

**Iceland Water Chemistry Group
presents the chemical speciation program**

WATCH

The computer program WATCH is mainly intended to serve as a tool for interpreting the chemical composition of geothermal fluids, although it is also useful for non-thermal waters. The program reads chemical analyses of water, gas, and steam condensate samples collected at the surface and computes the chemical composition of downhole, or aquifer, fluids. This includes the pH, aqueous speciation, partial pressures of gases, redox potentials, and activity products for mineral dissolution reactions. The program is briefly described below.

I. General description.

The input to the program is from a file containing a component analysis of each phase of the geothermal fluids at the surface, including the water pH and the temperature at which it was measured. Other input, which is provided interactively from the terminal, includes a specification of the reference temperature, i.e. the temperature at which the aqueous speciation is to be calculated.

The concentrations of the species considered in the program are expressed in terms of the component concentrations by mass balance equations, and the chemical equilibria between the species are expressed as mass action equations. The two sets of equations are solved simultaneously by an iterative procedure. This procedure is carried out a few times during each run of the program. The program contains provisions for 67 different aqueous species, in addition to H^+ and OH^- , which are treated separately.

An initial estimate of the ionic strength of the water is obtained using only the concentrations of the major cations. This value of the ionic strength is used to compute activity coefficients, at the temperature of the pH measurement, using the extended Debye-Hückel equation. The chemical equilibria and mass balance equations are now solved simultaneously at this temperature to yield a distribution of species. From the new distribution of species, a proper ionic strength is computed. This ionic strength is used to recompute the activity coefficients and species concentrations, still at the temperature of the pH measurement.

The concentrations of the anions of the weak acids and their complexes are now added up, weighted by the number of protons that each can accept, to give a sum, SUMWA. This quantity, which is a measure of alkalinity, in some sense, is assumed to be constant for a given sample, independent of temperature. This property is used to compute the pH at the reference temperature. Before doing so, however, the steam phase, if one was collected, is added to yield a component concentration for the total discharge. The pH-

calculation, the calculation of the activity coefficients, the mass balance iteration, and the ionic strength calculation are all, in turn, carried out a number of times. The equilibrium gas pressures are then computed from the final equilibrium species concentrations.

The reference temperature mentioned above can be chosen in a few ways. It can be chosen as the measured temperature of the well or spring, or as a chalcedony, quartz, or sodium-potassium chemical geothermometer value. The geothermometer temperatures are calculated from the activities of the respective chemical species. This means that the pH and speciation calculations must be repeated each time the geothermometer temperature is updated. This is iterated until the temperature is self-consistent to within 0.01 degree. Finally, the reference temperature can also be chosen arbitrarily.

The output from the program lists the component and species concentrations at the reference temperature, as well as the activity coefficients. Ionic balance, geothermometer temperatures, partial pressures of gases, and redox potentials are also output. Finally, the ion activity products and solubility products of selected minerals are computed and printed. From these, the corresponding saturation indices can be trivially obtained.

The WATCH program can also be used to compute the resulting species concentrations, activity coefficients, and activity products and solubility products when the equilibrated fluid is allowed to cool conductively or by adiabatic boiling from the reference temperature to some lower temperature. This is particularly useful in the study of scaling.

It should be pointed out that since activity coefficients are obtained by the (extended) Debye-Hückel equation, the computed activities become less and less accurate at higher concentrations. Results of calculations of solutions with ionic strength in excess of 0.5, or so, should be treated with caution.

When calculating the aquifer composition, in particular the distribution and partial pressures of gases, the program uses one of three models. The first of these is applicable to wet-steam wells with "excess enthalpy", i.e. the case where liquid water and steam coexist in the reservoir. The second model is appropriate for hot-water wells, hot spring fluids that have not boiled before sample collection, and wet-steam wells in single-phase (liquid) aquifers. The third model describes boiling hot springs, where steam and gas have been lost prior to sampling by boiling of the fluid from the reference temperature down to an assumed final temperature. Here, the original composition is reconstructed by computing and adding back the steam and gas lost.

In older versions of WATCH these three models were covered by two distinct programs. WATCH1 handled all cases where samples of both water and steam were available, and thus dealt with the first model above (two-phase aquifer) as well as the wet-steam well instances of the second. WATCH3, on the other hand, was used for the second model when single-phase samples of the total discharge were available, in which case the program was often referred to as WATCH2. Finally, WATCH3 was also used when the third model was applicable.

