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Calibrating Geochemical Software Programs with Respect to Fe-Sulfides and Fe-Oxides Saturation Indices

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ABSTRACT

Saturation indices of common Fe-sulfides (pyrite, pyrrhotite) and Fe-oxides (magnetite, hematite, goethite) in geothermal setting are calculated by geochemical software programs WATCH and SOLVEQ/CHIM and then calibrated with actual documentation of petrologically identified scale minerals in surface facilities. This study aims to determine which geochemical modeling software yield reasonable saturation indices that are consistent with field data and can therefore be used to assess and predict scaling potential of geothermal fluids.

Results show that SOLVEQ yield lower and more reasonable saturation indices relative to WATCH. However, there is a discrepancy of saturation indices yielded by the software programs with actual data. In order to appreciate both the potential and extent of Fe-sulfide or Fe-oxide deposition, it is more useful to model the fluids using reaction path software CHIM-XPT that will yield predicted amount of supersaturated Fe-precipitates that are more consistent with actual observations. Due to significant variation of results, sensitivity of the calculated saturation indices to key parameters (temperature, pH, Fe and H_2S levels) is also explored. The saturation indices given by WATCH are very sensitive to the input solution pH and reference temperature and should therefore be validated and interpreted with caution to account for variation in these parameters that are common consequences of sampling, analytical procedures and assumed reference temperature.

1. INTRODUCTION

The occurrence of Fe-scales is common in geothermal environments but the extent of scaling varies depending on the environment. In systems dealing with neutral-pH geothermal fluids, Fe levels are typically <0.5 ppm and thus the quantity of Fe-scale formed is limited. FeIt does not pose scaling concerns and can even be beneficial as thin layers of corrosion products provide protection against further pipe corrosion. In some instances, the utilization of lower pH fluids discharged by some production wells led to Fe-scaling problems affecting steam production. Thus in addition to evaluating the occurrence of more ubiquitous common geothermal scales (e.g. am. silica, calcite, anhydrite), saturation indices of Fe-sulfides (pyrite and pyrrhotite) and Fe-oxides (magnetite, hematite and goethite) as yielded by standard geochemical softwares are investigated and compared to numerous field data to become meaningful tools for reservoir management. The scale samples were sent to the Petrology Laboratory for detailed petroanalysis. At the laboratory, the scales were first analyzed megascopically using binocular microscope. These samples were then processed into thin and polished sections and analyzed under a polarizing and reflected light microscopes, respectively. Additionally, XRD also helps in verifying the minerals present in the samples.

The speciation program WATCH by Arnórsson et al. (1982), version 2.1 of Bjarnason (1994) is a DOS-based software that computes for the chemical composition of fluid at the reference temperature including pH, aqueous speciation, partial pressure of gases, redox potentials and activity products of mineral dissolution reactions. WATCH 2.1 has a graphical-user interface version, WATCHWORKS, developed by Klein and Chappell of Geothermex. Another DOS-based version, WATCH 2.4, was introduced in April 2010 and incorporated Al species in the pH calculations, updated Henry's constants of CO_2, H_2S, H_2 and CH_4 and introduced dissociation constants of four aluminum hydroxyl species, aqueous CO_2, bicarbonate and H_2S. Using analytical data of separated vapor and separated liquid samples (at the same sampling pressure), common modeling procedures (reduction to reservoir condition, adiabatic boiling of reservoir fluid to the wellhead, conductive heating/cooling) are easy and straightforward which makes WATCH a popular tool for geochemists. No mineral precipitation or dissolution is assumed while modeling the fluid.

SOLVEQ by Reed et al. (2012), version XPT, is also a DOS-based speciation program with a more comprehensive and updated database (SOLTHERM). A special version of the database SOLTHERM was utilized in one of the procedures to consider only gas solubility reactions involving the gas species CH_4, H_2, N_2 and NH_3 but not their associated redox gas-equilibrium reactions. SOLVEQ is used primarily as a work horse for processing the separated vapor and separated water samples into the reference temperature (e.g., reservoir condition, line condition) prior to modeling using the reaction path software CHIM (adiabatic boiling, conductive heating/cooling, fluid mixing). For a given temperature, pressure, and total composition of a chemical system, CHIM computes not only the compositions of the aqueous and gas phases but also the solid phases at equilibrium.

2. METHODOLOGY

Fluid chemistry data were selected based on availability of documented scales and petrological analysis of the scale samples. Two types of fluids and scenarios were considered in the calibration procedure.

