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CALCULATION OF CALCITE AND ANHYDRITE SCALING POTENTIAL IN GEOTHERMAL WELLS

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ABSTRACT

Both calcite and anhydrite deposition occurs in geothermal wells in the Philippines. In an attempt to predict calcite deposition and deternine a deposition mechanism for anhydrite the solubilities of these minerals have been calculated using a computer algorithm which calculates chemical speciation in saline fluids at high temperatures and which can model the processes of flashing and mixing.

Calcite and anhydrite are both close to saturation in preflashed geothermal fluids in the Philippine geothermal fields studied. After flashing however, calcite is computed to become significantly oversaturated in the majority of wells studied whereas anhydrite is computed to become significantly undersaturated. Calcite scaling problems, however, have been restricted to low temperature wells.

Mixing of high sulphate waters with moderately calcium rich reservoir fluids is concluded to be a strong depositional mechanism for anhydrite deposition in wells and may provide a technique to control high sulphate inflows.

INTRODUCTION

Calcite scaling within the wellbore of geothermal wells in response to flashing of reservoir fluids is a common problem, particularly in lower temperature fields. In the Philippines calcite scaling problems have been experienced in a number of relatively low temperature (<220°C) exploration wells.

Anhydrite deposition within the wellbore is a much less common phenomena but has been experienced in a significant number of wells in the Philippines. In contrast to calcite deposition, anhydrite deposition has been observed to occur more commonly when a well is shut in after a discharge test.

At Bacon-Manito, in the Philippines, downhole sampling has identified high sulphate inflows in a number of wells, all of which have developed anhydrite blockages at (or near) the inflow depth.

In an attempt to predict the onset of calcite scaling and to establish a depositional mechanism for anhydrite, the solubilities of calcite and anhydrite were calculated for geothermal fluids under downhole conditions using a downhole chemistry computer program. Two sets of conditions were considered; where a single phase fluid from a single feed. flashes in the wellbore and where separate feed zones of different chemistry mix.

METHOD

The computer algorithm used is a modified and updated version of the downhole chemistry program of Truesdell and Singers (1971). This program calculates the concentrations of chemical components and speciation in a hot geothermal brine from separated steam and water analyses collected from a discharging well.

In sampling a discharging well, samples of separated steam and water are normally taken off the horizontal discharge pipe. A knowledge of the discharge enthalpy of the well is required in order to combine the analyses of the two phases and hence derive the composition of the reservoir fluid prior to separation.

An alternative sampling technique involves running a downhole sampler into the well at low mass-flow rates to obtain a sample of reservoir fluid prior to flashing. However, there are problems associated with this sampling technique. It is often difficult to obtain representative samples due to differential flashing of fluids into the sampler or leakages while running in or out. It is also difficult to obtain satisfactory non-condensible gas concentrations in downhole samples and a reliable method for doing this has yet to be devised.

A number of assumptions are inherent in any attempt to combine steam and water analyses to calculate the chemical composition of the preflashed reservoir fluid. Assumptions are made that flashing occurs adiabatically and in one stage, that no deposition or leaching of minerals occurs and that equilibrium conditions exist for all chemical and physical processes.

If the well discharge enthalpy is equal to the enthalpy of water at the reservoir temperature then the well is feeding from a single phase, liquid water reservoir and calculation of speciation at the reservoir temperature is relatively straightforward. If, however, the discharge enthalpy is significantly higher than the enthalpy of water at the reservoir temperature than the situation is more complex.

Excess discharge enthalpy occurs when phase separation in the reservoir results in a well discharge that contains excess steam. Three basic models for excess enthalpy discharges can be invoked; a steam cap, two feed zones and flashing flow (Grant and Glover, 1984).

The first two models are, in practical terms, largely indistinguishable and are modelled in the same way by a downhole chemistry program. The program assumes that phase separation has occurred in the reservoir and hence calculates the fraction of steam present in the reservoir from the discharge enthalpy of the well. The gas content in the total discharge is assumed to be partitioned between the two phases in the reservoir and downhole speciation is calculated on this basis.

In the case of flashing flow the downhole chemistry program assumes that the gases in the total discharge are dissolved in the reservoir liquid water away from the well-bore and speciation is calculated on this basis.

There is a reasonable degree of uncertainty in establishing whether excess discharge enthalpy derives from a steam zone or flashing flow and this decreases the reliability of calculated mineral solubilities in such wells.

In order to eliininate as many areas of uncertainty as possible, the modelling studies reported on here only include data Erom wells which do not have excess discharge enthalpy and which have only one major inflow zone under discharging conditions.

