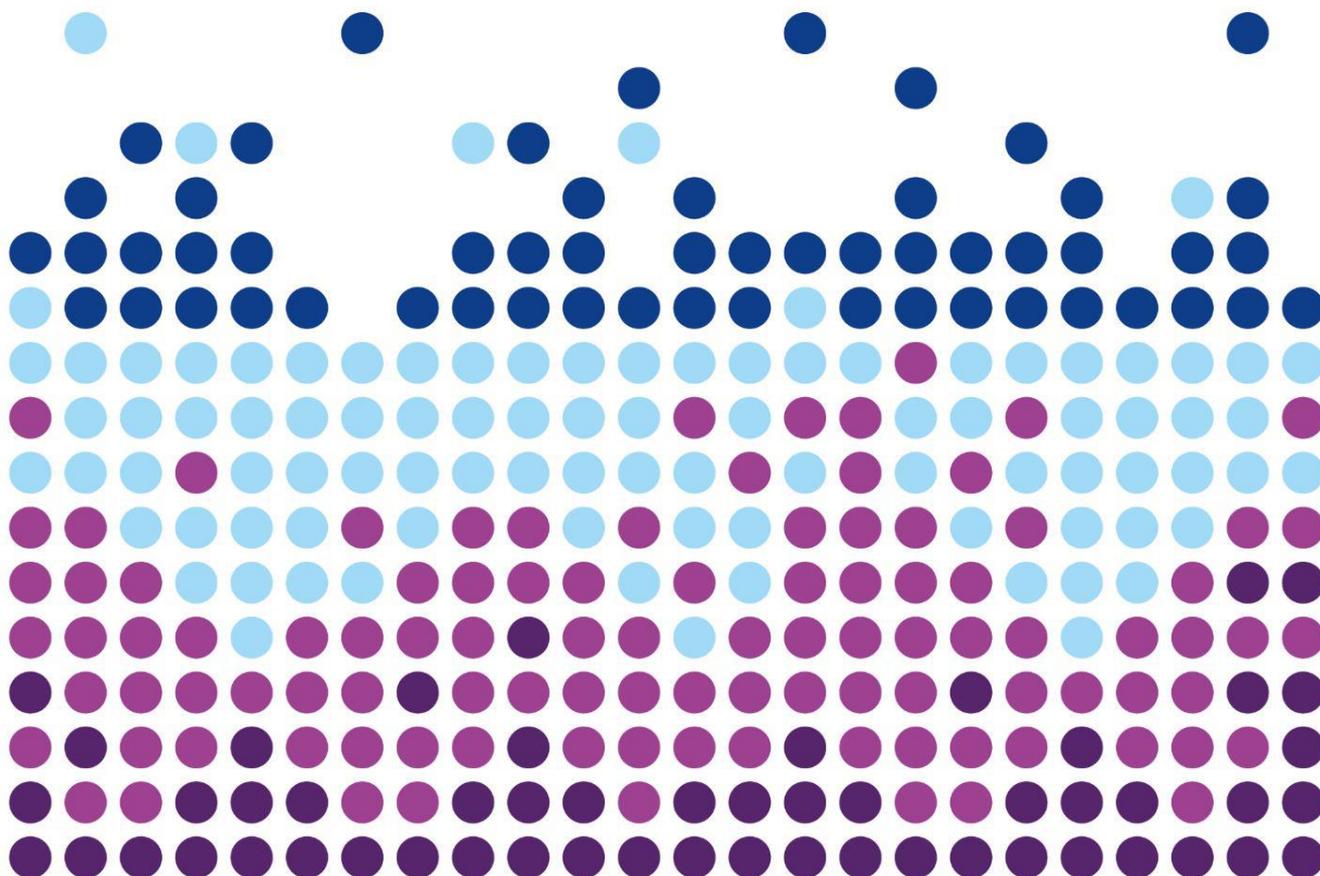
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## Glossary of abbreviations

%v/v	volume percentage
%w/w	weight percentage
BFS	Blast Furnace Slag
CASH	Calcium Aluminium Silicate Hydrate
cAt	(Radioactive waste of) Category A
CEMIII/C	Cement of class III, type C
CILVA	Centrale Infrastructuur voor Laagactief Vast Afval (Central Installation for Low-level Solid Waste)
CSH	Calcium Silicate Hydrate
DoE	Design of Experiments
Eh	standard redox potential
IC	Ion Chromatography
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
ICP-OES	Inductively Coupled Plasma - Optical Emission Spectrometry
ISA	Isosaccharinic acid
$K_d$	solid - liquid distribution coefficient at equilibrium
LSC	Liquid Scintillation Counting
NPOC	Non Purgeable Organic Carbon
ONDRAF/NIRAS	Organisme national belge des Déchets radioactifs et des Matières Fissiles enrichies / Nationale Instelling voor Radioactief Afval en verrijkte Splijtstoffen
OPC	Ordinary Portland Cement
ORP	Oxidation-Reduction Potential
PB	Plackett-Burman
PFE	Pore Fluid Extraction
pH	potential of hydrogen
Pu	Plutonium
Rd	solid - liquid distribution coefficient outside equilibrium
RDD	Research & Development Disposal Unit at SCK CEN
RN	Radionuclide
S/L	Solid to Liquid ratio
SCK CEN	Belgian Nuclear Research Centre (StudieCentrum voor Kernenergie – Centre d'Etude Nucleaire)
SCPW	Synthetic CILVA Pore Water
TOC	Total Organic Carbon

## Abstract

In the frame of the safe disposal of nuclear waste, ONDRAF/NIRAS has submitted a license application for the building of a near surface facility for the disposal of short-lived low and intermediate level waste (category A (cAt) waste). A significant part of the cAt waste, including Pu-contaminated cAt waste, has been conditioned in the CILVA-installation of Belgoprocess. Sorption data for Pu to cementitious matrices are available (Wang, 2009), and used in the safety case for near surface disposal, but uncertainties persist concerning the sorption values of Pu specifically on the CILVA-mortar. In this respect, ONDRAF/NIRAS has launched an experimental program to determine sorption values for Pu specifically to the CILVA-mortar, in order to obtain more representative sorption values. This experimental program is divided in two phases. A first phase focuses on the sorption on fresh CILVA mortar. A second phase focuses on oxidized CILVA mortar. This report is part of the first phase (fresh CILVA mortar).

At the start of the experimental program, the pore water of the fresh CILVA matrix was characterized, in order to define the prerequisite chemical conditions and boundaries in which the experimental set-up should fit. Preliminary tests were then carried out to define the analytical and practical boundary conditions for the experiments. Based on these data and previously gained knowledge on the conditions affecting radionuclide (RN) sorption (and Pu-sorption in particular), an experimental matrix was defined to screen for variables affecting Pu sorption to the fresh CILVA matrix.

The aim of this first part of the experimental program is to define which factors would affect sorption of Pu to the fresh CILVA immobilization matrix. The different factors are variables related to the CILVA pore water composition on one hand (concentrations of  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{S}^{2-}$ ,  $\text{K}^+$  and  $\text{OH}^-$  (pH)), and variables characteristic for batch sorption experiments on the other hand ([Pu], S/L and equilibration time).

From these 9 variables, only  $[\text{Ca}^{2+}]$  was found to be an active factor, and as such affecting Pu-sorption. In a next step (not included in this report), the extent of the impact of the  $[\text{Ca}^{2+}]$ , together with the effect of [ISA], will be the subject of a more elaborate experimental set-up, following a central composite design.

