Evaluations of Various Organic Inhibitors in Controlling Silica Fouling At the CFE Cerro Prieto Geothermal Field

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ABSTRACT

At the CFE geothermal complex in Cerro Prieto, México, fouling by silica represents a costly problem to the efficient production of steam. From the producing zones, through areas critical to the release and separation of steam from the geothermal brine, to the discharge canals and lagoons, silica deposition reduces the operating efficiency of the site, and increases the costs required to maintain the level of steam generation from the field's 150 wells.

In an effort to minimize the degree of silica fouling in the complex's geothermal fluid handling equipment, as well as to reduce the associated production well downtime and maintenance and cleaning costs, various organic inhibitors were tested for their ability to control silica deposition.

This paper reports on the ongoing collaborative efforts of CFE and Ashland Specialty Chemical Company in evaluating several of these antiscalant technologies in some of the production wells in the Cerro Prieto geothermal field. The results thus far are quite promising in that it is quite apparent that 100% inhibition of silica fouling of the surface equipment can be achieved, at treatment levels that represent significant savings in the operating costs of the site. Additionally, the possibilities of both increased steam and binary heat recovery, as well as increased well injection, all of which would further improve the economics of the Cerro Prieto operation, appear more feasible as silica deposition can be reduced and even eliminated.

Introduction

The Cerro Prieto geothermal field, located in the Mexicali Valley in the Mexican state of Baja California, 30 km south of the border with US state of California, celebrates its 30th anniversary of electrical production this year. Encompassing an area of approximately 14 km^2, Cerro Prieto is the second largest geothermal operation in the world. It is owned and operated by the government-run national company, Comisión Federal de Electricidad, CFE.

The Cerro Prieto geothermal field started producing electricity in April, 1973, in the area known as Cerro Prieto 1 (CP-1), with a generating unit of 37.5 MW. Today, there are four power plants (CP-1 through CP-4), with thirteen generating units, and a combined total electrical output of 720 MW. With much of the formation reservoir still yielding conditions as high as 200 bars pressure and 300°C temperature, the Cerro Prieto geothermal field has been, and will continue to be, a significant, reliable source of electricity to the Baja California power grid.

Currently, approximately 250 wells have been drilled since exploration of the geothermal reservoir began; of these, there are presently some 150 wells in production. Thirteen (13) wells are being used for spent brine reinjection, as part of an ongoing feasibility project; several of the remaining wells are used for monitoring the conditions of the reservoir. The continuous monitoring of the reservoir over the past 30 years, examining pressures, temperatures, and brine characteristics, indicates that the Cerro Prieto field can maintain, and perhaps increase, its current capacity of 720 MW, at least until the year 2030.

Inherent to maintaining capacity is controlling the operating costs associated with producing steam and generating electricity. Annually, nearly 20% of the geothermal field's produced steam, or approximately 1,200 tons per hour, needs to be replaced, primarily due to silica in the reservoir and its subsequent fouling within the production zone. On the average, 10-15 new wells are drilled and 15-20 wells are cleaned or reworked each year, because of silica, to meet the steam requirements of the site. Silica not only presents a problem in the geothermal reservoir, but also on the surface in much of the brine handling and discharge equipment. At Cerro Prieto, surface fouling by silica is prevalent in between 15-25% of the producing wells in CP-2, CP-3, and CP-4. Some of the fouling is minimal, and is controlled in many production wells by maintaining a high separation pressure at the well and minimizing the degree of flashing of the geothermal brine into steam. In this manner, the fluid can remain in a less-than-saturated condition; i.e., at a Silica Saturation Index (SSI) less than 1.0. In approximately 10% of the production wells at Cerro Prieto, the silica problem is much more severe, and SSI values in these well operations run between 1.5-2.2. In these systems, fluid handling equipment and pipelines need to be taken out of service and mechanically cleaned, perhaps as frequently as once per month. Additionally, there is continuous manual removal of silica scale from the silencer discharge canals that permeate the complex and are used to transfer the spent brine to the surface ponds, where additional silica is periodically excavated and removed. Currently, nearly 10,000 tons per hour of spent brine are sent to the ponds, yielding more than 8 tons per hour of silica waste that is precipitating throughout the system.

