Cold water extraction (CWE)

Procedure for the determination of the alkali content and pore solution composition

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REPORT

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Summary

This document describes the cold water extraction (CWE) procedure which allows to determine the free alkali content of hydrated cement paste, mortar or concrete. The calculation of the pH using the thermodynamic modelling software PhreeqC is presented in the appendix.

Indexing terms	Stikkord
Concrete	*Betong*
Pore solution	*Pore løsning*
Free alkali content	*Fri alkaliinnhold*

Table of contents content

Preface

This document describes the cold water extraction (CWE) procedure which allows to determine the free alkali content of hydrated cement paste, mortar or concrete.

This procedure includes 1) the preparation of the sample, 2) the extraction of the ions of the pore solution, 3) the analysis of the extracted solution and 4) how to calculate the free alkali content and the composition of the pore solution. Finally, a form for reporting the results is presented.

The calculation of the pH using the thermodynamic modelling software PhreeqC is presented in the appendix.

This document is meant as a practical guide to perform the CWE analysis. More information regarding the validation of the method can be found in Plusquellec et al. (2017).

The work has been performed with the ASR KPN project n° 236661 (2014-2018) "ASR – Alkali-silica reaction in concrete – reliable concept for performance testing" managed by SINTEF Building and Infrastructure and supported by the Norwegian Research Council and its industrial partners: Norcem, NorStone, Norsk Stein, Hydro Energy, Axion and the Norwegian Public Roads Administration.

If you wish to refer to this method, please use the following reference:
Plusquellec, Geiker, Lindgård, Duchesne, Fournier and De Weerdt, 'Determination of the pH and the Free Alkali Content in the Pore Solution of Concrete: Review and Experimental Comparison', Cement and Concrete Research 96 (2017), 13-26.

Brief description of the method

Cold water extraction (CWE) includes the following steps (Figure 1): 1) grinding the concrete to powder; 2) leaching of the powdered sample by introducing it to a known amount of deionized water for 5 min and filtration; 3) analysing the extracted solution; and 4) calculation.

The objective is to extract the elements present in the pore solution
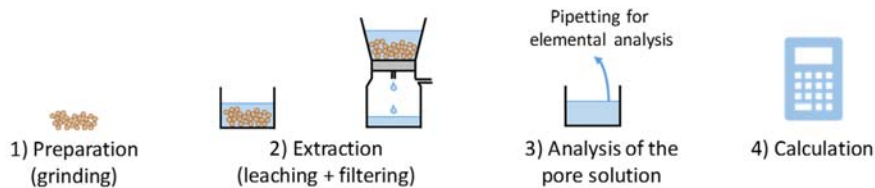

Figure 1: The 4 steps of the cold water extraction (CWE) method.

General recommendations

Storing of samples

In order to avoid carbonation, all the material (original sample and powdered samples) should be stored in a desiccator containing soda lime.

The liquid samples, i.e. the extracted solution, have to be acidified with HNO_3, giving a concentration of $[HNO_3] = 0.1$ mol/l in the sample in order to avoid precipitation.

Aggregate contribution

Besides the cement paste, aggregates can also release alkalis during CWE. When the concrete is ground fine for CWE the exposed surface of the aggregates is increased considerable compared to that in the concrete. This might lead to an overestimation of the alkali released by aggregates in the concrete. If one assumes that all alkalis originate from the cement paste and does not take into account a potential contribution of the aggregates, one might overestimate the alkali content of the concrete. In order to have an idea of the release of alkali by aggregates during CWE, one is advised to perform the extraction on the aggregates separately.

Ca concentration

It should also be noted that when applying CWE on hydrated cement, mortar or concrete, hydrates may partly dissolve, resulting in a high Ca concentration in the final solution. This concentration is not representative of the pore solution of the studied sample. Hence, it should not be considered. The Ca concentration of the pore solution can however be estimated by performing CWE using methanol instead of deionized water. For more information see Plusquellec et al. (2017).

Equipment

The instruments listed in the description below require training by authorized personnel or could be ordered as a service of the respective laboratories. The table below lists the instruments and the contact persons.

Table 1: Overview over instruments or services required for CWE as well as the laboratories providing them and the contact persons.

	Instrument	Laboratory	Contact person
1	Jaw crusher	SINTEF Building infrastructure and architecture	Knut Lervik Roger Leistad
2	Powder mill	NTNU Department of structural engineering	Steinar Seehuus
3	Surface grinder	SINTEF Building infrastructure and architecture	Knut Lervik Roger Leistad
3	Filtration unit	NTNU Department of structural engineering	Klaartje De Weerdt
4	Flame spectrometry	SINTEF Building infrastructure and architecture	Tone Østnor Anne Kristine Møen
5	High resolution ICP-MS, Element 2 from Thermo Scientific	NTNU Department of material science	Syverin Lierhagen

Other equipment/materials requested:
- Soda lime
- Silica gel
- Freshly deionized water (resistivity of 18.2 MΩ.cm)
- Permanent marker
- Desiccator
- Steel brush
- Aerated oven at 105°C
- Balance with accuracy 0.001 g
- Spatula
- 80 μm sieve and brush
- Small plastics bags with zip-lock (100 ml)
- Metallic sponge
- Glas beakers x2 (100 ml)
- Magnetic stirrer
- Magnet for magnetic stirrer
- Filtration unit: vacuum Erlenmeyer (500 ml) connected to a water pump + sintered glass filter from Whatmann
- Whatmann cellulose filter 8 μm, grade 40
- Timer set on 5 min
- Plastic vials (centrifuge tubes) with lid (15 ml)
- Micropipette (1-5 ml) with plastic pipette tips (1 ml)
- Nitric acid HNO_3 65%

1. Sample preparation

1.1. Determination of the free water content

The determination of the free water content is only necessary if the pore solution composition or pH has to be calculated based on the CWE results. If not, the reader can directly go to the next step.

