Proceedings Ninth Workshop Geothermal Reservoir Engineering
Stanford University, Stanford, California, December 1983
SGP-TR-74

DISPOSAL OF FLASHED BRINE DOSED WITH $CaCO_3$ SCALE INHIBITOR: WHAT HAPPENS WHEN THE INHIBITOR IS EXHAUSTED?

D. E. MICHELS
REPUBLIC GEOTHERMAL, INC.

in cooperation with

EG&G, IDAHO, INC.,
AND
UNIVERSITY OF UTAH RESEARCH INSTITUTE

ABSTRACT

A freshly flashed geothermal liquid, previously dosed with inhibitor and supersaturated with calcite was injected into another well where it displaced an unflashed counterpart of itself around the wellbore. Back-production of the injectate, and subsequently the native fluid, has yielded data for the rate that a scale inhibitor is degraded after injection. The circumstance also displays a novel mechanism whereby two fluids that do not physically mix nevertheless react with one another through the reservoir rock's serving a role of intermediary. The results have been further interpreted to conclude that in some circumstances a short lifetime for the scale inhibitor is not necessarily a problem for long-term injection.

INTRODUCTION

Commercialization of a geothermal resource requires that several different perspectives be pursued in regard to what happens when the reservoir fluids are moved around by production and disposal. Emphasis on reservoir management via hydraulic principles currently tends to dominate the issue despite examples where permeability changes are due to chemical reactions of injected fluids, mainly involving silica. Although $CaCO_3$ deposition has generally been regarded as a production problem, successful inhibitors displace that concern to the context of injection. It is that aspect of $CaCO_3$ deposition which is addressed in this report.

Flashed brine, dosed with inhibitor to retard deposition of $CaCO_3$ is, nevertheless, thermodynamically poised to deposit it. Eventually the scale inhibitor may be overcome. For example, an effective lifetime of less than 14 hours was indicated for one inhibitor. Consequences to the reservoir which receives the fluid apparently have not been previously explored. However, Huff-Puff tests (monitored backflow of injected tracers), carried out at East Mesa in the summer of 1983, have provided a starting point for addressing the questions.

Geothermal liquid for the 1983 Huff-Puff tests was produced by natural flow from a commercial-quality well (No. 38-30) at East Mesa. Although the liquid was available at the wellhead in an unflashed condition, the overall system required that steam flashing be allowed. Such flashing activates the $CaCO_3$ scale deposition reactions, hence scale inhibitor was added, before the flash.

Since the functional mechanism of the inhibitor does not affect the thermodynamic drive for scale deposition, one should anticipate deposition whenever the residual inhibitor in the brine diminishes to below a critical minimum concentration. Although the inhibitor has long-term stability at the temperature of flashed brine, its stability at rock temperatures in the injection zone is in question. Additionally, the large rock surface area of the injection zone may sorb some inhibitor from the injectate. Furthermore, a slow, but finite overgrowth of $CaCO_3$ on "inhibited" crystals also consumes some of the inhibitor. There may be other factors including some which intervene to limit deposition.

The engineering questions raised by this eventuality are: (1) How far is the fluid from the wellbore when the deposition occurs; (2) how much $CaCO_3$ will deposit compared to available space in the rock's porosity; and (3) what factors may limit deposition.

Huff-Puff experiments provide a means for direct measurement of the time involved with decay/degradation of the inhibitor's function in the real context of a receiver well. More significantly, these experiments have also provided insights about water-water reactions between the injectate and native fluid. We have obtained additional implications about chemical reactions between the reservoir rock and the injectate and also about what happens when native fluid returns to rocks that have previously reacted with injectate.

The present experimental results deserve to be viewed at two levels. Firstly, the data are site-specific and reflect an early attempt to discover what sorts of things can be learned. These are experiments in the truest sense, in that the eventual outcome was predicted only vaguely at the start.

Secondly, the experiments identify a new class of studies that yield important data not provided by any counterparts. These new data are complementary, without being redundant, to more traditional kinds of information in the issue of resource evaluation and reservoir management.