During its history, Cerro Prieto has examined various means to alleviate its silica problems. In 1980, CFE initiated a study with the United States Department of Energy (USDOE) to explore the possibilities of blending the waste silica with cement for road surfacing, or with other additives to make highly insulating bricks. To date, this study is still in an experimental stage.

Much more recently, in the 1990's, several proprietary organic materials were evaluated, both in the laboratory and in the field at Cerro Prieto, for their ability to reduce silica deposition. Several of these compounds were found to actually enhance scale formation rather than retard it; only one product, GPC-129, from Betz Company, was found to show some effectiveness in reducing silica fouling. However, the limited efficacy of the product – approximately 20% - resulted in no further action being taken by CFE.

Thus, the problem of silica deposition and excess silica production still plague both the operation and generation of electricity at Cerro Prieto, and may pose a potential hazard to the environment in the future, should there be an inability to dispose of all the waste silica that is produced.

As will be described in the remainder of this paper, CFE Cerro Prieto, with the assistance of Ashland Specialty Chemical Company and Ashland Chemical de México, has performed several field evaluations during the past 18 months that show promise as a solution to the problem of silica fouling. The successful applications of new, proprietary scale control additives represent an exciting opportunity for CFE Cerro Prieto to immediately benefit from reduced maintenance costs, in that silica is not fouling the surface equipment and discharge canals.

Mechanism of Silica Deposit Formation

In a geothermal operation, the formation of silica and siliceous deposits follows a complex process, related to brine temperature, pH, salinity, nature and level of metal ion contaminants, and the flowrate of the brine through the system. How these parameters affect both the nature of the deposit and its rate of formation are described below.

In a typical geothermal operation, the temperature of the brine decreases as it passes through the surface equipment installation. Silica is less soluble at lower temperatures; as steam is flashed and the brine is cooled, it becomes saturated and then supersaturated with silica. During these stages, dissolved monomers of silica ($Si(OH)_4$) undergo polymerization to form polysilicic compounds that continue to polymerize and eventually coalesce to form colloids. These colloids agglomerate, and in the process, they can precipitate as amorphous silica scale, or they can interact with various metal ions in the brine, such as calcium, magnesium, and iron, to form siliceous compounds.

The degree of supersaturation greatly influences the process: highly over-saturated brines (e.g., brines with an SSI value near or greater than 2.0) tend to quickly form a less "dense" amorphous silica in the bulk water, while brines with SSI values between 1-2 tend to yield scale that is more dense and tenacious, forms more slowly, and is more apt to contain metal ions in the deposit matrix.

Methods of Silica Deposit Control

Both physical and chemical means have been employed by geothermal operations to minimize, with varying degrees of success, deposits formed by silica and siliceous compounds on their surface equipment.

The most common physical method is to restrict the steam separation to a temperature at which the silica level remains at or below saturation. This is currently being employed in some wells at CFE Cerro Prieto. A drawback here is that more production wells would be required to achieve the full power generation potential of the geothermal brine.

The most prevalent chemical method to prevent silica deposition is through pH modification of the brine, typically after an initial extraction of steam. Lowering the pH to 3-4 with acid (typically, either hydrochloric or sulfuric acid), decreases the rate of silica polymerization quite effectively. Drawbacks of this approach include the hazards in handling and feeding the acid, the increased system corrosion rates associated with the low pH, and the costs of special corrosion-resistant feed equipment and brine handling equipment.

To a lesser extent, a method known as the Crystallizer-Reactor-Clarifier (CRC) Process has been successfully employed to control silica. In this procedure, the brine is actually seeded with fine particulate silica, to promote its precipitation. The precipitated silica is removed through the clarifier; the remaining level of dissolved silica is below saturation, thereby minimizing fouling of downstream equipment. The drawbacks to this process have been the capital and operational costs of the equipment used to precipitate, concentrate, recirculate, and remove the silica.

A third chemical method utilizes organic additives, commonly referred to as "scale inhibitors," "antiscalants," or "antifoulants," to control deposition of silica and siliceous compounds. Treatments of this type that are currently being promoted for the geothermal market usually entail proprietary blends of synthetic polymers, chelants, or sequestrants.