The amount of free water can be determined by oven-drying at 105°C. This approach is based on the method described by Sellevold and Farstad[1]. It should be noted that the temperature chosen for drying the sample induces a decomposition of the ettringite and C-S-H. The amount of free water will thus be slightly overestimated. However, a lower temperature, e.g. 40 °C, would considerably increase the drying time, and might allow further hydration for the young, not fully hydrated samples.

Equipment and materials needed:
- Steel brush
- Marker
- Aerated oven at 105 °C (available at NTNU and SINTEF)
- Balance with accuracy 0.001 g
- Desiccator with silica gel

Procedure:
- Collect samples of approx. 150 to 400 cm^3. Preferably collect some parallel samples.
- Brush the samples with a steel brush to remove all lose parts
- Mark the samples and weigh them as received
- Put the samples in a 105 °C aerated oven.
- Remove the samples from the oven and let them cool down to room temperature in a desiccator over silica gel, prior to weighing. After weighing put the samples back in the oven.
- Repeat the weighing of the samples until reaching approx. constant weight (mass difference < 0.01% / 24 h). About 7 days is normally sufficient, but the time needed can vary depending on the porosity of the material and the size of the sample.

The mass percentage of free water or free water content can then be calculated using the following formula:

$$\%m_{\text{free water}} = \frac{m_{\text{initial}} - m_{\text{dried}}}{m_{\text{initial}}} \cdot 100 \tag{1}$$

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[1] Erik J Sellevold and Tom Farstad, 'The Pf-Method – a Simple Way to Estimate the W/C-Ratio and Air Content of Hardened Concrete', in *Proceedings of ConMat'05 and Mindess Symposium. Vancouver, Canada: The University of British Colombia. ISBN 0-88865-810-0,* (2005).

1.2. Powdering of the sample

Note: the samples which have been used for the determination of the free water content can NOT be used for another purpose.

Equipment and materials needed:
- Jaw crusher (available at SINTEF)
- Powder mill (e.g. the vibratory disc mill RS 200 from Retsch (see Figure 2) available at NTNU)
- Spatula
- 80 μm sieve and brush
- Small plastics bags with zip-lock (100 ml)
- Permanent marker
- Desiccator
- Soda lime
- Metallic sponge

Note: a surface grinder (available at SINTEF) can be used instead of the jaw crusher and the powder mill.

Procedure:
- Check if the jaw crusher and its component are correctly cleaned.
- Crush the concrete to pieces < 10 mm with a jaw crusher. Collect the crushed material in a bag, seal and store in a desiccator over soda lime until further grinding.
- Check if the powder mill and its component are correctly cleaned.
- Put the crushed material to be fine-ground in the device (max = 50 g).
- Seal and close the mill.
- Select the program "1500 rpm – 30 secs" and launch it.
  Note: the grinding time depends on the initial material (aggregates, hydrated cement paste, mortar or concrete), but a minimum of 30 seconds is required.
- Scratch the grinding elements with a spatula to recover most of the powder.
- Check the size of the particles using the 80 μm sieve and a brush. If not all the material passes through the sieves, a longer grinding time is required.
- Put the powder in plastics bags, seal and label correctly.
- Put the plastics bags in a desiccator containing soda lime.
- Clean and dry all the used equipment before grinding another sample. A metallic sponge is used to clean the grinding elements of the mill.

Figure 2: Vibratory disc mill RS 200 (Retsch). Photos by H. Vurucu.

2. Cold water extraction

2.1. Leaching and filtration

Equipment and materials needed:
- Balance (precision 0.001 g)
- Glas beakers x2 (100 ml)
- Spatula
- Freshly deionized water (resistivity of 18.2 MΩ.cm)
- Magnetic stirrer (RH basic 2 from IKA)
- Magnet for magnetic stirrer
- Filtration unit: vacuum Erlenmeyer (500 ml) connected to a water pump + sintered glass filter from Whatmann (Figure 3).
- Whatmann cellulose filter 8 μm, grade 40 (other filters can be used, but they should be tested for potential alkali retention)
- Timer set on 5 min
- Plastic vials (centrifuge tubes) with lid (15 ml)
- Permanent marker

Procedure:
- Prepare and install the filtration unit (Figure 3)
- Weigh carefully and precisely 20.000 g of the powdered sample using a spatula in a beaker. Write down the mass.
- Weigh carefully and precisely 20.000 g of the freshly deionized water in the second beaker. A Pasteur pipette is used at the end to obtain small drops and be precise enough. Write down the mass.
  Notes:
  o If the total sample mass is < 20.000 g, a lower amount can be used. The same mass of water has to be weighed to ensure a liquid-to-solid ratio of 1.
  o The weighing has to be done as fast as possible to avoid carbonation.
- The magnet is put in the beaker containing the powder, which is placed on the magnetic stirrer.

- Put the magnetic stirrer on at a low speed, i.e. 1. The heating mode has to be turned off.
- Add slowly the deionized water and start the timer. Adjust the speed of the stirrer: high enough to ensure good mixing, but splashing must be avoided. The mixing can be helped by carefully moving the beaker on the stirrer.[2]
- After stirring 5 min, the suspension is immediately filtered using the filter device.
- When all the solution has passed through the filter, it is poured from the Erlenmeyer into a 15 ml centrifuge tube properly labelled. The remaining filtrate is discarded.

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[2] Some water will remain in the beaker. To know precisely the amount of water added to the powder, the beaker can be weighted dry and after the mixing.
However, some tests showed that the results are not significantly influenced by this correction.

2.2. Dilution and acidification

It is recommended to dilute 10 times the solution and to acidify it prior to ICP analysis. The required dilution depends on the expected concentration of K and Na.

