

CHAPTER 4. Materials and methods

4.1. Hydrated C_3S samples manufacture

Materials:

- C_3S provided by M.R. Pro Mineral Research Processing.
- Deionised water Milli-Q quality ($18,2 M\Omega \cdot cm$).
- Isopropyl alcohol.

Equipments:

- Mixer; IKA RW11 basic with R1002 screw-type stirrer.
- Precision balance; A&D Instrument Ltd, model GX400EC. Resolution 0.001g. Max. capacity 410g.
- Agate mortar.



Figure 4.1. Mixer used for samples preparation.

Methods:

a) C_3S pastes preparation ($W/C=0.42$)

- I. Placing the beaker on the balance, humming it and pouring 6.3 g of Milli-Q water.
- II. Pouring 15 g of C_3S in another beaker to obtain a 0.42 water/cement relation.
- III. Placing the baker that contains C_3S under the stirrer.
- IV. Adding the water gradually while mixing for 15 min.
- V. Pouring the resulting mass in cylindrical-shaped casts (reused from the pharmaceutical industry).
- VI. Beginning the curing process placing the samples in humidity room (at small scale) at RH 95%, and a temperature of $24 \pm 0.5^\circ C$. For this purpose, using some plastic plaques with rounded-filters periodically humidified with Milli-Q water. To ensure the inside humidity, covering the plaques with plastic film.
- VII. Turning the samples out from the cast at 24 h (hardened enough to do it) and covering the plaques with plastic film one more time.
- VIII. Considered hydration times: 7, 14, 28 and 56 days.

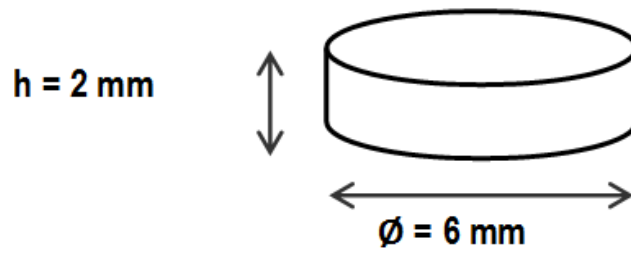


Figure 4.2. Sizes of hydrated C_3S samples.



Figure 4.3. Hydrated C_3S samples placed in the humidity room.

b) Stopping hydration

The procedure followed to stop samples hydration is performed in accordance with conclusions reached in previous related works [Correa, 2010], consisting in solvent exchange method application:

- I. Placing 3-4 specimens in a little screw plastic container.
- II. Filling it with isopropyl alcohol, completely covering the specimens.
- III. Covering the pots with plastic film.
- IV. Removing the samples after 72 h, drying them in the oven at 60°C temperature for 15 min.

c) Powdering samples

Some experimental tests require powdered samples.

- I. Powdering some samples manually with the aid of an Agate mortar until reaching very fine powder.
- II. Following an order, placing the samples distinguishing by different hydration times and, if applicable, manufacture date.

4.2. Analysis and characterization methods

4.2.1. Thermogravimetric Analysis (TGA)

Materials:

- Powdered hydrated C_3S samples (section 4.1).

Equipments:

- Thermogravimetric analyser (TGA); TA Instruments, model TGA Q50 v.6.5 Build 196.

Method:

Each thermogravimetric test is carried out by the same procedure as the software support for the instrument allows the introduction and permanent configuration of required routines.

- I. Putting the amount of sample to be analyzed on a platinum support provided, which is part of the instrument.
- II. Placing the support in the analyzer furnace.
- III. Waiting for the atmospheric nitrogen that surrounds the sample to be stable. Nitrogen prevents the sample to react with other elements while temperature rises.
- IV. Heating up to 40°C and maintaining this temperature constantly for 1 min.
- V. Starting temperature and masses record, while heating from 40 to 1000°C at a constant rate of $20^{\circ}\text{C}/\text{min}$.
- VI. Once achieving 1000°C , the instrument cools down, and also stops recording data, automatically.
- VII. Once cooled ($\sim 50^{\circ}\text{C}$), removing the sample from the furnace.
- VIII. Remaining dust is not profitable.

