

CHAPTER 8. Annex – Leaching experiments

It must be taken into account that, in the present work, leaching (long-term) experiments have been performed in parallel to sorption experiments, as additional work to the thesis, to start assessing the release mechanisms from cement hydrates. It is important to know and understand how cementitious materials may affect the environment once exposed to such conditions. However, as cited later, the results have not been the expected ones.

8.1. Introduction

Leaching is the process by which some components of a solid material are totally or partially dissolved in a liquid media (normally water) when entering in contact [Van der Sloot et al, 2003]. Consequently, leaching characterisation is the most relevant way to evaluate the environmental properties of construction materials which are in direct or indirect contact with soil and ground water [Engelsen et al, 2010].

Therefore, leaching tests are of utmost importance to [De Windt et al, 2006]:

- Better characterize the cementitious waste long-term evolution,
- Understanding of leaching mechanisms to extrapolate the laboratory results to engineered systems (decommissioning, disposal) or waste/environment interactions (disposal, recycling).

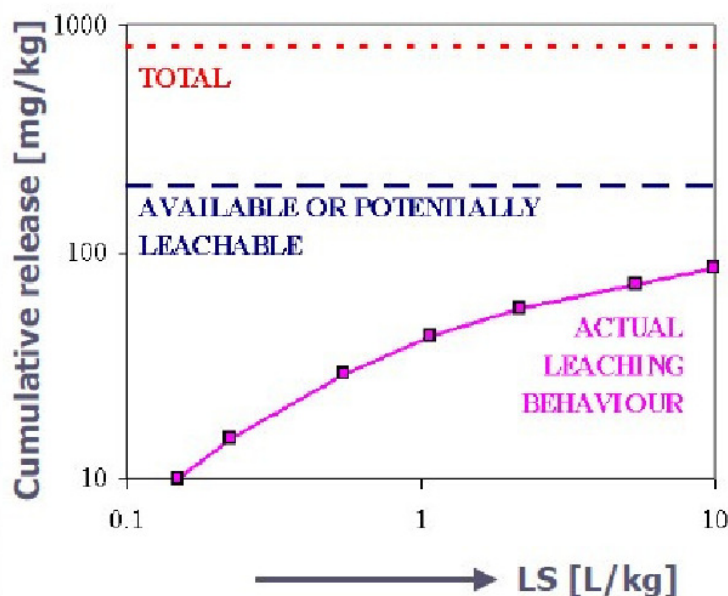


Figure 8.1. General release representation including usual terms [Van der Sloot et al, 2003].

As already demonstrated, cement-based materials are used for the S/S of toxic metal waste because they present good physical and chemical containment properties. As water is the main environmental pollution vector, their short and long-term behaviours in the scope of disposal and recycling

scenarios are evaluated by extensive leaching tests. On the one hand, *batch leaching experiments*, performed on crushed materials, are simple tests useful for determining the intrinsic properties of the waste with respect to one or several controlled parameters. Batch tests are widely used for sorption, partitioning and leaching experiments between solid and aqueous phases. On the other, *dynamic leaching tests*, made on monolithic samples, are more specifically used to determine the long-term waste evolution and pollutant release under accelerated alteration processes. Coupling between diffusion, dissolution-precipitation and sorption processes has been clearly identified during such leaching of cement-based waste [De Windt and Badreddine, 2007].

Assessing the environmental quality of cement and cementitious products is usually based on leaching characteristics, i.e. the release of constituents such as trace elements or organic compounds when the materials are in contact with groundwater or soil. However, the relationship between release of substances like trace elements or organic components under specific laboratory test conditions and actual field situations may lead to some contradictions.

The trace element contents of commercial cements may vary broadly as a consequence of the use of various natural fuels and raw materials. Increasing concern has been raised with the use of alternative (waste derived) fuels and raw materials which may both increase or decrease the trace element content in cement.

These studies have also shown that the release of constituents (trace elements) from cement based products in contact with water during service life is mainly diffusion-controlled and affected by various physical and chemical retention mechanisms. Mechanisms holding the key in defining environmentally sound trace element levels in clinker and cement are:

- *Physical retention* of the potentially leachable fraction,
- *Chemical retention* of elements fixed in the hardened cement paste matrix (solubility limitation, sorption reactions, solid solutions), and
- *Changes in conditions* controlling trace element release such as the decrease of the pH value due to carbonation.