Flashing was modelled in 20°C single stage steps from the flash point temperature in each well down to 100°C.

Mixing was modelled by combining downhole samples of acid sulphate waters with a computed downhole neutral chloride reservoir fluid obtained from surface samples.

Because of a lack of gas analyses €or downhole samples it was not possible to model the effect on calcite saturation of mixing a bicarbonate water with neutral chloride fluid. A nominal gas content was assumed for the acid sulphate downhole samples.

The solubility of calcite and anhydrite was determined by comparing the product of the appropriate ion activities with thermodynamically derived equilibrium constants for the reactions:

$$Ca^{2+} + CO_3^{=} = CaCO_3 \text{ (calcite)}$$

$$Ca^{2+} + SO_4^{-} = CaSO_4 \text{ (anhydrite)}$$

where $K_{sp}\ (CaCO_3) = aCa^{2+}.aCO_3^{=}$

$$Ksp\ (CaSO_4) = aCa^{2+}.aSO_4^{=}$$

This follows the method used by Arnorssen et al (1382) which is the source of the equilibrium constants used. This method differs from others which evaluate such variables as pH or pCO_2 to calculate calcite solubility only in the variable evaluated.

RESULTS OF WELL MODELLING

All the wells used in this study are from the Bacon-Manito geothermal field in Luzon except for BN-2 which is on Biliran Island, off the coast of Leyte.

One of the low temperature (<220°C) exploration wells at Tongonan, Leyte (TGE-4) formed a calcite scale at the flashpoint upon discharge but is not included here because of the very close similarity between the modelling data for this well and MO-2.

Wells at Southern Negros have developed both calcite and anhydrite scales but were excluded from this study on the basis of excess enthalpy,. multi feed zones or insufficient chemical data. Some work has been carried out, however, on calculation of mineral solubilities in Southern Negros wells. (Jordan, 1982)

Chemical analyses for the wells chosen are shown in Table 1 and the results of modelling the effects of adiabatic flashing on anhydrite and calcite solubility are shown in Figures 1 and 2 respectively.

Figure 1 suggests that reservoir fluids at Bacon-Manito are close to saturation with respect to anhydrite and this is supported by the occurrence of this mineral in reservoir rocks. Geothermal fluids at Tongonan and Southern Negros have also been found to be close to saturation with respect to anhydrite, valididating the use of anhydrite as a geothermometer in these fields (Bogie, 1983).

As the flash temperature decreases there is a trend towards increased solubility of anhydrite as a result of the inverse solubility of this mineral. A net increase in solubility with declining temperature occurs in a flashing brine. This is despite a counteracting decrease in solubility caused by; an increase in the activity of $SO_4^{=}$ (through increased dissociation of HSO_4^{-}) as the pH rises due to gas dissolution, and the concentration of the brine after stem separation.

Isothermal boiling could give rise to anhydrite deposition but there are no known occurrences of anhydrite deposition in wells as a result of this process.

Figure 2 shows the modelling of calcite saturation after single stage flashing (in 20°C steps) from the reservoir temperature at the flash point down to 100°C. Reservoir fluids prior to flashing for all wells except IM-1 are calculated to be significantly undersaturated with respect to calcite. The reservoir temperature at the inflow point to the well is, in most cases, a little higher than the flash point temperature and it is assumed that the fluid cools conductively from the inflow temperature down to the flash temperature. Because calcite has an inverse solubility-temperature relationship, most of the well-bore fluids plotted in Figure 1 will be closer to saturation with respect to calcite at the reservoir temperature than shown. However, it must be borne in mind that the calculated degree of saturation of unflashed reservoir fluid with respect to calcite is determined empirically, not absolutely; as outlined by Arnorsson et al (1982) in their discussion on their choice of association constant for $CaHCO_3$.

The rapid decrease in the solubility of calcite that occurs with the onset of flashing results from a large increase in the activity of $CO_3^{=}$ in response to the rising pH due to gas dissolution. This more than overcomes the increased solubility at lower temperatures.

The effects of mixing an acid-sulphate water with neutral chloride reservoir fluid can also be modelled with the downhole chemistry program, despite the limitations of this program for the calculation of high temperature speciation in acidic fluids. (Due to a lack of analytical data for aluminium and inadequate thermodynamic data for iron and aluminium complexes at high temperatures.)

The well CN-1 developed on anhydrite blockage at around 1600 mm depth soon afer being shut-in after a discharge test. The analyses of two downhole samples taken at 1150 m and 1400 m depth are shown in Table 1. These acid waters only flow into the well under shut-in conditions, permeable zones at these depths being underpressured relative to the major producing zone (2300-2450 m) under discharging conditions.