In the first scenario, analysis of purely water phase samples and their corresponding scales were used. The procedure involves only "re-heating" or re-evaluating the water chemistry from the sampling temperature into the line temperature and thus uses only the speciation capabilities of WATCH and SOLVEQ. In this way, other processes (e.g., boiling) should not affect the modeling results. Two types of water sample were used: (1) an Fe-scale forming fluid (Water 1) yielding scales consisting of 15% amorphous silica, 25% Fe-oxides and 60% amorphous materials and (2) non-Fe-scale forming fluids (Water 2 and Water 3) with 100% amorphous silica scales which served as control samples. Scale samples were obtained from their respectivepipelines, as shown in Figure 1.

Figure 1: Fe-oxide/sulfide (left) and am. silica (center and right) scales documented in the geothermal water pipelines.

The water chemistry samples (Table 1) were run through three geochemical software programs, WATCH 2.1, WATCH 2.4 and SOLVEQ-XPT. They were evaluated at their respective line temperatures to determine the saturation indices of the following Fe-sulfide (pyrite, pyrrhotite) and Fe-oxide (magnetite and goethite) minerals.

Table 1: Water chemistry of Fe-scale forming (Water 1) and Am. Silica-forming (Water 2 and 3) geothermal brine samples.

	Line T(C)	pH/ T(C)	ppm												
			CO2	H2S	NH3	B	SiO2	Na	K	Mg	Ca	Cl	SO4	Fe	HCO3
Water 1	160	4.13/ 22.2	0	1.77	26.3	42.3	1112	3127	900	5.04	232	6502	68.9	38.8	0
Water 2	45	7.77/ 22.3	11.3	0.06	32.3	24.1	282	995	186	0.13	17.9	1775	142	0.79	14.2
Water 3	188	5.9/ 23.6	40	2	4.5	244	671	3980	817	0.20	106	7231	35	0.35	0

In the second calibration scenario, two-phase fluid samples that are confirmed to form Fe-scales in the wellhead or branchline are selected. Fluid 1 scale samples from the branchline were composed of 50% Sulfides, 20% Barite, 20% Magnetite and 10% Anhydrite. Fluid 2 scales from the upper sections of the well casing were composed of 45% Galena, 35% Magnetite, 15% Barite, 5% Pyrite and 1% Chalcopyrite.

Figure 2: Fe-oxide/sulfide scales documented in Fluid 1 (left) and Fluid 2 (right) in the geothermal two-phase pipelines.

Separated water (Table 2) and separated gas (Table 3) samples of the Fe-scale forming two-phase fluids which were obtained using a double-cyclone Webre separator were run through the same three softwares (WATCH 2.1, WATCH 2.4 and SOLVEQ-

XPT/CHIM-XPT) by combining the two phases and recalculating the liquid aquifer back to the reservoir temperatures (Tqtz) and then adiabatically boiled back to the wellhead or branchline conditions (188.5°C). The saturation indices of pyrite, pyrrhotite, magnetite and goethite were then obtained from five temperature points along the wellbore conditions.

Table 2: Separated water sample chemistry of Fe-scale forming two-phase fluids.

	pH/T(C)	ppm											
		H2S	NH3	B	SiO2	Na	K	Mg	Ca	Cl	SO4	Fe	F
Fluid 1	3.59/25	1.17	18.2	41.7	1194	3449	958	5.21	237	6879	19.4	34	1.4
Fluid 2	3.45/25	1.45	47.4	51.8	1008	3235	856	19.6	134	6357	47	32.4	1.86

Table 3: Separated gas chemistry of Fe-scale forming two-phase fluids.

	pH/T(C)	mmol/100 mol steam					
		CO2	H2S	NH3	H2	N2	CH4
Fluid 1	3.59/25	618	42.2	0.3	0.167	0.539	0.307
Fluid 2	3.45/25	464	44.4	0.16	0.304	0.904	0.349

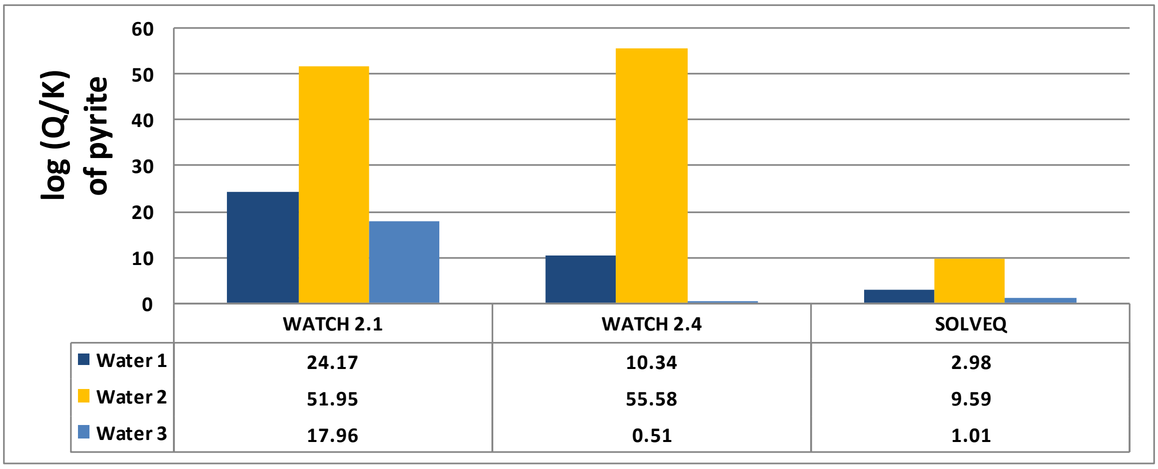
Saturation index sensitivity was also tested for Water 1, Water 2 and Fluid 1. This was done by varying the parameters (line temperature, measured pH, hydrogen sulfide (H2S) content and iron (Fe) content) and plotting the saturation index values using the same three software programs (WATCH 2.1, WATCH 2.4, SOLVEQ-XPT).