The antiscalant program may be engineered to reduce or eliminate scale through one or more of the following mechanisms: 1) inhibiting the formation of metal silicates, through threshold inhibition; 2) inhibiting the agglomeration of silica, through dispersion; 3) inhibiting the actual polymerization of monomeric silica; 4) inhibiting the adherence of silica and silicate particulates to equipment surfaces, through crystal lattice distortion; 5) extending the solubility of silica and silicates through sequestration; or 6) minimizing the corrosion products, which may serve as binding sites for monomeric and polymeric silica, in the system. The key drawback to this approach has been, until recently, the actual effectiveness of the antiscalants available to the marketplace. As noted earlier, in 1990, CFE Cerro Prieto evaluated many different antiscalant materials available at the time, both in the laboratory and in a field pilot test unit. None of the inhibitors showed any applicable success, and several of them appeared to enhance precipitation of silica versus no brine treatment.

Perhaps a decade ago, a breakthrough was made in silica inhibition in geothermal systems with the development of Geogard[1]® SX scale inhibitor, a proprietary blend of organic polymers, pioneered in a research and field effort between the Philippine National Oil Company – Energy Development Corporation (PNOC-EDC), a geothermal energy producer, of the Philippines, and Biolab Water Additives, a developer and manufacturer of water treatment additives, of the United Kingdom. Geogard SX has successfully prevented the formation of scale in several high silica brine applications of PNOC, and numerous papers have been presented on its excellent performance.

Outside of the Asia Pacific geography, Geogard SX is marketed and promoted as MILLSPERSE[2]® SX antiscalant, by Ashland Specialty Chemical Company, of the United States, a developer and supplier of specialty technologies and programs, including chemical treatment products and services for the geothermal market.

Table 1. Chemical analyses of the brines in the test wells.

Well	Wellhead Pressure, bars / psi	pH	Conductivity mmhos	Sodium ppm	Potassium, ppm	Calcium ppm	Chloride ppm	Silica ppm
E-54	27.6/400	7.83	40,700	8,950	2,375	300	17,370	1,420
427	50/725	8.00	43,000	7,830	2,134	279	15,383	1,070

Field Studies

In 2002, CFE Cerro Prieto, in collaboration with Ashland, began to re-examine the efficacy of silica antiscalant technologies in its geothermal brine. The first production well selected was Well E-54, located in CP-2. Here, the brine in the formation reaches the surface at 550 psi (247°C), and flows at a rate of 75 tons per hour. It passes through both a high pressure (185 psi, 191°C) and a low pressure (55 psi, 142°C) steam separator. The spent brine is then diverted to either of two silencers, which operate at atmospheric pressure (0 psi, 100°C). From either silencer, the brine discharges to a canal, which eventually connects with other discharge canals that flow to a retention pond to allow for suspended silica to eventually settle out.

Deposition of silica has long been a problem in the surface equipment of Well E-54. Typically, deposits begin to form between the first and second stages of steam separation, and are quite prevalent after the second stage. The rate of scale buildup in the 30-cm diameter line leading from the second separator to the silencer has been on the order of 2 cm per month. Mechanical cleaning of the equipment usually occurs two or more times per year, in order to regain unimpeded throughput of the brine and generation of steam and electricity. With two silencers, the well can continuously operate while maintenance work can be performed on the equipment downstream of the second steam separator. Cleaning this separator of deposits is required annually, necessitating a temporary shutdown of the well.

The silica level in the brine has been analyzed to be approximately 1,400 ppm, corresponding to an SSI value of 1.9, and an excess level of silica of about 650 ppm above the saturation point. This excess would polymerize to hard, slightly porous deposits. An analysis of the brine for Well E-54 is included in Table 1.

Four chemical products were evaluated by CFE and Ashland: MILLSPERSE® SX antiscalant, THERMSPERSE[2]® 300 antiscalant, THERMSPERSE 350 antiscalant, and DREWFAX[2]® 269 deposit control agent. As noted, MILLSPERSE SX antiscalant represents technology that has been proven effective for silica control in geothermal wells in the Philippines. The other three products were included in the study to determine if new antiscalant materials developed in recent years for water treatment might show efficacy in the stressful brine conditions, and more importantly, against silica deposition.

The antiscalant feed location selected for the evaluations at Well E-54 was between the first and second steam separators, upstream of the control valve to the second unit. To determine product effectiveness, an actual 4 meter, 30-cm diameter, section of pipe between the low pressure separator and one of the silencers was used as a test spool. This spool was the only section of the pipeline cleaned before each antiscalant trial. Figure 1 shows a schematic of Well E-54, as well as the locations of the inhibitor feedpoint and the test spool.

