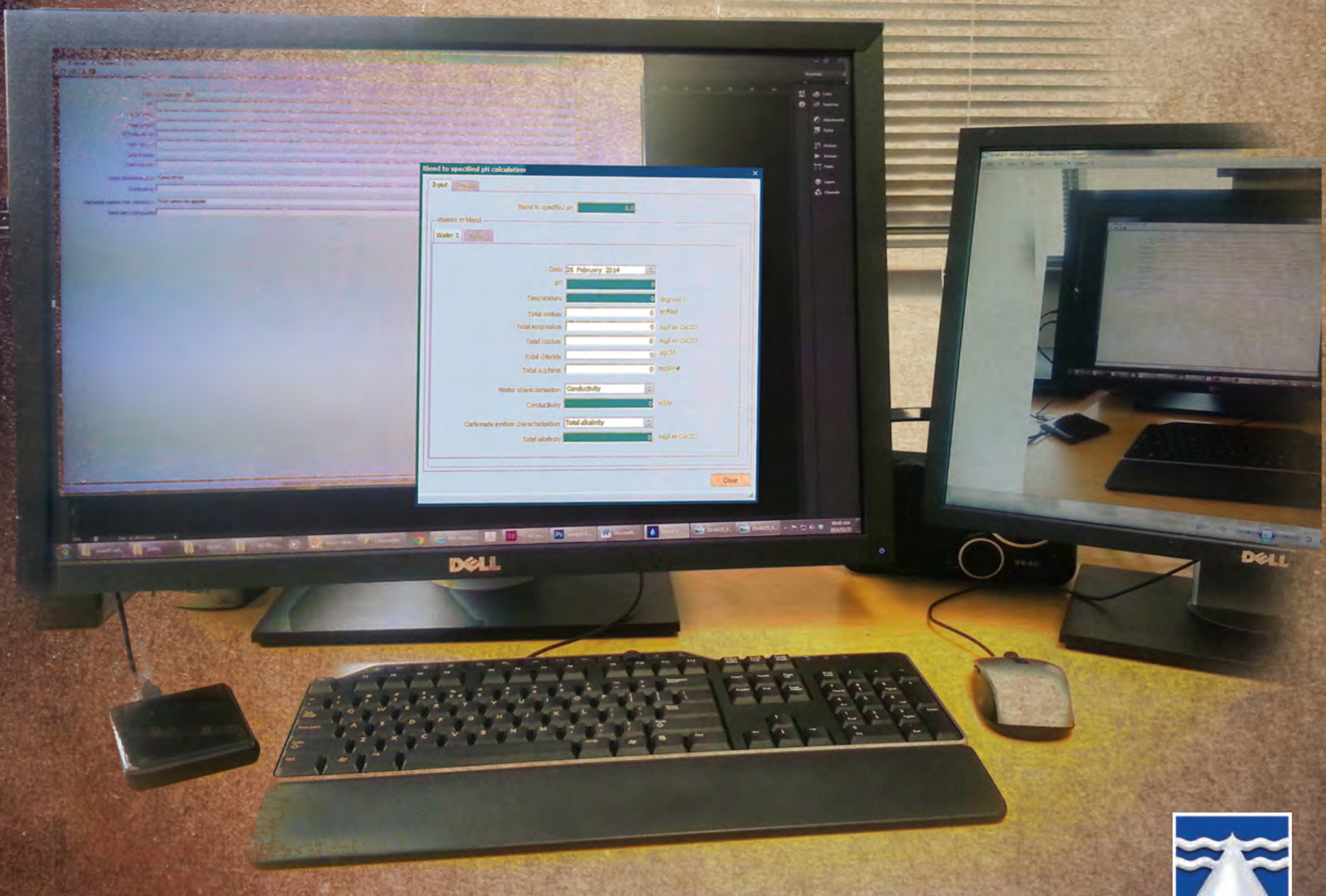
# Stasoft V User Manual

## JFC Friend



Blend to specified pH: 0.0

Waters to blend

Date: 25 February 2014
pH: 0
Temperature: 0 degrees C
Total sodium: 0 mgNa/l
Total magnesium: 0 mg/l as CaCO3
Total calcium: 0 mg/l as CaCO3
Total chloride: 0 mgCl/l
Total sulphate: 0 mgSO4/l
Water characterisation: Conductivity
Conductivity: 0 mS/m
Carbonate system characterisation: Total alkalinity
Total alkalinity: 0 mg/l as CaCO3

WATER RESEARCH COMMISSION
TT 585/13

# Stasoft V
# user manual

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Report to the
**Water Research Commission**

by

**Softchem**

**WRC Report No. TT 585/13**

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This report contains a CD at the back that contains the Stasoft V computer software.

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## SYNOPSIS

The program Stasoft V addresses water conditioning problems in aqueous media with a total dissolved solids concentration of up to about 15 000 mg/ℓ and with the carbonate system as the only weak acid system in solution.

Algorithms are developed and presented for solving conditioning problems encompassing the aqueous phase only (pH and $CaCO_3$ precipitation potential control), or aqueous-gas phases (changes in pH and mineral precipitation potential where groundwaters are aerated and in the treatment of cooling waters), or aqueous-solid phases ($Ca^{2+}$ and $Mg^{2+}$ softening) or aqueous-solid-gaseous phases (three-phase equilibrium situations arising with treatment of underground waters).

The Stasoft V computer program addresses a wide range of chemical conditioning problems likely to arise in the treatment of municipal waters, cooling waters and mining wastewaters.

## ACKNOWLEDGEMENTS

Mr Wynand Wolmarans, from Enerweb (Pty) Ltd, for his infinite patience, prompt response times and development of the new Windows-based menu system for Stasoft V.

# TABLE OF CONTENTS

# 1 INTRODUCTION

The chemical quality of a water can have a major impact on the system storing and conveying the water, and on the use of the water. Waters from underground sources in dolomitic areas, when brought to the surface, in contact with air, may become oversaturated with respect to calcium carbonate ($CaCO_3$) and cause excessive precipitation in storage dams, canals and pipes. Some waters may attack (be aggressive to) cement type materials and/or be corrosive to ferrous and other metals. Other waters may have unduly high concentrations of calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) ions, termed hard waters, giving rise to high soap demand in washing, furring of hot water appliances and deleterious effects within some industrial processes. All these waters need to be treated to remove or minimise the various adverse effects. The difficulties with any water are to assess its characteristics and to devise an appropriate treatment to give a non-scaling, non-aggressive, non-corrosive water.

To attain the desired water quality usually requires the addition of chemicals to the water (chemical conditioning). A prerequisite to conditioning is to determine the chemical state of the water (characterisation), to that level of detail sufficient to calculate the sources of corrective chemicals to be added to the water (dosing estimation).

Characterisation and dosing estimation are based on equilibrium chemistry of the calcium-magnesium-carbonate ($Ca\text{-}Mg\text{-}CO_3$) system. This is a complex weak acid/base system existing in three phases, gas, aqueous and solid. Both characterisation and dosing estimation may require satisfying equilibria in one, two or three phases, that is aqueous, aqueous-solid, aqueous-gas, or aqueous-gas-solid phases.

Procedures for characterisation and dosing estimation can be developed from the basic equations defining capacities and equilibria of the $Ca\text{-}Mg\text{-}CO_3$ system. However, the procedures are cumbersome in the extreme. To overcome this problem, ancillary capacity parameters have been developed (for example, $H_2CO_3^*$ alkalinity, $CO_3^{2-}$ acidity), which have greatly reduced the problems of characterisation and chemical conditioning.

A major advance in characterisation and in solving conditioning problems was the development of graphically aided procedures. Using these procedures, solutions have become readily available and practical for field use. The development of the graphically aided procedures and their application to a wide range of conditioning problems have been dealt with in detail by Loewenthal *et al.* (1986).

Even though graphically aided procedures are relatively simple, their application still demands a fairly comprehensive understanding of the $Ca\text{-}Mg\text{-}CO_3$ system. Also, graphically aided procedures are relatively slow and finding an optimal solution often demands repeated calculations. To address this Loewenthal *et al*. (1988) presented an interactive user-friendly computer program, Stasoft. This program was based on the chemical equilibrium model of the $Ca\text{-}Mg\text{-}CO_3$ system. It provided rapid numerical solutions to characterisation of a water and the dosing requirements to obtain the desired chemical water quality for a prescribed input. The model, however, was appropriate only for low salinity waters, that is, waters that have a total inorganic dissolved solids concentration (TDS) of less than 1 000 mg/ℓ. In such waters ion pairing effects usually are negligible and their effect has been neglected. In waters with TDS concentrations above 1 000 mg/ℓ, as the TDS increases ion pairing effects become increasingly significant and the model predictions become increasingly approximate.

In 1992 an updated version of the program, Stasoft III, was brought out in which the Ca-Mg-$CO_3$ equilibrium model was extended to incorporate ion pairing between principal cation species ($Ca^{2+}$, $Mg^{2+}$ and $Na^+$) and anion species ($SO_4^{2-}$, $CO_3^{2-}$ and $HCO_3^-$). As such, the model was acceptable for application to waters with TDS up to about 15 000 mg/ℓ. Weak acid and ion pair equilibrium constants used in the computations are listed in Appendix A; deviations from ideality arising from activity coefficient effects are determined as set out in Appendices B and C (Friend and Loewenthal 1992).

Stasoft III was designed for application to both "terrestrial" waters (that is, those where ion pairing effects are negligible and the TDS less than about 1 000 mg/ℓ) and "higher" salinity waters (that is, those where ion pairing effects are significant). For both types of water the program was designed to provide solutions to a broad range of problems the water chemist or engineer is likely to encounter in practice, and included the following:

- calcium and magnesium softening and restabilisation,
- pH adjustment of water through chemical dosing,
- stabilisation of waters to a specified calcium carbonate precipitation potential,
- blending of two or more waters with different chemical characteristics,
- effects of temperature and concentration changes on water's characterisation,
- evaluation of underground or treated waters when achieving two- or three-phase equilibrium, and
- treatment of calcium and alkalinity deficient waters.

The Stasoft program was further enhanced during 2000 when Stasoft 4 came out that included more functional menus and a larger selection of chemicals for dosing purposes (Morrison and Loewenthal 2000). However, with the advent of newer operating systems (Windows Vista and later), the previous versions of Stasoft no longer functioned on the new operating platforms.

The new Stasoft V program was developed to be functional on new operating platforms (Windows 7 and higher). The program has the same calculation functions that were available in Stasoft III, with enhanced menu and help facilities.

# 2 PROGRAM STRUCTURE

## 2.1 Introduction

The computational aspects of the program (that is, the algorithms) were written in Turbo Pascal. These algorithms were incorporated into a new 32-bit Windows program with a modern user interface written using Delphi Version XE5. The program is compatible with all Windows 7 and higher operating systems.

Stasoft V was developed with an integrated menu system, consisting of three main menu items, namely Data set, Calculations and Help. Input to the program is via either the Data set menu option or the four taskbar icons below the main menu items. The various available solution procedures (tasks) of the program may be selected from the Calculations menu option, with assistance on any of the program's features provided within the Help menu option.

## 2.2 Data input

Data is entered into the program via an input window, see Section 4. The following data (with relevant units) may be entered into the program:

- date of the input in format DD MMM YYYY (optional),
- pH of the water,
- temperature of the water in degrees Celsius,
- total sodium ($Na^+$) concentration in mg Na/ℓ (necessary for characterisation of medium salinity waters)[#],
- total magnesium ($Mg^{2+}$) concentration in mg/ℓ as $CaCO_3$ (necessary for softening calculations and for characterisation of medium salinity waters),
- total calcium ($Ca^{2+}$) concentration in mg/ℓ ac $CaCO_3$,
- total chloride ($Cl^-$) concentration in mg/ℓ (necessary for characterisation of medium salinity waters)[#],
- total sulphate ($SO_4^{2-}$) concentration in mg $SO_4$/ℓ (necessary for characterisation of medium salinity waters)[#],
- ionic nature of the water (necessary for characterisation of low salinity waters) via either TDS (in mg/ℓ) or conductivity (in mS/m) or ionic strength, and
- value for a parameter to characterise the carbonate system, that is, any one of the following:
  - Total alkalinity (also termed $H_2CO_3$* alkalinity, in mg/ℓ as $CaCO_3$),
  - total carbonate species concentration ($C_T$) in mg/ℓ as $CaCO_3$,
  - $HCO_3^-$ acidity in mg/ℓ as $CaCO_3$, or
  - partial pressure of $CO_2$ in atmospheres.

[#]Note *For low salinity waters the input data entered into the program must contain pH, temperature, magnesium concentration if the magnesium softening task(s) is to be addressed, calcium concentration, ionic nature of the water and a value for one parameter to characterise the carbonate system. Any other species concentrations (that is, $Na^+$, $Cl^-$ and $SO_4^{2-}$) can be entered but are not utilised in the computational procedures.*

*For medium salinity waters the concentration of all the species constituting the principal ionic matrix (that is, $Na^+$, $Mg^{2+,}$ $Ca^{2+}$, $Cl^-$ and $SO_4^{2-}$) must be entered. In addition, pH, temperature and the value for one parameter to characterise the carbonate system also must be entered. If a value for the ionic nature of the water is entered, it will be* *overwritten by an ionic strength value determined by the program from the calculated free and ion paired species concentration of the principal ionic matrix.*

### 2.3 Tasks available in the program

The following tasks are available in the program and are explained in detail in Section 4:

- softening,
- pH adjustment by chemical conditioning,
- stabilisation to a desired $CaCO_3$ precipitation potential by chemical conditioning,
- blending of waters,
- change in state due to attainment of equilibrium with the air,
- temperature change of water,
- concentration change resulting from evaporation,
- change in state of underground waters brought into contact with the air, and
- treatment of calcium and carbonate species deficient waters

### 2.4 Output from the program

The output from the program after execution of a particular task is displayed on the screen and subsequently can be either printed or exported to a Microsoft Excel csv file (see Section 4). The following output regarding the water and conditioning chemical(s) is displayed to the user on completion of a task:

- total concentration of each of the dissolved species present ($Na^+$, $Mg^{2+}$, $Ca^{2+}$, $Cl^-$, and $SO_4^{2-}$),
- final pH and temperature,
- TDS, conductivity and ionic strength values,
- Total alkalinity, $CO_3^{2-}$ acidity and $CaCO_3$ precipitation potential, and
- dosage of the selected chemical needed to effect the desired task.

Note that output data obtained from any one task can be used as input data for any subsequent selected task (see Section 4)

## 3 PROGRAM LIMITATIONS

By extending the Stasoft program (since Version III) to include ion pairing effects, several program limitations of the earlier version were eliminated. However, certain limitations still exist for use of the extended program and are listed below.

- The TDS of the water should not exceed 15 000 mg/ℓ. At higher salinities ionic hydration becomes significant in estimation of activity coefficients, and a residual liquid junction potential causes the pH reading to deviate appreciably from the true pH. These waters can be characterised and conditioned by means of graphical aids, as discussed by Loewenthal and Marais (1984).

- In water reclamation, for the calculation of lime requirements in the high lime treatment stage of biologically treated secondary effluents. The presence of organic material increases the apparent $CaCO_3$ solubility product by an order of magnitude. No provision has been made in the program for changes of the solubility product due to the presence of organic material and hence the changes in state in the high lime treatment phase cannot be determined (see Wiechers 1977 and Wiechers *et al.* 1980 for a solution using graphically aided procedures). After carbon filter treatment the organic content is greatly reduced, the solubility product reverts to that for normal water and conditioning problems can be solved using the program.

- Stabilisation of natural soft brown waters containing humic and fulvic acids. These acids give rise to two effects:

    - The humic and fulvic acids contribute acidities and alkalinities additional to those due to the carbonate system. The theoretical relationships in the program include the carbonate system only. In consequence, dosage calculation from inputs of alkalinity and pH, determined on the natural brown waters using the methods developed for the carbonate system, will be in error.

    - The humic material slows down the rates of dissolution and precipitation of solid $CaCO_3$; in practical terms these are equivalent to an apparent high solubility product for dissolution of $CaCO_3$ (see Loewenthal *et al.* 1986 for detail). Once colour has been removed, the program procedures apply.

- The only weak acid system species considered to affect pH are those of the carbonate system. As such, the program cannot be used for situations where weak acid systems other than the carbonate system are present. For example, in anaerobic digestion in addition to the carbonate system the volatile fatty acid, phosphate, ammonium and sulphide weak acid systems may also be present in significant concentrations.

- In the assessment of underground waters, the iron (Fe) and manganese (Mn) systems have not been incorporated into the program. Consequently, if high concentrations of iron and manganese are present, the program cannot be used to characterise and/or condition such waters with any accuracy.

Based on the relevant algorithms and executing functions used within Stasoft V, it should be noted that some differences between values calculated for $CaCO_3$ precipitation potential exist for values determined via the previous Stasoft 4 and the new Stasoft V. Three examples for different waters with associated characteristics are provided in Table 1, with values for the calcium carbonate precipitation potential (CCPP) calculated from Stasoft 4 and Stasoft V provided for comparison.

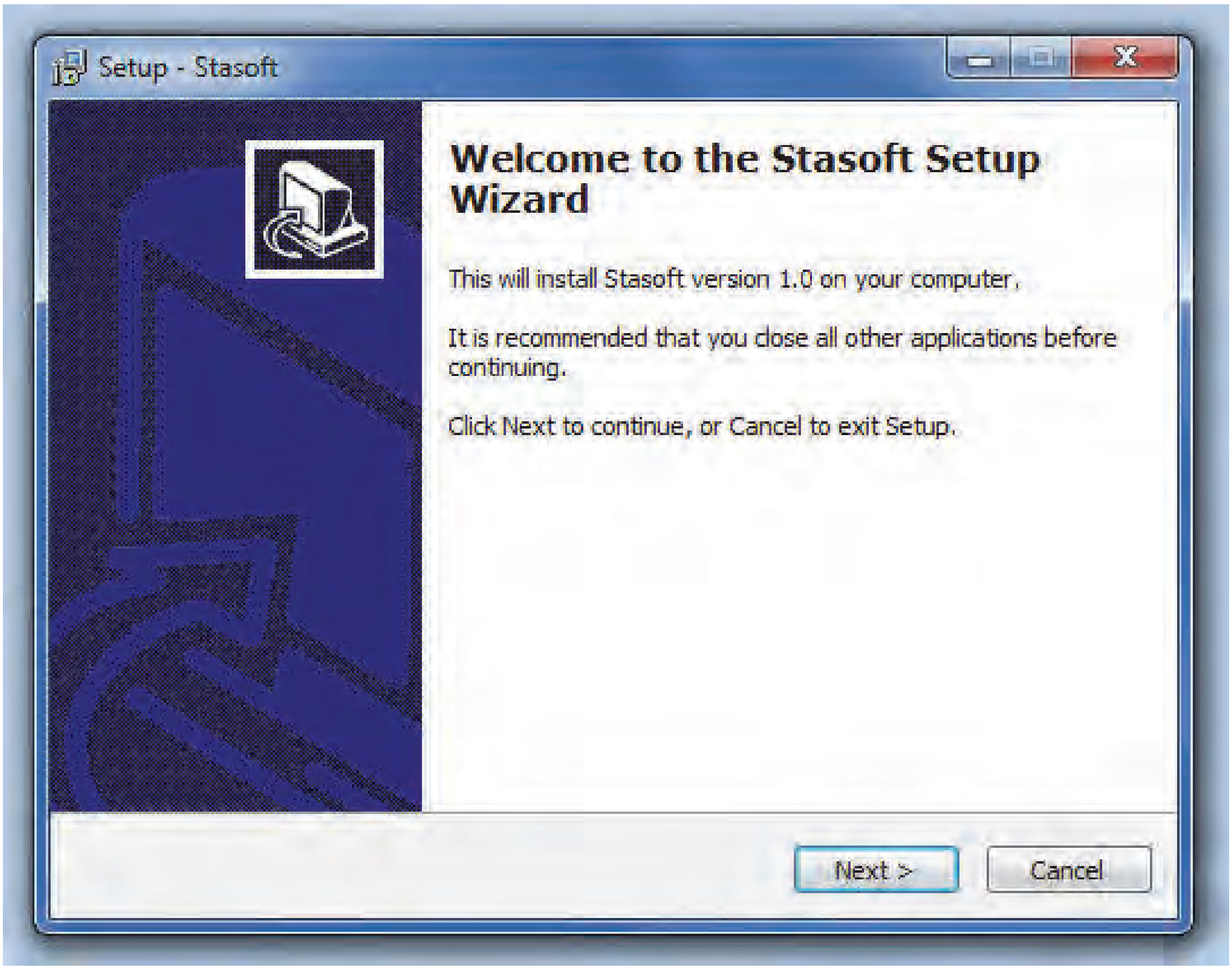
**Table 1: Calculation comparison between Stasoft 4 and Stasoft V.**

| Water characteristics | Water 1 | Water 2 | Water 3 |
|---|---|---|---|
| **pH** | 7 | 8 | 8,5 |
| **Temperature ($^oC$)** | 15 | 20 | 20 |
| **Ca (mg/ℓ as $CaCO_3$)** | 25 | 50 | 75 |
| **Alkalinity (mg/ℓ as $CaCO_3$)** | 20 | 80 | 120 |
| **Conductivity (mS/m)** | 20 | 25 | 25 |
| **CCPP (Stasoft 4)** | -12,1 | -1,1 | 9,0 |
| **CCPP (Stasoft V)** | -11,65 | -1,46 | 7,82 |

# 4 USER MANUAL

## 4.1 Installing the program

The Stasoft V software is distributed as a self-extracting file "Stasoft-setup.exe". Running this executable file the **Welcome to the Stasoft Setup Wizard** window comes up, as illustrated in Figure 1. (Depending on a user's antivirus software installed on his/her computer, the user may be asked to allow the program to make changes to his/her computer. Select <Yes> to continue.) Selecting <Next> the user has the opportunity of selecting the program's destination from the **Select Destination Location** window (Figure 2). Continue with the installation by selecting <Next> that brings up the **Select Start Menu Folder** window onto the screen (Figure 3). In this window the user may select the folder to place the program's shortcuts, with the default being "Stasoft".



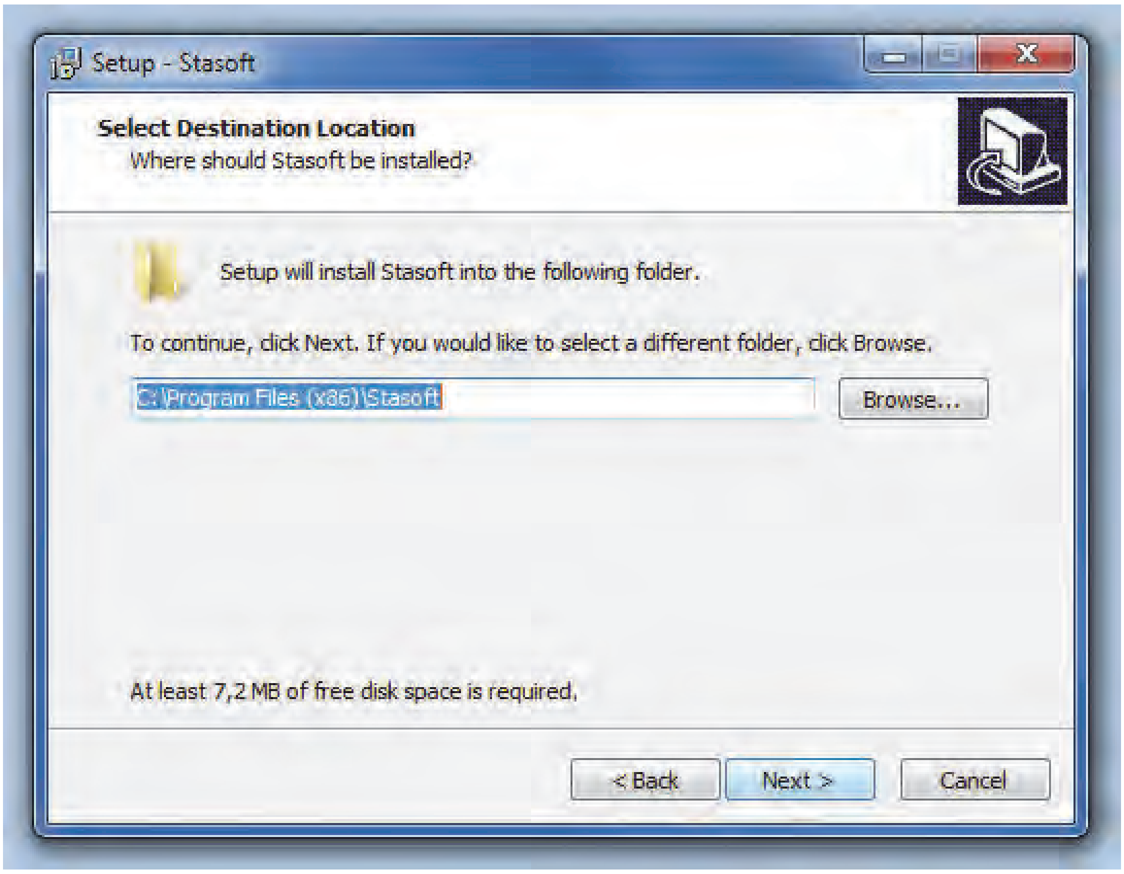
Welcome to the Stasoft Setup Wizard

This will install Stasoft version 1.0 on your computer.

It is recommended that you close all other applications before continuing.

Click Next to continue, or Cancel to exit Setup.

Figure 1: Welcome to the Stasoft Setup Wizard window.



Setup - Stasoft

**Select Destination Location**

Where should Stasoft be installed?

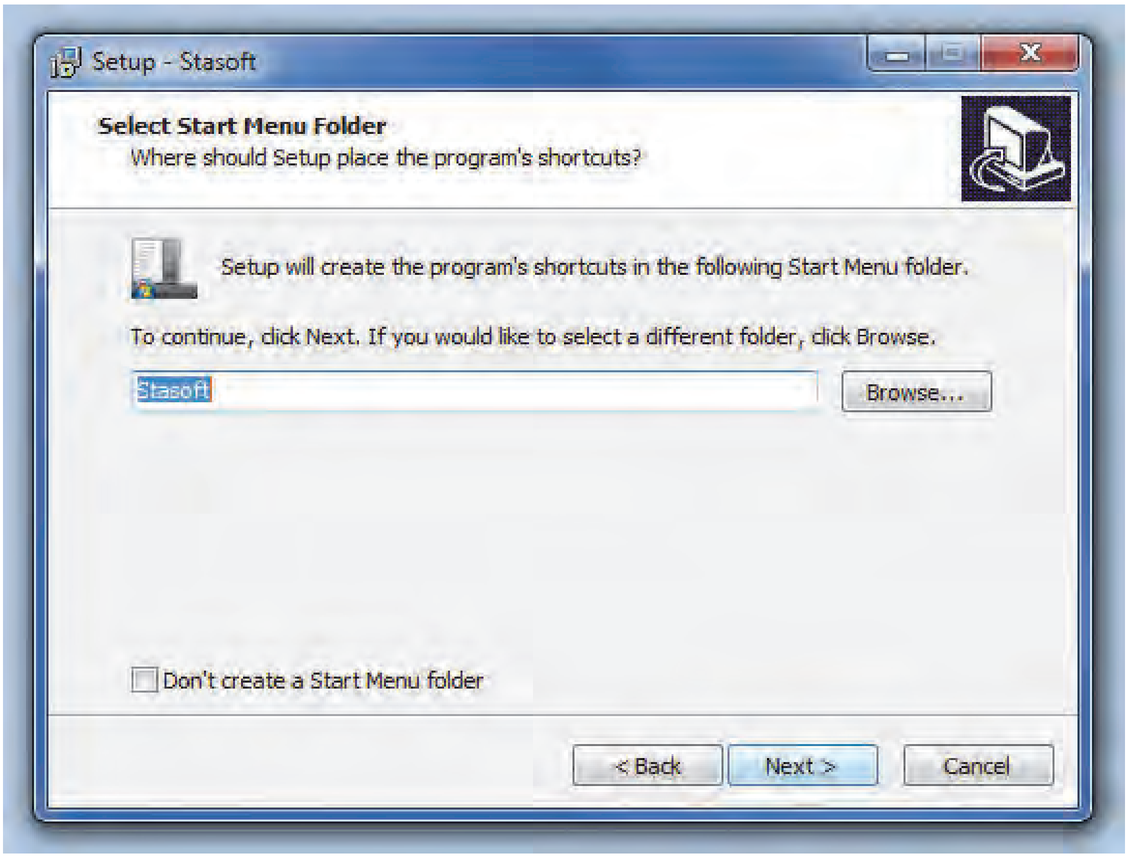
Setup will install Stasoft into the following folder.

