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Chemical Modeling of Fluids from the Las Tres Vírgenes B. C. S. (México) Geothermal Field

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ABSTRACT

The Las Tres Vírgenes geothermal field is a liquid-dominated resource located in the Baja California Peninsula (México) that currently has an installed power capacity of 10 MWe. The exploitation of this field has been limited because of a large, mostly calcite scaling potential of produced fluids which makes necessary the use of commercial inhibitors that suppress calcite and anhydrite deposition, in most of the wells. In this work the chemical composition of fluids from wells of the Las Tres Vírgenes field was used to perform equilibrium modeling for a wide range of temperatures to investigate the saturation indices of hydrothermal minerals and to identify desirable production conditions for the wells at which calcite scaling could be avoided. The wells studied were LV-1, LV-3, LV-4, LV-5, LV-11 and LV-13 while input data corresponded to an early production stage of the wells. Chemical speciation was calculated by using the WATCH program, the temperature ranged from 150 to 300°C with calculations every 2°C. The behavior of the saturation indices of minerals vs temperature for the wells LV-1, LV-3 and LV-5 suggested more than one fluid-mineral equilibrium temperature, (at about 180, 220 and 240°C for well LV-1; 220, 250 and 270°C for well LV-3 and 180, 200 and 240°C for well LV-5) indicating the occurrence of multiple fluid entries. This is consistent with the temperature differences obtained when using different (Na/K, Na-K-Ca and quartz) geothermometers. We conclude that observed scaling phenomena in these wells is probably due to mixing of different fluids in the well. In well LV-4 the mineral equilibrium temperatures were found within the relatively narrow interval 257-268°C, indicating no significant multiple fluid entries and reservoir fluid temperature in the feeding area of this well in its early production stage. Based on fluid-mineral equilibria, the reservoir temperature for wells LV-11 and LV-13 could be at least 290°C, quartz equilibrium occurs at 290 and 300°C respectively, and as was stated for well LV-4, no multiple entries were identified at early production conditions in both wells. Calcite was found to be oversaturated in the wells LV-1 and LV-3 for almost all the studied temperatures; for the wells LV-4 and LV-11 calcite showed equilibrium at 190°C; for the well LV-5 at 180°C while for the well LV-13 such equilibrium occurs at 225°C. Anhydrite showed equilibrium at 200°C in well LV-5; 220°C in LV-1; 230°C in LV-13; 250°C in LV-3 and LV-4 and 290°C in LV-11. Our results show oversaturation of calcite and anhydrite at higher temperatures, consistently with the reverse solubility of these minerals. Based on these results, separation pressures for the fluids were recommended although it is well known that the separation process itself could promote calcite precipitation, because of fluid degassing.

1. INTRODUCTION

The Las Tres Vírgenes geothermal field is located in the state of Baja California Sur (México) in the Baja California Peninsula (Figure 1). At present it has an installed power capacity of 10 MWe (Gutiérrez-Negrín, 2007) while a capacity of 10-20 MWe for the field has been estimated (Flores-Armenta and Jaimes-Maldonado, 2001). Exploration studies in the area started in 1982 and the first exploratory well (LV-2) was drilled in 1988 (Flores-Armenta and Jaimes-Maldonado, 2001). To date, at least nine wells have been drilled in two separated zones: LV-1, LV-2 and LV-5 (which are not longer producers) in the northern zone; LV-3, LV-4, LV-11 and LV-13 in the southern zone and wells LV-7 and LV-8 are located to the east of the field (Figure 1). The wells LV-2, LV-7 and LV-8 are used as injectors. The wells in the southern zone produce hotter and more saline fluids than the northern wells (Flores-Armenta and Jaimes-Maldonado, 2001). Truesdell (1998) and Portugal et al, (2000) have proposed geochemical models for the Las Tres Vírgenes reservoir. At the Las Tres Vírgenes field severe scaling has been observed to occur in some wells making necessary the use of a commercial inhibitor (Flores-Armenta and Jaimes-Maldonado, 2001).

In 2007 a study was developed to investigate the main reservoir processes occurring due to exploitation at Las Tres Vírgenes, (Iglesias et al, 2007). Important processes were characterized including the mixing of fluids and dilution occurring at Las Tres Vírgenes reservoir (Barragán et al, 2009). The objective of this work is to perform chemical equilibrium modeling of fluids including the calculation of the saturation indices of hydrothermal minerals in a wide range of temperatures in order to define optimal separation conditions in the wells tending to minimize scaling processes. This study included data for wells LV-1, LV-3, LV-4, LV-5, LV-11 and LV-13 provided by Comisión Federal de Electricidad.