Initially, a blank (no treatment) was run for 28 days, after which the test spool was examined, photographed, and cleaned. MILLSPERSE SX antiscalant was then injected into the brine at a dosage of 10 ppm, for 28 days. By the fourth day, it was observed that the spent brine leaving the silencer had turned clear,

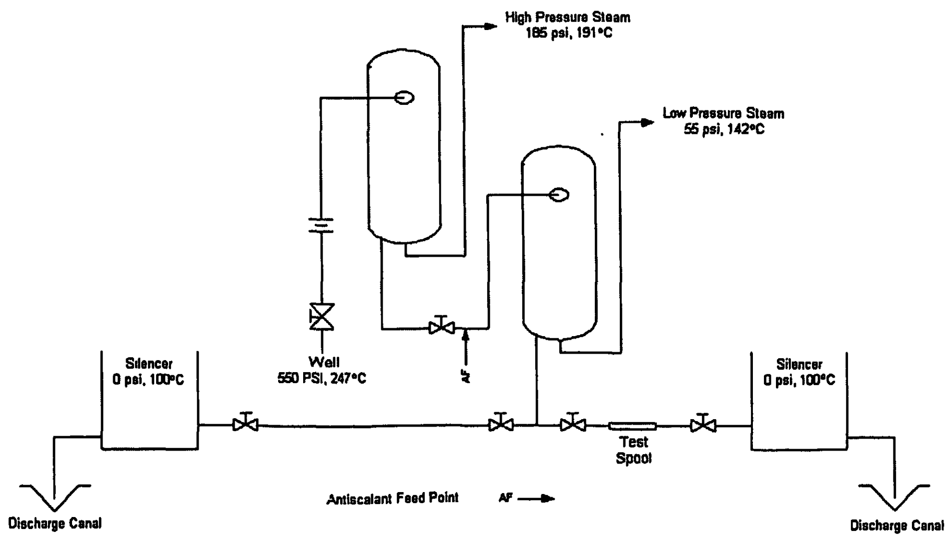

Figure 1. Schematic of Well E-54, with antiscalant feed and test spool locations.

and it remained so for the duration of the test. The brine in the discharge canal after the silencer was seen to be clear for at least 50 meters before any initial cloudiness could be observed. This cloudiness may have been due to silica from either the brine or the discharge canal itself, which was totally encrusted with deposits. It also appeared that, close to the discharge of the silencer, the MILLSPERSE SX antiscalant had both reduced the amount of silica present as well as altered the morphology of the existing deposit in the canal.

After the completion of the test, the test spool was removed, examined, and photographed. There was virtually no scale formed inside the test spool; a number that had been painted on the bare metal of the spool was still plainly visible, indicating the excellent performance of the MILLSPERSE SX antiscalant to inhibit deposition of silica.

Figures 2 and 3 show the condition of the test spool and discharge canal after the 28 days without treatment. Figures 4 and 5 show the results of these same two locations after 28 days of treating the brine with MILLSPERSE SX antiscalant.

THERMSPERSE 300 antiscalant was evaluated next. Its technology is based on proprietary chemistries developed initially for controlling silica and silicates in boiler and cooling water, and process mining and oilfield applications, indicating that its components are thermally stable as well as salinity and suspended solids-tolerant. The product was dosed to the brine at a treatment level of 20 ppm. The higher feedrate was selected as a starting point due to its activity relative to that of the other antiscalants involved in the evaluation. The duration of the test was 14 days.

By the fourth day of the test, the brine in the discharge canal from the silencer was observed to be clear, for approximately 50 meters, indicating, preliminarily, that THERMSPERSE® 300 antiscalant was a successful technology for preventing the formation and deposition of colloidal silica. The brine remained clear for the duration of the evaluation period. At the end of the trial period, it was observed that the valves before and after the test spool could be shut easily, signifying minimal, if any, deposition. The valve after the spool, leading to the silencer, was removed, examined,

