

Evaluation of Chemical Equilibria of Calcite Deposition in a Geothermal Well at Northern Negros Geothermal Project, Philippines

Dennis R. Sanchez, Aristeo S. J. Baltasar, and Mayflor N. R. Candelaria

Philippines National Oil Company-Energy Development Corporation (PNOC-EDC),

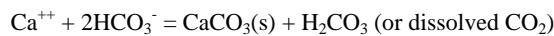
Geoscientific Department, Merritt Road, Ft. Bonifacio, Makati City, Philippines

sngpf_geoservices@energy.com.ph

Keywords: Calcite, chemical equilibria, WatchworksTM,

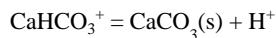
ABSTRACT

Calcite deposition in geothermal wells is commonly expressed as:



For calcite supersaturated reservoir fluids, at constant reservoir and boiling temperatures, deposition was triggered by boiling and release of dissolved CO₂. This paper evaluates this equilibrium based on gas and water samples collected in one of the calciting wells, PT2D, in the Northern Negros Geothermal Project. This type of study was possible because water and gas data were available as the well's massflow and wellhead pressure declined due to calcite deposition.

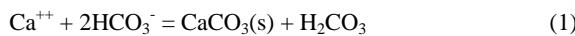
Through the series of time-plots of chemical species' activities related to calcite, and comparison of Gibb's Free energy from each postulated equilibria, calcite deposition was likely through dissociation of CaHCO₃⁺:



In this reaction, deposition of calcite from supersaturated reservoir fluids was possible in the wellbore because there was an increase in reservoir temperature during discharge, as manifested by an increase in quartz geothermometer (Tqtz) with time. It is not clear whether calcite deposition was caused by mixing of the supersaturated fluids and the hotter up-flowing fluids or by heating of the reservoir fluids in the wellbore.

1. INTRODUCTION

This study evaluated calcite equilibria commonly used in describing calcite deposition in geothermal wells. Through the years, calcite deposition is assumed to occur by boiling and release of CO₂ gas as expressed in Equation 1 (Cowan and Weinritt, 1976; Granados, 1983):



For calcite supersaturated reservoir fluids, boiling and release of dissolved CO₂ shifts the equilibrium to the right triggering deposition. In geothermal environments, this chemical reaction is commonly accepted as the mechanism of calcite deposition, specifically in discharging geothermal wells. This paper describes this equilibrium from the gas and water data collected at PT2D well in Northern Negros Geothermal Project during its test. Equation 1 is examined, by determining the changes in reservoir's molal activities of dissolved species that are related to deposition. It is also envisaged that other possible equilibria may be identified controlling calcite deposition.

1.1 Discharge History

PT2D is the second well drilled in the production sector of Northern Negros Geothermal project (Figure 1). It was first discharged in February 1996 and attained a stable but non-commercial well-head-pressure of 0.10 MPaa and water flow of 7.5 kg/s. No steam flow and enthalpy measurements were taken because of the non-commercial nature of the discharge. The test lasted for 29 days with the objective of cleaning the well of its drilling fluids prior to a work-over and acidizing.

Its second test commenced on July 1997 after a mechanical work-over and acidizing conducted a year before. The well was put to full-open for a week. However, there were indications that massflow and well-head-pressure started to decline. The well was throttled to attain and maintain a commercial well-head-pressure and to decrease the degree of boiling or release of CO₂ while in a throttled state.

The well was returned to full wellhead-pressure and the massflow showed a distinct decline from 0.68 to 0.52 MPaa and 59 to 53 kg/s, respectively. Again the well was put to a throttled state, this time using back-pressure plates. Throttling the well was aimed at preventing calcite deposition by minimizing extensive boiling, hence release of CO₂ gas (Granados, 1983). This condition lasted for ten days until the pressure and flow dropped to zero. Critical gas and water samples were collected at each phase of discharge to evaluate calcite deposition.