Calculations and justification:

One of the main objectives to achieve through TGA analysis is the confirmation of the C_3S pastes manufacturing process reproducibility in order to be sure that samples are produced in the same way. If so, it is possible to state that the samples (even if manufactured in different campaigns) are completely identical. Through the interpretation of TGA results, it's possible to determine the hydration degree for each considered hydration time (when C_3S hydration is stopped: 7, 14, 28 and 56 days).

According to the stoichiometry of the reaction that takes place each thermal zone (detailed in section 3.3.3), as shown in Figure 4.4, the present amount of portlandite can be calculated.

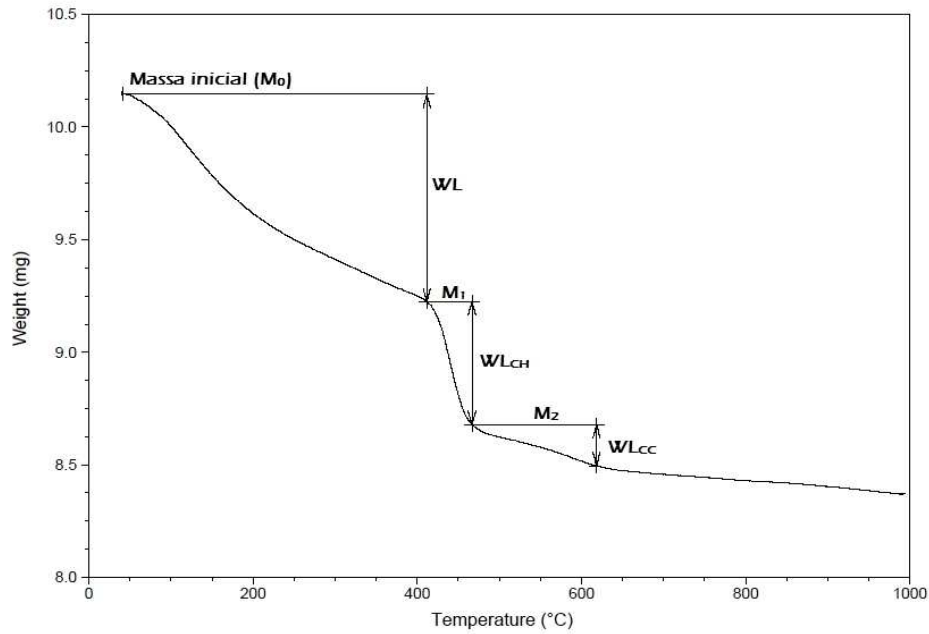
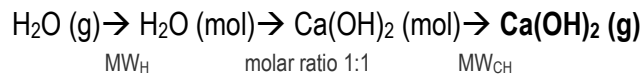
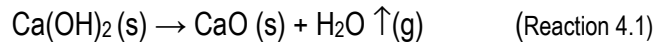


Figure 4.4. Characteristic graphic obtained from TGA measurements.

Following steps must be considered to know the total amount of portlandite in the sample [Chen et al, 2008]:

I. Calculation of portlandite amount decomposed in ~400°C → ~500°C range:



$$\frac{\text{WL}_{\text{CH}} \cdot \frac{\text{MW}_{\text{CH}}}{\text{MW}_{\text{H}}}}{\text{M}_0} = \text{CH} (\%) \quad (\text{Equation 4.1})$$

Where:

WL_{CH} is weight loss (mg) due to water evaporation when occurring Reaction 4.1

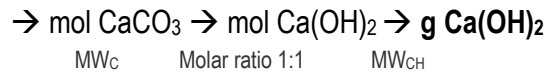
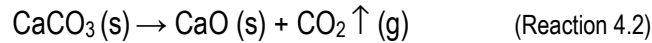
MW_H is water molecular weight (18 g/mol).

