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Geothermal Chemistry Thermodynamics: The Watchworks Program For MS-Windows™

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ABSTRACT

The WATCH computer code, which calculates composition and aqueous speciation in geothermal reservoir waters, has been upgraded and transferred to MS-Windows™ under the name WatchWorks. Program output includes pH, redox potential, the partial pressures of dissolved gases, and mineral solubilities. WatchWorks assists analyses of scaling and corrosion potential, calculates reservoir steam composition, effects of boiling and cooling, and excess steam in the wellflow. The amount of acid, base or CO₂ gas needed to adjust brine pH can be calculated, as may be needed to inhibit scale formation or neutralize a low pH. The Windows environment provides for extensive input-output control and on-screen recalculation of data units. Examples of applications are provided.

Introduction

A capability to calculate geothermal fluid characteristics such as aqueous speciation, scaling potential, pH, and gas partial pressure can be useful in geothermal exploration, resource assessment, project design and production/injection fluids management. The WATCH computer program, which provides such capabilities, was originally developed at the University of Iceland (Amorsson and Sigurdsson, 1982, Amorsson and others, 1983a and 1983b). WATCH has recently been upgraded at the Icelandic National Energy Institute, Orkustofnun, as WATCH ver.2.1, and transferred to the MS-Windows™ environment by GeothermEx, Inc., as WatchWorks.

Program Features

WatchWorks is specifically suited to handle chemical data from two-phase wells, hot water wells and boiling hot springs, but equally well accepts any theoretical cold or hot water and gas composition. The code allows study of the chemical changes which accompany heating or cooling, boiling and vari-

able degassing, and how these changes affect solution/mineral equilibria. WatchWorks can generate a pickup file, which allows using the output from one boiling or heating/cooling process as input to another. Thermal mass balance features include the ability to calculate aquifer steam fraction and gas composition.

Activity coefficients are calculated using the extended Debye-Hückel equation. The chemical thermodynamics database is essentially equivalent to that in the original WATCH program.

The basis species modeled are Ca, Mg, Na, K, SO₄, Cl, F, B, Al, Fe, H₂S, NH₃, CO₂, HCO₃, CO₃, Alkalinity, H₂, O₂, CH₄ and N₂. pH may be in the range 2 to 11, temperature in the range 0° to 370°C. Density may be entered to control conversions between different concentration units systems.

Input Features Include:

- Temperature data in °C or °F
- Pressure in bar, ksc, psi or MPa
- Enthalpy in joules/gm, cal/gm or BTU/lb
- Water compositions in mg or m-moles per liter, kg solution or kg of H₂O
- Gas/steam compositions in 10 different units systems, including various combinations of mg, m-moles, mole%, ppm-wt, liters gas, condensate and total steam composition, and
- Control over the degassing coefficient, to allow modeling non-equilibrium gas/steam distributions.

Data Management and Analysis Tools Include:

- Instant on-screen recalculations between units systems

- A choice of carbon species entry as total CO₂, true H₂CO₃-HCO₃⁻-CO₃⁼ or alkalinity;
- Control of steam fraction by temperature or pressure
- A boiling springs model to estimate reservoir gases when no separate steam sample is available, and
- Multiple boiling or cooling steps in a single run.

There is an on-screen instant display of analytical ion balance and ionic strength, as data are entered, and samples may be completely balanced by transfer of speciated ion balance results on output back into a new input run, with an adjustment of Cl or some other species.

Program Output Includes:

- Aquifer water composition
- Aquifer gas partial pressures
- Aquifer steam composition (if present)
- Chemical geothermometers
- Ionic strength and ion balance (analytical and speciated)
- Activity coefficients (48 species)
- Speciation in ppm and log moles (69 species)
- Mineral solubility saturation points (29 species), and
- Oxidation potential.

