

SALSOLCHEMIS: a spreadsheet application to calculate the ionic speciation of saline soil solutions and irrigation waters

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Abstract

SALSOLCHEMIS (SALine SOLution CHEMistry Ionic Speciation) is a computer program developed to calculate the equilibrium properties of saline, calcareous and gypsiferous soil solutions and irrigation waters at 25°C, pH between 3 and 11 and electrical conductivity lower than 20 dS m⁻¹. SALSOLCHEMIS is an ion-association model for the ions sodium, potassium, magnesium, calcium, chloride, nitrate, sulphate, bicarbonate and carbonate. SALSOLCHEMIS is able to carry out calculations of ionic speciation, ionic activities, ionic activity products, and electrical conductivity (EC₂₅).

SALSOLCHEMIS is written in Microsoft Visual Basic® and developed as a spreadsheet application. Input data to the model are entered in the sheets of a Microsoft Excel® workbook, from which SALSOLCHEMIS is called. Following calculations output data are written in the same workbook.

Table of contents

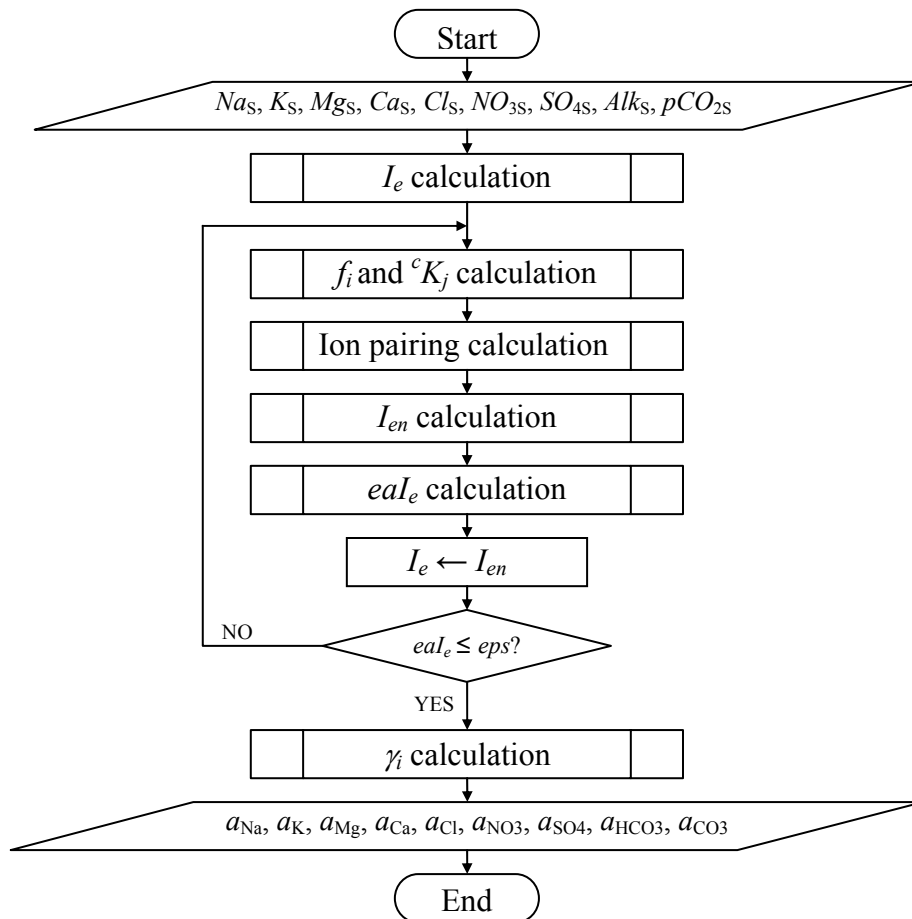
Model description.....	2
Flowchart.....	3
Electrical conductivity calculation.....	5
Novel characteristics of SALSOLCHEMIS.....	6
The computer program.....	6
Files.....	6
Software requirements.....	7
Structure of the SALSOLCHEMIS.xls workbook	8
Sheet "Main"	8
Sheet "Batch"	8
Sheet "Constants"	9

