

## **NOTICE CONCERNING COPYRIGHT RESTRICTIONS**

This document may contain copyrighted materials. These materials have been made available for use in research, teaching, and private study, but may not be used for any commercial purpose. Users may not otherwise copy, reproduce, retransmit, distribute, publish, commercially exploit or otherwise transfer any material.

The copyright law of the United States (Title 17, United States Code) governs the making of photocopies or other reproductions of copyrighted material.

Under certain conditions specified in the law, libraries and archives are authorized to furnish a photocopy or other reproduction. One of these specific conditions is that the photocopy or reproduction is not to be "used for any purpose other than private study, scholarship, or research." If a user makes a request for, or later uses, a photocopy or reproduction for purposes in excess of "fair use," that user may be liable for copyright infringement.

This institution reserves the right to refuse to accept a copying order if, in its judgment, fulfillment of the order would involve violation of copyright law.

## CALCIUM CARBONATE SCALE CONTROL IN GEOTHERMAL WELLS

Marcus Vaska<sup>(1)</sup> and Norm Kellogg<sup>(2)</sup>

(1) Drew Industrial Division, Ashland Chemical Company  
One Drew Plaza, Boonton, NJ 07005  
(2) Drew Industrial Division, Ashland Chemical Company  
16168 Beach Blvd., Suite 241, Huntington Beach, CA 92647

### ABSTRACT

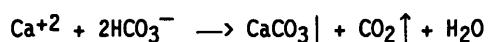
Scaling of wells represents a major problem to many geothermal power plants. Geothermal brines contain dissolved minerals that have a high tendency to precipitate in critical areas. In particular, formation and growth of calcium carbonate scales are harmful to operations by restricting brine flow and causing a decrease in power generating efficiency. Removal of the scale involves taking the well off-line and physically cleaning the deposits downhole. This process restores the well efficiency but is extremely costly and time consuming.

This paper explores the technology behind how polymeric antiscalant additives effectively and economically prevent downhole scale formation and allow for uninterrupted, efficient power generation. Feeding methods, monitoring techniques and results from geothermal developers in the Imperial Valley, Coso Hot Springs, Steamboat Springs and Beowawe resource areas will also be discussed.

### INTRODUCTION

Calcium-based scale precipitation is a common problem in geothermal fluids and brines. The area most prone to scaling is at the flash point inside geothermal wells. Reinjection pumps, lines and equipment can also be susceptible to scale formation. An accumulation of these adherent deposits can result in rapid reduction of brine flow, loss of efficiency and eventual interruption of well production or plant operation.

One of the most common causes of scaling in geothermal fluids is the relative insolubility of calcium carbonate. The presence of the calcium ion and bicarbonate alkalinity is common in almost every water source. When the temperature of the water increases, the bicarbonate breaks down to carbonate and combines with calcium by the following reaction:



As the hot brine rises toward the surface in a well, an equilibrium is reached between the pressure and boiling point of the brine which causes flashing to occur. The liquid brine at the flashpoint therefore experiences an increase in solids concentration. In addition, carbon dioxide is liberated which along with the previous factor drives the above equilibrium reaction to the right and causes precipitation of calcium carbonate scale.

Other commonly encountered deposits in geothermal operations are metal sulfides and silica scales. This paper, however, will discuss control of calcium carbonate scale only.

In the absence of effective antiscalant reagents, expensive cleaning techniques are required to restore scaled wells to full production efficiency. This involves taking the well off-line and either dissolving the scale with an acidic solution or mechanically removing scale from the affected areas. Neither option is attractive due to cost and downtime considerations. The development of polymer technology over the last few years has enabled plants to feed these reagents in the low part per million range and effectively prevent or minimize scale formation. A properly treated system can now typically function for many months or even years without interruption for cleaning due to calcium carbonate scale.

In formulating an effective maintenance program to combat the problems of scale formation, there are a number of steps that can be taken to optimize this goal. Although most all brines are scale forming in nature, due to specific operating parameters and differences in brine makeup characteristics, some may be far more severe than others. A complete brine analysis, both before and after flashing, including calcium concentration, alkalinity, silica, pH and total dissolved solids should be determined. This information, along with the temperature and pressure of the geothermal fluid, will help determine the best treatment approach. A history of well-scaling severity from production reports, hole caliper logs and ring gauge runs is also helpful in formulating an effective antiscalant maintenance program.