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## Keywords

Pu, Sorption, Cement, CILVA,  $K_d$ , Factorial Design, Calcium

## Introduction

In the frame of the safe disposal of nuclear waste, ONDRAF/NIRAS has submitted a license application for the building of a near surface facility for the disposal of short-lived low and intermediate level waste (category A (cAt) waste). When processing different types of waste, including radioactive waste, cementitious materials have been widely used as solidification/stabilization agents (Atkins, 1992; Chen, 2009). One of the benefits of using cement is its high sorption capacity towards toxic elements and radionuclides. To assess the safety of such cAt disposal facility, sorption values for various radionuclides on cementitious components are used in safety calculations (ONDRAF/NIRAS, 2019a, b).

A significant part of the cAt waste, including Pu-contaminated cAt waste, has been conditioned in the CILVA-installation of Belgoprocess. Sorption data for Pu to cementitious matrices are available (Wang, 2009), and used in the safety case for near surface disposal, but uncertainties persist concerning the sorption values of Pu specifically on the CILVA-mortar. In this respect, ONDRAF/NIRAS has launched an experimental program to determine sorption values for Pu specifically on the CILVA-mortar in both reduced and oxidized conditions, in order to obtain more representative sorption values. This document is part of the first phase of the experimental program, which focuses on the reducing conditions by using fresh CILVA mortar. In the second phase, the CILVA mortar will be treated to obtain oxidizing conditions.

Before starting the experimental program a literature and database review was carried out by Wang (2020) in support of these sorption studies. Earlier, different reviews were published on sorption values of actinides for some benchmark cements (Ochs, 2010, 2016; Wang, 2009). A common issue in these reviews is the often-lacking knowledge concerning the oxidation state of Pu. Pu is a redox sensitive element and can be (simultaneously) present as Pu (III), Pu (IV), Pu (V) and Pu (VI), each with different solubility and sorption behaviour. In the context of near surface disposal facility, sorption values were estimated for Pu (IV) and Pu (VI) based on the available published data (Ochs, 2016; Wang, 2009). Yet it is not entirely known in which (combination of) oxidation states Pu will be present in the lifespan of near surface disposal.

In the different reviews, sorption values of Pu to cementitious components are reported to be high, around  $10^5$  L/kg, considering Pu (IV), fresh cement and reducing conditions. For some other conditions, the reported sorption values were based on chemical analogies with other actinides. In those cases, sorption seems similarly high in some cases, but other sorption values range from  $3 \cdot 10^4$  L/kg for cement at degradation state II and III in both oxidizing and reducing conditions, to as low as 50 and 300 L/kg for cement at degradation state IV under oxidizing and reducing conditions respectively (Haussler et al., 2018; Wieland, 2014). The reviews also suggest the impact of elevated concentrations of calcium ( $\text{Ca}^{2+}$ ) and organics (from cellulose degradation and cement additives) on solubility and sorption of actinides. Overall, sorption of actinides seems linear at low loadings, reversible and fast (1 to 7 days, with a maximum of 30 days). Plausible sorption mechanisms are surface sorption, interlayer incorporation and co-precipitation.

Based on these reviews, the redox state and composition of the cementitious matrix and its pore water could affect Pu solubility and sorption. Therefore, a detailed experimental program on sorption of Pu to a specific cementitious matrix (the CILVA mortar), which takes into account different variables including pH, redox potential, concentration of major ions and organics, was designed.

At the start of the experimental program, the CILVA matrix, and more specifically, its pore water, was characterized, in order to define the prerequisite chemical conditions and boundaries in which the experimental set-up should fit. Preliminary tests were then carried out to define the analytical and practical boundary conditions for the experiments. Based on these data and previously gained knowledge on the conditions influencing radionuclide (RN) sorption (and Pu-sorption in particular), an experimental matrix was defined to screen for variables affecting Pu sorption to the fresh CILVA matrix.

Ultimately, this report aims at identifying the variables affecting sorption of Pu to the fresh CILVA matrix. The output of this first part of the experimental program is used to outline an experimental matrix, which targets to describe the correlation between these variables on one hand and Pu sorption to the CILVA matrix on the other hand.

# 1 General design of experiments

Traditionally, experiments are designed to determine the effect of one variable on a certain response. For example, at the start of the experimental program, it was agreed to study the effect of chloride (Cl<sup>-</sup>) and isosaccharinic acid (ISA) concentrations (=variables) on Pu sorption values ( $K_d$ ) (=response). However, because other variables (for example, pH) were discussed to possibly have an impact as well, the number of experiments needed to additionally address these uncertainties, would dramatically increase. In this respect, a Design of Experiments (DoE) approach was adopted. In such experimental design, variables are often referred to as factors. A factor is defined as an independent variable that can be tweaked by the experimentalist, independently from other variables.

Because there was little knowledge on whether certain factors would have an effect on the response (sorption) or not, a screening step was included in the experimental set-up. Such screening can be considered as a preliminary experiment in which the extreme values of the factors are addressed in a minimal number of tests. After screening, factors are flagged 'active' or not, meaning they are most likely to have an effect on the response, while the other factors most likely do not have a significant impact.

Based on this information, a follow-up experimental design can be drafted focused solely on the active factors, to investigate the extent of their impact on the response. This follow-up experiment might be an interaction study or a surface-response study, depending on the outcome of the screening.

## 1.1 Plackett-Burman

By using factorial design, the effects of multiple variables can be addressed in one experimental set-up, thereby significantly reducing the number of tests needed, compared to the more traditional and intuitive "one-factor-at-a-time-approach". Additionally, factorial design can both show independent effects of the different variables and interaction effects.

Since a full factorial design would still demand for a significant amount of tests, all the while also delivering information not needed at this stage of the research program (screening), a Plackett-Burman (PB) design was selected (some of the PB designs are a fractional factorial). Indeed, for a screening study (*i.e.* the identification of active factors) the following model is postulated for each response (Equation 1):

$$y = b_0 + \sum_{i=1}^p b_i * x_i$$

*Equation 1: Postulated model for a screening study, according to Plackett-Burman design*

with:

- $b_i$  being the unknown coefficients of the model;
- $x_i$  being the factor associated with the coefficient  $b_i$ ;
- $y$  being the response in question.

These models are by no means aimed to be phenomenological nor do they have any predictive quality. They can be used solely to identify the main effect of the factors under study. A PB design allows estimating the coefficients associated to the factors with great precision by making use of only a very limited amount of experiments. However, in a PB design, all main effects are confounded (aliased) with many interaction effects. This is often considered a drawback of these matrices. However, with a clever analysis of the results this drawback can be turned into an advantage and as such can allow identifying strong interactions. A very nice practical example of this is reported by (Cau Dit Coumes et al., 2018).

## 2 CILVA matrix

The CILVA immobilization matrix consists of CEMIII/C and two types of sand, as presented in Table 1 (Vanherck, 2017). As can be deduced from the table, the CILVA mortar has a w/c ratio of 0.38.

Table 1: Composition of the CILVA immobilisation matrix

Component	kg	%
Sand 1 (Sibelco Wessem)	250	44.3
Sand 2 (Sibelco M32)	83.3	14.8
CEMIII/C (see Table 2)	166.7	29.5
Water	63.4	11.2
Additive (MasterGlenium27)	1.314	0.2

CEMIII/C is a highly reducing cement containing 81 to 95% of blast furnace slag (BFS). Upon hydration, it produces *a.o.* calcium silicate hydrates (C-S-H), calcium aluminium silicate hydrates C-A-S-H and portlandite phases.

The average elemental composition (oxides and chloride) of Holcim CEMIII/C 32.5 N-LH/SR LA and the corresponding average composition of the CILVA mortar, can be consulted in Table 2. The alkali content (Na<sub>2</sub>O-equivalent) of CEMIII/C 32.5 N-LH/SR LA is limited to a maximum of 2%. Likewise, there is an upper threshold of the SO<sub>3</sub> content, set at 4.5%. The chloride content is above 0.1%, which is allowed according to the European EN197-1 norm, provided it is clearly mentioned.