To continue, click Next. If you would like to select a different folder, click Browse.

C:\Program Files (x86)\Stasoft

At least 7,2 MB of free disk space is required.

Figure 2: Select Destination Location window.



Setup - Stasoft

**Select Start Menu Folder**

Where should Setup place the program's shortcuts?

Setup will create the program's shortcuts in the following Start Menu folder.

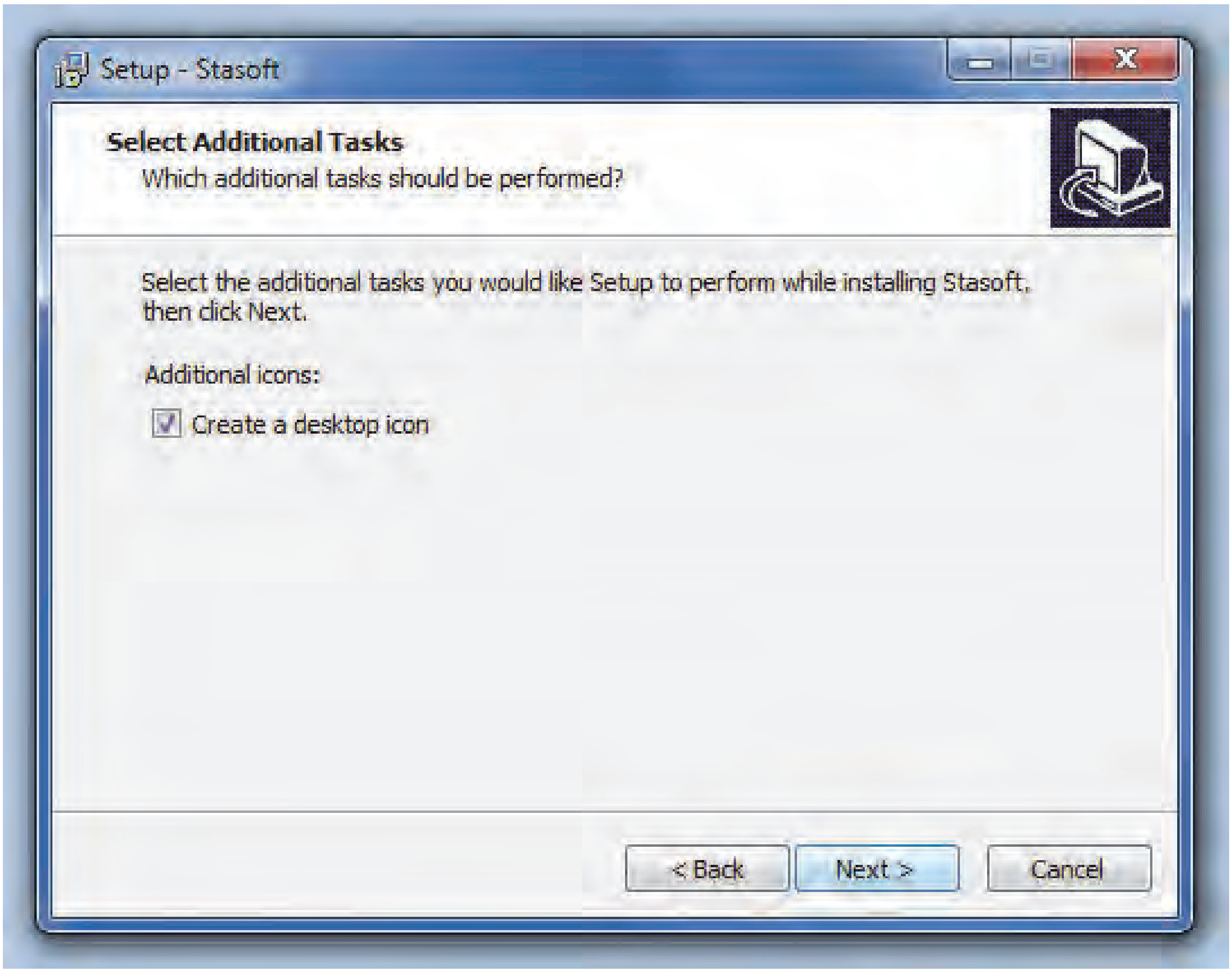
To continue, click Next. If you would like to select a different folder, click Browse.

Stasoft

☐ Don't create a Start Menu folder

Figure 3: Select Start Menu Folder window.

By selecting <Next> the **Select Additional Tasks** window is brought up (Figure 4). Here the user may select to create a desktop icon (default is selected). Selecting <Next> the **Ready to Install** screen comes up (Figure 5) and the user selects <Install> to complete the installation process. Once installation is complete the **Completing the Stasoft Setup Wizard** window comes up (Figure 6), providing the opportunity to launch Stasoft directly or the user may exit by selecting <Finish>.



Select Additional Tasks

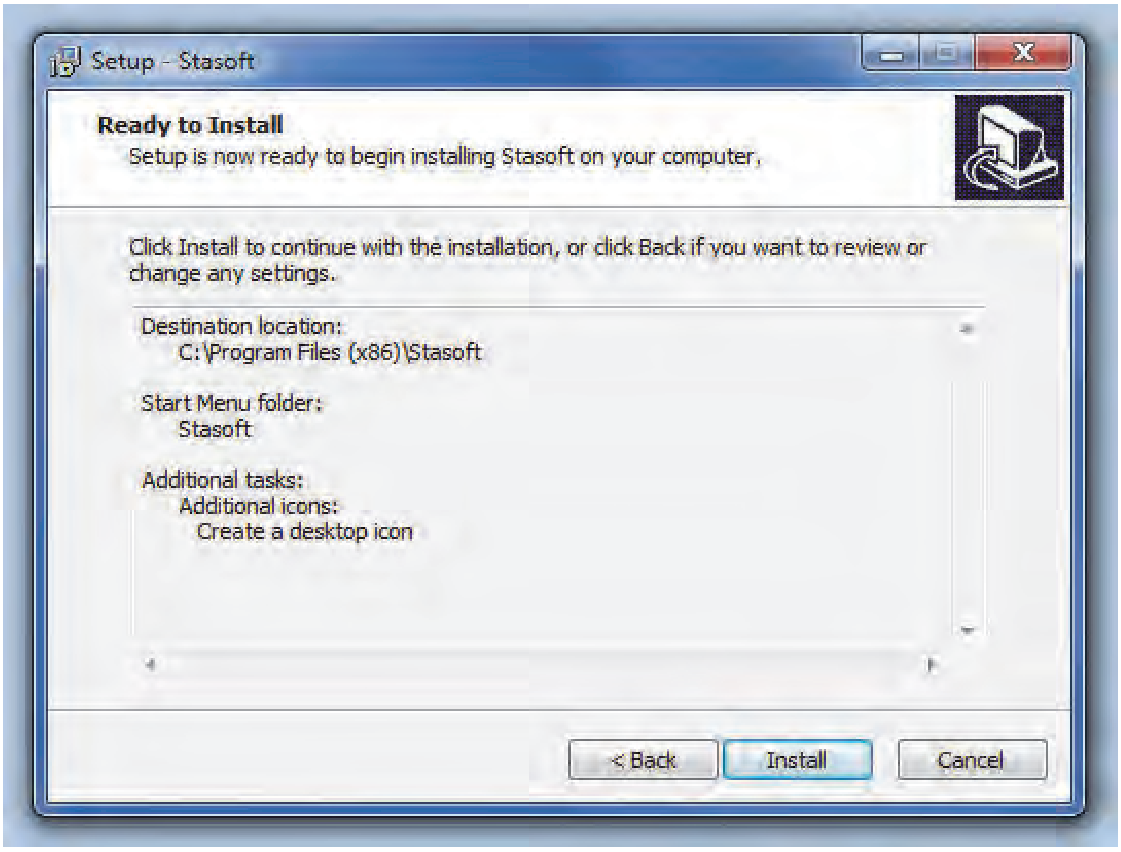
Which additional tasks should be performed?

Select the additional tasks you would like Setup to perform while installing Stasoft, then click Next.

Additional icons:

☑ Create a desktop icon

Figure 4: Select Additional Tasks window.



**Ready to Install**

Setup is now ready to begin installing Stasoft on your computer.

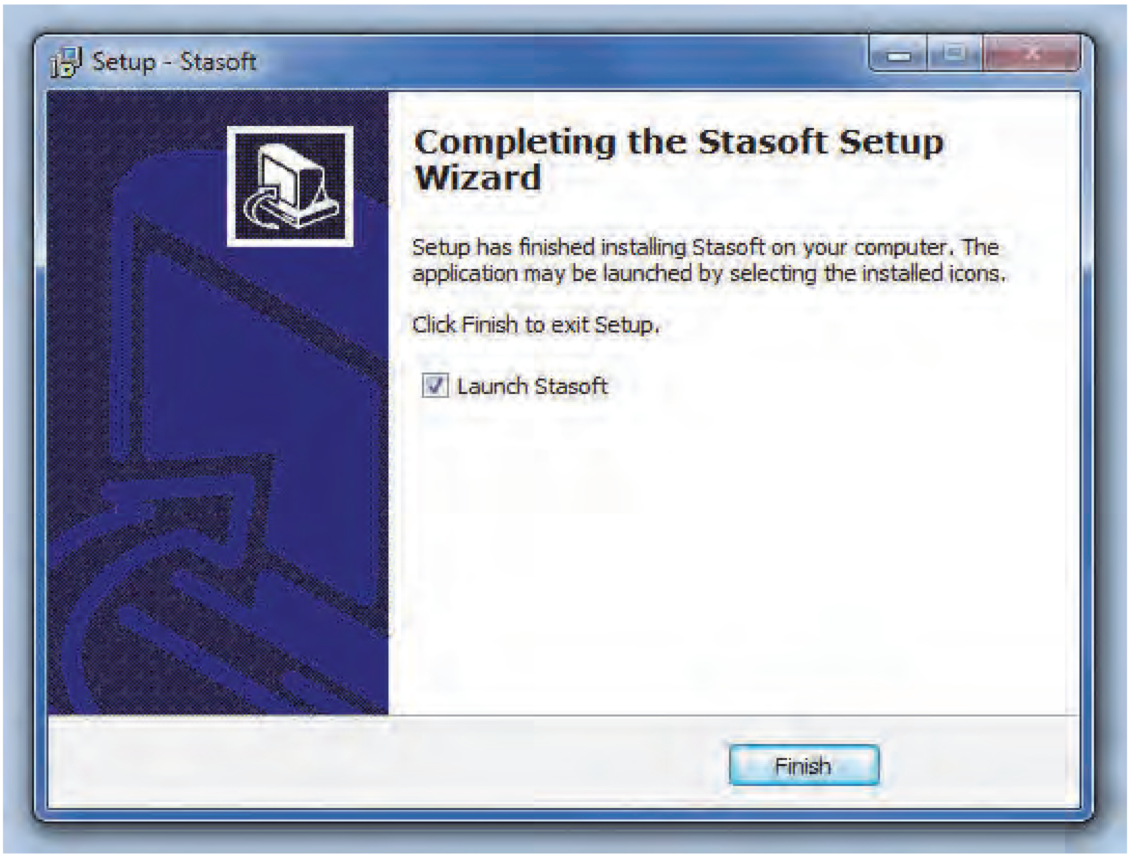
Click Install to continue with the installation, or click Back if you want to review or change any settings.

Destination location:
C:\Program Files (x86)\Stasoft

Start Menu folder:
Stasoft

Additional tasks:
Additional icons:
Create a desktop icon

Figure 5: Ready to Install window.



**Completing the Stasoft Setup Wizard**

Setup has finished installing Stasoft on your computer. The application may be launched by selecting the installed icons.

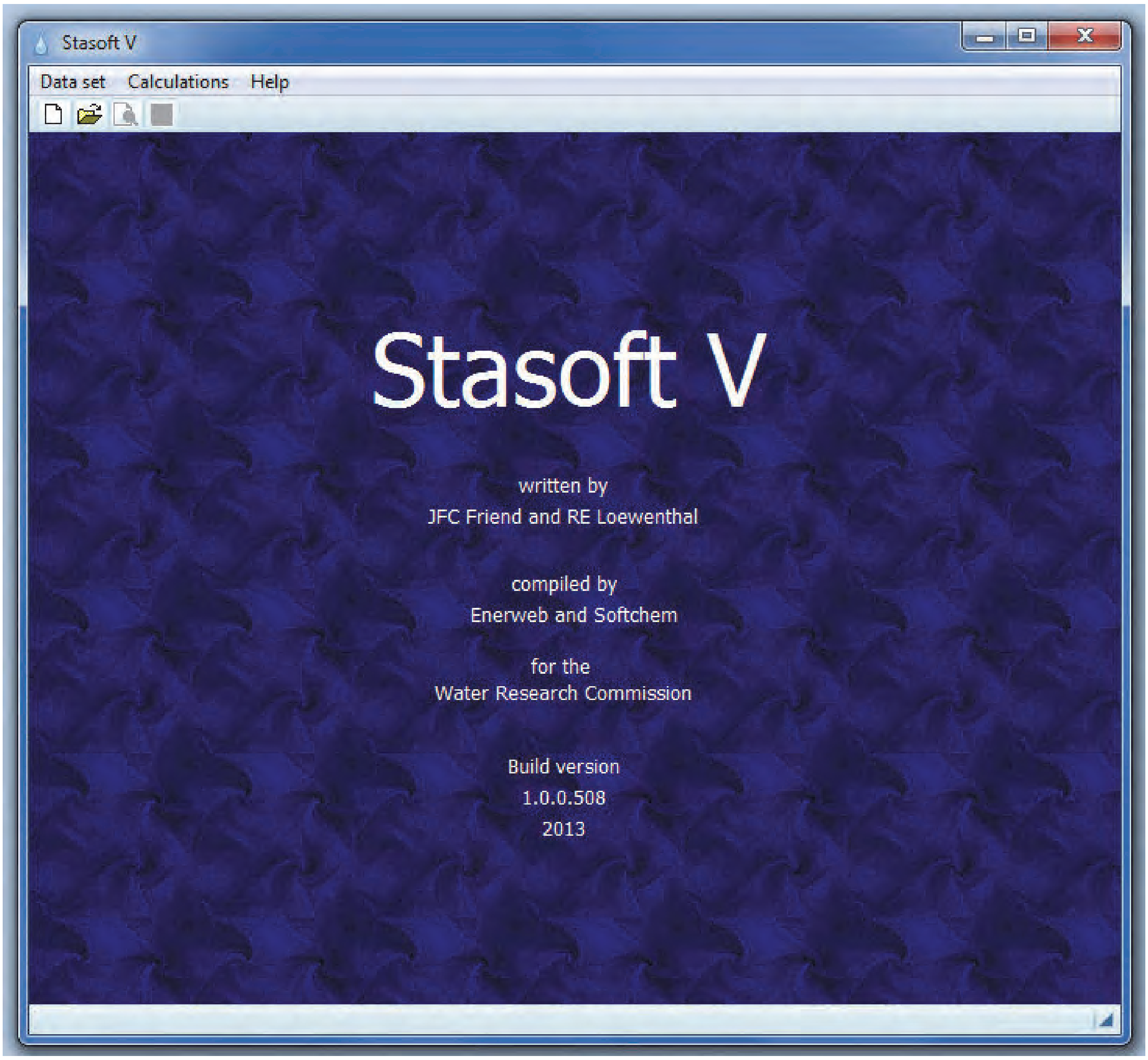
Click Finish to exit Setup.

☑ Launch Stasoft

Figure 6: Completing the Stasoft Setup Wizard window.

## 4.2 Using the program

By double clicking on the Stasoft desktop icon, see right, the program opens to display the title page, as shown in Figure 7.



Stasoft V

written by
JFC Friend and RE Loewenthal

compiled by
Enerweb and Softchem

for the
Water Research Commission

Build version
1.0.0.508
2013

Figure 7: Title page of the Stasoft V program.

### 4.2.1 The Data set menu option

By selecting the data set option, a pull-down menu appears on the screen as shown in Figure 8. A data set is a set of input values for a particular water. This data set will contain values for independent parameters describing the state of a water, for example, pH, Total alkalinity, temperature and conductivity.

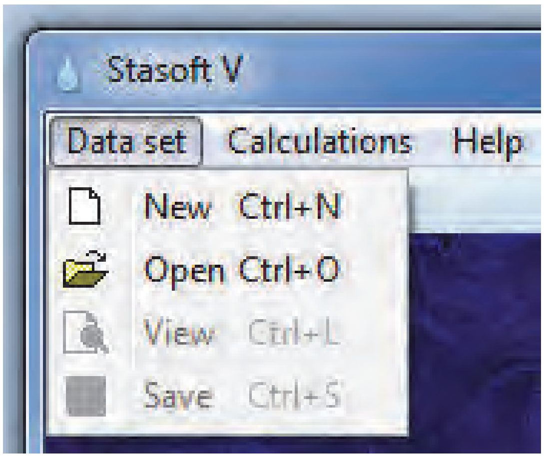
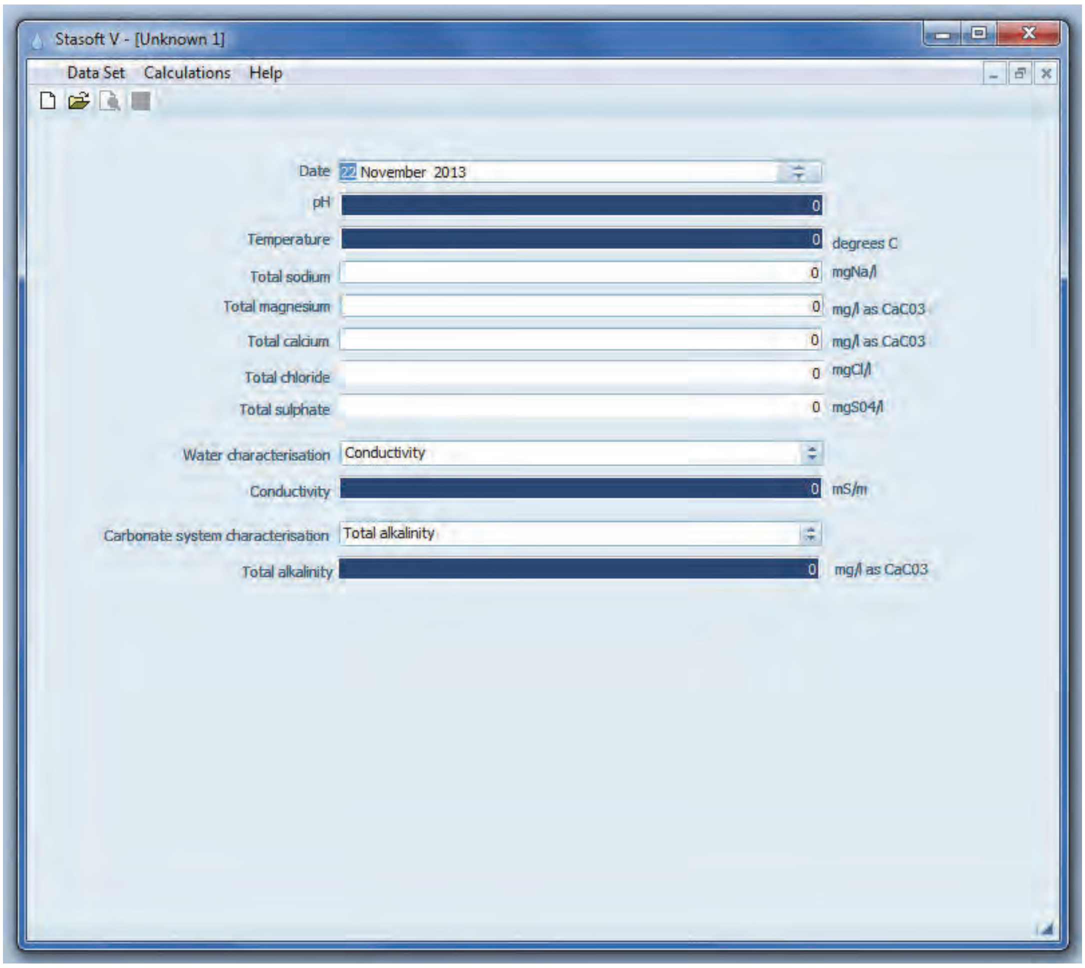


Figure 8: The Data set submenu.

All task calculations, except for the blending tasks, require a data set for a water. A data set either can be created by entering data via the <New> command on the data set submenu, or a previously saved data set can be selected via the <Open> command. Selecting the <New> option opens the **data set input** window, as shown in Figure 9.



Date 22 November 2013
pH 0
Temperature 0 degrees C
Total sodium 0 mgNa/l
Total magnesium 0 mg/l as CaC03
Total calcium 0 mg/l as CaC03
Total chloride 0 mgCl/l
Total sulphate 0 mgS04/l
Water characterisation Conductivity
Conductivity 0 mS/m
Carbonate system characterisation Total alkalinity
Total alkalinity 0 mg/l as CaC03

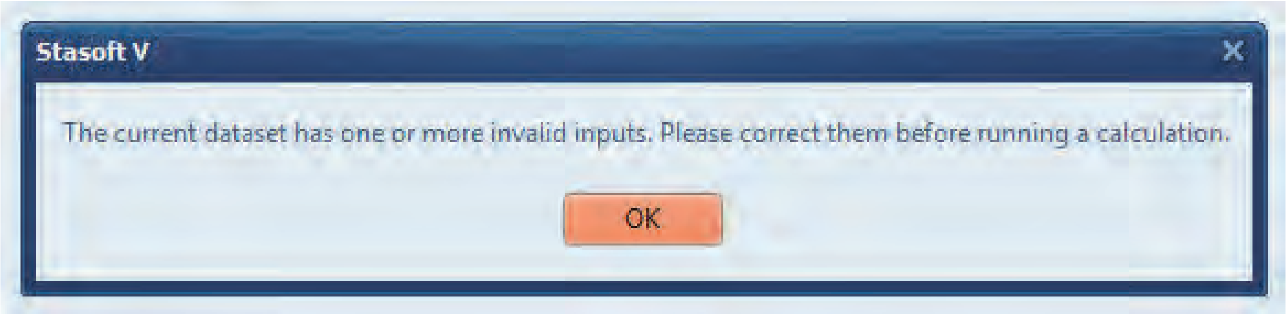
Figure 9: Data set input window.

For complete characterisation of low salinity waters and for subsequent conditioning calculations, the data set must contain values for the following:

- pH and temperature,
- the ionic nature of the water (either TDS, conductivity or ionic strength),
- a parameter characterising the carbonate system (either Total alkalinity, total carbonate species concentration, $HCO3^-$ acidity or partial pressure of $CO_2$ in the air), and
- Total alkalinity, $CO_3^{2-}$ acidity and $CaCO_3$ precipitation potential, and
- if softening of the water is required, the calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) concentrations must be entered.

For complete characterisation of medium salinity waters, the concentrations of the species constituting the principal ionic matrix ($Na^+$, $Mg^2$, $Ca^{2+}$, $Cl^-$ and $SO_4^{2-}$) must be entered.

If the **data set input** window is exited and the data set is either incomplete or contain some invalid inputs, the **notification message** in Figure 10 will appear on the screen and no subsequent calculations may be executed prior to a complete data set input. (Note that valid entries for different data are given at the bottom of the **data set input** window when a data entry box is activated.)



The current dataset has one or more invalid inputs. Please correct them before running a calculation.

**Figure 10: Notification message for incomplete/invalid inputs.**

When selecting the <Open> option the **file name input** window will appear, see Figure 11, and the user may select a previously saved file. (Note that all Stasoft files will have the extension xxxx.sft.) Once a file is loaded the data of the relevant file will appear within a **data set input** window. All data within this window, whether new or from a previously saved file, can be edited within this window.