Equipment and materials needed:
- Plastic vials (centrifuge tubes) with lid (15 ml)
- Micropipette (1-5 ml) with plastic pipette tips (1 ml)
- Freshly deionized water (resistivity of 18.2 MΩ.cm)
- Nitric acid HNO_3 65%
- Permanent marker

Procedure:
- The nitric acid HNO_3 65% has to be first diluted by 2 with deionized water.
  When performing the dilution, remember to always measure the deionized water <u>first</u>, and then add the acid to the water.
- Pipette 1 ml of the filtrate in the centrifuge tube.
- Pipette 9 ml of deionized water in the same tube.
- For a diluted sample of 10 ml sample, 0.140 ml of the diluted HNO_3 has to be added in order to obtain 0.1 mol/l of HNO_3 in the sample.[3]
  It has to be kept in mind that the addition of acid induces a dilution which has to be taken into account. For example, the acidification of a 10 times diluted solution will increase the dilution factor to 10.14.
- All tubes have to be properly labelled (sample name, date, dilution, acidification etc).

Figure 3: The filtration unit used for CWE. Photo by H. Vurucu.

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[3] 65 % HNO_3 acid contains 65 % by mass HNO_3. The density of 65 % HNO_3 is 1.39 kg/l. The molar mass of HNO_3 is 63.01 g/mol.
Mass of HNO_3 in 1l of acid = 1.39 kg/l · 0.65 = 0.9035 kg/l.
The concentration of HNO_3 is 0.9035 kg/l / 63.01 g/mol = 14.34 mol/l.
When we dilute the acid by 2 the concentration becomes 7.17 mol/l.

In order to achieve a 10 ml solution with a concentration of 0.1 mol/l we need 0.010 l · 0.1 mol/l = 0.001 mol HNO_3. That is equal to a volume of 0.001 mol / 7.17 mol/l = 0.00014 l = 0.140 ml of the diluted acid.

3. Analysis of the solution

If only the alkali metals K and Na are required, the filtrate can be analysed by flame spectrometry. If additional elements are required such as Ca, S, Al, Si, Mg, or Fe, the analysis is done by inductively coupled plasma mass spectrometry (ICP-MS). The analyses are done by trained technicians and are therefore not described.

The following information has to be delivered with the samples:
- Sample name
- Dilution
- Acidification
- Expected composition of the solution, in order to take into account the matrix effect. Not only the elements that one wants to analyse should be mentioned here.

The elemental concentrations in the filtrate obtained from flame spectrometry or ICP-MS are given in [g/l].

4. Calculation of the results

4.1. Free alkali content of concrete in [mol/g], [g/g] or [Na_2O_{eq}%]

Based on the result obtained by flame spectrometry or ICP, the content of the element x (e.g. K or Na) of the sample can be calculated as follows:

$$x\,[g/g] = [x]_{measured} \cdot D \cdot \frac{m_{water}}{m_{powder}} \cdot 10^{-6} \tag{2}$$

or

$$x\,[mol/g] = \frac{[x]_{measured} \cdot D}{M(x)} \cdot \frac{m_{water}}{m_{powder}} \cdot 10^{-6} \tag{3}$$

With:

- x, measured element, i.e. Na or K.
- $[x]_{measured}$, the concentration of the element x measured by flame spectrometry or ICP in [mg/l].
- D, the dilution factor.
- $M(x)$, the molar mass of the element x in g/mol (22.99 g/mol for Na, 39,10 g/mol for K and 61.98 g/mol for Na_2O).
- m_{water}, the mass of deionized water added to the powder during CWE in [g].
- m_{powder}, the mass of powdered material used in [g].

It should be noted that m_{water} should also include the amount of free water contained in the material. However, the amount of free water is very little compared (4 – 5%) to the added amount of water and can therefore be omitted as demonstrated in Plusquellec et al. (2017). However, if one would like to correct for the free water available in the sample, one could determine the free water content by drying the powdered sample in the TGA at 105 °C until constant mass as described in Plusquellec et al. (2017) and include this in the m_{water} in equation (2) and (3).

In structural engineering, the alkali content of concrete is often expressed as the Na_2O_{eq} per m^3. This can be calculated as follows using the free alkali contents calculated above with the molar mass of Na_2O, $M(Na_2O)$ = 61.98 g/mol and assuming a density of the concrete of 2400 kg/m^3:

$$Na_2O_{eq}\text{ per }m^3 = \left(\frac{1}{2} \cdot K\,[mol/g] \cdot M(Na_2O) + \frac{1}{2} \cdot Na\,[mol/g] \cdot M(Na_2O)\right) \cdot 2400\ ^{kg}/_{m^3} \tag{4}$$

4.2. Pore solution composition in [mol/l]

The concentration of Na and K in mol/l in the pore solution can be calculated as follows:

$$[x]_{pore\ solution} = \frac{[x]_{measured} \cdot D \cdot 10^{-3}}{M(x)} \cdot \frac{m_{water\ added} + m_{powder} \cdot \%m_{free\ water}/100}{m_{powder} \cdot \%m_{free\ water}/100} \qquad (5)$$

With:
- $[x]_{pore\ solution}$ is the concentration of Na and K in the pore solution [mol/l]
- x, measured element, i.e. Na or K.
- $[x]_{measured}$, the concentration of the element x measured by flame spectrometry or ICP in [mg/l].
- D, the dilution factor.
- $M(x)$, the molar mass of the element x in [g/mol].
- $m_{water\ added}$, the mass of deionized water added to the powder during CWE in [g]. This can be assumed similar as V_{water} in [ml] as described above.
- m_{powder}, the mass of powdered material used in [g].
- $\%m_{free\ water}$, the amount of free water in the material in [wt%].

Based on the pore solution composition the pH can be calculated using a thermodynamic modelling software such as PhreeqC. This is described in the appendix.

5. Data reporting

The following section gives a form to be filled-out (light grey areas) when performing CWE.