These programs, WATCH1 and WATCH3, were originally written in the 1970's by Stefán Arnórsson, Sven Sigurðsson, and Hörður Svavarson. They were all at

Orkustofnun, the National Energy Authority of Iceland, during the early stages of the work, but the first two authors joined the University of Iceland during the later stages. The programs have now been completely rewritten to yield the present WATCH, version 2.0. This new program does the same calculations as the previous ones, and uses the same thermodynamic data, but the FORTRAN code has been rewritten from scratch. This was done by Jón Örn Bjarnason, also of Orkustofnun, and completed in 1993. In particular, the roles of WATCH1 and WATCH3 have been conflated in the present program, WATCH, which supersedes both of them. A few errors, mostly minor, have been corrected in the process. The most serious of these was an extra multiplication by the liquid fraction in the case of a two-phase sample from a well fed by a single-phase reservoir. This error became particularly significant if the sampling temperature was low compared to the reference temperature.

Furthermore, a few improvements in the program have been made along the way: the form of the input file has been made more transparent, a pickup file capability for boiling and cooling steps has been added, and the fluoride, ammonia, borate, and sulfate species have been included in the pH calculation. This last addition can lead to significant differences between the new WATCH version and the older programs, in cases involving acid water with very high concentrations of sulfate. Finally, talc, chrysotile, and amorphous silica have been added to the mineral saturation list. Saturation data for talc and chrysotile were obtained from the SUPCRT program of Helgeson et al., and amorphous silica solubility data from Fournier (Geothermics, 5, pp. 41-50, 1977).

It has also turned out to be desirable to tighten the convergence criteria in various calculations, and to increase the number of iterations in some parts of the program. This is necessary to attain self-consistency in the calculations for some types of waters, especially some acid sulfate waters, though quite superfluous for many common types of geothermal waters. As a result, the program is somewhat slower than the original ones. This should present no problems, however, since computer speed and cost have improved vastly in the last few years.

A substantial amount of internal documentation, largely absent from the older programs, has been added to the present version. Most importantly, however, it is hoped that the new code, though somewhat longer, is easier to read and make changes to than the original programs.

The present version is written in FORTRAN 77, though it does not adhere strictly to the ANSI standard. The extensions used have become "almost standard", however, and are widely available in FORTRAN compilers. Even so, minor modifications in the program may have to be made for many compilers.

The background to the program and the methods of calculation used were described by Stefan Arnorsson, Sven Sigurdsson, and Hordur Svavarsson in their paper "The chemistry of geothermal waters in Iceland. I. Calculation of aqueous speciation from 0°C to 370°C", which appeared in 1982 in *Geochimica et Cosmochimica Acta*, on pages 1513 to 1532 of volume 46. The paper gives complete references for the thermodynamic data used.

II. User's guide.

A. Input file.

To run the WATCH program, one must first create an input file. There are two ways of doing this. One is to run the program WAIN, which prompts the user for the concentration values of individual components and other data and writes the replies to a properly formatted file. The other way is to edit an already existing file, using it as a template. The input file need only contain the component composition of one sample, but a sequence of many samples can be included in a file; as many as desired, in fact.

The first line of an input file is a fixed heading introducing the file as a WATCH input file. The remainder of the file consists of sets of three records each. The first record of each set is blank, for readability. The second line of the set identifies the component whose value goes into the third record, directly below the identification. The value can be entered anywhere in the space under the identification, on the third line of the set, up to and including the angular brackets that enclose it. This third line of the set will be referred to as the data line.

The first data line has space for a sample number (or other identification of a similar nature) and for the sample location. The measured temperature, pressure, enthalpy, and discharge go on the next data line. The discharge is there for the printout only and is never used in the calculation. The temperature value is only used if so desired at runtime. The pressure and enthalpy values are used only in the case of a two-phase sample from a high temperature steam-water well. Even then, an enthalpy value can be omitted, in which case WATCH will assume the enthalpy of the fluid to be that of saturated water at the reference temperature. The pressure is in bar-gauge. The next five data lines list the component concentrations in the water phase, and the following two the gas phase concentrations. Condensate phase and whole steam data are given on the final two data lines. Specifically, the next to last data line gives the concentrations of CO₂ and H₂S in total steam. These values are typically obtained by collection into an alkaline solution in an otherwise evacuated flask. If non-zero, they override the gas phase CO₂ and H₂S concentrations. If the file contains the data for another sample, the headline and first set of records for this sample immediately follow.

For running the program, the data in the file need not be complete. In particular, the data lines for the gas, steam, and condensate phases can be left blank. In this case the sample will be treated as a single-phase water sample. The program will, furthermore, run even if this water analysis is itself also incomplete. If many components, or major ones, are missing, the results may not be very meaningful, of course, but this is left to the judgement of the user.

B. Running the program.

If an input file is already available, the program can be run. After invoking the program, the user is first prompted for the name of the input file. The default value for this is WATCH.IN, and the program will search for a file with this name if the user replies to the prompt with <RETURN> or <ENTER>. Otherwise the filename given will be used.