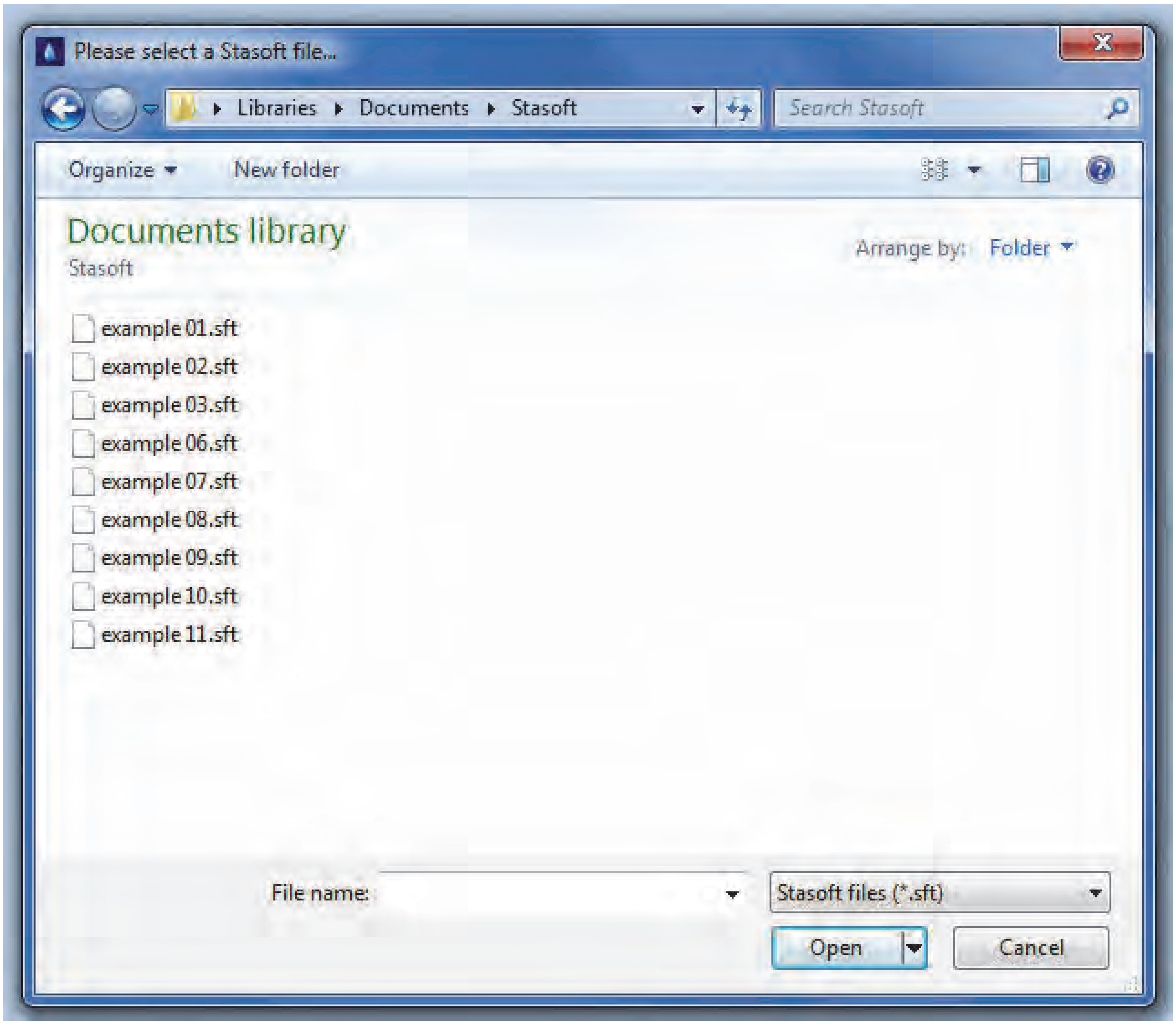
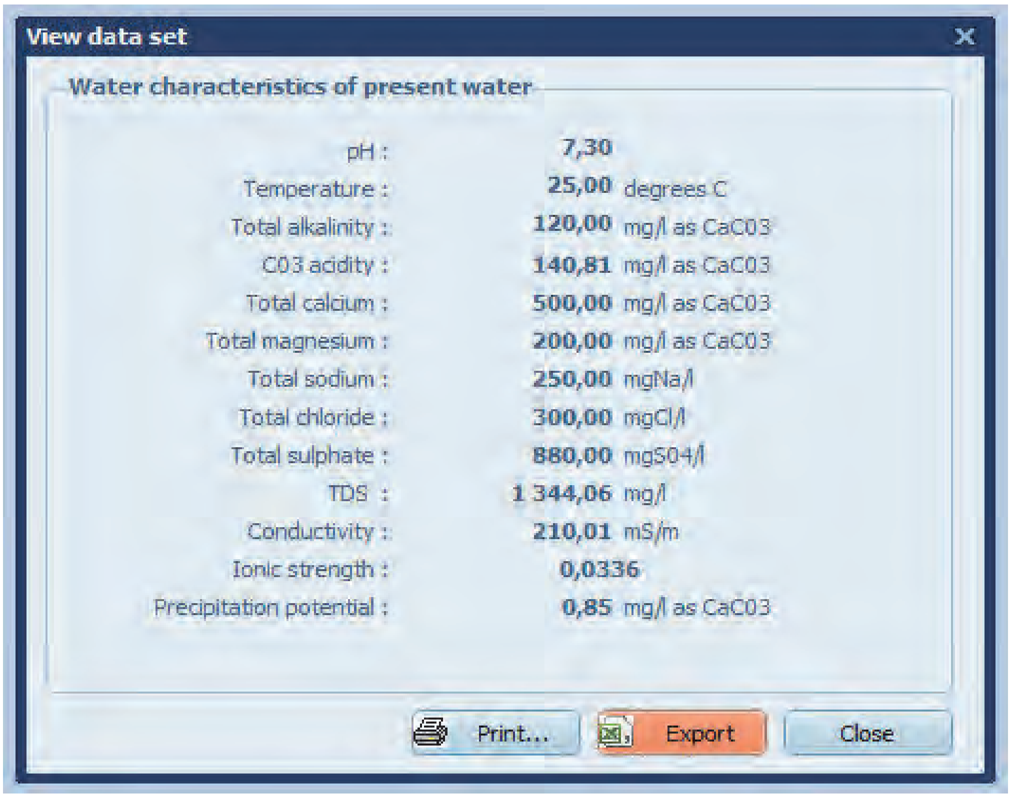


Figure 11: File name input window.

The third command of the Data set menu option allows the user to view the current characteristics of a water (for example, the $CaCO_3$ precipitation potential) by selecting the <View> command, resulting in the **water characteristics** window to appear onto the screen (see Figure 12). The information displayed on the screen can be either printed or exported to a Microsoft Excel csv file.

With the final command of the Data set menu option an active/current data set can be saved to a relevant folder. Selecting the <Save> command will open the **data set save** window (see Figure 13) that allows the user to save the relevant data set to a selected folder.

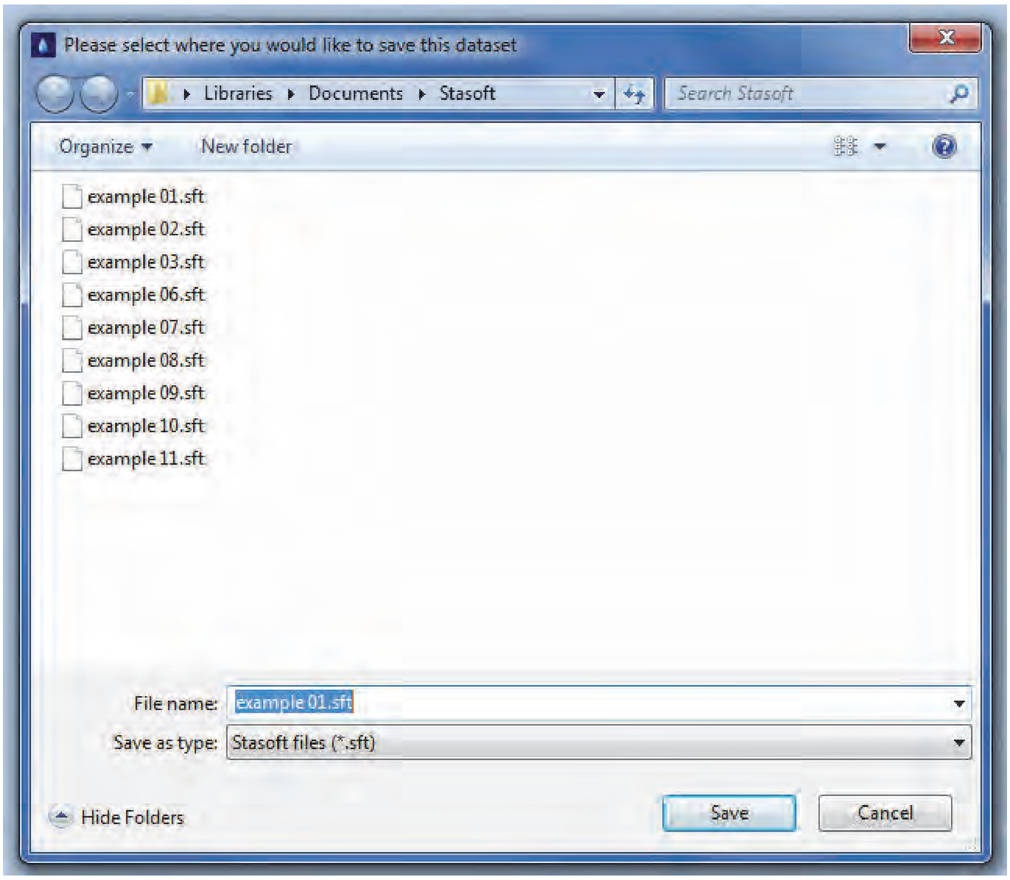
All four submenu commands of the Data set menu option are also available as taskbar icons below the main menu, as seen below for the New, Open, View and Save submenus respectively:



Water characteristics of present water

| | | |
|---|---|---|
| pH : | 7,30 | |
| Temperature : | 25,00 | degrees C |
| Total alkalinity : | 120,00 | mg/l as CaC03 |
| C03 acidity : | 140,81 | mg/l as CaC03 |
| Total calcium : | 500,00 | mg/l as CaC03 |
| Total magnesium : | 200,00 | mg/l as CaC03 |
| Total sodium : | 250,00 | mgNa/l |
| Total chloride : | 300,00 | mgCl/l |
| Total sulphate : | 880,00 | mgS04/l |
| TDS : | 1 344,06 | mg/l |
| Conductivity : | 210,01 | mS/m |
| Ionic strength : | 0,0336 | |
| Precipitation potential : | 0,85 | mg/l as CaC03 |

Figure 12: Water characteristics window.



example 01.sft
example 02.sft
example 03.sft
example 06.sft
example 07.sft
example 08.sft
example 09.sft
example 10.sft
example 11.sft

File name: example 01.sft
Save as type: Stasoft files (*.sft)

Figure 13: Data set save window.

### 4.2.2 The Calculations menu option

By selecting the calculation menu option, a pull-down menu appears on the screen as shown in Figure 14. Nine menu options are available from the Calculations submenu, with each being described in more detail below.

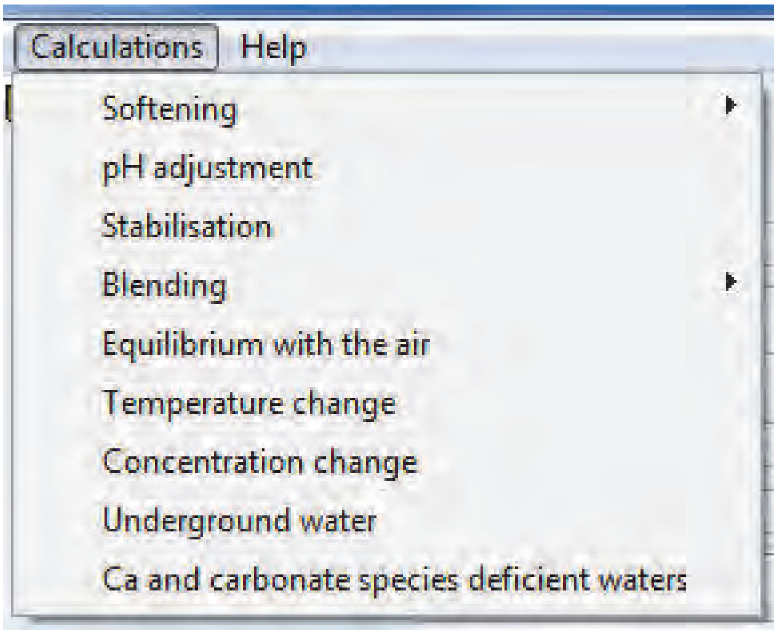


Figure 14: The Calculations submenu.

### 4.2.3 Softening

In this option the dosages of lime and/or soda ash required to soften a water to a desired calcium and/or magnesium value are determined. Three options are available once this menu option is selected, namely softening to a desired Ca value, to a desired Mg value and to both Ca and Mg desired values (see Figure 15).

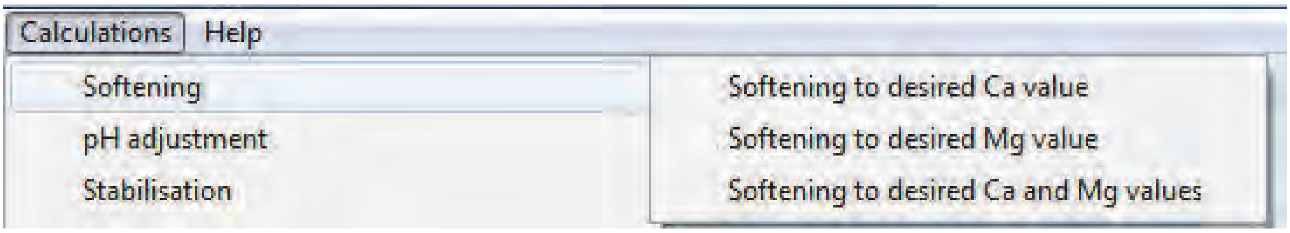


Figure 15: Softening options window.

### 4.2.4 pH adjustment

In this option the chemical dosage required to adjust the pH is determined. Six chemicals are available for dosage:

- lime - $Ca(OH)_2$,
- soda ash - $Na_2CO_3$,
- caustic soda - NaOH,
- carbon dioxide - $CO_2$,
- either hydrochloric acid - HCl or sulphuric acid - $H_2SO_4$, and

- bicarbonate of soda - $NaHCO_3$.

### 4.2.5 Stabilisation

In this option the chemical dosage required to stabilise a water to a desired $CaCO_3$ precipitation potential is determined. The same chemicals that are available for pH adjustment, except bicarbonate of soda, are available for dosage.

### 4.2.6 Blending

In this option either the fractions required to blend two waters to a specified pH or the final state of a water after blending several waters (maximum 20) can be determined. The two blending options become available after selection of this option, as illustrated in Figure 16.

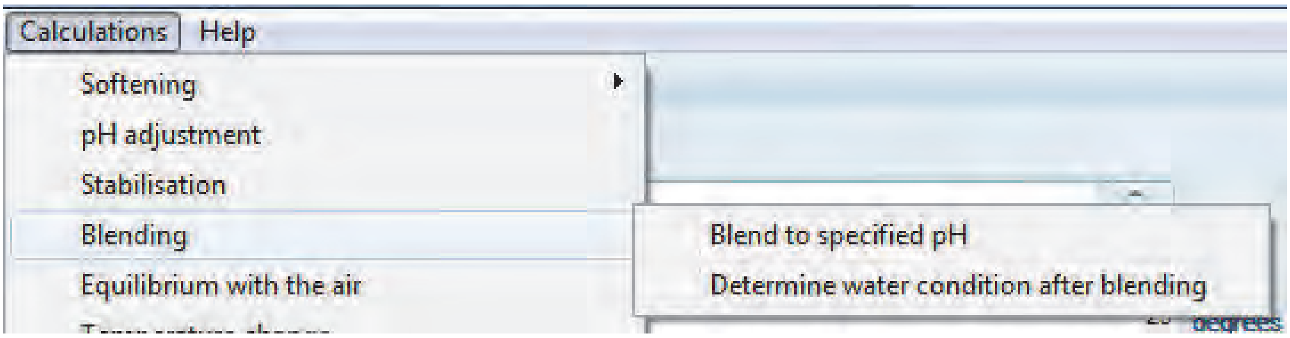


Figure 16: Blending options window.

### 4.2.7 Equilibrium with the air

In this option the final state of a water, after equilibrium with the air has been established, is determined.

### 4.2.8 Temperature change

In this option the final state of a water after a change in temperature is determined.

### 4.2.9 Concentration change

In this option the final state of a water after a change in concentration, due to evaporation, is determined.

### 4.2.10 Underground water

In this option two tasks are executed with results available in two consecutive windows:

- the equilibrium state that the water will attain if allowed to come to equilibrium with $CO_2$ in the air, that is, two phase equilibrium (aqueous-gas), is determined; and

- the equilibrium state that the water will attain if allowed to come to equilibrium with $CO_2$ in the air and solid $CaCO_3$ in solution, that is, three phase equilibrium (solid-aqueous-gas), is determined.

#### 4.2.11 Ca and carbonate species deficient waters

In this option the dosage of lime required to increase the calcium concentration and alkalinity values of a calcium and carbonate deficient water is determined. In addition the amount of $CO_2$ required to adjust the water to a prescribed $CaCO_3$ precipitation potential is determined.

All options introduced above are described in detail in the examples set out in Section 4.3.

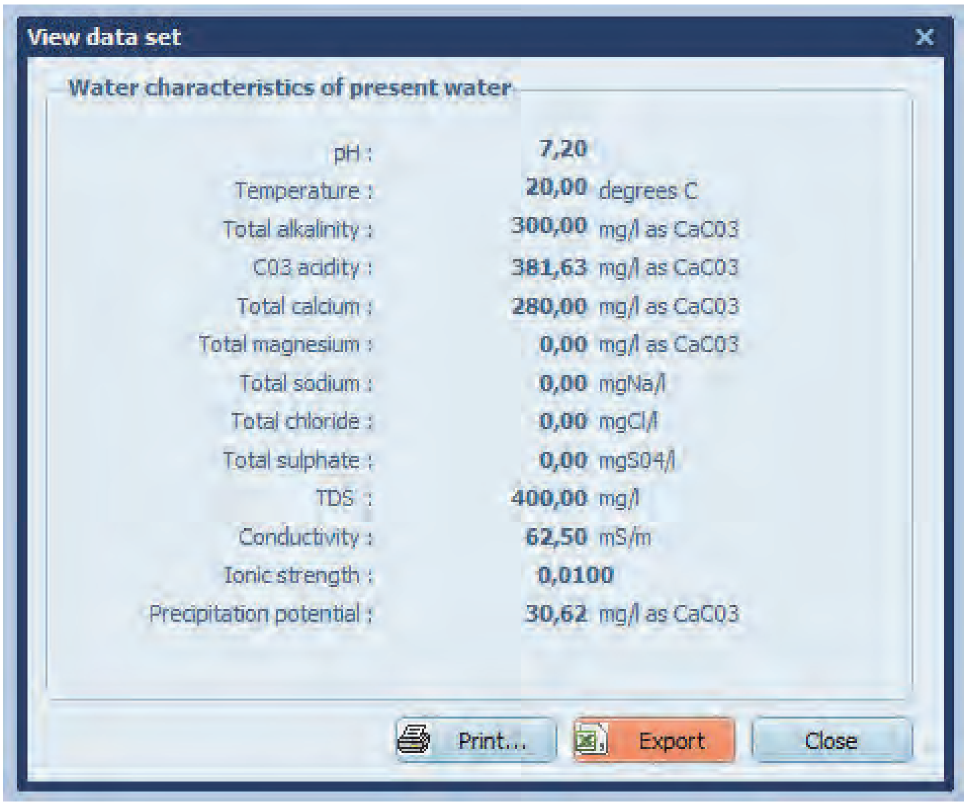
### 4.3 Examples

A number of typical conditioning problems are presented to illustrate the program capability and to serve as benchmarks for the program user. In each example the user is directed in the use of the menus to obtain the required results.

#### 4.3.1 Example 1: Calcium softening using lime

Analyses of a water gives Total alkalinity 300 mg/ℓ, calcium 280 mg/ℓ (both as $CaCO_3$), pH 7,2, TDS 400 mg/ℓ ($\mu$ = 0,01) and temperature 20°C. Determine the $Ca(OH)_2$ dosage to soften the water to $Ca^{2+}$ 100 mg/ℓ as $CaCO_3$. The solution procedure using the Stasoft program is set out below.

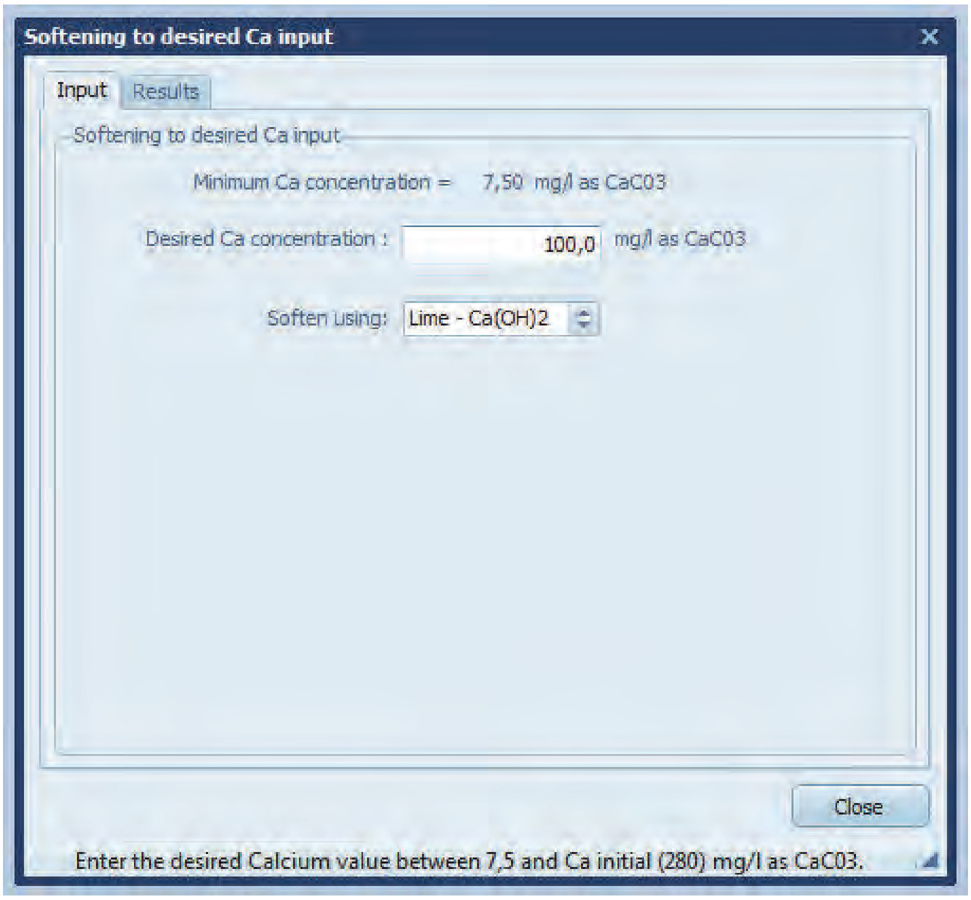
After entering the data into the **data set input** window (Figure 9), selection of the <View> option will bring the window displaying the characteristics of the present water onto the screen (Figure 17). Close the window and select <Softening> and <Softening to desired Ca value> from the Calculations menu. This will bring up the **Softening to desired Ca input** window onto the screen (Figure 18). The minimum and maximum calcium concentrations that the water can be softened to are displayed in the window (the maximum is less than the initial calcium input concentration). Enter the specified final calcium concentration of 100 mg/ℓ as $CaCO_3$ by typing **100** in the input box and select the lime option, as illustrated in Figure 18.



Water characteristics of present water

pH : 7,20
Temperature : 20,00 degrees C
Total alkalinity : 300,00 mg/l as CaC03
C03 acidity : 381,63 mg/l as CaC03
Total calcium : 280,00 mg/l as CaC03
Total magnesium : 0,00 mg/l as CaC03
Total sodium : 0,00 mgNa/l
Total chloride : 0,00 mgCl/l
Total sulphate : 0,00 mgS04/l
TDS : 400,00 mg/l
Conductivity : 62,50 mS/m
Ionic strength : 0,0100
Precipitation potential : 30,62 mg/l as CaC03

Figure 17: Window displaying the characteristic of the water used in Example 1.



Softening to desired Ca input

Minimum Ca concentration = 7,50 mg/l as CaC03

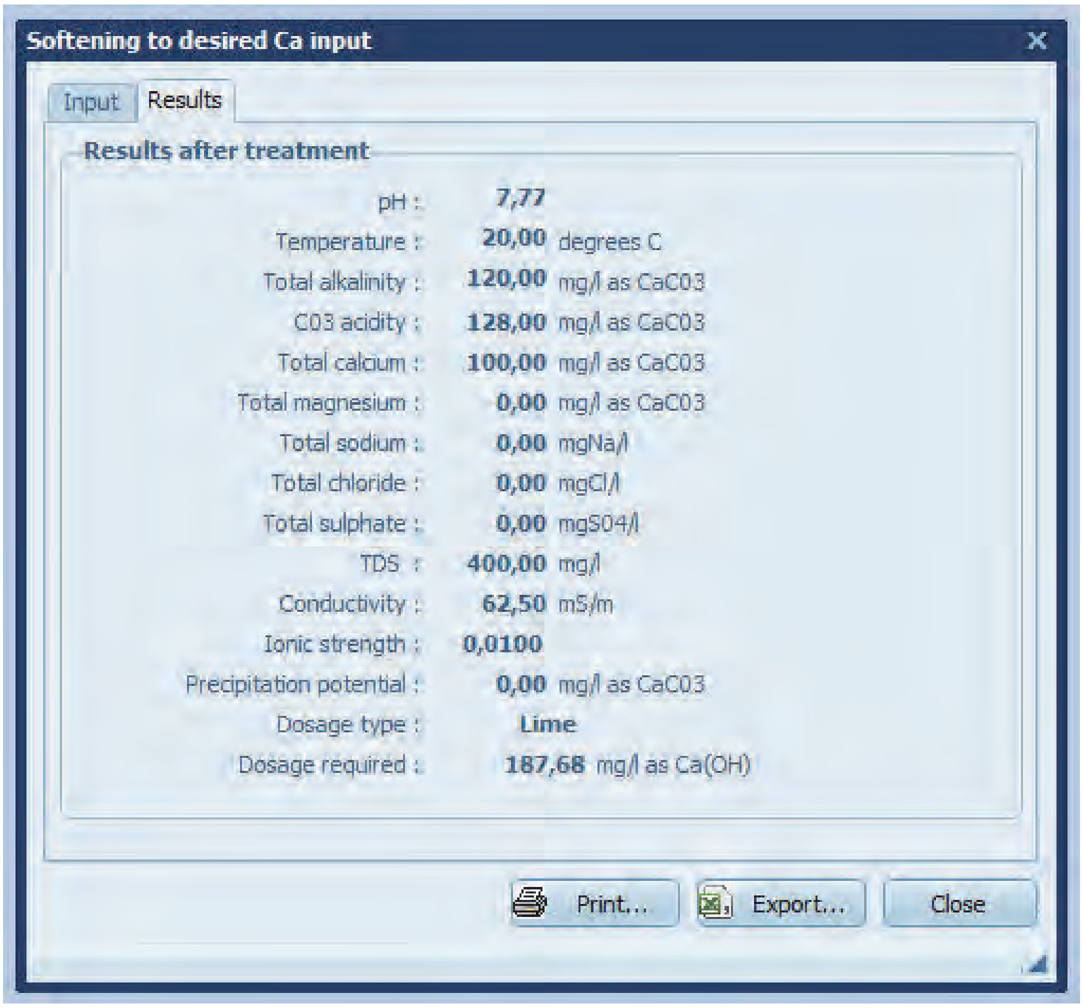
Desired Ca concentration : 100,0 mg/l as CaC03

Soften using: Lime - Ca(OH)2

Enter the desired Calcium value between 7,5 and Ca initial (280) mg/l as CaC03.

Figure 18: Softening to desired Ca input window.

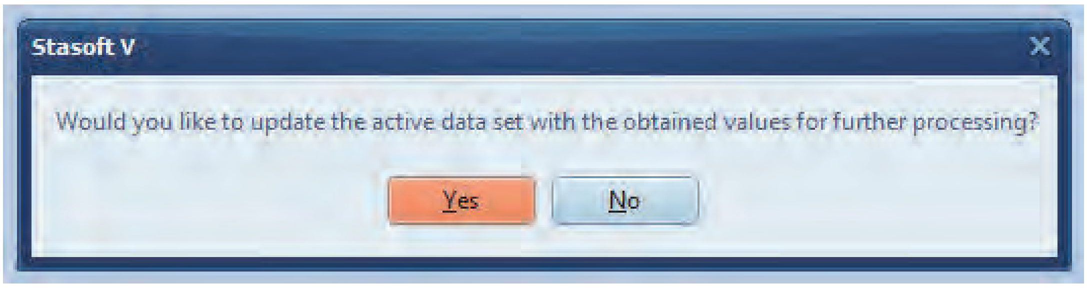
Selection of the <Results> menu option will bring the **results after treatment** window onto the screen with values for the new state of the water and the dosage of lime required to soften the water to the prescribed calcium concentration, as shown in Figure 19. The results displayed on the screen can be either printed or exported to a Microsoft Excel csv file. Selecting the <Close> option allows the user to update the active data set with the present water's characteristics for further processing (for example, pH adjustment or stabilisation) in the **update data set** window (Figure 20).



