CALCITE SCALING FIELD EXPERIMENTS TO 120°C AT WAIRAKEI

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SUMMARY – Preliminary field experiments were undertaken at Wairakei Geothermal Field to measure calcite scaling between 50 and 120°C. The geothermal fluid was saturated with respect to calcite by injecting sodium bicarbonate solutions into the base of a 1m long, 50mm diameter fluidized bed reactor. The reactor was filled with 1.5 kg of calcite with a BET specific surface area of 0.0695 m^2/g. The experimental technique, with high turbulence, high ratio of volume over surface area, and high supersaturation should have resulted in maximum deposition rates. However, the deposition appeared to be inhibited at lower temperature and thermodynamic calculations overestimated the propensity for scaling.

1. INTRODUCTION

The deposition of calcium carbonate scales is a serious and costly impediment to the utilization of high-enthalpy geothermal resources where the aquifer fluids are bicarbonate-dominated (Kindle et al. 1984; Gudmundsson and Thomas, 1989). Calcite is the crystalline form that deposits but aragonite can also from but is much less common. The solubility of calcite has been measured over a range of temperatures and as a function of salt concentration and CO_2 gas pressure (Henley et al., 1984). The solubility decreases with increasing temperature and increases with increasing salinity.

The driving force for deposition of calcite during discharge of geothermal brine is usually the loss of non-condensible CO_2. Precipitation occurs inside a well from the wellhead down to a depth where the bicarbonate-carbonate equilibrium is disturbed due to the evolvement of gas. However, at Ohaaki calcite deposition has been observed as a calcite saturated flow meets a higher hotter inflow (Hedenquist, Pers. Comms.) and in two-phase lines and separation plants where mixing of incompatible fluids may occur, e.g. high calcium and high bicarbonate respectively (Lew Bacon, Pers. Comms.). High CO_2 fluids which are normally also rich in Ca are more likely to deposit calcite compared to fluid poor in CO_2. This is because the higher CO_2 gas pressure enables a fluid to flash at smaller drawdowns and a larger portion of Ca is thermodynamically ready to deposit for a given percent of flash (Michels, 1981). The equilibrium reactions may be represented as :

$$2HCO_3^- \rightleftharpoons CO_3^= + CO_2(g) + H_2O \quad (1)$$

$$Ca^{++} + CO_3^= \rightleftharpoons CaCO_3 \quad (2)$$

$$Ca^{++} + 2HCO_3^- \rightleftharpoons CaCO_3 + CO_2(g) + H_2O \quad (3)$$

A extensive study by Michels on deposition of $CaCO_3$ in porous materials (Michels, 1981) showed the importance of kinetic effects in determining the degree of scaling. The deposition was always less than what an equilibrium calculation would show, in that the deposition of $CaCO_3$ appeared to lag behind the vaporisation of H_2O-CO_2. This was thought to be due to the speed of transfer of CO_2 into the steam phase. The flow regimes occurring in the well would have an important bearing on the effectiveness of this process (Henley et al., 1984). Non-equilibrium during flashing also included inefficient removal of Ca from the liquid. Michels's experiments showed that in some cases only 20% calcium was removed whereas equilibrium would be expected to achieve more than 90%. Slower depressurization for the flashing appeared to favour a closer approach to equilibrium.

How the fluid enters the well bore can also determine the severity of scaling. Fluid entering through fractures can provide a longer pressure drop path during flow and may result in a longer zone of calcite deposition. It may be difficult to recover from this situation as acid entry into the production fractures may be blocked. Arnórsson (1989) speculated that wide-spread boiling and consequent calcium carbonate deposition out into the formation would not degrade permeability of lifetime of the individual wells to the extent that production is affected. However this would be highly dependent on the aquifer properties and chemistry of the fluids.