	Id.	Measured	Calculated
Sample name:			
Date:			
Performed by:			
Mass sample on arrival [g]	m_i		-
Mass sample after drying at 105 °C [g] – 4 days	$m_{105, 4}$		-
Difference	-	-	m_i- $m_{105, 4}$
Mass sample after drying at 105 °C [g] – 5 days	$m_{105, 5}$		-
Difference	-	-	m_i- $m_{105, 5}$
Mass sample after drying at 105 °C [g] – 6 days	$m_{105, 6}$		-
Difference	-	-	m_i- $m_{105, 6}$
Mass sample after drying at 105 °C [g] – 7 days	$m_{105, 7}$		-
Difference	-	-	m_i- $m_{105, 7}$
Mass sample after drying at 105 °C [g] – 8 days	$m_{105, 8}$		-
Difference	-	-	m_i- $m_{105, 8}$
Mass sample after drying at 105 °C [g] – 9 days	$m_{105, 9}$		-
Difference	-	-	m_i- $m_{105, 9}$
Free water content	$\%m_{free\ water}$	-	$\frac{m_i - m_{105,7}}{m_i} \cdot 100$
Total amount of ground powder	$m_{powder\ tot}$		-
Amount of ground powder for CWE (20 g)	m_{powder}		-
Amount of deionized water for CWE (20 g)	m_{water}		-
Sample size filtrate (e.g. 10 ml)	$V_{filtrate\ tot}$		-
Amount of used filtrate (e.g. 1ml)	$V_{filtrate}$		-
Added deionized water (e.g. 9 ml)	$V_{dilution}$		-
Acidification – added HNO$_3$ (e.g. 0.14 ml)	V_{acid}		-
Dilution	D	-	$\frac{V_{filtrate} + V_{dilution} + V_{acid}}{V_{filtrate}}$
K concentration from ICP [µg/l]	$[K]_{measured}$		-
Na concentration from ICP [µg/l]	$[Na]_{measured}$		-
K concentration in the filtrate (mmol/l)	$[K]_{filtrate}$	-	$([K]_{measured} \cdot D)/(39.1 \cdot 1000)$
Na concentration in the filtrate (mmol/l)	$[Na]_{filtrate}$	-	$([Na]_{measured} \cdot D)/(22.99 \cdot 1000)$
K content of the sample [g/g] or [mol/g]	K_{sample}	-	Eq. 2 or Eq.3
Na content of the sample [g/g] or [mol/g]	Na_{sample}	-	Eq. 2 or Eq.3
Alkali content of the sample [kg/m^3, Na$_2$O$_{eq}$]	$Na_2O_{eq, sample}$	-	Eq. 4
K concentration in the pore solution (mol/l)	$[K]_{pore\ solution}$	-	Eq. 5
Na concentration in the pore solution (mol/l)	$[Na]_{pore\ solution}$	-	Eq. 5

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6. References

CWE is based on:
- M.C. Alonso, J.L. García Calvo, C. Walker, M. Naito, S. Pettersson, I. Puigdomenech, M.A. Cuñado, M. Vuorio, H. Weber, H. Ueda, K. Fujisaki, Development of an accurate pH measurement methodology for the pore fluids of low pH cementitious materials (2012).
- V. Räsänen, V. Penttala, The pH measurement of concrete and smoothing mortar using a concrete powder suspension, Cement and Concrete Research, 34 (2004) 813-820.
- L. Li, J. Nam, W.H. Hartt, Ex situ leaching measurement of concrete alkalinity, Cement and Concrete Research, 35 (2005) 277-283.

If you wish to refer to this method, please use the following reference:
G. Plusquellec, M.R. Geiker, J. Lindgård, J. Duchesne, B. Fournier and K. De Weerdt, 'Determination of the pH and the Free Alkali Content in the Pore Solution of Concrete: Review and Experimental Comparison', Cement and Concrete Research 96 (2017), 13-26.

Appendix: pH calculation using PhreeqC - quick user manual

Installation of the software

PhreeqC and its database can be downloaded on the USGS website at:

http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/PhreeqC/

The software is available on different platforms: Windows, MacOS and Linux.
PhreeqC is installed in C:\Program Files (x86)\USGS\PhreeqC Interactive 3.3.0-10251 (Figure 4).
The numbers at the end only indicate the current version which is installed. Documentations and database files are also provided. The database used here (pitzer_updated.dat) is an updated version and is available on demand.
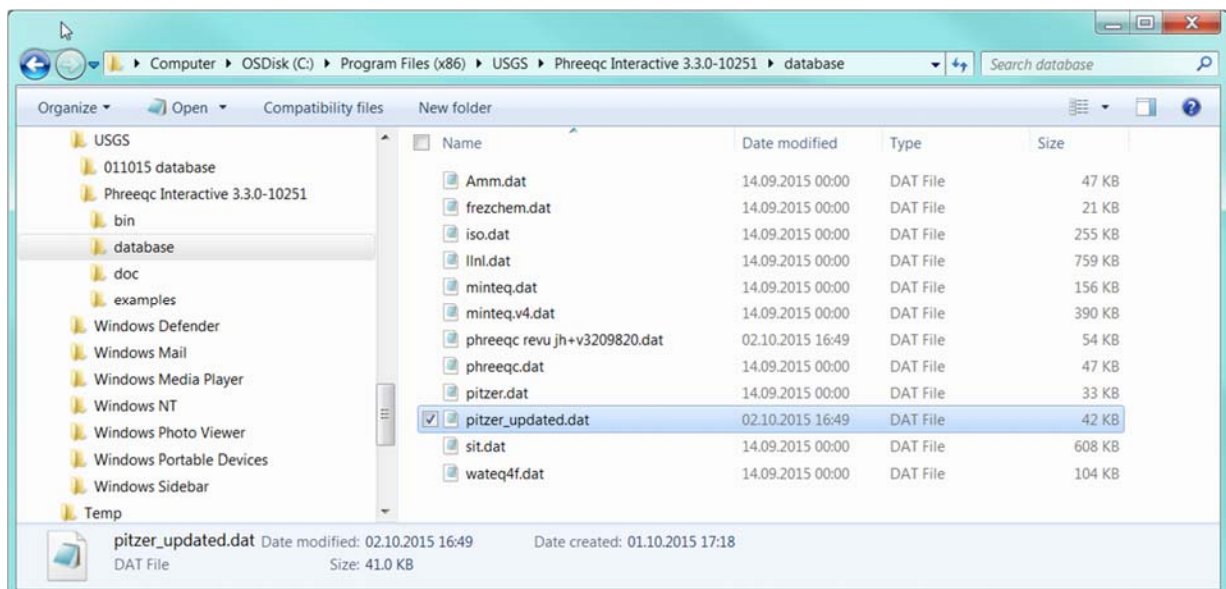
Figure 4.