Results after treatment

pH : 7,77
Temperature : 20,00 degrees C
Total alkalinity : 120,00 mg/l as CaC03
C03 acidity : 128,00 mg/l as CaC03
Total calcium : 100,00 mg/l as CaC03
Total magnesium : 0,00 mg/l as CaC03
Total sodium : 0,00 mgNa/l
Total chloride : 0,00 mgCl/l
Total sulphate : 0,00 mgS04/l
TDS : 400,00 mg/l
Conductivity : 62,50 mS/m
Ionic strength : 0,0100
Precipitation potential : 0,00 mg/l as CaC03
Dosage type : Lime
Dosage required : 187,68 mg/l as Ca(OH)

**Figure 19: Results after treatment window for Example 1.**



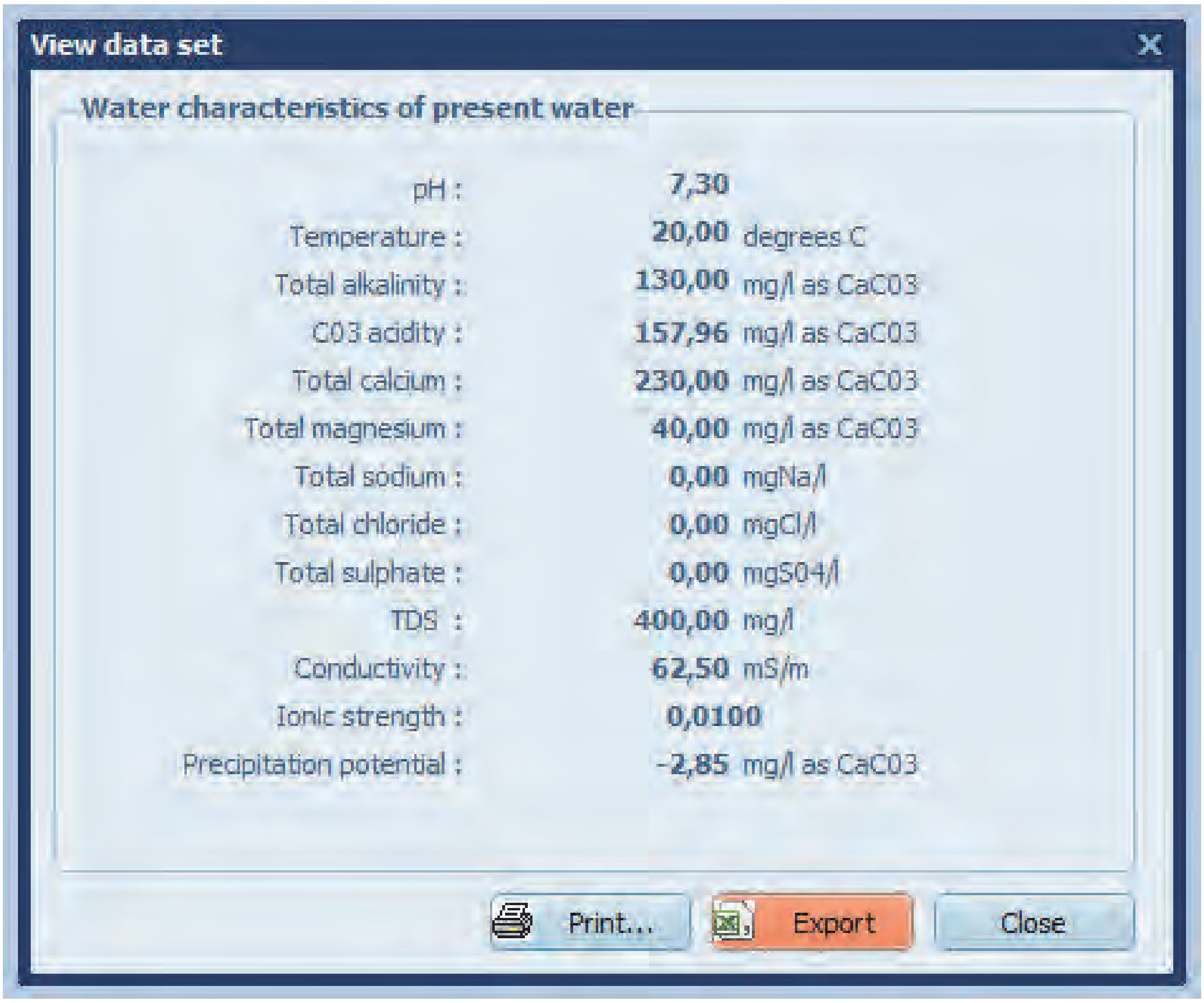
Would you like to update the active data set with the obtained values for further processing?

**Figure 20: Update data set window.**

### 4.3.2 Example 2: Calcium and magnesium softening using lime and soda ash

A water has the following characteristics: Total alkalinity 130 mg/ℓ, calcium 230 mg/ℓ, magnesium 40 mg/ℓ (all as $CaCO_3$), pH 7,3, TDS 400 mg/ℓ and temperature 20°C. The water is to be softened, using lime and soda ash, to calcium 60 mg/ℓ and magnesium 4 mg/ℓ (both as $CaCO_3$). Thereafter the water is to be stabilised using $CO_2$ to give a $CaCO_3$ precipitation potential of 5 mg/ℓ as $CaCO_3$. Determine the chemical dosages and the final state of the water. A solution procedure is set out below.

After entering the data into the **data set input** window (Figure 9), selection of the <View> option will bring the window displaying the characteristics of the present water onto the screen (Figure 21). Close the window and select <Softening> and <Softening to desired Ca and Mg values> from the Calculations menu. This will bring up the **Softening to desired Ca and Mg inputs** window onto the screen (Figure 22).

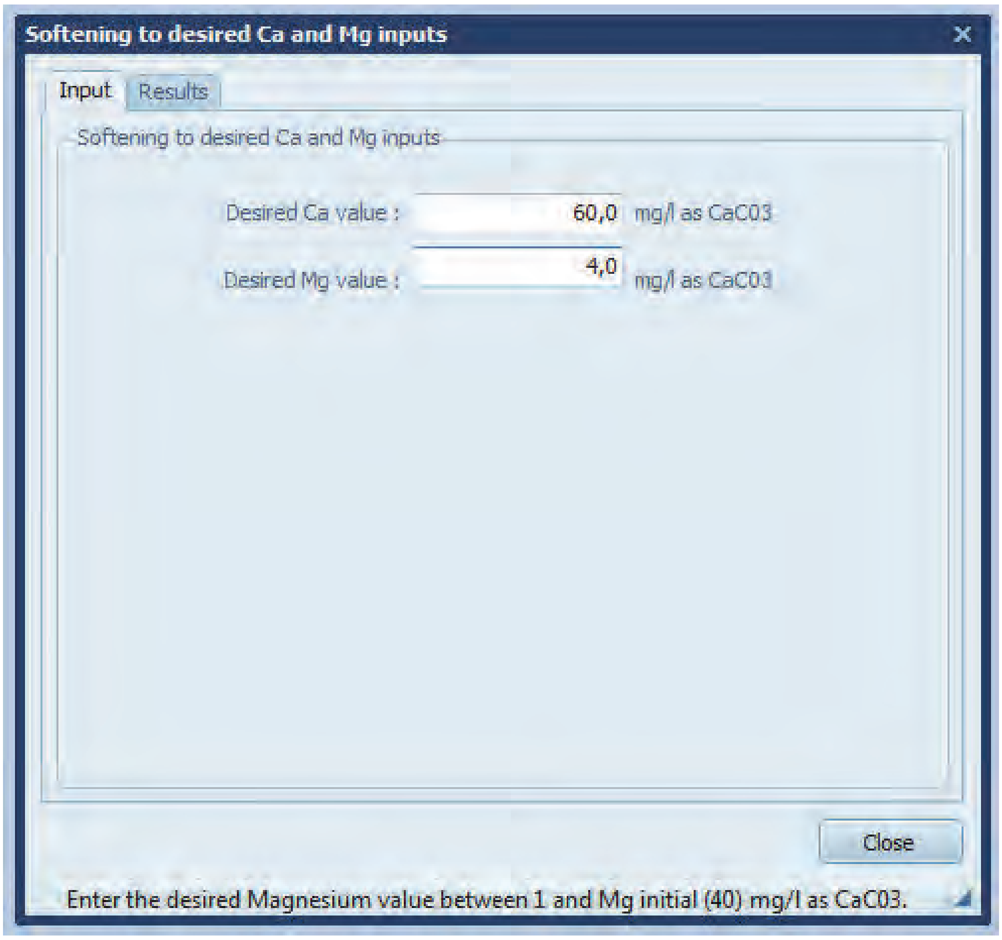


pH : 7,30
Temperature : 20,00 degrees C
Total alkalinity : 130,00 mg/l as CaC03
C03 acidity : 157,96 mg/l as CaC03
Total calcium : 230,00 mg/l as CaC03
Total magnesium : 40,00 mg/l as CaC03
Total sodium : 0,00 mgNa/l
Total chloride : 0,00 mgCl/l
Total sulphate : 0,00 mgS04/l
TDS : 400,00 mg/l
Conductivity : 62,50 mS/m
Ionic strength : 0,0100
Precipitation potential : -2,85 mg/l as CaC03

Figure 21: Window displaying the characteristics of the water used in Example 2.

Enter the specified final calcium concentration of 60 mg/ℓ as $CaCO_3$ by typing **60** into the desired Ca value input box (the desired calcium concentration must be greater than 2 mg/ℓ as $CaCO_3$ and smaller than the initial calcium concentration). Enter the specified final magnesium concentration of 4 mg/ℓ as $CaCO_3$ by typing **4** into the desired Mg value input box (the desired magnesium concentration must be smaller than the initial magnesium concentration and greater than 1 mg/ℓ as $CaCO_3$). Both entries illustrated in Figure 22.

Selection of the <Results> menu option will bring the **results after treatment** window onto the screen with values for the new state of the water and the dosages of lime and soda ash required to soften the water to the prescribed calcium and magnesium concentrations, as shown in Figure 23. The results displayed on the screen can be either printed or exported to a Microsoft Excel csv file. Selecting the <Close> option allows the user to update the active data set with the present water's characteristics for further processing in the **update data set** window (Figure 20). Select <Yes> and then select the <Stabilisation> option from the Calculations menu, bringing up the **stabilisation inputs** window for recarbonation of the present/active water, as illustrated in Figure 24.

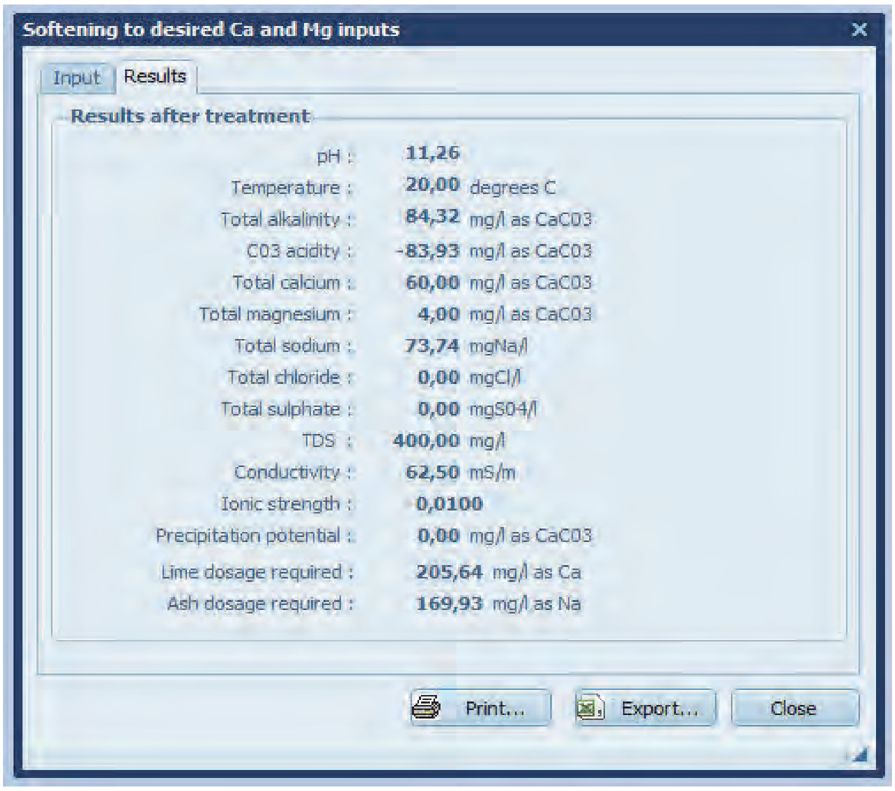


Desired Ca value : 60,0 mg/l as CaC03

Desired Mg value : 4,0 mg/l as CaC03

Enter the desired Magnesium value between 1 and Mg initial (40) mg/l as CaC03.

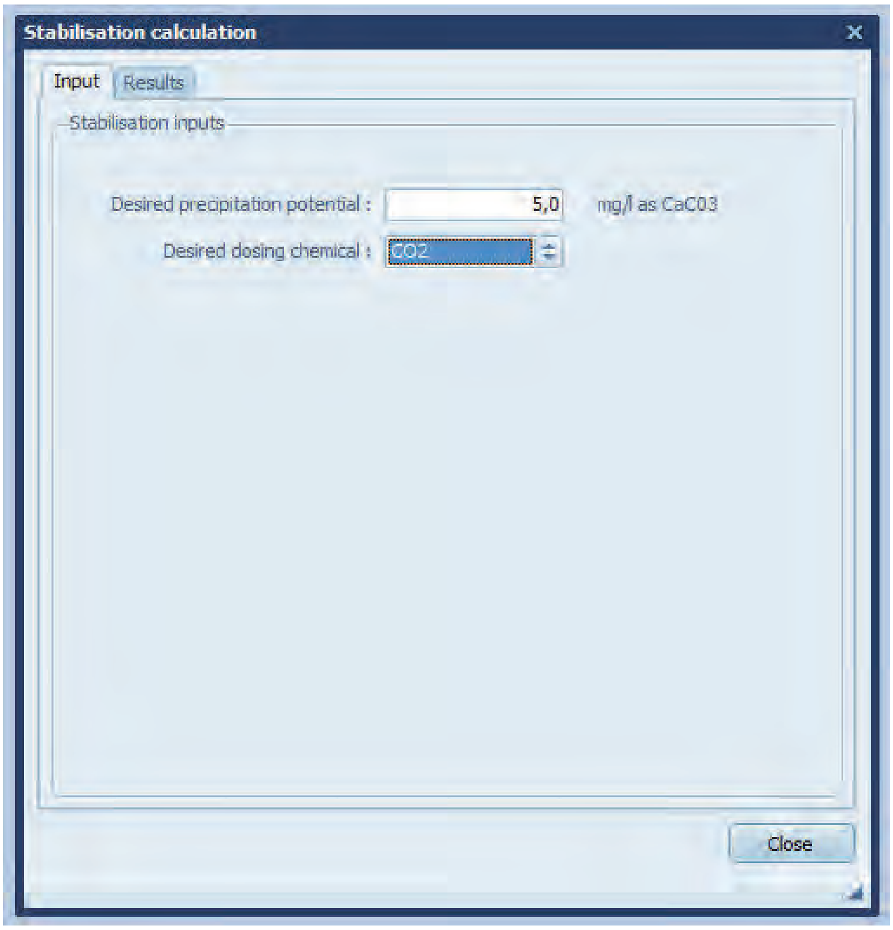
Figure 22: Softening to desired Ca and Mg inputs window.



Results after treatment

pH : 11,26
Temperature : 20,00 degrees C
Total alkalinity : 84,32 mg/l as CaC03
C03 acidity : -83,93 mg/l as CaC03
Total calcium : 60,00 mg/l as CaC03
Total magnesium : 4,00 mg/l as CaC03
Total sodium : 73,74 mgNa/l
Total chloride : 0,00 mgCl/l
Total sulphate : 0,00 mgS04/l
TDS : 400,00 mg/l
Conductivity : 62,50 mS/m
Ionic strength : 0,0100
Precipitation potential : 0,00 mg/l as CaC03
Lime dosage required : 205,64 mg/l as Ca
Ash dosage required : 169,93 mg/l as Na

Figure 23: Results after treatment window for Example 2 (softening).

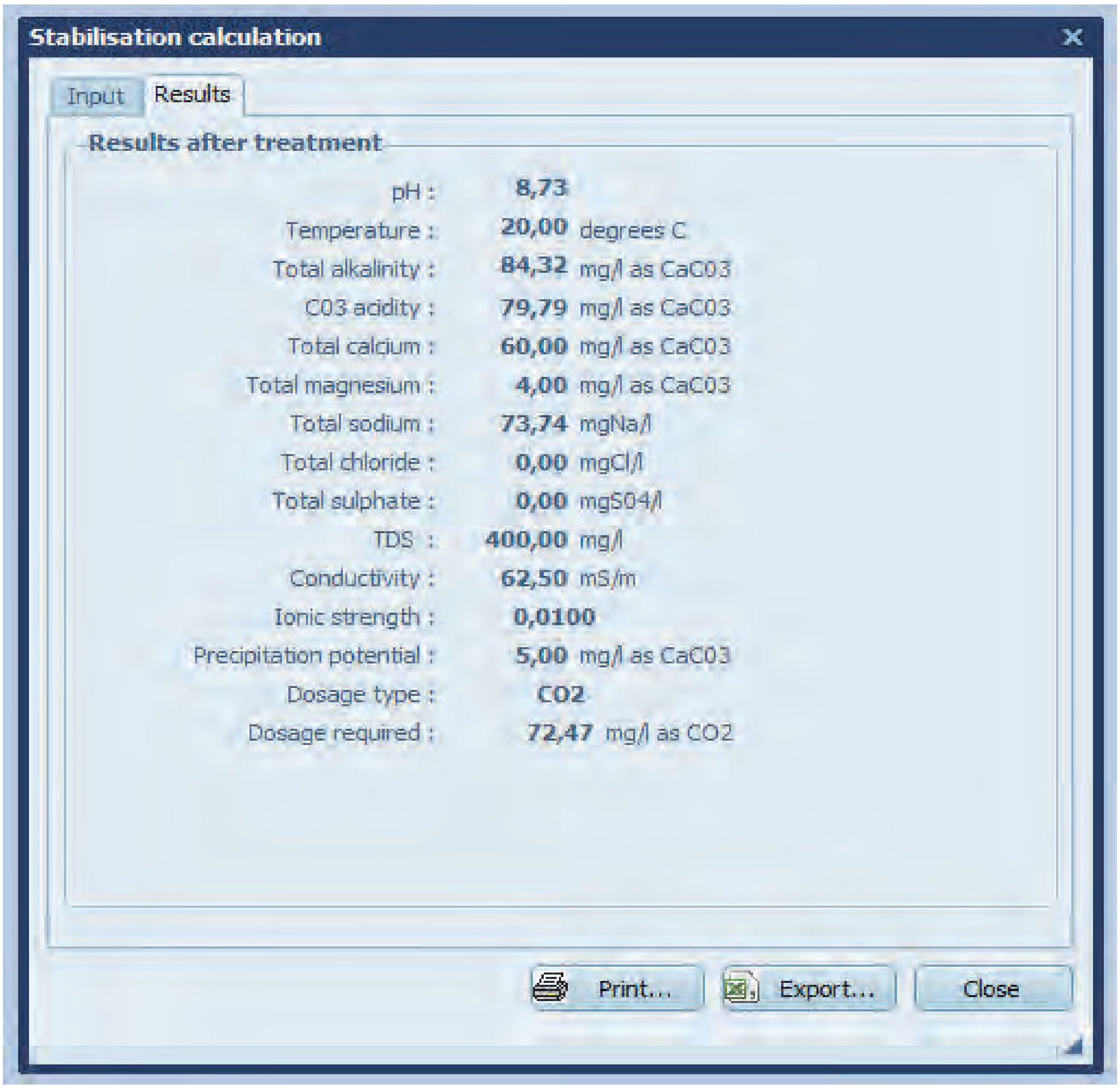


Stabilisation inputs

Desired precipitation potential : 5,0 mg/l as CaC03
Desired dosing chemical : CO2

Figure 24: Stabilisation inputs window.

Enter the specified final $CaCO_3$ precipitation potential of 5 mg/ℓ as $CaCO_3$ by typing **5** into the desired precipitation potential input box and select the $CO_2$ option (Figure 24). Selection of the <Results> menu option will bring the **results after treatment** window onto the screen with values for the new state of the water and the dosage of $CO_2$ required to adjust the water to the specified $CaCO_3$ precipitation potential, as shown in Figure 25.



Results after treatment

pH : 8,73
Temperature : 20,00 degrees C
Total alkalinity : 84,32 mg/l as CaC03
C03 acidity : 79,79 mg/l as CaC03
Total calcium : 60,00 mg/l as CaC03
Total magnesium : 4,00 mg/l as CaC03
Total sodium : 73,74 mgNa/l
Total chloride : 0,00 mgCl/l
Total sulphate : 0,00 mgS04/l
TDS : 400,00 mg/l
Conductivity : 62,50 mS/m
Ionic strength : 0,0100
Precipitation potential : 5,00 mg/l as CaC03
Dosage type : CO2
Dosage required : 72,47 mg/l as CO2

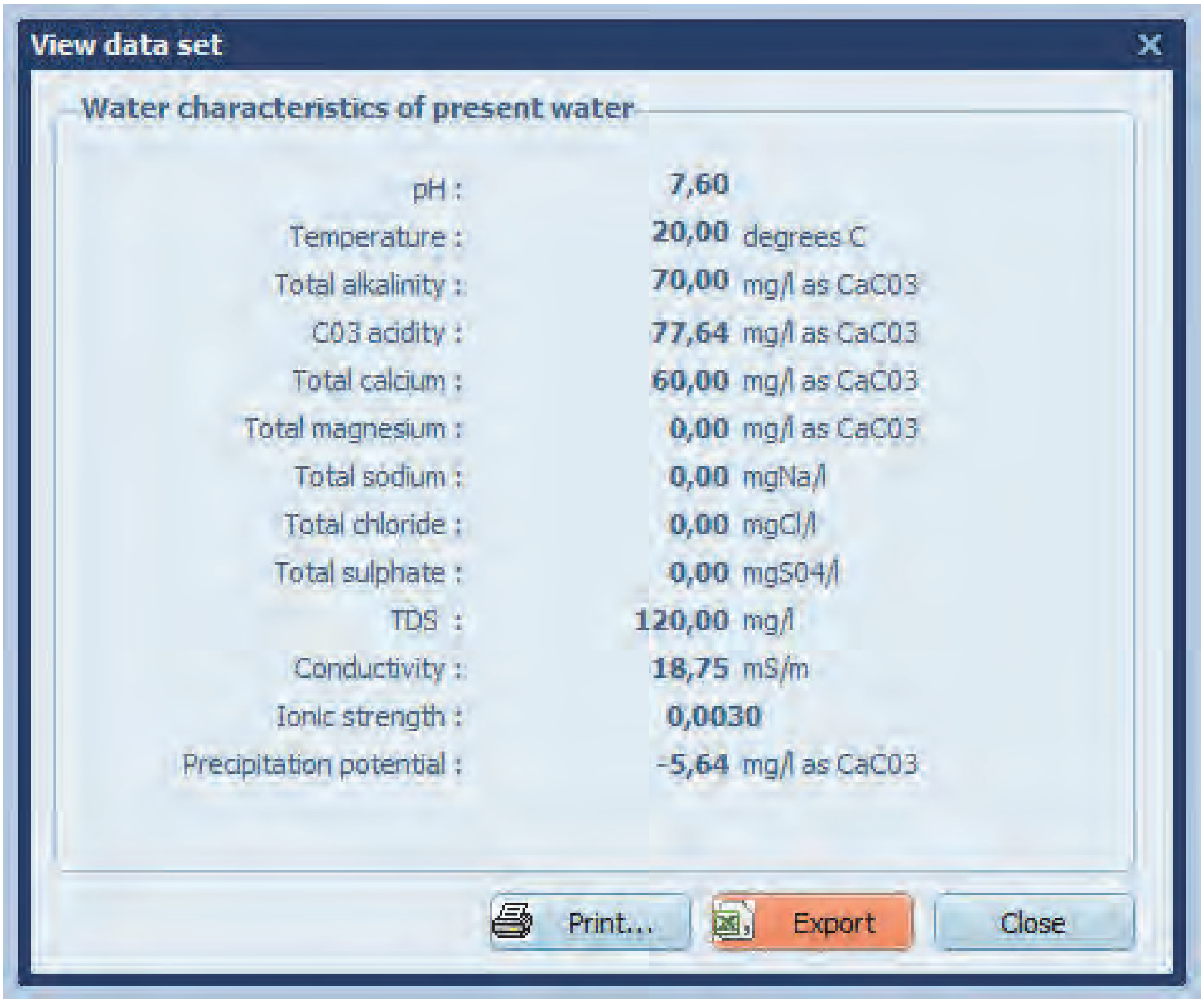
**Figure 25: The results after treatment window for Example 2 (recarbonation).**

### 4.3.3 Example 3: Stabilising a water to a specified $CaCO_3$ precipitation potential using lime

A water has the following characteristics: Total alkalinity 70 mg/ℓ, calcium 60 mg/ℓl (both as $CaCO_3$), pH 7,6, TDS 120 mg/ℓ and temperature 20°C. It is required to stabilise the water to have a $CaCO_3$ precipitation potential of 4 mg/ℓ ac $CaCO_3$ using lime. A solution procedure using the Stasoft program is set out below.

After entering the data into the **data set input** window (Figure 9), selection of the <View> option will bring the window displaying the characteristics of the present water onto the screen (Figure 26). Close the window and select the <Stabilisation> option from the Calculations menu, bringing up the **stabilisation inputs** window for recarbonation of the present/active water (as illustrated in Figure 24).

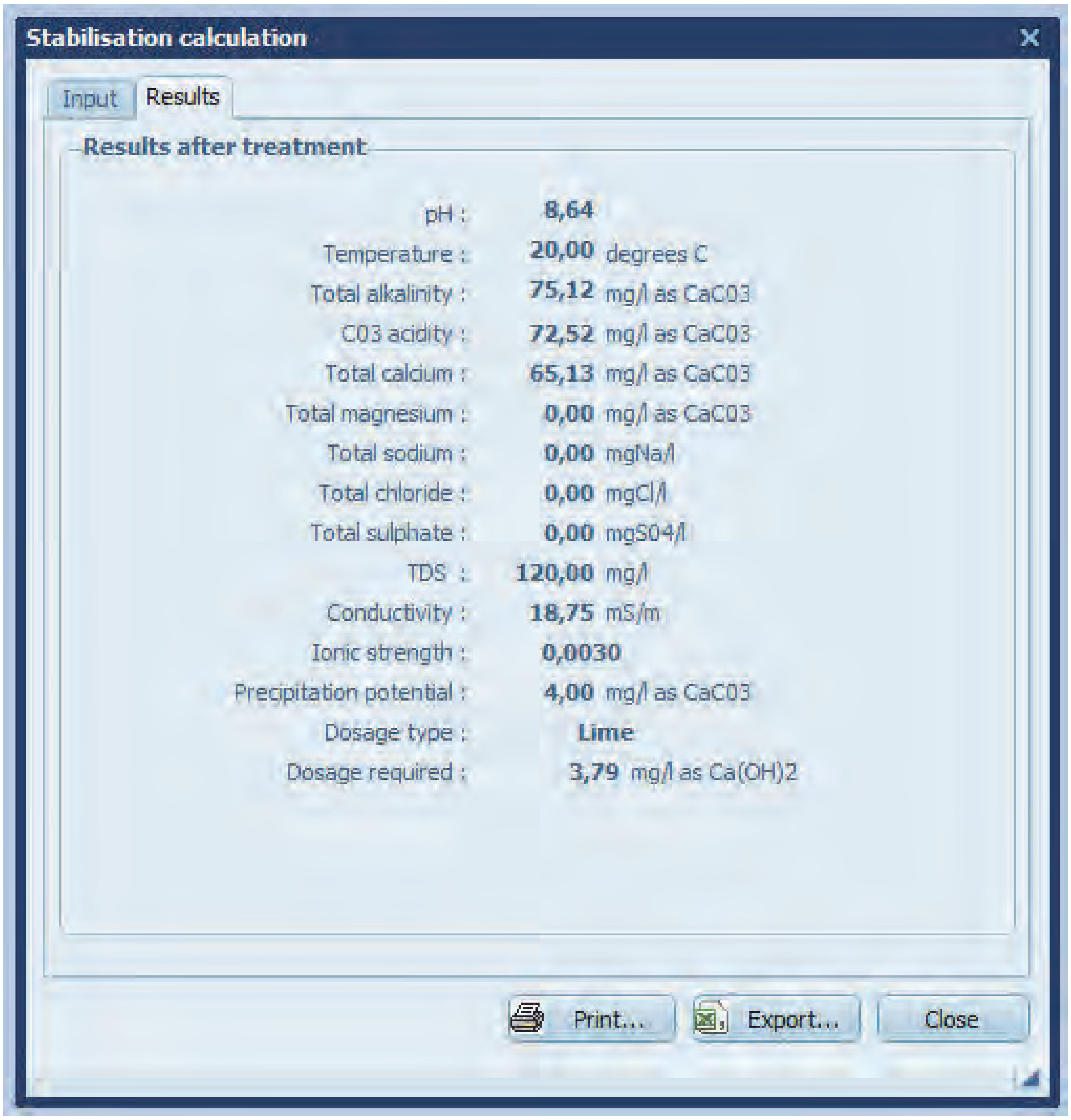
Enter the specified final $CaCO_3$ precipitation potential of 4 mg/ℓ as $CaCO_3$ into the desired precipitation potential input box and select the lime option (similar to Figure 24). Selection of the <Results> menu option will bring the **results after treatment** window onto the screen with values for the new state of the water and the dosage of lime required to stabilise the water to the prescribed $CaCO_3$ precipitation potential, as shown in Figure 27.