MW_{CH} is portlandite molecular weight (74.08 g/mol).

M₀ is initial mass (mg) of the sample.

CH (%) is percentage of portlandite decomposed in ~400°C → ~500°C thermal zone.

II. Calculation of calcium carbonate amount decomposed $\sim 500^{\circ}\text{C} \rightarrow \sim 750^{\circ}\text{C}$ range:



$$\frac{\text{WL}_{\text{CC}} \cdot \frac{\text{MW}_{\text{CC}}}{\text{MW}_{\text{C}}}}{M_0} = \text{CC} (\%) \quad (\text{Equation 4.2})$$

Where:

WL_{CC} is weight loss (mg) due to carbon dioxide dissipation when occurring Reaction 4.2.

MW_{C} is carbon dioxide molecular weight (44 g/mol).

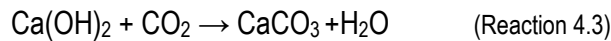
MW_{CC} is calcium carbonate molecular weight (100.089 g/mol).

M_0 is initial mass (mg) of the sample.

CC (%) is calcium carbonate percentage decomposed in $\sim 500^{\circ}\text{C} \rightarrow \sim 750^{\circ}\text{C}$ thermal zone.

III. Calculation of portlandite amount becoming calcium carbonate:

Calcium carbonate appears in the sample when portlandite undergoes through a carbonation process because of the atmospheric CO_2 . Molar ratio between portlandite and calcium carbonate is 1:1 according to the following expression [Kocaba, 2009]:



Accordingly, it is possible to calculate the amount of portlandite that becomes calcium carbonate due to carbonation process.

$$\text{CC} (\%) \cdot \frac{\text{MW}_{\text{CH}}}{\text{MW}_{\text{CC}}} = \text{CH}' (\%) \quad (\text{Equation 4.3})$$

Where:

MW_{CH} is portlandite molecular weight (74.08 g/mol).

MW_{CC} is calcium carbonate molecular weight (100.089 g/mol).

CC (%) is calcium carbonate percentage decomposed in the $\sim 500^{\circ}\text{C} \rightarrow \sim 750^{\circ}\text{C}$ thermal zone.

CH' (%) is portlandite carbonated in the sample, becoming calcium carbonate, decomposed in the $\sim 500^{\circ}\text{C} \rightarrow \sim 750^{\circ}\text{C}$ thermal zone

IV. Calculation of total portlandite amount formed in the sample:

$$CH_T (\%) = CH (\%) + CH' (\%) \quad (\text{Equation 4.4})$$

Where:

CH_T (%) is total amount of portlandite in the C_3S hydrated sample.

CH (%) is portlandite in the sample decomposed in the $\sim 400^\circ C \rightarrow \sim 500^\circ C$ thermal zone.

CH' (%) is portlandite carbonated in the sample, becoming calcium carbonate, decomposed in $\sim 500^\circ C \rightarrow \sim 750^\circ C$ thermal zone.

4.2.2. X-Ray Diffraction (XRD)

Materials:

- Powdered hydrated C_3S samples (section 4.1).

Equipments:

- Diffractometer (XRD); Bruker; model D83 with Cu anode.

Method:

The X-ray diffraction was carried out by CRnE (UPC) technicians, in a range values for 2θ of $5-50^\circ$. CrystalDiffractTM and Pananalytical X'Pert High Score softwares helped with results interpretation.

4.2.3. Scanning Electron Microscopy (SEM)

Materials:

- Powdered hydrated C_3S samples (section 4.1).
- Epoxy resin; Buehler Epothin.
- Epoxy resin hardener; Epothin Buehler.
- Release agent; Buehler.
- Sandpaper; SiC Grinding paper for metallography wet or dry, Buehler ($\varnothing 305\text{mm}$) P240 ($58.5\text{ }\mu\text{m}$), P600 ($25.8\text{ }\mu\text{m}$) and P1200 ($15.3\text{ }\mu\text{m}$).
- Diamond suspension; Buehl MetaDi Monocrystalline Diamond Suspension 9, 3 and $1\text{ }\mu\text{m}$.