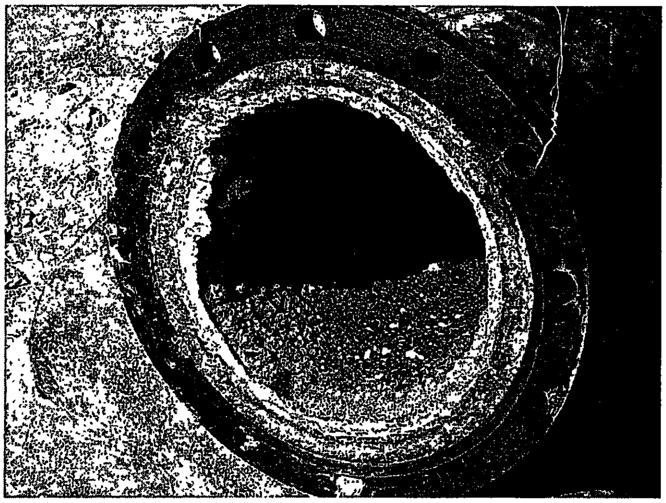

Figure 2. Well E-54 Test Spool after 28 days with no antiscalant treatment.

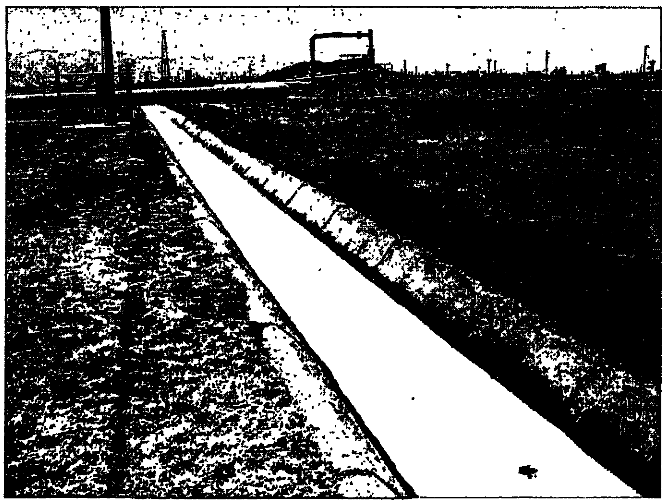

Figure 3. Well E-54 Discharge Canal after 28 days with no antiscalant treatment.

Figure 4. Well E-54 Test Spool after 28 days of treatment with MILLSPERSE® SX antiscalant

Figure 5. Well E-54 Discharge Canal after 28 days of treatment with MILLSPERSE SX antiscalant.

and photographed. There was minimal deposition observed on the valve. The test spool was also removed and inspected. Bare metal and minimal deposition were seen on the internal surface of the spool. The pipeline before and after the test spool showed no buildup in the amount of silica present. As seen in Figures 6 and 7, the visual evidence indicated that the THERMSPERSE 300 antiscalant can effectively control silica deposition in a highly scale-forming geothermal brine.

THERMSPERSE 350 antiscalant, which is based on chemistry similar to some of the components of the THERMSPERSE 300 antiscalant, but engineered more toward dispersion, was evaluated next. The targeted treatment level for the product was 10 ppm to the brine, based on the product's activity. A dosing pump malfunction during the evaluation resulted in the 14-day supply of product being consumed within seven days, with much of the antiscalant being fed in just three days. While the trial was considered too short in duration to be 100% conclusive on the antiscalant's performance, the following observations were made.

The brine leaving the silencer turned clear within the first four days of antiscalant feed; however, the outer edges of the discharge canal, where the brine had cooled, showed some deposition. This might indicate that there is more to effective inhibition of silica than strictly dispersion, as the brine cools to ambient conditions.

The test spool was dismantled, inspected, and photographed. It was observed to be clean and free of deposits. Sections of the pipeline before and after the test spool did not show any buildup of deposits. Figures 8 and 9 show the canal and test spool during the trial of THERMSPERSE 350 antiscalant.

DREWFAX® 269 scale control agent was the fourth product to be evaluated in Well E-54. Its chemistry is based on inhibition of hardness-based salts of both an organic and inorganic nature. The antiscalant was dosed at a 10 ppm feedrate to the brine, for 14 days. During the trial, the clarity of the discharge canal did not appear to change significantly. At the end of the evaluation, examination of the test spool showed approximately 1 cm of

Figure 6. Well E-54 Test Spool after 14 days of treatment with THERMSPERSE® 300 antiscalant.