The next two prompts can be answered with carriage returns if so desired. The items sought are: first, the user name, or the date, or other similar label for the printout; and second, a printout heading. These are, of course, not essential for the running of the program. The fourth prompt is for the name of the output file. A default of WATCH.OUT is provided. Note that an existing file with the same name will be overwritten, and so should be copied to a different name if it is to be saved.

After these prompts, data for the first sample are displayed on the screen, and the user is prompted for an action to take. There are three choices. Typing q or Q, followed by a carriage return, will end the program run. Typing n or N, followed by carriage return, will cause the program to skip calculation of the sample displayed and move on to the next sample, if there is one, and exit otherwise. The default choice, however, is to carry out the calculation.

When this default choice is made, which is presumably most of the time, the program asks how the reference temperature is to be chosen. This is the temperature at which the speciation calculation is carried out in the program. There are five ways of choosing this temperature, and the choices are distinguished by the numbers 0, 1, 2, 3, and 4. The default choice, i.e. 0 or <RETURN>, is to use a measured temperature. If this choice is made, the program prompts for the value of the measured temperature. The default reply to this prompt, <RETURN>, causes the program to read the measured temperature from the input data file; otherwise the value supplied is used. To select an arbitrary reference temperature, one types 1 in response to the temperature type prompt. The program then prompts for the temperature value. The only difference between these two choices of reference temperature type, 0 and 1, is on the printout; the fixed value of the temperature is treated identically in the calculation in the two cases. The remaining three possibilities, 2, 3, and 4, represent chalcedony, quartz, and sodium-potassium geothermometer temperatures, respectively. Since the geothermometer temperature is computed by the program, the user need not supply a temperature value with these choices.

If, in the case of a two-phase sample, the value of the reference temperature chosen is lower than the separation (collection) temperature, the gas, steam, and condensate phases are ignored, and the calculation is carried out on the water phase only. Thus if a two-phase sample of a fluid at a high temperature is available, and the composition of the whole fluid at some lower temperature is desired, one should carry out an equilibration at a temperature higher than the sampling temperature, and then use the boiling or the cooling option (see below) to find the composition at the lower temperature.

After the reference temperature has been chosen, the program will prompt for the temperature at which the water is assumed to have boiled and lost steam before sampling, such as may be the case for boiling springs. If such a separation temperature is given, the program computes the composition of a steam phase that would have been in equilibrium with the water sample at the separation temperature. This steam is then added to the water phase. This prompt only appears if the sample in the input file is single-phase. (If the sample is two-phase, as is generally the case for high-temperature wells, the composition of the separated steam is, of course, already known and need not be calculated.) If the single-phase sample is believed not to have suffered steam loss, the prompt is answered by a simple carriage return. If a boiling temperature is given,

however, the user is also prompted for a degassing coefficient. This coefficient is a measure of incomplete degassing and can only be guessed at. This option is, however, useful when studying the effect of incomplete degassing on the aqueous species distribution. The default value of unity corresponds to equilibrium degassing, but the program will accept values in the range 0.01 - 1. Other values are set to 1 by the program.

The remaining prompts from the program involve boiling and cooling of the fluid equilibrated at the reference temperature down to some different temperature. The first of these prompts is for the temperatures to which adiabatic boiling is assumed to bring the equilibrated fluid. This prompt is answered by the number of boiling steps and the temperature values, separated by commas. Thus, if one desires the steam and water composition resulting from the adiabatic boiling to 220°C, 150°C, and 100°C, of a fluid equilibrated at 235°C, the prompt is answered with 3,220,150,100. Note that for each step the initial fluid composition is the original equilibrated fluid at the reference temperature, not the liquid in the previous step. If calculation of adiabatic boiling is not desired, the prompt is answered with a carriage return.

If a boiling calculation is wanted, the program prompts for a degassing coefficient. Generally, the default value of unity is chosen, corresponding to equilibrium degassing. The permitted range for this coefficient, which is a measure of incomplete degassing, is 0.01 to 1. Values outside this range are set to 1 by the program.

The final prompt is for the number of cooling steps and the temperatures to which the fluid equilibrated at the reference temperature is allowed to cool conductively. Thus, if one wishes to find the composition of a fluid that has just been equilibrated at, say, 235°C, after cooling to 200°C and 150°C, one enters 2,200,150 in response to the cooling prompt. This cooling calculation is intended to simulate cooling without boiling, such as takes place in a heat exchanger or a channel or a fracture in the ground. If the fluid equilibrated at the reference temperature is two-phase, it is assumed quenched to a single-phase in the process of cooling. As a result, the component composition resulting from this calculation is always identical to the total discharge composition. If this calculation is not desired, the response to the prompt is a carriage return.