Water characteristics of present water

pH : 7,60
Temperature : 20,00 degrees C
Total alkalinity : 70,00 mg/l as CaC03
C03 acidity : 77,64 mg/l as CaC03
Total calcium : 60,00 mg/l as CaC03
Total magnesium : 0,00 mg/l as CaC03
Total sodium : 0,00 mgNa/l
Total chloride : 0,00 mgCl/l
Total sulphate : 0,00 mgS04/l
TDS : 120,00 mg/l
Conductivity : 18,75 mS/m
Ionic strength : 0,0030
Precipitation potential : -5,64 mg/l as CaC03

**Figure 26: Window displaying the characteristics of the water used in Example 3.**



Results after treatment

pH : 8,64
Temperature : 20,00 degrees C
Total alkalinity : 75,12 mg/l as CaC03
C03 acidity : 72,52 mg/l as CaC03
Total calcium : 65,13 mg/l as CaC03
Total magnesium : 0,00 mg/l as CaC03
Total sodium : 0,00 mgNa/l
Total chloride : 0,00 mgCl/l
Total sulphate : 0,00 mgS04/l
TDS : 120,00 mg/l
Conductivity : 18,75 mS/m
Ionic strength : 0,0030
Precipitation potential : 4,00 mg/l as CaC03
Dosage type : Lime
Dosage required : 3,79 mg/l as Ca(OH)2

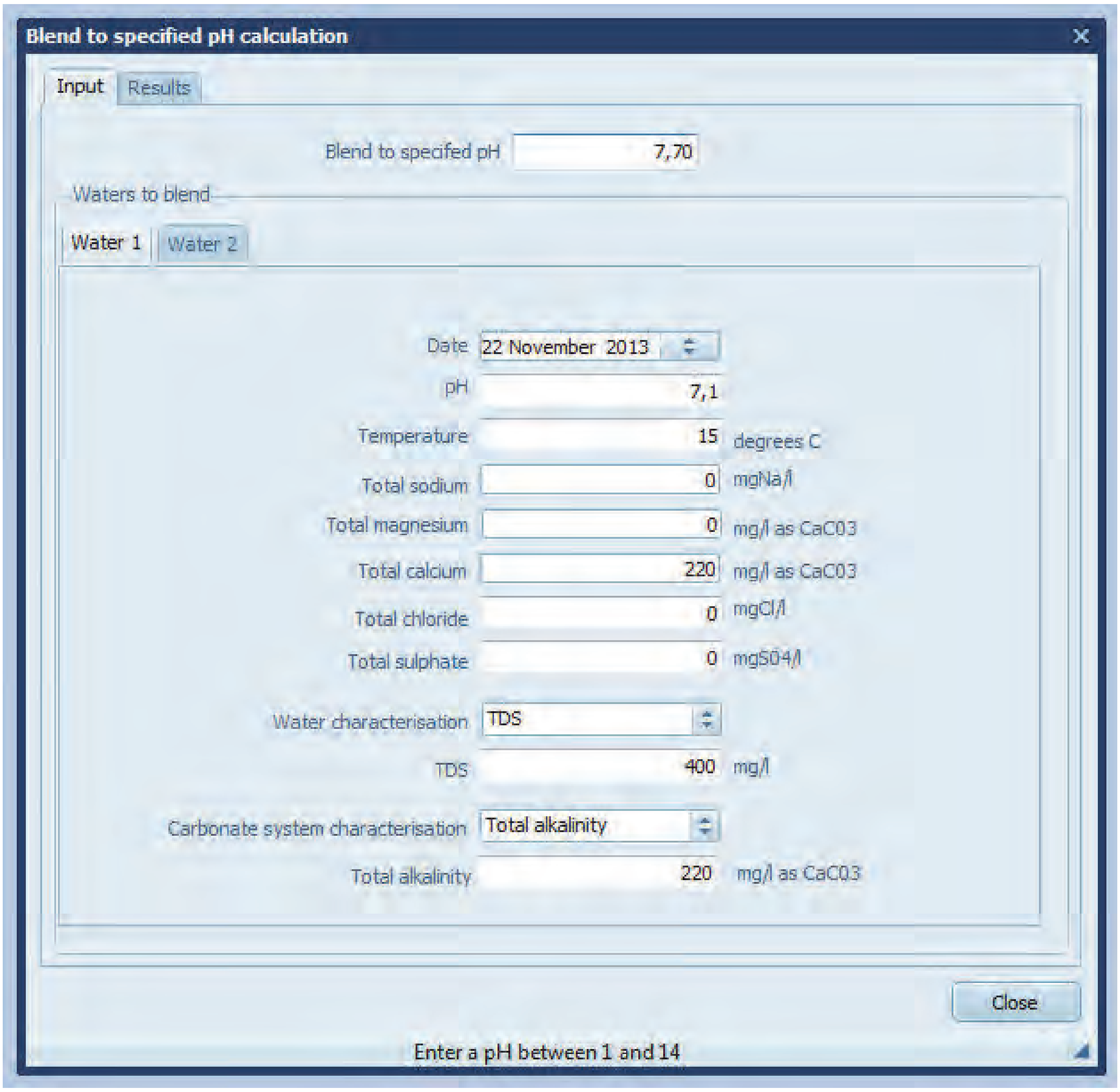
**Figure 27: The results after treatment window for Example 3.**

### 4.3.4 Example 4: Blending two waters to a specified pH

Water 1 has the following characteristics: Total alkalinity 220 mg/ℓ, calcium 220 mg/ℓ (both as $CaCO_3$), pH 7,1, TDS 400 mg/ℓ and temperature 15°C. Water 2 has the following characteristics: Total alkalinity 60 mg/ℓ, calcium 140 mg/ℓ (both as $CaCO_3$), pH 11,5, TDS 300 mg/ℓ and temperature 20°C. It is required to determine the fraction of each water necessary to give a final pH equal to 7,7 for the blended water. The solution procedure is set out below.

**NOTE**: *An active data set is not required to execute either of the two blending calculations. However, the active data set at the time of selecting one of the blending options is overwritten by the program, even if the blending option is later aborted before completion of a calculation.*

Selecting the <Blend to specified pH> option from the Blending menu (see Figure 16) will bring the **blend to specified pH input** window onto the screen, as shown in Figure 28. Enter the desired pH value by typing **7,7** into the desired pH of blended water input box, and then complete the data set input for Water 1 (Figure 28). After the data for Water 1 has been entered, select the <Water 2> tab and enter the relevant data for Water 2 (Figure 29).



Blend to specifed pH 7,70

Date 22 November 2013

pH 7,1

Temperature 15 degrees C

Total sodium 0 mgNa/l

Total magnesium 0 mg/l as CaC03

Total calcium 220 mg/l as CaC03

Total chloride 0 mgCl/l

Total sulphate 0 mgS04/l

Water characterisation TDS

TDS 400 mg/l

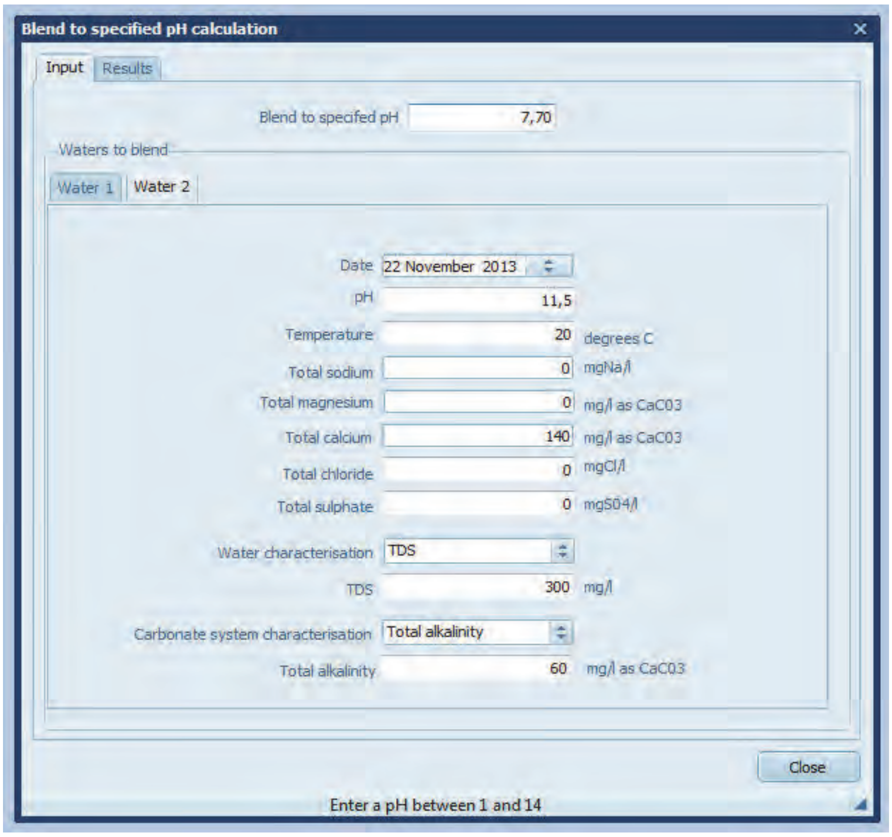
Carbonate system characterisation Total alkalinity

Total alkalinity 220 mg/l as CaC03

Enter a pH between 1 and 14

**Figure 28: Blend to specified pH input window (Water 1) in Example 4.**

Selection of the <Results> menu option will bring the **results after treatment** window onto the screen with values for the final state of the blended water and the fraction of each water required to give the prescribed pH, as shown in Figure 30.



Blend to specifed pH 7,70

Date 22 November 2013

pH 11,5

Temperature 20 degrees C

Total sodium 0 mgNa/l

Total magnesium 0 mg/l as CaC03

Total calcium 140 mg/l as CaC03

Total chloride 0 mgCl/l

Total sulphate 0 mgS04/l

Water characterisation TDS

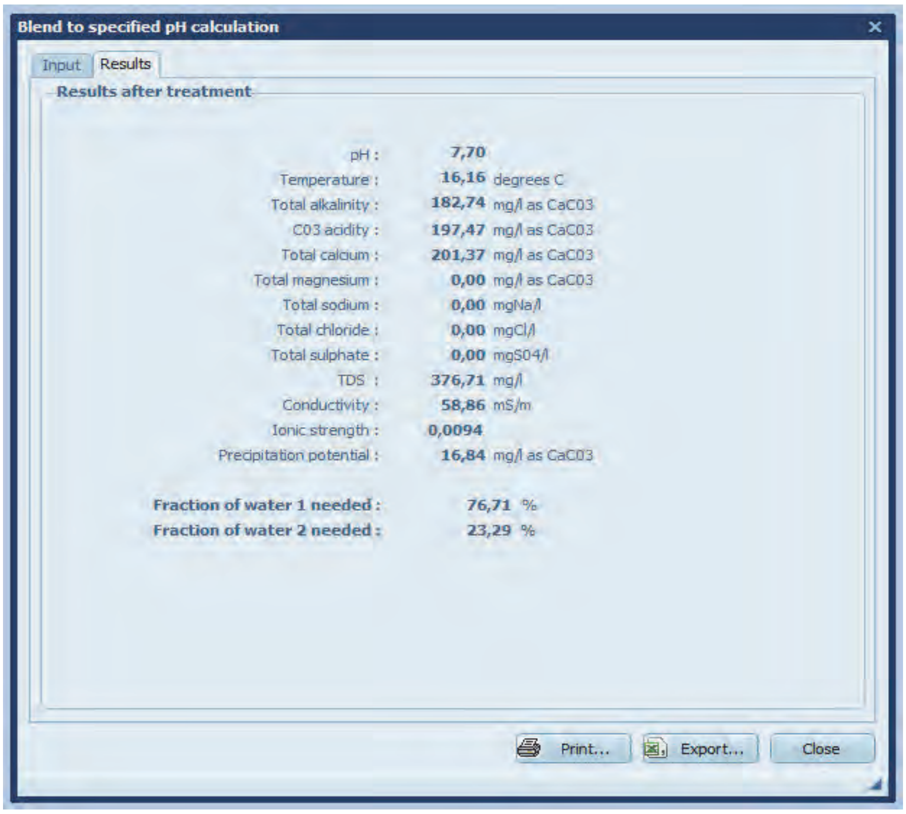
TDS 300 mg/l

Carbonate system characterisation Total alkalinity

Total alkalinity 60 mg/l as CaC03

Enter a pH between 1 and 14

Figure 29: Blend to specified pH input window (Water 2) in Example 4.



pH : 7,70

Temperature : 16,16 degrees C

Total alkalinity : 182,74 mg/l as CaC03

C03 acidity : 197,47 mg/l as CaC03

Total calcium : 201,37 mg/l as CaC03

Total magnesium : 0,00 mg/l as CaC03

Total sodium : 0,00 mgNa/l

Total chloride : 0,00 mgCl/l

Total sulphate : 0,00 mgS04/l

TDS : 376,71 mg/l

Conductivity : 58,86 mS/m

Ionic strength : 0,0094

Precipitation potential : 16,84 mg/l as CaC03

**Fraction of water 1 needed :** 76,71 %

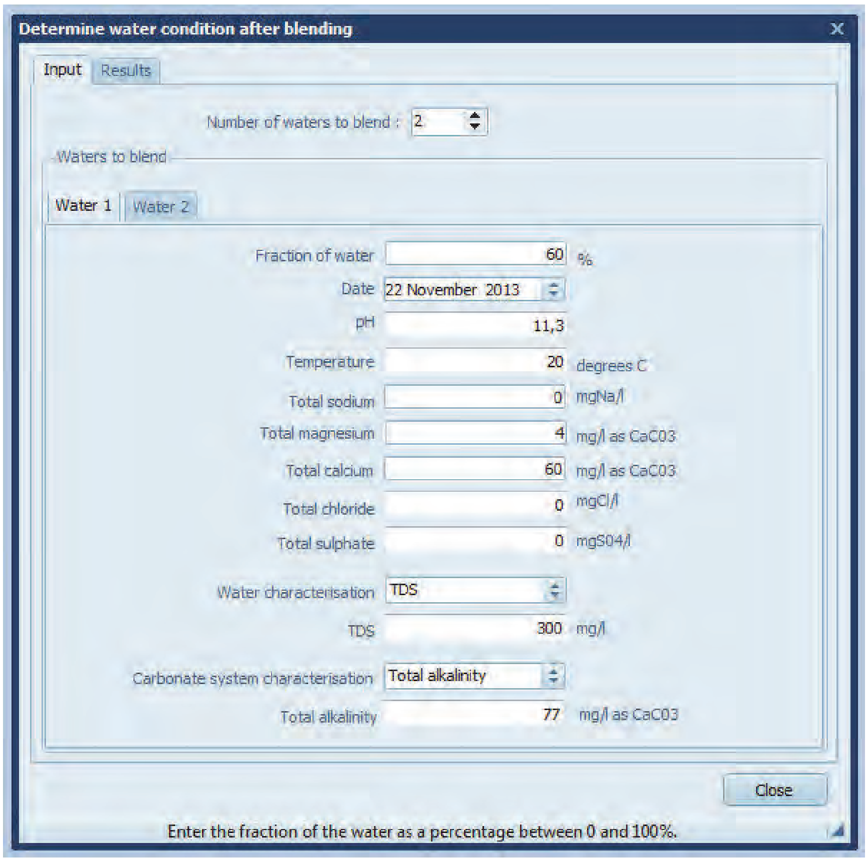
**Fraction of water 2 needed :** 23,29 %

Figure 30: The results after treatment window for Example 4.

### 4.3.5 Example 5: Determining the final state of a water after blending two waters

A high lime softened water (Water 1) is to be blended with an untreated (unsoftened) raw water (Water 2). Water 1 has the following characteristics: Total alkalinity 77 mg/ℓ, calcium 60 mg/ℓ, magnesium 4 mg/ℓ (all as $CaCO_3$), pH 11,3, TDS 300 mg/ℓ and temperature 20°C. Water 2 has the following characteristics: Total alkalinity 130 mg/ℓ, calcium 230 mg/ℓ, magnesium 40 mg/ℓ (all as $CaCO_3$), pH 7,30, TDS 400 mg/ℓ and temperature 20°C. Determine the chemical characteristics of the blend if 60% of Water 1 is blended with 40% of Water 2. The solution procedure is set out below.

Selecting the <Determine water condition after blending> option from the Blending menu (see Figure 16) will bring the **determine water condition after blending input** window onto the screen, as shown in Figure 31. Enter the number of water to blend (2) into the input box, and then complete the relevant data for Water 1 (Figure 31). After the data for Water 1 has been entered, select the <Water 2> tab and enter the relevant data for Water 2 (Figure 32).



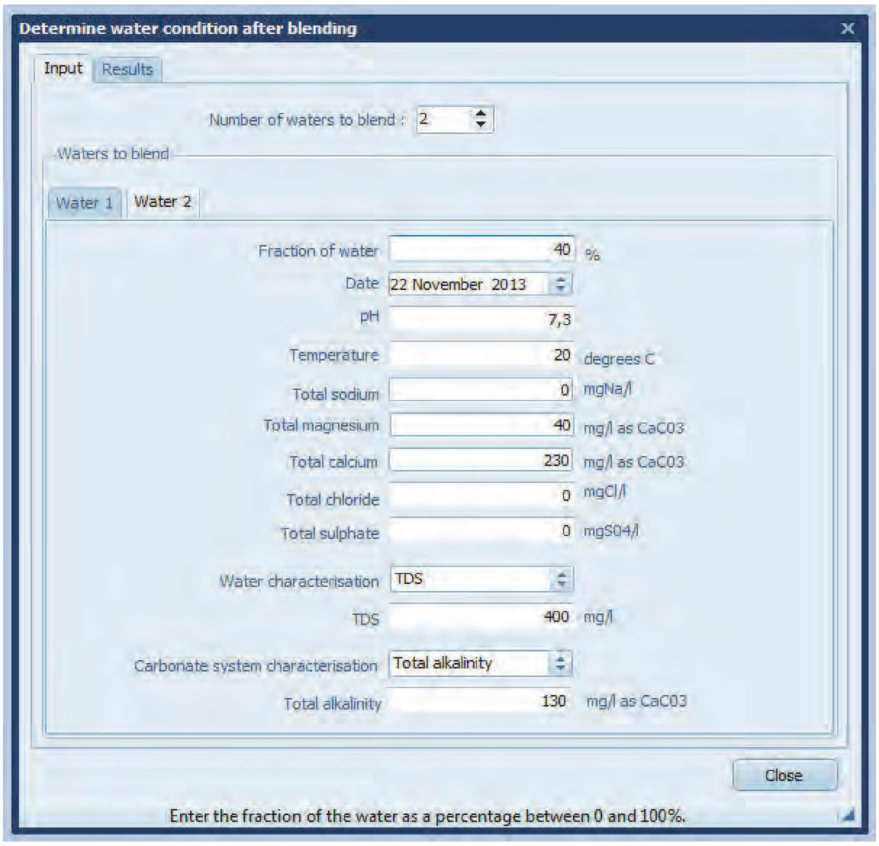
Number of waters to blend : 2

Fraction of water 60 %
Date 22 November 2013
pH 11,3
Temperature 20 degrees C
Total sodium 0 mgNa/l
Total magnesium 4 mg/l as CaC03
Total calcium 60 mg/l as CaC03
Total chloride 0 mgCl/l
Total sulphate 0 mgS04/l
Water characterisation TDS
TDS 300 mg/l
Carbonate system characterisation Total alkalinity
Total alkalinity 77 mg/l as CaC03

Enter the fraction of the water as a percentage between 0 and 100%.

**Figure 31: Determine water condition after blending input window (Water 1) in Example 5.**

Selection of the <Results> menu option will bring the **results after treatment** window onto the screen with values for the final state of the blended water, as shown in Figure 33.

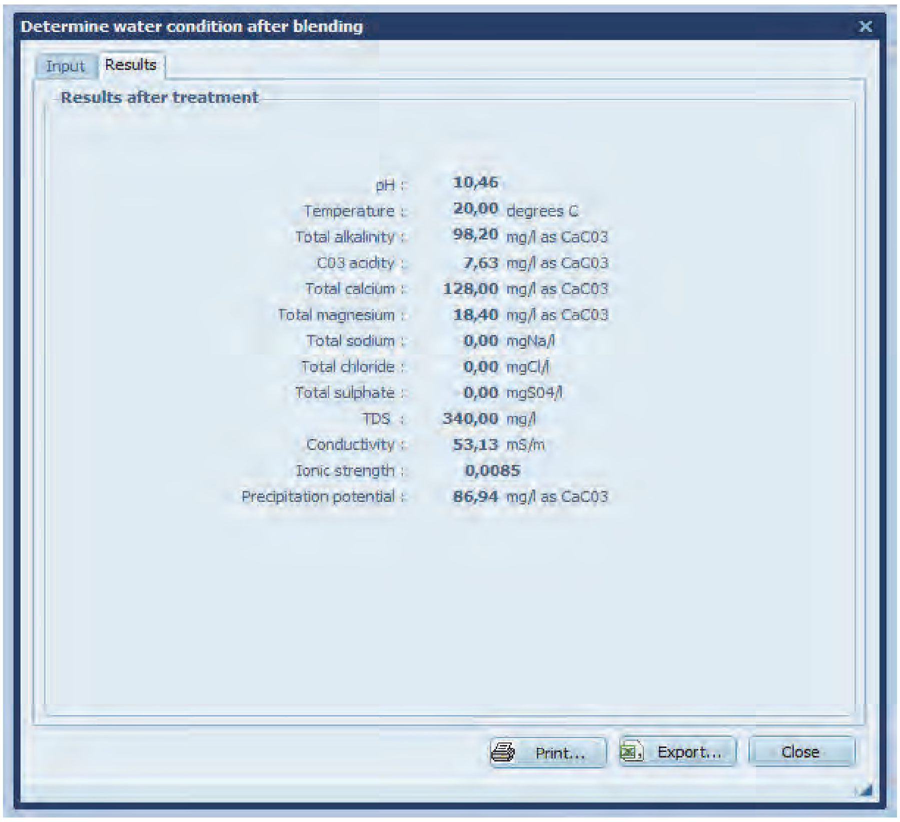


Number of waters to blend : 2

Fraction of water 40 %
Date 22 November 2013
pH 7,3
Temperature 20 degrees C
Total sodium 0 mgNa/l
Total magnesium 40 mg/l as CaC03
Total calcium 230 mg/l as CaC03
Total chloride 0 mgCl/l
Total sulphate 0 mgS04/l
Water characterisation TDS
TDS 400 mg/l
Carbonate system characterisation Total alkalinity
Total alkalinity 130 mg/l as CaC03

Enter the fraction of the water as a percentage between 0 and 100%.

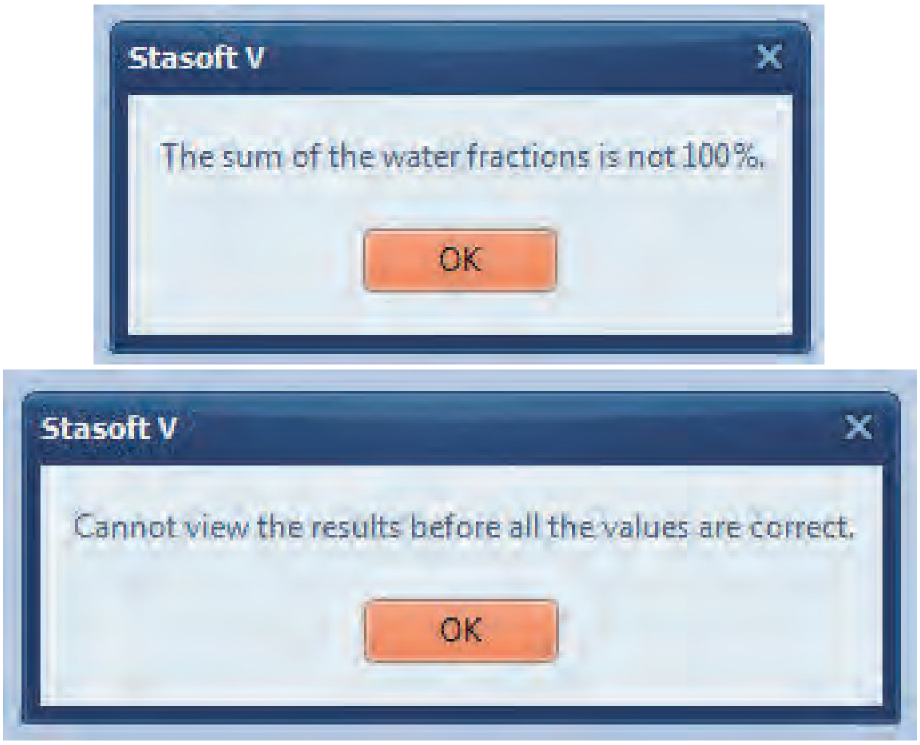
**Figure 32: Determine water condition after blending input window (Water 2) in Example 4.**



pH : 10,46
Temperature : 20,00 degrees C
Total alkalinity : 98,20 mg/l as CaC03
C03 acidity : 7,63 mg/l as CaC03
Total calcium : 128,00 mg/l as CaC03
Total magnesium : 18,40 mg/l as CaC03
Total sodium : 0,00 mgNa/l
Total chloride : 0,00 mgCl/l
Total sulphate : 0,00 mgS04/l
TDS : 340,00 mg/l
Conductivity : 53,13 mS/m
Ionic strength : 0,0085
Precipitation potential : 86,94 mg/l as CaC03

**Figure 33: The results after treatment window for Example 5.**

In the event of incorrect water fractions entered for the relevant two or more waters to be blended, the **notification messages** in Figure 34 will appear sequentially on the screen and no results will be calculated until corrected.



The sum of the water fractions is not 100%.

