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DEVELOPMENT OF A CARBONATE SCALE INHIBITION PROGRAM AT DIXIE VALLEY, NEVADA

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ABSTRACT

A scale inhibition program was initiated at Dixie Valley in late 1988 to reduce the high annual cost of removing carbonate scale from the production wellbores. An exceptionally low calcium content in the fluid allowed an inexpensive and quick test of six different polymeric antiscalants. Nalco 1340, a polyacrylate, was selected as the most efficient and cost effective chemical. A dosage rate near 3 mg/l appears to result in 100% inhibition. The most difficult problem in implementing the program was development of a hardware system that allows uninterrupted delivery of chemical. These problems were solved by protecting the stainless tubing actually transporting the chemical within a larger diameter hang-down tubing string. The main remaining problem is long-term corrosion of the stainless tubing and plugging by the corrosion products.

At Dixie Valley, Nevada the total annual cost of allowing carbonate scale to precipitate in the wellbores is estimated to be about \$ 1.8 million (US), based on one years operating experience. This includes about \$800,000 for actual drilling costs and about \$ 1.0 million of lost production during the cleanouts. Note this does not include the cost of diminishing production while the well is scaling. For 6 to 8 production wells it appeared that about 20 mechanical cleanouts per year at an average cost of \$ 40,000 would actually be performed. If the risk of damaging a well during a scale cleanout is only 1% this indicates that over a 5 year period the chances of damaging a well were about 100 %. These actual and potential costs provided the incentive for Oxbow Geothermal Corp. to develop a carbonate scale inhibition program at the earliest possible time.

INTRODUCTION

Carbonate scale in production wells is perhaps the most common chronic world-wide problem associated with flash-type geothermal power plants. The severity of the problem varies widely, with wells in some fields such as Desert Peak, Nevada being able to flow a year between scale cleanouts (Faulder and Johnson, 1987) while wells in other fields such as Miravalles, Costa Rica may only flow a few weeks (Vaca, 1989).

Of necessity operators have developed mechanical or chemical scale removal techniques that allow the fields to be economically produced. However, these techniques still have a significant economic impact in that at a minimum the wells must be removed from production for scale cleanout operations. Generally in the United States wells are actually shut down while the scale is drilled out or removed by acid. These operations also run a risk of damaging or possibly even destroying a viable production well. The preferable method for dealing with carbonate scale in production wells is to keep it from forming.

PREVIOUS INHIBITION STRATEGIES AND RESULTS

A number of techniques have been tried at many different geothermal fields to reduce or eliminate carbonate scale with varying limitations and degrees of success. Maintaining pressure by pumping is not an option at Dixie Valley due to the 480°F (249°C) temperature and the fact the flash points are below 1883' (574 m). Locating producing intervals with little or no scaling potential such as can be done at Krafla (Armannsson, 1989) is not feasible as all thermal fluids at Dixie Valley produce scale. Injection along with scrubbing and recycling of CO₂ such as was experimentally demonstrated at Desert Peak (Kuwada, 1982) was not deemed economically viable for the dual flash plant at Dixie Valley where the wells and separators are over 2 miles apart. Use of acid is not desirable due to the presence of exposed cemented liner laps. The well known phosphonate based chemicals bearing the Dequest series names have been shown to be effective in inhibiting scale but have the side effect problems of being highly corrosive, requiring teflon lined delivery equipment

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(Pieri, et al., 1989), and depositing orthophosphate scales (Vaska and Kellogg, 1989).

The most promising scale inhibition development in the United States in 1988 was the field testing of polymeric antiscalants that had originally been developed for scale control in power plant cooling water systems. Three chemical companies, Betz Industrial, Drew Industrial Division, and Nalco Chemical Company had begun marketing polymeric antiscalants to the geothermal industry in the United States and long-term tests of the chemicals were underway at Heber in the Imperial Valley (Johnson, pers comm.1988) and at Coso in eastern California (Chesney, pers comm 1988).

The chemical characteristics of these two areas required long term testing as the brines at Coso contain 80 to 100 mg/l calcium and at Heber the brines contain 900 mg/l calcium. There is no rapid or accurate way to determine if only a few mg/l of calcium are being inhibited against this high background. Testing of the inhibition results was determined by caliper logging after flowing periods of approximately one month. All products being tested were indicating good inhibition at dosage rates less than 10 mg/l.