Table 2: Average elemental composition of Holcim CEMIII/C 32.5 N-LH/SR LA and CILVA mortar

	% in CEMIII/C	mg/g CEM III/C	mg/g CILVA
CaO	46.4	464	137.0
SiO <sub>2</sub>	31.8	318	93.9
Al <sub>2</sub> O <sub>3</sub>	10	100	29.5
Fe <sub>2</sub> O <sub>3</sub>	1	10	3.0
MgO	5.8	58	17.1
Na <sub>2</sub> O	0.5	5	1.5
K <sub>2</sub> O	0.56	5.6	1.7
Cl <sup>-</sup>	0.3	3	0.9
Na <sub>2</sub> O-equivalent	0.87	8.7	2.6
SO <sub>3</sub>	1.6	16	4.7
Na <sub>2</sub> O-equivalent upper threshold	2	20	5.9
SO <sub>3</sub> upper threshold	4.5	45	13.3

The CILVA matrix was produced at BelgoProcess (Dessel, Belgium), following the protocol by Vanherck (2017), where it was allowed to hydrate for 12 months, while being kept under water. At 12 months, the samples were transferred to SCK CEN, where they were stored in inert atmosphere (N<sub>2</sub> glovebox) at 95-98% RH, achieved by providing a saturated K<sub>2</sub>SO<sub>4</sub> solution in a closed cabinet inside the glovebox.

### 2.1 CILVA pore water

Batch sorption experiments are performed by bringing the radionuclide (RN) in contact with the sorbing matrix, *i.e.* the CILVA mortar. Such contact typically takes place in a relevant background solution (Van Laer, 2017; Wouters et al., 2022a). To avoid alteration of the mortar through cement degradation, the background solution should be close to the CILVA pore water. With respect to RN speciation and solubility, using a proper background solution is crucial as well. In addition, knowledge on the pore water composition is needed to define the factors possibly affecting Pu sorption in the frame of factorial design.

### 2.1.1 Pore fluid extraction

In order to characterize the CILVA pore water and to define an appropriate background solution, pore water was extracted by squeezing from a prism of CILVA mortar after approximately 1 year of hydration. This pore fluid extraction (PFE) was performed at the Magnel laboratory of UGent, using a hydraulic press. Applying a force of 2\*900 kN to a prism of 7\*4\*4 cm yielded approximately 400 µL of pore solution, which was subsequently subjected to analyses.

### 2.1.2 Pore water composition

#### 2.1.2.1 Major anions and cations

The pore water sample extracted by PFE, was analysed by ICP-OES (Thermo Scientific iCAP 7400 rad) for the cations and by IC (Thermo Scientific Dionex Aquion IonPac AS22) for the anions, by SCK CEN's ISO 17025 certified Radiochemical Analysis Labs (RCA). The total amount of S was determined by complete oxidation of all S to SO<sub>4</sub><sup>2-</sup> by adding 10 %v/v H<sub>2</sub>O<sub>2</sub> in a subsample, and subsequent analysis of SO<sub>4</sub><sup>2-</sup> in the subsample by IC.

Ions detected in the pore water were Ca<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup> (Table 3).

Table 3: Major ions detected in the CILVA pore water, extracted by PFE

ICP/IC	mM
<b>Ca</b>	1.2 ± 0.85
<b>K</b>	42.7 ± 5.63
<b>Na</b>	84.8 ± 21.75
<b>Cl</b>	20.3 ± 0.52
<b>SO<sub>4</sub><sup>2-</sup></b>	1.6 ± 0.10
<b>Total S</b>	9.7 ± 0.31

#### 2.1.2.2 pH

Unfortunately, the sample volume was too low for pH measurement. The expected pH was therefore calculated, based on the charge imbalance imposed by the major cations and anions detected. Replacing the pH as the charge balance species, *i.e.* H<sup>+</sup> (or OH<sup>-</sup>) as the balancing species, resulted in a pH of 12.82 at an assumed temperature of 25°C. Alternatively, based on the solubility of both portlandite and calcite in the cementitious phase, a similar pH of 12.86 is predicted (ThermoChimie v10a). Such calculation would however coincide with a [Ca<sup>2+</sup>] of 6 mM, which is considerably higher than observed. An experimental underestimation of the [Ca<sup>2+</sup>] could be attributed to the precipitation of Ca<sup>2+</sup> in the form of CaCO<sub>3</sub> upon ingress of CO<sub>2</sub> from the atmosphere in the pore fluid sample during or after the extraction.

In later PFE efforts of CEMIII/C hardened cement paste with a w/c ratio of 0.5, the cementitious component of the CILVA mortar, the pH was confirmed to be 12.89 after 12 months of hydration. A higher w/c ratio of 0.5, as opposed to a 0.38 w/c ratio in the CILVA mortar, was chosen for these pastes, to allow extraction of a higher volume of pore fluid, sufficient for pH analysis.

An estimated pH between 12.8 and 12.9 is significantly lower than the pH reported in literature for pore fluid of Ordinary Portland Cement (OPC), which would be >pH 13,5 (Vollpracht et al., 2016). However, a lower pH is consistent with the observed lower concentrations of alkalis, *e.g.* 84.8 mM of Na and 42.7 mM of K, as compared to respectively 1500 mM of Na and 400-600 mM of K in an OPC pore fluid (Vollpracht et al., 2016). Indeed, depending on the kind of cement used, the initial pH and pore water composition is expected to differ. In BFS or pozzolanic cements, the pH of fresh cement pore water is generally lower, *a.o.* due to the 'dilution' of the OPC (Cau Dit Coumes et al., 2006; Lothenbach et al., 2012).

Based on calculations, the measured pH of CEMIII/C pore water samples and literature, a pH of around 12.85 - 12.86 is therefore assumed the most accurate estimate.

### 2.1.2.3 Eh

Likewise, the redox potential (Eh) could not be measured in the pore fluid sample. Eh estimation is not possible based solely on the measured fluid composition, as no speciation measurements are available for any redox couples. It is however possible to scope the Eh by assuming that the measured total sulphur is composed only of sulphate and sulphide and that the couple  $\text{SO}_4^{2-}/\text{S}^{2-}$  controls the redox potential of the system. This assumption is reasonable as literature suggests that a BFS cement is rich in sulphide, and partial oxidation of sulphide to sulphate always occurs (Roy, 2009).

Based on the  $\text{SO}_4^{2-}/\text{S}^{2-}$  redox couple, the Eh is estimated at -615 mV at a pH of 12.85, and may gradually increase to around -400 mV upon atmospheric  $\text{CO}_2$  ingress in the pore fluid. In case other S-species than  $\text{S}^{2-}$  are present (e.g. intermediate oxidation species like sulphite), the Eh is expected to be higher.

### 2.1.2.4 Organic carbon

To assess whether organic carbon is present in the CILVA pore water (Section 0), a subsample of the PFE extract was analysed for Non-Purgeable Organic Carbon, using a carbon analyser (Shimadzu TOC-L CPH analyser) available at RDD (Group R&D Disposal, SCK CEN) after treatment of the samples with 1M HCl, sufficient to reach a pH < 2. This pre-treatment was needed to remove all inorganic and so-called purgeable organic carbon, i.e. carbon that can be turned into a volatile compound by acidification. The NPOC analyses showed an amount of approximately 790 mg/L NPOC in the CILVA pore water.

### 2.1.3 Synthetic CILVA pore water

Based on the above analyses and calculations, the CILVA pore water can be considered NaOH/KOH dominated, with a pH between 12.8 and 12.9, and additionally containing  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{S}^{2-}$ . In order to prepare synthetic CILVA pore water (SCPW) as a background solution to perform sorption experiments, a combination of Na-, K- and Ca-salts is needed. A rudimentary composition of SCPW around pH 12.86 is provided in Table 4, in which the  $[\text{OH}^-]$  is calculated based on the activity coefficients of the ions according to the Debye-Hückel equation (Debye and Hückel, 1923).