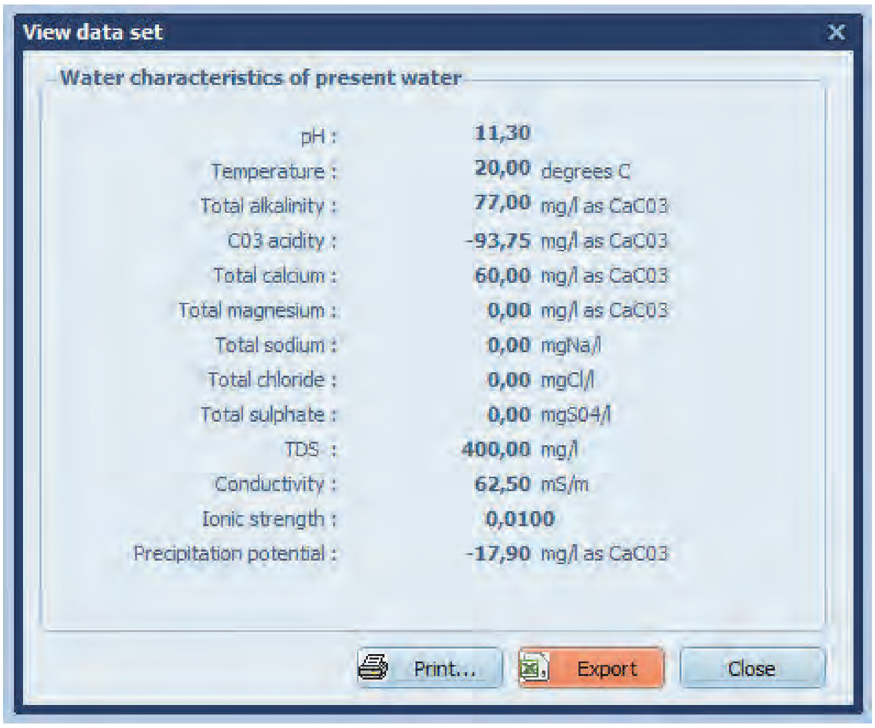
Cannot view the results before all the values are correct.

**Figure 34: Sequential notification messages for incorrect entered water fractions.**

### 4.3.6 Example 6: Determining the final state of a water after equilibrium with the air has been established

After high lime treatment, the analysis of a water gives Total alkalinity 77 mg/ℓ, calcium 60 mg/ℓ (both as $CaCO_3$), pH 11,3, TDS 400 mg/ℓ and temperature 20°C. After aeration of the water determine the final state of the water after $CO_2$ equilibrium with the air is attained. The solution procedure is set out below.

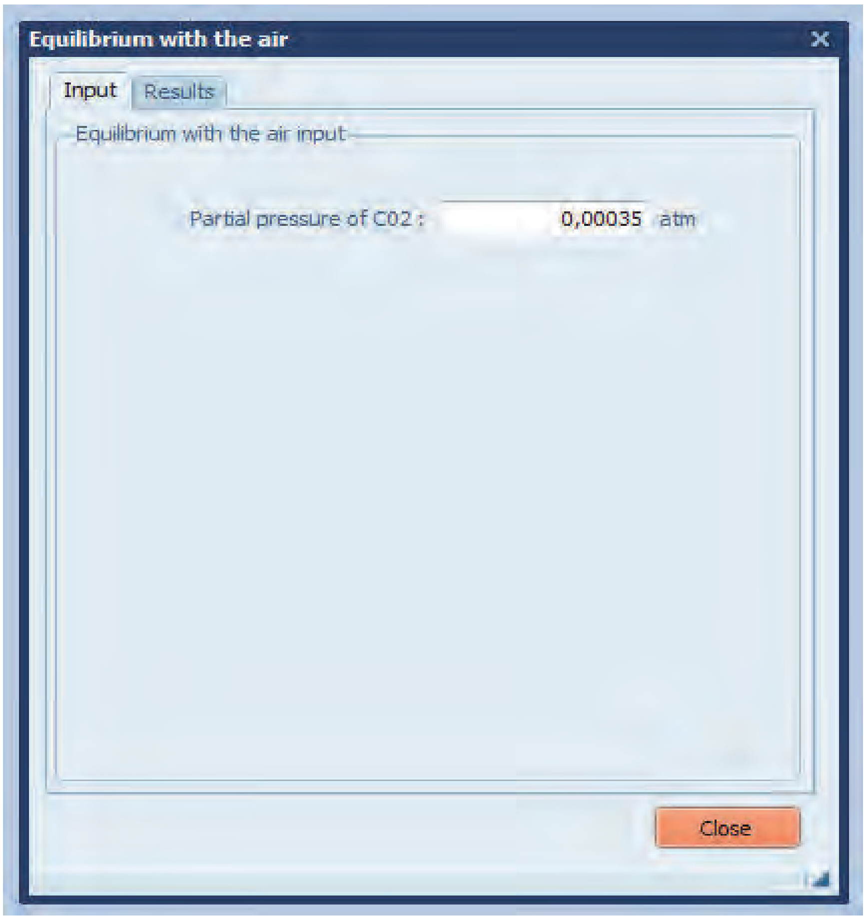
After entering the data into the **data set input** window (Figure 9), selection of the <View> option will bring the window displaying the characteristics of the present water onto the screen (Figure 35). Close the window and select the <Equilibrium with the air> option from the Calculations menu, bringing up the **equilibrium with the air input** window as shown in Figure 36. Enter partial pressure of $CO_2$ in the air by typing **0,00035** (or accepting the default value; see also range available in the help file) into the partial pressure of $CO_2$ input box, as illustrated in Figure 36.



Water characteristics of present water

pH : 11,30
Temperature : 20,00 degrees C
Total alkalinity : 77,00 mg/l as CaC03
C03 acidity : -93,75 mg/l as CaC03
Total calcium : 60,00 mg/l as CaC03
Total magnesium : 0,00 mg/l as CaC03
Total sodium : 0,00 mgNa/l
Total chloride : 0,00 mgCl/l
Total sulphate : 0,00 mgS04/l
TDS : 400,00 mg/l
Conductivity : 62,50 mS/m
Ionic strength : 0,0100
Precipitation potential : -17,90 mg/l as CaC03

Figure 35: Window displaying the characteristics of the water used in Example 6.

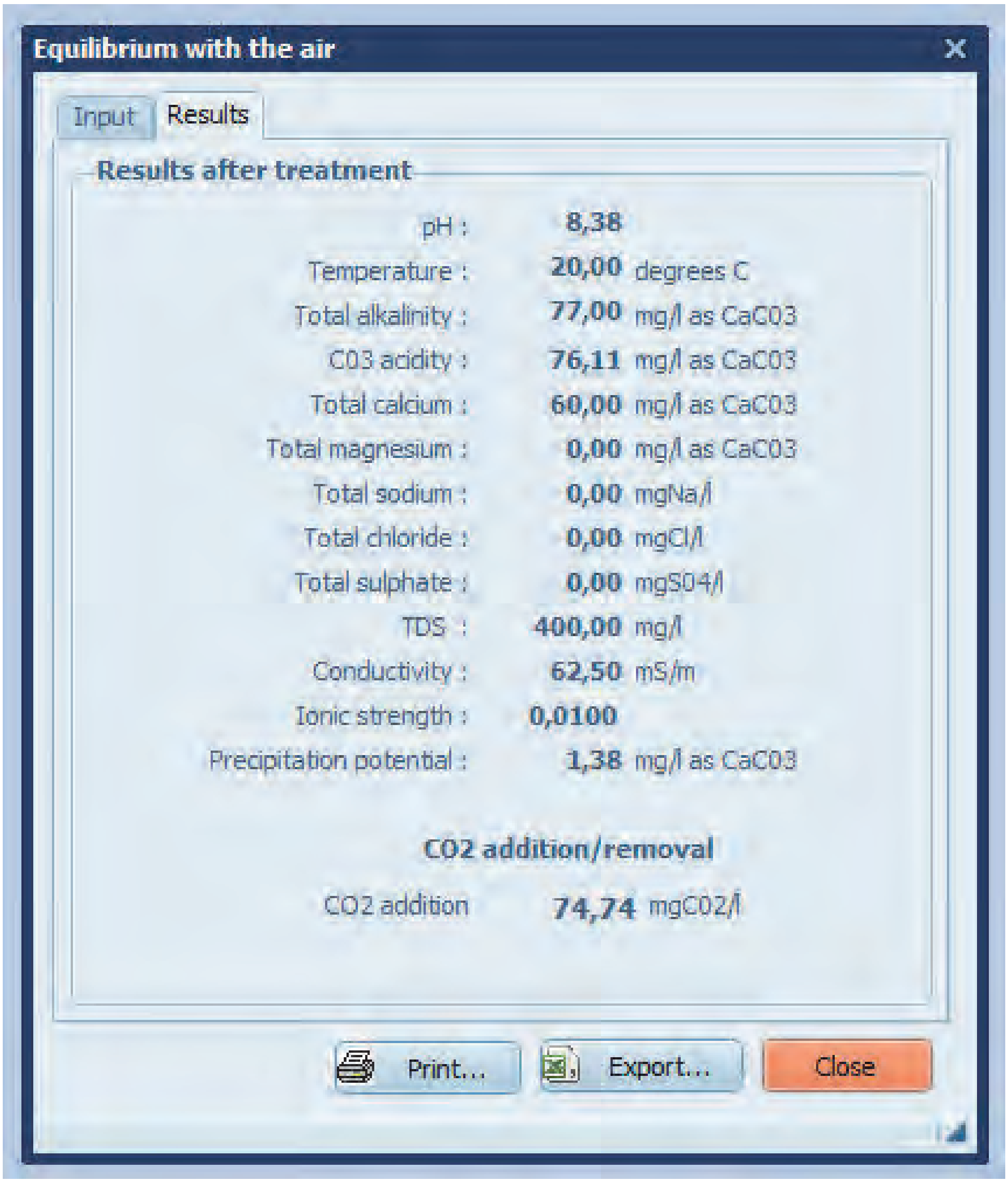


Equilibrium with the air input

Partial pressure of C02 : 0,00035 atm

Figure 36: Equilibrium with the air input window.

Selection of the <Results> menu option will bring the **results after treatment** window onto the screen with values for the new state of the water and the amount of $CO_2$ lost or gained by the water, as shown in Figure 37.



Results after treatment

pH : 8,38
Temperature : 20,00 degrees C
Total alkalinity : 77,00 mg/l as CaCO3
CO3 acidity : 76,11 mg/l as CaCO3
Total calcium : 60,00 mg/l as CaCO3
Total magnesium : 0,00 mg/l as CaCO3
Total sodium : 0,00 mgNa/l
Total chloride : 0,00 mgCl/l
Total sulphate : 0,00 mgSO4/l
TDS : 400,00 mg/l
Conductivity : 62,50 mS/m
Ionic strength : 0,0100
Precipitation potential : 1,38 mg/l as CaCO3

CO2 addition/removal

CO2 addition 74,74 mgCO2/l

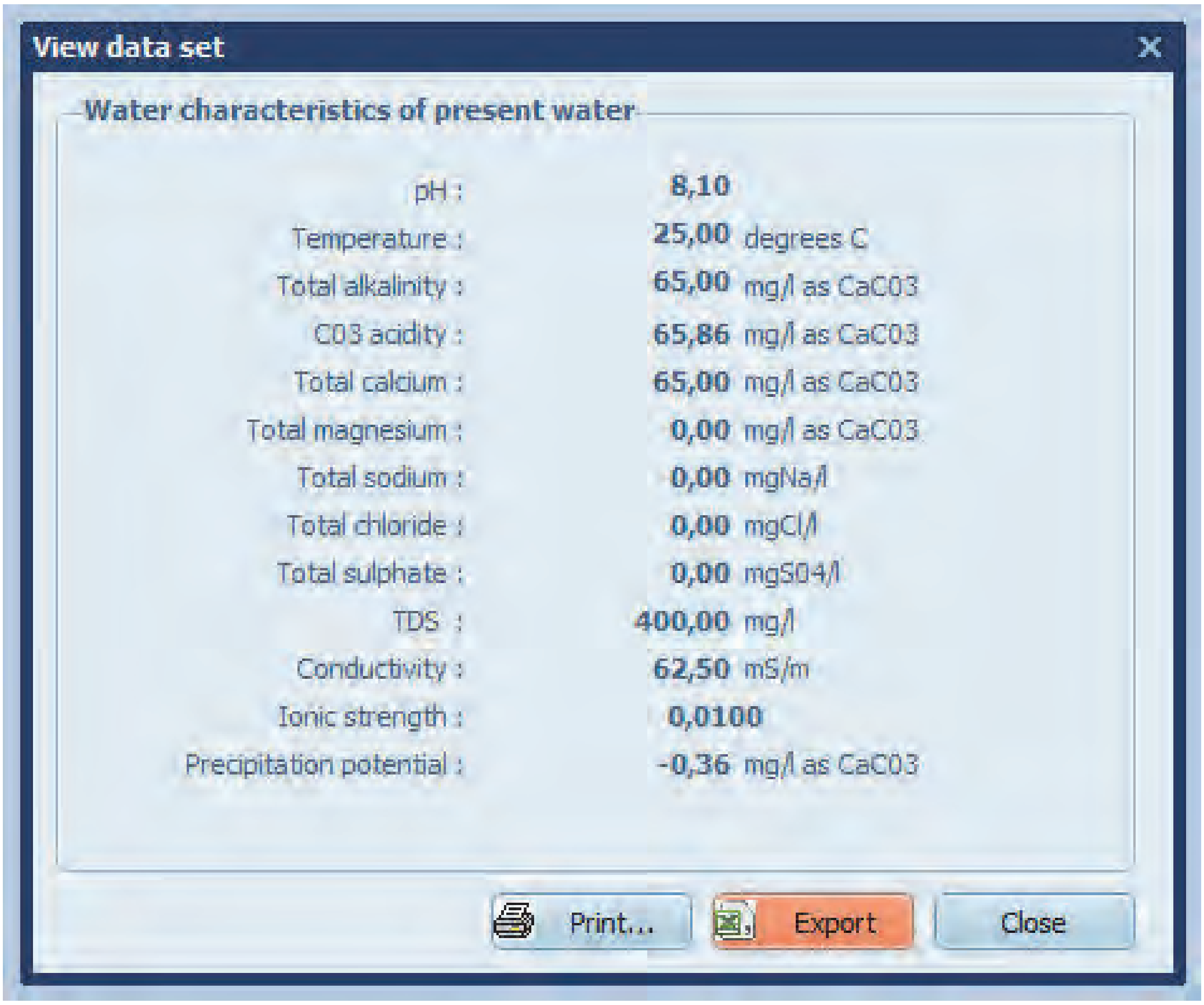
**Figure 37: The results after treatment window for Example 6.**

### 4.3.7 Example 7: Determining the final state of a water after a change in temperature

Analysis of a water gives Total alkalinity 65 mg/ℓ, calcium 65 mg/ℓ (both as $CaCO_3$), pH 8,1, TDS 400 mg/ℓ and temperature 25°C. This water is to be used as a cooling water where its temperature will increase to 90°C. Determine the final state of the water at 90°C. The solution procedure is set out below.

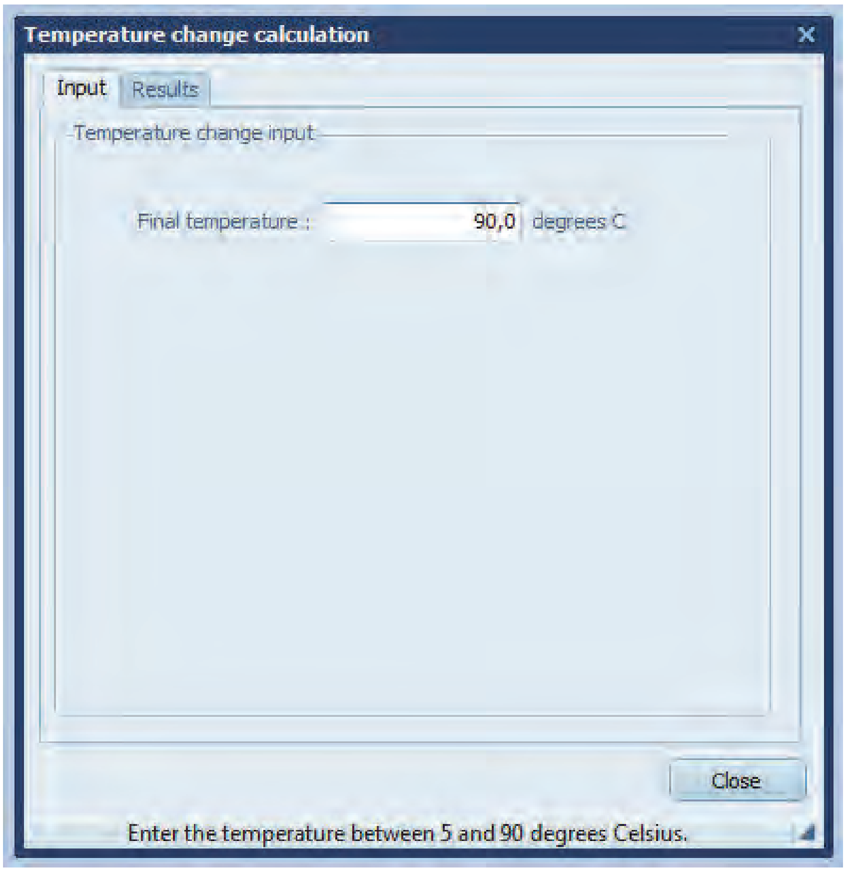
After entering the data into the **data set input** window (Figure 9), selection of the <View> option will bring the window displaying the characteristics of the present water onto the screen (Figure 38). Close the window and select the <Temperature change> option from the Calculations menu, bringing up the **temperature change input** window as shown in Figure 39.

Enter the final state temperature by typing **90** into the final temperature input box (see Figure 39). Selection of the <Results> menu option will bring the **results after treatment** window onto the screen with values for the new state of the water, as shown in Figure 40.



| | | |
|---|---|---|
| pH : | 8,10 | |
| Temperature : | 25,00 | degrees C |
| Total alkalinity : | 65,00 | mg/l as CaC03 |
| C03 acidity : | 65,86 | mg/l as CaC03 |
| Total calcium : | 65,00 | mg/l as CaC03 |
| Total magnesium : | 0,00 | mg/l as CaC03 |
| Total sodium : | 0,00 | mgNa/l |
| Total chloride : | 0,00 | mgCl/l |
| Total sulphate : | 0,00 | mgS04/l |
| TDS : | 400,00 | mg/l |
| Conductivity : | 62,50 | mS/m |
| Ionic strength : | 0,0100 | |
| Precipitation potential : | -0,36 | mg/l as CaC03 |

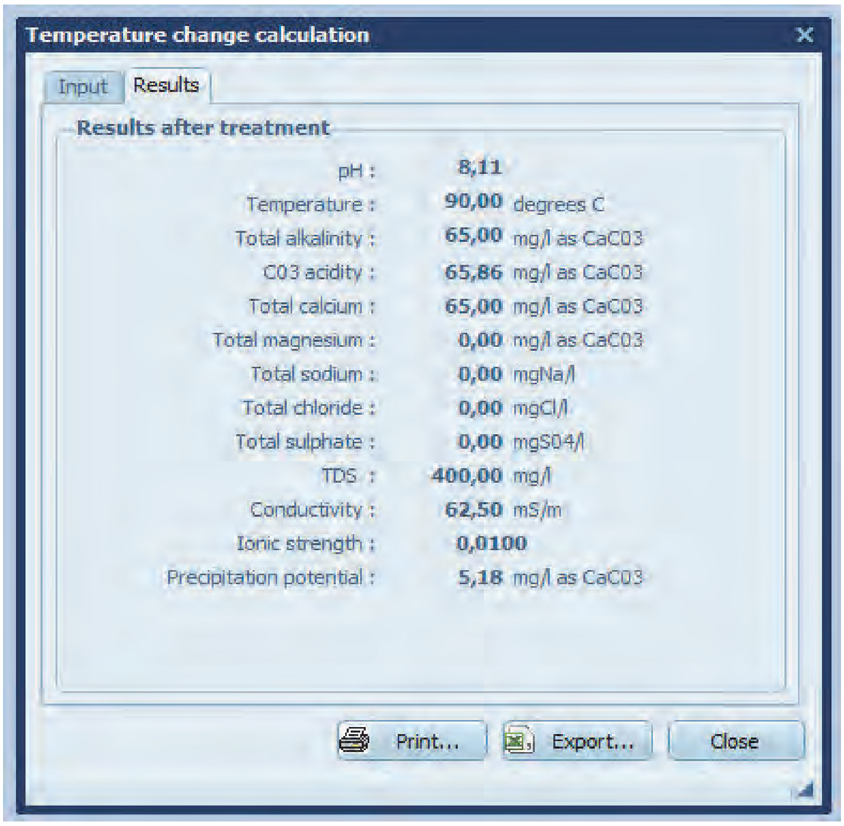
**Figure 38: Window displaying the characteristics of the water used in Example 7.**



Final temperature : 90,0 degrees C

Enter the temperature between 5 and 90 degrees Celsius.

Figure 39: Temperature change input window.



Results after treatment

pH : 8,11
Temperature : 90,00 degrees C
Total alkalinity : 65,00 mg/l as CaC03
C03 acidity : 65,86 mg/l as CaC03
Total calcium : 65,00 mg/l as CaC03
Total magnesium : 0,00 mg/l as CaC03
Total sodium : 0,00 mgNa/l
Total chloride : 0,00 mgCl/l
Total sulphate : 0,00 mgS04/l
TDS : 400,00 mg/l
Conductivity : 62,50 mS/m
Ionic strength : 0,0100
Precipitation potential : 5,18 mg/l as CaC03

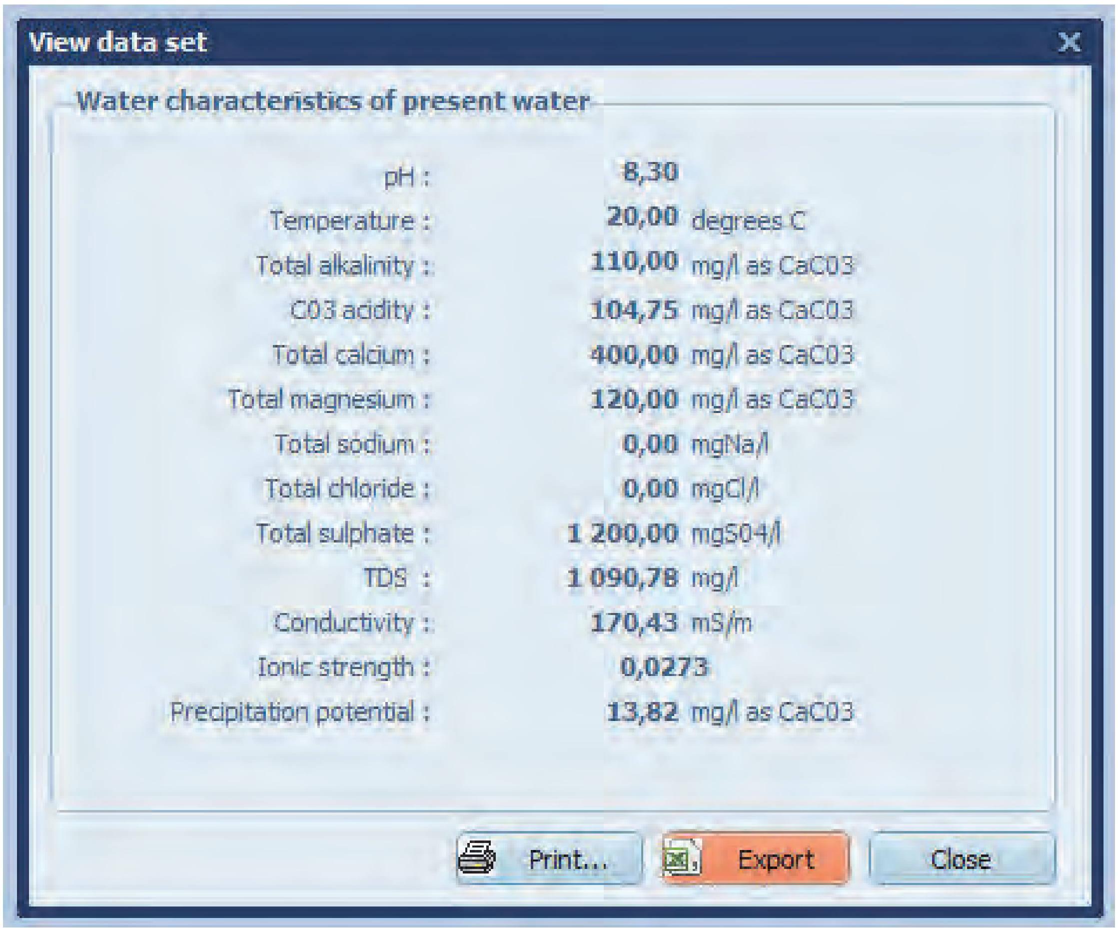
Figure 40: The results after treatment window for Example 7.

### 4.3.8 Example 8: Determining the final state of a water after a change in concentration due to evaporation

Analysis of a water gives Total alkalinity 110 mg/ℓ, calcium 400 mg/ℓ, magnesium 120 mg/ℓ (all as $CaCO_3$), sulphate 1 200 mg/ℓ, pH 8,3, TDS 1 200 mg/ℓ and temperature 20°C. This water is to be used in a cooling cycle where 40% of the water is evaporated. Determine the final state of the water after evaporation. The solution procedure is set out below.

After entering the data into the **data set input** window (Figure 9), selection of the <View> option will bring the window displaying the characteristics of the present water onto the screen (Figure 41). Close the window and select the <Concentration change> option from the Calculations menu, bringing up the **concentration change input** window as shown in Figure 42.

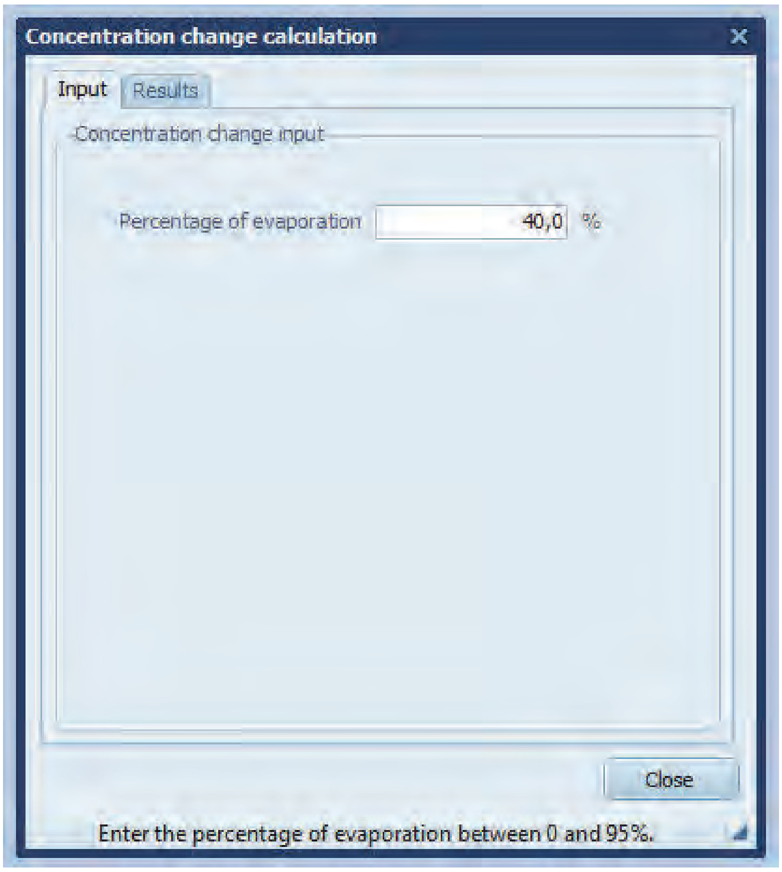
Enter the percentage of water that is evaporated by typing **40** into the percentage of evaporation input box (see Figure 42). Selection of the <Results> menu option will bring the **results after treatment** window onto the screen with values for the new state of the water, as shown in Figure 43.