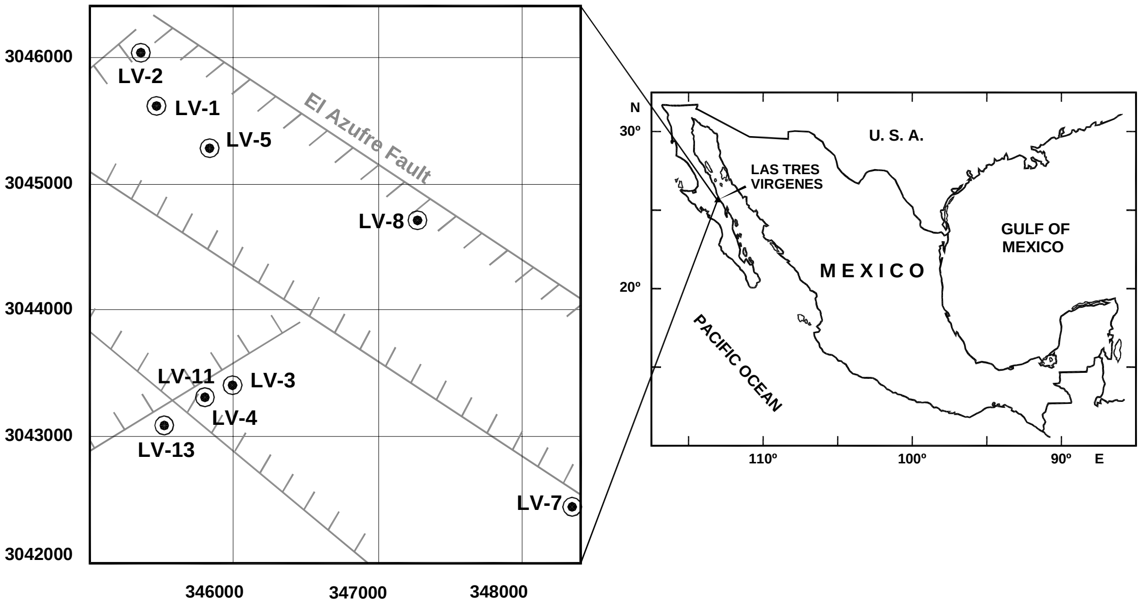

Figure 1: Location of the Las Tres Vírgenes geothermal field and locations of the wells in the field.

2. CHEMICAL MODELING

The equilibrium state is expressed in terms of equations that govern the behavior of the species in a given system. These equations are referred to: (a) the mass action law; (b) mass balances; (c) ionic charge balances; (d) energy balances; (e) partition processes of volatile species between steam and liquid phases and (f) the calculation of equilibrium quotients that describe the minerals dissolution which are compared with appropriate equilibrium constants to indicate the degree of saturation of the minerals in the fluid.

For chemical equilibrium modeling of solutions there are two types of approaches: the ionic association model and the ionic interaction model. The former utilizes either the Debye-Hückel equation or modified expressions based on that equation and are suitable to be used for waters with a ionic strength values less than one molal (Henley et al, 1984). In this approach the activity coefficients depend on both the ionic size and on the solution ionic strength. The second type of approach is based on virial methods which utilize coefficients that take into account the interactions among the individual components of the solution instead of consider the species in the solution (Bethke, 1996). These methods are complex and require a great deal of data but provide scarce information regarding the species distribution in the solution. However they are reliable to predict the solubility of mineral phases in concentrated brines. The semi-empiric equations used by virial methods, also called Pitzer equations can be utilized in geochemical modeling of solutions with a high ionic strength.

At present a number of computer programs are available to provide the aqueous speciation of reservoir fluids through chemical equilibrium modeling some of them are specially suited for geothermal wells data, i. e. ENTHALP (Truesdell and Singers, 1976); EQ3/EQ6 (Wolery, 1979); WATCH (Arnórsson et al, 1982); EQQYAC (Barragán and Nieva, 1989); GWB (Bethke, 1996) among others. According to Truesdell et al, (1987) the results of equilibrium modeling at reservoir provided by different programs could be different, due to considerations made by the user on the nature of “excess enthalpy” discharges and also due to the use of different thermodynamic databases.

3. METHODOLOGY AND DATA

Early chemical data of the wells were selected to perform modeling along with physical data, regarding the operation conditions of the wells.

The WATCH program (Arnorsson et al, 1982), Version 2.1 released in 1994 by the Icelandic Water Chemistry Group, was used to perform the chemical modeling at given temperatures and the calculations of saturation indices of hydrothermal minerals. The WATCH program utilizes the ionic association method and is specially suited to handle data of fluids from geothermal wells, when solute concentrations are less than one molal. This program was selected because of its capability to perform calculations of saturation indices of minerals and also because no excess enthalpy discharges occur at Las Tres Vírgenes reservoir.

As separated water samples were taken at ambient conditions (atmospheric pressure) the WATCH program was first used to estimate aqueous speciation including pH of the separated water at the conditions (temperature, pressure) corresponding to those of the steam sample separation. These results together with the steam phase chemical composition, constituted the input data for the WATCH program to perform fluid-mineral equilibrium modeling. The temperatures studied started from the separation temperature at which the steam sample was collected to 300°C, with 2°C steps. For every temperature the equilibrium composition of the fluid was obtained and the saturation indices of typical hydrothermal minerals (SI) were also obtained as follows:

$$SI = \log Q - \log K = \log (Q/K)$$

where (Q) is referred to the ion activity product and (K) is the mineral solubility product constant. Negative values for SI indicate subsaturation of the mineral in the solution, positive values indicate oversaturation of the mineral and zero indicates exact saturation.