1.2 Calcite deposition history

Figure 2 shows the temperature-pressure profile of the well taken in 1995 before its first discharge test. Three feed zones were identified:

Minor zone: ~1590-1600mMD (Mambucal A fault)

Minor zone: ~2100-2240mMD (Kinabkaban A fault)

Major zone: ~2400-2500mMD (Dinagaan fault)

The heat-up surveys of PT2D showed that the well had a good rate of thermal recovery with a maximum recorded temperature of 242°C from ~2300-2500mMD after 62 days-shut. The heat-up profiles indicated that in a shut condition, fluid enters at the 2100-2240mMD minor feed zone and exits at the 2400-2500mMD major bottom zone, masking the true temperature of the bottom feed. However, during the discharge, the bottom zone dominated the flow, revealing its true temperature. Unfortunately, this bottom temperature can only be inferred from geochemical geothermometers (i.e. quartz geothermometer or Tqtz), since no flowing or discharge measurements were conducted. The fluid coming from the bottom zone was assessed at 270°C using Tqtz.

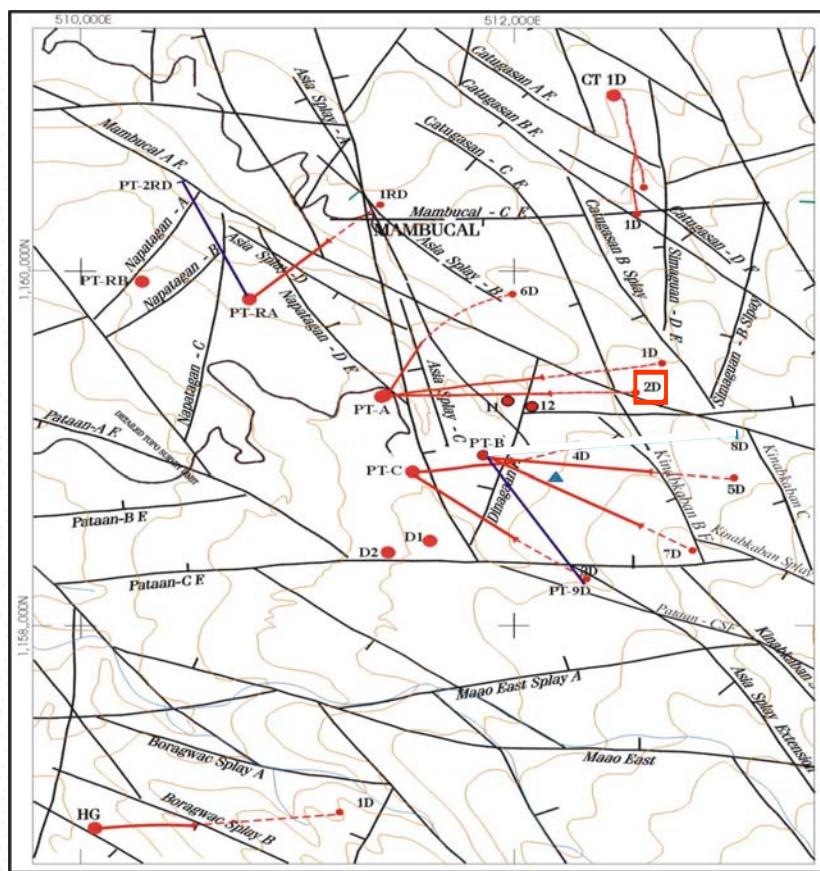


Figure 1: Location map of PT2D at Northern Negros Geothermal Project, Philippines