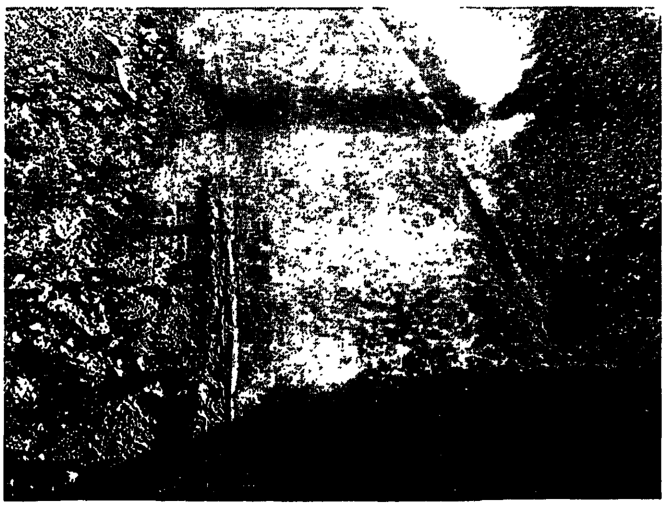

Figure 7. Well E-54 Discharge Canal after 14 days of treatment with THERMSPERSE 300 antiscalant.

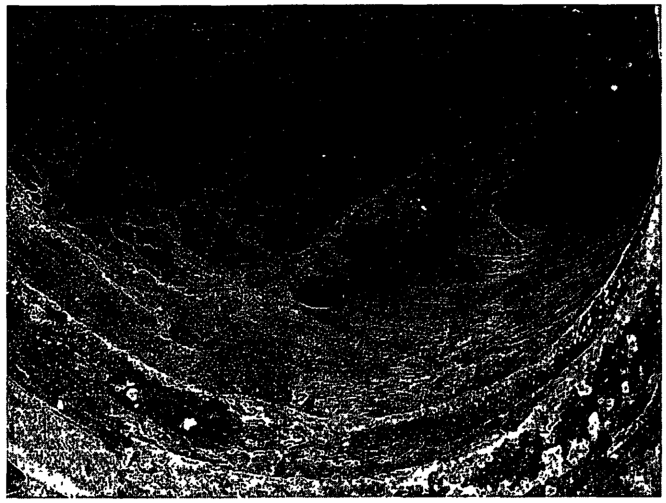

Figure 8. Well E-54 Test Spool after 7 days of treatment with THERMSPERSE 350 antiscalant.

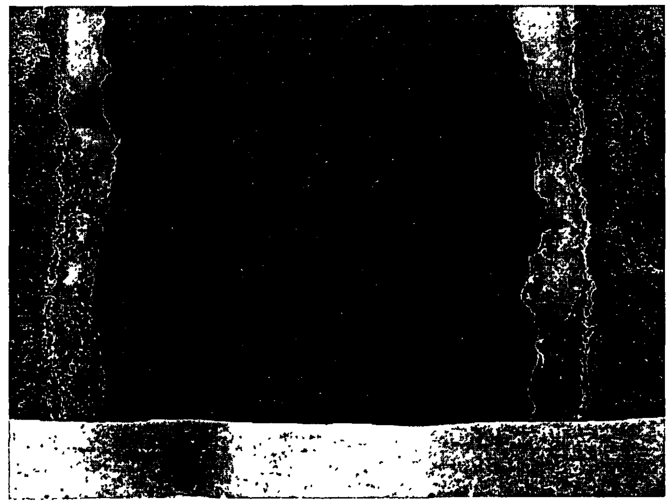

Figure 9. Well E-54 Discharge Canal after 7 days of treatment with THERMSPERSE 350 antiscalant.

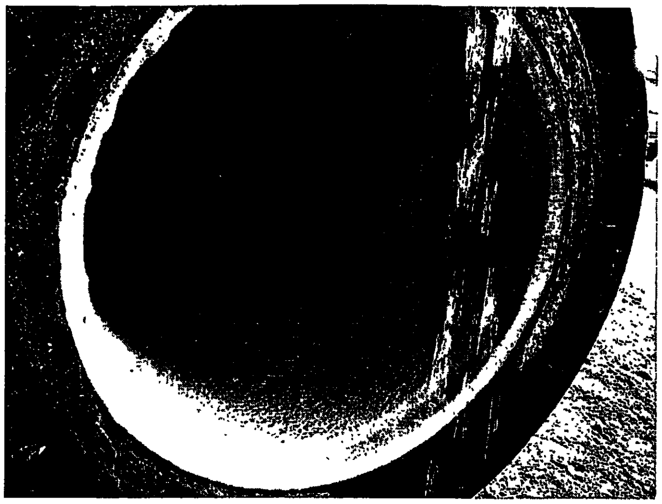

Figure 10. Well E-54 Test Spool after 14 days of treatment with DREWFAX® 269 antiscalant.

