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Application of Calcite Precipitation Rate in Predicting the Utilization Period of Calciting Wells in the Mindanao Geothermal Field, Philippines

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ABSTRACT

The empirically determined precipitation rate law (Shiraki and Brantley, 1995) was applied to calculate the utilization period of calciting wells where pipe geometry and varying boiling temperatures were considered. The results using the empirical precipitation rate law method showed extended utilization periods for saturation ratio (Q/K) less than or equal to 1.72, while shorter periods were calculated for saturation ratio above 1.72 as compared to direct deposition of excess calcite method. The applicability of the calcite precipitation rate law method in predicting the utilization period of calciting wells depends on the determination of the actual flash point temperature and calibration of the empirical equation to the field observations. The empirical equation was derived at laboratory conditions using reactor tanks with stirring at 100oC and modified (extrapolated) to include higher temperatures (Andre et al., 2006). The laboratory test set-up is perceived to be an approximation but does not mimic the complex flow regime observed in geothermal wells. Information on the utilization period of a calciting well derived from the modified rate law method will help in refining steam availability evaluation of the geothermal field as well as devise appropriate work over schedule.

1. INTRODUCTION

In the absence of calcite inhibition system, the utilization period of the calciting wells is uncertain. Majority of the speciation software available only reveal the characteristic of the geothermal fluids in terms of degree of saturation with respect to calcite mineral. This does not directly translate to duration the well will sustain the discharge. Utilization period of calciting wells can be derived from the discharge history if we assume that the well has stable chemistry. The changes are inevitable particularly in fluid chemistry since the geothermal reservoir is very dynamic due to the effects of mass extraction and injection. Therefore, variation in utilization period through time is expected.

Initially the methodology being done is to assume that all of the excess calcite from the solution will be deposited in a predetermined volume of the geothermal pipe. This approach is conservative considering that calcite deposition is an instantaneous process. However, numerous literatures state that calcite deposition is kinetically-controlled where the process of deposition could either be slower or faster (Morse, 1978; Berner and Morse, 1974; Plummer et al., 1978; Sjorberg and Rickard, 1984; Busenberg and Plummer, 1986; Compton and Urwin, 1990 and Lebron, 1996). Shiraki and Brantley in 1996 developed a precipitation rate equation for high salinity fluid in laboratory condition at temperature of 100^{o}C using a reactor tank. This was modified through extrapolation to extend the application up to 300oC and currently used in the program code of *FRACHEM* (Andre et. al., 2006).

This paper will evaluate the applicability of the modified precipitation rate equation in predicting the discharge duration of a calciting well, in comparison to the observed utilization history and to the results of the conservative method from direct deposition of excess calcite. Three wells in Mindanao Geothermal Production Field (MGPF) with documented output decline due to calcite deposition were studied, namely APO1D, SP4D and MD1D.

2. THE GEOTHERMAL FIELD

The Mindanao Geothermal Production Field (MGPF), with an area of ~30 km^2, is situated on the northwest flanks of Mt. Apo volcano located in the southwestern part of Mindanao Island in the Philippines (Fig. 1). Commercial operation of the field started in March 1997 with the commissioning of the 52-MWe Mindanao-1 geothermal power plant (M1). An additional 52-MWe power plant (M2) commissioned in June 1999, and increased the total capacity of the field to 104 MWe. Each power plant requires a annual minimum energy off-take; this necessitates an updated total steam availability of the field and realistic forecast to ensure realization of steam production. The unexpected drop in the output of the calcite-affected wells upsets the steam availability of the field requiring immediate rig mobilization to work-over and regain the lost production capacity.