The mineral species are: adularia, anhydrite, Mg-chlorite, laumontite, Ca-montmorillonite, Na-montmorillonite, pyrrhotite, wairakite, epidote, chrysotile, low albite, calcite, fluorite, microcline, K-montmorillonite, muscovite, pyrite, wollastonite, marcasite, amorphous silica, analcime, chalcedony, goethite, magnetite, Mg-montmorillonite, prehnite, quartz, zoisite and talc

Any calculated parameter can be automatically tabulated at each step of a multi-step boiling or cooling process, into an ASCII (text) file which is readable by (external) graphing software. There is easy, direct Windows control of screen and printer fonts, and input/output windows can be open simultaneously.

Practical Examples

Figure 1 is an example of how the program can be used to evaluate calcite scaling potential. Boiling steps track the level of calcite saturation in two different cases at the same well, where reservoir temperature is about 228°C and boiling proceeds from left to right. The first case shows saturation in the total wellflow as measured, which includes excess (reservoir) steam. The maximum level of calcite oversaturation at any temperature is very small, and scaling is not expected so long as the well flow is well-mixed. The cause of this is the partial pressure of CO₂ gas in the steam fraction.

The second case shows saturation in the boiling reservoir liquid fraction, without reservoir steam. There is extreme oversaturation and scaling is likely. It follows that scale may deposit

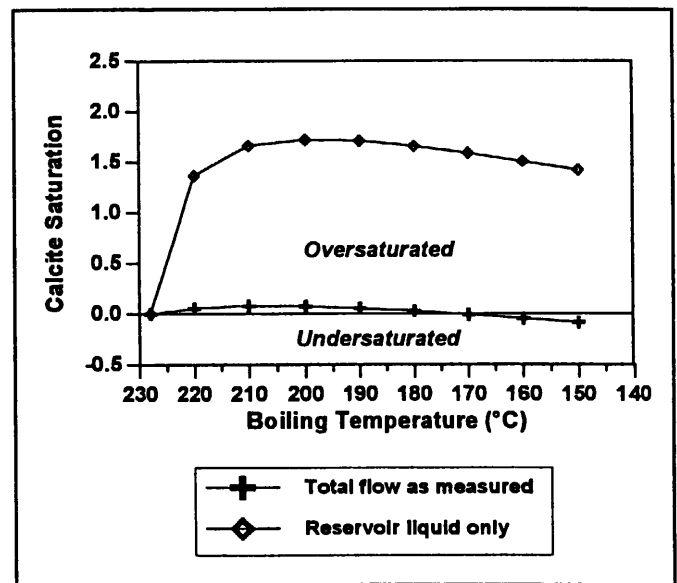


Figure 1. Calcite saturation versus boiling temperature in a wellflow with and without reservoir steam fraction.

in the well between upper and lower production zones, if reservoir steam enters the flow from an upper production zone, while water alone enters from a lower production zone.

Figure 2 shows how the program can be used to evaluate mixing of CO₂ gas into a brine injection line, with a resulting drop of pH which is needed to inhibit silica scaling. pH in the 175°C water is calculated at various levels of total CO₂. The re-