There are significant differences in the generic leaching characteristics of different trace elements. Confirming the results from previous studies, three different categories of elements can be identified with regard to their generic leaching behaviour [Van der Sloot et al, 2008]:

- I. *Regular* metals, like Pb, Cu, Cd, Ni, and Zn, showing a minimum leachability in the pH 8-11.
- II. Elements occurring as *oxyanions*, such as Cr, Mo, As, Sb, and V (i.e. chromate CrO_4^- , arsenate AsO_4^{3-} or molybdate MoO_4^-) featuring a maximum leachability at neutral to slightly alkaline pH.
- III. *Soluble salts* showing no relationship with pH at all. Only a few constituents behave like this in cement based systems.

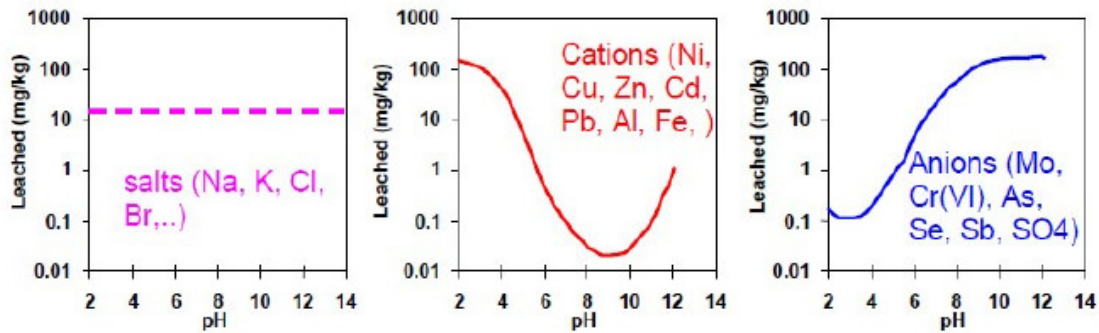


Figure 8.2. Generic leaching behaviour of regular metals, oxyanions and soluble salts (obtained from pH dependence tests on different crushed cement mortars) [Van der Sloot et al, 2008].

In highly alkaline cementitious systems, meaning $\text{pH} \approx 12-13$, CSH has the ability to bind oxyanions and metal cations (as has been demonstrated in the present work), although previous studies state that specific binding mechanisms are not clear [Engelsen et al, 2010]. Consequently, in order to analyse if such systems can be permanent reservoirs of heavy metals like vanadium, leaching experiments must be carried out to give proof of the environmental impact that could be caused. Observing the figure above, anions (like in the case of HVO_4^{2-}) achieve its maximum leaching values at $\text{pH} \approx 12-13$, which is in fact the pH in cementitious systems. Due to the potential risk to the environment, such experiments with oxyanions must be taken into account.

8.2. Materials and methods for *Batch* leaching experiments

Materials:

- Powdered hydrated C_3S samples (section 4.1).
- Deionised water Milli-Q quality ($18,2 \text{ M}\Omega \cdot \text{cm}$).

Equipments:

- Micropipette; Nahita, model ECO-66610310. Max. capacity 1000 μL . Accuracy $\pm 1.0\%$. Precision $< 0.3\%$.
- Precision balance; A&D Instrument Ltd, model GX400EC. Resolution 0.001g. Max. capacity 410g.
- pH-meter; Crison, model BASIC 20+. Resolution 0.01.
- Spectrometer ICP-MS; Perkin Elmer Elan – 6000.



Figure 8.3. Plastic screw bottles where leaching tests are carried out.

Method:

The experiment is done in duplicate in order to obtain a more reliable database and to detect possible errors. For each sample, the steps to consider are the following:

- I. Pouring 10 mg of powdered hydrated C_3S at 28 days in a plastic screw bottle of 600 ml.
- II. Adding 200 ml in weight of deionised water ($L/S=20$).
- III. Shaking the mix manually for 10 min.
- IV. Periodically, extracting 2 ml aliquots and pouring them in a test tube clearly marked. *Note:* It is essential and of utmost importance an organised labelling for the substrates to be used and the containers to be analysed. Moreover, writing the day, time and mass extracted.
- V. Measuring and writing down the pH value for each sample taken by aliquot.
- VI. After each extraction, adding 2 ml of Milli-Q water in the plastic bottles to maintain $L/S=20$.
- VII. Shaking manually for 10 min.
- VIII. Diluting the 2 ml samples by adding 8 ml in weight of Milli-Q water to facilitate the analysis with ICP-MS and acidifying by adding HNO_3 (~2 drops with a dropper).
- IX. Analyzing Ca and Si concentrations in each test tube by ICP-MS.