Table 4: Exemplary composition of Synthetic CILVA Pore Water at pH 12.859

pH <b>12.859</b>								
[OH <sup>-</sup> ] 96.9 mM		<b>NaCl</b>	<b>K<sub>2</sub>SO<sub>4</sub></b>	<b>Ca(OH)<sub>2</sub></b>	<b>KOH</b>	<b>NaOH</b>	<b>Na<sub>2</sub>S</b>	<b>SUM</b>
		<b>20.3</b>	<b>1.6</b>	<b>1.2</b>	<b>44.42</b>	<b>50.08</b>	<b>8.1</b>	<b>mM</b>
<b>Ca</b>	1.2			1.2				1.2
<b>K</b>	42.7		3.2		44.42			47.62
<b>Na</b>	84.8	20.3				50.08	16.2	86.58
<b>Cl</b>	20.3	20.3						20.3
<b>SO<sub>4</sub></b>	1.6		1.6					1.6
<b>OH</b>	96.9			2.4	44.42	50.08		96.9
<b>S</b>	8.1						8.1	8.1

The salt composition provided in Table 4 is considered a base recipe for SCPW, and assumes it is prepared under inert atmosphere (no  $\text{CO}_2$ ). Yet there are uncertainties regarding the exact composition of the pore water (for example the pH and Eh). The significance of this uncertainty for the experimental program was unknown. To account for this uncertainty, the methodology of factorial design was adopted, as described in Section 1 of this report.

## 2.1.4 Variables for factorial design

Based on the pore water composition of the CILVA matrix, the corresponding calculations and literature, six pore water variables were selected as factors potentially affecting Pu sorption to the matrix (Table 5).

Table 5: Boundary values for six variables associated with CILVA pore water, identified for factorial design (screening)

Factor	Min	Max	Unit
Cl <sup>-</sup>	0.02	1.25	M
S <sup>2-</sup>	0.0001	0.015	M
Ca <sup>2+</sup>	0.0005	0.005	M
pH	12.5	13.2	-
SO <sub>4</sub> <sup>2-</sup>	0.0001	0.015	M
K <sup>+</sup>	0.035	0.05	M

The impact of Cl<sup>-</sup> on Pu sorption was already considered a point of interest with regard to RN sorption, yet based on literature it was unclear to what extent it could impact the Pu-sorption ( $K_d$ ) (Altmaier et al., 2013; Altmaier et al., 2009). Therefore, it was included as factor to screen. As a minimum value, the background value of the SCPW is chosen (20 mM), while a conservatively high value (1.25 M) is selected as the maximum value to screen against.

Based on the review preceding the experimental program (Wang, 2020), and from a cement degradation point of view, the impact of Ca<sup>2+</sup> is considered an important variable to screen for as well. As a minimum value, less than half of the measured [Ca<sup>2+</sup>] is selected (0.5 mM), while a value close to saturation is chosen as a maximum value (5 mM).

Because of the impact of the redox potential on Pu speciation (Section 0), and the uncertainty regarding the actual redox conditions of the CILVA pore water and the speciation of S, the SO<sub>4</sub><sup>2-</sup>/S<sup>2-</sup> couple was included as a factor as well. Both [S<sup>2-</sup>] and [SO<sub>4</sub><sup>2-</sup>] were chosen to range from close to zero (0.1 mM) to a little over double the total S concentration measured (15 mM).

As the pH was mostly estimated based on calculations and literature, and since both Pu speciation and cement chemistry are likely to be impacted by pH (Section 0), the pH was selected as a factor as well, ranging from pH 12.5 to 13.2, with the estimated pH of ca. 12.85 (Section 2.1.2.2) as the intermediate value.

Finally, the [K<sup>+</sup>] was included in the design. Although alkalis are not expected to affect RN sorption, it was considered useful to confirm this as such, since the alkali account for most of the ionic content of the pore water. [K<sup>+</sup>] was selected to range between 35 and 50 mM, which are values balanced around the measured value of 42.7 mM.

To allow for the actual preparation of the synthetic pore water with differences in the above ion contents, the [Na<sup>+</sup>] was assigned as a so-called floating factor. Such floating factor is needed to change 'freely', to compensate the charge imbalance imposed by the combinations of anions and cations proposed in the factorial design.

Note that zero concentrations were never chosen to allow for a maximum of flexibility and potential re-use of data in potential future follow-up studies (e.g. Surface Response Measurement). In addition, minor adaptations of minimum and maximum values were allowed when designing the screening experiments.

### 3 Sorption experiments

Sorption includes all processes that take place at the interface of the sorbent and the background solution, and results in a specific distribution of the radionuclide between the solid and liquid phase. In this respect, the solid-to-liquid distribution represents the sorption behaviour of the sorbate (Pu) towards the sorbent (CILVA matrix). Other processes that might affect the presence of the sorbate in the liquid phase (e.g. precipitates, colloids...), should not be included in this distribution representation, and should be addressed separately if relevant.

In literature, the solid-liquid distribution coefficient is expressed as either  $K_d$  or  $R_d$ , and is defined as the ratio between on one hand the concentration of the element sorbed to the solid phase and on the other hand the concentration of the element in the liquid phase (Equation 2):

$$K_d \text{ (or } R_d) = \frac{C_{ads}}{C_{sol}}$$

Equation 2: Calculation of  $K_d/R_d$

with  $C_{ads}$  and  $C_{sol}$  being respectively, the concentration of the element sorbed to the cementitious phase, and its concentration in the liquid phase.

In general,  $K_d$  is used when the partitioning of an element between the solid and the liquid phase is considered to be at equilibrium, while  $R_d$  is preferred when the partitioning is not in considered to be at equilibrium. Throughout this report, the solid-liquid distribution coefficient will be referred to as the  $K_d$  though the reversibility of the sorption was not assessed

#### 3.1 Batch sorption tests

The most common way to study sorption is through batch experiments, which broadly consist of bringing the sorbate and sorbent in contact with each other inside a background solution, and as such determining the concentration of the sorbate in the background solution at the beginning and after a certain equilibration time. The amount of the element sorbed to the sorbent ( $C_{ads}$ ) is calculated as its concentration in solution at the beginning versus its concentration in solution at the end of the equilibration time. As this report focuses on sorption of Pu, concentration is interpreted from radiometric analysis, so the  $K_d$  is expressed as the ratio of activities, taking into account the amount of background solution and sorbent available (Equation 3):

$$K_d = \frac{A_{init} - A_{eq}}{A_{eq}} \cdot \frac{V}{m}$$

Equation 3: Calculation of  $K_d$  using RN activity and taking into account the solid to liquid ratio of the suspension

with  $A_{init}$  being the initial activity of the RN in solution (Bq),  $A_{eq}$  the activity of the RN in solution at equilibrium (Bq),  $V$  the volume of the liquid phase (L) and  $m$  the dry weight of the added solid phase (kg).

An elaborate protocol on how to perform batch sorption experiments of RN (sorbate) to a cementitious matrix (sorbent), and more specifically of Pu to the CILVA mortar, is provided in Wouters et al. (2022a).

#### 3.2 Selection of Pu concentration, S/L and equilibration time

When performing RN sorption experiments, it is advisable to perform preliminary experiments and/or calculations to estimate the relevant Solid to Liquid ratio (S/L) (i.e. the amount of CILVA matrix in the background solution) and RN concentrations to focus on. Some combinations of S/L and RN concentration might lead to invalid results (Van Laer, 2017; Wouters et al., 2022a).

As such, statistics, detection limits and Pu solubility will determine in which 'window' of S/L and Pu concentrations the experiments should take place. The limits of this window can furthermore be selected as the minima and maxima for the factorial design.