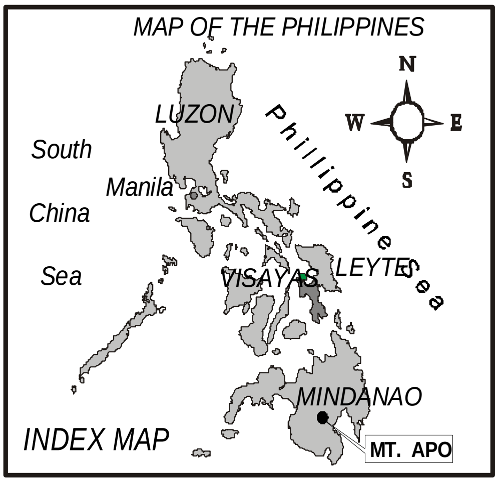

Figure 1: Philippine map showing the location of the project site.

3. METHODOLOGY

Three production wells are considered in the evaluation of the calcite precipitation rate equation for its applicability in predicting the utilization period, namely APO1D, SP4D and

MD1D. The outputs of these wells were intermittently affected by calcite deposition in the well bore when operated without the calcite inhibition system (CIS), requiring periodic work-over to regain productivity. Wells APO1D and SP4D are wells supplying steam to M1 power plant while MD1D supplies steam to M2 power plant but also contribute steam to M1 through steam-sharing system.

For each well the utilization period was calculated using the precipitation rate equation as well as direct deposition of the excess calcite mineral. The discharge fluid chemistry is initially evaluated to reservoir condition and simulated to boil at different temperatures. Each boiling temperature produced different saturation values (Q/K) with respect to calcite mineral requiring individual calculation of utilization period. If the flash point temperature of the well is available during the episode of active calcite deposition, the calculated utilization period at this temperature is compared to the historical value.

The speciation software used to evaluate boiling to obtain calcite saturation ratios, concentrations of aqueous Ca^{2+} and CO_2 species, activity coefficients and equilibrium constants is WATCHWORKS. This geochemical software, designed to do geothermal chemistry simulation, was initially programmed by Stefan Arnorsson in DOS based operating systems, and eventually reprogrammed by the GeothermEx Inc.-Icelandic Water Chemistry Group (Klein, et al. 1998) to create graphical user interface to make it more user-friendly.

3.1 Precipitation Rate

The general rate law equation is given by:

$$Rate = Kp(\Omega - 1)^n A_{kgw} \qquad (1)$$

where:

Rate – precipitation rate, mole/kgw-s

Kp – rate contant, mole/m^2-s

Ω - saturation ratio (Q/K)

A_{kgw} – surface area for deposition per kilogram water

n – empirically determined

The following equations are derived from Eq. 1 depending on the saturation levels (Q/K) which is modified to include higher temperature range:

For Q/K < 1.72:

$$R_p = 1.927x10^{-2} T \exp^{\left(\frac{-41840}{RT}\right)} A_{kgw}\left(\frac{Q}{K}-1\right)^{1.93} \qquad (2)$$

For Q/K > 1.72:

$$R_p = 1.011T \exp^{\left(\frac{-41840}{RT}\right)} A_{kgw} \exp\left(\frac{-2.36}{\ln\left(\frac{Q}{K}\right)}\right) \qquad (3)$$

where:

R – 8.315 J/mol-K

T – Temperature in Kelvin

Q/K – Saturation ratio taken from *WATCHWORKS*

A_{kgw} – Surface area for deposition per kilogram water in m2

R_p – Precipitation rate, mole/Kgw-s

Equations 2 and 3 are used to calculate the precipitation rate of the thermal fluid at varying boiling temperatures using the actual pipe diameter. The boiling calculations are done by the speciation software *WATCHWORKS*. The output of this program also includes the calcite saturation ratios, the activity coefficients of the water species and the equilibrium constants. The surface area for deposition per kilogram of water is obtained using Eq. 4 given the diameter of the pipe where calcite blockages were detected. This is the surface area of the inner wall of the pipe occupied by 1 kg water.