Figure 11. Well E-54 Discharge Canal after 14 days of treatment with DREWFAX 269 antiscalant.

uniform deposition throughout the pipe. The results, as seen in Figures 10 and 11, indicate that DREWFAX 269 scale control agent is not effective for inhibiting silica.

The next antiscalant evaluation involved Well 427, located in geothermal field CP-4. This area is the most recently developed section of Cerro Prieto, and certainly the most active with regard to zone formation. Surface pressures for some of the wells exceed 1,200 psi, and the problem of silica deposition is readily apparent throughout the field. Well 427, for example, needs to be temporarily shut down every 2-3 weeks in order to clean a 30-cm diameter orifice plate, located about 1 meter from the wellhead, due to severe silica incrustation restricting the brine flow. In the period between cleanings, deposits as deep as 6-8 cm form on the internal surface of the plate, reducing flow by nearly one-half.

The wellhead pressure at Well 427 is approximately 725 psi, with a corresponding brine temperature of 264°C. The level of silica in the brine has been analyzed to be approximately 1,000 ppm, corresponding to an SSI value of 1.3. Due to the initial precipitation of silica on the orifice plate, the wellhead itself was selected as the antiscalant injection point. In such an evaluation, the pressure and temperature stability of the scale inhibitor would be tested, as well as its ability to control silica. A chemical analysis of the brine is presented in Table 1.

MILLSPERSE® SX antiscalant was dosed to the wellhead for a period of 28 days, at a feedrate of 10 ppm to the brine. A high-pressure pump and feedquill were used to inject the additive. Sixteen days into the evaluation, the well was briefly shut down to inspect, remove, and replace a valve that controlled the brine flow from the high pressure separator to a collection vessel. This action was performed because the valve appeared obstructed. In the inspection, no appreciable scale was observed on either side of the valve. As well, the pipeline sections at the entrance and exit of the valve, which had not been cleaned before the trial, showed minimal deposition.

During the trial, the discharge effluent of the silencer never changed clarity. This was presumed to be due to the fact that the brine from Well 427 passes to a collection vessel, where it mixes with brines from three other wells, all untreated with antiscalant, prior to flowing to the second separator and silencer.

Although the antiscalant feed was terminated on the 28th day, the well continued to operate for 36 hours more before the unit could be shut down and inspected. The orifice plate was then opened and examined. There was less than 0.1 mm deposition present, indicating that MILLSPERSE SX antiscalant is stable to both high temperature and pressure in its ability to inhibit the formation of silica deposits. Additionally, the new valve that had been put into service sixteen days into the trial was inspected. There was no evidence of deposition, after twelve days of exposure to treated brine.

Figures 12, 13, and 14 show some of the results of the trial, including the appearance of the wellhead at the end of the trial, with minimal deposition, the new valve after twelve days of treatment, with no deposition, and the reduction pipe upstream of the valve to the collection vessel, beyond the valve, with minimal deposition.

At this point in time, work is underway to begin evaluations of THERMSPERSE® 300 antiscalant in the same location.

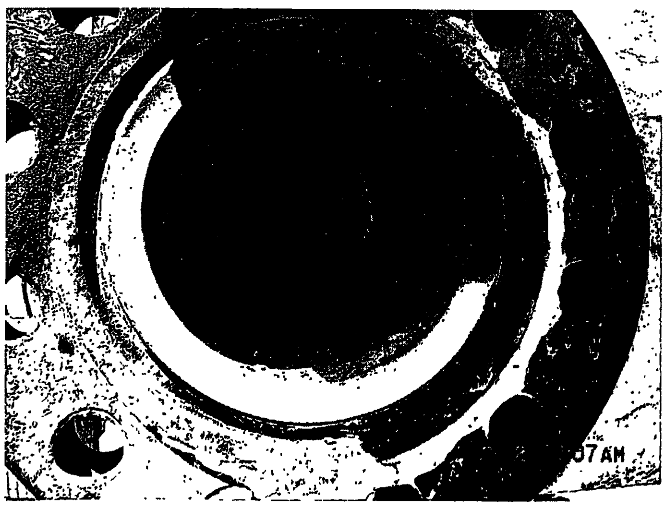

Figure 12. Well 427 Wellhead after 28 days of treatment with MILLSPERSE SX antiscalant.