The saturation indices of the minerals were then plotted vs temperature in order to investigate the water-rock equilibrium temperatures by the convergences of saturation curves of representative minerals to the zero value saturation index line of the plot, according to the method proposed by Bethke, (1996).

The input data at the steam separation conditions of the wells LV-1 (27 January 1996), LV-3 (20 April 1995), LV-4 (5 October 1999), LV-5 (14 March 1997), LV-11 (25 September 2000) and LV-13 (27 January 2003) used in this study are given in Table 1. For reference, in Figure 2 a Schöeller diagram for the separated water collected at ambient conditions of the Las Tres Vírgenes wells is given together with the compositions of seawater, well M-19A from Cerro Prieto and well AZ-9 from Los Azufres. These data sets were chosen considering an early stage of production of the wells, completeness of data and controlled sampling conditions.

Table 1: Chemical composition of fluids from wells at separation conditions (T_{SEP}). Na/K (N) and Na-K-Ca reservoir temperature estimations are also given.

Separation Conditions	Wells (LV-)					
	1	3	4	5	11	13
Enthalpy (kJ/kg)	930	1359	1296	1184	1078	1347
T_{SEP} (°C)	146	152	154	128	155	151
y_{SEP}	0.15	0.34	0.39	0.30	0.2	0.34
pH/T_{SEP}	6.71	6.62	6.76	7.0	6.79	6.46
$T_{Na/K}$ (N) (°C)	249.5	255	255	253	256	275
$T_{Na-K-Ca}$ (°C)	254	267	277	249	260	276
Liquid (mg/kg)						
Na^+	4026	3531	4237	4637	4988	4825
K^+	662	615	733	790	878	1018
Ca^{+2}	224	90	190	361	291	232
Mg^{+2}	0.53	0.8	0.026	0.2	0.07	0.23
Al	0.046	0.04	0.044	0.05	0.05	0.05
Cl^-	7399	6124	7694	8296	9166	8932
$SO4^{2-}$	66	50.3	36.8	89	12.4	48.0
SiO_2	650	434	725	437	909	979
B	146	159	149	136	178	219
CO_2	35.2	224.4	4.66	2.18	2.12	4.66
H_2S	1.93	4.97	0.41	0.37	0.5	0.34
NH_3	0.63	4.16	1.05	1.54	1.94	2.26
Steam (mg/kg)						
CO_2	12778	46484	1801	784	718	2883
H_2S	243.4	320.5	51.6	53.8	58.4	68.3
NH_3	4.63	30.91	7.6	10.1	14.3	10.3
H_2	0.24	1.55	0.38	0.27	0.61	0.02
CH_4	3.28	16.25	4.48	0.58	1.0	3.46
N_2	9.83	549.3	22.1	12.1	27.4	9.10

4. RESULTS

4.1 Reservoir Aqueous Speciation

Some of the important results obtained for the aqueous speciation including pH of the studied wells (LV-1, LV-3, LV-5, LV-11 and LV-13) at the silica (quartz) reservoir temperatures are given in Table 2.

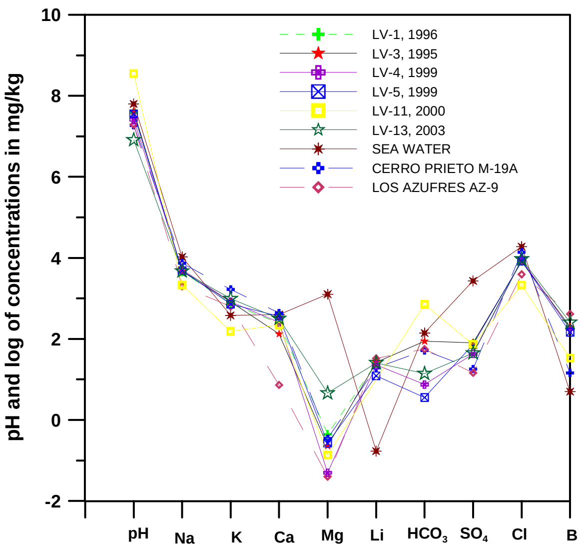

Figure 2: Schöeller diagram for separated water from Las Tres Vírgenes wells. Seawater and water from wells M-19A (Cerro Prieto) and AZ-9 (Los Azufres) are also shown.

Table 2: Chemical composition of reservoir fluids at the silica, (quartz) reservoir temperatures (T_{RES}) for the wells according to the WATCH program. Concentrations in ppm.

Reservoir Conditions	Wells (LV-)					
	1	3	4	5	11	13
T_{RES} (°C)	265	245	270	220	290	295
pH	5.4	6.0	6.5	6.8	6.3	5.9
Na^+	2950	3284	2818	3558	2842	2608
K^+	503	584	510	616	554	618
Ca^{+2}	154	71	133	280	192	149
Mg^{+2}	0.40	0.07	0.02	0.14	0.04	0.14
Cl^-	5490	5720	5182	6402	5359	4972
$SO4^{2-}$	21.3	25. 7	11.6	34.7	3.1	11.0
HCO_3^-	30.6	59.4	7.9	4.3	8.6	6.0
H_4SiO_4	844	690	860	553	1010	1060
H_3BO_3	680	906	631	623	706	848
H_2CO_3	4548	1365	114	9.4	279	682

4.2 Saturation Indices of Minerals

4.2.1 Well LV-1

In Figure 3 the saturation indices of hydrothermal minerals vs temperature for the well LV-1 are shown.

