ASSESSMENT OF CALCITE SCALING POTENTIAL IN THE GEOTHERMAL WELLS OF THE NW-SABALAN GEOTHERMAL PROSPECT, NW-IRAN

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ABSTRACT

Three deep exploration wells have been drilled in the northwest Sabalan geothermal field in Iran. Two of them (NWS-1 and NWS-4) are productive. The aquifer temperature for both wells is between 220 and 230°C. During discharge tests of these wells, a decline in fluid discharge calcium concentration was observed that was thought to be due to calcite scaling. Also, traces of calcite scale were observed in the wells' installed surface test equipment. Assessment of the calcite scaling potential in wells NWS-1 and NWS-4 is the object of this study. The large variation in the reported pH, especially in samples from well NWS-1, was considered to be a consequence of inadequate sampling and an analytical error which, in turn, led to large variations in the calculated calcite saturation state of the aquifer waters. The speciation program WATCH was used to calculate aquifer water composition for wells NWS-1 and NWS-4 as well as changes in calcite saturation during adiabatic boiling. At the aquifer temperature, one would expect the un-boiled aquifer water to be close to saturation with respect to calcite. For initially calcite-saturated aquifer water, adiabatic boiling leads to calcite over-saturation and therefore calcite precipitation. Maximum super-saturation is attained at about 180°C in both wells. For equilibrium, (maximum) degassing over-saturation by a factor of about 10 is produced at 180°C. In contrast, 10% of maximum degassing does not produce significant over-saturation. Degassing by boiling, causes the pH and carbonate ion concentrations to increase sharply in the boiled water with a slight increase in free calcium ion concentrations, while CO_2 concentrations decrease. The sharp increase in the carbonate ion concentrations is largely responsible for the calcite over-saturation produced by boiling. When the water has been largely degassed (at about 180°C for maximum degassing), further cooling by boiling leads to progressively less over-saturation due to the retrograde solubility of calcite with respect to temperature. Two methods are recommended to cope with calcite scaling in these wells. If the calcite deposition rate is not very fast, regular mechanical cleaning may prove to be satisfactory, but if scale formation is faster, the use of an inhibitor needs to be considered.

1. INTRODUCTION

Geothermal exploration in north and northwest Iran was started by the Iran's Ministry of Energy in 1975. A contract was made between the Iranian Ministry of Energy and the Electric Company of Italy (ENEL). The Khoy-Maku, Mount Sabalan, Sahand and Damavand regions were proposed for detailed geothermal exploration.

Since 1998 detailed investigations have been undertaken in the Mt. Sabalan area in northwest Iran (Figure 1). The investigations were undertaken jointly by the Renewable Energy Organization of Iran (SUNA) and a company from New Zealand, Sinclair Knight Merz (SKM). The work was divided into two stages, *Stage 1: Exploration and development programme* and *Stage 2: Exploration drilling programme.* Activities in Stage 1 included a review of previously collected

FIGURE1: Location of the Sabalan geothermal prospect

geothermal field data, sampling and analyses of all surface geothermal manifestations, a detailed MT geophysical survey over the greater Sabalan area which identified five geothermal anomalies (the most prospective being located in the Moil Valley on the northwest flanks of Mt. Sabalan), detailed geological mapping of the Moil geophysical anomaly and preparation of a predrilling exploration model. An overview of the Stage 1 exploration programme concluded that the NW-Sabalan area was sufficiently prospective for high temperatures to warrant conducting an exploration drilling programme (Sahabi et al., 1999). In Stage 2, three deep exploration and two shallow injection wells were drilled. The drillings and well testing were carried out in the northwest Sabalan area between 2002 and 2004. Two of the three exploration wells, NWS-1 and NWS-4, are productive. Deposition of calcite has been observed in test equipment that was installed in these wells. Also, a decline in fluid discharge calcium concentration was observed for both wells, likely the consequence of calcite scaling. It is considered possible that well-bore calcite deposition may become a future production problem.

Assessment of calcite scaling potential in wells NWS-1 and NWS-4 is the object of this study. The speciation program WATCH was used to determine the composition of the aquifer water and also the composition of adiabatically boiled water ascending wells NWS-1 and NWS-4 during their discharge.

2. GEOTHERMAL FEATURES

The NW-Sabalan geothermal prospect is located in the Moil valley on the northwest slopes of Sabalan volcano in the northwest of Iran (Figure 1). Mt. Sabalan is a trachyandestic stratovolcano, with which geothermal fields are associated. The NW- Sabalan geothermal field is one of them. The Sabalan volcano was last active in Holocene times. A shallow magma chamber exists beneath the mountain, as indicated by rock chemistry and Ar-Ar and K-Ar dating (Bogie et al., 2000). Moil valley has several thermal springs with temperatures ranging from 15 to 85°C. The hottest is the Gheynarge spring. The

spring waters are of acid SO_4, acid Cl-SO_4 and neutral Cl-SO_4 types. Hydrothermal alteration is seen at the surface. The main hydrothermal alteration is associated with the Valhazir formation.

3. DRILLING AND WELL TESTING

Three deep exploration wells named NWS-1, NWS-3 and NWS-4 with depths of 3197, 3170 and 2265.5 m, respectively, and two shallow reinjection wells, each 600 m deep, were drilled in this area (Figure 2). Well NWS-1 was drilled vertically while NWS-3 and NWS-4 are deviated wells with throws of 1503 and 818 m, respectively.

3.1 Geology of wells

3.1.1 NWS-1

The Dizu formation is found down to 200 m

FIGURE 2: Geological cross-section through the Sabalan geothermal field (Bogie et al., 2005)

depth. This formation consists of terrace deposits mainly made up of conglomerates with some sand intercalations. The terraces themselves were formed by a combination of fluviatile processes, particularly during flash floods and by mass flow from the surrounding slopes. The conglomerates consist predominantly of rounded clasts of andesite, trachyandesite and subordinate trachydacite. The conglomerates are very poorly sorted and clasts range from granule to boulder size, with a matrix of sand so they are sandy granule conglomerates, sandy cobble conglomerates and sandy cobble boulder conglomerates. They are un-cemented and are not hydrothermally altered, although rare clasts of chalcedonic quartz have been reported, but these are erosional products from the hydrothermally altered parts of the Valhazir formation, rather than the product of in situ hydrothermal alteration. The Valhazir formation exists between 200 and 655 m depth. This formation includes andesitic lava flows, tuffs and tuff breccias. Pyroclastics predominate in the upper parts of the unit with lavas beneath. There is a variety of tuffs with variable clast composition with crystal clasts of feldspar and hornblende, along with vitric clasts. These are enclosed in a very fine grained matrix, the exact nature of which has been obscured by alteration. From 655 to 1021m depth, a strongly altered unit named Epa occurs. Its original nature is apparent only in thin section, where it has glomeroporphyritic clots of plagioclase and mafics in a groundmass that contains sub-aligned microphenocrysts of hornblende. Monzonite is a regional intrusive unit at 1021-3197m. Other units that are encountered in the well are a young porphyritic diorite dyke between 1262 and 1268 m and intermittently down to 1536 m, an old porphyritic diorite dyke from 1271 to 1327 m and a unit of hornfels intermittently from 1698 to 3197 m (SKM, 2003).