### 3.3 Organic carbon

In the pore water of cementitious stabilization matrices, a certain amount of organic components could be present as well. As shown in Section 2.1.2.4, indeed approximately 790 mg/L of NPOC was detected in the CILVA pore water. Organic compounds can be derived from organic cement additives, or can leach out from the nuclear waste itself (e.g. cellulose degradation products). In the CILVA mortar, the organic carbon is most likely derived from the MasterGlenium27 additive (see Table 1), and/or natural organic impurities from the Sibelco sands. In the review from Wang (2020), recent literature on the impact of such organic degradation products on Pu sorption is presented. Central in these studies stands the significant impact of isosaccharinic acid (ISA) on RN solubility and hence RN sorption. Indeed, above a critical concentration of  $10^{-4}$  M of ISA, a significant reduction of Pu sorption is to be expected, as described earlier for similar systems (Tasi et al., 2021; Wang, 2009; Wieland, 2014).

### 3.4 Variables for factorial design

Because of the current uncertainties regarding their impact on  $K_d$  values, the three variables inherent to batch sorption experiments, namely RN concentration, S/L ratio and equilibration time, are included in the factorial design as summarized in Table 6. Together with the factors related to the CILVA pore water (Section 0, Table 5), this means a total of 9 factors were identified.

Table 6: Boundary values of [Pu], S/L and equilibration time, identified for factorial design (screening)

Factor	Min	Max	Unit
Pu	$7 \cdot 10^{-11}$	$1 \cdot 10^{-9}$	M
S/L	0.1	0.5	g/L
Eq. time	7	21	days

As for ISA, it is already abundantly clear from literature and preliminary scoping calculations (Section 0), that it has a significant impact on Pu-sorption. It was therefore concluded that [ISA] should certainly be accounted for in the experimental program, in a broad range of concentrations ( $10^{-1}$  to  $10^{-5}$  M). Organic compounds other than ISA are at this point not yet included in the experimental program.

However, it's not needed to include [ISA] as a factor to screen in the preliminary step. As mentioned before (Section 1), the goal of screening is to identify which factors are 'active'. Because the [ISA] is assumed to be an active factor, it will merely be added to the screening experiments as a fixed 'background' variable, at an intermediate concentration of  $10^{-3}$  M.

## 4 Design of the Plackett-Burman plan

Based on the preliminary tests and calculations discussed in the previous paragraphs, an experimental plan was designed in order to screen for active factors.

The following factors were identified each with their lower and upper limit (Sections 0 and 3.2):

1. Concentration of chlorides, ranging from 0.02 to 1.25 M;
2. Concentration of reduced sulphur species, ranging from 0.0001 to 0.015 M;
3. Concentration of calcium, ranging from 0.0005 to 0.0049 M
4. pH-value, ranging from pH 12.5 to 13.2;
5. Equilibration time, ranging from 7 to 21 days;
6. Concentration of sulphates, ranging from 0.0001 to 0.0151 M;
7. Concentration of Pu, ranging from  $7E-11$  to  $1E-9$  M;
8. Ratio S/L, ranging from 0.100 to 0.501;
9. Concentration of potassium, ranging from 0.035 to 0.050 M;

In the screening study, all factors, except equilibrium time and pH, are log-transformed before being normalized. The physical boundaries of the experimental domain are normalized over the n-dimensional vector space, with n being the numbers of factors.

Since it is established before that the [ISA] has an impact on Pu-sorption (Section 0), it will not be included as a factor in the screening step (as already noted in Section 3.4). Instead, it will be kept constant, at an intermediate level of  $10^{-3}$  M. The addition of ISA will take place at the same time as Pu, to minimize bias caused by their order of addition and *a.o.* subsequent preferential sorption or competition effects.

As mentioned before (Section 0), the concentration of sodium ( $Na^+$ ) is not among the factors. In order to overcome practical issues associated with a design heavily relying on varying combinations of different ions, and thus to allow adjustments for electro neutrality, it was opted to keep the  $[Na^+]$  as free-floating, ranging between  $3.08 \cdot 10^{-2}$  M and 1.40 M. The choice for sodium as free-floating element was driven by the fact that this element is, together with  $OH^-$ , the most abundant ion in the CILVA pore water.

To limit the number of experiments, three factors (factor 7, 8 and 9), which are considered the least likely to affect the response, are combined in one grouped variable ([Pu], S/L and  $[K^+]$ ). This means they are all varied interdependently and evaluated as one factor. Only if this factor is shown to be active, a new experimental plan is needed to find which of the three variables causes the impact on Pu sorption. As such, grouping factors in one factor is considered a calculated risk in the hope of lowering the total amount of tests needed, because none of the factors in this group is expected to affect Pu sorption.

Seven factors can be assessed by a PB-matrix in eight runs. However, this would not allow assessment of the experimental error since no degrees of freedom are left. Indeed, without knowledge on the experimental error one cannot judge whether the estimates for the coefficients are significantly different from zero or not. Therefore, the PB-design is complemented with repetitions of the centre point. The centre point is executed three times (independent repetitions).

The experiments of the PB-design are randomized to block a time effect, and the centre points are added to this plan - one at the start, one in the middle and one at the end - in order to account for potential drift. The resulting experimental plan, expressed in coded (normalized) factors, is presented in Table 7.

Table 7: Experimental matrix for screening. -1, 1 and 0 correspond to the lower, upper and centre of the factor value ranges.

[Cl <sup>-</sup> ]	[S <sup>2-</sup> ]	[Ca <sup>2+</sup> ]	pH	Equil. time	[SO <sub>4</sub> <sup>2-</sup> ]	Grouped factor
1	1	1	-1	1	-1	-1
-1	1	1	1	-1	1	-1
-1	-1	1	1	1	-1	1
1	-1	-1	1	1	1	-1
-1	1	-1	-1	1	1	1
1	-1	1	-1	-1	1	1
1	1	-1	1	-1	-1	1
-1	-1	-1	-1	-1	-1	-1
0	0	0	0	0	0	0
0	0	0	0	0	0	0
0	0	0	0	0	0	0

Power calculations revealed that such an experimental plan would, when analysed by ANOVA with a significance level of 5%, detect active factors in 80% of the cases as long as the effect size<sup>1</sup> is 3 (or greater). For an effect size of 4, the power increases to 95%.

The resulting experimental plan, expressed in physical units, is shown in Table 8. This plan includes a combination of lower, intermediate and upper limits of the variables, based on the levels defined before (Table 5 and Table 6), and, as mentioned above, includes three replicates of the same conditions to enable evaluation of the experimental accuracy and asses drift. As discussed before, the [ISA] is kept constant, and the [Na<sup>+</sup>] varies depending on the composition of the solution, as a floating factor to ensure charge balance.