As shown in Figure 3, one of the acid-sulphate samples is calculated to be undersaturated and the other considerably oversaturated with respect to anhydrite at the temperature of inflow into the well. The nixing of a small percentage of these acid waters with the neutral chloride reservoir fluids is sufficient to cause significant over-saturation to occur.

DISCUSSION

Of the wells shown in Figure 2 only two had calcite scaling problems; NO-2 developed a calcite scale at the flash-point which eventually constricted the discharge, and BN-2 developed an aragonite scale in the horizontal discharge pipe. The deposition of aragonite instead of calcite in the discharge pipe of BN-2 can be attributed to the low Ca/Mg ratio of fluids from this well. Although calcite is less soluble than aragonite normally, when the Ca/Mg ratio is low aragonite becomes the favoured phase due to the increased solubility of magnesium calcite (Stumm and Morgan, 1981). Mg can be considered as a deposition inhibitor in this instance, the greater solubility of aragonite over calcite accounting for the fact that scaling occurred well above the flash point.

This example indicates that kinetic factors can exert considerable control over deposition and that kinetic factors may be the controlling factors affecting scale build up. Such factors may include inhibitors to crystal growth, the presence of favourable nucleation sites, fluid flow velocity, the degree of turbulence in the well-bore and two phase fluid flow regime.

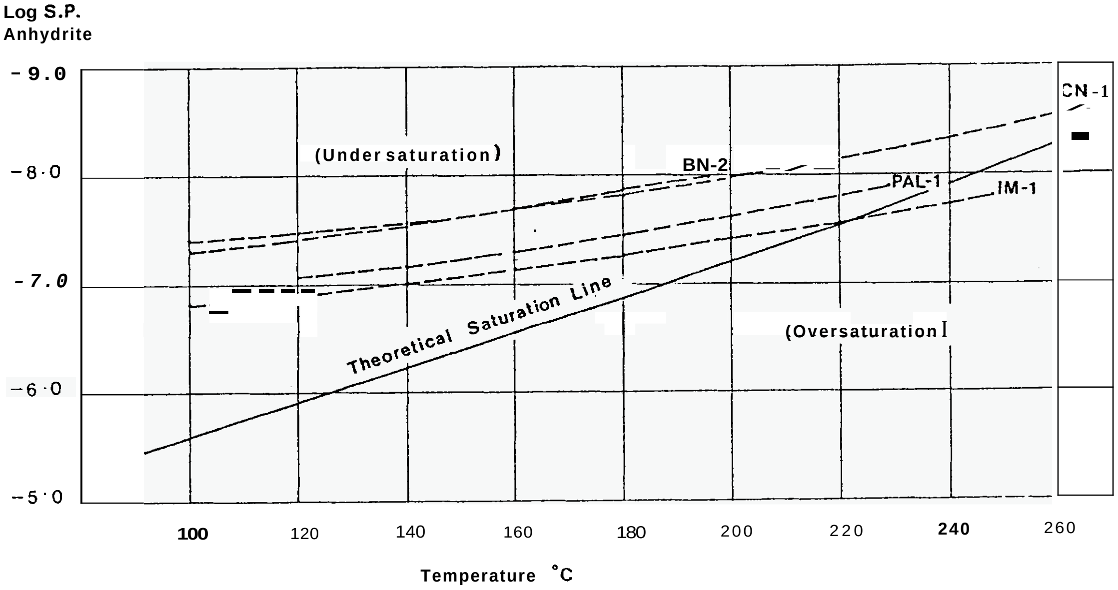

FIGURE 1. The effects of adiabatic boiling on Anhydrite solubility as modeled by DHCHEM.

TABLE 1 : CHEMICAL DATA FROM WELLS INVESTIGATED IN THIS STUDY

WELL	H^O J/G	pH (20^oC)	Li	Na	K	Ca	Mg	Cl	SO_4	B	HCO_3	SiO_2	CO_2^*	H_2S^*
			CONCENTRATIONS IN MG/KG											
RES FLUID		7.8	5.3	30G0	588	115	0.3	5710	16	25.0	10	560	40	1.7
CN-1(1150m)		3.0	0.0	1170	87	34.7	102.0	355	3040	11.6	0	425	1	0.1
CN-1(1400m)		3.1	0.0	1130	104	4.5	17.2	833	1955	10.7	0	425	1	0.1
CM-1	1200	7.8	8.0	4647	914	167	0.1	8721	25	36.4	9	800	40	1.7
PAL-1	995	6.3	6.3	4520	572	176	0.5	2254	41	30.6	36	604	134	0.9
IM-1	1060	7.7	5.3	3394	452	149	0.7	6080	67	34.5	35	560	52	1.5
MO-2	850	7.0	6.3	3351	408	268	0.5	6208	42	28.3	29	2no	37	0.4
BN-2	850	8.3	1.5	1627	45	9.3	1.8	2136	247	58.6	560	379	508	3.0