3.1.2 NWS-4

The Dizu formation in well NWS-4, as in well NWS-1, consists of terrace deposits mainly made up of conglomerates with some sand intercalations that extend from 0 to 63 m. The characteristics of this
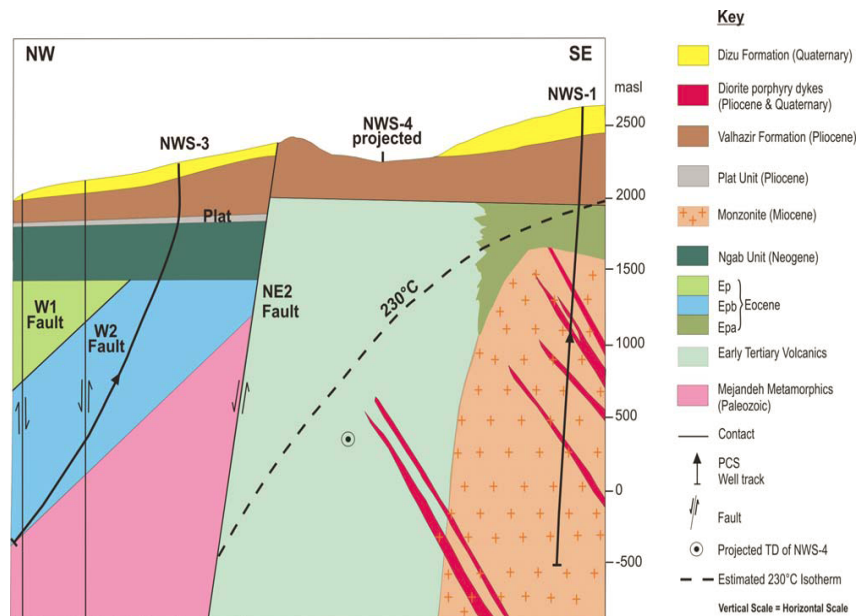
unit reflect those in the previous section. Also as in NWS-1, a unit of andesitic lava flows and tuff breccias of the Valhazir formation underlies the Dizu formation. This unit occurs at 63-383m depth. Well NWS-4 encountered Early Tertiary volcanics between 383 and 1840 m and then an intrusive contact zone that extends from 1840 to 2265 m. The intense hydrothermal alteration and blind drilling from 1613 m have obscured stratigraphic features in the deeper parts of the well. Parts of the sequence between 383 and 1613 m are very similar to the Epa unit found in NWS-1. A core, taken at 2265 m, is altered porphyritic diorite. Although there is no clear evidence of contiguity, it is likely to be related to the older porphyritic diorite dyke identified in NWS-1. Its form is not defined in NWS-4, because the sample is from a bottom-hole core, but there is a decrease in the rate of penetration (ROP) from 1840 m that may be indicative of the presence of an intrusive. Partial returns from 1955 m included volcanic material, possibly dyke material and veins, so it is likely that the interval from 1840 m down could be a dyke complex at the margins of a larger porphyritic diorite body. Other than having a sufficiently porphyritic texture to identify the rock as porphyritic diorite, little further can be established due to the intense alteration of the rock (SKM, 2004a).

3.2 Well testing

3.2.1 NWS-1

Well NWS-1 was successfully discharged by air-lifting and flowed for a period of 21 days. The discharge enthalpy in this well was initially about 960 kJ/kg and stabilised at 980-1000 kJ/kg. The measured mass flow of well NWS-1 was 30 kg/s at 3.4 bar-g wellhead pressure, equivalent to 5.5 kg/s of separated steam flow or 2.2 MWe. The spinner surveys in well NWS-1 confirmed the major zone as being at 2500-2900 m depth, with an inflow temperature initially of 223°C, rising to 226.5°C prior to closure. The secondary feed zone at 1500-1600 m yielded hotter water and the combined feed temperature inside the casing was initially 224.5°C, rising to 228°C prior to closure. The calculated productivity declined from 7 to 5 kg/s/MPa, presumably because of localised drawdown during the test (SKM, 2004b). The measured discharge enthalpy equals that of steam-saturated water of the aquifer temperature, taking into account errors in measurement.

3.2.2 NWS-4

Well NWS-4 also was successfully discharged by air-lifting. Four brief full open discharge measurements were made to determine the producing capacity of the well. NWS-4 has been left on heavily throttled discharge and the discharge test is on-going. The steam differential pressure gauge appeared to drift out of calibration, giving low readings for steam flow from the separator. The silencer measurements at higher flows appeared to be accurate. The discharge enthalpy was stable at 940-950 kJ/kg. The maximum mass flow measured was 56 kg/s at 5.5 bar-g wellhead pressure, equivalent to 7.9 kg/s of separated steam flow or 3.9 MWe. This rate was maintained for one hour only because of brine disposal limitations. The spinner survey confirmed a major producing zone at about1550 m MD (1403 m VD), with an inflow temperature of 222.5°C. A secondary feed zone near 1400 m MD contributed hotter water and the combined feed temperature inside the casing was initially 223.8°C, decreasing to 222°C at the flash point. The calculated productivity was 14 kg/s or 16.9 l/s which was close to the measured injectivity (SKM, 2005a).

Injection tests have been conducted on wells NWS-1 and NWS-4. These have generally been short-term completion tests designed to provide initial information on reservoir conditions in the vicinity of the wells. The injectivity and transmissivity values obtained from these tests are only moderate but are expected to be higher in future wells as the nature of the reservoir permeability is now better understood. The injectivity indices for wells NWS-1 and NWS-4 are 7 l/s-MPa and 16 l/s-MPa, respectively (Barnett et al., 2005).

4. FLUID CHEMISTRY OF WELL DISCHARGES

4.1 NWS-1

Water samples of the well discharge were collected from the discharge brine line, in most cases, but also from the weirbox. Samples included untreated and acidified water (unfiltered). Gas samples were collected from the steam-line using evacuated gas flasks containing 50 ml of 4N sodium hydroxide solution.   The local atmospheric pressure at NWS-1 (2632 m a.s.l.) is about 735 mbar. At this pressure, the steam flash to atmospheric and solute concentrations are about 5% higher than at sea level. Well NWS-1 produces from a single-phase, reservoir liquid, predominantly at 2500-2900 m VD at a temperature of 225°C. Analytical results are presented in Table 1. The water discharged from NWS-1 can be classified as an alkaline-pH, medium-salinity, sodium-chloride water with total dissolved solids of about 5000 mg/kg.