Table 8: Experimental matrix expressed in physical units

Order	[Cl <sup>-</sup> ] mol/l	[S <sup>2-</sup> ] mol/l	[Ca <sup>2+</sup> ] mol/l	pH -	Equil. time days	[SO <sub>4</sub> <sup>2-</sup> ] mol/l	[Pu] mol/l	S/L g/l	[K <sup>+</sup> ] mol/l	[ISA] mol/l	[Na <sup>+</sup> ] mol/l
1	1.25E+00	1.0E-04	4.9E-03	12.5	7	1.51E-02	1.00E-09	5.01E-01	5.00E-02	1.00E-03	1.25E+00
2	2.00E-02	1.5E-02	5.0E-04	12.5	21	1.51E-02	1.00E-09	5.01E-01	5.00E-02	1.00E-03	3.08E-02
3	2.00E-02	1.5E-02	4.9E-03	13.2	7	1.51E-02	7.00E-11	1.00E-01	3.50E-02	1.00E-03	1.64E-01
4	1.58E-01	1.2E-03	1.6E-03	12.85	14	1.23E-03	2.65E-10	2.24E-01	4.18E-02	1.00E-03	1.86E-01
5	2.00E-02	1.0E-04	5.0E-04	12.5	7	1.00E-04	7.00E-11	1.00E-01	3.50E-02	1.00E-03	1.58E-01
6	1.25E+00	1.5E-02	4.9E-03	12.5	21	1.00E-04	7.00E-11	1.00E-01	3.50E-02	1.00E-03	1.24E+00
7	2.00E-02	1.0E-04	4.9E-03	13.2	21	1.00E-04	1.00E-09	5.01E-01	5.00E-02	1.00E-03	1.19E-01
8	1.58E-01	1.2E-03	1.6E-03	12.85	14	1.23E-03	2.65E-10	2.24E-01	4.18E-02	1.00E-03	1.86E-01
9	1.25E+00	1.5E-02	5.0E-04	13.2	7	1.00E-04	1.00E-09	5.01E-01	5.00E-02	1.00E-03	1.36E+00
10	1.25E+00	1.0E-04	5.0E-04	13.2	21	1.51E-02	7.00E-11	1.00E-01	3.50E-02	1.00E-03	1.40E+00
11	1.58E-01	1.2E-03	1.6E-03	12.85	14	1.23E-03	2.65E-10	2.24E-01	4.18E-02	1.00E-03	1.86E-01

When performing the screening experiments, care was taken to perform all experiments independently from each other, in order to limit experimental bias and interdependency. This means it was not allowed to use a general stock solution of a 'background' SCPW to start from. Each of the 11 solutions, including the 3 replicates, was thus prepared separately. For each experiment, CILVA powder was weighed separately, and added to the corresponding background solution as a suspension, which was also prepared in the respective solution (see Wouters et al. (2022a) for more details on the protocol). On the other hand, using stock solutions of the individual salts and of a Pu- and ISA-spike was allowed for practical reasons (e.g. cost and inventory of RN stock solutions). All experiments were started on the same day, and ended after 7, 14 or 21 days.

<sup>1</sup> Effect size: the effect a factor has on the response when it changes from its lowest to its upper value compared to the standard deviation of the experimental error.

## 5 Experimental Methods

The 11 sorption experiments were executed according to the recommendations provided in (Wouters et al., 2022a). The most important steps are summarized below.

### 5.1 Preparation of solid phase

#### 5.1.1 Treatment of the cementitious matrix

The CILVA matrix was prepared by BelgoProcess according to the recipe detailed in Section 2 and in Vanherck (2017). It had been hydrated for one year, and was as such available as a solid matrix. In order to address sorption in suspension, the cementitious matrix was reduced to a powder with grain size  $<74 \mu\text{m}$ . This was achieved by using hammer and chisel in a first step, followed by an iteration of manual grinding (mortar and pestle) and sieving, in inert atmosphere to avoid carbonation.

#### 5.1.2 Water content

When calculating the solid to liquid ratio (S/L), the mass of the solid fraction refers to the oven dry mass. To correct the added mass of cementitious powder for the weight of the pore water, the pore water content was determined. When doing so, it is important to determine water content on the same sample type as used in the sorption experiments, since the effort of crushing and sieving the cement as such, could already cause partial water loss. In this case, the water content of powdered CILVA was determined to be 3.3 %w/w.

### 5.2 Preparation of synthetic cement pore water

Based on the experimental plan (Table 8), 11 SCPW solutions were prepared. In addition to the six salts mentioned in Table 4 (NaCl,  $\text{K}_2\text{SO}_4$ ,  $\text{Ca}(\text{OH})_2$ , KOH, NaOH and  $\text{Na}_2\text{S}$ ), KCl and  $\text{Na}_2\text{SO}_4$  were added to the SCPW recipe, to allow mass balance corrections resulting in the ion concentrations reported in Table 8.

When preparing the synthetic pore water for the sorption experiments, care was taken with regard to the atmosphere, pH and equilibration with the solid phase as detailed in the following sections

#### 5.2.1 Inert atmosphere

Keeping in mind the alteration/degradation of cementitious materials when exposed to *a.o.*  $\text{CO}_2$ , sorption experiments should be performed in an inert atmosphere (*i.e.* in a glovebox with inert,  $\text{N}_2$  atmosphere). As such, all stock solutions and SCPW solutions were prepared in the glovebox using degassed water.

#### 5.2.2 pH

Knowing and/or regulating pH at which sorption occurs is important, on one hand because it might play a role in the sorption mechanism and the speciation of the RN, and on the other hand because it might affect the state/degradation of the cementitious phases. Since pH is one of the variables that is being screened a careful adjustment of the pH of the synthetic cement pore water is crucial.

In this respect, it's key to take into account the alkali error when measuring high pHs such as those of cement pore water. At high pH, *i.e.* low concentration of hydrogen ions, alkali metals like  $\text{Na}^+$  and  $\text{K}^+$  can contribute to the electrochemical signal picked up by the pH-electrode. In these conditions, the correlation between the electrochemical potential (ECP) and the pH is not linear anymore, and as such, standard calibration of the electrode is not valid.

To remediate this, the pH electrode was calibrated with a series of NaOH and/or KOH concentrations, using the protocol and readily available Excel file published by (Traynor et al., 2020). As such, a more accurate pH could be calculated based on the measured ECP of each solution and this calibration.

### 5.2.3 ORP/Eh

The Oxidation-Reduction Potential (ORP) of the synthetic pore water was measured with an ORP electrode (Ag/Pt). Because absolute potentials are difficult to measure directly, the ORP is defined relative to a reference electrode, in this case an Argenthal Ag/AgCl electrode. To allow comparison with other redox measurements, ORP readings were converted to the potential of the Standard Hydrogen Electrode (SHE) to obtain the Eh (Equation 4):

$$E0(25^{\circ}C) = Et - 0.198 * (T - 25) + \sqrt{a - b * T}$$

Equation 4: Conversion of ORP to Eh

with a and b constants determined by the electrode and its reference electrolyte, and T the temperature at the time of the ORP reading. For the Argenthal Ag/AgCl reference electrode with a 3M KCl electrolyte, values for a and b are 50301 and 297 respectively. The electrode was not calibrated, but its accuracy was checked before and after each reading with a commercially available standard of 225 mV. Deviations up to 60 mV were allowed; if deviations exceeded 60 mV, the electrode was cleaned with commercial toothpaste and thoroughly rinsed with ultrapure water, followed by a new reading of the standard, until satisfactory.

As mentioned in Section 2.1.2.3, Eh of the CILVA pore water could not be measured, so it was estimated at -617 mV, based on the  $SO_4^{2-}/S^{2-}$  redox couple. The Eh measurements of the synthetic pore water however, were slightly higher, ranging from -320 mV to -280 mV. Although higher than estimated, these values are still considered to represent a 'reducing' environment in which Pu would for the most part be available as Pu (IV) (see Figure 1).

### 5.2.4 Equilibration with cementitious phase

When brought into contact with each other, the cementitious phase and the SCPW might not be in complete equilibrium, as the experimental matrix accounts for a range of ion concentrations in the background solution. It was therefore decided to let the cementitious phase equilibrate with the synthetic pore water for a period of two weeks prior to the start of the sorption experiments, at the targeted S/L ratio (Tits and Wieland, 2018). The samples were left to equilibrate on a shaker inside a glovebox with  $N_2$  atmosphere. Every two days, the samples were vortexed to keep the solid phase from developing pellets or adhering to the test vials.

## 5.3 Addition of Pu and ISA

After a first equilibration period of 2 weeks, Pu and ISA were added to the 11 suspensions at the same time. Pu was added as a spike in 1 M  $HNO_3$ , while ISA was added as a solution in ultrapure water. To correct for the addition of  $HNO_3$ , a corresponding volume of 5 M NaOH was added (1/5 of the  $HNO_3$  volume). pH was not measured after addition of Pu and ISA, to avoid loss of Pu to the pH electrode. Instead, pH was measured after the prescribed equilibration time (7, 14 or 21 days), in the leftover solution after sampling (see protocol in Wouters et al. (2022a)).