Step by step calculation of the pH

General comment:

All the numbers indicated on the figures refer to the different steps described in the text below.
When the software starts, the window presented in Figure 5 will open.

1) The first step is to describe the solution(s) of which you want to calculate the pH. Click on the icon called "SOLUTION" (Figure 6), represented as a volumetric flask (first icon in the command blocks).

2) A new window will pop up. In the first tab, "General", change the temperature if needed (25°C by default), depending at which temperature the experiments you want to simulate have been done (Figure 6).

3) The description of solution is made in the "Individual element input" tab (Figure 7):
   a) Selection of the unit (mmol/kg water by default)
   b) Selection of the charge balance: pH (none by default)
   c) Selection of the present species. Na, K, Ca, Al, Si and S in this example
   d) Description of the solution by setting the concentrations

4) After confirmation, the main window will be similar as the one in Figure 8. It is possible to make changes directly in the right area with the keyboard.
   Several solutions can be described, just make sure that each one of them has a different number. At the end, the word "END" must be added.

5) To execute the program, click on "Run…". (Figure 8)
   a) A message to save the file will appear. Click on "OK" and save and name your file in the desired file.
   b) Choose the database (pitzer_updated.dat in this example) (Figure 9).
   c) Click on "Start", then "OK" and finally "Dismiss" at the end of the calculation (Figure 9).

6) The main window automatically opens the "Output" tab (Figure 10).
   Scroll down the window to see the results. You will find:
   - The solution composition with the molality of the present species.
   - The description of the solution, including the pH.
   - The distribution of the different species.
   - The saturation indices (SI) of the phases present in the database (a positive SI indicates a precipitation of the concerned phase at equilibrium).
   The result of each solution is presented one after another.