Notes :

CO_2^* and H_2S^* concentrations : mmoles/100 moles in Total. Discharge

RES FLUID data is averaged from discharge data from well CN-1 and represents typical reservoir fluid composition in Bacon-Manito field.

CN-1(1150m) and CN-1(1400m) are downhole samples taken at acid sulphate inflow depths under shut-in conditions.

All other data was separated at atmospheric pressure from discharging wells.

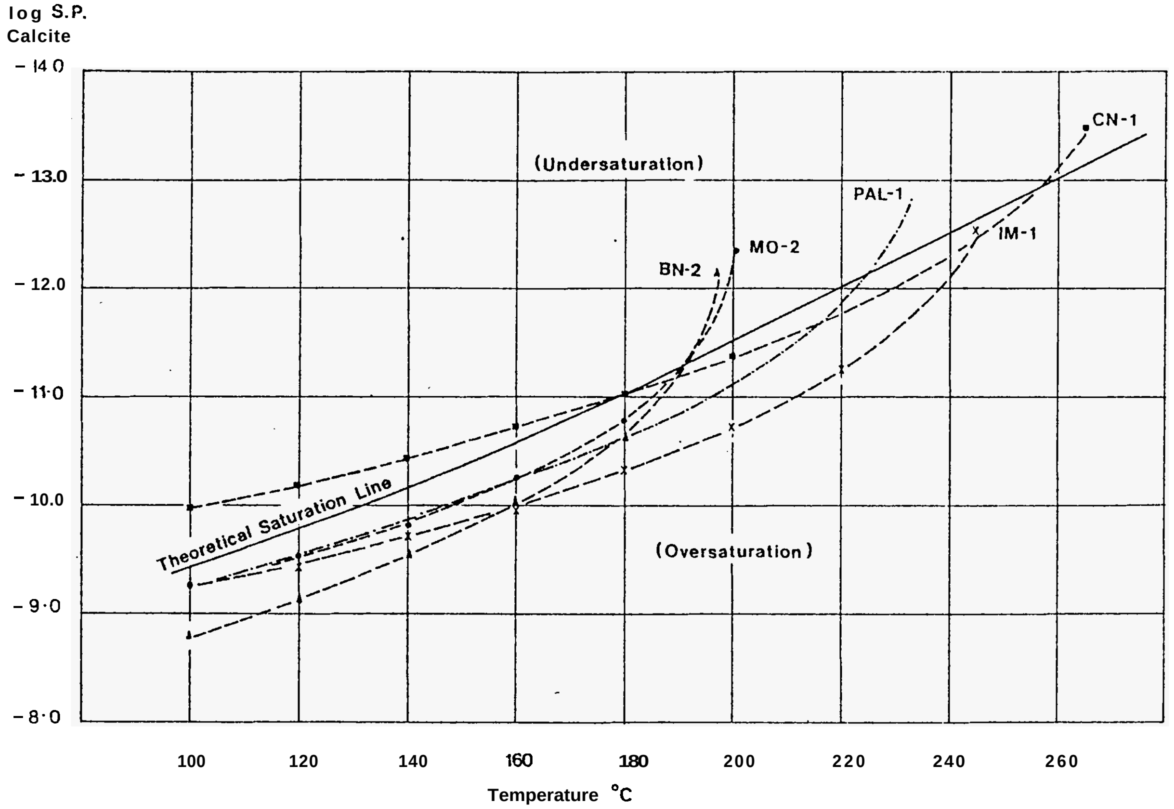

FIGURE 2. The effects of adiabatic boiling on Calcite solubility as modeled by DHCHEM.