After addition of Pu and ISA, the samples were returned to the shaker and left to equilibrate for 1, 2 or 3 weeks, according to the experimental plan.

### 5.3.1 $^{238}Pu$

The 3.7 MBq  $^{238}Pu$  source was purchased from Eckert and Ziegler Nuclitec GmbH. The source was reported to yield >99.9%  $\alpha$ -activity and had  $^{241}Am$  removed prior to shipping (<0.0005%  $^{241}Am$ ). Upon arrival, a subsample was diluted in 1 M  $HNO_3$  for further use. The activity and purity of the subsample was confirmed by alpha spectrometry and its concentration by ICP-MS (Inductively Coupled Plasma – Mass Spectrometry).

### 5.3.2 Na- $\alpha$ -ISA

Although two isomers of ISA are reported to be produced upon cellulose degradation, the focus of most studies is on  $\alpha$ -ISA rather than  $\beta$ -ISA, because the latter seems to have a lower impact on RN sorption (Van Loon and Glaus, 1998; Van Loon et al., 1999).  $\alpha$ -ISA is added as a Na-salt, as this is the most soluble and stable form of ISA. The synthesis of pure Na- $\alpha$ -ISA is based on the protocol provided by (Van Loon and Glaus, 1998) and is described in detail in Wouters et al. (2022b).

## 5.4 Sampling

In order to determine the concentration of Pu in solution, it should be adequately separated from the RN sorbed to the cementitious phase. Separation of liquid and solid phase was achieved by centrifugation (Section 5.4.1). After sampling of the liquid phase (inside the glovebox, see Wouters et al. (2022a)), an additional effort was needed to account for the Pu sorbed to the plastic recipient in which the experiments took place. This was done by HCl desorption of Pu (Section 5.4.2). Both SCPW and HCl sampling was performed in duplicate.

### 5.4.1 Centrifugation

In Wouters et al. (2022a), a detailed calculation of the optimal centrifugation conditions for a suspension of powdered cementitious sorbents, is provided. As a reference, the particle density of C-S-H particles was used ( $2.6 \text{ g/cm}^3$ ) (Pellenq, 2009), and a C-S-H nanoparticle size of 40 nm (Wang et al., 2019). For these conditions, centrifugation for 30 minutes at  $21000 \text{ *g}$  was selected as sufficient to spin down the crushed CILVA mortar.

It should be noted that at this centrifugation speed and time, (hypothetical) Pu-colloids larger than 18 nm diameter would be separated from the liquid phase as well, given a particle density of  $9 \text{ g/cm}^3$  (Rundberg, 1987). Intrinsic spherical Pu-colloids of a reported diameter of 2 nm (Micheau, 2020) should however still be in solution after the centrifugation effort. Because there is no evidence of large Pu-colloids ( $> 18 \text{ nm}$ ) in the given experimental conditions, the centrifugation effort is assumed to only target Pu sorbed to the cementitious phase.

### 5.4.2 HCl desorption

When working with high pH systems, sorption of the RN to the test tubes can be considerable. Indeed, up to 75% of the Pu added to the matrix was found to sorb on the test tubes, but with varying percentages for different test conditions (e.g. different S/L ratio of the cementitious sorbent, different pH ...). Therefore, using a blanc without CILVA as a reference for Pu loss to the plastic vessel, was deemed inaccurate. Instead, Pu was recovered from the test tubes after centrifugation and sampling (Wouters et al., 2022a).

By adding HCl (0.1M) after removing the solution and CILVA matrix, and allowing to desorb for 24h, all Pu could be accounted for (with an efficiency of 96.7%, according to a first test without cementitious sorbent), hence allowing a calculation of the Pu available for sorption to the cementitious matrix for each of the 11 sorption experiments.

This way, it can be calculated how much of the Pu was available for sorption at the equilibrium, and as such, how much was sorbed to the CILVA matrix. The distribution coefficient can be calculated as:

$$K_d = \frac{A_{init} - A_{acid} - A_{eq}}{A_{eq}} \cdot \frac{V}{m}$$

*Equation 5: Calculation of  $K_d$  using low pH desorption of RN from tube walls*

with  $A_{acid}$  being the amount of RN (expressed as activity in Bq) desorbed from the test tube with a low pH (acid) solution.

## 5.5 Liquid Scintillation Counting

Activity of Pu in the samples (both SCPW solution after centrifugation and HCl desorption) was determined by liquid scintillation counting. A volume of 5 mL (SCPW solution) or 2 mL (HCl solution) was mixed with respectively 15 or 18 mL of dedicated LSC cocktail (Optiphase HiSafe 3, Perkin Elmer). Pu activity was detected in the 200 – 700 keV window on a TRI-CARB 2100TR LSC counter (Packard), available at the RDD group, with a maximum time of 90 minutes per sample and a  $2\sigma$  of 0.5%. The efficiency of  $^{238}\text{Pu}$  detection in both background solutions was determined at 95-96%.

## 6 Experimental results

The complete overview of the experimental results, including all unprocessed LSC data and their corrections for volumes, counting efficiencies and averaging of duplicates, can be consulted in the embedded Excel file below, and on the dedicated network locations:

- ONDRAF/NIRAS: <https://nirond-km.be/gm/document-1.9.420813>;
- SCK CEN: <https://ecm.sckcen.be/OTCS/llisapi.dll?func=ll&objaction=overview&objid=44002750>;



D4 (part) \_ Results Kd  
Pu-CILVA DoE screenii

In the end, the response needed to evaluate the screening effort, are the  $K_d$  values corresponding to the 11 experiments of the experimental plan outlined in Table 8. These 11  $K_d$  values are presented in Table 9. Results of the triplicate experiments are presented in bold.

Table 9:  $K_d$  values for the 11 experiments of the PB design

Experiment Number	$K_d$
1	2.14E+03
2	2.30E+04
3	4.00E+03
4	<b>3.28E+03</b>
5	2.48E+04
6	3.44E+03
7	2.97E+02
8	<b>4.06E+03</b>
9	3.85E+04
10	2.49E+04
11	<b>5.07E+03</b>

### 6.1 Data processing techniques

The response was analysed with the NEMRODW software (Mathieu et al., 2007). The responses are analysed with and without a log-transformation. The model coefficients of the linear model are estimated by least squares regression. The analyses start by an ANOVA. The power of this experimental design is recalled in combination with ANOVA and a significance level of 5%. It was at least 80% for effect sizes not lower than 3 and increased to 95% for an effect size of 4. Consequently, the ANOVA-test is complemented by an effect-analysis by making use of a Half-Normal or a Normal-plot, and a Bayesian analysis.

The half-normal probability plot, proposed by Daniel (1959), is based on the fact that if all estimated effects were noise, they would have a normal distribution and, when plotted on a normal cumulative plot, would fall on a straight line. Hence, effects significantly different from zero should fall outside of the normal line. If more than two effects seem to be significant, we referred to the alias structure to identify susceptible interactions.

The Bayesian analysis used here was proposed by Box and Meyer (1986). It involves computing a posterior probability that an effect is active. The prior information is summarized in two parameters,  $\alpha$  (the proportion of factors postulated as active) and  $k$  (the inflation in the standard deviation produced by an active effect). The calculations were performed for  $\alpha$  and  $k$  ranging between 0.1-0.4 and 5-15 respectively. The result of these calculations are typically presented as a bar graph showing the posterior probabilities. Factors for which the a posterior probability is more than 50% are regarded as active.

## 6.2 Active factors

Since the above procedure allows to assess for each factor the activity through three statistical instruments, a distinction can be made between *i*) factors that are active according to both ANOVA and all other instruments, *ii*) factors that are active according to ANOVA but not to other instruments or *iii*) factors that are not active according to ANOVA but are according to other instruments.