$$SA = \frac{2V}{r} \qquad (4)$$

All of the calcite blockages of the wells studied were found within the slotted liner with diameter of 7-⅝ inches. After evaluating the precipitation rate (mole calcite /Kgw-s), the value is multiplied by the formula weight of calcite mineral at 100 g/mole and the total water flow, and divided by 1000 to obtain the amount of calcite mineral deposited in kilogram per second. The amount of calcite needed to choke the well (i.e. the well is no longer flowing) is derived from the mass of calcite required to fill the volume occupied by the water flow (kg/s). The water flow (kg/s) is multiplied with the calcite mineral density of 2.71 kg/L to get the target amount of calcite assuming the density of water of 1 kg/L. Finally, the utilization period is obtained by dividing the target amount of calcite needed to choke the well with the amount of calcite deposited per second; the resulting value is then transformed to a more convenient time unit (either days or months).

The following are the assumptions made in applying the precipitation rate equation.

- Deposition occurs at the boiling point
- The fluid is supersaturated with calcite mineral
- Complete adhesion of the calcite mineral in the inner wall of the pipe when formed
- Moderate flow in the pipe to mimic the stirring experiment

The last two assumptions may not be true in the actual conditions where instantaneous boiling and turbulent flow in the pipe occur. These conditions do not allow certain calcite crystals to deposit immediately and fractions may be removed by the fluid.

3.2 Direct Deposition of Excess Calcite

The expected mole of excess calcite deposited per kilogram of fluid is determined using the equation below.

$$mole\_CaCO_3 / kgw = \left(\frac{(\Omega-1)K}{(\gamma_{Ca}\gamma_{CO_3})}\right)^{1/2} \qquad (5)$$

where:

Ω - saturation ratio (Q/K)

K – equilibrium constant

γ - activity coefficient

Subsequently, the mole of the excess calcite obtained from Eq. 5 is multiplied with the formula weight of Ct (100 g/mole) and with the water flow (kg/s) then divided by 1000 to get the amount of calcite precipitated in kilogram per second. Similar to the precipitation rate, the target amount of calcite needed to choke the well is calculated by multiplying the water flow (L/s) with the calcite mineral density (kg/L). Lastly, the utilization period is acquired by dividing the target amount of calcite with the amount of the calcite deposited.

3.3 Drop in Concentration of Species

The impact of the calcite deposition to the concentrations of Ca^{2+} and CO_2 is evaluated using the mass balance equation (Eq. 6 below). This was done to check the possibility of knowing the on-set of calcite deposition by monitoring the drop in the concentration of either Ca^{2+} or CO_2.

$$\text{Residual Amount} = \text{Initial Amount} - \text{Deposited Amount} \qquad (6)$$

4. RESULTS AND DISCUSSION

4.1 Fluid Chemistry

The physical and geochemical data used in the simulation of the fluid chemistry and characteristic of the wells at different boiling temperatures are shown in Table 1. The Ca^{2+} concentrations of the near neutral to slightly alkaline pH well waters range between 87 to 211 mg/L. The Ca^{2+} concentrations appear to inversely correlate with reservoir temperature as estimated from the quartz geothermometer. For instance, APO1D having the lowest reservoir temperature at 228°C, has the highest calcium value of 211 mg/L among the three. This is followed by SP4D with a temperature of 236°C and Ca^{2+} value of 139 mg/L while the hottest well MD1D with reservoir temperature of 270°C has the least Ca^{2+} value of 87 mg/L. Except for MD1D, the wells at reservoir condition are just about saturated with respect to calcite minerals but the residual liquid becomes oversaturated following boiling upon flow through the well. Boiling process as triggering mechanism for calcite formation is proven from the location depths of the calcite minerals. Majority of the calcite blockages were found at the flash point depths of the production wells.