Sheet "Parameters"	9
How to use the program	10
References	11

Model description

SALSOLCHEMIS is applicable for the research of the chemical properties of soil solutions and irrigation waters from arid, semi-arid and dry subhumid regions, specifically those under risk of salinization. SALSOLCHEMIS presents several similar features with other programs developed with the same purpose, and also some novel characteristics which are stated below.

Figure 1. Flowchart of the SALSOLCHEMIS algorithm.



Flowchart

SALSOLCHEMIS is an ion-association model that uses the adaptation carried out by Davies (1962) of the Debye-Hückel equation to calculate the activities of free ions and ion pairs in aqueous solution. A flowchart for SALSOLCHEMIS is shown in figure 1 (Visconti, 2009).

The input data to the model are the major ion composition of the aqueous solution, the equilibrium thermodynamic constants and the ion parameters required to calculate the electrical conductivity. The composition of the aqueous solution is expressed as the concentrations in mmol/L of sodium, potassium, calcium, magnesium, chloride, nitrate and sulphate, together with the value of one of the following three pairs of data.

- A. pH and alkalinity in meq/L,
- B. $p\text{CO}_2$ in atm and alkalinity in meq/L, or
- C. bicarbonate and carbonate molar concentrations in mmol/L.

The thermodynamic constants are the Henry solubility constant of carbon dioxide in water (K_H), the constant of water ionization (K_w), the first and second ionization constants of the carbonic acid (K_{a1} and K_{a2}), and the constants of ion pair formation shown in table 1. These last values have been taken from Lindsay (1979) except for the formation of the ion pairs $\text{Ca}(\text{HCO}_3)^+$ and CaCO_3° (Visconti *et al.*, 2009).

Table 1. Ion pair formation constants ($\log K_f$): after Lindsay (1979)

	Na	K	Ca	Mg
HO	-0,2	-0,5	1,3	2,55
Cl	-0,48	-0,7	-1	—
NO_3	—	—	-4,8	—
SO_4	0,7	0,85	2,31	2,23
HCO_3	—	—	—	1,06
CO_3	1,26	—	—	3,23

Following the flowchart (figure 1), from the composition of the aqueous system SALSOLCHEMIS calculates the effective ionic strength (I_e) of the aqueous solution by means of the following equation

$$I_e = \frac{1}{2} \sum c_i z_i^2 \quad [1]$$

Where c_i and z_i are, respectively, the analytical concentration and charge of the ionic species i , which could be a free ion or an ion pair. From the effective ionic strength, the free ion activity coefficients (f_i) of each ion are calculated next using the following equation.

$$\log f_i = -0,512 z_i^2 \left[\frac{I_e^{1/2}}{1 + I_e^{1/2}} - 0,3 I_e \right] \quad [2]$$

The activity coefficients of non-charged species such as carbonic acid are calculated by means of this equation.

$$\log \gamma_i = 0.1I_e \quad [3]$$

The total activity coefficients of the charged ion pairs are calculated by means of equation 2. On the other hand, those of the non-charged ion pairs are calculated by means of the equations in table 2 depending on their composition, i.e. they are formed by divalent (Eq. 4) or monovalent (Eq. 5) ions.

Table 2. Equations used to calculate the total activity coefficients of non-charged ion pairs (Sposito and Traina, 1987).