7) If an important number of solutions is going to be simulated, it is possible to generate an excel file containing the desired information.
   a) Activate the "Printing and numerical method" task bar using a right click (Figure 11).
   b) Click on the "SELECTED_OUTPUT" icon, a new window will open. In the "General" tab, first name the excel file and do not forget the ".xls" extension. The file will be created by default in the same folder as the Input PhreeqC file, but it can be changed using "Browse…". Put the value for "simulation" and "pH" on "True", and some other if of interest in. Click on "OK" (Figure 12).
   c) Do not forget "END" at the end of the program and "Run" it (Figure 13).
   d) Open the excel file (Figure 14).
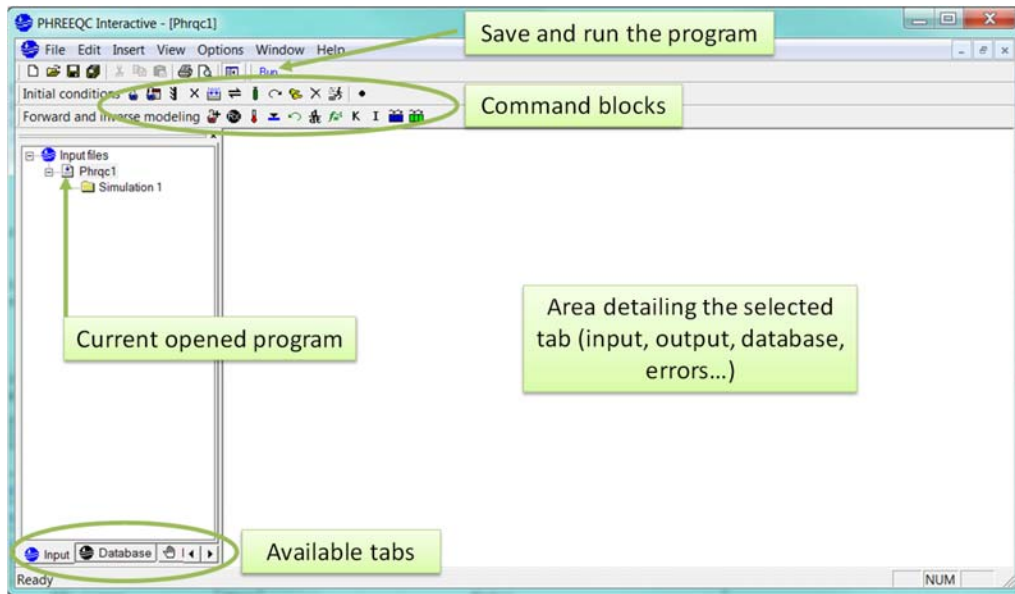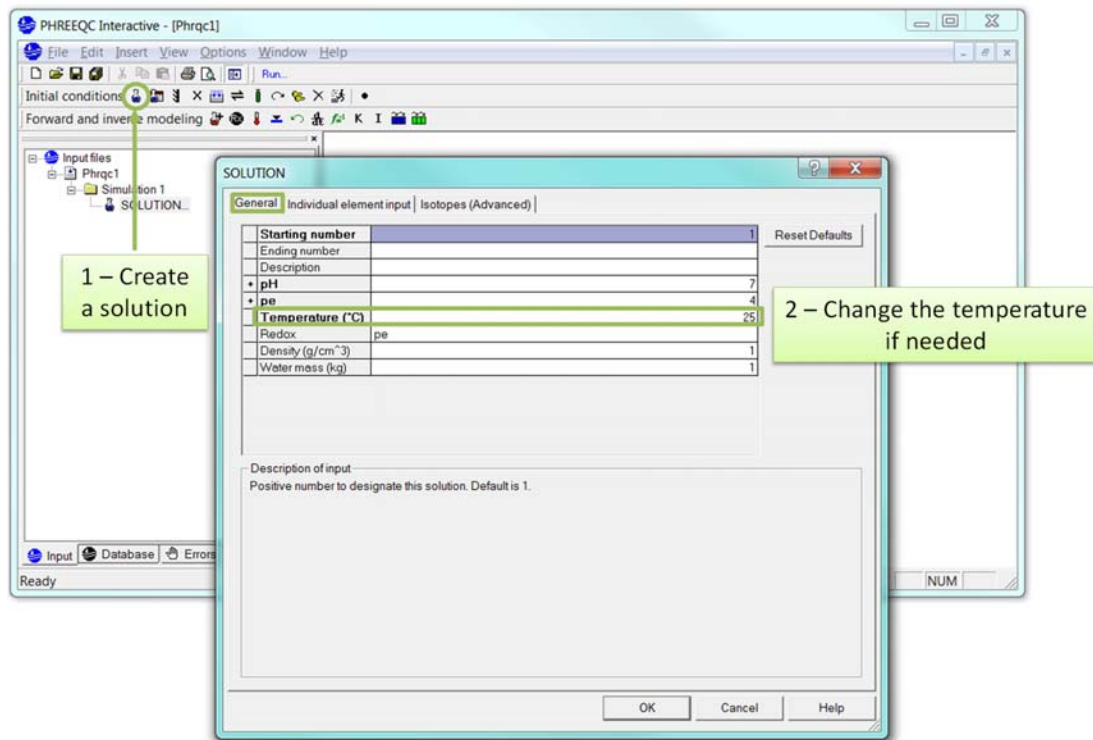   e) It is important to close the excel file if the programme has to be restart.
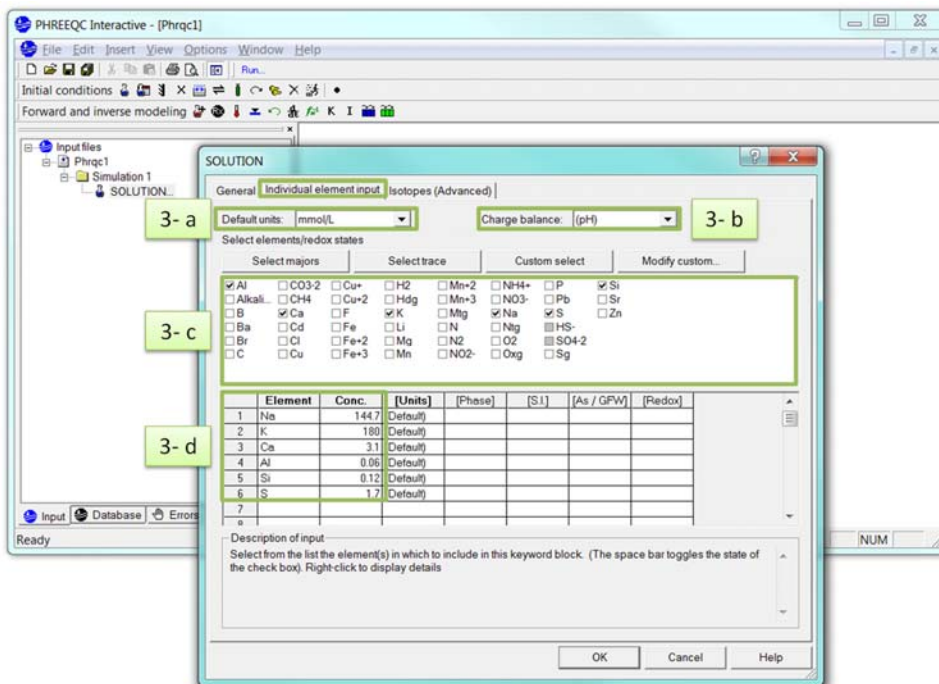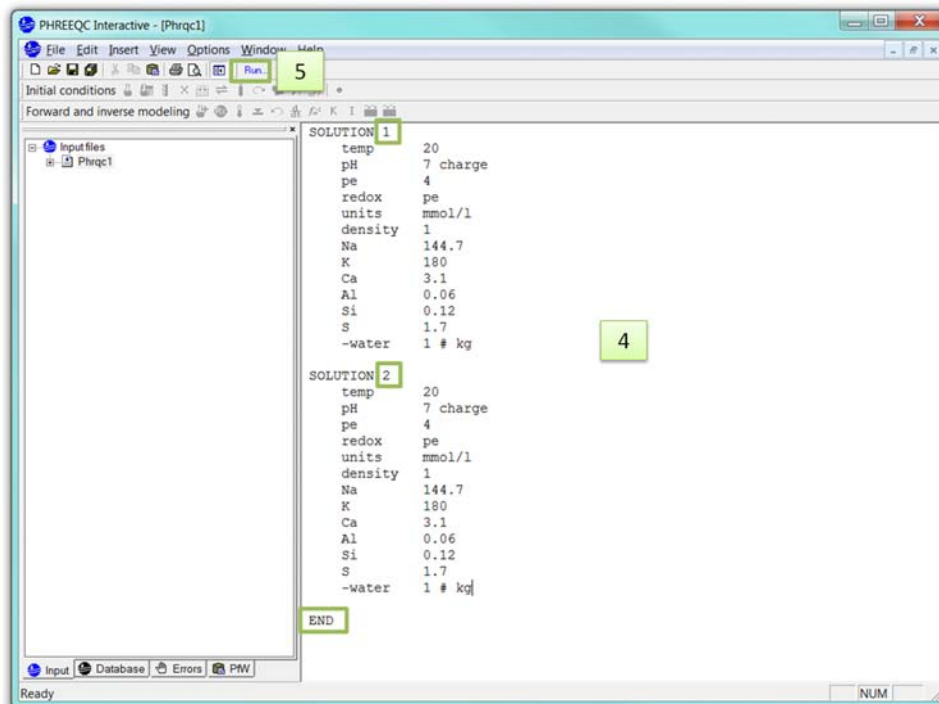
Figure 5.