EXPERIMENTAL

Two test Wells, 56-30 and 56-19, and the supply well 38-30, were used in the overall program, but this report is limited to a test where fluid from 38-30 was dosed with scale inhibitor, allowed to flash, and separated liquid was then dosed with tracers and pumped into 56-30. The amount injected was not sufficient to enable a breakthrough into 38-30.

After injection, the fluid was allowed to rest there for 12 hours before back-production began. Back-production was made at the same rate as injection, but lasted longer, so that nearly five times the injected volume was removed. The injected volume (IV) constitutes a natural unit of volume when describing the results of these experiments.

During back-production, many liquid samples were collected to quantify the behavior of tracers, both added and natural. Several other physical measurements were made also, but this report is limited to selected chemical results and fluid volumes.

For the overall experimental program the calcium content in the supply liquid was about 7.0± 0.1 ppm before flashing and about 6± 1ppm after flashing when inhibitor was present. Table 1 shows compositions for the fluids involved. All inhibitors used were incompletely effective within the space of the surface equipment (this aspect will be covered in a separate report). Without inhibitor, the calcium content of flashed brine was about 2.0 ± 0.5 ppm.

The calcium serves as a tracer of the injectate's reactivity, hence also of the inhibitors effectiveness. Inhibited liquid shows a loss of calcium from its concentration at the time of injection to a lower concentration characteristic of uninhibited liquid.

Test 3 provides the subject for this report. It involved 11.5 hours of injection of inhibited, flashed liquid from 38-30 into 56-30 at a rate of 300 gpm (0.78 million liters total injected volume). The injectate was also dosed with a level increment of chloride intended to track the nature of the mixing front. After the 12-hour quiescence, 56-30 was back-produced at a rate of 300 gpm and samples were collected for chemical analysis.

Samples were taken from the wellhead through a probe that reached into the mainstream flow. Liquid entering the probe passed, without flashing, through a stainless steel tubing formed into a coil. The assembly was cooled by immersion in cool water. A valve downstream from the cooling coil controlled the flow. The liquid sample was then collected, briefly open to the atmosphere, into a glass vial with screw cap. The calcium contents of samples collected this way are stable. Samples were analyzed one to 20 hours later using atomic absorption calibrated with standards.

Results are shown in Figure 1 where the ordinate X/X_0 represents a normalized calcium or chloride concentration. Specifically, the observed concentration X, in a sample is divided by the concentration in unaltered native fluid X_0.

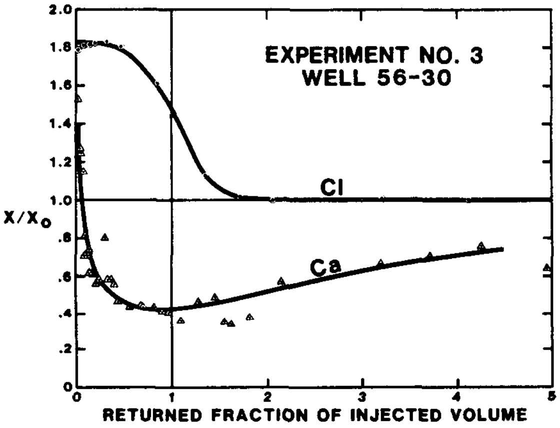

FIGURE 1. CALCIUM AND CHLORIDE IN BACKFLOW

The chloride concentrations initially exceeded the X_0 values because KCl was added as a level tracer to the injected liquid. The native concentration of calcium in 56-30 is 6.55 ± .08 ppm, based on seven samples collected before Test 3 began. Several features of Figure 1 are worth noting.

1. The chloride returns indicate that unmixed native fluid was obtained by the time two injection volumes had been back-produced; the inflection point for chloride is distinct and near 1 IV.
2. The ordinate function for calcium decreases sharply and remains well below unity throughout all of the back-production. The inflection point is not distinct.
3. The calcium concentration is still small and near its minimum value after back-production of two injection volumes.
4. The overall deficit of calcium in the back-produced liquid is several times the amount that could have been stripped from the original injected liquid.