The program now carries out the calculations requested. The results are written to the output file WATCH.OUT. Note that this file is overwritten each time the program is run, so it must be copied to a different name if it is to be saved.

If one or more boiling steps are selected, the component composition of the liquid phase at the last boiling step is written to the file BOIL.OUT. This file is overwritten the next time the program is run with a boiling step calculation. The file BOIL.OUT allows one to do calculations on a liquid phase separated in a boiling step without having to reenter the liquid composition by hand. Thus one could, for example, start with a sample of geothermal fluid at a wellhead, compute its equilibrium composition at some downhole temperature, say 235°C, then compute the composition of the fluid after flashing at 150°C, as in a separator, and have the liquid composition written to BOIL.OUT. This file could be copied to WATCH.IN and used as an input file for a second run of the program, in which the composition of the separated liquid would be explored under other conditions, such as in a second flashing stage, or in a heat exchanger.

If one or more cooling steps are selected, the resulting component composition is written to the file COOL.OUT. The temperature written to the file is that of the last cooling step. This is particularly useful if one wants a pickup file containing the total discharge composition of a fluid from a two-phase well. By editing such a file and using it as input for a new calculation, one could thus e.g. explore the consequences of changes in the inflow to the well.

For further information on WATCH, please contact

Stefán Arnórsson	or	Jón Örn Bjarnason
Science Institute		Orkustofnun
University of Iceland		Grensásvegur 9
Dunhagi 3		108 Reykjavík
107 Reykjavík		ICELAND
ICELAND		

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Program upgrade: Version 2.1, October 1994.

In version 2.0 of WATCH, improper initialization caused the logarithms of activity products for mineral dissolution to be carried over from a previous sample in the same input file, instead of being set to 99.999, if concentration values necessary for the calculation were missing. This has been corrected in version 2.1.

When the calculated enthalpy exceeded the measured enthalpy very slightly and a geothermometer temperature was chosen as the reference temperature, version 2.0 would sometimes give small but nonzero aquifer steam fractions. This has been fixed in version 2.1.

Several other modifications, mostly very minor, have been carried out.

Note that the name of the companion program used to create input files has been changed from WIN to WAIN, in order to avoid conflict with MS-WINDOWS.

October 1994

Program upgrade: Version 2.2, April 2002.

The temperature functions for the dissociation constants of the iron hydroxyl species and the aluminum hydroxyl species have been updated. This was deemed necessary in light of thermodynamic data that has been published in recent years.

The temperature functions for the Henrys law constants have likewise been updated.

In previous versions of WATCH, the ion activity products that included aluminum were

calculated by setting the concentration of the Al(OH)_4^- species equal to the total aluminum concentration. With the inclusion of the new dissociation constants for the aluminum hydroxyl species, this approach has been dropped, and the computed Al(OH)_4^- concentration is used instead.

In versions 2.0 and 2.1 of WATCH, improper initialization would cause the oxidation potentials for four couples to be carried over from a previous sample in the same input file instead of being set to 99.999, if concentration values necessary for the calculation were missing. This has been corrected in the present version.

The aluminum hydroxyl species, as well as the calcium and magnesium hydroxyl species, have been included in the pH calculations.

The printout has been modified slightly. In particular, the format for boron, aluminum, and iron on the first page has been expanded to four decimal places. The format for CO_2 in the vapor phase has been expanded to cover extremely high concentrations. On the second page, some headings have been modified, and columns have been realigned to facilitate importing the file into spreadsheet programs.

April 2002

Program upgrade: Version 2.3, January 2004.

In previous versions of the program, the quartz geothermometer temperature option would sometimes give wrong results if the silica concentration in the input file was extremely high. For two-phase samples, in particular, an incorrect reference temperature and an inconsistent steam fraction might be calculated. For still higher silica values the program would crash. This has been corrected in the present version.

January 2004

Program upgrade: Version 2.4, April 2010.

The contribution of the aluminum species to the pH calculation was not properly formulated in versions 2.2 and 2.3 of WATCH. This led to convergence problems in the pH calculation, and resulted in erroneous species distributions. The problem was most pronounced at high aluminum concentrations. This defect has been corrected in version 2.4.

Previous versions of the program would sometimes crash when the computed NaK-geothermometer temperatures were above 350°C or below 0°C. The handling of such cases has been modified in the present version to allow the application to exit gracefully, when necessary.

A test has been included to ensure that the reference temperature will never be lower than the separation temperature of a two-phase sample, since this would cause the steam fraction at collection to become negative.

Updated values for the Henrys constants of CO₂, H₂S, H₂, and CH₄ have been included. New values have also been introduced for the dissociation constants of the four aluminum hydroxyl species, aqueous carbon dioxide, bicarbonate, and hydrogen sulfide.

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