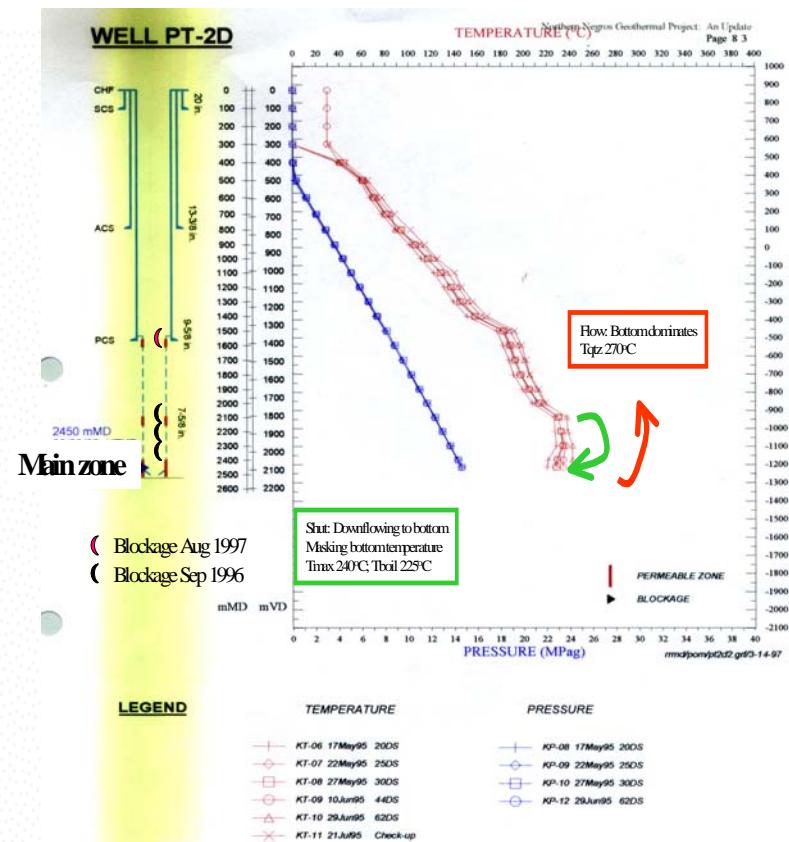


Figure 2: Well temperature/pressure profile showing flow of fluids at shut and flow conditions and calcite tags.

Figure 2 shows the history of calcite deposition as tagged in its respective depths. Calcite deposits were found at these following depths (mMD): ~2100-2150, 2380-2400, and 2440-2460. These deposits were detected by downhole surveys as early as January 1996, months before the first discharge test.

A sample was collected at the top of the blockage (~2100mMD) with a maximum measured temperature of 225°C. The sample was ~0.50cm, cylindrically shaped and cream-colored. It was consisted of 90% calcite and 10% aragonite. Fluid inclusion temperatures from the samples agree with the measured temperature at similar depth (PNOC-EDC, 1998). It was inferred that the initial scales were formed during boiling but this is arguable since this blockage was detected even before it was discharged.

A mechanical work-over was conducted in September-1996 to clean the well of these obstructions. After clearing, the blockage reformed, possibly days before the succeeding surveys after the completion tests. This suggests that calcite did “recur” in spite of the mechanical work-over and even in the absence of boiling. The well was acidized on June 1997. However, just after clearing the well, blockages were detected during the heat-up at 2232mMD prior to discharge.

After a month of testing, a blockage was tagged at a shallower depth of 1550mMD. Unfortunately, no sample was collected. Presumably it was calcite and did exhibit a peculiar nature: it can recur in spite of acidizing and even, possibly, absence of boiling. This phenomenon led to an evaluation of how calcite deposited in PT2D. Below are the results of the investigation.

2. THEORY

At constant temperature and pressure, a chemical reaction is postulated to be at equilibrium if there is no tendency for the activities of reactants and products to change. Let us examine Equation 1 as represented in Figure 3.