ANTISCALANT CHEMICAL TESTING

Oxbow held discussions with all three chemical companies and it soon became clear that there was no way to determine which chemical would be most effective at Dixie Valley. Betz had success with a combination of polyacrylate and phosphonate. Drew had success with polymaleic anhydride. Nalco's polyacrylate had also been proven successful. These discussions created enough confusion that Oxbow decided to actually field test the various chemicals.

Dixie Valley has a rather unique brine chemistry in that at the surface, after flashing in the wellbore, the brines contain only about 1 mg/l of calcium (Reed, 1989). Previous studies had shown that between 3 and 6 mg/l of calcium were entering the wellbore (Benoit, 1989). Therefore, it was anticipated that the effectiveness of the inhibitors could be easily and quickly determined in the field by varying the amount of chemical injected and measuring the amount of calcium at the wellhead. Field titrations using EDTA are sufficiently accurate to determine the difference between 1 and 3 mg/l of calcium.

The test was performed over one week in late October 1988. A total of six chemicals were tested with the assistance of all three chemical companies. Samples

were analyzed in the field by titration with EDTA and duplicate samples were collected for later ICP analysis. The testing was performed on well 27-33 because it had been cleaned out just prior to the start of the test. The brine samples were collected from the bottom of a long straight run of two phase flowline a short distance downstream of the wellhead. Previous sampling from this port and comparison with samples collected after full flow separation had proven that the flow line was acting as a separator and that good quality separated brine samples would be obtained.

The test apparatus was very simple, consisting of a 55 gallon (208 l) drum of chemical, a 2.7 gallon per hour (10.2 l/hr) Milton Roy metering pump, and a 3750 foot (1143 m) string of 1/4 inch (6.35 mm) OD 316 stainless low carbon steel capillary tubing to deliver the chemical about 300 feet (100 m) below the flash point in the well. The chemical flow rate was determined periodically and repeatedly by pumping through a calibration cylinder. The well flow rate was read from the power plant metering equipment and remained constant during the test.

The testing strategy was to pump a chemical overnight at the maximum pump rate to flush the capillary tubing and have a steady state condition ready for sampling the next morning. The well was then sampled and the pump rate reduced. After an hour, which was 4 times as long as it should have taken the inhibited fluid to reach the surface from the bottom of the capillary tubing, another sample was collected and the pump rate was again reduced. The reductions continued until the amount of calcium at the wellhead showed a significant decline.

Initially the first chemical was pumped in undiluted form and it quickly became apparent that inhibition was effectively working at extremely low injection rates. Then it was noticed that full inhibition continued even after the pump was shut off. This proved that there was a problem with the chemical draining out of the capillary tubing faster than it was being pumped in the top at low injection rates. It is now known that drainage becomes a problem in 1/4 inch (6.35 mm) OD tubing below an injection rate of about 10 ml/min. Consequently the chemicals were all diluted 3:1 with unfiltered condensed steam from the cooling tower basin. All the tested chemicals are highly soluble in water so dilution posed no problems.

CHEMICAL TESTING RESULTS

The testing proved that all the chemicals provided maximum inhibition at dosage rates of 5 parts per

million and higher (Figure 1). The expected calcium content at the surface with complete inhibition was previously estimated to be 3.76 mg/l based on caliper logging of adjacent well 45-33 (Benoit, 1989). This caliper logging technique was based on a number of measurements, most of which could easily be in error by 5 or 10%. Thus, finding 3.5 mg/l maximum calcium at the wellhead probably signifies that maximum inhibition is very close to full or complete inhibition and the words will be used interchangeably.