4.2 Precipitation Rate Constant

The calcite mineral has retrograde solubility where the amount of calcite that can be dissolved in a certain volume of water decreases as the temperature increases. The behavior is indirectly shown in Fig. 2 where the plots of the calcite precipitation rate are constant at saturation ratio below and above 1.72. Precipitation is the opposite of solubility thus lower solubility favors the formation of calcite mineral. Based on Fig. 2, the calcite precipitation rate constant is increasing with increasing temperature. Two regimes of calcite formation, dependent on the saturation ratio, were discussed by Shiraki & Brantley. At saturation ratio <1.72, the precipitation rate of calcite has parabolic behavior (spiral growth) while at >1.72, the rate increased exponentially or the rate law adhere to the surface nucleation as growth mechanism (Fig. 3). Thus, the precipitation of calcite mineral has slower rate at saturation ratio < 1.72 compared to the saturation ratio > 1.72.

Table 1: Chemistry of calciting wells used in the simulation.

	APO1D	SP4D	MD1D
Sampling Pressure, Mpaa	0.869	0.967	0.870
WF, kg/s	35	40	20
TQtz, °C	228	236	270
Water Chemistry (mg/L except pH)			
pH	7.34	7.33	6.59
Na	3328	2974	3623
K	379	390	794
Ca	211	139	87.4
Mg	0.14	0.09	0.05
Cl	5546	5274	6057
SO_4	35.4	37.2	101
SiO_2	417	462	708
NH_3	0.46	0.44	0.19
H_2S	4.66	4.11	3.82
B	108	105	127
TCO_2	13.1	9.29	46.3
Gas Chemistry (mmole/100 mole steam)			
CO_2	116	81.4	256
H_2S	6.4	2.0	13.7
NH_3	0.4	0.3	0.60

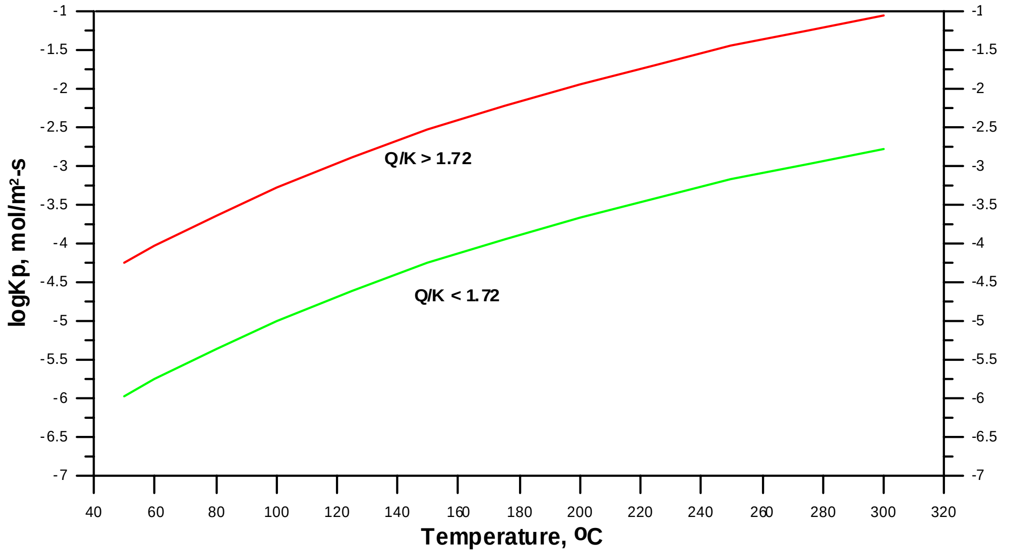

Figure 2: Calcite saturation rate constant at saturation below and above 1.72.