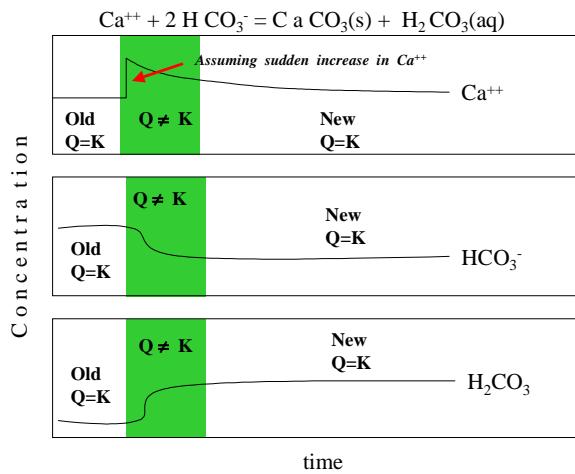


Figure 3: Demonstration of calcite deposition by Equation 1 assuming excess Ca^{++} and readjustment of HCO_3^- and H_2CO_3 to form calcite

At reservoir conditions, the state of old equilibrium is manifested by constant concentration of dissolved species of reactants, Ca^{++} and HCO_3^- , and product, H_2CO_3 . Assuming there is a sudden increase in Ca^{++} , rendering a stress to old equilibrium, the HCO_3^- will readjust to compensate as additional H_2CO_3 (and calcite as CaCO_3) is formed. A new state of equilibrium will then be established

to compensate for the excess Ca^{++} . Of course, another source of stress is the removal of dissolved CO_2 as H_2CO_3 as the fluid boils. Although this mechanism is possible, but highly contested in the field. Considering that almost all geothermal fluids boil to generate steam, not all of them developed calcite. It is likely that if Equation 1 is the dominant equilibrium controlling calcite, then a state of supersaturation on the reactant-side, either from excess Ca^{++} or HCO_3^- species at reservoir conditions, must first exist before any calcite deposition can occur. Boiling or release of CO_2 gas is just a tipping point of an already supersaturated fluid.

Another factor that may contribute to deposition is a change in either temperature or partial pressure of CO_2 . At constant partial CO_2 reservoir pressure, calcite deposits at increasing temperatures (Cowan and Weinritt, 1976). However, this may involve a different set of reaction aside from Equation 1.

This paper focuses in evaluating the calcite deposition in PT2D assuming it was controlled by Equation 1. This type of study was possible because of available gas and water data while the well's massflow and wellhead pressure declined due to calcite deposition. In assessing Equation 1, the reservoir temperature is set at 240°C while the boiling temperature is at 225°C. Both temperatures are from the measured survey before the test. A detailed discussion of the method is given below.

3. METHODOLOGY

All the data used in this study are from PNOC-EDC (1998). These are the brine and gas chemistry collected at each critical phase during July 1997. The methods used in this study are outlined below:

Step 1: From the latest survey, the measured reservoir temperature and derived boiling temperatures were used at 240 and 225°C, respectively.

Step 2: Using the available gas/water samples, data was processed using Watchworks™ (Arnorsson et al., 1982) in computing the chemistry at reservoir (240°C) and boiling (225°C) conditions

Step 3: From the output files of each run, calcite's solubility ($\log Q/K$), molal activities of HCO_3^- , Ca^{++} and its complexes, H_2CO_3 , and pH were computed

Step 4: Time plots for each computed parameters (at reservoir and boiled conditions) were then generated

Step 5: Changes with time of each parameters were determined

Step 6: For each change the possible equilibria were evaluated for spontaneity by computing Gibb's free energy

In this evaluation the following assumptions were invoked:

- Temperatures at 240 and 225°C are constant
- Even at different discharge states, all the fluids came from the major zone. Since there are at least three zones present in the production casing, there was no interplay of feed zones nor there was there a significant difference in each zone's chemistry.