These results are startling because they show a substantial loss of calcium from native fluid that never mixed with the injectate that must have induced the loss.

DISCUSSION

1. Inhibitor Lifetime

Figure 1 shows that the calcium concentration in samples of returned fluid plunged sharply with the first increments of production. All the samples for which X/X_0 exceeds unity are from "injectate" that remained in the wellbore through the 12-hour hiatus between injection and back-production. These large values are taken to indicate dissolution of calcium-containing minerals from the wellbore. This is extraneous to the issue of water-rock reaction or stability of inhibitor in the reservoir and will not be discussed further.

Values of X/X_0 less the unity all pertain to the fluid which was exposed to reservoir rocks. The minimum values of about 0.4 correspond to actual calcium concentrations of about 2 ppm. This is the level expected for calcium in flashed brine which has not been dosed with inhibitor. Accordingly, such results indicate complete exhaustion of the inhibitor.

The time involved to reach exhaustion is indicated by the minimum in the trend line of Figure 1, namely, a return of about 0.8 IV. (Notwithstanding the scatter of data and a few lower values of X/X_0 between IV's of 1 and 2.) This is about 9.2 hours after start of backflow and about 21.2 hours after injection ceased. By symmetry the fluid involved with the minimum X/X_0 was dosed with inhibitor 9.2 hours before injection ceased, thus, the total time to complete exhaustion is about 30 hours.

On the other hand, even the first sample of fluid which contacted rock shows a loss of calcium. Since that sample was taken only about one hour into backflow, we can conclude that the inhibitor was detectably degraded in less than 14 hours.

A more sophisticated approach presumes that the inhibitor function degrades in the sense of a first order reaction. To measure this, one may plot X/X_0 vs IV on semi-log paper and examine it for linearity. Figure 2 shows that the 17 data points between 0.08 and 0.7 IV do indeed suggest linearity. Smaller IV values can be excluded because they involve fluid returning only from the wellbore; larger volumes can be excluded because a sensitivity limit has apparently been reached where the inhibitor's effect, if any, can no longer be resolved by the analytical results.

The slope of a least squares fitted line to those data yield a value of 0.65 IV for the half-volume, the amount of fluid production involved with a two-fold change in X/X_0.

Since the value of 0.0 IV belongs to fluid dosed 12 hours earlier and 1.0 IV is obtained 36 hours after dosing with inhibitor, a time half-life for the inhibitor of 15.7 hours can be deduced.

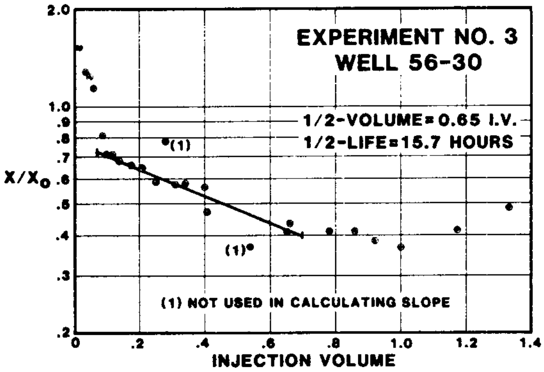

FIGURE 2. NORMALIZED CONCENTRATION OF CALCIUM vs. RETURNED FRACTION OF INJECTION VOLUME

This appears to be reasonable, considering that inhibitor dosage was nominally 3 ppm and that concentrations above about 1 ppm are without significant effect. In principle, a half-life of 15.7 hours would reduce 3 ppm of inhibitor to the 1 ppm threshold in about 25 hours. Thereafter, continued degradation of inhibitor would be discernible through the variable analytical results for residual calcium. That calculated 25-hour delay is larger than the apparent 14 hour delay described earlier, but not unreasonably so because neither the 3 ppm nor 1 ppm nominal values are precisely identified for this experiment. Also, the scatter of data in Figure 2 yields some uncertainty for the half-life calculated above.