Ion pairs	Equation	Number
From divalent ions	$\log \gamma_i = -0.3I_e + 0.033I_e^2$	[4]
From monovalent ions*	$\log \gamma_i = -k \left[\frac{I_e}{1 + aI_e} - bI_e^2 \right] + cI_e^3$	[5]

* $k = 11.7021$, $a = 60.8128 \text{ L mol}^{-1}$, $b = 0.0319 \text{ L}^2 \text{ mol}^{-2}$ and $c = -0.044 \text{ L}^3 \text{ mol}^{-3}$

From the activity coefficients and the thermodynamic equilibrium constants, the concentration equilibrium constants (cK_j) are calculated. The values of the concentration equilibrium constants are substituted in the mass balance equations of every of the ions in solution. These equations are next solved to find out the ion pair concentrations by means of a continued fraction algorithm (Nordstrom *et al.*, 1979). From the ion pair concentrations a new value for the effective ionic strength is calculated. This new value is compared with the previous one calculating the relative difference in percentage terms (eaI_e) between both as is expressed by equation 6.

$$eaI_e = 100 \left| \frac{I_{en} - I_e}{I_{en}} \right| \quad [6]$$

Where I_{en} and I_e stand for the new and the previous value of the ionic strength, respectively. When eaI_e is larger than the machine epsilon, the smallest number the computer distinguishes from zero, the calculation is repeated, starting from the new value of the effective ionic strength. On the contrary, the calculation is finished and the total ion coefficients are calculated subsequently.

Electrical conductivity calculation

Starting from the ionic species concentrations, the electrical conductivity at 25°C is calculated by means of the following equation (Visconti, 2009).

$$EC_{25} / \text{dS m}^{-1} = \left[0.21 + 0.681 \left(\sum_{i=1}^n |z_i| \lambda_i [i] \right) \right] \pm 0.28 \quad [7]$$

Where z_i , λ_i and $[i]$ stand for the charge, the equivalent ionic conductivity at infinite dilution, and the concentration of ion species i , respectively. The values of the ionic conductivities at infinite dilution of free ions are shown in table 3.

Table 3. Ionic conductivity of various ions at the limit of infinite dilution in $\text{S cm}^2 \text{mmol}^{-1}$.

Ion	H ⁺	HO ⁻	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	HCO ₃ ⁻	CO ₃ ²⁻
λ_i^0	0.337	0.192	0.050	0.074	0.053	0.060	0.076	0.071	0.080	0.044	0.072

The ionic conductivities of the ion pairs are calculated multiplying their ionic mobility by the Faraday constant. In order to calculate the ionic mobility of every ion pair the following equation is used (Anderko and Lencka, 1997).

$$u_{pi} = \frac{|z_{pi}|}{\sqrt[3]{\sum_i \left(\frac{|z_{pi}|}{u_i} \right)^3}} \quad [8]$$

Where u_{pi} and z_{pi} are the ionic mobility and the electrical charge of the ion pair pi and u_i is the ionic mobility of ion i . The summation in the denominator of equation 8 extends to the both ions that form the ion pair.

Novel characteristics of SALSOLCHEMIS

SALSOLCHEMIS presents several advantages, which are stated below, compared to other similar programs.

1. SALSOLCHEMIS calculates the electrical conductivity at 25°C of aqueous systems. Other programs do not calculate the electrical conductivity, or conversely, they use the electrical conductivity as an input datum to estimate the ionic strength.
2. The data required to characterise the carbonic-carbonate system can be entered in three distinct ways.

3. All data required to run the model (equilibrium constants, ion parameters, etc) are entered in a spreadsheet workbook, which name is SALSOLCHEMIS.xls.
4. All this information can be modified to the user's discretion.
5. SALSOLCHEMIS writes the results in the same workbook, which makes data processing easier.
6. A high number of aqueous systems can be processed in a batch-run.

Furthermore, in SALSOLCHEMIS there is no restriction regarding the charge balance of the working solutions. Nevertheless, users must be aware of the lack of reliability of the results obtained for systems with a charge balance that significantly departs from zero.