- Since we employed Watchworks TM (Arnorsson et al., 1982), the program's working assumptions such as chemical equilibria of the each dissolved species were also invoked in each run
- Boiling at 225°C was adiabatic and each gas attained equilibrium degassing

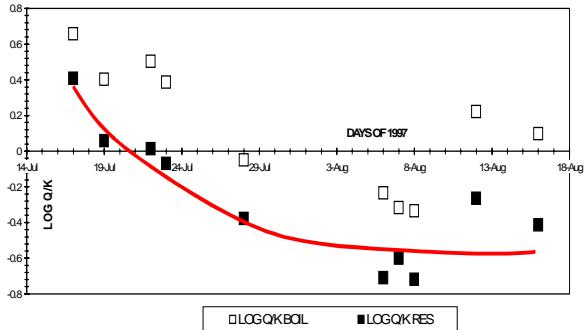


Figure 4: Time plot of calcite solubility ($\log Q/K$) computed from product of Ca^{++} and $\text{CO}_3^=$ of the fluids. Closed squares (\blacklozenge) are reservoir while open (\blacklozenge) squares are boiled conditions.

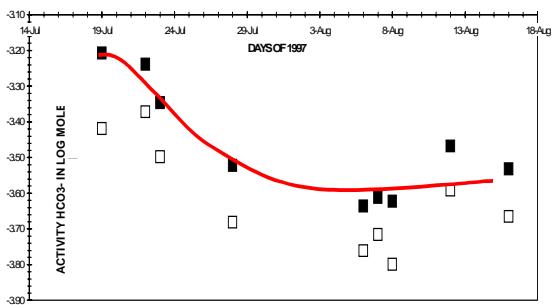


Figure 5: Time plot of activity of HCO_3^-

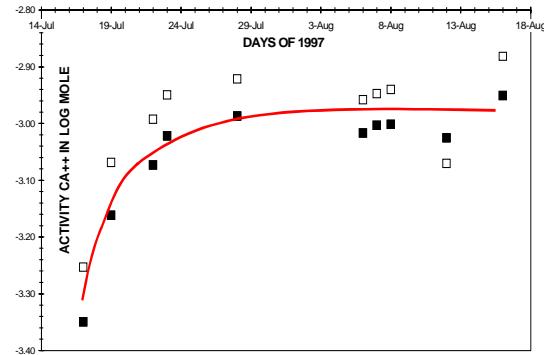


Figure 6: Time plot of activity of Ca^{++}

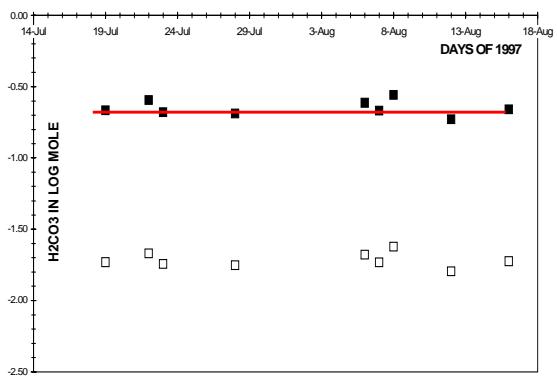


Figure 7: Time plot of activity of H_2CO_3

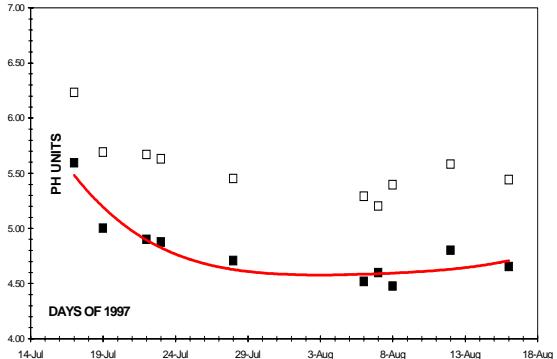


Figure 8: Time plot of activity of pH

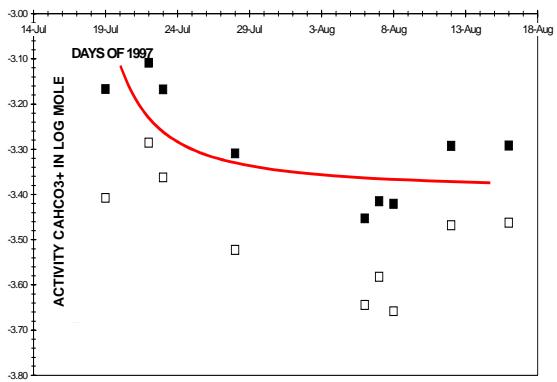


Figure 9: Time plot of activity of CaHCO_3^+

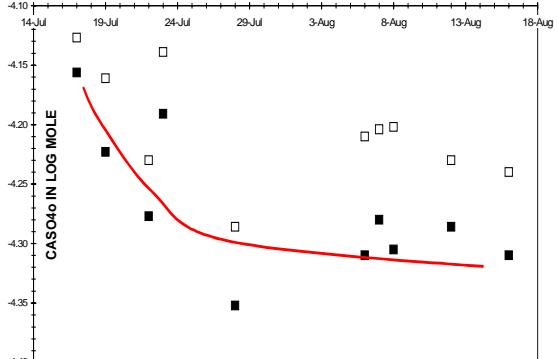


Figure 10: Time plot of activity of CaSO_4^0

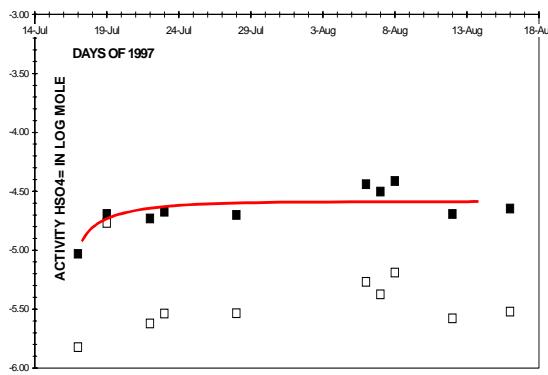


Figure 11: Time plot of activity of HSO_4^-

4. RESULTS AND DISCUSSION

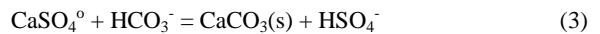