The concept of half-life for the inhibitor, using units of time, might be appropriate for a degradation mechanism due to temperature instabilities. However, the maximum temperatures in 56-30 are approximately 175°C for which the inhibitors have elsewhere shown good stability in seawater-like salinities. Thus, unless there is a synergistic effect between temperature and some factor in the reservoir rocks, exposure temperature may be disregarded. Therefore, it would seem useful to interpret the half-life from Figure 2 in units of volume. Accordingly it would then be plausible to consider the degradation as being due to a water-rock reaction, perhaps akin to sorption, not readily reversible, but involving amounts of liquid on the order of the injection volume. This conclusion will be considered later in regard to where the calcium deposits.

2. Water-Rock Reaction

If the reactive potential of the injected liquid were truly transferred to the native fluid, beyond the extent to which they were physically mixed, then an intermediary must have been involved. The intermediary in this case would appear to be the rocks of the reservoir.

The nature of an intermediary is to respond in a chemically reversible way, in this case with a reaction that can also participate with the calcite deposition reaction. This statement is not intended to imply that the rocks react directly with calcium or calcium carbonate. Rather, it is proposed here that the acid-base exchange capacity of the rocks, which exists mainly in the clays, participates with the acid-base properties of the injectate and native fluid.

Specifically, the pH of native fluid, charged as it is with CO_2, and at an elevated temperature, is much lower than the pH of the flashed counterpart that has not only lost its free CO_2, but also carries significant $CO_3^=$ due to decomposition of HCO_3^- according to Equation 1.

$$2HCO_3^- \rightarrow H_2O + CO_2 + CO_3^= \qquad (1)$$

In the case at hand, pH in the native reservoir condition is calculated to be 6.7 whereas, pH of the flashed brine at the injection temperature is on the order of 9.0. The base capacity of the flashed brine is about 0.8 milliequivalents per kilogram (meq/kg) to pH's near 7. By contrast, the calcium content of native fluid is about 0.33 meq/kg.

The reservoir rocks, on the other hand, contain clays in variable amounts up to a few percent by weight. Of course, the active part of the injection zone must be a clay-poor region, but none of the East Mesa production zones are considered clay-free.

The acid-base exchange capacity of the clays there have not been measured, but published values for kaolinite between pH 6.7 and 9 suggest that 0.2 meq per gram of clay would be a reasonable presumption. If we further presume five weight percent clay in the reservoir sandstone and a 30 percent porosity, the rock's acid-base capacity would be 19 meq/liter of rock volume. This is about 80 times the acid-base capacity of flashed brine that could fill the porosity.

Two concepts derive from this approximation. The rock's over-capacity to react with injectate assures that the injection front which displaces native fluid will be largely equilibrated with the rock before much fluid-fluid mixing can occur. Since we would expect that two fluids in equilibrium with the same rock are also in equilibrium with each other, little water-water reaction can be expected as the injectate displaces native fluid. Furthermore, it appears that a unit of injectate will lose its thermodynamic drive to deposit calcite due to chemical equilibration with the rock and without deposition of calcite.

Secondly, the chemical base capacity carried by the injectate will be consumed near the wellbore. The estimated 80:1 capacity ratio suggests that the 0.78 million liters of injectate were titrated by only 9.8 cubic meters of rock. Since only about 120 meters of wellbore length are involved with significant production, the nominal depth of water-rock reaction, assuming radial symmetry, is about 0.090 meters. A somewhat larger estimate of chemical penetration depth can be derived for part of the well by noting that about 70 percent of the reservoir flow in 56-30 is associated with a 40-meter long interval of wellbore. For that zone, depth of water-rock reaction would be 0.154 meters.

By comparison, the total fluid injected into the rocks would involve 2,600 cubic meters of rock volume with radial penetrations corresponding to 2.6 and 3.8 meters, respectively.

Thus, although a zone of transition between unaffected rock and totally reacted rock may be expected for several reasons, its practical width would seem to be small relative to the gross depth of fluid penetration. Therefore, the calcium burden in the injectate would appear to soon become stable during injection, irrespective of whether inhibitor remained present.