Scaling can be controlled by adjusting the thermodynamic equilibrium through acidification or maintaining excess CO_2 pressure through well throttling or downhole injection of CO_2. Both these methods have been used to prevent scaling (Auerbach et al., 1983, Corsi et al., 1985). However acidification causes problems with corrosion and may not be economic as usually large amounts of acid are required to sufficiently reduce the pH. Well throttling results in decreased output while downhole injection of CO_2 has not been tested at pressures greater than 10 bars due to the unavailability of high pressure pumps (Corsi et al., 1985). The usual method of clearing a well is by mechanical cleaning a few times a year. This is usually an expensive exercise that cannot be undertaken during production. Failure to recover injectivity through mechanical cleaning can usually be rectified by acidizing the well. Typically HCl is pumped into the well to dissolve the carbonate scales. This is a different technique to the acid control treatment discussed above. Perhaps the most effective method to prevent build-up of calcite in geothermal wells and associated piping to inject an antiscalant chemical at depth below flash zone. The inhibitors work by acting as chelating agents or by inhibiting crystal growth. The major problems are inhibitor costs, choosing the most suitable inhibitor and the system for injecting it into the well. Invariably mechanical cleaning is still required, albeit at a reduced rate, which offsets the high cost of the chemicals.

At the conclusion of the 1988 conference "Deposition of Solids in Geothermal Systems" the Carbonate Depositions Working Group identified the deficiencies in the current understanding and control of carbonate scaling and recommended possible research directions (Thomas and Gudmundsson, **1989).** In particular that little is known how the complex geothermal fluid matrix affects the mineralogy, rate and morphology of the scale and how the substrate surface chemistry affects the rate of nucleation and deposition. In the intervening period little kinetic data has been published that could be applied to geothermal conditions, that is at temperatures above 100°C in chemically complex solutions. At present scaling rates are "predicted" thermodynamically by determining how much mineral will be precipitated to reach equilibrium (for example see Todaka et al., *1995;* Ramos-Candelaria et al., 2000). This is inadequate, particularly given the comments by Michels (1981) above, for accurate prediction of scaling rates in aquifers and wellbores. Predicting deposition gives the ability to control the scaling.

There are no kinetic models to estimate calcite scaling under geothermal conditions. To rectify the dearth of data, we have begun a series of field experiments in an attempt to measure calcite scaling rates under typical geothermal conditions of mixing and boiling. The measured rates will then be compared to literature values and applied to geothermal systems using reactive transport computer codes (White, 1995).

In this paper we describe the preliminary experiments which were designed to test the methodology and to model the **mixing** of a high bicarbonate fluid with geothermal fluid at temperatures between 50 and 120°C.

2. EXPERIMENTAL

The aim of the experiments is to measure deposition rates of calcite from geothermal fluid but this has so far proved to be very difficult. The problem is that the geothermal fluid at the well head is not saturated with respect to calcite due to the fluids being cooler than in the aquifer. So to measure deposition rates first requires the solutions to be saturated with respect to calcite.

Initial experiments were conducted at Ohaaki Geothermal Field where a large 1.5m long, 50 mm diameter SS pipe was packed with lime through which was passed hot geothermal fluid. The calcium concentrations Ohaaki fluid well BR15 were low (< 2 ppm) and the experimental configuration proved to be inadequate as the fluid did not saturate with respect to calcite rapidly enough. In addition major impurities dissolved into the water, which are not naturally found in geothermal fluids (e.g. phosphate).

In our next attempt we moved the experiment to Wairakei Flash Plant 10 where the geothermal calcium concentrations are high, about 15-20 ppm. The temperatures at FPlO are low but the primary purpose of these initial experiments was to test the experimental methodology and obtain results which could be easily compared with low temperature literature results.

A plug flow reactor, consisting of a 1m long, 25 mm diameter SS pipe, was packed with inert **1.4-2.4** mm diameter zirconia beads. The geothermal fluid was saturated with respect to calcite, by injecting sodium bicarbonate upstream of the reactor. Unfortunately the reactor quickly blocked (– 30 minutes) with a very fine white powder (assumed to be calcite) primarily at the inlet of the bed. It was impossible to interpret the data and calculate reaction rates where the flow through the reactor was constantly decreasing.