In the present case, only the concentration of  $\text{Ca}^{2+}$  revealed to be an active factor towards the sorption of Pu to the CILVA mortar. When the response was expressed in  $\log(\text{L/kg})$ , *i.e.*  $\log(K_d)$ , the p-value for ANOVA was below 1% while this activity was also observed by the other instruments. The effect size of this factor on the response is question is estimated at a Cohen's d-value of 5.7 (Cohen, 1988). When expressed as  $K_d$ , *i.e.* in L/kg (no transformation) however, the p-value of ANOVA was greater than 1%, but lower than 5%, while the other instruments revealed also the activity of the concentration of  $\text{Ca}^{2+}$ . For the other factors, the ANOVA did not result in a p-value below 5% nor did the other instruments indicate an activity. For this response, the effect size of that factor is estimated at a Cohen's d-value of 2.7 (Cohen, 1988).

### 6.2.1 Analysis of Pu-sorption without transformation

In Figure 2, the ANOVA-table is given at the top. Only the third coefficient  $b_3$ , associated with the concentration of  $[\text{Ca}^{2+}]$ , differs significantly from zero. A similar conclusion can be drawn based on the Bayesian-analysis (bottom left of Figure 2) and the Half-Normal plot (bottom right of Figure 2).

Since the best estimate for the coefficient of  $b_3$  is negative, the sorption of Pu decreases when the concentration of calcium changes from its lower to its upper value.

For this response the standard deviation of the experimental error is estimated to be 9599.5, and therefore the effect size of this factor, when being changed from the coded level -1 to +1 is estimated at a Cohen's d-value of 2.7 (Cohen, 1988).

Nom	Coefficient	F.Inflation	Ecart-Type	t.exp.	Signif. %
b0	12336.6		2894.4	4.26	2.37 *
b1	2284.6	1.00	3393.9	0.67	54.9
b2	2354.6	1.00	3393.9	0.69	53.8
b3	-12852.1	1.00	3393.9	-3.79	3.23 *
b4	2015.4	1.00	3393.9	0.59	59.4
b5	-2452.1	1.00	3393.9	-0.72	52.2
b6	-1797.9	1.00	3393.9	-0.53	63.3
b7	1045.4	1.00	3393.9	0.31	77.8

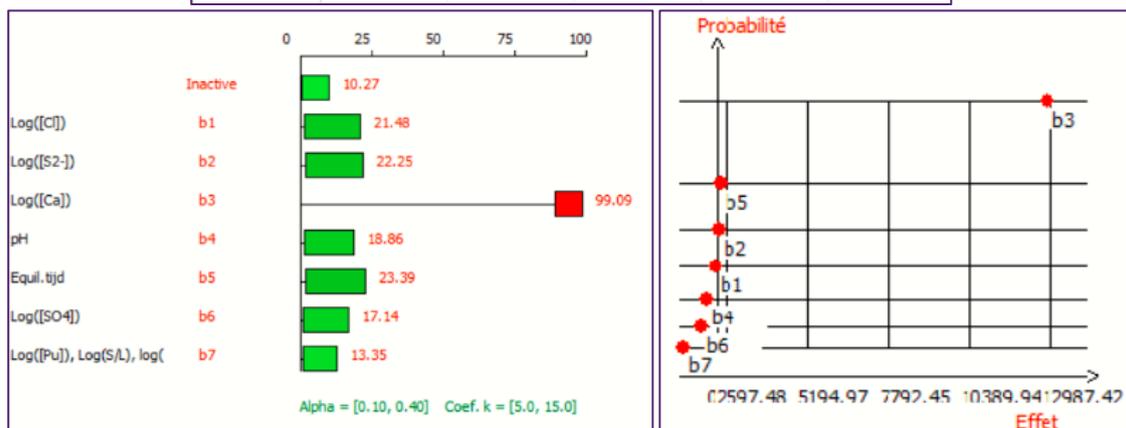


Figure 2: Analysis of Pu-sorption without transformation

### 6.2.2 Analysis of Pu-sorption with a log transformation

In Figure 3, the ANOVA-table is given at the top. The third coefficient  $b_3$ , associated with  $[Ca^{2+}]$ , differs significantly from zero. As in Section 6.2.1., this is confirmed by the other instruments (bottom left and right of Figure 3).

Again, since the best estimate for the coefficient of  $b_3$  is negative, the sorption of plutonium decreases when the concentration of calcium changes from its lowest to its upper value.

For this transformed response, the standard deviation of the experimental error is estimated to be 0.211, and hence the effect size of this factor, when being changed from the coded level-1 to +1 is estimated at a Cohen's d-value of 5.7 (Cohen, 1988).

Nom	Coefficient	F.Inflation	Ecart-Type	t.exp.	Signif. %
b0	3.782		0.063	59.60	< 0.01 ***
b1	0.124	1.00	0.074	1.67	19.3
b2	0.189	1.00	0.074	2.54	8.4
b3	-0.595	1.00	0.074	-8.00	0.408 **
b4	-0.064	1.00	0.074	-0.86	45.5
b5	-0.146	1.00	0.074	-1.96	14.5
b6	0.086	1.00	0.074	1.15	33.2
b7	-0.145	1.00	0.074	-1.95	14.6

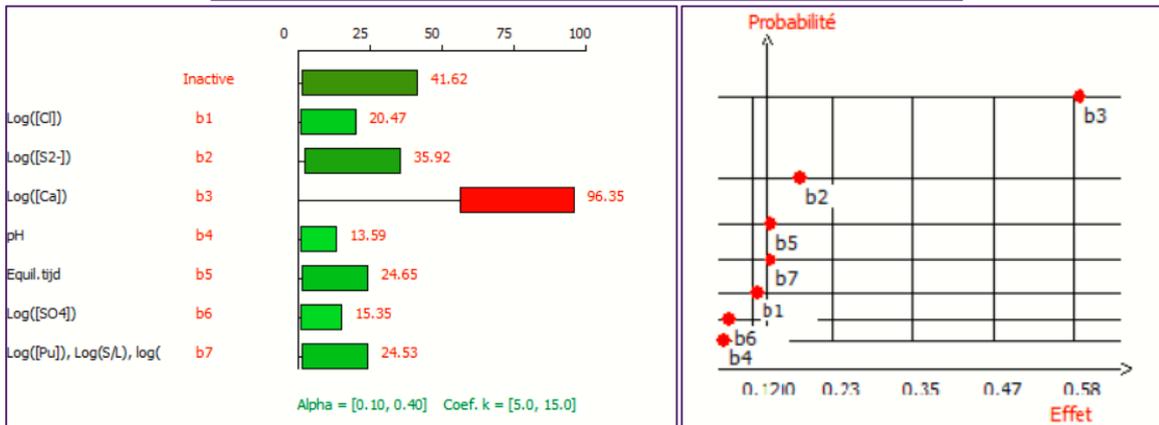


Figure 3: Analysis of Pu-sorption with log transformation

## 7 Conclusion

The aim of this first part of the experimental program in the frame of cAt disposability, was to define which factors would affect sorption of Pu to the CILVA immobilization matrix, within the investigated ranges. The different factors are related to the CILVA pore water composition on one hand (concentrations of  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{S}^{2-}$ ,  $\text{K}^+$  and  $\text{OH}^-$  (pH)), and to characteristics for batch sorption experiments on the other hand ([Pu], S/L and equilibration time).

From these 9 factors, only  $[\text{Ca}^{2+}]$  was found to be active, in the ranges considered, and as such affecting Pu-sorption. In a next step, the extent of the impact of the  $[\text{Ca}^{2+}]$ , together with the effect of [ISA], will be subject of a more elaborate experimental set-up.

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