Figure 4 is the plot of calcite solubility ($\log Q/K$) computed from Watchworks™. The plot shows calcite's tendency to deposit: from the initial supersaturated state it decreased and approached saturation. A similar trend is also observed using boiled fluids. Although this plot may be related to Equation 1, it does not imply that Equation 1 is the controlling reaction in calcite deposition. It simply shows the state of calcite solubility relative to the fluid's Ca^{++} and $\text{CO}_3^{=}$ contents, and not the fluid's tendency to deposit or dissolve calcite.

Assuming constant temperatures, Equation 1 is investigated by plotting activities of HCO_3^- , Ca^{++} , and H_2CO_3 (dissolved CO_2) with time as shown in Figures 5, 6, and 7. For HCO_3^- , its activity decreased with time. However, the predicted decrease in Ca^{++} and increase in H_2CO_3 are not realized to support Equation 1's calcite equilibrium, instead, Ca^{++} increased while H_2CO_3 remained constant. A similar trend is also observed for boiled fluids indicating boiling had not affected their activities. These trends imply that Equation 1 was not the reaction controlling calcite deposition. To identify other possible equilibria, activities of other species were investigated. These include pH, activities of, complexes of Ca (as CaHCO_3^+ , CaSO_4^0), and HSO_4^- . The results of these plots are shown in Figures 8 to 11.