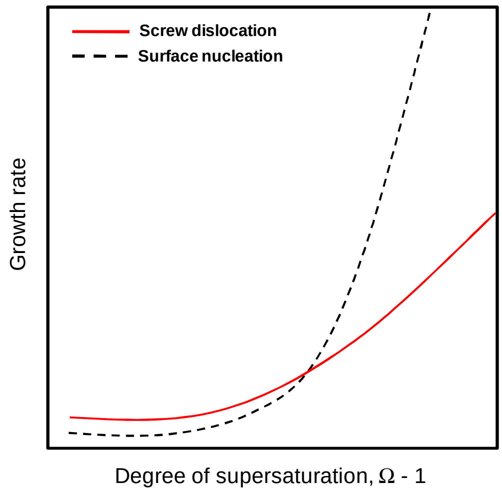

Figure 3: Schematic diagram of crystal growth rate and degree of supersaturation for the two mechanisms.

4.3 Utilization Period

4.3.1 Well APO1D

Figure 4 and Table 2 show the summary of the results of calculations done for well APO1D. The utilization periods given by the direct deposition of the excess calcite has a minimum of 1 month and maximum of 6 months. Since this is deposition of the excess calcite the value obtained from this method provided the minimum duration of well utilization. It can be noted that the calcite precipitation rate equation at saturation ratio above 1.72 provided shorter utilization time than the direct deposition method which means the rate law overestimated the amount of calcite deposited. However, at saturation ratio below 1.72 the rate law indicated longer utilization period which was expected since calcite deposition is kinetically controlled rather than instantaneous deposition of the excess calcite.

Table 2: Results of APO1D utilization period calculations.

Boiling Temp., ^{o}C	Q/K	log K	γCa	γCO_3	Utilization Period, months	
					Rate Equation	Excess Calcite
227	1.12	-12.186	0.186	0.150	73.6	6.2
226	1.48	-12.161	0.187	0.151	5.2	3.1
225	1.78	-12.136	0.188	0.151	1.5	2.3
224	2.02	-12.111	0.188	0.152	0.7	2.0
223	2.23	-12.086	0.189	0.153	0.5	1.8
218	2.80	-11.962	0.192	0.156	0.3	1.3
213	2.94	-11.840	0.196	0.159	0.3	1.1
208	2.84	-11.718	0.199	0.162	0.3	1.0
203	2.64	-11.598	0.202	0.165	0.5	0.9
198	2.39	-11.478	0.206	0.168	0.7	0.9
183	1.62	-11.128	0.216	0.177	9	1.0
178	1.40	-11.013	0.219	0.180	24	1.1

Based on the utilization history of APO1D, periodic work-over was done in the well after 7-8 months of continuous utilization. With this actual range of utilization period, it could be estimated that the first boiling temperature of the well was above 226^{o}C having calcite saturation ratio < 1.48. Temperatures < 200^{o}C were not considered since the values reflected surface conditions. The calcite precipitation equation is very sensitive as the saturation ratio approaches unity. A comparison of the utilization period of 226^{o}C and 227^{o}C with saturation ratio of 1.48 and 1.12, respectively, shows the difference in the duration period is 68 months. Though the behaviour was also manifested in direct deposition of excess calcite, the duration period was doubled.

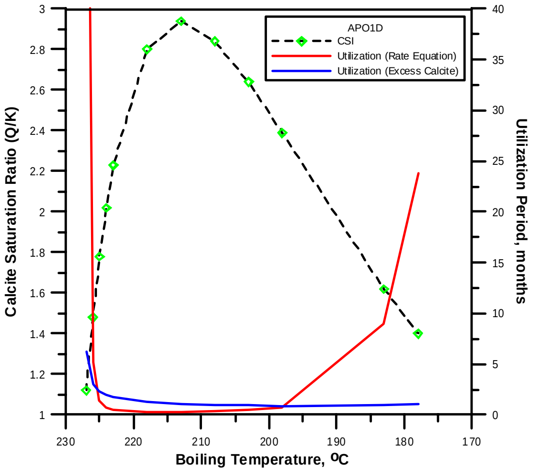

Figure 4: APO1D saturation ratio and utilization period at different boiling temperatures.