The water has a moderate bicarbonate concentration of about 100 ppm and a calcium concentration of 15-20 ppm. When calculating reservoir conditions by correcting for steam loss, the reservoir chloride concentration in NWS-1 was about 2000 ppm. Although the discharge chemistry was generally stable for most of the discharge test, there were some significant changes. Over the first few days reservoir chloride concentration decreased from about 2200 to 1950 mg/kg but then remained stable for the rest of the test. The trend suggests the first water discharged may have had different zone contributions than later in the test. Also, calcium declined relative to chloride over the first week of discharge. Since the decline occurred while other parameters were stable, calcite scaling was thought to be responsible. Another possibility is that the early samples contained higher calcium concentrations from dissolution of suspended solids in the samples (the samples were not filtered). With all gas dissolved, the pH of the water was about 5.8 which is close to neutral at this temperature. With a calcium concentration of about 14 ppm, measured at the end of the discharge test, the water was calculated to be slightly but not significantly under-saturated with respect to calcite (log Q/K = -0.2). Using higher calcium values of 20 ppm measured early in the discharge, the water is close to saturation with respect to calcite (-0.04). Figure 3 shows the computer-simulated calcite saturation as the reservoir water flows up the well and boils adiabatically. The water becomes significantly over-saturated which suggests that the water in NWS-1 tends to deposit calcite. Discharge silica concentrations were in the range 520-540 ppm in the weirbox (SKM, 2005b).
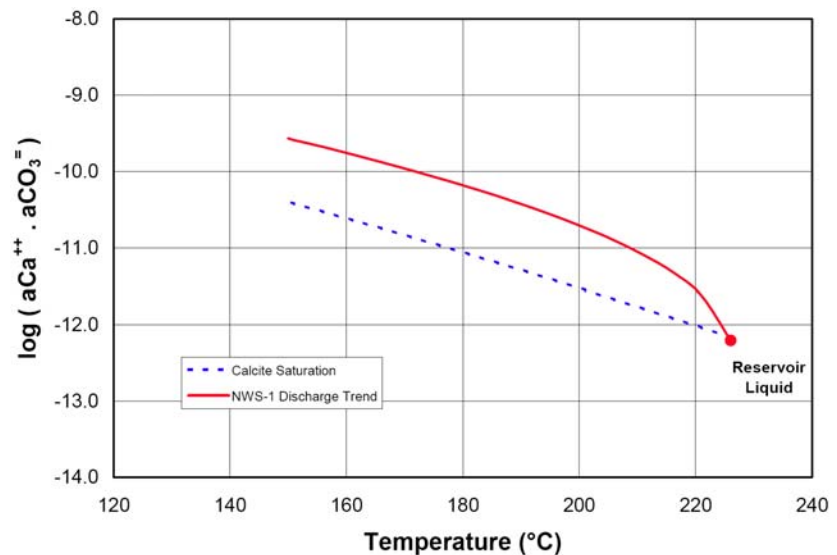

FIGURE 3: Simulation of calcite saturation in variably flashed water from well NWS-1 (SKM, 2005b)

Gas chemistry is presented in Table 1. About 98% of the total gas content is CO_2 with H_2S and N_2 making up the rest. Ar, H_2 and CH_4 are all present but in very low concentrations. The gas chemistry is characterized by relatively high helium content. Steam separated at a wellhead separator at a pressure of about 5 bar-g has a total gas content of about 2.5% by volume. The corresponding concentration in the deep reservoir is about 0.35%. The gas chemistry is notable for the low H_2 concentration (0.02% by volume of the total gas) (SKM, 2005b).

TABLE 1: Analysis of liquid and vapour samples collected from the discharge of well NWS-1 (concentration in mg/kg for water samples and in mmole/kg for steam samples)

	Sampling conditions					Water analysis															Gas analysis							
Date	WHP (bar-g)	DEPY (kJ/kg)	TMF (kg/s)	CP (bar-g)	SCP (bar-g)	No.	pH	Na	K	Ca	Mg	Fe	Cl	SO$_4$	tHCO$_3$	CO$_2$	B	SiO$_2$	NH$_3$	TDS	CO$_2$	H$_2$S	NH$_3$	H$_2$	O$_2$	N$_2$	CH$_4$	Total
31May04	3.3	960	27.8	0.85	0.85	6	7.91	1495	264	41	0.11	2.40	2,517	159	117	84.4	22.0	522		5150	229	3.3						232
1Jun04	3.3	960	27.8	0.80	0.85	7	8.02	1461	265	20	0.19	0.26	2,483	112	114	82.2	22.0	527	0.20	5010	342	3		0.1	0.1	6.1	0.05	351
2Jun04	3.3	960	27.8	0.80	0.80	8	8.14	1468	263	17	0.11	0.17	2,483	123	103	74.3	22.0	530		5020	465	1.7	2.5					469
3Jun04	3.3	960	27.8	0.80	0.80	9	8.25	1455	262	17	0.07	0.18	2,519	116	105	75.7	22.0	527		5030	400	1.4	2.3					404
4Jun04	3.3	960	27.8	0.78	0.78	10	8.23	1456	266	17	0.08	0.06	2,499	114	104	75	22.0	527		5010	419	1.4	1.8					422
6Jun04	3.3	960	27.8	0.80	0.85	11	8.22	1444	263	16	0.09	0.09	2,470	109	101	72.9	22.0	537	0.14	4970	396	4.2		0.1	<0.0005	3	0.06	403
7Jun04	3.2	960	27.8	0.75	0.75	12	8.18	1461	266	16	0.11	0.07	2,482	110	106	76.5	22.0	531		5000	402	1.4	2.3					406
8Jun04	3.3	920		0.75	0.75	14	8.77	1466	267	15	0.12	0.05	2,454	117	105	75.7	22.0	529		4980	367	2.3	1.8					371
10Jun04	3.3	986	29.2	0.79	0.79	17	8.84	1457	265	14	0.12	0.09	2,482	120	103	74.3	22.0	544		5020	461	2	2.1					465
12Jun04	3.5	955	28.6	1.79	1.79	19	8.84	1443	262	15	0.11	<0.02	2,446	119	109	78.6	22.0	531		4960	560	3	2.2					565
13Jun04	3.5	934	28.3	1.80	1.80	20	8.82	1414	257	15	0.11	0.10	2,411	117	105	75.7	22.0	520		4870	427	2.3	2.3					431
14Jun04	3.7	910	27.2	2.40	2.40	21	8.88	1414	257	15	0.11	0.10	2,411	117	105	75.7	22.0	520		4870	509	3.2	2.3					514
15Jun04	3.8	924	27.5	2.55	2.55	22	8.70	1402	254	15	0.10	0.05	2,375	117	113	81.5	22.0	519		4820	477	2.1	2.3					481
16Jun04	4.0	902	25.6	3.10	3.10	23	8.56	1382	255	14	0.09	0.02	2,336	118	130	93.8	21.0	506	0.22	4770	556	2.7						559
18Jun04	4.1	895	27.2	3.00	0.85	24	8.63	1385	252	14	0.09	0.04	2,384	114	115	83	21.0	522		4820	571	5.1		0.3	3.5	25.4	0.07	606