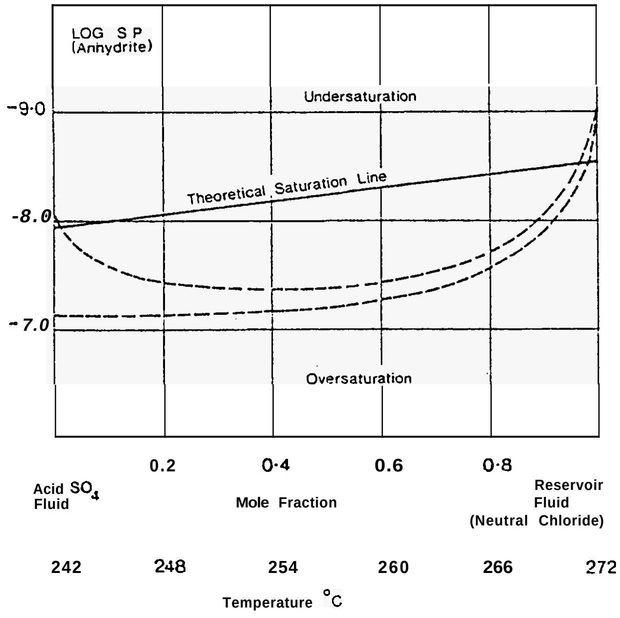

FIGURE 3 : Mixing of 272°C Reservoir Fluid with 242°C Acid Sulphate Fluid in Well CN-1. The effects on Anhydrite solubility as modelled by DHCHEM.

The accuracy of downhole computer algorithms in determining the solubility of the minerals calcite and anhydrite is subject to the validity of the thermodynamic data used and to an adequate knowledge of speciation in high temperature saline solutions. A case in point is the dissociation constant for $CaHCO_3^+$. Arnorsson et al (1982) noted that this ion pair has a significant effect on calculated calcite saturation and had to incorporate empirical high temperaure values for Iceland geothermal fluids over those values extrapolated from low temperature thermodynamic data.

They obtained their emperical data by assuming that geothermal fluids at Svartsengi were just saturated with respect to calcite and adjusted the dissociation constant of $CaHCO_3$ to an appropriate value at the reservoir temperature so that the output from their WATCH computer program agreed with this assumption. Therefore, the degree of saturation calculated for other geothermal fluids using the $CaHCO_3^+$ dissociation constant data of Arnorsson et al (1982) is dependent on their basic assumption regarding calcite saturation at Svartsengi and the applicability of this assumption to other fields.

However, it may be the rate of change of saturation with the onset of flashing which is important in predicting scaling rather than the calculated degree of saturation prior to flashing. As calcite scaling tends to occur very close to the flash point in a well, the very early stage of flashing is the process which should be examined in most detail.

As shown in figure 2, the rate of change of saturation at the onset of flashing for MO-2 is much greater than for the higher temperature wells at Bacon–Manito. In YO-2 a 2°C temperature drop upon flashing results in an increase in the activity solubility product of 0.5 log unit whereas for CN-1 the increase is only 0.1 log unit. This difference is a consequence of the lower solubility of CO_2 in the MO-2 fluids at 200°C than in the 270°C CN-1 fluids.

Another factor that needs consideration is the decrease in the slope of the boiling point for depth curve at lower temperatures.

A temperature drop of 2°C from 270°C on the B.P.D. curve will occur over a vertical distance of 21.8 m whereas the same temperature drop from 200°C will occur over 7.5 m. This would result in a more rapid rate of scaling in lower temperature wells.

Anhydrite is not predicted to form as a result of flashing of geothermal fluids and this is consistent with field experience, anhydrite blockages being found at or near to zones at which acid–sulphate waters flow into a well but not at the flash–point of discharging wells. Philippine geothermal fluids are quite saline by comparison with the majority of known geothermal fields and anhydrite scaling problems appear more prevalent in higher salinity fluids due to the high Ca^{2+} concentrations in these fluids. An increase in H^+ activity occurs as the salinity rises in order to balance increased cation concentrations, the cation/H^+ activity ratio being constrained by mineralogical buffers. (Henley et al, 1984) High Ca^{2+} concentrations are maintained in more saline geothermal fluids because of the increased H^+ activity and hence decreased CO_3 activity.

Anhydrite, as a vein filling and groundmass mineral is quite common in the upper part of the Bacon–Manito reservoir (Leach and Beaza, 1985) where acid–sulphate waters produced above the water table encroach on to the neutral reservoir. Acid–sulphate waters have been found to percolate as deep as 1600 m into the reservoir, principally down restricted structural channels; the chemical and isotopic composition remaining remarkable intact as a result of a hydrologic barrier between the fluid types formed through anhydrite deposition.

It is suggested that the anhydrite blockages that have been encountered in geothermal wells could be either controlled or eliminated by injecting Ca+

rich fluids into wells which have blockages or high sulphate inflows.

The mixing of the two fluid types within permeable fractures which contain acid–sulphate waters may result in these zones becoming blocked up with anhydrite.

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