As inferred from the utilization periods given by the direct deposition method the first boiling temperature of the well did not occur in the higher range of the calcite saturation ratios (226^{o}C-180^{o}C). Upon simulation of calcite saturation index of the production well the highest saturation value is usually reported. The available simulated flashed temperature of APO1D in 1998 was 235^{o}C and the reservoir temperature of the well in this period was 238^{o}C. This validated that the first boiling point temperature of the well was just a few degrees lower than the reservoir temperature. But it would still be possible that the first boiling temperature occurred in this high saturation range if there were crystal losses through fluid carry-over or a more fitting calcite precipitation rate equation may be created and applied at this condition.

4.3.2 Well SP4D

The actual utilization period of the well prior to work-over ranged from 10 to 15 months. Using the calcite precipitation rate equation, the utilization period coincided (at 235^{o}C first boiling temperature) was 11 months (Fig. 5 and Table 3). Again the 205^{o}C was not considered here since it occurred at the surface pipeline and the calcite blockages were found in the production liner. The equivalent utilization period for the direct deposition of excess calcite at this condition is only 5 months. The simulated flashed temperature of SP4D was 234^{o}C which is very close to the value derived from correlating the actual and calculated utilization periods. Similar to APO1D, the calculated utilization periods for saturation ratio above 1.72 indicated shorter duration than the direct deposition of excess calcite.

4.3.3 Well MD1D

Well MD1D is unique among the three wells since the calcite saturation ratios are always > 1 even at reservoir condition. The well has no saturation value obtained below 1.72, thus the utilization period based on the rate equation consistently resulted to short duration at maximum of 15 days only compared to the values from the direct deposition of excess calcite at 6 months as maximum value.

The historical utilization period of MD1D is around 6 months. This actual utilization period corresponded to the value from the direct deposition of excess calcite at the boiling temperature of 270^{o}C. It is interesting to note that well MD1D has high calcite saturation values and yet produce longer calculated utilization periods than APO1D and SP4D using the direct deposition method (Table 4 and Figure 6). This is attributed to the lower equilibrium constant of calcite mineral (reference value) at higher temperature. Thus, despite of the inherently lower calcium concentration of MD1D the well has high degree of saturation.

Table 3: Results of SP4D utilization period calculations.

Boiling Temp., ^oC	Q/K	log K	γCa	γCO_3	Utilization Period, months	
					Rate Equation	Excess Calcite
235	1.29	-12.387	0.188	0.152	11.3	5.1
230	2.19	-12.261	0.191	0.156	0.4	2.2
225	2.33	-12.136	0.195	0.159	0.4	1.9
220	2.19	-12.012	0.198	0.162	0.6	1.7
215	1.96	-11.889	0.202	0.165	1.0	1.7
210	1.71	-11.767	0.205	0.168	3.5	1.8
205	1.46	-11.646	0.209	0.171	9.1	1.9
200	1.24	-11.526	0.212	0.174	36	2.4

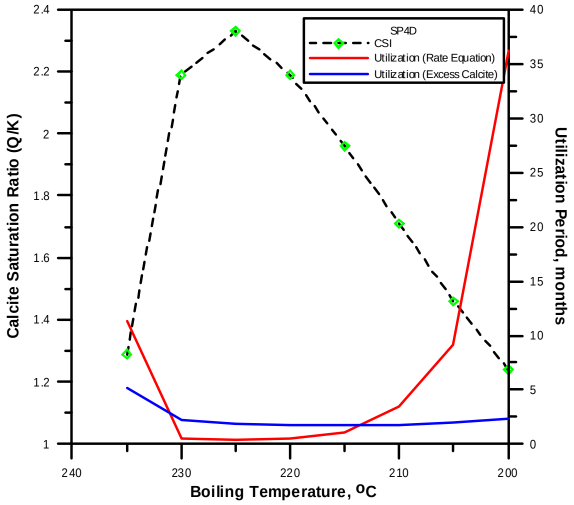

Figure 5: SP4D saturation ratio and utilization period at different boiling temperatures.