Equipments:

- Vacuum system; Buehler, model Cast'n'Vac 20-3510-250.
- Polishing machine; Buehler, model PHOENIX 4000.
- Manual turbo evaporator; EMITECH K950X.
- Scanning Electron Microscopy; Zeiss, model Neon 40 with a column 4 pA-20 nA $0.1-30\text{ kV}$. Resolution 1.1 nm . EDS detector for elemental detection.

Method:**a) Fixing the sample to the resin support**

For SEM analysis, samples must be impregnated with an epoxy resin in order to be holding on an easy to handle support.

- In a cup, preparing epoxy mix in a ratio of 3.9/10 g (hardener/resin) for 2-4 min
- Placing a hydrated C_3S sample (the observation plane at the bottom) in the middle of a cylindrical mold from the vacuum system, that will give shape to the resin support, and pouring the solution carefully.
- The epoxy mix is fed from its cup outside the vacuum chamber to the top of the specimen via a plastic tube. After some minutes, air is gradually let into the vacuum chamber to push the epoxy further.
- Leaving the sample at atmospheric pressure and room temperature for 24 h to cure.

b) Grinding and polishing

In this work, the objective is to obtain SEM images from a flat sample surface. Such diffraction is named *X-ray backscattering spectroscopy*, which has the peculiarity that the incident beam rebounds in the same direction it comes. So, samples should be accurately grinded and polished in order to remove surplus epoxy for exposing a planar hydrated C_3S surface.

In the following Table 4.1, three grinding stages of different grit size followed by three different grades of diamond polishing are listed.

Table 4.1. Materials used for several grinding and polishing stages.

	Material	Grit size (μm)	Time (min)	Strength (N)	Frequency (rpm)
Grinding^{a,b}	Grinding paper P240	58.5	10	~10	100
	Grinding paper P600	25.8	5	~10	100
	Grinding paper P1200	15.3	5	~10	100
Polishing^a	Diamond suspension	9	10	~8	100
	Diamond suspension	3	10	~8	100
	Diamond suspension	1	10	~8	100

^a: Using compressed air between the different stages to dislodge any grinding material from the surface.

^b: Water as lubricant.

c) Carbon coating

SEM examination needs the specimens to be coated by carbon sputtering to make the top surface conductive, with a manual turbo evaporator, and later sticking the sample (by the side not to be analyzed) to a conductive metal support. Finally, the side to be imaged must be painted with an aluminium conductive paint.

4.3. Experimental procedures for studying vanadium retention

4.3.1. Experimental planning

The agreed components over which its vanadium sorption capacity wants to be studied, being all of them major compounds in cementitious materials, are:

- **Hydrated C_3S samples** (also referred to in the following as **CSH** for being its major compound and the only one containing CSH)
- **CH**
- **CaO**

As a result, the scheduled experiments are the following, considering that some experiments have been done several times (with the solution concentration as a variable parameter) in order to obtain comparable results and more data for getting more reliable explanations. In order to reach the equilibrium situation of each system, several time intervals were considered, while changing them depending on the results obtained in each series carried out.

Note: Scheduled planning time for analysis gets extended because first results are insufficient, even being programmed in advance according to previous research works.

Table 4.2. Planning for studying vanadium retention on CSH, portlandite and CaO.

Experiment procedure	Substrate	[V] solution (ppm)	Time analysed (min)
Section 4.3.2	CH	500	120
		1000	240
	CSH	500	120
		1000	240
		1000	480
Section 4.3.3	CaO	0 (control)	180
		1000	180

Tests conducted for the vanadium retention study have been carried out up to 240 min for portlandite and CSH substrates, by following the same procedure as shown in Table 4.2, except one test on CSH which is extended up to 8 h. Contrary, tests for vanadium retention on CaO have been considered separately from the ones on CSH and CH because includes *insitu* portlandite formation process which is not studied in any of the other cases. Hence, the experiments with CaO are planned as the following, bearing in mind that there's a pure water solution for the control sample and another one of 1000 ppm of vanadium.