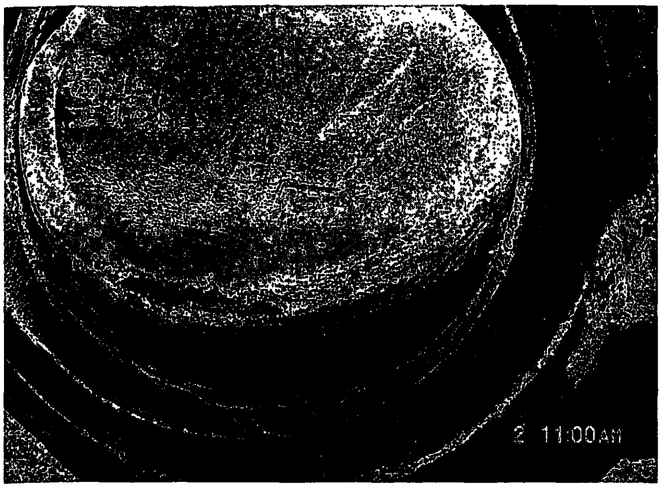

Figure 13. Well 427 Control Valve to Collection Vessel after 12 days of treatment with MILLSPERSE SX antiscalant.

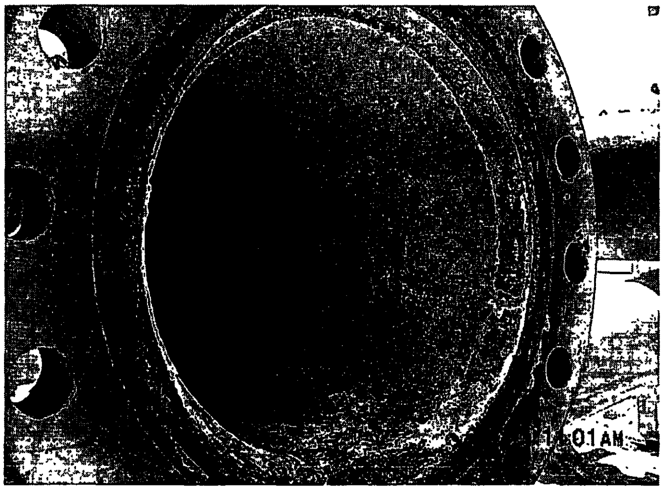

Figure 14. Well 427 Reduction Pipe to the Control Valve, after 28 days of treatment with MILLSPERSE SX antiscalant.

Summary and Conclusions

The field results at CFE Cerro Prieto indicate that geothermal brines severely oversaturated with silica can be effectively treated with low levels of organic chemical inhibitors to minimize fouling of surface fluid handling and discharge equipment. Both MILLSPERSE® SX and THERMSPERSE® 300 antiscalants were found to inhibit the formation of silica deposits under conditions of temperature and pressure, and to maintain the brine free of scale as the pressure and temperature were reduced to ambient conditions.

Work is currently ongoing at CFE Cerro Prieto in a collaborative effort with Ashland to examine and achieve a number of objectives, including feeding MILLSPERSE SX and THERMSPERSE 300 antiscalant to very extremely high pressure wells (1,500+ psi) and to wells of higher silica concentrations (1,500 ppm). Additionally, projects are underway to optimize the feedrate of the antiscalants, in order to optimize the economics of the treatment program.

The successful trials to inhibit silica show great promise for both the short- and long-term future of Cerro Prieto. Immediately, the frequency and duration of outages to clean surface equipment can be reduced, as can the associated maintenance expenses and lost production. In the long-term, the possibility of increased steam recovery, as well as the potential of a successful binary program, are much more feasible. Additionally, the possibility of increased brine reinjection to replenish the formation, appears more likely. These ambitious, yet now achievable, initiatives for Cerro Prieto will make its next thirty years of geothermal development an exciting time.

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Footnotes:

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