Lastly, to determine the actual amounts of scales that may form within the pipeline, CHIM-XPT runs were conducted on Water 1 and Water 3. This was to compare between the Fe-scale forming and non-Fe-scale forming fluids and their resulting calculated mass of deposits. These two fluids were chosen due to their similar line temperatures.

3. RESULTS AND DISCUSSION

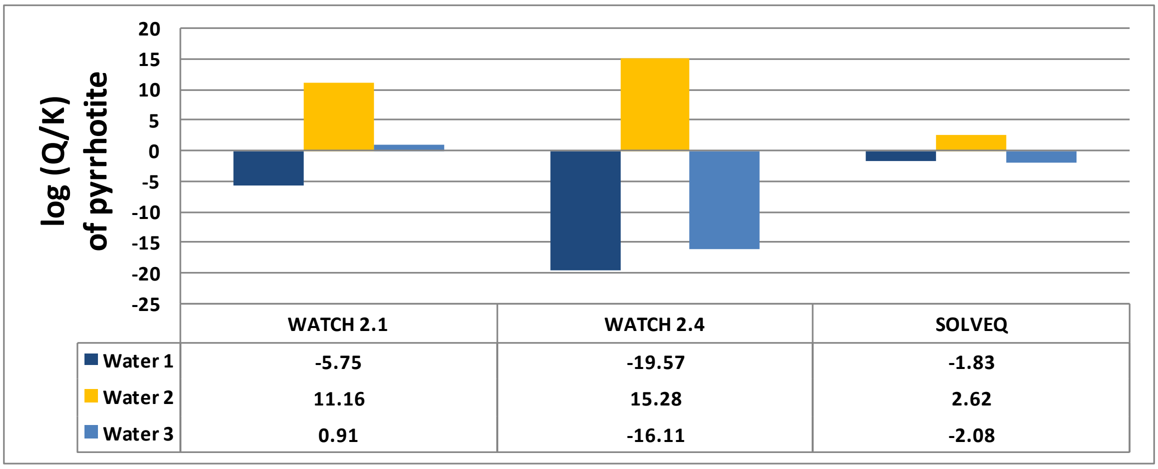
3.1 Heating of geothermal water phases

Comparative saturation indices of Fe-sulphides: Figure 3 (pyrite) and Figure 4 (pyrrhotite) ; and Fe-oxides: Figure 5 (magnetite) and Figure 6 (goethite) are shown below. Unexpectedly, all three softwares yielded contrasting results for Water 1 and 2. Results show supersaturation of the Fe-sulphides and the Fe-oxides in the non-Fe-scale forming chemistry of Water 2 (100% am. silica) and undersaturation of the Fe-scales from the chemistry of Water 1 which yielded Fe-sulphide and Fe-oxide scales in the lines. For Water 3, undersaturation of the Fe-scales is consistent with actual line observations. The modeling results show predicted supersaturation of pyrite for Water 1, which are also consistent. However, all three softwares predicted supersaturation of pyrite even in the non-Fe-scale forming chemistry of Water 2 and 3. Both versions of WATCH yield very high supersaturation values in the Fe-sulphides (especially pyrite) compared to SOLVEQ results. These confounding results provided the motivation to do the sensitivity analysis discussed in section 3.3, especially with measured pH values, as Water 1 is acidic whereas Water 2 is neutral.