4.3.2. Vanadium retention experiments

Materials:

- Powdered hydrated C₃S samples (section 4.1).
- Portlandite (CH), provided by Panreac Química S.A.U.
- Deionised water Milli-Q quality (18,2MΩ·cm).
- Vanadium, provided by Panreac Química S.A.U as ammonium metavanadate (NH₄VO₃), M=116.98 PRS. 98.0% purity.
- Nitric acid (HNO₃), 67%.

Equipments:

- Micropipette; Nahita, model ECO- 66610310. Maximum capacity 1000 µL. Accuracy ±1.0%. Precision <0.3%.
- pH-meter; Crison, model BASIC 20+. Resolution 0.01.
- Balance; Mettler Toledo, model SB8001. Resolution 0.1 g. Max.capacity 8100 g, Min.capacity 5 g.
- Spectrometer ICP-OES; Perkin Elmer Optima 3200 RL.

Method:

The same procedure is followed for each substrate (powdered CSH and CH), performed at 24±1°C.

- I. Preparing two vanadium dilutions: 500 ppm and 1000 ppm (both adjusted at pH 12 by adding NaOH to simulate pH conditions in a cement paste).
- II. Weighting 0.5 g of the substrate on plastic screw containers (previously hummed) where the test will be performed. Chosen liquid/solid ratio (vanadium solution/substrate) is L/S = 200.
- III. Adding 100 ml in weight of vanadium solutions in each screw container.
- IV. Shaking the mix manually for 10 min.
- V. Every 30 min, 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.
- VI. Measuring and writing down the pH value for each sample taken by aliquot.
- VII. After each extraction, shaking the containers manually for 10 min.
- VIII. Repeating points IV and V at fixed time intervals. Test performance duration is 8 h, depending on the variables.
- IX. Diluting the 2 ml samples by adding 8 ml in weight of Milli-Q water to facilitate the analysis with ICP and acidifying by adding HNO₃ (~2 drops with a dropper).
- X. Analyzing vanadium concentrations in each test tube by ICP-OES, and also Ca and Si concentrations for CSH.
- XI. Calculating % of vanadium removal:

$$\text{a. Dilution factor elimination: } [V] = \frac{[V_{\text{ICP}}]}{10 \text{ ml}} \cdot 2 \text{ ml} \quad (\text{Equation 4.5})$$

$$\text{b. V-removal percentage: } \%_{\text{V elimination}} = \frac{[V_0] - [V]}{[V_0]} \cdot 100 \quad (\text{Equation 4.6})$$

where:

$[V_{ICP}]$ = concentration (mg/l) provided by ICP-OES results.

$[V_0]$ = Initial solution concentration (mg/l), corresponding to 500ppm or 1000ppm.

$[V]$ = corrected sample concentration (mg/l).

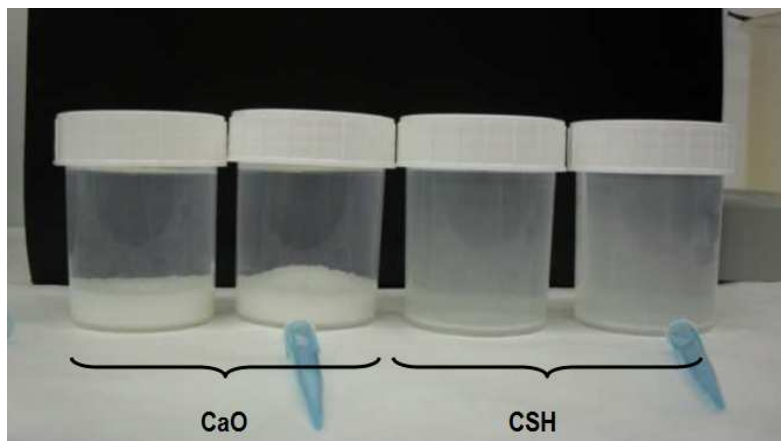


Figure 4.5. Examples of plastic vessels filled with 500 ppm or 1000 ppm vanadium solutions and (left) CaO (detailed in next section) and (right) CSH.