The results of these plots, in both reservoir and boiled fluids, are listed below:

- (a) pH decreased,
- (b) activities of Ca-complexes, as CaHCO_3^+ and CaSO_4^0 , both decreased, while,
- (c) activity of HSO_4^- increased,

For all these plots boiled fluids have similar trends with reservoir fluids, indicating that boiling had not affected their respective activities. Below are the postulated equilibria related to calcite deposition to explain these trends:

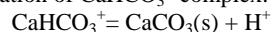


The spontaneity of Equations 1, 2, and 3 is then compared by computing each equilibrium's Gibb's Free energy (ΔG) as illustrated in Figure 12. The ΔG is a measure of the amount of work that can be extracted from the system at constant pressure and temperature. For the reaction to be spontaneous, reaction's ΔG must be negative. The lower the energy requirement to do that work, say to form one mole of calcite, from the available and yet limited free energy of the system, the greater is its possibility to be spontaneous. From the results of Figure 12, Equation 2 is the most likely to proceed spontaneously because it has the lowest energy requirement to form one mole of calcite; at the maximum, it just needed 7.5 kJ/mole, while Equation 1 needed 25.5 kJ/mole and Equation 3 needed 13.0 kJ/mole. Moreover, in the early days of discharge, the ΔG is close to zero with respect to fluid's equilibrium of Equation 2. From these results, calcite that was formed in PT2D was likely through Equation 2.

The spontaneity of Equation 2 also has an implication with respect to the reservoir temperature of the system. For Equation 2 to form calcite, additional energy was required. The availability of this energy was manifested in terms of reservoir temperature. Figure 13 shows the increasing trend of T_{Qtz} with time, from 240 to 270°C. The increase in reservoir temperature provided an opportunity for calcite to deposit. However, it is not clear whether mixing of the supersaturated fluids and the hotter upflowing fluids, or heating of the reservoir fluids in the wellbore caused calcite deposition found in the bore.

5. CONCLUSION

The evaluation of the commonly used calcite equilibrium in geothermal wells resulted to identification of another calcite chemical deposition reaction. In this case, deposition through dissociation of CaHCO_3^+ complex:



The spontaneity of this reaction was investigated by computing Gibb's Free energy. From the results, it can be seen that the dissociation of CaHCO_3^+ complex was more spontaneous because it had the lowest energy requirement, as compared to other equilibria. Moreover, in the early days of PT2D discharge, the fluids' ΔG was close to zero with respect to this reaction indicating equilibrium. From these results, calcite that was formed in PT2D was likely through dissociation of CaHCO_3^+ . However, the spontaneity of this reaction required energy, such as increase in reservoir temperature. The availability of this energy was manifested by increase of T_{Qtz} with time, from 240 to 270°C. As the reservoir temperature increased, hence more available energy, the calcite formed. Calcite in the bore could either form by mixing of the supersaturated fluids and the hotter up-flowing fluids or heating of the reservoir fluids.

