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CARBONATE SCALE INHIBITION IN REPUBLIC'S EAST MESA GEOTHERMAL OPERATIONS

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ABSTRACT

Republic Geothermal, Inc., Lawrence Berkeley Laboratory and Monsanto Chemical Company have jointly funded a study by Vetter Research to evaluate and control carbonate scale in geothermal surface production and injection equipment. Republic's East Mesa geothermal field was chosen for the field experiments because of the utilization of down-hole pumps in this field. Pumping prevents carbonate scale formation within the producing wellbore and shifts the entire scale problem into the surface equipment. Field experiments designed to control the scale problem consisted of pumping the wells for extended periods of time and adding a phosphonate scale inhibitor (Monsanto's Dequest 2060) at the wellhead. Fluid flow was directed through a test loop which simulated a flash cycle power plant. It was found that all carbonate scales can be avoided at a cost of less than 0.3 mills/KWhr in a planned 64 MW power plant. The critical range of scale inhibitor concentration is very small. Field studies were backed up by laboratory studies using the same inhibitor labeled with radioactive carbon (C-14). The pseudo-scale collected in the field was analyzed and attempts were made to duplicate the field results in the laboratory.

INTRODUCTION

Lawrence Berkeley Laboratories (LBL) manages a comprehensive program concerned with the development of geothermal resources for the United States Department of Energy, Division of Geothermal Energy (DOE/DGE). They are therefore interested in research and field methods leading to an effective control of scale in geothermal operations. Republic Geothermal, Inc. (RGI), a geothermal operator in East Mesa, California, was confronted with a calcium carbonate ($CaCO_3$) scale problem. Monsanto Chemical Company (MCC) is a major manufacturer of chemical scale inhibitors and wanted to evaluate the effectiveness of its products in a geothermal field. In late 1978, a contract was awarded to Vetter Research (VR) to continue studies begun by RGI and MCC on the feasibility of effective scale control in East Mesa with inhibitors. This work was funded by LBL (DOE), RGI and MCC.

Two series of inhibitor tests were performed. Both tests had the same basic objective: to prevent carbonate scale formation in the field at a reasonable cost without generating problems due to undesired side effects caused by the addition of the inhibitor. The inhibitor used was Dequest 2060, a Monsanto chemical.

The first field test at well #16-29 was conducted between March 25, 1978 and April 7, 1978. This test was prematurely terminated because of a down-hole pump failure. To finish the project, a new scale inhibition field test at well #56-30 was conducted between February 8, 1979 and March 6, 1979. This latter test completed RGI's program on scale inhibitor evaluation because the carbonate scale problems at East Mesa were solved in a technically and economically feasible way.

CARBONATE SCALE PREVENTION IN SURFACE OPERATIONS AT EAST MESA

RGI had an "ideal" candidate for the planned field tests. Its wells in East Mesa have a fairly low temperature (320-340°F) and are produced by down-hole pumping. This production method prevents the dissolved CO_2 from breaking out of solution within the wellbore. This, in turn, prevents scale from forming within the wellbore and shifts the location of the entire scale problem into the surface equipment where it is more accessible. In a way, the surface equipment becomes an accessible extension of the wellbore. This set-up is ideally suited for experiments of this nature. The shift of the CO_2 flash zones due to the installed down-hole pumps allow inhibitor and other experiments in inexpensive and conveniently operatable test loops on the surface.

In addition to the foregoing advantages, the brines produced at East Mesa have four extremely important favorable properties for these types of experiments:

1) The formation of carbonate scales is significant. For example, a flow rate of 650,000 lbs/hr can deposit as much as 1.5 inches of scale at the flash point in less than 100 hours of flow. Thus, scale inhibitor efficiencies can be studied in fairly short experiment times.

2) The calcium, magnesium and iron content of the brines is very low; thus, no serious interference between the inhibitor molecules and divalent ions (pseudo-scale) are expected.

3) The low iron content does not act as an inhibitor poison.

4) The composition of the reservoir brine is easy to determine without the need for lengthy and, possibly, wrong calculations because no interfering scale is formed downhole.

BASE LINE TEST WITHOUT INJECTION OF SCALE INHIBITOR AT WELL NO. 16-29

During this first test period, no inhibitor was injected. This was done in order to determine the base line data, namely, the deposition rates of the carbonate scale in the absence of an inhibitor. The test loop (Figure 1) was operated for 92 hours and 45 minutes and then shut down for visual inspection and collection of samples.

The loop incorporated orifice plates of predetermined sizes to control the pressure and temperature within the four test spools. The orifice sizes were 2.5, 3.5, 5.0 and 7.0 inches. The average flow rate was 375,000 lbs/hr. An effort was made to maintain constant conditions during the test. No appreciable steam flash was encountered until downstream of the first spool. On the other hand, CO_2 flashing was definitely experienced at all locations within the test loop. This was confirmed by actual measurements and theoretical calculations.