SALSOLCHEMIS presents also some limitations: i) only 11 inorganic ions are included in the calculations: hydronium, hydroxyl, sodium, potassium, magnesium, calcium, chloride, nitrate, sulphate, bicarbonate and carbonate, and ii) aqueous mineral equilibrium with calcite and gypsum is not considered in the calculations, iii) the ion activity calculations are reliable until 20 dS m⁻¹, and iv) the electrical conductivity calculations are reliable until 30 dS m⁻¹.

The computer program

Files

SALSOLCHEMIS is distributed with the following four files:

1. README.txt, a brief explanatory ASCII document
2. SALSOLCHEMIS.doc, the present explanatory document,
3. SALSOLCHEMIS.xls, a Microsoft Excel worksheet file, with which users interact, and
4. SALSOLCHEMIS.exe, the application file.

Software requirements

In order to correctly run SALSOLCHEMIS the following software requirements must be met: i) Windows XP or Vista operating system, ii) Microsoft Excel 2003 or better, iii) location of the four SALSOLCHEMIS files in the same folder in the hard drive, iv) to enable the macros of the SALSOLCHEMIS.xls workbook. In order to enable Excel macros in our computer the security level of Microsoft Excel probably has to be changed. It is advisable to have a medium security level. In Microsoft Excel 2003 open the "Security" dialog box in the menu Tools → Macro → Security...

(figure 2). Click the Security Level tab, select "Medium" and click the "Accept" button.

Figure 2. Configuración del nivel de seguridad de Microsoft Excel 2003

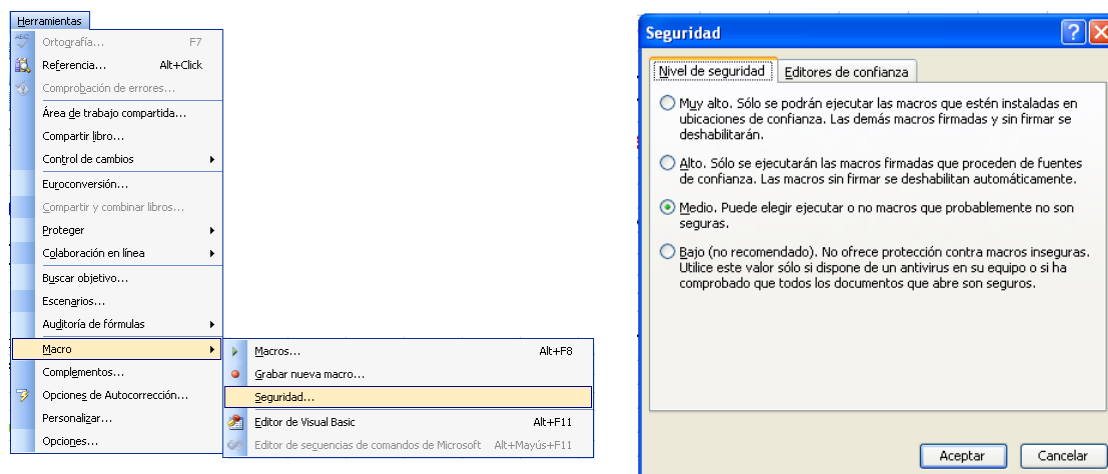
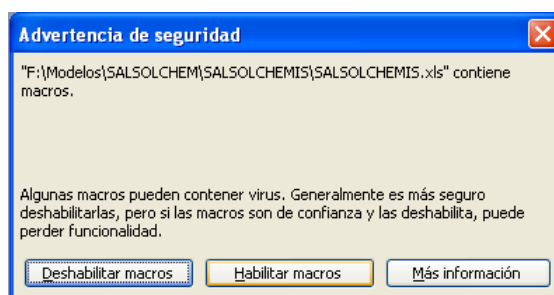


Figure 3. Advertencia de seguridad de Microsoft Excel



How to enable macros in Microsoft Excel 2007 can be looked up in the Microsoft Office online help in the following URL <http://office.microsoft.com/en-us/excel/HP100969191033.aspx?pid=CH101001571033>

When the security level has been established to "Medium" every time the SALSOLCHEMIS.xls workbook is open Excel will show us the box "Security warning" which is shown in figure 3. After it has been read click the "Enable macros" button.