The applicability of the calcite precipitation rate in predicting the utilization period is only limited to saturation ratio below 1.72 based on the results of the three calciting wells. If the flash point temperature of the well is initially known and the calculated calcite saturation ratio is above 1.72, the method of direct deposition of excess calcite is better used in predicting the utilization period. The calcite precipitation rate equation should be calibrated to what is really observed in the field particularly for calcite saturation above 1.72. The empirical equation was derived at laboratory conditions using reactor tanks with stirring at 100^oC and modified (extrapolated) to include higher temperatures (Andre et al. 2006). The laboratory test set-up is perceived to be an approximation but does not mimic the complex flow regime observed in geothermal wells.

4.4 Drop in Concentration of Species

The impact of the calcite deposition to the chemistry of the residual liquid was determined through mass balance equation. Figures 7 and 8 show the expected drop in the calcium and total CO_2 concentrations during calcite deposition in the well bore for precipitation governed by the rate law and direct deposition of excess calcite. The expected maximum drop in calcium is about 2 ppm at the highest saturation ratio of well APO1D. Considering that the as- analyzed calcium concentration for APO1D is 211 mg/L, this drop will not be manifested in the surface since it is within the uncertainty of analysis and normal fluctuation of the fluid chemistry which is also the same case with total dissolved CO_2. Thus determining the onset of calcite deposition through drop in concentration of either Ca^{2+} or total CO_2 is not viable. Furthermore, the on-set of calcite deposition based on these parameters will be indistinct if the well is affected by other reservoir processes such as inflow of degassed cooler fluids which increases the calcium and decreases the total CO_2.

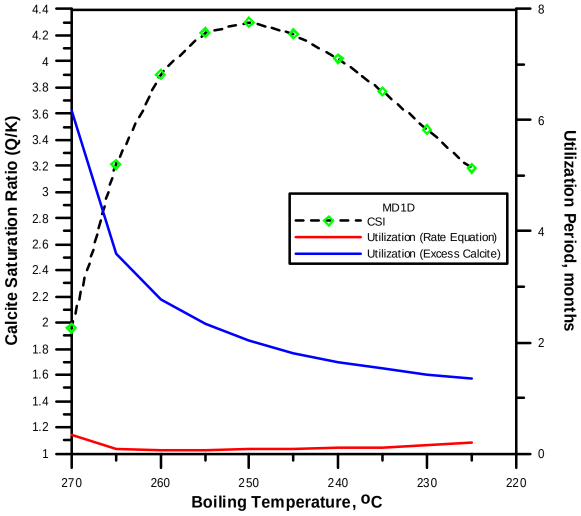

Figure 6: MD1D saturation ratio and utilization period at different boiling temperatures.

Table 3: Results of MD1D utilization period calculations.

Boiling Temp., ^oC	Q/K	log K	γCa	γCO_3	Utilization Period, months	
					Rate Equation	Excess Calcite
270	1.96	-13.295	0.147	0.115	0.32	6.2
265	3.21	-13.162	0.151	0.119	0.08	3.6
260	3.90	-13.031	0.155	0.122	0.07	2.8
255	4.22	-12.900	0.159	0.126	0.07	2.3
250	4.30	-12.771	0.163	0.129	0.07	2.0
245	4.21	-12.642	0.167	0.132	0.08	1.8
240	4.02	-12.514	0.170	0.136	0.10	1.7
235	3.77	-12.387	0.174	0.139	0.12	1.5
230	3.48	-12.261	0.178	0.142	0.15	1.4
225	3.18	-12.136	0.181	0.145	0.19	1.3

Dulce et al. (2000) observed that in general, the calcite saturation of the well shifts from oversaturated to undersaturated during active calcite deposition. Why then was there a change in the calcite saturation ratio if the expected change in the Ca^{2+} and total CO_2 are very minimal? Through sensitivity analysis, it was found out that the calcite saturation ratio is significantly affected by the pH of the fluid. A variance of 0.1 pH unit will translate to 1 to 2 unit change in the ratio. Thus, the noted shifting of the saturation ratio during deposition could be attributed to the change in the pH brought by the calcite deposition.