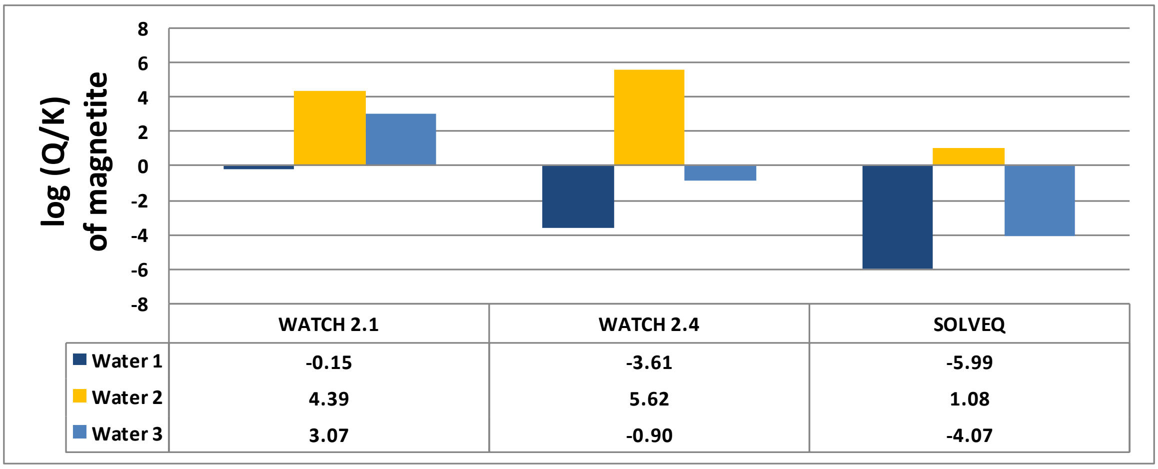
	WATCH 2.1	WATCH 2.4	SOLVEQ
■ Water 1	24.17	10.34	2.98
■ Water 2	51.95	55.58	9.59
■ Water 3	17.96	0.51	1.01

Figure 3: Pyrite saturation indices from analyses of purely water phases evaluated at line conditions. Water 1 (160°C) is the Fe-rich water, and Water 2 (45°C) and 3 (188°C) are the fluid yielding only am. silica scales.



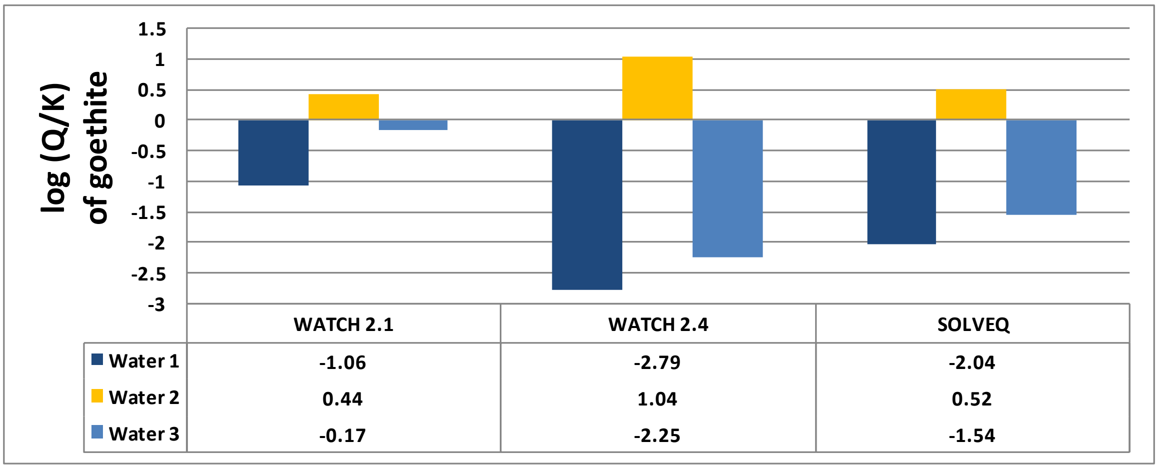
	WATCH 2.1	WATCH 2.4	SOLVEQ
Water 1	-5.75	-19.57	-1.83
Water 2	11.16	15.28	2.62
Water 3	0.91	-16.11	-2.08

Figure 4: Pyrrhotite saturation indices from analyses of purely water phases evaluated at line conditions. Water 1 (160°C) is the Fe-rich water, and Water 2 (45°C) and 3 (188°C) is the fluid yielding only am. silica scales.



	WATCH 2.1	WATCH 2.4	SOLVEQ
Water 1	-0.15	-3.61	-5.99
Water 2	4.39	5.62	1.08
Water 3	3.07	-0.90	-4.07

Figure 5: Magnetite saturation indices from analyses of purely water phases evaluated at line conditions. Water 1 (160°C) is the Fe-rich water, and Water 2 (45°C) and 3 (188°C) is the fluid yielding only am. silica scales.



	WATCH 2.1	WATCH 2.4	SOLVEQ
Water 1	-1.06	-2.79	-2.04
Water 2	0.44	1.04	0.52
Water 3	-0.17	-2.25	-1.54

Figure 6: Goethite saturation indices from analyses of purely water phases evaluated at line conditions. Water 1 (160°C) is the Fe-rich water, and Water 2 (45°C) and 3 (188°C) is the fluid yielding only am. silica scales.