Water characteristics of present water

pH : 8,30
Temperature : 20,00 degrees C
Total alkalinity : 110,00 mg/l as CaC03
C03 acidity : 104,75 mg/l as CaC03
Total calcium : 400,00 mg/l as CaC03
Total magnesium : 120,00 mg/l as CaC03
Total sodium : 0,00 mgNa/l
Total chloride : 0,00 mgCl/l
Total sulphate : 1 200,00 mgS04/l
TDS : 1 090,78 mg/l
Conductivity : 170,43 mS/m
Ionic strength : 0,0273
Precipitation potential : 13,82 mg/l as CaC03

**Figure 41: Window displaying the characteristics of the water used in Example 8.**

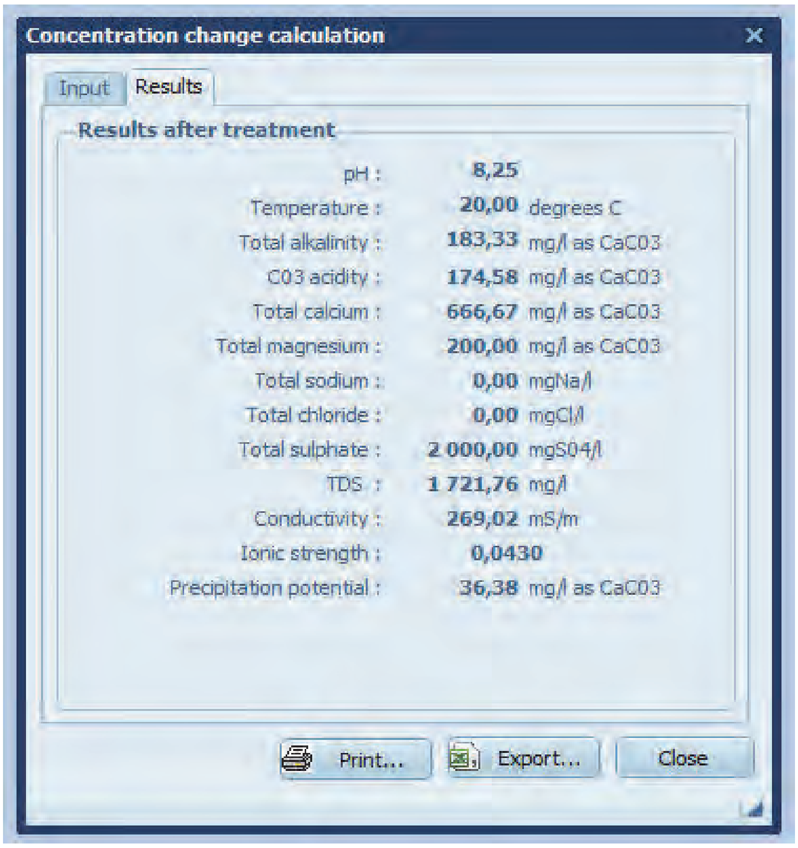


Concentration change input

Percentage of evaporation 40,0 %

Enter the percentage of evaporation between 0 and 95%.

Figure 42: Concentration change input window.



**Results after treatment**

pH : 8,25
Temperature : 20,00 degrees C
Total alkalinity : 183,33 mg/l as CaC03
C03 acidity : 174,58 mg/l as CaC03
Total calcium : 666,67 mg/l as CaC03
Total magnesium : 200,00 mg/l as CaC03
Total sodium : 0,00 mgNa/l
Total chloride : 0,00 mgCl/l
Total sulphate : 2 000,00 mgS04/l
TDS : 1 721,76 mg/l
Conductivity : 269,02 mS/m
Ionic strength : 0,0430
Precipitation potential : 36,38 mg/l as CaC03

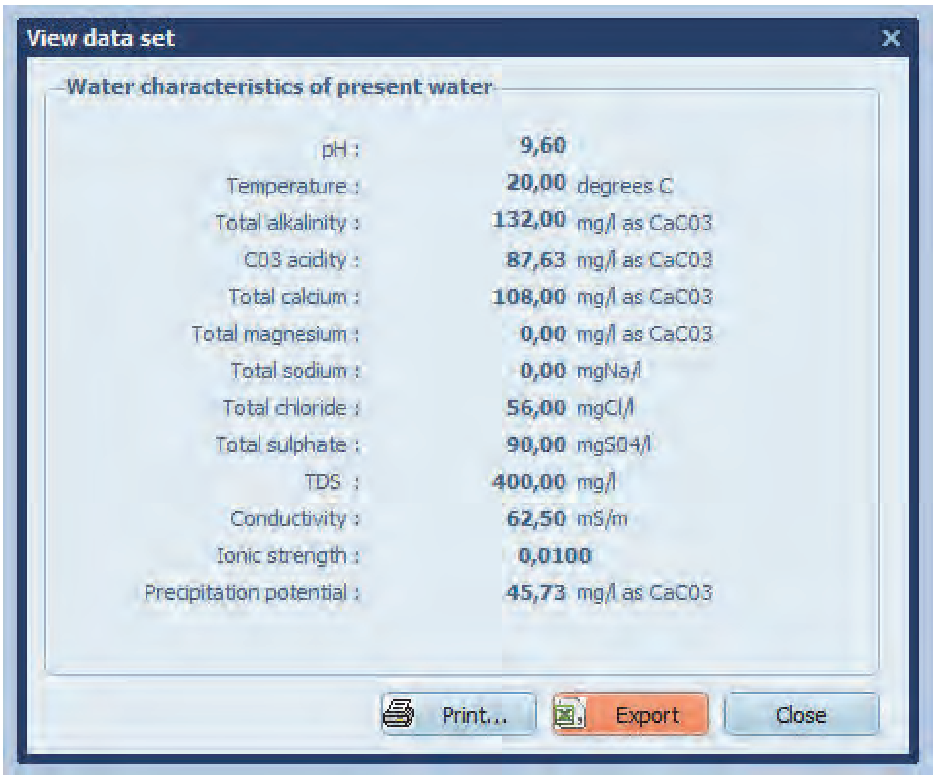
Figure 43: The results after treatment window for Example 8.

### 4.3.9 Example 9: Adjusting the pH of a water using hydrochloric acid

The analysis of a raw water gives Total alkalinity 132 mg/ℓ, calcium 108 mg/ℓ (both as $CaCO_3$), chloride 56 mg/ℓ, sulphate 90 mg/ℓ, pH 9,6, TDS 400 mg/ℓ and temperature of 20°C. Determine the dosage of hydrochloric acid to adjust the water to a pH of 7,2. The solution procedure is set out below.

After entering the data into the **data set input** window (Figure 9), selection of the <View> option will bring the window displaying the characteristics of the present water onto the screen (Figure 44). Close the window and select the <Concentration change> option from the Calculations menu, bringing up the **pH adjustment inputs** window as shown in Figure 45. Enter the specified pH of **7,2** into the desired pH input box and select the hydrochloric acid dosage option (see Figure 45). Selection of the <Results> menu option will bring the **results after treatment** window onto the screen with values for the final state of the water and the dosage of hydrochloric acid required to adjust the water to the prescribed pH, as shown in Figure 46.

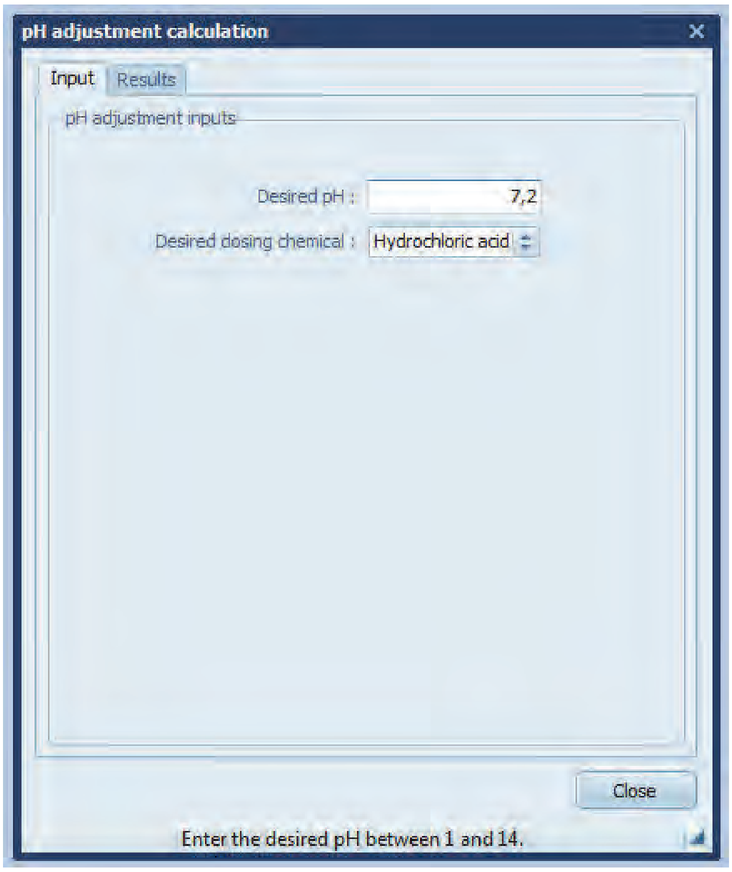
**NOTE:** *In this case hydrochloric acid was required as the dosage chemical. However, if the required chemical to adjust the pH is sulphuric acid, the same procedure can be adopted as above for the hydrochloric acid. In the help information on the pH adjustment option, a conversion factor is given that can be used to convert the calculated value for the dosage of hydrochloric acid to that of sulphuric acid.*



Water characteristics of present water

pH : 9,60
Temperature : 20,00 degrees C
Total alkalinity : 132,00 mg/l as CaC03
C03 acidity : 87,63 mg/l as CaC03
Total calcium : 108,00 mg/l as CaC03
Total magnesium : 0,00 mg/l as CaC03
Total sodium : 0,00 mgNa/l
Total chloride : 56,00 mgCl/l
Total sulphate : 90,00 mgS04/l
TDS : 400,00 mg/l
Conductivity : 62,50 mS/m
Ionic strength : 0,0100
Precipitation potential : 45,73 mg/l as CaC03

**Figure 44: Window displaying the characteristics of the water used in Example 9.**



Desired pH : 7,2

Desired dosing chemical : Hydrochloric acid

Enter the desired pH between 1 and 14.

Figure 45: The pH adjustment inputs window.

pH : 7,20
Temperature : 20,00 degrees C
Total alkalinity : 96,67 mg/l as CaC03
C03 acidity : 122,97 mg/l as CaC03
Total calcium : 108,00 mg/l as CaC03
Total magnesium : 0,00 mg/l as CaC03
Total sodium : 0,00 mgNa/l
Total chloride : 81,05 mgCl/l
Total sulphate : 90,00 mgS04/l
TDS : 400,00 mg/l
Conductivity : 62,50 mS/m
Ionic strength : 0,0100
Precipitation potential : -17,03 mg/l as CaC03
Dosage type : Hydrochloric acid
Dosage required : 25,44 mg/l as HC

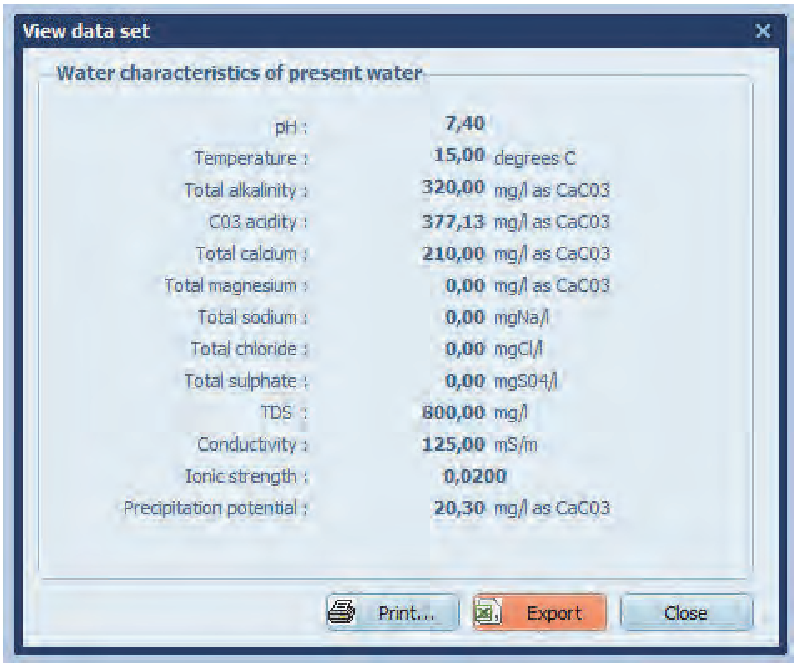
Figure 46: The results after treatment window for Example 9.

### 4.3.10 Example 10: Determining the final state of an underground water after three-phase equilibrium is attained

Analysis of an underground water, to be pumped to the surface, is Total alkalinity 320 mg/ℓ, calcium 210 mg/ℓ (both as $CaCO_3$), pH 7,4, TDS 800 mg/ℓ and a temperature of 15°C. The water is exposed to the air. Determine the chemical state of the water after it has achieved equilibrium with the air, and has attained equilibrium with solid $CaCO_3$ in solution. The solution procedure is set out below.

After entering the data into the **data set input** window (Figure 9), selection of the <View> option will bring the window displaying the characteristics of the present water onto the screen (Figure 47). Close the window and select the <Underground water> option from the Calculations menu, bringing up the **underground water input** window, which is similar to the **equilibrium with the air input** window as shown in Figure 36.

Enter partial pressure of $CO_2$ in the air by typing **0,00035** (or accepting the default value) into the partial pressure of $CO_2$ input box, as illustrated in Figure 36. Selection of the <Results> menu option will bring the **results after treatment** window onto the screen with values for the state of the water and the amount of $CO_2$ lost or gained by the water after equilibrium with the air has been attained, as shown in Figure 48. Selecting the <Close> menu option will bring the final **results after treatment** window onto the screen with values for the final state of the water and the amount of $CaCO_3$ that will precipitate after three-phase equilibrium has been attained by the water, as shown in Figure 49.



Water characteristics of present water

pH : 7,40
Temperature : 15,00 degrees C
Total alkalinity : 320,00 mg/l as CaC03
C03 acidity : 377,13 mg/l as CaC03
Total calcium : 210,00 mg/l as CaC03
Total magnesium : 0,00 mg/l as CaC03
Total sodium : 0,00 mgNa/l
Total chloride : 0,00 mgCl/l
Total sulphate : 0,00 mgS04/l
TDS : 800,00 mg/l
Conductivity : 125,00 mS/m
Ionic strength : 0,0200
Precipitation potential : 20,30 mg/l as CaC03

**Figure 47: Window displaying the characteristics of the water used in Example 10.**

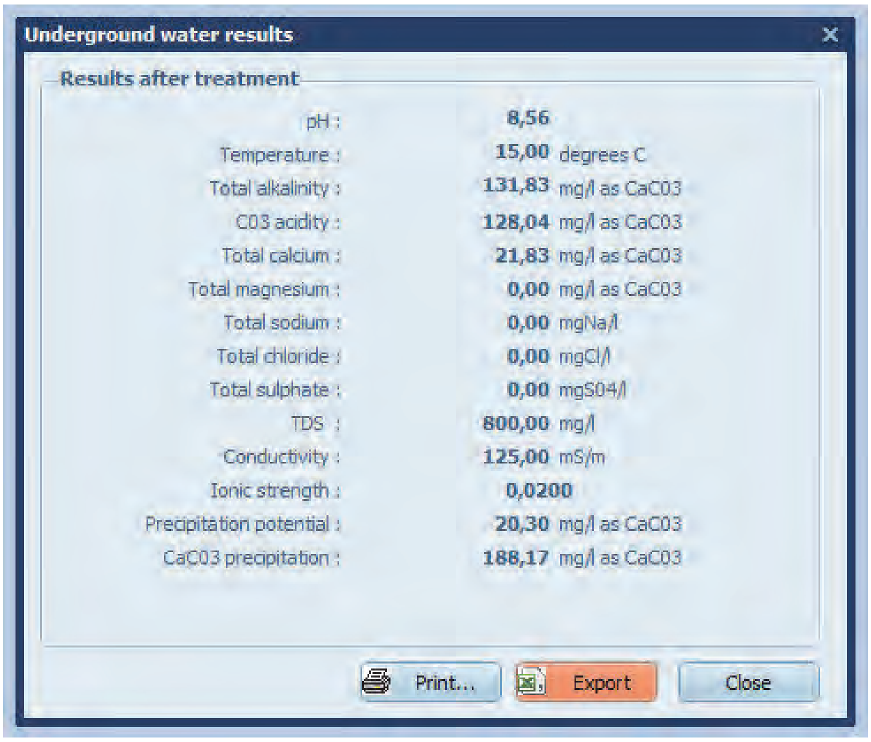
Results after treatment

pH : 8,92
Temperature : 15,00 degrees C
Total alkalinity : 320,00 mg/l as CaCO3
CO3 acidity : 293,57 mg/l as CaCO3
Total calcium : 210,00 mg/l as CaCO3
Total magnesium : 0,00 mg/l as CaCO3
Total sodium : 0,00 mgNa/l
Total chloride : 0,00 mgCl/l
Total sulphate : 0,00 mgSO4/l
TDS : 800,00 mg/l
Conductivity : 125,00 mS/m
Ionic strength : 0,0200
Precipitation potential : 67,29 mg/l as CaCO3

CO2 addition/removal

CO2 expelled 36.77 mgCO2/l

Figure 48: The results after treatment window for Example 10 (when equilibrium is attained between gaseous [air] and aqueous phases).



Results after treatment

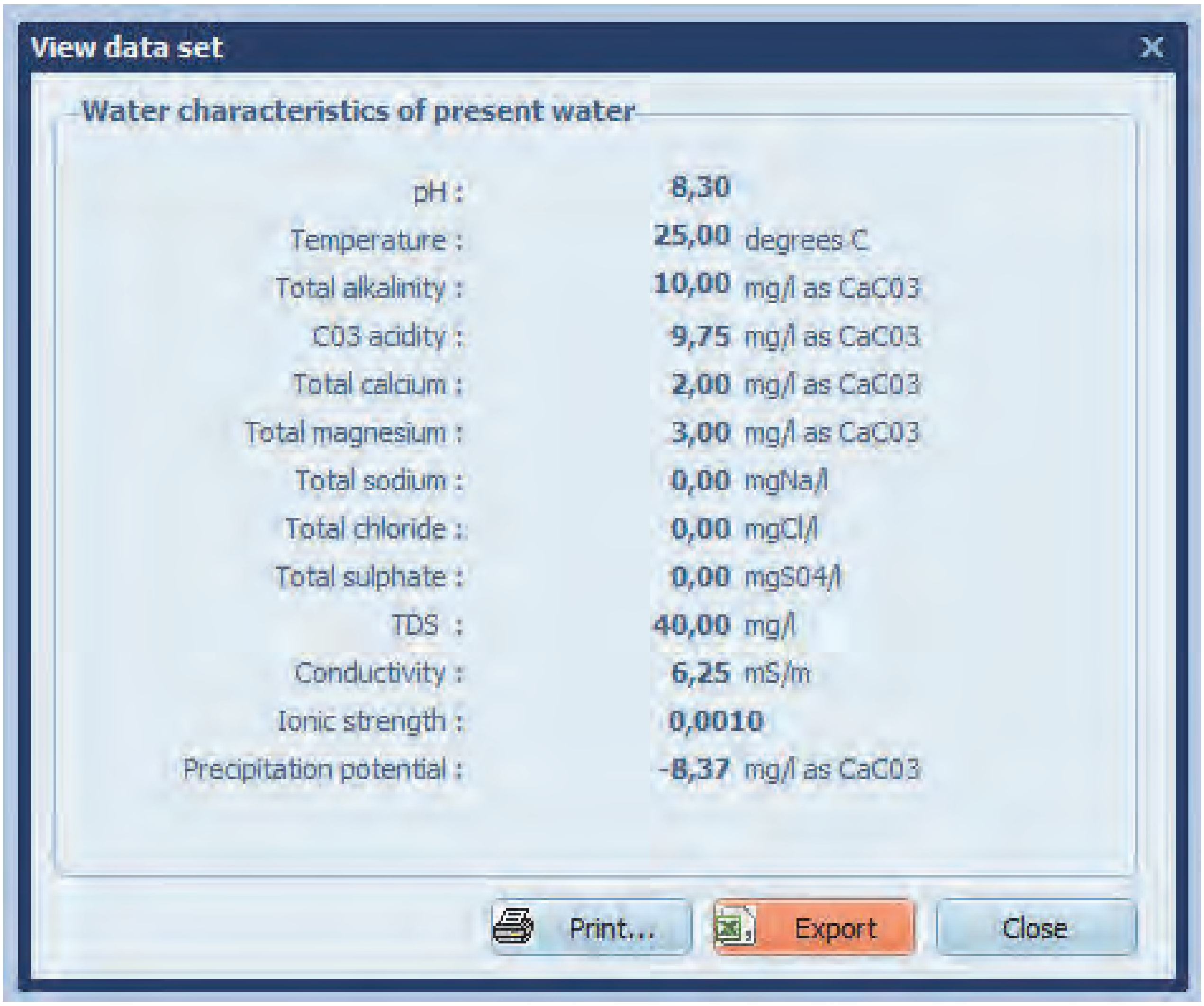
pH : 8,56
Temperature : 15,00 degrees C
Total alkalinity : 131,83 mg/l as CaCO3
CO3 acidity : 128,04 mg/l as CaCO3
Total calcium : 21,83 mg/l as CaCO3
Total magnesium : 0,00 mg/l as CaCO3
Total sodium : 0,00 mgNa/l
Total chloride : 0,00 mgCl/l
Total sulphate : 0,00 mgSO4/l
TDS : 800,00 mg/l
Conductivity : 125,00 mS/m
Ionic strength : 0,0200
Precipitation potential : 20,30 mg/l as CaCO3
CaCO3 precipitation : 188,17 mg/l as CaCO3

Figure 49: The results after treatment window for Example 10 (when equilibrium is attained between aqueous, gaseous and solid phases).

### 4.3.11 Example 11: Stabilisation of a calcium and carbonate species deficient water

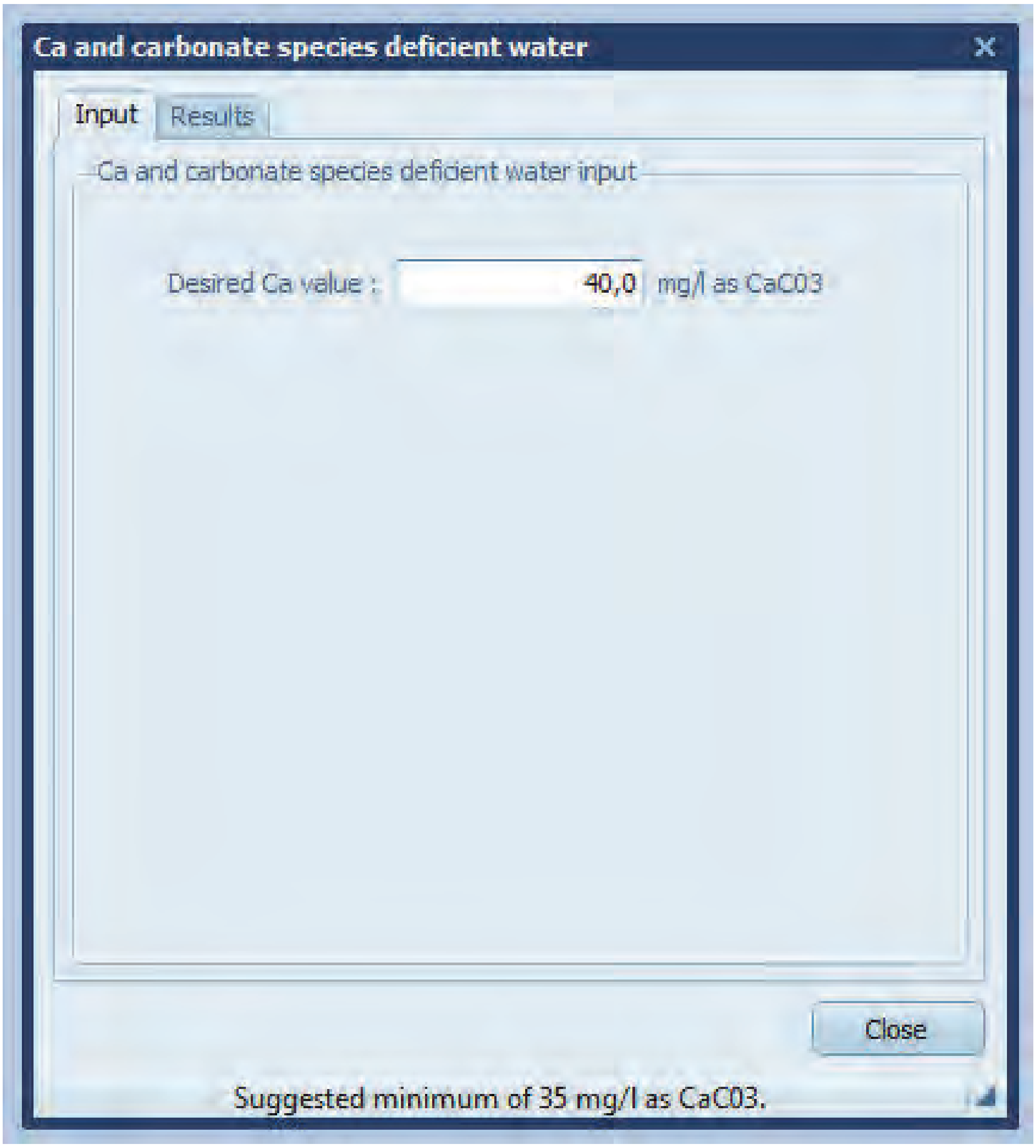
A water has the following characteristics: Total alkalinity 10 mg/ℓ, calcium 2 mg/ℓ, magnesium 3 mg/ℓ (all as $CaCO_3$), pH 8,3, TDS 40 mg/ℓ and temperature 25°C. This water needs to be stabilised to give a $CaCO_3$ precipitation potential of 5 mg/ℓ $CaCO_3$ and alkalinity and/or calcium not less than 40 mg/ℓ as $CaCO_3$. The solution procedure is set out below.