Figure 6.

Figure 7.

Figure 8.
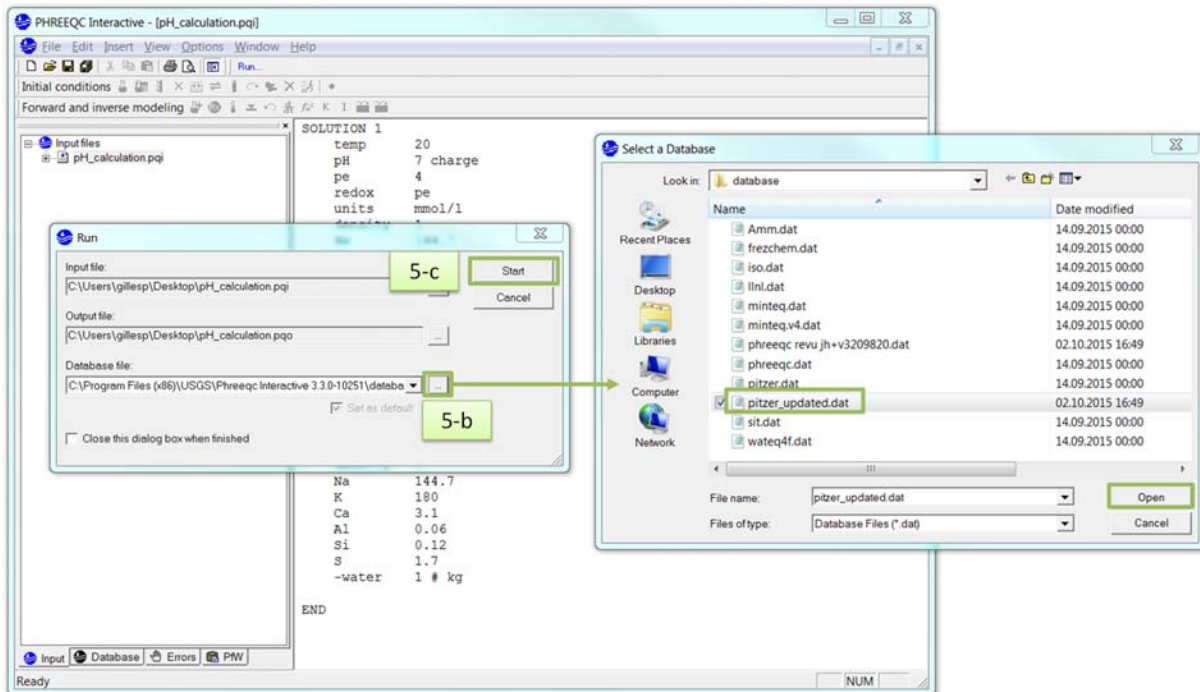
Figure 9.
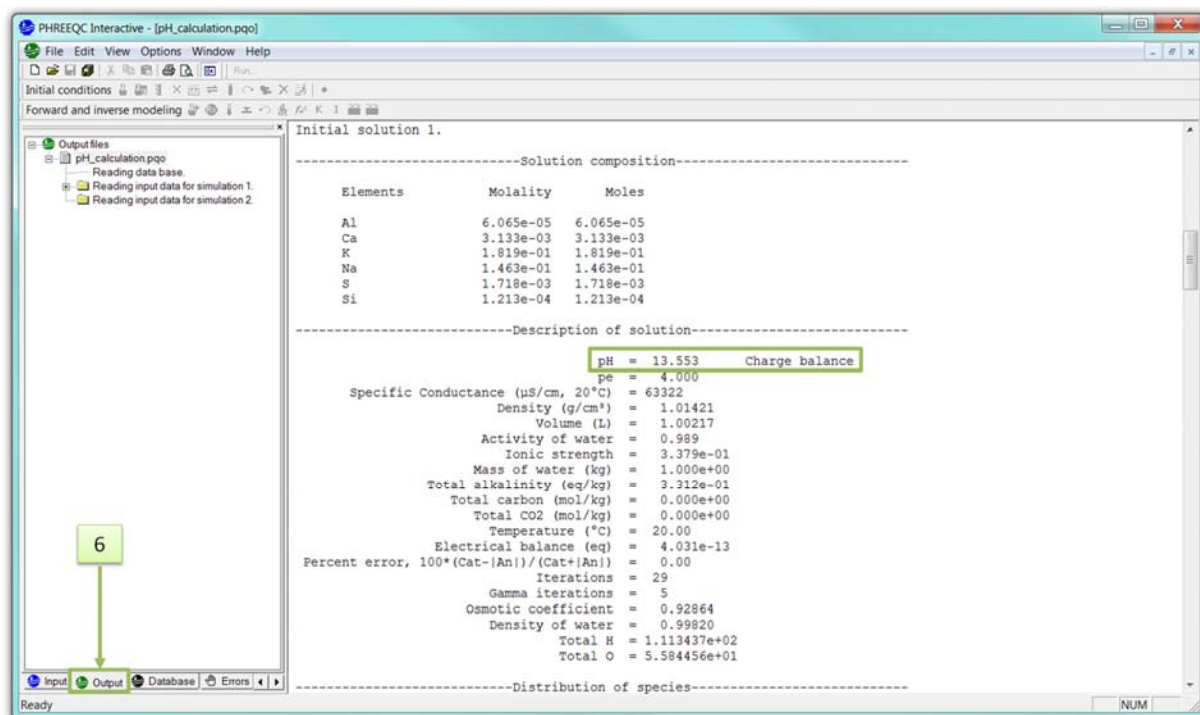
Figure 10.