3.2 Adiabatic boiling of the geothermal two-phase fluids

For the Fe-scale forming two-phase samples, the water and gas chemistries were adiabatically boiled from T-quartz to the wellhead using WATCH 2.1, WATCH 2.4 and the combined procedures of SOLVEQ (for recalculation to reservoir condition) and CHIM (for adiabatic boiling). Adiabatic boiling using CHIM was also done at two variations where redox reactions involving CH4, H2 and NH3 species were either allowed or suppressed. Supersaturation, at least in pyrite, pyrrhotite and magnetite, were initially expected since these minerals were documented in the surface. However, in all runs, Figure 7shows that pyrite is the only mineral that supersaturates as the fluid temperature decreases when using WATCH 2.1 which makes this software consistent with actual occurrence in the pipelines. In contrast, WATCH 2.4 and SOLVEQ/CHIM saturation index values are all unsaturated. There is also no significant difference whether redox is allowed or suppressed in the SOLVEQ/CHIM runs.

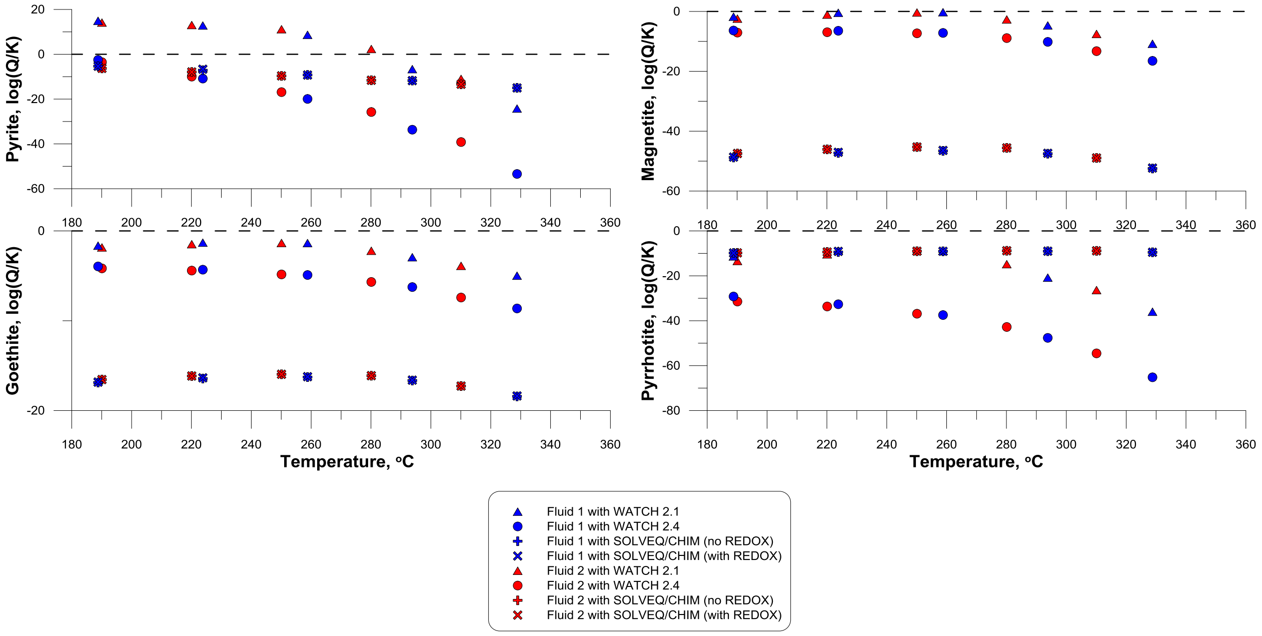


Figure 7: Saturation indices of pyrite, pyrrhotite, magnetite and goethite of the Fe-scale forming two-phase samples of Fluid 1 and Fluid 2 while adiabatically boiling from reservoir (Tquartz is 328.8°C and 310.1°C, respectively, xxx?) to the wellhead (188.5°C) conditions.

3.3 Sensitivity analysis

Saturation index sensitivity runs were done for water phase samples of geothermal brine (Water 1 and Water 2) and two-phase Fluid 1 with respect to temperature (Figure 8), measured water pH (Figure 9), H2S level in the water (Figure 10) and total Fe concentration in the water (Figure 11). In all the plots, open symbols represent the actual parameter value of the respective samples. Data points to the left or right of the open symbols are the ranges of the variables based on the actual line parameters and the minimum-maximum historical values of the water samples. In dealing with the two-phase Fluid 1, recalculation to reservoir condition and adiabatic boiling into the wellhead are repeatedly done while varying the mentioned parameters in the separated water sample.