After entering the data into the **data set input** window (Figure 9), selection of the <View> option will bring the window displaying the characteristics of the present water onto the screen (Figure 50). Close the window and select the <Ca and carbonate species deficient waters> option from the Calculations menu, bringing up the **Ca and carbonate species deficient waters input** window as shown in Figure 51.



pH : 8,30
Temperature : 25,00 degrees C
Total alkalinity : 10,00 mg/l as CaC03
C03 acidity : 9,75 mg/l as CaC03
Total calcium : 2,00 mg/l as CaC03
Total magnesium : 3,00 mg/l as CaC03
Total sodium : 0,00 mgNa/l
Total chloride : 0,00 mgCl/l
Total sulphate : 0,00 mgS04/l
TDS : 40,00 mg/l
Conductivity : 6,25 mS/m
Ionic strength : 0,0010
Precipitation potential : -8,37 mg/l as CaC03

**Figure 50: Window displaying the characteristics of the water used in Example 11.**



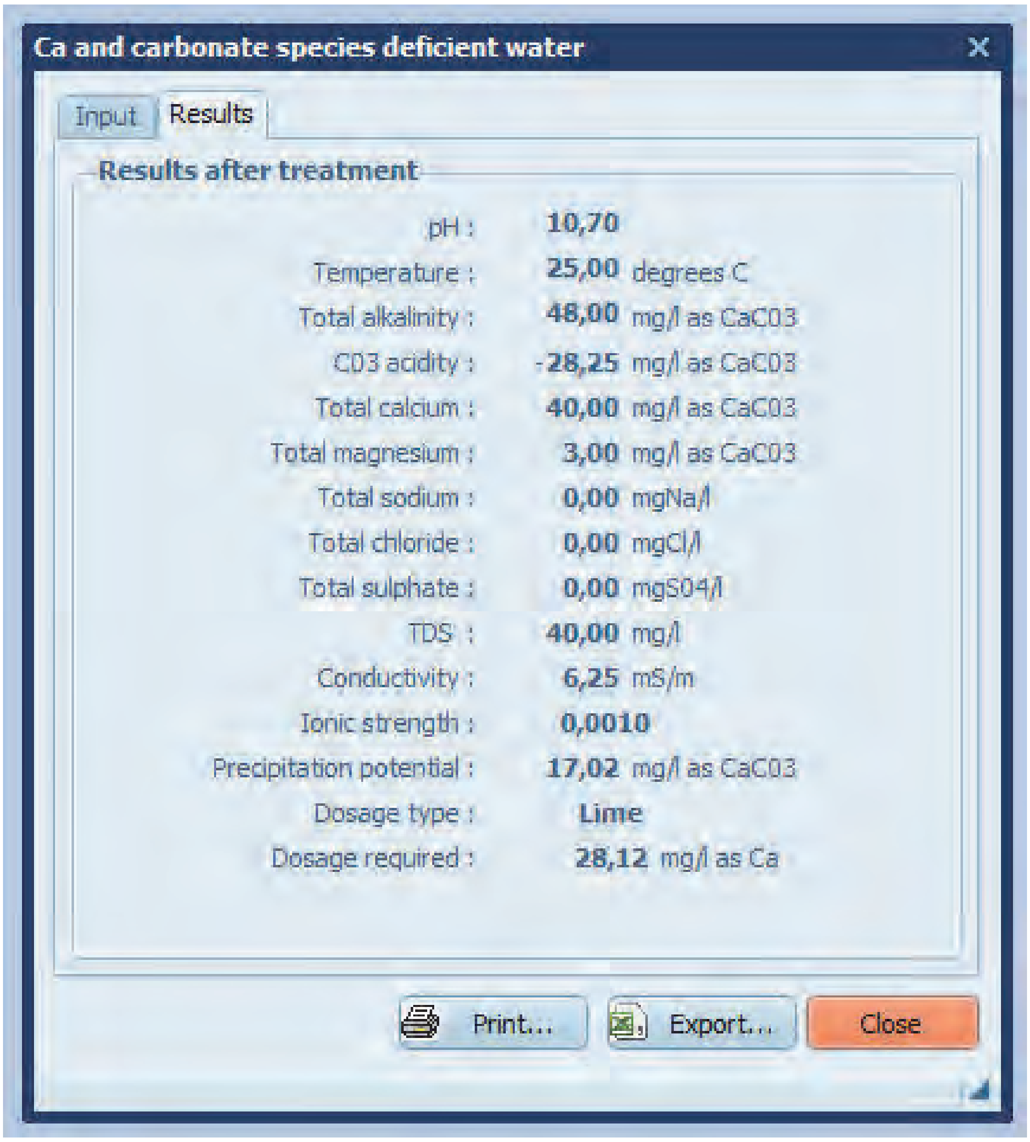
Desired Ca value : 40,0 mg/l as CaC03

Suggested minimum of 35 mg/l as CaC03.

**Figure 51: Ca and carbonate species deficient waters input window.**

In this particular case, because the calcium concentration is less than the Total alkalinity value, only the input box for a desired calcium value appears on the screen. Enter the required calcium concentration of 40 mg/ℓ as $CaCO_3$ by typing **40** into the desired calcium value input box (Figure 51).

Selection of the <Results> menu option will bring the **results after treatment** window onto the screen with values for the state of the water after lime dosage and the dosage of lime required to increase the calcium value to the desired concentration, as shown in Figure 52.



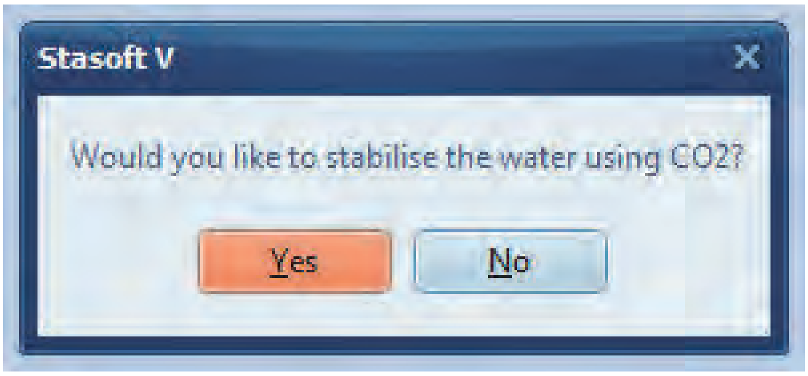
Results after treatment

pH : 10,70
Temperature : 25,00 degrees C
Total alkalinity : 48,00 mg/l as CaC03
C03 acidity : -28,25 mg/l as CaC03
Total calcium : 40,00 mg/l as CaC03
Total magnesium : 3,00 mg/l as CaC03
Total sodium : 0,00 mgNa/l
Total chloride : 0,00 mgCl/l
Total sulphate : 0,00 mgS04/l
TDS : 40,00 mg/l
Conductivity : 6,25 mS/m
Ionic strength : 0,0010
Precipitation potential : 17,02 mg/l as CaC03
Dosage type : Lime
Dosage required : 28,12 mg/l as Ca

**Figure 52: The results after treatment window for Example 11 (lime dosing).**

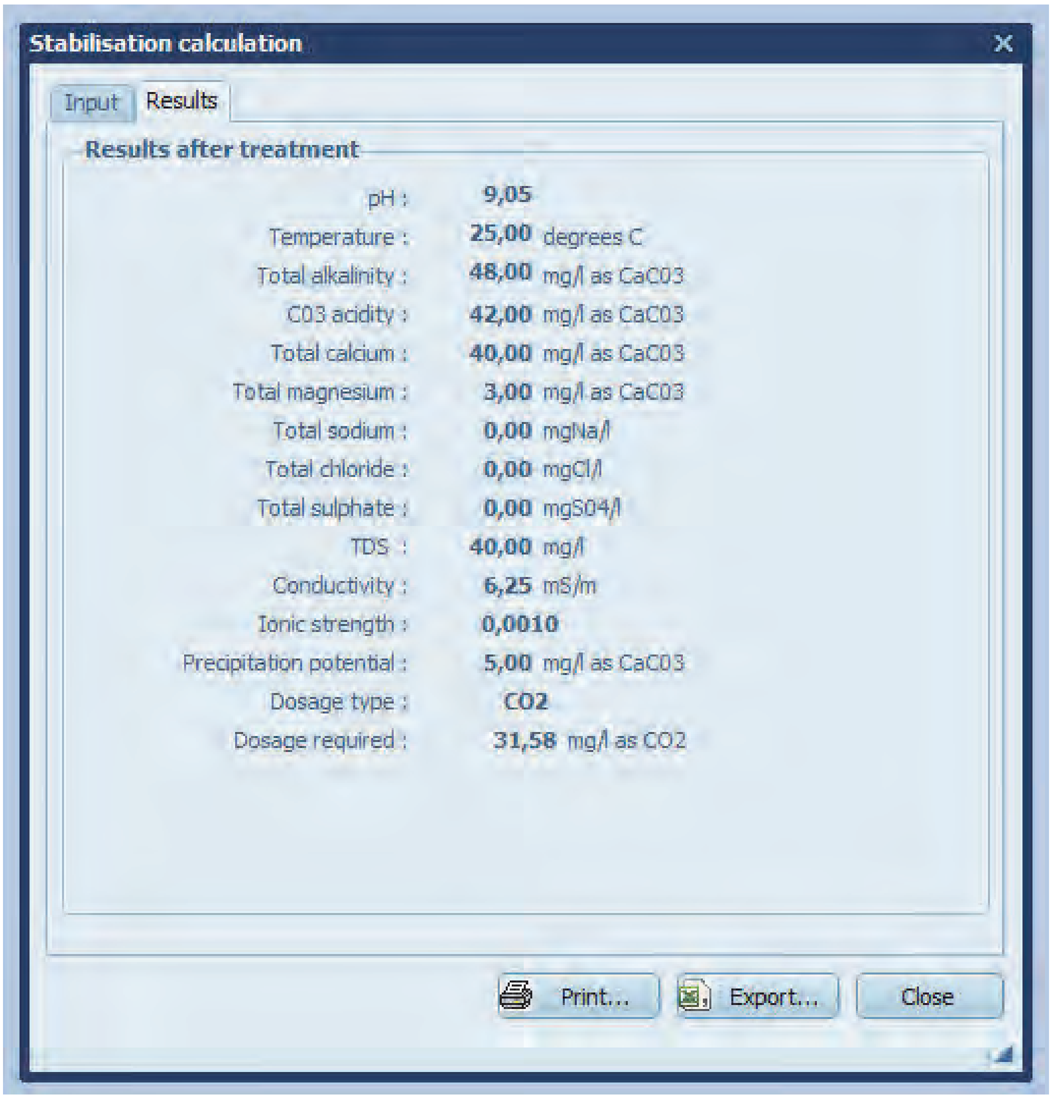
Selecting the <Close> option will bring the **stabilise enquiry** window onto the screen, allowing the user to recarbonate the water with $CO_2$ (Figure 53). Select <Yes> and the **stabilisation inputs** window for recarbonation of the present/active water will come onto the screen (similar to Figure 24, however, only allowing input for $CaCO_3$ precipitation input as $CO_2$ is used for recarbonation). If recarbonation of the water after lime dosing is not required, the user can simply type <No> to continue with other program functions.

Enter the required $CaCO_3$ precipitation potential of 5 mg/ℓ as $CaCO_3$ by typing **5** into the desired precipitation potential input box. Selection of the <Results> menu option will bring the **results after treatment** window onto the screen with values for the final state of the water and for the dosage of $CO_2$ required to adjust the water to the specified $CaCO_3$ precipitation potential, as shown in Figure 54.



Would you like to stabilise the water using CO2?

Figure 53: The stabilise enquiry window.



Results after treatment

pH : 9,05
Temperature : 25,00 degrees C
Total alkalinity : 48,00 mg/l as CaCO3
CO3 acidity : 42,00 mg/l as CaCO3
Total calcium : 40,00 mg/l as CaCO3
Total magnesium : 3,00 mg/l as CaCO3
Total sodium : 0,00 mgNa/l
Total chloride : 0,00 mgCl/l
Total sulphate : 0,00 mgSO4/l
TDS : 40,00 mg/l
Conductivity : 6,25 mS/m
Ionic strength : 0,0010
Precipitation potential : 5,00 mg/l as CaCO3
Dosage type : CO2
Dosage required : 31,58 mg/l as CO2

Figure 54: The results after treatment window for Example 11 (after recarbonation).

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# APPENDIX A

## DETERMINATION OF THERMODYNAMIC EQUILIBRIUM CONSTANTS

### Equilibrium constants

Chemical equilibrium is a dynamic state of balance in a reaction between reactants and products; at equilibrium the rate of formation of products equals the rate of formation of reactants. The law of mass action states that the rate of a reaction is proportional to the product of the reactants each raised to their stoichiometric coefficients. For example, if the reaction of a moles of A with b moles of B producing product c moles of C and d moles of D has reached equilibrium, then the reaction is depicted as:

$$aA + bB \leftrightarrow cC + dD$$

and the corresponding equilibrium equation is:

$$\frac{(C)^c (D)^d}{(A)^a (B)^b} = K$$

where ( ) = activity on the molar scale, and
K = temperature dependent thermodynamic equilibrium constant.

Values at 25°C for the various weak acid, ion pairing and solubility product equilibrium constants used in this monograph are listed in logarithmic format in Table A.2. Values for the constants at other temperatures can be determined using the van't Hoff equation. This equation is developed as follows:

From thermodynamic considerations (see Garrels and Christ 1965):

$$d\ln K = -\Delta\frac{H_r^0}{R} d\left(\frac{1}{T}\right) \qquad \text{(A.1)}$$

where R = universal gas constant, 0,008319 kJ/K.mole;
T = absolute temperature in Kelvin;
$\Delta H_r^0$ = change in reaction enthalpy; kJ/mole; and
$\ln K$ = natural logarithm of the thermodynamic equilibrium constant.

Integrating this expression and assuming that change in reaction enthalpy, $\Delta H_r^0$, is constant over the temperature range considered, gives the required expression:

$$\ln K_2 - \ln K_1 \; -\Delta\frac{H_r^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad \text{(A.2)}$$

where $T_1$ = reference temperature, 298 Kelvin;
$T_2$ = given temperature in Kelvin;

lnK$_1$ = natural logarithm of the thermodynamic equilibrium constant at temperature T$_1$; and
lnK$_2$ = natural logarithm of the thermodynamic equilibrium constant at given temperature

Converting to common logarithms and rearranging Equation (A.2) gives:

$$\log K_2 = \log K_1 + \frac{\Delta H_r^0}{2{,}303RT_1} - \frac{\Delta H_r^0}{2{,}303RT_2}$$

Substituting T$_1$ = 298 K and R = 0,008319 kJ/K.mole into the above equation gives:

$$\log K_2 = \log K_1 + \frac{\Delta H_r^0}{5{,}709} - \frac{\Delta H_r^0}{5{,}709}\left[\frac{298}{T_2}\right] \qquad \text{(A.3)}$$

Determination of equilibrium constants at temperatures other than 25°C is effected in this monograph using Equation (A.3). The $\Delta H_r^0$ values listed in Table A.2 are either those values quoted in the literature or values determined by fitting Equation (A.3) to reported data.

**Assessment of values for equilibrium constant**

The literature abounds with values determined for the various equilibrium constants pertinent to this monograph (see Table A.1). A problem arises in selecting which of these give the best description of species concentrations (speciation) in a particular aqueous solution.

In practice, this can only be done by comparison with data obtained in the laboratory (that is, by comparison with established benchmarks). However, recognising that this work is restricted to waters with TDS below 15 000 mg/ℓ, and that values for equilibrium constants for any particular reaction do not differ radically, it was assumed that insignificant differences in speciation arose between the various sets of equilibrium constants used.

This assumption was tested for a typical cooling water with Total alkalinity 120 mg/ℓ, calcium 600 mg/ℓ, magnesium 200 mg/ℓ (all as $CaCO_3$) , sodium 250 mg/ℓ, chloride 300 mg/ℓ sulphate 880 mg/ℓ, pH 7.3, TDS 2 400 mg/ℓ and temperature 25°C as follows:

- The changes in pH and $CaCo_3$ precipitation potential with chemical treatment were assessed using the equilibrium constants listed in Table A.2; the calculation was then repeated using the highest and lowest values for one of the equilibrium constants listed in Table A.1 and maintaining the values for the remaining constants equal to the values listed in Table A.2. This procedure was repeated for each of the equilibrium reactions.

- Generally, it was found that irrespective of the equilibrium constants used, the $CaCO_3$ precipitation potential did not vary more than 0,42 mg/ℓ, and the difference in the predicted pH varied by less than 0,04 units.

Consequently, for the purposes of this work, any of the reported constants could be used with minimal error involved. The values selected here (see Table A.2) are drawn from reported data in the literature where both the value at 25°C and the effects of temperature are given.

**Table A.1 A spectrum of values for equilibrium constants at 25°C from Loewenthal and Marais 1984.**

| Ion pair | pK value of ion pair | | References |
|---|---|---|---|
| $CaSO_4^0$ | 2,44[2] | 2,31[1] | 1. Garrels, Thompson and Siever (1961)<br>2. Loewenthal and Marais (1984)<br>3. Plummer and Busenberg (1982)<br>4. Lafon (1970)<br>5. Nakayama (1971)<br>6. Nakayama (1968)<br>7. McGee and Hostetler (1973)<br>8. Larson, Sollo and McGurk (1973)<br>9. Baes and Mesmer (1976) |
| $CaCO_3^0$ | 3,22[3] | 3,10[4] | |
| $CaHCO_3^+$ | 1,25[6] | 0,59[2] | |
| $CaOH^+$ | 1,38[8] | 1,15[9] | |
| $MgSO_4^0$ | 2,40[2] | 2,25[1] | |
| $MgCO_3^0$ | 3,4[1] | 2,90[8] | |
| $MgHCO_3^+$ | 1,23[5] | 0,51[2] | |
| $MgOH^+$ | 2,21[7] | 2,08[8] | |
| $NaSO_4^-$ | 1,06[2] | | |
| $NaCO_3^-$ | 1,27[1] | 0,65[2] | |

**Table A.2 Relevant logK and change in enthalpy values for certain reactions at 25°C (Truesdell and Jones 1973).**

| Reaction | logK | $\Delta H_r^0$ (kJ) |
|---|---|---|
| $H_2CO^*_{3aq} \leftrightarrow H^+_{aq} + HCO^-_{3aq}$ | (1) | |
| $HCO^-_{3aq} \leftrightarrow H^+_{aq} + CO^{2-}_{3aq}$ | (2) | |
| $H_2O_l \leftrightarrow H^+_{aq} + OH^-_{aq}$ | -14,0 | 55,873 |
| $NH^+_{4aq} \leftrightarrow H^+_{aq} + NH_{3aq}$ | -9,252 | 52,25 |
| $HSO^-_{4aq} \leftrightarrow H^+_{aq} + SO^{2-}_{4aq}$ | -1,987 | -20,56 |
| $CaCO_{3s} \leftrightarrow Ca^{2+}_{aq} + CO^{2-}_{3aq}$ | (3) | |
| $CaSO_{4s} \leftrightarrow Ca^{2+}_{aq} + SO^{2-}_{4aq}$ | -4,637 | -15,78 |
| $Mg(OH)_{2s} \leftrightarrow Mg^{2+}_{aq} + 2OH^-_{aq}$ | -10,204 | 3,56 |
| $CaSO^0_{4aq} \leftrightarrow Ca^{2+}_{aq} + SO^{2-}_{4aq}$ | -2,309 | -6,91 |
| $CaCO^0_{3aq} \leftrightarrow Ca^{2+}_{aq} + CO^{2-}_{3aq}$ | -3,22 | -13,10 |
| $CaHCO^+_{3aq} \leftrightarrow Ca^{2+}_{aq} + HCO^-_{3aq}$ | -1,11 | -26,507 |
| $CaOH^+_{aq} \leftrightarrow Ca^{2+}_{aq} + OH^-_{aq}$ | -1,4 | -4,98 |
| $MgSO^0_{4aq} \leftrightarrow Mg^{2+}_{aq} + SO^{2-}_{4aq}$ | -2,238 | -20,60 |
| $MgCO^0_{3aq} \leftrightarrow Mg^{2+}_{aq} + CO^{2-}_{3aq}$ | -3,398 | -0,243 |
| $MgHCO^+_{3aq} \leftrightarrow Mg^{2+}_{aq} + HCO^-_{3aq}$ | -0,928 | -43,42 |
| $MgOH^+_{aq} \leftrightarrow Mg^{2+}_{aq} + OH^-_{aq}$ | -2,6 | -8,96 |
| $NaSO^-_{4aq} \leftrightarrow Na^+_{aq} + SO^{2-}_{4aq}$ | -0,226 | -9,332 |
| $NaCO^-_{3aq} \leftrightarrow Na^+_{aq} + CO^{2-}_{3aq}$ | -1,268 | -37,309 |
| $NaSO^0_{4aq} \leftrightarrow 2Na^-_{aq} + SO^{2-}_{aq}$ | -1,512 | -11,05 |
| $Na_2CO^0_{3aq} \leftrightarrow 2Na^+_{aq} + CO^{2-}_{3aq}$ | -0,67 | 0,0 |
| $CO_{2g} \leftrightarrow CO_{2aq}$ | (4) | |

(1) The temperature dependence for the logK value for this reaction is (from data reported by Plummer and Busenberg 1982):

$$\log K = -356{,}3094 - 0{,}0609196T + 21834{,}37/T + 126{,}8339\log_{10}T - 1684915{,}0/T^2$$

(2) The temperature dependence for the logK value for this reaction is (from data reported by Plummer and Busenberg 1982):

$$\log K = -107{,}8871 - 0{,}03252849T + 5151{,}79/T + 38{,}92561\log_{10}T - 563713{,}9/T^2$$

(3) The temperature dependence for the logK value for this reaction is (from data reported by Plummer and Busenberg 1982):

$$\log K = -171{,}9065 - 0{,}077993T + 2839{,}32/T + 71{,}595\log_{10}T$$

(4) The temperature dependence for the logK value for this reaction is (from data reported by Stumm and Morgan 1970):

$$\log K = 2025{,}3/T + 0{,}0104T - 11{,}362$$

with T = absolute temperature in Kelvin.

# APPENDIX B

## DETERMINATION OF APPARENT EQUILIBRIUM CONSTANTS FOR LOW SALINITY WATERS

The equilibrium equation formulated in Appendix A is expressed in terms of species activities and the thermodynamic equilibrium constant. However, computational procedures in the various algorithms reported in this monograph use mass and proton balance equations in conjunction with equilibrium equations to resolve the various problems addressed. Recognising that the mass and proton balance equations are formulated in terms of molarities, it is necessary to link species activities and molarities.

The link between activity and molarity for a particular species, species X, is via the activity coefficient for species X, $\gamma_X$, that is:

$$\gamma_X = (X)/[X] \qquad \text{(B.1)}$$

where $\gamma_X$ = activity coefficient of species X,
(X) = activity of species X, and
[X] = molar concentration of species X.

In low salinity waters activity coefficients of ions can be determined from the Debye-Hückel theory, or some modification of it. The most widely used modification is that by Davies (Loewenthal *et al.* 1989); viz.

$$\log\gamma_i = -AZ_i^2\left[\frac{\mu^{\frac{1}{2}}}{1+\mu^{\frac{1}{2}}} - 0{,}2\mu\right] \qquad \text{(B.2)}$$

where $\gamma_i$ = activity coefficient for ionic species i, written as $\gamma_m$ and $\gamma_d$ for mono- and divalent ions respectively;
A = temperature dependent constant = $1{,}825.10^6(78{,}3T)^{-1{,}5}$ = 0,512 at 25°C;
T = temperature in Kelvin;
$Z_i$ = charge of the i^th species, equal to 1 for monovalent and 2 for divalent ions;
μ = ionic strength
= $\frac{1}{2}\,\Sigma C_i Z_i^2$ (B.3); and
$C_i$ = concentration of the ith ionic species in mol/ℓ.

To calculate the ionic strength, μ, using Equation (B.3), requires a complete analysis of the water. However, the activity coefficients determined from the Davies equation are relatively insensitive to ionic strength so that an approximate estimate for μ from empirical methods usually is sufficient. Two empirical equations valid for TDS up to ~ 1 000 mg/ℓ are available (Loewenthal *et al.* 1989), namely:

$$\mu \approx 2{,}5.10^{-5}.\text{TDS} \qquad \text{(B.4)}$$

where TDS = total inorganic dissolved solids in mg/ℓ and

$$\mu \approx 1{,}68.10^{-4}.\text{SC} \qquad \text{(B.5)}$$

where SC = specific conductance in mS/m (1 mS/m = 10 $\mu$S/cm).

Once activity coefficients have been determined, the equilibrium equations can be reformulated with species in terms of molarities by appropriately adjusting the thermodynamic equilibrium constants to incorporate activity coefficients (the Debye-Hückel effect) to give an apparent equilibrium constant. For example, for dissociation of the ion pair $CaCO_3$ at equilibrium, the reaction is:

$$CaCO_3^0 = Ca^{2+} + CO_3^{2-}$$

And the corresponding dissociation equilibrium equation, incorporating activity coefficients, is as follows:

$$\frac{[Ca^{2+}][CO_3^{2-}]}{[CaCO_3^0]} = \frac{K_{cc}}{\gamma_{d^2}} = K_{cc}$$

In the case of weak acid equilibrium equations it is more convenient to maintain the hydrogen ion species, $H^+$, in the activity form and adjust weak acid species to the molar form (Friend 1990). For example, for the first dissociation equation of carbonic acid ($H_2CO_3^*$), the desired equation is:

$$\frac{(H^+)[HCO_3^-]}{[H_2CO_3^*]} = \frac{K_{c1}}{\gamma_m} = K_{c1}$$

Note that the above formulations (applying to both low and medium salinity waters) the assumption is used that the activity and molarity are equal for neutral species, that is, their activity coefficients equal unity.

## APPENDIX C

## DETERMINATION OF APPARENT EQUILIBRIUM CONSTANTS AND SPECIES RATIOS FOR MEDIUM SALINITY WATERS

In medium salinity waters the form of the Debye-Hückel equation used to determine activity coefficients of ionic species follows that due to the extended Debye-Hückel law (Butler 1964), namely:

$$\log\gamma_i = -AZ_i^2\left[\frac{\mu^{\frac{1}{2}}}{1+Ba\mu^{\frac{1}{2}}}\right] \qquad (C.1)$$

where $\gamma_i$ = activity coefficient for ionic species i;
$A$ = temperature dependent constant = $1{,}825.10^6(78{,}3T)^{-1{,}5}$ = 0,512 at 25°C;
$T$ = temperature in Kelvin;
$Z_i$ = charge of the $i^{th}$ species, equal to 1 for monovalent and 2 for divalent ions;
$\mu$ = ionic strength;
$B$ = a function of the absolute temperature T = $50{,}3(78{,}3T)^{-½}$ = 0,33 at 25°C; and
$a$ = variable parameter measured in Angstrom units ($10^{-8}$ cm), which corresponds roughly to the effective size of the hydrated ion (see Table C.1).

**Table C.1 Values of the parameter a used in Equation (C.1) for selected ions. (from Butler 1964).**

| Ion | a |
|---|---|
| $OH^-$, $NH_4^+$ | 3 |
| $Na^+$, $HCO_3^-$, $SO_4^{2-}$ | 4 |
| $CO_3^{2-}$ | 5 |
| $Ca^{2+}$ | 6 |
| $Mg^{2+}$ | 8 |
| $H^+$ | 9 |

The form of equilibrium equations in medium salinity waters depends on the nature of the equilibrium reaction considered. For ion pairing and solubility product reactions, the equilibrium equations are formulated in terms of activities of free species; consequently, for these equations the apparent equilibrium constants are obtained by adjusting the thermodynamic constants in the same fashion as for low salinity waters. For weak acid equilibrium reactions, the equations are formulated in terms of the activity of hydrogen ion and for weak acid species in terms of the total species concentrations, the apparent equilibrium constants taking due account of this formulation, are set out in Friend (1990).

Activity coefficients in medium-salinity waters cannot be determined because initially the distribution of free and ion paired species concentrations is unknown. Consequently, speciation of the water, determination of ionic strength and hence determination of activity coefficients via Equation (C.1) are carried out simultaneously, Friend (1990).

The resultant speciation allows determination of the ratio ‘total to free species concentration’ for those species forming ion pairs in the solution, and these ratios are used in several of the algorithms presented by Friend (1990),

$$\mathrm{MGK} = [\mathrm{Mg}^{2+}]_T / [\mathrm{Mg}^{2+}]$$

$$\mathrm{CAK} = [\mathrm{Ca}^{2+}]_T / [\mathrm{Ca}^{2+}]$$

$$\mathrm{CO3K} = [\mathrm{CO}_3^{2-}]_T / [\mathrm{CO}_3^{2-}]$$

where MGK = ratio of total to free $Mg^{2+}$ concentration,
CAK = ratio of total to free $Ca^{2+}$ concentration, and
CO3K = ratio of total to free $CO_3^{2-}$ concentration.

In low-salinity waters the effects of ion pairing are insignificant, so that each of the ratios above equals unity.