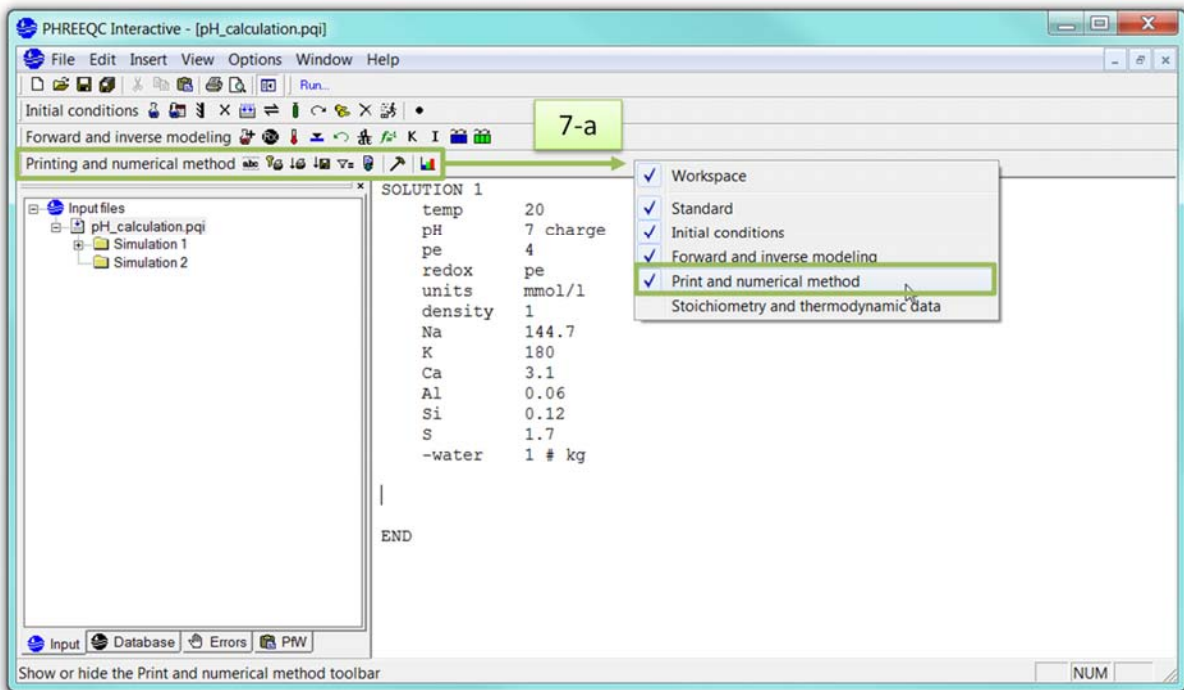
Figure 11.
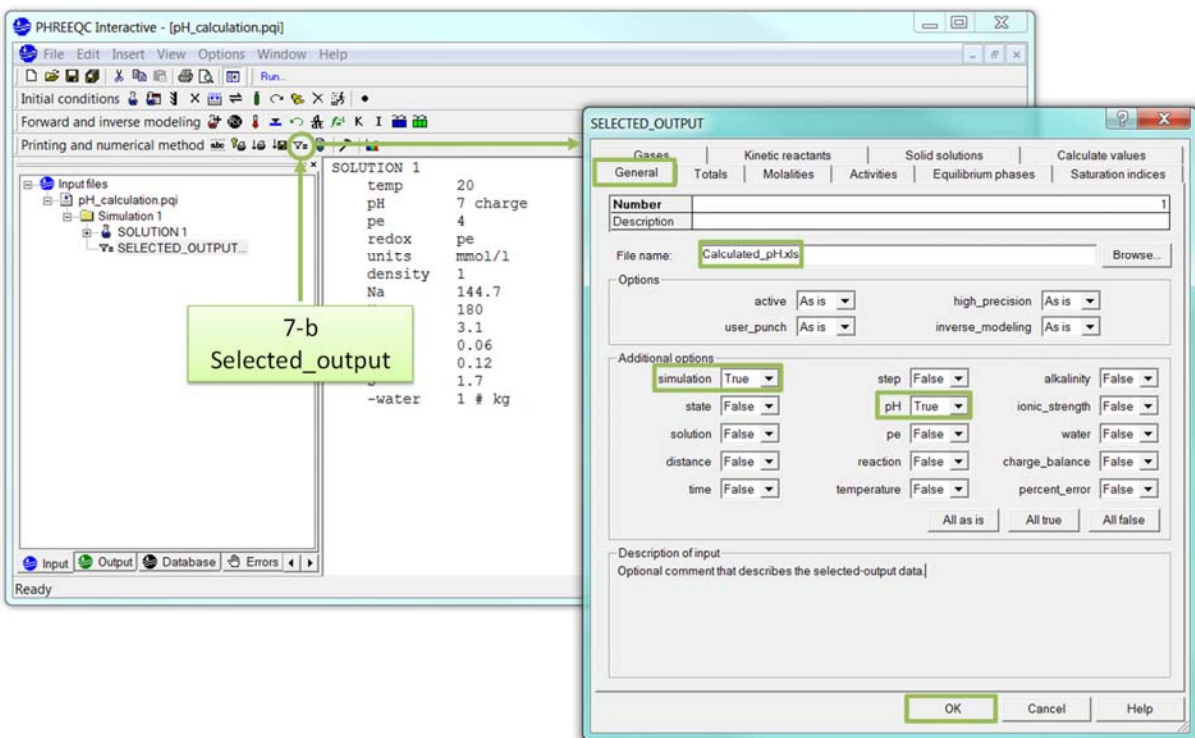
Figure 12.

Figure 13.

Figure 14.