DEPY: Discharge enthalpy; TMF: Total mass flow; CP: Water collection pressure; SCP: Steam collection pressure;
Concentration of He in samples 7, 11 and 24 is 0.008, 0.009 and 0.015 mmole/kg, respectively, and concentration of Ar in samples 7, 11 and 24 is 0.08, 0.05 and 0.3 mmole/kg, respectively

4.2 NWS-4

Discharge water samples were collected either from the atmospheric silencer (weirbox samples) or from the separator. Samples included untreated and filtered-acidified water (0.45 μm filters and nitric acid). Gas samples were collected from the steam-line using evacuated gas flasks containing 50 ml of 4N sodium hydroxide solution. The local atmospheric pressure in NWS-4 is about 748 mbar. At this pressure, the steam flash to the atmospheric silencer is about 5% greater than at sea level.

Well measurements show that NWS-4 produces from a single-phase, liquid reservoir at 1400 m VD, with a temperature of 223°C. Discharge water analyses are presented in Table 2. Well NWS-4 discharges water that has alkaline-pH, medium salinity, and is a sodium-chloride type water with total dissolved solids of about 5000 mg/kg. The water has moderate bicarbonate (60-80 ppm) reflecting the moderate gas content of the reservoir waters. The calcium concentration of 25-30 ppm is, in turn, controlled by calcite solubility. The calculated reservoir chloride concentration in NWS-4 is about 2000 ppm. The water chemistry of wells NWS-1 and NWS-4 is very similar with the notable exception of calcium which has twice the concentration in NWS-4 compared to NWS-1. The discharge water chemistry during a one day flow test showed only a slight increase in salinity. The only significant change in chemistry during the test was a small but consistent change in Cl/Ca ratio. During periods of high flow, the Cl/Ca ratio increased (i.e. showed relatively less calcium). This was confirmed by duplicate calcium analyses. There are two possible reasons for this, multi-zone effect or loss of calcium through calcite deposition. The discharge water is significantly over-saturated with respect to calcite. Calcite scaling is, therefore, expected to be caused by depressurization boiling within the wellbore. The increase in Cl/Ca may also have been produced by

TABLE 2: Analysis of liquid and vapour samples collected from the discharge of well NWS-4 (concentration in mg/kg for water samples and in mmole/kg for steam samples)

| | Sampling conditions | | | | | | Water analysis | | | | | | | | | | | | | | Gas analysis | | | | | | | |
Date	WHP (bar-g)	DEPY (kJ/kg)	TMF (kg/s)	CP (bar-g)	SCP (bar-g)	No.	pH	Na	K	Ca	Mg	Fe	Cl	SO$_4$	tHCO$_3$	CO$_2$	B	SiO$_2$	TDS	CO$_2$	H$_2$S	NH$_3$	H$_2$	O$_2$	N$_2$	CH$_4$	Total
7Sept04	8.0	940		0.5	0.50	2	8.71			27			2,430	104	67	48.3	20.7	473	3120	342	1.7						344
8Sept04	8.3	920		0.0	0.50	3	8.62	1465	270	26	0.21	0.03	2,520	104	71	51.2	21.1	536	5030	381	2.1						383
9Sept04	8.8	944	18.9	0.0	0.50	5	8.58	1440	272	28	0.27	0.03	2,570	111	70	50.5	21.8	547	5070	428	1.8	0.06	0.1	<0.0005	9		439
9Sept04	9.0	920		0.0	0.50	6	8.82	1419	284	29	0.27	0.02	2,590	108	62	44.7	22.4	539	5070	438	2.5						441
10Sept04	9.5	920		0.0	1.00	7	8.61	1414	282	26	0.24	0.08	2,570	104	74	53.4	21.1	558	5060	461	2.9	0.06	0.1	<0.0005	6.5	0.05	471
11Sept04	5.4	950	56.1	1.7	1.50	8	8.10	1312	261	22	0.33	1.20	2,390	122	80	57.7	19.4	516	4740	434	2.8	0.2	0.1	<0.0005	5.4	0.06	443
14Sept04	6.8	920		0.0	0.00	11	8.39	1382	260	29	0.26	0.09	2,482	109	85	61.3	21.4	518	4900	420	3.4						423
16Sept04	7.3	954	48.1	0.0	1.45	13	8.04	1441	270	24	0.10	0.07	2,430	107	73	52.7	21.1	542	4920	458	1.9	0.2	0.06	0.53	18.9	0.05	480
16Sept04	5.5	950	56.1	1.5	1.45	14	8.42	1350	253	26	0.09	0.10	2,570	116	78	56.3	21.6	500	4930	412	2.6						415

DEPY: Discharge enthalpy;   TMF: Total mass flow;   CP: Water collection pressure;   SCP: Steam collection pressure;
Concentration of He in each sample 5, 7, 8 and 13 is 0.01 mmole/kg, and concentration of Ar in samples 5, 7, 8 and 13 is 0.1, 0.08, 0.07 and 0.2 mmole/kg, respectively

an increase in the relative flow of a second, lower-calcium zone, probably deeper in the well. Discharge silica concentrations are in the range of 520-540 ppm in the weirbox. Chemical speciation of reservoir water at 230°C was calculated. With all gas dissolved, the water has a pH of about 5.6, which is near neutral at this temperature. The water calculates to be slightly under-saturated with respect to calcite ($CaCO_3$) and anhydrite ($CaSO_4$). Upon discharge, the NWS-4 reservoir water becomes significantly over-saturated with respect to calcite and calculations indicate that the water has a high potential for depositing calcite. However, there is no direct evidence that scaling actually occurred (SKM, 2004c). Figure 4 shows the computer-simulated calcite saturation as the reservoir water flows up the well and boils.
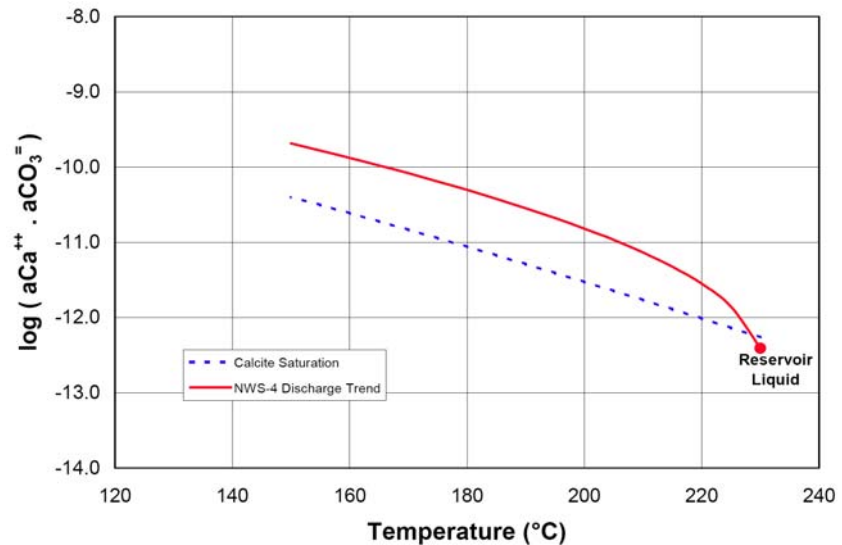
FIGURE 4: Simulation of calcite saturation in variably flashed water from well NWS-4 (SKM, 2004c)