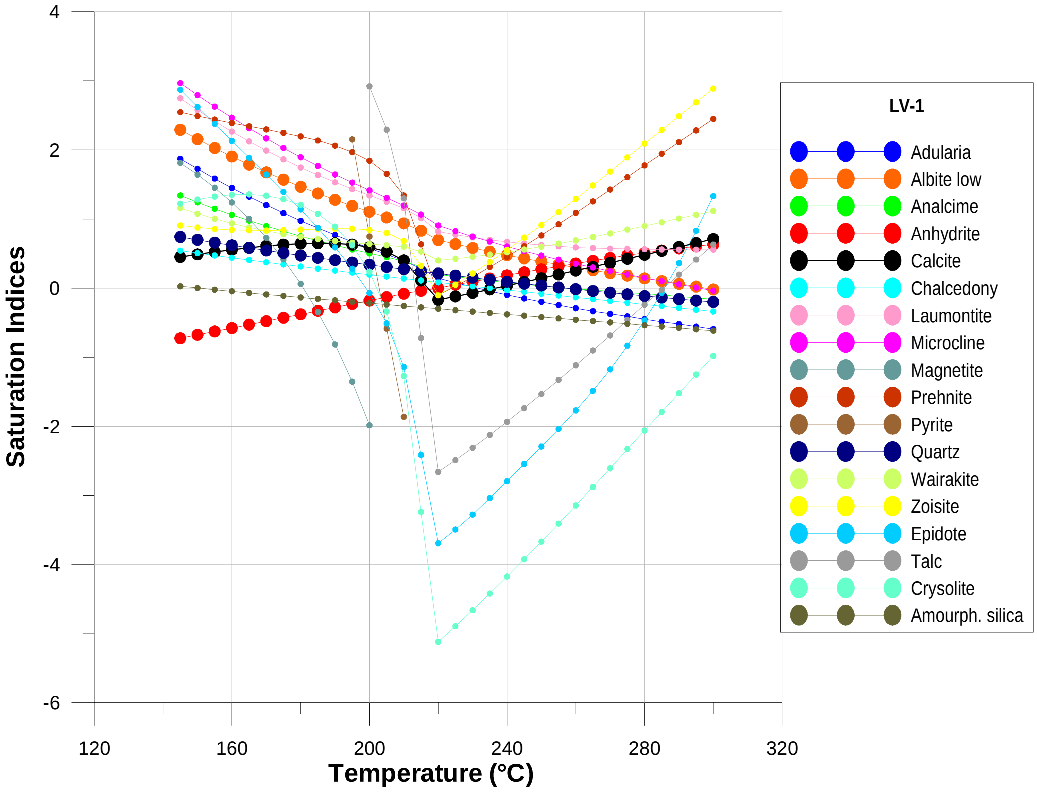

Figure 3: Saturation indices of hydrothermal minerals vs temperature for the well LV-1.

As seen in Figure 3 the saturation indices for calcite indicate oversaturation for temperatures from 140°C (separation temperature) while at about 220°C calcite shows slightly subsaturation and for temperatures higher than 240°C this phase becomes oversaturated. The behavior of silico-aluminate minerals like zoisite and prehnite show similar trends than that mentioned for calcite while minerals such as talc and crysolite (both Mg silicates) and epidote (Fe-aluminum-calcium silicate) show minimum saturation indices at 220°C. Talc and epidote show another equilibration at a rather high temperature, 290°C. Anhydrite ($CaSO_4$) attains equilibrium at 220°C, at lower temperatures is undersaturated while it becomes oversaturated at higher temperatures. The saturation indices of quartz change from positive to negative values at 257°C being this temperature that estimated by the quartz geothermometer. Chalcedony shows equilibrium at 240°C and amorphous silica at 160°C. When reservoir fluids have attained total equilibrium with the host rock, saturation indices lines tend to converge to the saturation zero line, indicating the reservoir temperature (Bethke, 1996). Following this approach, it is seen in Figure 3 that there is not a single temperature (or a relatively small temperature range) for well LV-1 where saturation indices converge to the zero saturation line, instead there are at least three points where saturation indices converge to the zero saturation line. One equilibrium seems to occur at 180°C, other at 220°C and another at 240°C, this result suggest that there could be different entries of fluids to the well producing a mixture of fluids. These results can explain the differences obtained in reservoir temperature estimations by using different geothermometers such as quartz (Fournier and Potter II, 1982) (Table 2), Na-K-Ca (Fournier and Truesdell, 1973) and Na/K (N) (Nieva and Nieva, 1987) (Table 1) (Barragán et al, 2009). On the other hand, a geochemical study based on chemical and isotopic variations of fluids over time, suggested that mixing and dilution processes occur in the wells due to exploitation (Barragán et al, 2009). A temperature of about 187°C was estimated for the shallower, less saline fluid. Therefore the equilibrium results seem to confirm that the entry of shallower waters occurred in this well since early production. At the same time, it has been noticed that fluid mixing promotes mineral scaling (Arnorsson, 1992; Bethke, 1996) thus, it is possible that this process could have enhanced calcite deposition processes in the well. Since October 2003 the well LV-1 is no longer producer in the field.