Figure 8and Figure 9show that Water 1, Water 2 and Fluid 1 samples show considerable sensitivity to both temperature and pH variations. Temperature sensitivity (Figure 8) is most prominent in WATCH 2.1 and WATCH 2.4 for all the minerals. In contrast, SOLVEQ/CHIM results are not very sensitive especially for Fe-sulfides (pyrite, pyrrhotite).

All the software programs have significant saturation index sensitivity to changes in pH (Figure 9) wherein an increasing saturation index value is observed as the pH value increases. Thus choosing the reference temperature at which the samples were evaluated and the inputted pH at the time of measurement is critical parameters that will affect Fe-scale Saturation Indices.

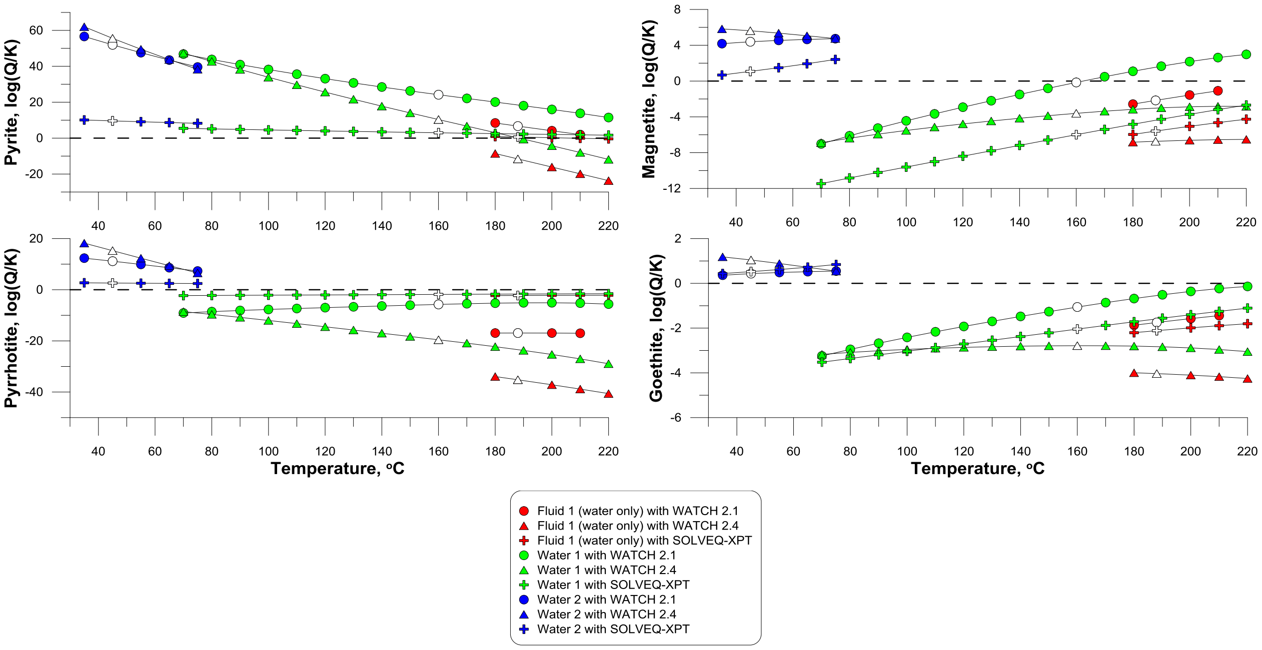


Figure 8: Sensitivity of mineral saturation indices (pyrite, pyrrhotite, magnetite and goethite) using WATCH 2.1, WATCH 2.4 and SOLVEQ/CHIM to reference temperature.