Gas chemistry is presented in Table 2. CO_2 constitutes about 98% by volume of the total gases, with H_2S and N_2 making up about 2%. Ar, H_2 and CH_4 are all present in very low concentrations. The total gas concentration in NWS-4 steam, separated at about 5 bar-g, is 3.0%, based on a steam mass percentage of about 20%. This equates to 0.4% in the deep reservoir. Overall, the gas chemistry for NWS-4 is very similar to that of NWS-1, both in terms of the total gas content and the relative proportions of the gases. The gas chemistry was reasonably stable throughout the discharge test with no significant changes in response to WHP changes or mass flow. The NWS-4 gas chemistry is notable for the low H_2 concentration (0.02% by volume of the total gas) and in particular with respect to argon (SKM, 2004c).

5. THEORY OF CALCIUM CARBONATE SCALE FORMATION

Scale formation of geothermal waters may occur in production wells, injection wells and surface equipment. In extreme cases, intense scale formation observed during testing of exploration wells has led to a cessation of further development (Arnórsson, 2004). Scale formation occurs largely in response to the cooling and degassing of geothermal water, as it boils by depressurization. The most common type of troublesome scale is that of amorphous silica and calcium carbonate. Calcite is unusual in that it has retrograde solubility. It becomes more soluble upon a decrease in solution temperature and also when dissolved carbon dioxide (CO_2) is present in the solution.

Geothermal reservoir waters are close to calcite saturation. Degassing of such water, which occurs in response to boiling, leads to a sharp rise in the pH of water. This in turn causes the activity of the carbonate ion (CO_3^{2-}) to increase significantly, leading to over-saturation (Arnórsson 1989):

$$CaCO_{3,\,s} = Ca^{2+} + CO_3^{2-}$$
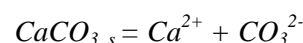
Cooling, which occurs during depressurization boiling, counteracts the effect of CO_2 degassing with respect to the state of calcite saturation. The release of CO_2 and deposition of calcite is conveniently expressed as:

$$Ca^{2+} + 2HCO_3^- = CaCO_{3,\,s} + CO_2 + H_2O$$

During the early stages of boiling, the effect of degassing dominates, but after the water has been largely degassed with respect to CO_2, the effects of further cooling by boiling takes over, steadily decreasing the degree of over-saturation. Many observations have shown that calcium carbonate deposition in wells is only troublesome at the first depth level of boiling and that the deposition is strongest just above this level. Calcite scale formation is most troublesome around 200°C because CO_2 solubility is at a minimum at this temperature; it decreases at both higher and lower temperatures.

The intensity of calcite scale formation increases with increasing salt content of the water (Arnórsson, 2004). Aragonite, which is slightly more soluble than calcite, has also been identified as scale. It seems that aragonite forms at the expense of calcite, when CO_2 degassing causes strong over-saturation (Arnórsson, 1989). However, the deposition of aragonite scale in geothermal waters is less than that of calcite.

6. ASSESSMENT OF CALCITE SCALING IN WELLS NWS-1 AND NWS-4

6.1 NWS-1

There is a strong correlation between the calculated aquifer water pH and the value taken by the saturation index for calcite. The SI / pH slope of the line is about 1.2 for well NWS-1 (Figure 5). The calculated aquifer water pH is largely determined by the measured pH of water samples collected at the surface and analysed CO_2 concentrations in steam samples. In the report from which the analytical data are extracted for this study (SKM, 2005b), detailed information on sampling techniques and analytical precision for the pH measurement are not given. However, in light of the constant composition of all major species in water samples, the large variation in the reported pH must be considerably larger than expected analytical error. At the high temperature in the producing aquifers at Sabalan, one would expect the unboiled water to be close to saturation with respect to calcite. This must be kept in mind when changes in calcite saturation upon boiling are considered. These changes are calculated more accurately than the absolute calcite saturation state.

Figure 6 shows how calcite saturation varies during adiabatic boiling of water entering NWS-1 for variable extents of degassing. During the early stages of boiling, equilibrium degassing causes a sharp rise in the calcite saturation index values. For the initially calcite equilibrated aquifer water, maximum over-saturation is attained at about 180°C and the degree of over-saturation amounts to almost 1 SI unit. For successively less degassing, the degree of over-saturation produced during the early stages of boiling
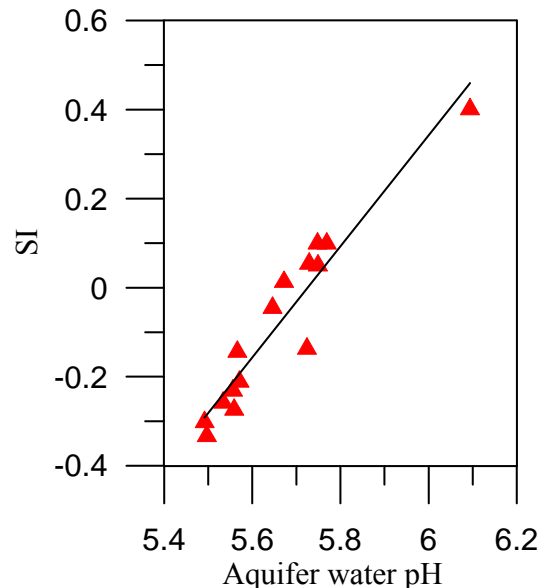
FIGURE 5: Aquifer water pH vs. saturation index for calcite in well NWS-1; the line represents a best fit through the data points
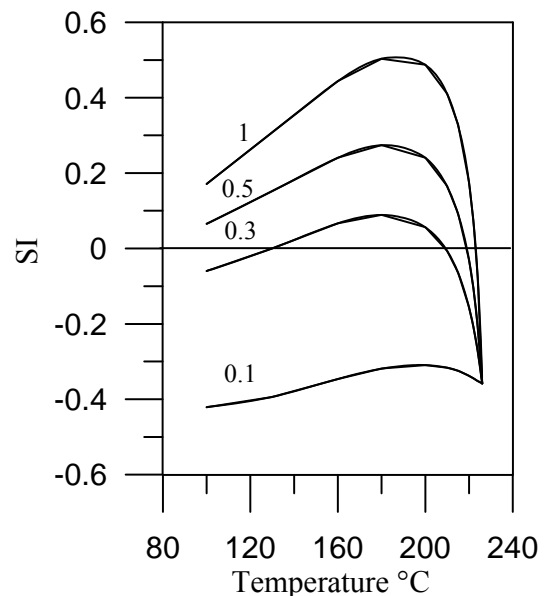
FIGURE 6: The variation in the saturation index for calcite for variable CO_2 degassing of water in well NWS-1; the numbers represent the extent of CO_2 degassing, 1 indicating equilibrium degassing, while 0.5, 0.3 and 0.1 represent 50%, 30% and 10% of equilibrium degassing, respectively