4.2.2 Well LV-3

In Figure 4 the saturation indices of hydrothermal minerals vs temperature for the well LV-3 are shown. As it is seen in the figure, the phase calcite is found oversaturated for all the temperature range studied showing a small inflexion at a temperature of about 250°C. Crysolite attains equilibrium at 220°C while epidote and talc at 250°C. Epidote shows a new equilibration at about 270°C.

Quartz equilibrates at 245°C and anhydrite at 257°C showing oversaturation at higher temperatures. Equilibrium for albite-low, laumontite and microcline is shown at 280°C. In this well, as in well LV-1, the saturation indices do not indicate a single equilibrium temperature, thus multiple entries of fluids to the well, is also proposed. Since June, 2006 this well is no longer producer in the field.

4.2.3 Well LV-4

The saturation indices of minerals found for well LV-4 vs temperature are given in Figure 5. As seen in the figure, the saturation indices show a more stable behavior regarding these for the wells LV-1 and LV-3.

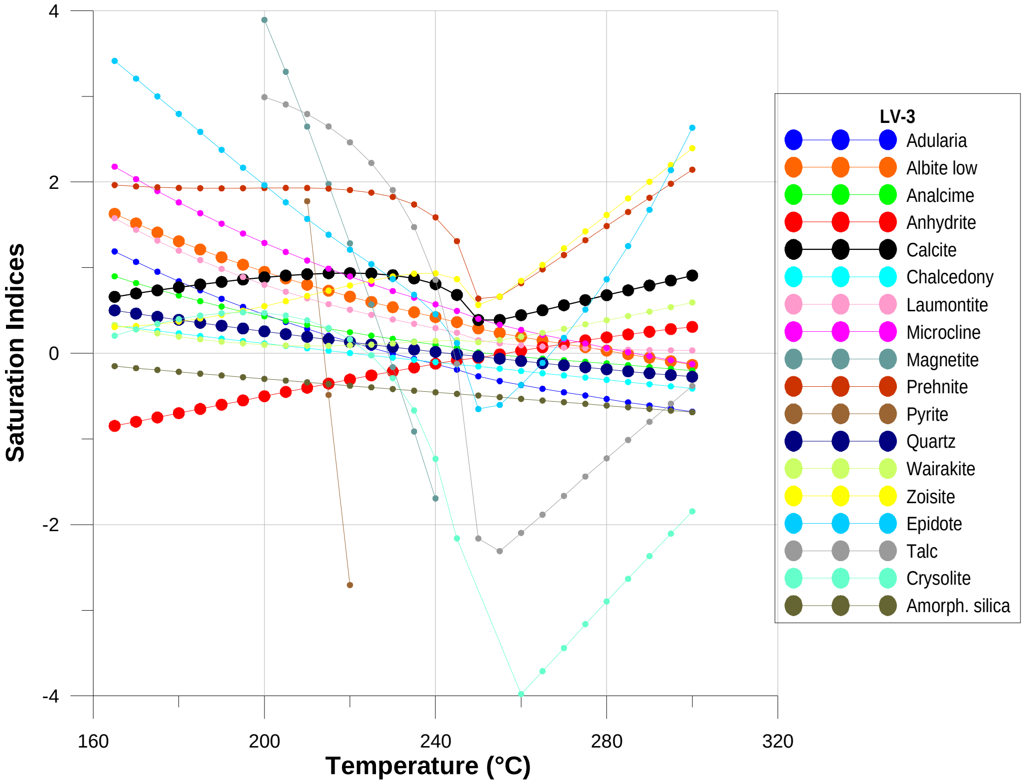

Figure 4: Saturation indices of hydrothermal minerals vs. temperature for the well LV-3.