After shutting down the test loop, it was taken apart and each spool and orifice plate was thoroughly examined visually, the thickness of the scale at various points in the loop was measured, and samples were taken to be analyzed for their composition in the laboratory.

THE EXPERIMENTAL SET-UP

The set-up of the inhibitor injection equipment at the wellsite was very similar to that used for previous acid injection experiments. Two 50-gallon plastic containers were used as the storage for the diluted inhibitor. A dilution of one part inhibitor to three parts produced water was used. A Pulsafeeder pump model 7120 was used for the injection. A stainless steel filter was mounted in the suction line to prevent a failure of the ball check valves in the suction and discharge. A back pressure regulator in the discharge line was installed and set at 500 psig to achieve constant flow conditions. The pump rate was monitored through a three-liter calibrated lucite vessel installed in the suction line of the pump. This lucite vessel was also connected to the 50-gallon drums and could easily be filled through a valve manifold in the suction line. A very constant pump rate was necessary to obtain a constant injection rate of the inhibitor. The injection nipple was installed approximately 10 feet downstream of the wellhead.

SCALE DEPOSITION RATE

The rate of scale formation in the test loop was significant. An average of 0.22 inches was found throughout the length of the test loop. The total length of the eight inch diameter pipr (OD) of the scaled portion of the loop is approxinately 54 ft. with an additional 25 ft. from the loop to the separator. A rough calculation shows that the total volume of deposited scale was approximately 3,360 cubic inches in the loop alone. A total of 3.48×10^7 pounds of cumulative flow was produced during this test. This volume is equivalent to 4.64×10^6 gallons of water. This means each liter of this water (total flow) produced has deposited 3.1×10^{-3} cm^3 or approximately 6.5 mg of carbonate scale in the test loop assuming a specific weight of only 2.1.

The amount of scale deposited per liter of water is fairly small, but illustrates a common problem in most geothermal operations. The detrimental effects of scale formation may be very small per volume unit of produced water. However, the overall effects become large due to the extremely large amounts of fluid produced in power generating operations. A 64 Mw power plant at East Mesa requires approximately 1.85×10^6 liters of total flow per hour. This flow would deposit 4.55×10^4 grams of approximately 100 pounds of carbonate per hour.

THE DEQUEST 2060 INJECTION

The test loop was cleaned of previously deposited scale by acidizing. Dequest 2060 injection was started on April 1, 1978. The rate of injection was adjusted to the predetermined Dequest 2060 concentration of 10 µl/liter in the water while the total flow was directed through the bypass line, i.e., not through the test loop. The test loop was opened and run for 122.5 hours under conditions similar to those described for the base run. The loop was then dissassembled, visually inspected for scale deposits and samples of deposited solids were taken. No carbonate scale was found. A short interval of a reaction product pseudo-scale (less than 1/8 inch thick) consisted of calcium phosphonate. A second test using an injection rate of 2.5 µl Dequest 2060 per liter of brine was abandoned because of a downhole pump failure.

INHIBITOR TEST AT WELL NO. 56-30

A second scale inhibitor injection test was performed at well #56-30. The chemical used in this new series of tests was again Monsanto's Dequest 2060. However, a dual test facility with a 12 inch test loop was used. Two separators, each capable of handling about 400,000 lbs/hr, were required because of the large flow rate (averaging 722,000 lbs/hr) employed during this test.

The analytical methods used to analyze the liquid and solid samples were different from those previously employed. Instead of using AA methods, an ARL ICAP spectrometer (inductively coupled argon plasma) was used for the analyses of the liquids and solids. This instrument allowed the simultaneous determination of 36 elements in each sample. Thus, major and minor components of a sample cannot easily escape detection and previously unknown components were automatically determined. For example, it was found that the scale was not only $CaCO_3$ with a small amount of SiO_2 as previously indicated by AA and X-ray diffraction analyses, but consisted of a mixture of calcium, strontium, barium and iron carbonates and SiO_2, with $CaCO_3$ being the major component.

BASE LINE TEST

The scale deposition rates in the various spools during the baseline run at well #56-30 were similar to those encountered during the base line test of the previous scale inhibition test work at well #16-29. Even though the thickness of the scale deposits was larger, the scaling rates per volume unit of flowing brine was approximately the same in both tests.

INHIBITOR INJECTION AT 7.5, 2.0 AND 1.0 µl DEQUEST 2060 PER LITER

The injection of 7.5 µl Dequest 2060 per liter of brine (total fluid flow) resulted in the total inhibition of carbonate scale. However, the phosphonate pseudo-scale was formed again. The inhibitor injection rate of 2.0 µl Dequest 2060 per liter of brine showed neither carbonate scale nor pseudo-scale. Thus, the maximum allowable inhibitor concentration lies between 2.0 and 7.5 µl Dequest 2060 per liter of brine. A final run was made with 1.0 µl Dequest 2060 per liter of brine. The result was also an absolutely scale free system at all pressures and temperatures. This latter rate is the equivalent in cost of 0.33 mills per KWhr for a commercial scale operation. Inhibitor injection must be considered an economical solution to the scale problems encountered in RGI's East Mesa field.