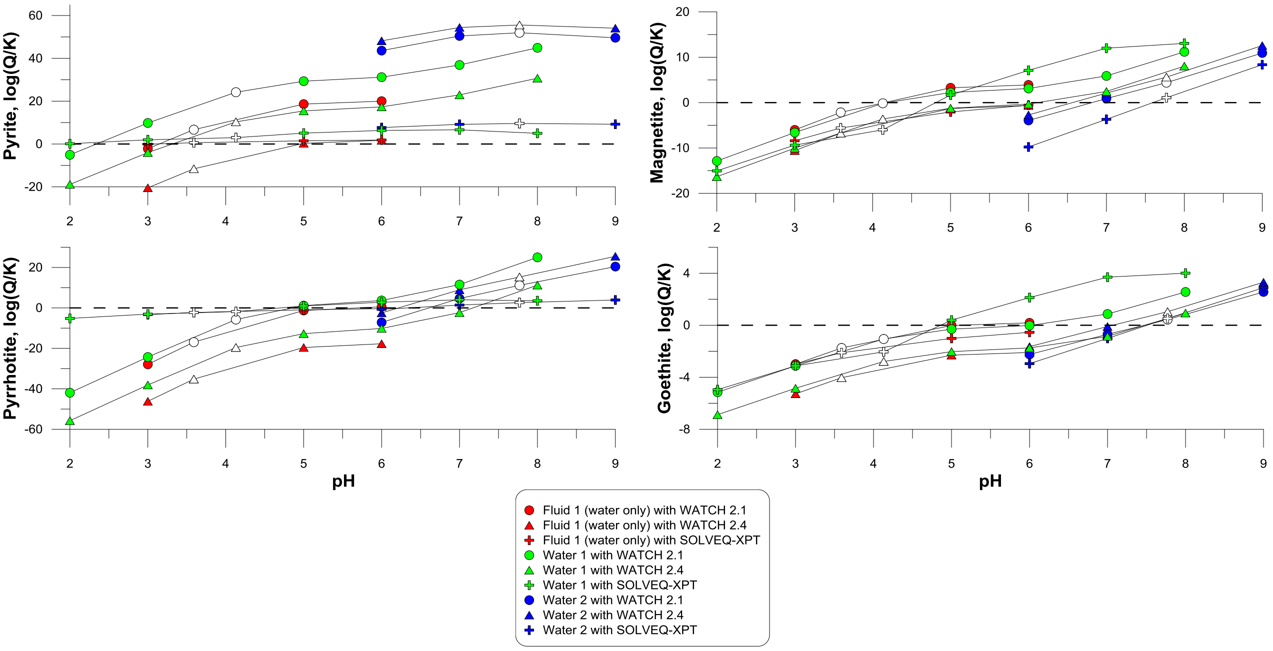


Figure 9: Sensitivity of mineral saturation indices (pyrite, pyrrhotite, magnetite and goethite) using WATCH 2.1, WATCH 2.4 and SOLVEQ/CHIM to measured pH of the water sample.

Using all softwares, variation in hydrogen sulfide (Figure 10) and iron (Figure 11) levels in the water samples do not significantly alter the saturation indices.

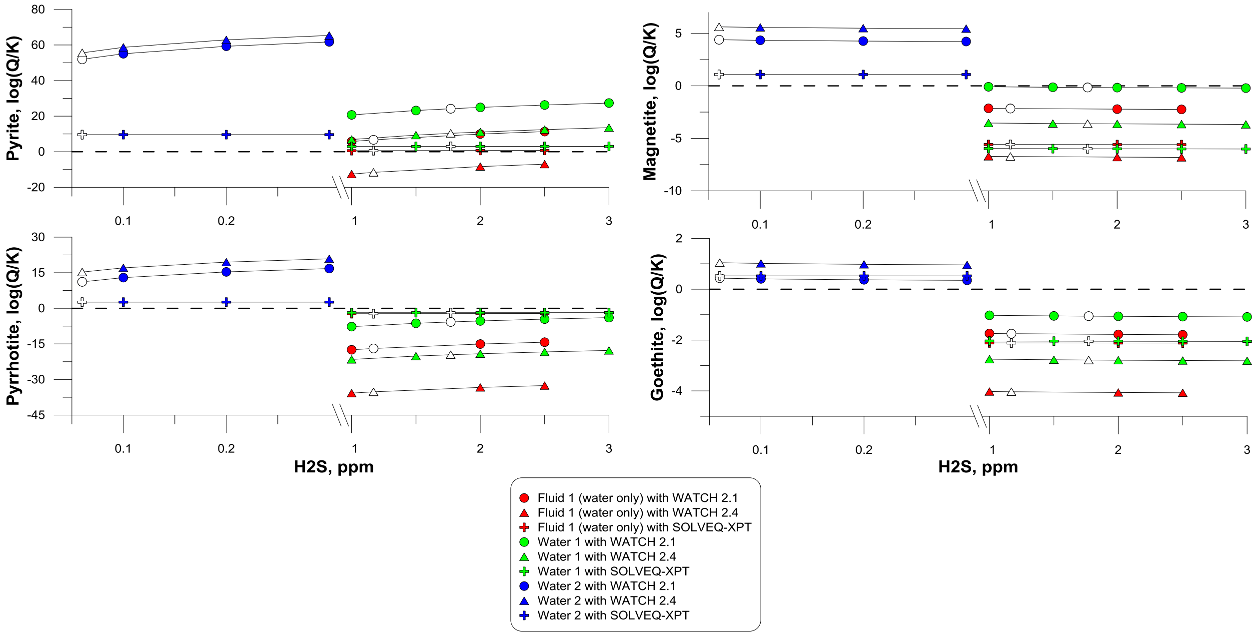


Figure 10: Sensitivity of mineral saturation indices (pyrite, pyrrhotite, magnetite and goethite) using WATCH 2.1, WATCH 2.4 and SOLVEQ/CHIM to H_2S level in the water sample.