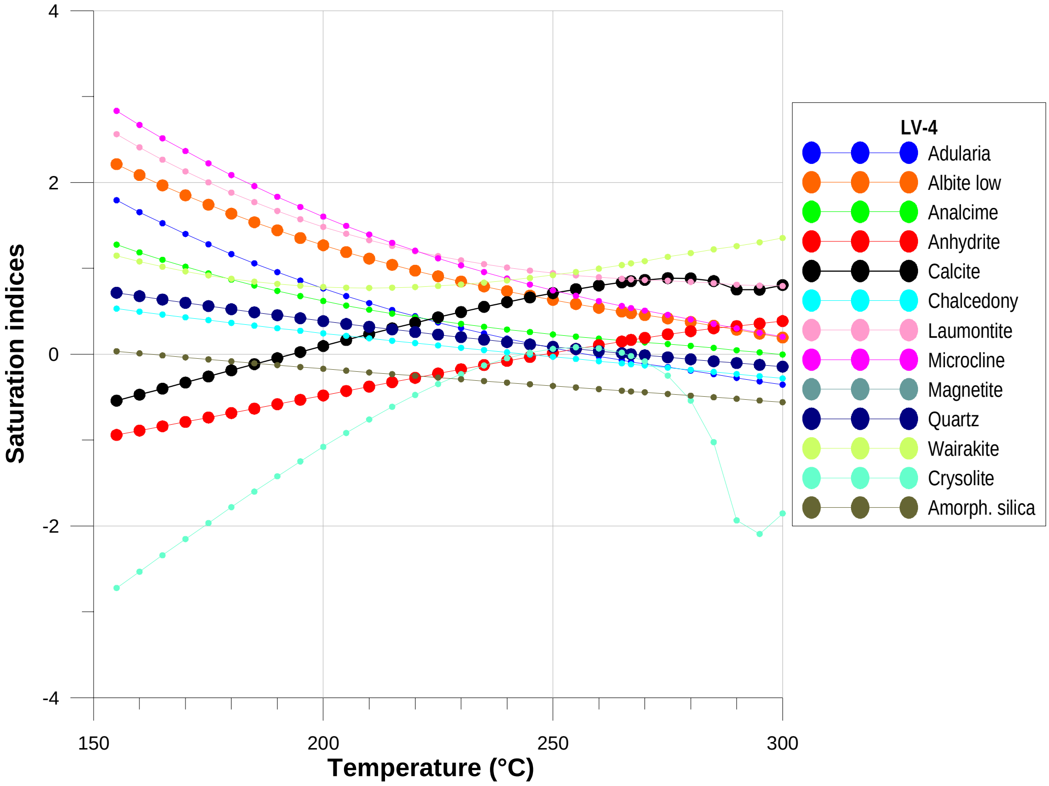

Figure 5: Saturation indices of hydrothermal minerals vs. temperature for the well LV-4.

Calcite attains equilibrium at 190°C while it is found subsaturated at lower temperatures but oversaturated at higher temperatures. For this reason, in order to try to overcome calcite deposition, it is recommended to operate the production separator at pressures lower than 12.5 bar. An “older” equilibration at 225°C is noticed through the convergence of saturation indices of amorphous silica, anhydrite and calcite to a slightly negative saturation index value. This could indicate an entry of a lower temperature water to the well. Anhydrite equilibrates at 250°C while at higher temperatures becomes oversaturated. Quartz is in equilibrium at 268°C while crysolite at 266°C; adularia attains equilibrium at 257°C and chalcedony at 243°C. In this well although different equilibrium temperatures are obtained from saturation indices of minerals, a range of temperatures occur (~257-268°C), in which saturation lines converge to the zero saturation line. The analysis of 2007 geochemical data indicated that some dilution effects have taken place in this well, which were attributed to exploitation (Barragán et al, 2009). However equilibrium modeling results of this work suggest that by 1999, a single fluid entry may have occurred.

4.2.4 Well LV-5

The well LV-5 is no longer producer, it was closed in 2002. The saturation indices of hydrothermal minerals vs temperature for the well LV-5 are given in Figure 6. As it is seen, calcite is found equilibrated at 180°C, subsaturated at lower temperatures and oversaturated at higher temperatures. Pyrite also shows equilibrium at 180°C while anhydrite, chalcedony and magnetite equilibrate at 200°C. Quartz attains equilibrium at a relatively low temperature, 220°C. Albite low equilibrates at 240°C and microcline at 250°C. As in this well a number of equilibrium temperatures are observed, multiple fluid entries to the well is proposed. Besides, it is noticeable that one equilibrium temperature is about 180°C, as was observed in well LV-1. This could support the hypothesis of dilution caused by the entry of shallower fluids (at about 187°C) to the well as was proposed for the well LV-1.

4.2.5 Well LV-11

The results of saturation indices of minerals vs temperature obtained for the well LV-11 are given in Figure 7. According to the results, calcite shows equilibration at 193°C while it becomes oversaturated at higher temperatures. For this reason recommended separation pressures should be lower than 13.4 bar to try to avoid calcite deposition. Amorphous silica also shows equilibration at 193°C and subsaturation at higher temperatures while pyrite equilibrates at a slightly lower temperature. It is interesting to notice that calcite-amorphous silica- pyrite partial equilibration takes place at a temperature close to that estimated for the shallower diluting water (187°C), suggesting a lower temperature fluid entry with minimum dilution effects in the well LV-11 in 2000. Chalcedony equilibrium is attained at 280°C while saturation curves of both quartz and anhydrite converge to the zero saturation line at 290°C. Other mineral phases such as albite low and microcline tend to converge each other to the zero saturation line at temperatures higher than 320°C. In general, the saturation indices of minerals show relatively stable behavior, except that of crysolite which exhibits important inflections showing subsaturation at temperatures between 250 and 270°C. In this well, the reservoir temperature could be estimated as high as 290°C.