4.3.3. Vanadium coprecipitation experiments

Materials:

- Calcium oxide (CaO), provided by Panreac Química S.A.U.
- Deionised water Milli-Q quality ($18,2\text{M}\Omega\cdot\text{cm}$).
- Vanadium, provided by Panreac Química S.A.U as ammonium metavanadate (NH_4VO_3), $M=116.98$ PRS. 98.0% purity.
- Nitric acid (HNO_3), 67%.

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.
- Thermogravimetric analyser (TGA); TA Instruments, model TGA Q50 v.6.5 Build 196.
- Spectrometer ICP-OES; Perkin Elmer Optima 3200 RL.

Method:

This experiments aims to study how the presence and availability of vanadium affects portlandite formation. For finding an answer, two situations (presence and absence of vanadium, while keeping the rest of variables identical) must be compared. It has to be noted that one individual plastic screw container is needed for each interval of time chosen to sample. In this experiment, considering that it's decided to sample every 60 min for 3 h for both control and contaminated systems, 3 different containers are used.

- I. Weighting 0.5 g of CaO on two plastic screw containers.
- II. In one container, adding 100 ml in weigh of Milli-Q water for the control test.
- III. In the other container, adding 100 ml in weight of 1000 ppm vanadium solution (the same one previously used for CSH and CH essays).
- IV. Shaking the mix manually for 10 min.
- V. After 30 min, extracting a 2 ml aliquot from the control container and pouring it in a test tube clearly marked. Measuring and writing down the pH value. *Note*: It is essential and of utmost importance an organised labelling for the substrates to be used and the containers to be analysed).
- VI. Shaking both containers manually for 10 min.
- VII. After 30 min from the extraction mentioned in step V, doing it again.
- VIII. After 60 min from the beginning of the test, filtering the content of the control container with the aid of a glass funnel and a conventional filter paper folded properly. The retained mass is CaO undergoing a process of hydration (also named *insitu* portlandite from now on). Placing the mass in a glass plaque.
- IX. Shaking the two remaining containers for 10 min.
- X. After one hour from previous step (i.e., within two hours of experiment), repeating all the steps from V to IX for the second container.
- XI. After one hour from the previous step (i.e., within three hours of experiment), repeating all the steps from V to IX for the second (last) container.
- XII. Diluting the 2 ml samples in test tubes by adding 8 ml in weight of Milli-Q water to facilitate the analysis with ICP and acidifying by adding HNO₃ (~2 drops with a dropper).
- XIII. Analyzing vanadium concentrations in each test tube by ICP-OES. For CSH, calcium and silicium are also analysed.
- XIV. Drying the three filtered quantities of *insitu* portlandite (on three different plaques) in the oven at 60°C for 15 min.
- XV. Once the filtered mass dried, powdering manually with the aid of an Agate mortar until reaching very fine powder, and proceeding to the *insitu* portlandite TGA and XRD characterisation.
- XVI. Calculating % of vanadium removal:

$$\text{a. Dilution factor elimination: } [V] = \frac{[V_{\text{ICP}}]}{10 \text{ ml}} \cdot 2 \text{ ml} \quad (\text{idem Equation 4.5})$$

$$\text{b. V-removal percentage: } \%_{\text{V elimination}} = \frac{[V_0] - [V]}{[V_0]} \cdot 100 \quad (\text{idem Equation 4.6})$$

where:

$[V_{\text{ICP}}]$ = concentration (mg/l) provided by I'ICP-OES results.

$[V_0]$ = Initial solution concentration (mg/l), corresponding to 500 ppm or 1000 ppm.

$[V]$ = corrected sample concentration (mg/l).