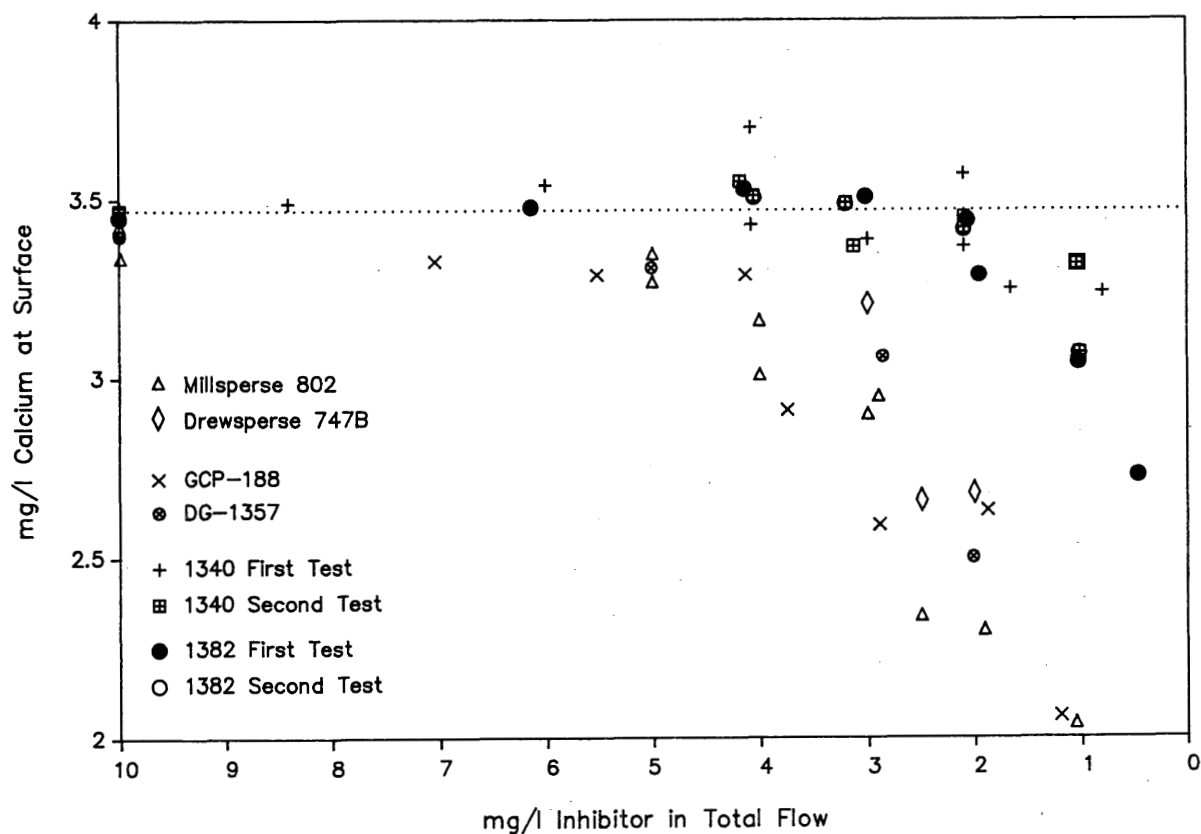
The two Nalco chemicals, 1340, a copolymer polyacrylate with a molecular weight of 2500, and 1382, a terpolymer mixture of two polyacrylate molecules, provided full inhibition at the lowest dosage rates, about 2 mg/l. The two Nalco chemicals were retested, confirming the results.

However, it must be pointed out that this test did not determine the inhibition efficiency of the different

molecules. It tested the effectiveness of the entire chemicals which appear to contain quite variable amounts of water (which is not expected to directly contribute to the inhibition process). All the chemical companies did not supply the activities or concentrations of the chemicals. To get some qualitative idea of the effectiveness of the actual molecules, the specific gravities of the individual chemicals are presented on Table 1. There is a solid correlation between the specific gravity of the chemical and the lowest dosage rate for full inhibition. The heavier the chemical the better the inhibition. This leaves open the possibility that the different molecules might have more or less equal inhibition efficiency but that this efficiency has simply been diluted to varying extents.

Further field testing with the same concentration or activities of the different molecules is needed to truly determine any differences in efficiency between the molecules. Vaska and Kellogg (1989 Table 1) show that

FIGURE 1 CARBONATE SCALE INHIBITION TEST
WELL 27-33 October 25-31, 1988



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PRODUCT NAME	CHEMICALS	SPECIFIC GRAVITY	LOWEST DOSAGE RATE FOR FULL INHIBITION
GCP-188	POLYACRYLATE AND PHOSPHONATE	1.053 AT 70° F.	4 PPM
DG-1357	PHOSPHONIC ACID	1.059 AT 70° F.	3-4 PPM
MILSPERSE 802	POLYMAELIC ANHYDRIDE	1.04 AT 77° F.	5 PPM
DREWSPERSE 747B	ACRYLIC COPOLYMER	1.02-1.05 AT 77° F.	3-4 PPM
NALCO 1340	POLYACRYLATE COPOLYMER	1.22 AT 50° F.	2 PPM
NALCO 1382	POLYACRYLATE AND SULFONATED POLYACRYLATE (TERPOLYMER)	1.16 AT 68° F.	2 PPM