5. CONCLUSIONS

The applicability of the calcite precipitation rate in predicting the utilization period of calciting wells was evaluated using wells with known history of calcite deposition and in comparison to the results obtained from the conservative method (deposition of excess calcite). The precipitation rate equation seemed to give reasonable values of utilization period at calcite saturation ratio below 1.72, since the results are closer to the actual utilization period. However, improbable values were obtained with calcite saturation ratios above the 1.72 because the calculated durations were consistently shorter than the values acquired from the direct deposition of excess calcite which was considered as the minimum possible value.

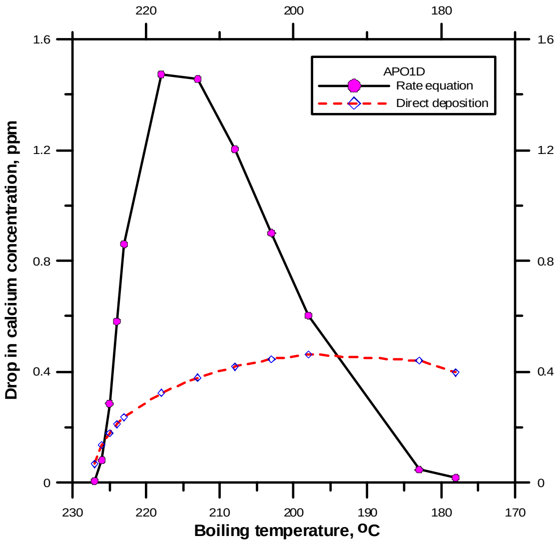

Figure 7: Expected drop in calcium concentration of APO1D during calcite deposition.

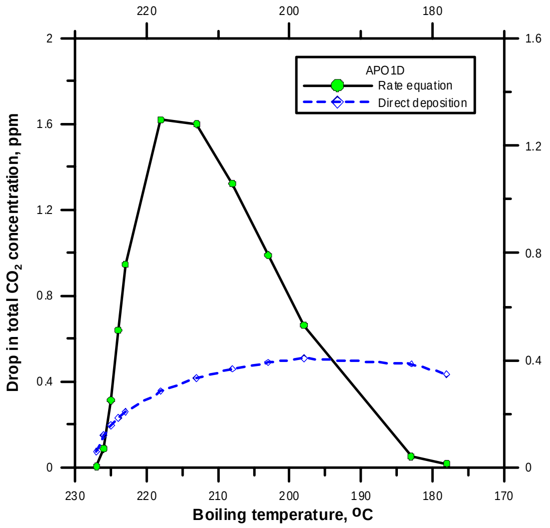

Figure 8: Expected drop in CO_2 concentration of APO1D during calcite deposition.

Monitoring the changes in concentrations of Ca^{2+} and total dissolved CO_2 to determine the onset of calcite deposition is impractical for wells with comparable chemistry to APO1D, SP4D and MD1D (> 80 mg/L Ca^{2+} and > 10 mg/L total CO_2) since the expected drop in concentrations are insignificant. This technique could be complicated by the effect of reservoir processes such as inflow of cooler degassed fluid which increases the calcium and decreases the total CO_2.

The calcite precipitation rate equation should be further refined by calibrating the equation to the field condition particularly for saturation ratio above 1.72. The calcite saturation ratio is more responsive in detecting the onset of calcite deposition through the sudden shift of the saturation ratio from consistently > 1 to < 1 as cited by Dulce (2002). The direct deposition of excess calcite method should be used in predicting the utilization period in cases where the flash point temperature of the well is known and the saturation ratio at this condition is above 1.72.

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