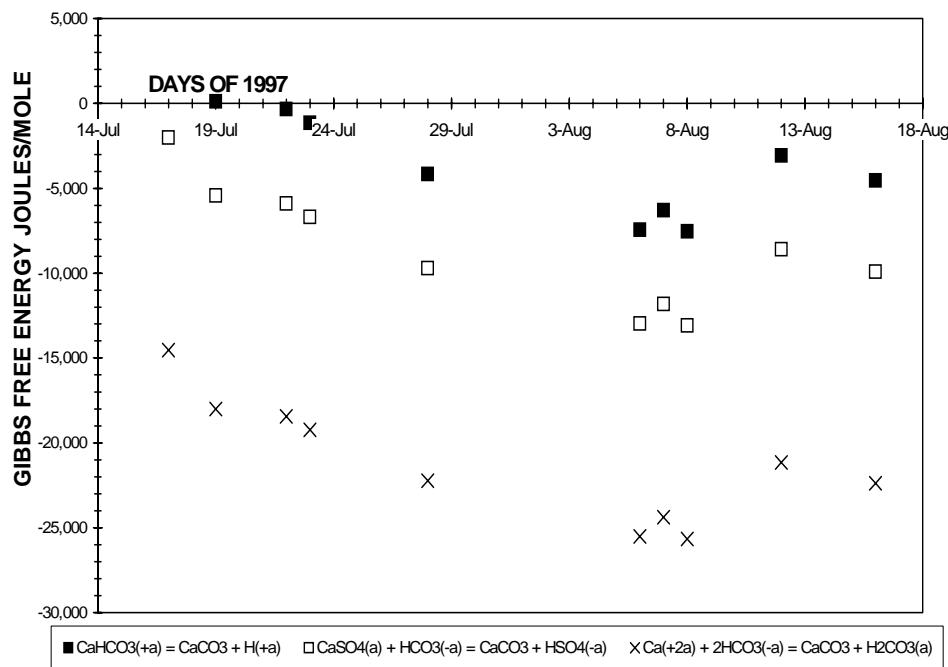


Figure 12: Time plot of Gibbs Free energy of each equilibria to test each spontaneity

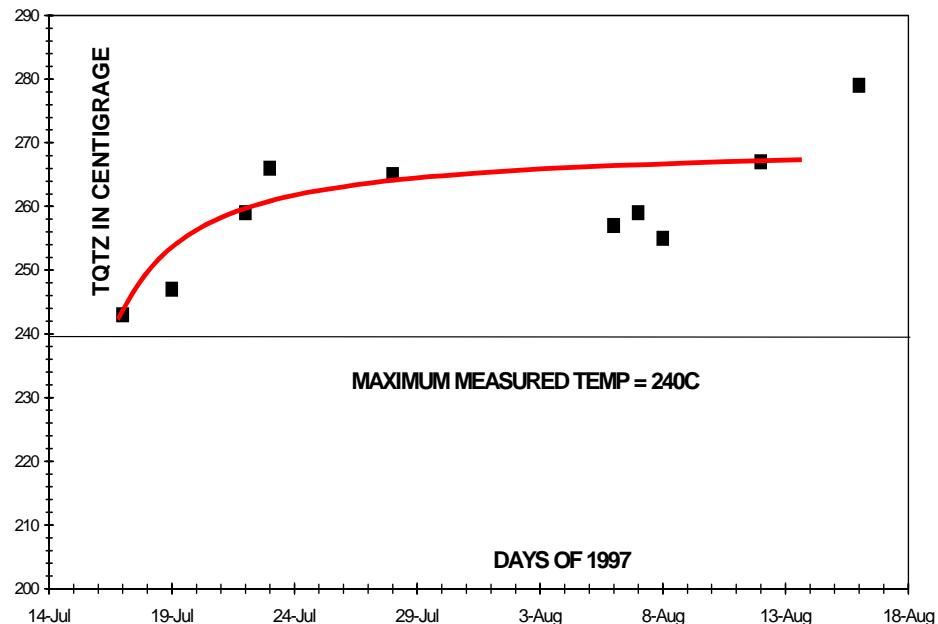


Figure 13: Time plot of Tqtz showing increase in reservoir temperature from 240 to 270°C

REFERENCES

Arnórsson, S., Sigurðsson, S., Svarvarsson, H., The chemistry of geothermal waters in Iceland. I. Calculation of aqueous speciation from 0 to 370°C, submitted to *Geochimica et Cosmochimica Acta*, 1982

Cowan, Jack C., and Weinritt, Donald J. Water-formed deposits. A comprehensive study of the prevention, control, removal, and use of mineral scale, Gulf Publishing Company, Book Division, Houston Texas (1976).

Granados, E., Calcium carbonate deposition in geothermal wellbores, Miravelles Geothermal Field, Costa Rica (MS Thesis). Stanford Geothermal Program, Stanford University, CA. (1983).

Philippine National Oil Company-Energy Development Corporation, Northern Negros Geothermal Project Resource Assessment Update. Internal report (1998)