becomes progressively less and is insignificant at 10% of equilibrium degassing. At maximum SI values, degassing is almost complete. Boiling to lower temperatures, therefore, causes limited degassing, but cooling causes a decrease in SI because calcite solubility increases with falling temperature. A strong increase in pH occurs during early boiling as a consequence of CO_2 degassing (Figure 7). When the water has been largely degassed, further cooling by boiling causes a decrease in the SI value for calcite, because calcite solubility increases with decreasing temperature. Also, degassing of CO_2 causes a rise in carbonate ion concentrations in well NWS-1 (Figure 8). It is mostly the increase in CO_3^{-2} that is responsible for the increase in the SI value. The limited increase in the concentration of Ca^{+2}, which largely occurs as a consequence of vapour formation, has much less effect (Figure 9). Figure 10 shows the variation of CO_2 for different extents of degassing, or from 10% of maximum degassing to equilibrium degassing. For the 10%, the CO_2 in the water decreases about a hundred-fold during boiling from the aquifer temperature to 100°C, but this decrease is about a thousand-fold for equilibrium degassing. During the rapid ascent of boiling water in a well, degassing may be incomplete; there is not enough time for the mass transfer of CO_2 to take place from the liquid water to the vapour that is continuously forming.
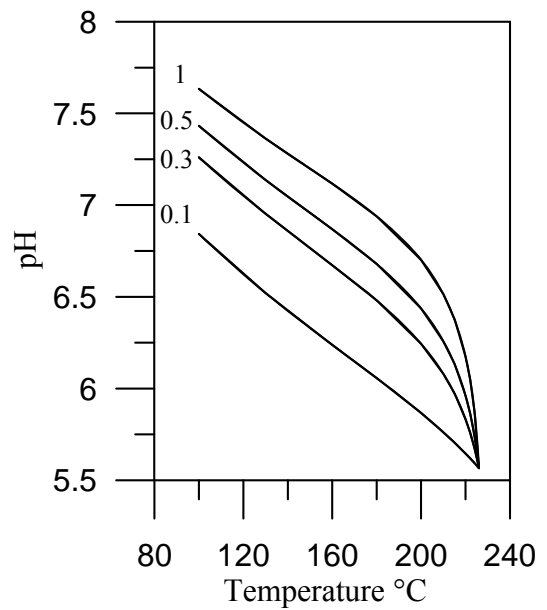
FIGURE 7: The variation in pH of water from well NWS-1 for variable CO_2 degassing; the numbers represent the extent of CO_2 degassing, 1 indicating equilibrium degassing, while 0.5, 0.3 and 0.1 represent 50%, 30% and 10% of equilibrium degassing, respectively
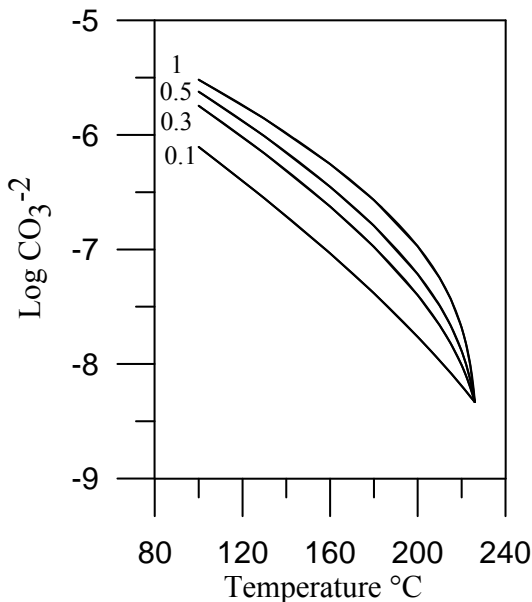
FIGURE 8: The variation in the concentration of CO_3^{-2} for variable CO_2 degassing of water in well NWS-1; the numbers represent the extent of CO_2 degassing, 1 indicating equilibrium degassing, while 0.5, 0.3 and 0.1 represent 50%, 30% and 10% of equilibrium degassing, respectively
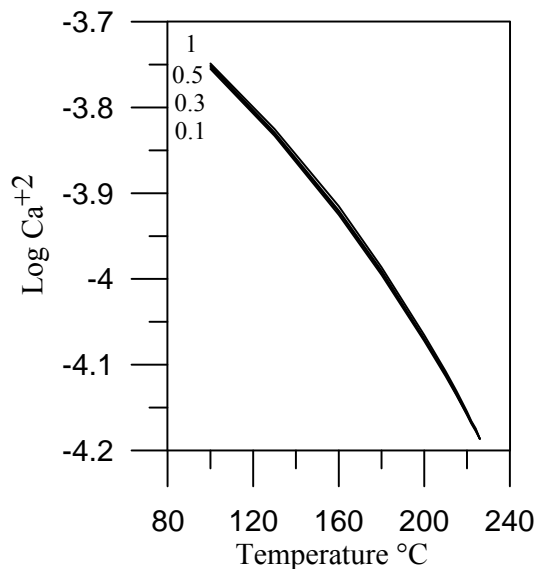
FIGURE 9: The variation in the concentration of Ca^{+2} for variable CO_2 degassing in well NWS-1; the numbers represent the extent of CO_2 degassing, 1 indicating equilibrium degassing, while 0.5, 0.3 and 0.1 represent 50%, 30% and 10% of equilibrium degassing, respectively
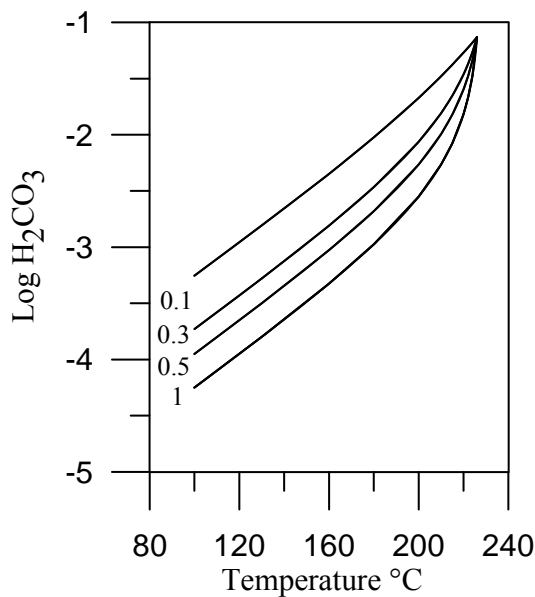
FIGURE 10: The variation in the concentration of CO_2 for variable CO_2 degassing in well NWS-1; the numbers represent the extent of CO_2 degassing, 1 indicating equilibrium degassing, while 0.5, 0.3 and 0.1 represent 50%, 30% and 10% of equilibrium degassing, respectively
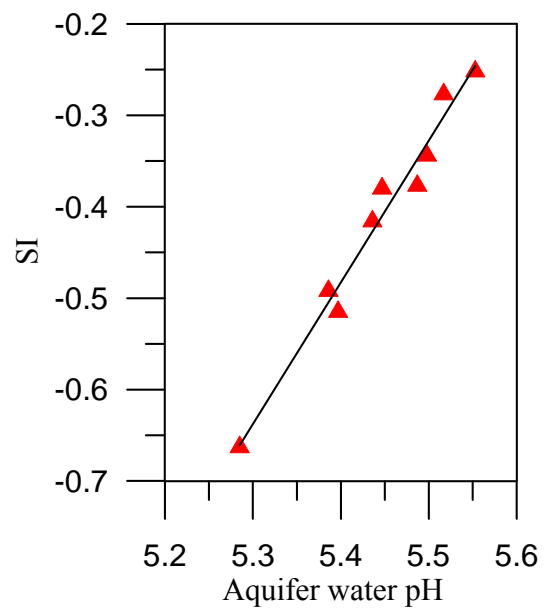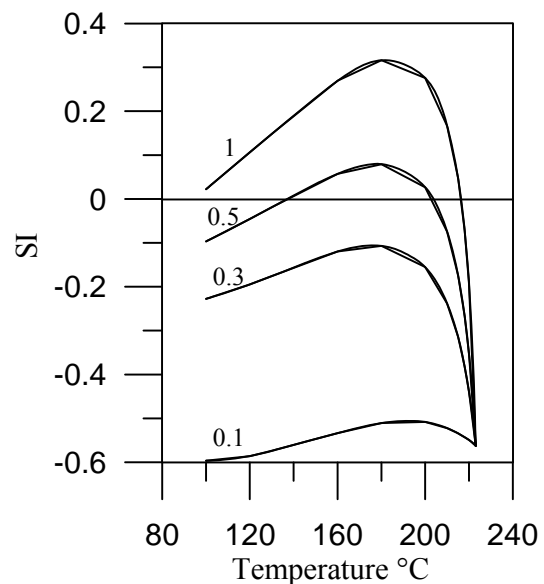