TABLE 1

polymaleic anhydride gives a significantly greater percentage of scale reduction than polyacrylic acid with the same molecular weight and concentration. The limited site specific field testing at Dixie Valley (admittedly without molecular weight and activity or concentration data) does not appear to support this.

DEVELOPMENT OF THE CHEMICAL DELIVERY SYSTEM

Prior to actually testing the chemicals it was expected that the delivery system technology was fairly mature and that few problems would be encountered. This was not the case. The delivery system problems were and to a certain extent remain the more difficult outstanding problems.

During the initial testing there fortunately were no problems with a Pruett Industries delivery system identical to those in use at several areas in the United States. The delivery system consisted of a 15 foot (4.6 m) lubricator made from 2 3/8 inch (6 cm) tubing and a stuffing box and shieves, a string of 1/4 inch (6.35 mm) OD 316 ssl capillary tubing, and a downhole assembly consisting of a dispersion head (attached to the capillary tubing) with 120 pounds (54.5 kg) of sinker bars attached to the bottom of the dispersion head. The system can be installed and retrieved under flowing conditions and under some conditions may be the ideal system in terms of convenience and cost.

The day after the chemical testing was completed the tubing appeared to be plugged and was pulled out of the well. Within a few feet of pulling, a hole was found worn in the tubing. The hole appeared to be where the tubing entered the wellbore through a nipple welded on the outside of a long radius elbow. The force of the flow in the wellbore apparently was pushing the capillary tubing against the sharp downstream edge of the hole cut through the elbow. On the same day a tubing string was run in well 84-7 to begin inhibition. It was pulled up a short distance the next day to check for wear but had already parted, apparently at the same location in the wellhead. The 84-7 tubing was recovered shortly thereafter during a 10 day fishing operation. On inspection of the long radius elbow from well 84-7 it was found the nipple was not centered over the cut hole which had very jagged edges. In late November one replacement tubing string was damaged when it floated in the 84-7 wellbore and one string was destroyed when it was blown out the 27-33 discharge line to the pit while being retrieved.

These problems forced a reevaluation of the adequacy of the delivery system for Dixie Valley and some changes were made. First, a larger and heavier delivery system was developed to help keep the capillary tubing from floating up the wellbore. This delivery system consisted of a 3 inch (7.6 cm) heavy wall, all welded lubricator and larger diameter sinker bars with a weight of 160 pounds (72.7 kg). This modification resulted in weight which was getting relatively close to the yield strength of the 1/4

inch tubing but still allowed the tubing to move around in the wellhead and abrade over periods of a few days.

Second, a 6 foot (2 m), 3 inch (7.6 cm) OD "stinger" was fabricated and installed in the wellhead so that the tubing would enter the flow stream in the center of the well just above the master gate valve and not be immediately forced downstream. The first stinger had no centralization for the tubing where it exited the stinger and the tubing experienced rapid abrasion as it rotated around the bottom of the stinger. A brass guide bushing was then fabricated to centralize the tubing within the bottom of the stinger. Brass was selected because it was available in Dixie Valley and was softer than the stainless steel tubing.

In spite of this precaution two tubing strings parted after being hung at a constant depth for between 26 and 40 days. The reason for these two partings is suspected to be fatigue as no evidence of wear was found on the broken ends of the tubing. When the wells were shut down to recover the tubing the brass guide bushings were found to have undergone serious erosion. Two later attempts with a split guide bushing with a soft silicon rubber ring and a graphite packing centralizing the tubing were unsuccessful when the silicon and graphite both failed in less than two days.

Perhaps additional sophistication will allow the stinger to work, but by this time the hang-down string concept was developed and management patience with costly fishing recovery operations was nearing an end. Breakage and loss of the unprotected small diameter tubing strings for a wide variety of reasons is common (Piere, et al., 1989) and is also one of the most expensive mishaps.