The second step in formulating a successful antiscalant treatment program is the selection of a cost-effective reagent that inhibits the formation of these troublesome deposits. There are a number of different generic materials available, each with inherent strengths and weaknesses. A full discussion will follow. Feeding of antiscalant reagents downhole is a difficult task and has itself evolved into a science. Typical methods will be detailed.

The last facet of a scale control program is monitoring its effectiveness. This represents the criterion by which success or failure can be judged and is an area in which new developments are constantly being made. Monitoring techniques that upgrade our ability to measure effectiveness will also be discussed.

#### Treatment Programs

The traditional treatment for scaling water has been to use reagents that act to sequester (solubilize) the calcium cation and prevent it from exhibiting its normal properties. Now, reagents termed "threshold" inhibitors are used to control large numbers of metal cations at stoichiometric concentrations. The exact mechanism of this "threshold effect" is not well understood; however, this phenomenon allows large volumes of geothermal fluid to be economically treated.

A well known approach to controlling calcium based deposits has been the use of organophosphorous compounds. Examples of two commonly used phosphonates are depicted in Figures 1 and 2.

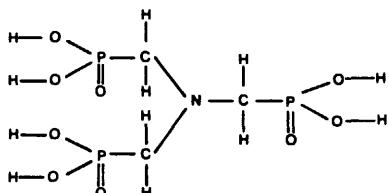


Figure 1. Aminomethylenephosphonate (AMP)

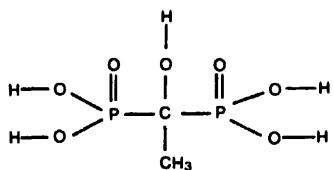


Figure 2. 1 Hydroxyethylidene-1, 1 diphosphonate (HEDP)

These compounds are referred to as AMP and HEDP phosphonate. Normally, they are fed at relatively low dosage rates and are often blended with polymeric compounds to increase their effectiveness. Phosphonates can function effectively as antiscalants but have the drawback of breaking down to orthophosphate and causing additional deposits. This breakdown or reversion

is dependent on the type of phosphonate, time, temperature and brine characteristics.

More recently, the technology of dealing with calcium carbonate has turned completely to polymeric type materials with carboxylic or sulfonic acid functionality. Examples of this would be polyacrylate, polymethacrylate, polymaleic anhydride, sulfonated polystyrene, as well as copolymers of various types. These compounds function by crystalline distortion, dispersion and modification mechanisms. Anionic polymers, such as sodium polyacrylate, which have a long extended charge network, become adsorbed into a growing crystal. The overall net negative charge then results in mutual particle repulsion. In achieving this dispersion, the molecular weight of a polymer is important. Too high a molecular weight will result in particle bridging and flocculation rather than dispersion. A polymer with too low a molecular weight will not function effectively as a crystal modifier and loses activity as shown in Table 1.

Table 1. Relation of molecular weight factor to scale reduction efficacy

Polymer	MW	Concen- tration	%Scale Reduction
Polyacrylic Acid	20,000	3	52
Polyacrylic Acid	10,000	3	61
Polyacrylic Acid	5,000	3	71
Polymethacrylic Acid	10,000	3	62
Polymethacrylic Acid	5,000	3	68
Polymaleic Anhydride	10,000	3	85
Polymaleic Anhydride	5,000	3	98
Polymaleic Anhydride	5,000	2	97

It has been determined through extensive research and cost comparisons of various polymer types that the optimum molecular weights for polymers used in preventing scale are between 1,000 and 10,000. All three types of polymers have been found thermally stable under conditions encountered in geothermal wells.

Other factors that affect the efficacy of a polymer on calcium carbonate scale formation are the type and orientation of the functional groups. For example, polymers with complex side chains may not be very effective for the control of compounds with small crystalline structures.

This is due to steric hindrance effects, which prevent a relatively large polymer structure from adsorbing onto a small crystal matrix. Polymer functional groups that have been most effective for control of mineral scales are the carboxylate and sulfonate varieties. Dosages required to control downhole scale formation vary widely, depending on brine and well characteristics, temperature, type of polymer (functionality), molecular weight and degree of activity. Dosages can range from one part per million or less up to 10 parts per million. Structures of polymer types commonly used for control of calcium carbonate scale are depicted in Figures 3, 4 and 5.