For long-term injection, the vicinity of the wellbore expandingly acquires the chemical and thermal nature of the injectate. Of the several modes of inhibitor failure, all except overgrowth would become suppressed, trending toward a maximum lifetime for the inhibitor's function. That would be timely since for longer term injection, the distance from wellbore to rock that still could neutralize the calcite deposition potential will become greater. In this East Mesa example, the possibility of inhibitor exhaustion appears to have a negligible consequence for long-term injectability.

3. Calcium Loss to the Rocks

There is a great contrast between the acid-base reactivity, which was neutralized in a rock volume estimated to be only 1/80th of the injection volume, and the 0.65 IV half-volume for the inhibitor. This suggests that the inhibitor moves much further through the rock than do the chemical base properties of the injectate.

Returning to Figure 2, the space between the plot for calcium and the line $X/X_0 = 1$ represents calcium lost from the liquids. The portion of that space to the right side of one IV, or more precisely, to the right of a vertical line through the inflection point in the chloride tracer curve, represents calcium lost from the native fluid.

The chemical equivalence of that calcium can be estimated by extrapolating the calcium recovery curve toward the right where it intersects $X/X_0 = 1$. Unfortunately, the data are a bit scattered, so only the simplest extrapolation will be considered at this time.

A liner least squares fit to the last 11 data yields $X/X_0 = 1$ at 7.1 IV.

The average calcium deficit is thereby calculable as 2.3 ppm. The total amount of calcium lost by the 7.1 IV is 636 chemical equivalents of calcium:

$$(780000\ \text{l/IV})\left(\frac{2.3 \times 2}{40.1}\ \text{meq/l}\right)(7.1\ \text{IV}) = 636\ \text{eq}$$

By comparison, the base capacity of the injected brine is 624 chemical equivalents.

$$(780000\ \text{l/IV})(.80\ \text{meq/l})(\text{IV}) = 624\ \text{eq}$$

This correspondence appears excellent, showing that the Huff-Puff techniques can yield quantitative results about water-rock interactions.

Significantly, the amount of calcite which deposits depends on the rock's base exchange capacity not on the volume of injectate or back-production.

The possibility of clogging the rock's porous space by this deposition mechanism appears slight. Using the approximation of rock reactivity applied earlier, namely 19 meq/l and 30 percent porosity, one can calculate that each liter of rock volume can become dosed with 0.95 gram of calcite. That amounts to about 0.35 ml of new calcite per 300 ml of porosity. Even accepting that deposition of calcite in the narrow throats which connect nodes of porosity has effects on permeability far beyond the volume proportions, it is difficult to expect a substantial effect. A laboratory verification of this matter would be simple to set up, however.

SUMMARY

The Huff-Puff experimental method has provided grist for several issues about how injected geothermal fluids behave in the reservoir rocks. Some data and estimates are provided for the survivability of an inhibitor, the fate of calcium that might be suspected to yield scale, the mixing of injectate with native fluid, and the nature of the water-rock reactions, including deposition of calcite in the porosity.

Significantly, some results are nonintuitive. It appears easy to design subsequent experiments for both field and laboratory, to yield still better tests of concepts.

The most significant result at this stage is that Huff-Puff experiments, as a class, are clearly powerful, experimental tools for applied geothermal engineering.

TABLE 1

NOMINAL LIQUID COMPOSITIONS*
ppm BY WEIGHT

	SUPPLY WELL 38-30		TEST WELL 56-30
COMPONENT	PRE-FLASH	POST-FLASH	PRE-FLASH
Sodium	630	698	597
Potassium	25	27	25
Calcium	7	2.0,6.0**	6.1
Ammonium	4.0	0.9	6***
Strontium	2.7	3.0	0.8
Lithium	0.6	0.7	0.3
Magnesium	0.2	0.2	-
Chloride	533	586	505
HCO_3	600	585	596
CO_3	0.03***	45***	0.03***
Sulfate	172	190	177
Boron	1.4	1.5	0.8
Fluoride	3.0	3.3	2.4
Silica	193	210	180
CO_2	440	1	430
Temp. °C	170	94****	165

* Electrically balanced based on several analyses

** Without and with $CaCO_3$ scale inhibitor added pre-flash

*** Estimated

**** Upon injection into 56-30