8.3. Modification on leaching experiments schedule

The schedule for leaching tests planned before starting the tests is as follows:

1st – Performing leaching experiments with powdered and hydrated C_3S samples (CSH^a , $[V]=0$ ppm) in water.

2nd – Performing leaching experiments with powdered and hydrated C_3S samples doped with vanadium in water.

^a: Hydrated C_3S samples are also referred to in the following as CSH for being its major compound.

To begin, batch leaching experiments have been performed in duplicate with CSH in order to assess elements release, mainly Ca^{2+} and Si^{4+} , from the powdered and hydrated C_3S samples. The first idea was, once known the release mechanisms and dynamic of CSH in water without any heavy metal content, performing the same experiment but with a vanadium solution in order to see how the presence of vanadium alters the leaching results and if it is retained in cementitious materials or not. For doing so, samples of hydrated C_3S doped with vanadium would have been synthesised. Anyway, the results obtained from batch tests with non doped samples are not the expected ones in any of the two samples, as discussed in the following section. For this reason, the experiment with doped samples has not been started.

8.4. Results and discussion

Obtained results are presented graphically in order to represent the following parameters: Ca/Si ratio evolution (in the solution), Ca^{2+} concentration evolutions and, finally, Si^{4+} concentration evolution. In

the three cases, X-axis values are represented in minutes up to ~130000 min, equivalent to ~90 days or ~3 months.

It must be noticed that the three parameters are indicated in molar concentrations, as all the results presented in this work in order to establish the comparisons, if necessary.

What would be expected is:

- Due to first portlandite dissolution, calcium ions should be released in the water, increasing calcium ions concentration in the media. Therefore, Ca/Si ratio would be higher at the beginning as silicon ions wouldn't still be released from CSH.
- Later on, CSH would start to dissolve releasing calcium ions in water but also silicon ions. Consequently, the Ca/Si ratio would be expected to decrease for having a greater denominator value.

However, results obtained with batch leaching tests are not the expected ones in any of the samples. Equilibrium state is not achieved and there are significant variations in Ca/Si ratio values, showing no specific trend over the time, although both series follow quite a similar trend. In addition, regarding calcium concentration and silicon concentration independently, no remarkable conclusions can be stated neither.

From these results, it seems clearly necessary to improve the design of the leaching experiments to evaluate such materials, i.e. hydrated C_3S samples in powder. From this point of view, other authors [Trapote-Barreira et al, 2010] have obtained good results performing *flow-through cell* experiments. In this case, liquid phase (water) would be continuously renewed, ensuring that the solution doesn't get saturated at any moment and the filtered liquid would also allow a continuous recollection data by analysing it.