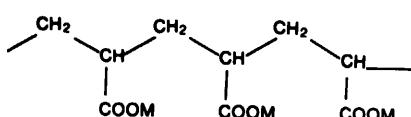


Figure 3. Polyacrylate

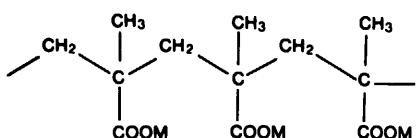


Figure 4. Polymethacrylate

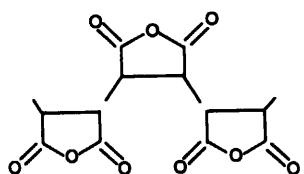


Figure 5. Polymaleic Anhydride

#### FEEDING METHODS

One of the most difficult aspects of downhole antiscalant treatment is feeding the reagent through thousands of feet of tubing inside the well. A typical geothermal well head consists of the casing head expansion spool, wing valves, master valves, flowline and crown valve as depicted in Figure 6.

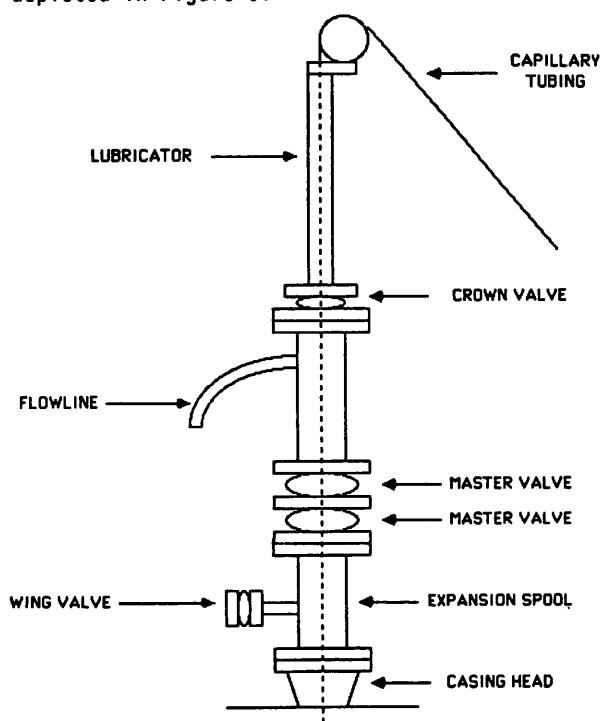


Figure 6. Geothermal well head.

Feeding antiscalant reagents downhole is an area of developing and changing technology and while there are many variations, a typical method is shown in Figure 7.

First, the well and well head need to be modified to allow the antiscalant to be fed into the well bore 200-400 feet below the lowest encountered scale formation as noted in Figure 7.

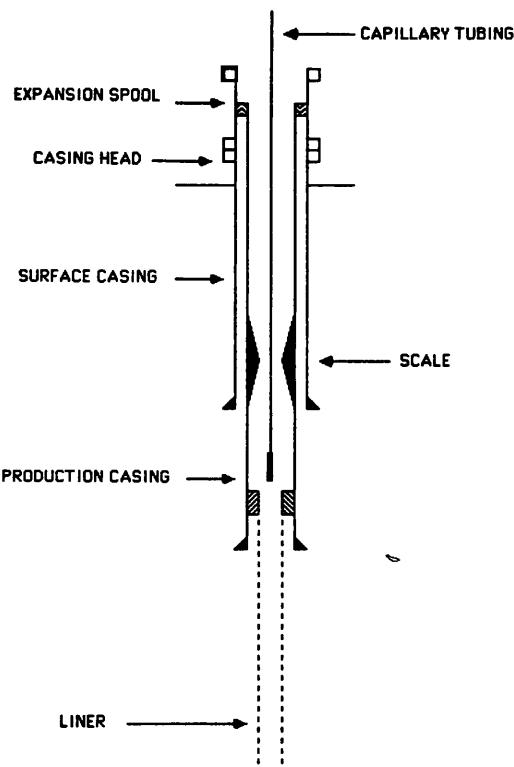


Figure 7. Geothermal well with antiscalant feed below flashpoint.

This requires pumping the reagent through 3,000-5,000 feet of stainless steel capillary tubing, usually 1/4" O.D. x 0.035" wall, that is lowered into the well bore through a lubricator mounted on the well head crown valve or an expansion spool wingvalve as shown in Figure 6. The end of the capillary tubing to be inserted into the well bore has a weight called a sinker bar which is attached to the capillary tubing via the mixing chamber. The purpose of the mixing chamber is to allow the antiscalant reagent to exit the tubing and flow into the well bore where it mixes with the geothermal fluid and prevents scaling deposits.