LABORATORY TESTS WITH RADIOACTIVELY LABELED DEQUEST 2060

Calcium ions and phosphonate inhibitors may form fairly insoluble calcium salts. These precipitating calcium salts of the inhibitors act precisely like scale in the field. As previously noted, these artificial scale deposits are termed "pseudo-scale".

Subsequent to the well #16-29 tests, a series of laboratory experiments were carried out prior to and during the additional inhibitor field tests funded by DOE (DGE) at well #56-30. The objective of these laboratory experiments was to determine the solubility of Dequest 2060 in the presence of calcium under conditions simulating some of the pressures, brine compositions and pH values expected to be encountered during the field work.

The critical part of these laboratory tests was the utilization of Dequest 2060 labeled with C-14. This radioactively labeled compound allowed the performance of solubility measurements at extremely low concentration levels. This was necessary because conventional analytical methods for determining the solubility products of the calcium phosphonates with the required accuracy at the extremely low concentration levels (e.g., 1-10 µl Dequest 2060 per liter brine) always failed in the past. Most of these analytical problems can be overcome by using C-14 labeled inhibitors and a very sensitive liquid scintillation spectrometer.

CONCLUSIONS AND SUMMARY

1) Scale deposition was prevented throughout the East Mesa test system by injection of 1.0 µl Dequest 2060 per liter of total flow. This is an important milestone in the area of scale handling in geothermal operations, and the data obtained during this test program are very encouraging. It is now proven that chemical inhibition of $CaCO_3$ scale formation can be achieved at temperatures up to at least 320°F.

2) Pseudo-scale (calcium phosphonate) formed at concentrations of greater than 7.5 µl Dequest 2060 per liter of brine. Thus, the application of the Dequest 2060 compound must be carefully tailored to the water:

    a) Too much chemical will cause formation of a pseudo-scale (calcium phosphonate); and

    b) Too little chemical will most likely not result in efficient scale inhibition.

3) New instrumentation used during the test at well #56-30 showed that while the scale at East Mesa is predominantly calcium carbonate, there are significant components of strontium, barium, iron and magnesium carbonates.

4) The pseudo-scale occurred in a totally unexpected location, i.e., at temperatures between 270°F and 320°F, and not at lower temperatures. This suggests that the calcium salt of the phosphonate has a "reversed" solubility like, e.g., anhydrite. This information must be carefully considered in future applications of Dequest 2060, especially for downhole applications and for waters having a high calcium content.

5) Even though the solubility product of the calcium phosphonate in East Mesa water at 320°F is very low and is exceeded at an injection of 7.5 µl Dequest 2060 per liter of brine, it is still high enough to ensure proper scale inhibition in the presence of pseudo-scale. This is encouraging information for possible formation squeezes with Dequest 2060 despite the formation of a calcium salt of the inhibitor. The precipitated calcium phosphonate will be redissolved by the reservoir fluid and will still act as a usable inhibitor. Thus, the formation of a calcium salt of the inhibitor in the reservoir may

not be as detrimental as normally assumed.

6) The test data show that scale inhibition using a chemical like Dequest 2060 can probably be more economical than any procedure using acids. Scale control at East Mesa using this method will most likely add less than 0.3 mills/KWhr to the cost of electricity.

7) Significant plugging of the injection well was experienced during the inhibitor test work at well #16-29 even though the carbonate scale was eliminated in the test loop. Premature termination of this test and analytical problems in the lab prevented identification of the plugging material. Little or no demonstrable plugging of the injector was experienced during the inhibitor injection tests at well #56-30. Filter analyses in the latter test showed that very little phosphonate containing particles penetrated the filter elements. The majority of the particles in the filter elements contained carbonates. It is therefore assumed that carbonate particles caused the injector plugging during the test at well #16-29.

8) Any application of scale inhibitors can cause the formation of pseudo-scale and/or injector plugging by scale particles. The inhibitor used should be preferably a "threshold" type inhibitor such as Dequest 2060 and not an inhibitor which prevents the adherence of the precipitated material without preventing the precipitation per se.

9) Laboratory tests with radioactive C-14 labeled Dequest 2060 showed an extremely complicated precipitation behavior of the compound. The critical precipitations of calcium phosphonate depend upon the: (a) temperature; (b) brine composition, particularly the calcium content; (c) pH; and (d) Dequest 2060 concentration.

10) The amount of calcium phosphonate precipitation in artificial brines created in the laboratory could be measured only at high calcium and Dequest 2060 concentrations. Using the actual field brine showed precipitations at fairly low calcium concentrations. It is not entirely clear why calcium phosphonate precipitates from the field brine at low calcium concentrations, while the artificial brines show precipitations only at much higher calcium concentrations. However, it was found that NaCl in the aqueous fluid enhances the precipitations of calcium phosphonate.

FIGURE 1

WELL TEST FACILITY