4.2.6 Well LV-13

The behavior of the saturation indices of minerals vs temperature for the well LV-13 are given in Figure 8. The results of saturation indices show the typical amorphous silica-pyrite partial equilibrium at 180°C giving evidence of the shallower fluid entry to the well. As seen in the figure, the saturation curves of calcite and anhydrite show the same shape, calcite equilibrates at 230°C while anhydrite at 240°C. The saturation curves of magnetite and amorphous silica intercept those for calcite and anhydrite at 230-235°C converging all of them at a slightly negative saturation index value probably indicating an “older” equilibration.

At higher temperatures both phases are found oversaturated. This result indicates that in this well at usual separation conditions (~ 150°C) no calcite precipitation should occur. Chalcedony attains equilibrium at 280° while quartz equilibrium occurs at 300°C. The phase adularia equilibrates at 320°C while microcline and albite low tend to equilibrate at even higher temperatures.

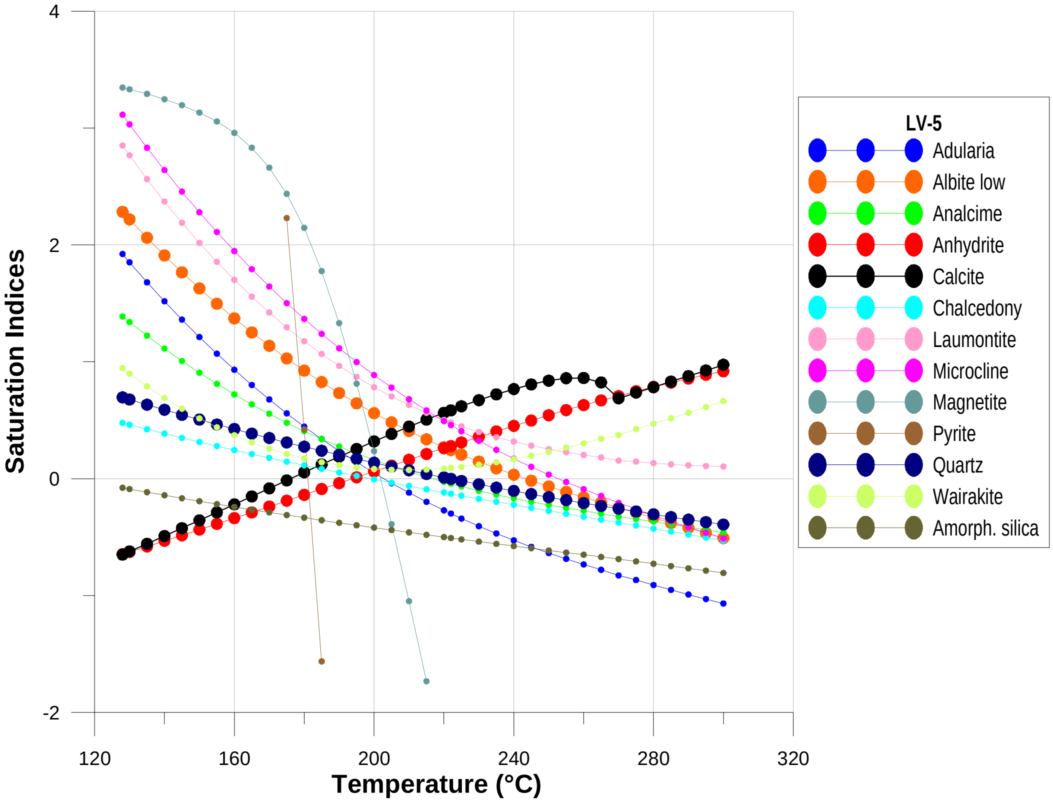

Figure 6: Saturation indices of hydrothermal minerals vs. temperature for the well LV-5.