Once the tubing abrasion problems were recognized it became necessary to develop a strategy for inhibiting the two wells in the field with damaged production casing. Wells 45-33 and 73-7 were both known to have jagged metal edges above the flash point. To protect the capillary tubing the most certain method seemed to be to run the tubing inside a larger more solid string of tubing such as some of the 2 3/8 inch (6.35 cm) that was already on location. Fortunately the well characteristics are such that the bottom of the hang-down string is deep enough to protect the entire tubing string yet shallow enough that a compressor could be used to kick off the wells.

This hang-down string also offered the opportunity to avoid further fishing for lost capillary tubing in the well by use of a relatively large "no go" ring attached just above the dispersion head and a smaller end nipple on the bottom of the hang-down string. To make this truly

effective, hollow sinker bar material was obtained so the bars would be above the no go ring and only the bottom of the dispersion head (also redesigned) would penetrate below the end nipple into the flow stream. The primary reason that all these modifications were necessary is that all the chemicals tested had low pH's and quickly dissolved carbon steel.

All production wells at Dixie Valley are now equipped with 1.9 inch (4.83 cm) OD hang-down strings which are simply screwed into the top flange on the wellhead. Hollow and lighter sinker bars can be used because there is no risk of the tubing floating inside the hang-down string unless there is a major lubricator failure (as happened once on well 73-7 when the shieve and stuffing box broke loose from a threaded connection). Since the hang-down strings were installed there has been no lost production due to fishing of capillary tubing. The hang-down strings have performed their primary mission well - that is to allow the delivery system to function continuously as it now has for over a year in a couple wells.

The hang-down strings do have drawbacks. The biggest economic drawback is that they do reduce the output of the wells by occupying up to 5 % of the cross sectional area of 9 5/8 inch (24.4 cm) casing and increasing the frictional resistance to two phase flow. The largest operational problem is that access to the lower part of the well is limited to a very small selection of tools that can pass through the 1.45 inch (3.68 cm) end nipple and should any modifications need to be made to the hang-down string the well must be shut down. This is somewhat mitigated by the fact that modifications such as lengthening or removal can be conducted in a day or two with minimal risk of major fishing operations. Also the wells can be kicked off with an air compressor rather than a much more costly nitrogen coiled tubing unit.

TUBING PLUGGING

Plugging of the small diameter tubing is another common problem (Pieri, et al., 1989). At Dixie Valley a number of tubing strings have plugged for various reasons. The first tubing string in use plugged. Possible reasons for this include the fact that a mixture of the chemicals were pumped through the tubing, unfiltered cooling tower basin water was used to dilute the chemicals, and a corroding galvanized fitting was in the surface system. This string was unplugged and placed in service again but parted about 70' down the wellbore after a short time. Upon retrieval of numerous fragments during another 10 day fishing operation the tubing was found to be severely corroded and cracked.

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Several other tubing strings plugged during the winter when the chemical in the tubing froze prior to getting inside the lubricator. Once the tubing freezes, pumping ceases and the chemical already inside tubing in the wellbore slowly drains down through the dispersion head. Gradually pressures within the tubing decrease to a point where the chemical is able to boil and it then polymerizes and dehydrates into a tar-like substance. There is apparently no way to remove one of these plugs which typically formed 1000 to 2000 feet (300 to 600 m) above the dispersion head, other than to cut the tubing.

The winter of 1988 - 89 had the coldest weather in Northern Nevada in 18 years. The power plant was operating through its first winter and occasionally manpower was not adequate to deal with freezing problems at the plant and at the wellheads. Nalco 1340 freezes at 20°F (-7°C) and the delivery system was winterized to the extent possible but these precautions could not prevent freezing of a temporary system that was basically exposed to the elements.

During the fall of 1989 insulated and heated structures were obtained to house the chemical tanks, pumps, and capillary tubing on the surface. An insulated covering over the entire lubricator has also been installed making it unnecessary to insulate and heat trace most of the above surface tubing. Pumping of the chemical can cease for a day and still be restarted but at no time has pumping restarted after a two day hiatus.