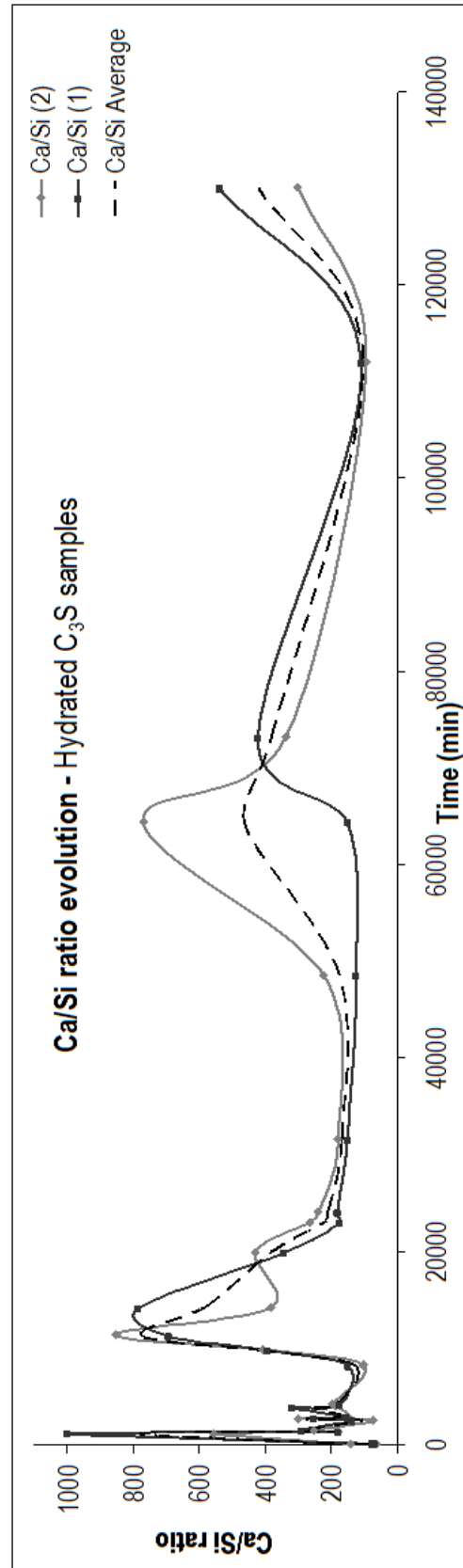
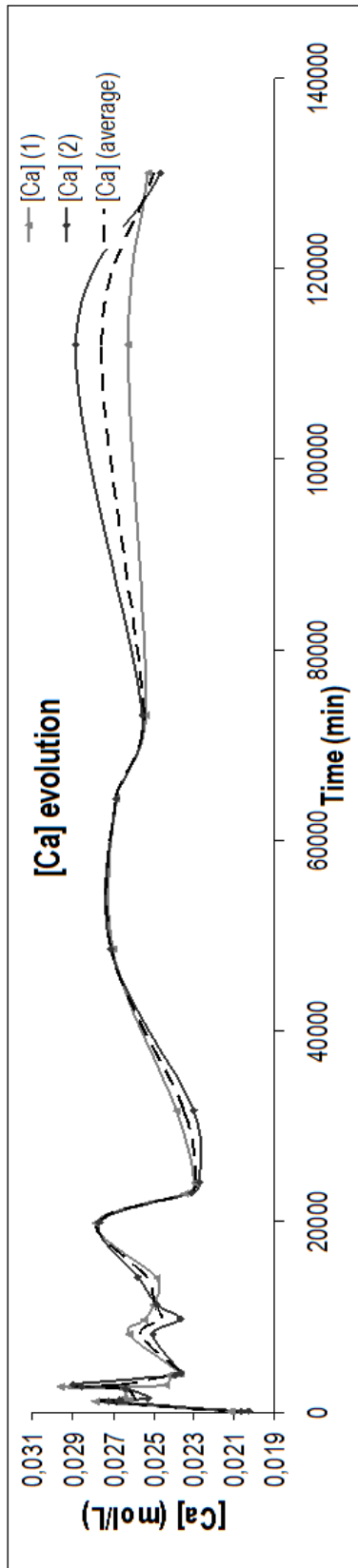
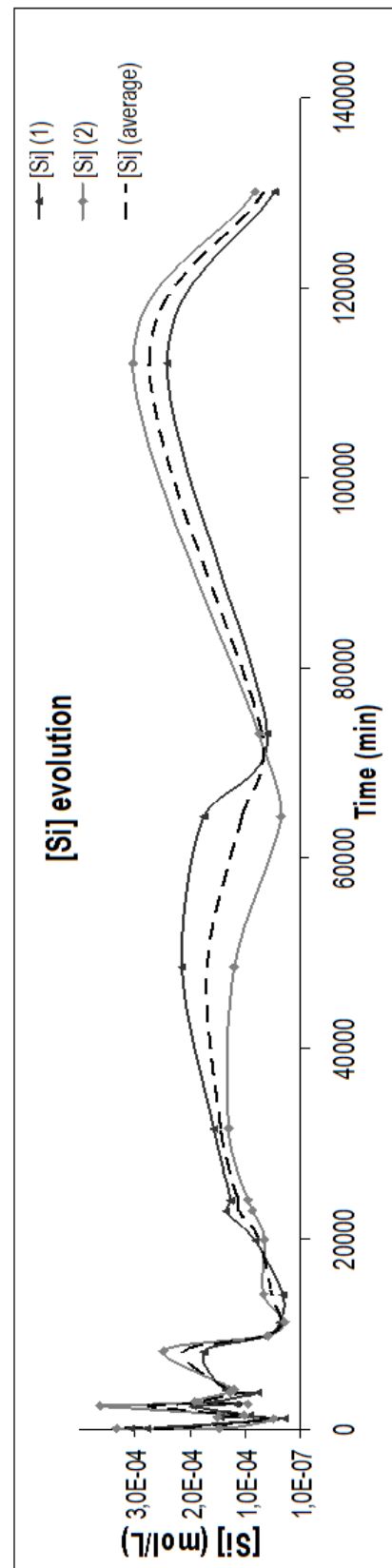


Figure 8.4. Ca/Si molar ratio evolution in time for the leaching experiments (in duplicate)

Figure 8.5. Ca^{2+} concentration evolution in timeFigure 8.6. Si^{4+} concentration evolution in time