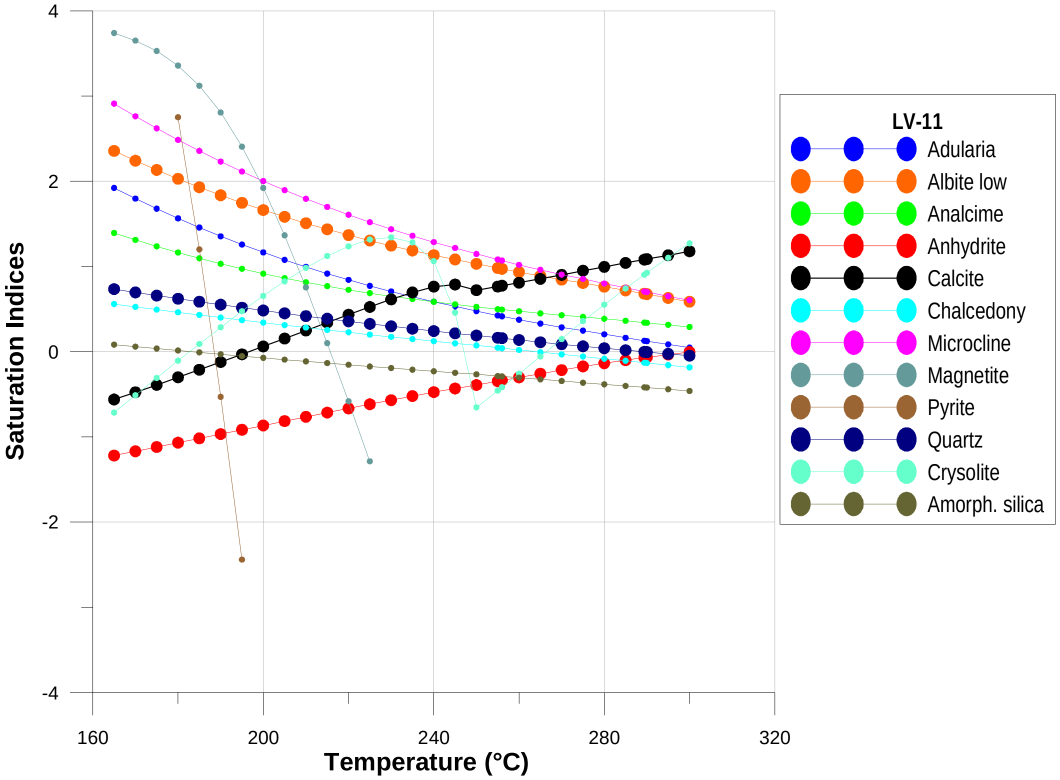

Figure 7: Saturation indices of hydrothermal minerals vs. temperature for the well LV-11.

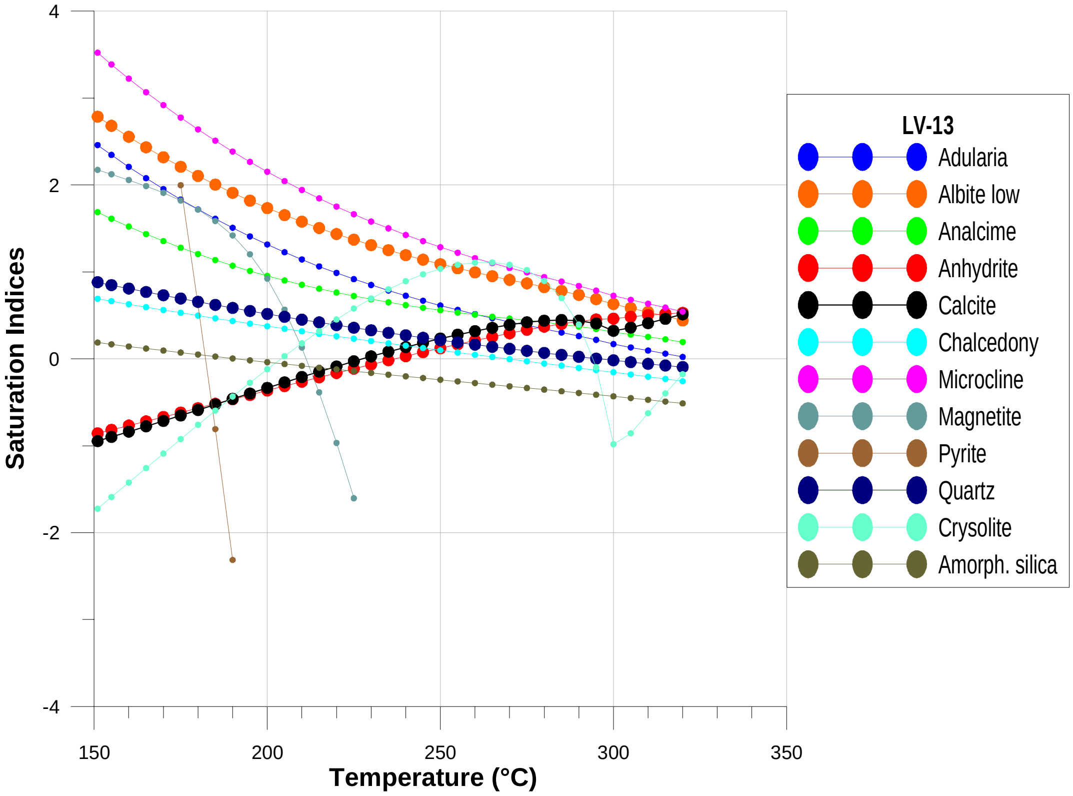

Figure 8: Saturation indices of hydrothermal minerals vs. temperature for the well LV-13.

5. CONCLUSIONS

The results of fluid-mineral equilibrium modeling with calculation of minerals saturation indices for fluids from the Las Tres Vírgenes wells allowed to better understand complex phenomena occurring in the field that limits the resource exploitation. Such phenomena includes calcite and other minerals scaling along with mixing effects caused by multiple fluid entries in the wells. As it is well known that mixing of fluids with different chemical compositions strongly promotes mineral deposition, it is possible that the scaling phenomena observed in the field is being enhanced by such processes. Based on calcite saturation indices results it was possible to estimate the optimal conditions (pressure and temperature) for the production separators of the wells in order to avoid calcite scaling. The behavior of the saturation indices of minerals vs temperature also allowed to explain the differences obtained in reservoir temperature estimations by using different geothermometers. The approach used in this work was useful to estimate the approximate temperatures of the shallower fluids entering the wells, which have caused dilution effects over time.

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