To potentially negate the freezing problem Nalco 1370 was tested in well 76-7 for two days. Nalco 1370 is simply Nalco 1340 that has been diluted 1:1 with deionized water and saturated with sodium hydroxide to bring the Ph from 3.8 to 13 and the freezing point down from 20°F (-7°C) to -12°F (-27°C). Nalco 1370 produced discouraging results in that for some unknown reason it was only 50 % effective in inhibiting scale, no matter what the dosage rate, and it destroyed the tubing string in less than three days by cracking it. The chemical escaped through the cracks into the annulus inside the hang-down string and deposited a sticky mess that required junking a few joints of tubing.

In a few instances there has been apparently spontaneous plugging of tubing. Initially the Nalco 1340, the chemical that has been used for over a year now, was pumped in its raw, and most concentrated form. But over time it became obvious that the chemical had plugging tendencies. Plugging is evidenced by increases in pumping pressure which can be treated by pumping the chemical at maximum rate for several hours. During the summer of 1989 a program of diluting the 1340 1:1 with

deionized water produced on site was instituted and the instances of attempted plugging decreased greatly. A 1:1 dilution was also successful for Pieri et al., (1989).

Dilution of the chemical, development of the hang-down string, and a resolve not to disturb operating inhibition systems have resulted in continuous operation of individual tubing strings for up to 11 months at the time this paper was submitted. This has allowed the discovery of long-term corrosion and plugging problems. In several instances operating systems were flushed with water from the cooling tower basin and then pulled out of the wells. After pulling or sometimes after running back in the well it was not possible to pump through the tubing. In several other instances the plugging occurred spontaneously after pumping for between 12 and 172 days. Two of the plugs have been retrieved and found to consist of black flaky deposits of iron sulfide, as determined from x-ray diffraction, with significant with chrome (Table 2). Nalco 1340 contains a small amount of sulphur used as a catalyst in producing the chemical. Oxbow plans to switch to a higher purity form of 1340 with little or no left over sulphur.

DEPOSIT ANALYSIS FROM WELL 76-7 (WEIGHT PERCENT)

SULFUR (% SO ₃)	72
CHROMIUM (% Cr ₂ O ₃)	12
IRON (% Fe ₂ O ₃)	5
SILICON (% SiO ₂)	3
NICKEL (% NiO)	2
COPPER (% CuO)	1
SODIUM (% Na ₂ O)	1
ZINC (% ZnO)	1
ALUMINUM (% Al ₂ O ₃)	1

Table 2

Apparently the iron sulfide particles are able to flake off the interior of the tubing and move downstream. Occasionally it has been possible to blow apparent plugs into the dispersion head and resume normal pumping or to cut them out if they occur near the bottom of the tubing. Attempts to chemically dissolve the iron sulfide have been unsuccessful. Among the compounds tested by Nalco at temperatures up to 140°F (60°C) for up to 12 hours are hydrochloric, sulfuric, and citric acids, sodium and potassium hydroxide, alcohol, formaldehyde, acetone, and NTA and EDTA chelate. No testing has been performed to find an inhibitor for the corrosion.

In anticipation of long-term corrosion problems one tubing string of Incoloy 825 was installed in well 27-33 on April 1, 1989. This string has remained undisturbed in the well with one attempted plugging incident for 350 days. Tubing strings of 316 ss have been in service for over 273 days. The data do not yet exist to determine whether Incoloy or stainless steel is most cost effective.

For various reasons a few of the hang-down strings have been pulled out of the wells for modifications after about seven months of operation. The hang-down strings showed only thin coatings of carbonate scale that can probably be attributed to times when inhibition was not occurring. The inhibition is operating at or near the 100% level.

CONCLUSIONS

Carbonate scale inhibition in 8 production wells at Dixie Valley has been successfully implemented with the level of inhibition at or near the 100% level. The costs of developing and implementing the program have been recovered in less than one year of inhibition. Nalco 1340, a copolymer polyacrylate has proven to be a very cost effective chemical although it is subject to plugging and long-term corrosion problems.

Unexpected hardware problems during development included abrasion, fatiguing, plugging, and corrosion. All of the problems with the exception of long-term corrosion have been dealt with by development of the hang-down strings, dilution of the chemical, and careful ongoing monitoring of the individual inhibition systems. The current system in place at Dixie Valley operates well but there is much room for improvements that will make the system less expensive, more versatile, and further reduce flow rate losses associated with the hang-down strings.

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