In an attempt to overcome the blocking packed pipe reactors the experimental technique was changed to a fluidised bed. A schematic of the piping arrangement is shown in Figure 1. Tracer tests showed that the fluidised bed approximated a well-mixed reactor. Calcite from Martha mine (Waihi) was crushed, cleaned and sieved (100 – 400 µm). The **50** mm diameter 1 m long pipe (excluding flow straightening and disengaging cones) was filled 1.5 kg of calcite with a BET specific surface area of 0.0695 m^2/g. The fluidized bed worked as expected with no blockages. The sodium bicarbonate was injected into the base of the fluidised bed and water samples were taken at the top of the 1 m column. The injection rate and total flow were determined by weighing the fluid over a known time interval. The filtered and acidified samples were **analysed** for calcium using ICP-OES. Samples were also collected in rubber sealed bottles for total bicarbonate analyses. A typical FPlO water analysis is given in Table 1 and the results of the first two successful experiments are given in Tables 2 and 3. The vagaries of fieldwork meant that in the second experiment the flash plant was operating at a lower separation pressure so the **maximum** temperature reached was approximately 10 °C less than in the first experiment. Continuing operational difficulties at FP 10 necessitated a shift to Flash Plant 2 where the composition of the fluid is similar to **FP10**. Table 4 gives the results at FP2 with an empty reactor while in Table 5 results are from the reactor filled with 1.46 kg of calcite.

Typical analytical errors are 5% for calcium and 3% for total bicarbonate. In the tables "Calcium Calculated" is the calcium concentration assuming the concentration change due solely due to dilution by the injected sodium bicarbonate solution. Similarly the "Extra Sodium" is the increase in sodium due to added bicarbonate solution. The pH of the sodium bicarbonate dosed fluids were between 8.4 to 8.5. The calcite saturation index was calculated using the computer code "Geochemists Workbench" with the "Calcium Calculated" and the measured bicarbonate concentration adjusted for the amount of calcium precipitated. There was negligible calcium in the sodium bicarbonate solutions.

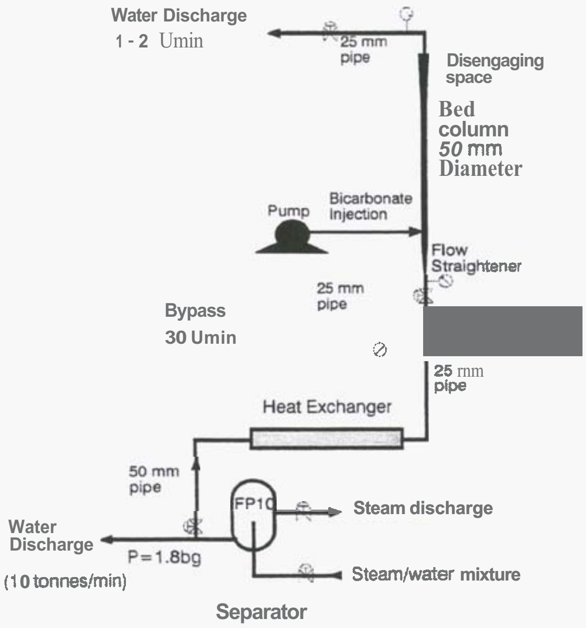

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Figure 1. Fluidized Bed Piping Arrangement, not to scale.

Table 1: Representative Wairakei FPlO Water Analysis (mg L^{-1}, except pH).

pH(@20°C)	**8.61**	Li	**12.6**
Na	**1279**	K	**190**
Ca	**18.7**	Mg	**0.010**
Rb	**2.55**	c s	**2.29**
Al	**0.33**	Fe	**<0.1**
Cl	**2068**	**SO_4**	**29**
B	**25.3**	SiO_2	**533**
tNH3	**0.3**	F	**8**
$tHCO_3$	**3**	tH_2S	**<1**

3. DISCUSSION

The precipitation and dissolution kinetics of calcite are extremely complex. The chemical reactions involved (1) and (2) are influenced by many factors such as solution saturation state, CO_2 partial pressure and involvement of a gas phase, pH, seed surface properties, solution ionic composition and any inhibitors as well as hydrodynamics (Zang and Dawe, 1998). Numerous experimental studies, nearly all at ambient temperatures but over a wide range of conditions, have been described in the literature (see for example Dreybrodt et al., 1997; Zang and Dawe, 1998; Nilsson and Sternbeck, 1999; and references therein). There are as yet insufficient results to develop a rate equation or to compare the results with published data. However there are observations that can be made with respect to the raw results obtained so far and the applicability with respect to applying the results to geothermal conditions. In the fluidized bed, the ratio of the volume of the solution to the mineral surface area (V/A) is relatively large ~ 2 cm so that the deposition rate is unlikely to be controlled by the slow dehydration reaction (1) of HCO_3^- to CO_2 but rather by the reactions at the calcite surface (Dreybrodt et al., 1997). The flow in the bed is turbulent so that the diffusional layer at the surface is absent or greatly reduced, i.e. essentially has the same chemistry as the bulk solution. The high supersaturation should also limit inhibition effects. All these factors suggest that the deposition rates measured in the fluidized bed should be at a maximum. Zang and Grattoni (1998) suggest that when the supersaturation of a $CaCO_3$ – saturated solution is above a critical value for homogeneous nucleation then the formation of extra nuclei can occur on other surfaces, including the calcite seed surfaces, so the deposition rate is unreliable as the "total" surface area in unknown. Indeed this must have been occurring in the initial packed pipe experiments which contained no calcite seed. Also, at times the flow from the fluidized bed was "milky" suggesting that homogenous nucleation may have been occurring. The solutions were never milky in the absence of bicarbonate injection so that