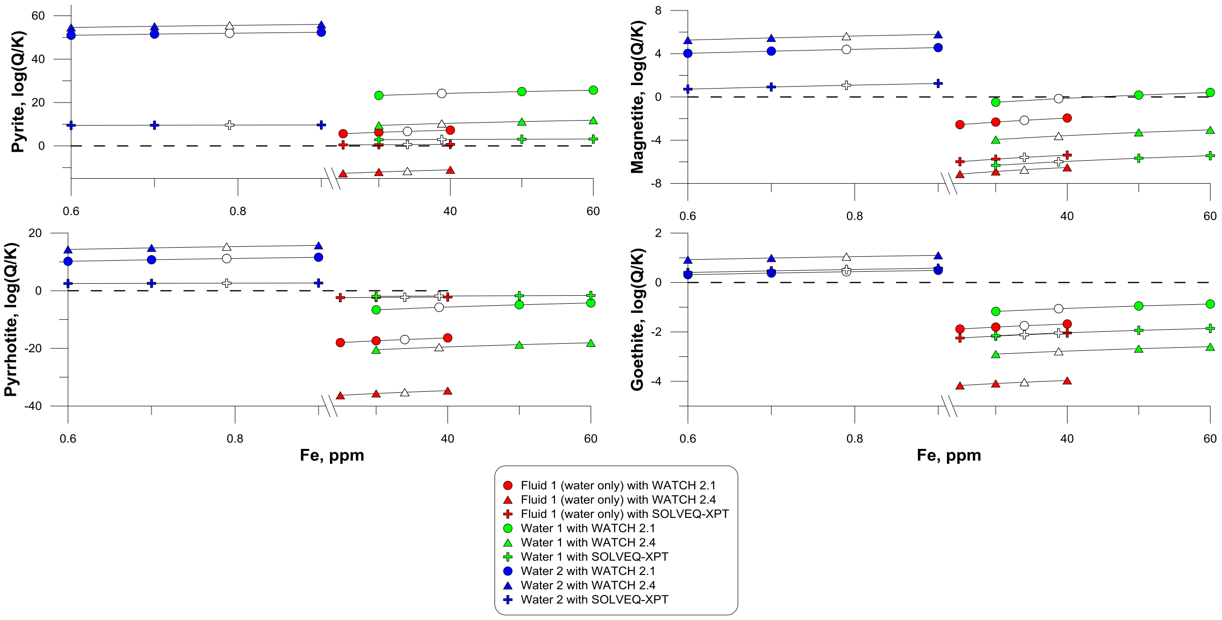


Figure 11: Sensitivity of mineral saturation indices (pyrite, pyrrhotite, magnetite and goethite) using WATCH 2.1, WATCH 2.4 and SOLVEQ/CHIM to total Fe concentration in the water sample.

4. SUMMARY AND CONCLUSION

Table 4 summarizes the resulting saturation indices of the two contrasting water samples (one Fe-scale forming, one non-Fe-scale forming) and two sets of two-phase fluids that are both Fe scale-forming.

Table 4: Summary of the mineral saturation index observations using different modeling software programs

	WATCH 2.1	**WATCH 2.4**	**SOLVEQ-XPT/CHIM-XPT**
Pyrite	Supersaturated in all subject fluids (including the non-Fe-scale forming fluid)	Supersaturated for non-Fe-scale forming fluids Undersaturated for Fe-scale forming fluids	Supersaturated in all subject fluids (including the non-Fe-scale forming fluid)
Pyrrhotite	Supersaturated for non-Fe-scale forming fluids Unsaturated for Fe-scale forming fluids		
Magnetite			
Goethite			

The seemingly inconsistent modeling results from actual documentation data demonstrate that caution must be exercised when predicting Fe-scale formation on the basis of saturation indices only from any geochemical softwares in this study. The log (Q/K) calculation of these iron-bearing minerals are very sensitive to temperature and pH variations which in turn largely affect the speciation distribution of the redox-affected Fe(II) and Fe(III). For example, Angcoy (2010) demonstrated limitations in the thermodynamic data on iron hydrolysis which yielded inconsistent trends on the saturation indices of minerals involving Fe when using WATCH 2.1.

Speciation softwares like WATCH 2.1, WATCH 2.4 and SOLVEQ only predicts if the potential for the fluid to form Fe-scales without considering other factors like kinetics. In order to appreciate both the potential and extent of Fe-sulfide or Fe-oxide deposition, it is more useful to model the fluids using reaction path software CHIM-XPT that yield predicted amount of supersaturated Fe-precipitates for calibration with actual observations. This is beyond the scope of the current study that will be later pursued.

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