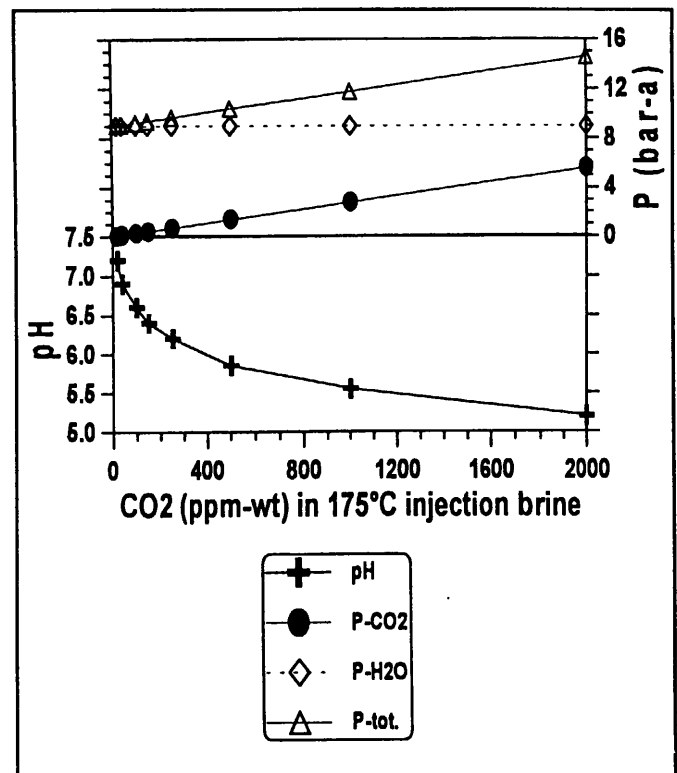


Figure 2. pH and gas partial pressures versus dissolved CO₂ in an injection water at 175°C.

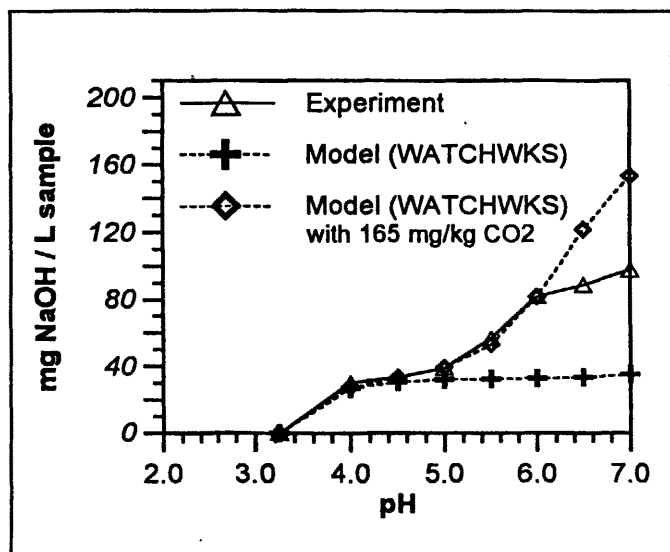


Figure 3. pH versus mg NaOH/L titrated into an acidic water sample.

sults indicate that pH could be lowered from 7.5 to 5.5 by injecting about 800 ppm-wt of CO₂. A related result is the calculation of gas partial pressure, which assists evaluating the bubble point in the injection line, and conditions needed to avoid gas break-out.

Figure 3 shows results of a study to determine whether acidic, corrosive well water could be neutralized downhole, to protect the casing and allow a long-term well test. The sample

was collected downhole at a geothermal field in Central America.

WatchWorks was used to match a laboratory titration of the acidic water with sodium hydroxide (NaOH).

The titration experiment was matched to pH 5 using the reported water analysis, and to pH 6 by adding 165 mg/kg of CO₂ gas. Considering that the sample was collected at pressure downhole, the presence of dissolved CO₂ (non-equilibrium at atmospheric pressure) is likely. The deviation of results at pH6 is explained by degassing and loss of CO₂ from part of the sample, or by precipitation of carbonate.

Acknowledgments

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References

- Arnorsson, S. and Sigurdsson, S., 1982. "The Chemistry of Geothermal Waters in Iceland. I. Calculation of aqueous speciation from 0° to 370°C," *Geochimica et Cosmochimica Acta*, Vol.46, p. 1513-1532.
- Arnorsson, S., Gunnlaugsson, E. and Svavarsson, H., 1983a. "The Chemistry of Geothermal Waters in Iceland. II. Mineral Equilibria and Independent Variables Controlling Water Compositions," *Geochimica et Cosmochimica Acta*, Vol.47, p. 547-566.
- Arnorsson, S., Gunnlaugsson, E. and Svavarsson, H., 1983b. "The Chemistry of Geothermal Waters in Iceland. III. Chemical Geothermometry in Geothermal Investigations," *Geochimica et Cosmochimica Acta*, Vol.47, p. 567-577.