Structure of the SALSOLCHEMIS.xls workbook

The SALSOLCHEMIS.xls workbook has four spreadsheets called "Main", "Batch", "Constants" and "Parameters".

Sheet "Main"

As its name says this is the main sheet of the program. This is the sheet from where the application SALSOLCHEMIS.exe is called, and where the equilibrium calculations are carried out for individual systems. In order to carry out these calculations the analytical data of the solution has to be typed in the framed cells of row 5 in the sheet under the heading "Total ion concentrations in the aqueous system in mmol/L". From this analytical information SALSOLCHEMIS carries out the calculations and writes the results of concentration of hydronium, hydroxyle, bicarbonate, carbonate, carbonic acid and total inorganic carbon in several cells next to the analytical data in row 5. In this row and under the heading "Other parameters" SALSOLCHEMIS writes the carbon dioxide partial pressure in equilibrium with the solution, the electrical conductivity, the ionic strength and the charge balance of the aqueous system. Under the heading "Ion activity coefficients and activities" SALSOLCHEMIS writes the activity coefficients (row 9) and the base-10 logarithm of ion activities (row 11). In the same row 11 and under the heading "Ion activity products" SALSOLCHEMIS writes the p value of the ionic activity products of gypsum, calcite and water. Finally within the matrix drawn under the heading "Ionic speciation in mmol/L" (rows 15 to 22 and columns D to I), SALSOLCHEMIS writes the concentrations of free ions and ion pairs.

Sheet "Batch"

The batch runs are carried out in this sheet. The first row is left for the column headings. The analytical data are entered in the second and subsequent rows. When SALSOLCHEMIS finishes the calculations it writes the results for every working solution in its corresponding row. Every aqueous system has to be labelled with some code significant for the user, which is introduced in the first column. SALSOLCHEMIS starts reading in the second row and stops when it finds a row with the first cell empty.

Sheet "Constants"

The values of the thermodynamic constants used by SALSOLCHEMIS are entered in this sheet. In row 5 there are several framed cells where the base-10 logarithm of the following constants has to be entered: Henry solubility constant of carbon dioxide in water (K_H), the constant of water ionization (K_w), the first and second ionization constants of the carbonic acid (K_{a1} and K_{a2}), and as supplemental information the solubility products of calcite and gypsum. In row 6, SALSOLCHEMIS writes the logarithm of the concentration equilibrium constant corresponding to each of the

thermodynamic equilibrium constants. In the framed matrix to the left of the sheet (rows 13 to 18 and columns D to F), the base-10 logarithm of the ion pair formation constants considered in this program have to be entered. An empty cell or containing a zero means that the ion pair does not form. In the matrix to the right of the sheet (rows 13 to 18 and columns J to M) SALSOLCHEMIS writes the logarithm of the concentration ion pair formation constants.

Sheet "Parameters"

The values of the parameters used by SALSOLCHEMIS to calculate the electrical conductivity at 25°C (EC_{25}) are entered in this sheet. This sheet is arranged in four frames. In the top frame (rows 4 to 7, columns B to M) the values of charge, ionic mobility and molar mass of the following free ions in addition to the neutral species carbonic acid, are entered: hydronium, hydroxide, sodium, potassium, calcium, magnesium, chloride, nitrate, sulphate, bicarbonate and carbonate. In the subsequent frames (rows 10 to 11, columns B to M and rows 14 to 15 and columns B to M) the values of charge and equivalent ionic mobility for each one of the ion pairs that can be formed by combination of the previous ions are entered. In the bottom frame the coefficients of the empirical equation used to calculate the electrical conductivity are entered, the intercept with the ordinate axis in cell E19 and the slope in cell E20.