FIGURE 11: Aquifer water pH vs. saturation index for calcite in well NWS-4; the line represents a best fit through the data points

The overall changes in degassing and the consequent increases in the activities of Ca^{+2} and CO_3^{-2} lead to a sharp increase in calcite over-saturation of an initially calcite-saturated water during the early stages of boiling, followed by a decrease in the calcite SI value caused by increased calcite solubility with falling temperature, except in the case of 10% equilibrium degassing. The effect of temperature on calcite saturation becomes evident when the water has been largely degassed.

6.2 NWS-4

For well NWS-4, the calculated SI for calcite varies linearly with the calculated aquifer water pH (Figure 11). The SI/pH slope of the line is about 1.5. As for well NWS-1, the report from which the analytical data were extracted for this study (SKM, 2004c) does not provide detailed information on sampling techniques and analytical precision for the pH measurement. Again, as for well NWS-1, the cause of the above relationship could be (a) error in the pH measurement or (b) error in analyzed CO_2 concentration in steam, or both.

Figure 12 shows how the calcite saturation index varies during adiabatic boiling of geothermal fluid in well NWS-4. Extensive degassing by boiling tends to cause an initially calcite-saturated aquifer water to become over-saturated. The calculated calcite saturation in the aquifer water of well NWS-4 is somewhat negative (Figure 12). This is considered to be a consequence of error in

FIGURE 12: The variation in the saturation index for calcite for variable CO_2 degassing of water in well NWS-4; the numbers represent the extent of CO_2 degassing, 1 indicating equilibrium degassing, while 0.5, 0.3 and 0.1 represent 50%, 30% and 10% of equilibrium degassing, respectively

calculating the aquifer water pH. The aquifer water is expected to be close to calcite saturation. During the early stages of boiling, equilibrium degassing causes a sharp rise in the saturation index with respect to calcite. As in well NWS-1, maximum over-saturation is attained at about 180°C. If degassing is less than ~10% of equilibrium degassing, boiling does not produce a significant increase in the calcite saturation index as it does when degassing is more efficient. Precipitation of calcite is expected to occur at all temperatures after the onset of boiling if degassing, with respect to CO_2 exceeds ~10% of equilibrium degassing. At maximum SI values, the water has been largely degassed, and the subsequent decline in SI is caused by increased calcite solubility with decreasing temperature. The initial increase in SI reflects an increase in pH due to CO_2 degassing (Figure 13). The pH increase causes a strong increase in CO_3^{-2} concentration in the flashed water of well NWS-4 (Figure 14).

It is mostly this latter increase that is responsible for making initially calcite-saturated aquifer

FIGURE 13: The variation in pH of water from well NWS-4 for variable CO_2 degassing; the numbers represent the extent of CO_2 degassing, 1 indicating equilibrium degassing, while 0.5, 0.3 and 0.1 represent 50%, 30% and 10% of equilibrium degassing, respectively