The surface feed equipment consists of a high pressure chemical metering pump, chemical storage tank and a metering gauge to measure the reagent feed rate.

## VASKA, KELLOGG

Feeding antiscalants to surface lines is a relatively simple task. The reagent should be fed far enough ahead of the scaling area to allow for sufficient mixing. This can best be achieved using an injector quill and a chemical feed pump.

### MONITORING TECHNIQUES

Many attempts to judge the effectiveness of adding chemical treatment to geothermal brines have been made. A common test consists of merely monitoring calcium concentrations across a system to measure loss of calcium ions due to precipitation. Unfortunately, this method has many inherent limitations. Establishing an accurate baseline for the calcium level of the brine is often difficult due to variations in brine characteristics. Additionally, with the volumes of brine involved, a relatively minor and difficult-to-detect reduction of calcium (1 ppm or less) could mean scaling is occurring. Another, more effective way to measure downhole scaling is by running caliper logs or ring gauges. These methods give accurate readings of well bore reduction but require removal of the antiscalant capillary tubing for several hours. During this period, the well is not protected and significant scaling can occur.

The simplest and most inexpensive method to monitor scale build-up is the use of scale coupons, which utilize a retractable injector. The test specimen consists of a stainless steel tube with holes in its surface. These scale coupons are placed into the brine flow and will show visually on inspection whether the system is scaling.

A key element in easily introducing the specimen to the system is the injector assembly. This device makes use of a retractable injection rod that draws the scale coupon within the thread housing. In this way, a simple gate valve in a circulating line can serve as the sampling point with the coupon being inserted into the brine solution flow after the housing has been tightened down and the valve opened. This procedure allows for rapid installation with no major piping alterations and also makes for easy inspection on a regular basis. Scale buildup is monitored easily and on a continuous basis. Adjustments can be made in reagent dosage and the effects measured by inspecting the test specimens. A singular advantage this type of monitoring device offers is the ability to measure various portions of the system with separate injectors.

This method is simple and effective but limited to areas of the system that are easily accessible such as brine reinjection lines. Several new and unique methods are currently being tried to monitor downhole scale formation so that antiscalant reagent dosages can be adjusted accordingly. At this writing, insufficient data are yet available to comment on these methods.

### CONCLUSION

Effective downhole and equipment scale control can be economically achieved by feeding low dosages of polymeric antiscalant reagents to the geothermal fluid. Feeding and monitoring techniques are being rapidly refined to optimize dosage rates and insure that wells and equipment are maintained at maximum production capacities.

### REFERENCES

1. "Principles of Industrial Water Treatment" (Drew Chemical Corporation, Boonton, New Jersey 1985) pages 77-84.
2. Harrar, J.E., Locke, F.E. and Lorenzen, L.E., 1980. Studies of Scale Formation and Scale Inhibitors at the Salton Sea Geothermal Field, NACE, Corrosion/80 (Chicago, March 3-7, 1980) Technical paper number 225.
3. Auerbach, M.H., Reimer, R.A., Olauder, R.G. and Rapier, P.M., 1983. A Calcium Carbonate Scale Inhibitor for Direct-Contact Binary Geothermal Service, Journal of Petroleum Technology, p. 1546-1552.
4. Hays, G.F., Thomas, P.A., Libutti, B.L., 1982. Fouling in Cooling Water Systems: State of the Art in Detection and Inhibition, Presented at the International Symposium on Fouling of Heat Transfer Surfaces, Whitehaven, PA (November, 1982)
5. Roti, J.S., Nulty, J.H., 1986. Scale Monitoring Techniques and Control in Alkaline Mill Water Systems, Presented at the American Institute of Mining Engineers Annual Meeting, New Orleans, LA (March 1986)
6. Townsend, J.R., Herman, K.W. 1978. Scale and Deposit Control in Cooling Water Systems, Presented at the 39th International Water Conference, Pittsburgh (October 31-November 2, 1978).
7. Masler, W.F., 1982. Characterization and Thermal Stability of Polymers for Boiler Treatment, Presented at the International Water Conference, Pittsburgh, PA (October 1982)
8. Panichi, C., 1989. Geothermal Research in Italy, Geothermal Resources Council Bulletin, March 1989, p. 15.