How to use the program

SALSOLCHEMIS is distributed with all the information necessary to carry out the equilibrium calculations, so it is ready to be used immediately. So as to use the program open the SALSOLCHEMIS.xls workbook. In the sheet "Main" the calculation for one solution at a time can be carried out. However, if we have several working solutions, in order to save time we can process several systems in the sheet "Batch". Whichever of the two options, enter the analytical data in the corresponding sheet. The analytical information about the carbonic system can be introduced following three distinct options which have been called A, B and C. What information and where it has to be introduced is specified in table 4.

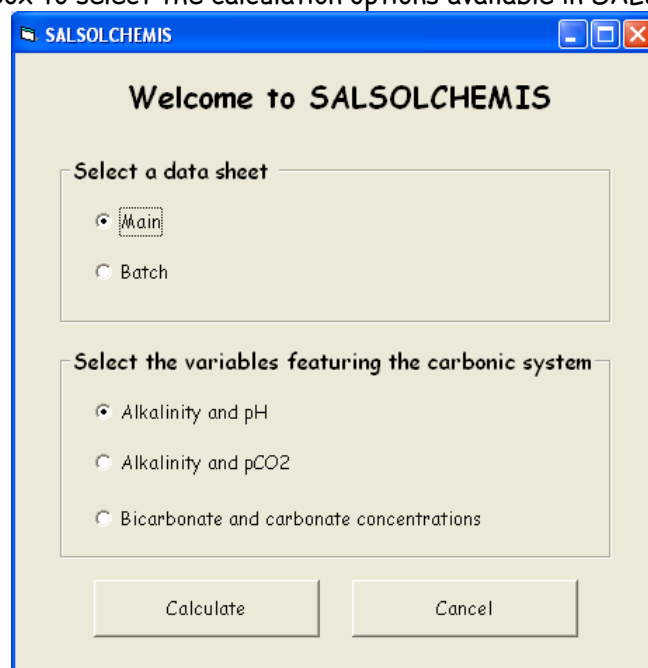
When the calculation option for the carbonic system is to be changed, the heading text in cells A4 and B4 in the sheet "Main" will not describe correctly the data in the cells below. This fact, however, is not of concern. SALSOLCHEMIS will change these headings once is informed about what option we selected. How-to is described in the lines below.

Table 4. Data to be introduced in the cells A5, B5, sheet "Main" and cells B1 and C1, sheet "Batch" depending on the option selected for carbonic system.

Option	Cells in the sheet "Main"		Cells in the sheet "Batch"	
	A5	B5	B2, B3, B4, etc.	C2, C3, C4, etc.
A	pH	alkalinity	pH	alkalinity
B	pCO ₂	alkalinity	pCO ₂	alkalinity
C	[CO ₃ ²⁻]	[HCO ₃ ⁻]	[CO ₃ ²⁻]	[HCO ₃ ⁻]

*pCO₂ in atm, alkalinity in meq/L, [CO₃²⁻] and [HCO₃⁻] in mmol/L

Figure 4. Dialog box to select the calculation options available in SALSOLCHEMIS



To run SALSOLCHEMIS click the button "Calculate" in the sheet "Main". A dialog box (figure 4) will appear. This box is arranged in two frames. In the frame "Select a data sheet" select the sheet where the data you want to run is located. In the frame "Select the variables featuring the carbonic system" select the calculation option for the carbonic system: A) "Alkalinity and pH", B) "Alkalinity and pCO₂" and C) "Bicarbonate and carbonate concentrations". Then click the "Calculate" button in the box and the program will be run.

Once the calculations have been carried out, SALSOLCHEMIS writes the results in the sheet "Main" or in the sheet "Batch" depending on our indications.

The program SALSOLCHEMIS is free distributed for educational and research purposes.

Comments and suggestions concerning problems or improvements of this program are welcomed and can be addressed to the e-mail provided at the beginning of this document

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