Table 2. FP10, Fluidized Bed Reactor filled with 1.5 kg Calcite.

Total Flow	t	Calcium Calculated	Calcium Measured	Bicarbonate Measured	Extra Sodium	Calcium Precipitated	Q/K Calcite
kg/min	"C	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	
1.53	48.2	14.3	14.0	799	301	0.3	6.3
1.38	73.4	14.2	14.1	842	317	0.1	11.0
1.56	104	14.3	8.4	784	299	5.9	17.9
1.39	119.3	14.0	2.7	870	334	11.3	31.7
1.41	122.8	15.4	4.8	421	165	10.6	17.2

Table 3. FP10, Fluidized Bed Reactor filled with 1.5 kg Calcite but with the FP operating at a different separation pressure.

Total Flow	t	Calcium Calculated	Calcium Measured	Bicarbonate Measured	Extra Sodium	Calcium Precipitated	Q/K Calcite
kg/min	"C	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	
1.38	82.6	14.2	13.9	933	352	0.3	14.1
1.57	107.7	14.4	4.8	871	333	9.6	23.0
1.70	109.0	16.0	14.6	341	130	1.4	9.4
1.67	110.5	16.5	16.4	196	74	0.1	6.6
1.41	110.2	16.9	18.2	59	21	-1.3	1.8

Table 4. FP2, "Empty" Fluidized Bed Reactor (plug flow!)

Total Flow	t	Calcium Calculated	Calcium Measured	Bicarbonate Measured	Extra Sodium	Calcium Precipitated	Q/K Calcite
kg/min	"C	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	
1.61	121.7	14.4	2.5	781	301	11.9	35.4
1.58	122.9	14.9	2.7	598	232	12.2	27.6
1.59	124.1	15.5	4.7	392	154	10.8	16.1
1.58	125.4	16.1	15	189	72	1.1	8.2
1.59	126.1	16.4	16.3	57	22	0.1	2.3

Table 5. FP2, Fluidized Bed Reactor filled with 1.46 kg Calcite

Total Flow	t	Calcium Calculated	Calcium Measured	Bicarbonate Measured	Extra Sodium	Calcium Precipitated	Q/K Calcite
kg/min	°C	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	
1.41	116.8	14.3	2.3	921	354	12.0	29.3
1.40	118.0	14.8	3.3	727	280	11.5	24.0
1.22	117.5	15.4	3.5	504	197	11.9	17.5
0.98	1118.8	16.1	8.8	285	112	7.3	11.2

grinding of the calcite during fluidisation was unlikely to have been the cause of the deposit.

The interesting result from these tests is that the prediction of the extent of scaling was not adequate by equilibrium thermodynamic calculations, even at relatively low temperatures where they may have been expected to be most reliable. In Table 3 at 110 °C at a calculated supersaturation index Q/K of 6 there appeared to be no removal of calcium. Reducing to a calculated supersaturation to 1.8 resulted in the calcite seed dissolving, i.e. the solutions must have actually been undersaturated with respect to calcite. Comparing the results fiom FP2 with the reactor empty (Table 4) and filled with calcite seed (Table 5) shows that the absence of calcite seed, at least at the higher supersaturations, did not appear to reduce the removal rate of calcium. Unfortunately the changing operational conditions at FP10 and then moving to FP2 makes it difficult to adequately compare the results between the experiments.

The complexity of the calcite kinetics and the results obtained in this study suggest that field experiments, where the control over all parameters is difficult, may not be successful. Future work will determine whether the calcite is depositing on the seed and then the experiments will be extended to higher temperatures to obtain rate data, which can be applied to geothermal conditions.

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