water supersaturated. The concentration of free calcium ions increases in the flashed water due to steam loss (Figure 15). This increase in Ca^{+2} has much less effect on the calcite saturation index than does the increase in CO_3^{-2} ion concentration. The reduction of CO_2 in the flashed water in well NWS-4 for 10% equilibrium degassing and equilibrium degassing from the aquifer temperature to 100°C is about 100 and 1000 times, respectively (Figure 16).
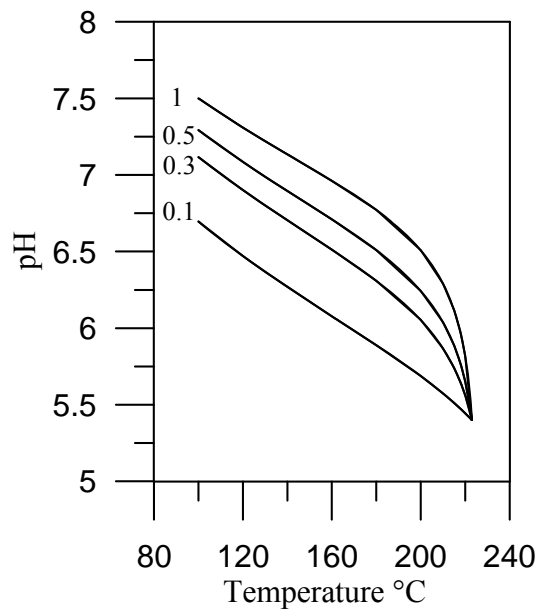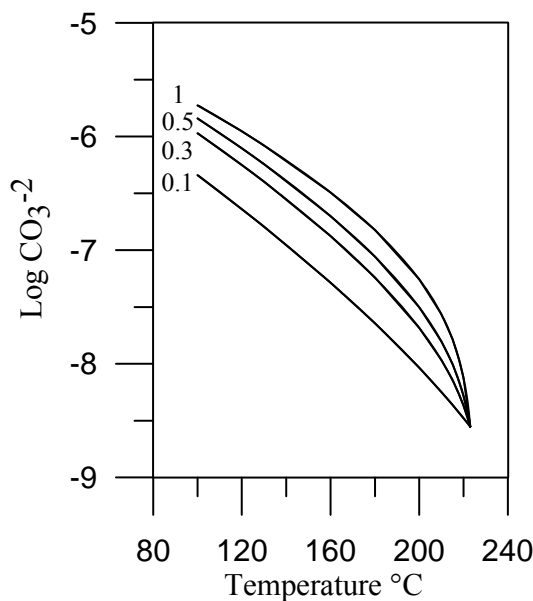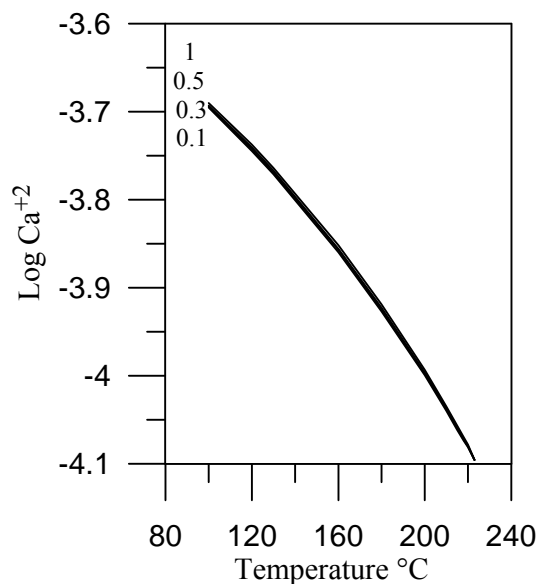

FIGURE 14: The variation in the concentration of CO_3^{-2} for variable CO_2 degassing of water in well NWS-4; the numbers represent the extent of CO_2 degassing, 1 indicating equilibrium degassing, while 0.5, 0.3 and 0.1 represent 50%, 30% and 10% of equilibrium degassing, respectively

FIGURE 15: The variation in the concentration of Ca^{+2} for variable CO_2 degassing in well NWS-4; the numbers represent the extent of CO_2 degassing, 1 indicating equilibrium degassing, while 0.5, 0.3 and 0.1 represent 50%, 30% and 10% of equilibrium degassing, respectively

7. CONCLUSIONS AND RECOMMENDATIONS

Silica scaling is not expected to occur in the wells because boiling of the aquifer water of wells NWS-1 and NWS-4 does not produce an amorphous silica over-saturation solution. In contrast, calcite scales are expected to form from the first level of boiling in the well and down to 100°C. Near calcite saturation is expected in the aquifer. The calculation of calcite saturation in aquifer waters is subject to many errors, including errors during sampling, analysis and in thermodynamic data. One would not expect thermodynamic data to produce large errors. On the other hand, both sampling of well discharges and subsequent analysis can produce substantial errors. For wells NWS-1 and NWS-4, the calculated saturation index for calcite varies linearly with the calculated aquifer water pH. The SI/pH slope of the lines is about 1.2 and 1.5 for wells NWS-1 and NWS-4, respectively. The cause of this relationship could be error in analysed CO_2 concentrations in steam or in the pH measurements, because the calculated aquifer water pH is largely determined by the measured pH of water samples collected at the surface and analysed CO_2 concentrations in steam samples. Generally, the variation in aquifer pH should be very slight. The large variation in the reported pH, especially for samples from well NWS-1, must be largely due to analytical error.
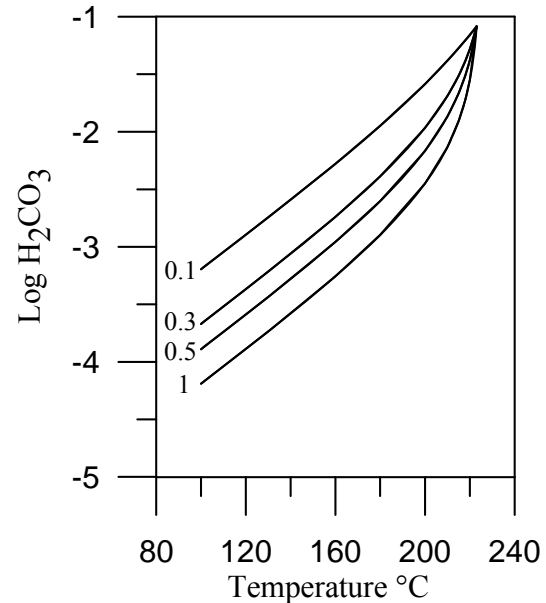

FIGURE 16: The variation in the concentration of CO_2 for variable CO_2 degassing in well NWS-4; the numbers represent the extent of CO_2 degassing, 1 indicating equilibrium degassing, while 0.5, 0.3 and 0.1 represent 50%, 30% and 10% of equilibrium degassing, respectively

During adiabatic boiling, initially calcite saturated waters become over-saturated, the degree of over-saturation being dependent on the extent of CO_2 degassing of the boiling water. CO_2 degassing by boiling causes pH and carbonate ions and calcium ion concentrations to increase in the flashed water for both wells NWS-1 and NWS-4. Maximum over-saturation is reached at about 180°C for both wells. Cooling by further boiling causes progressively decreasing over-saturation because the solubility of calcite increases with decreasing temperature. Calcite deposition will be confined to the well and wellhead equipment because the first depth level of boiling is in the well. It only takes a relatively limited deposition of calcite to clog a well. Two methods are recommended to cope with calcite scaling in these wells. If the calcite deposition rate is not very fast (cleaning required no more than about twice a year), regular mechanical cleaning is a good method, but if scale formation is faster the use of inhibitors is considered more attractive. The most successful mechanical cleaning method involves drilling out the scale with a truck-mounted rig while the well is producing. In the inhibitor method, the inhibitor must be injected into the well to a depth below the level of first boiling.

ACKNOWLEDGEMENTS

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