

SURVEY OF CHEMICAL INHIBITOR APPLICATIONS FOR CONTROLLING CALCITE DEPOSITION IN GEOTHERMAL WELLS

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ABSTRACT

After more than a decade of commercial application of the calcite inhibition technology in geothermal this paper attempts to: 1) review the present state of chemical inhibitors, 2) compare inhibition efficiencies of various inhibitors, 3) present case histories of applications to show their uniqueness and/or similarities, 4) discuss limitations or problems of the present technology, 5) provide options for improvement or avenues for research.

1.0 INTRODUCTION

Calcite scaling of production well bores drilled in reservoirs with $T \leq 240^\circ\text{C}$ is a common problem for geothermal field operators. In most cases, the fluids are already over saturated with calcite in the reservoir. Further, flashing of these fluids inside the well causes deposition. Gradual output declines occur with continued deposition until well becomes completely blocked and non-commercial. Rehabilitation of the well to recover output requires putting the well off-line for regular 1) work-over and/or 2) acidizing operations. These operations are costly due to the down time the well is off-line. Thus, from the early 1980's (Pierri, et al., 1989) to the present, testing and commercial field applications of calcite inhibitor chemicals has been undertaken. To date, several geothermal fields all over the world are applying on a commercial scale the downhole addition of chemical inhibitors as the solution to calcite scaling in production wells (Pierri et al., 1989; Benoit, 1990; Robson et al., 1990; Vaska and Kellog, 1989; Monette et al, 1991; Lovekin, 1990; Yoshida, 1991 and others).

After more than a decade of commercial application of calcite inhibition in geothermal, this paper attempts to: 1) review the present state of chemical inhibitors, 2) compare inhibition efficiencies of various chemicals, 3) present case histories of commercial applications, 4) discuss limitations or problems of the current technology, 5) provide options for improvement or avenues for research.

2.0 ANTI-SCALANT CHEMICALS

Several chemicals have already been tested for their anti-scalant properties. However, in more recent years the polymers with carboxylic functional groups have been the more popular. This is mainly due to their greater thermal stability at high temperatures. This group includes polymers from acrylic acid, maleic anhydride, methyl-acrylic acid and their copolymers (made up of 2 or more monomers or base units). The structures of the base units and polymers of these common calcite inhibitor chemicals are shown in Figure 1.

These are available in a wide range of molecular weights (depending on the number of monomers), but it is widely accepted that low MW (1,000-10,000) is useful for inhibition (Vaska and Kellog, 1989). Longer chain and higher MW polymers will cause bridging and deposition, rather than dispersion.

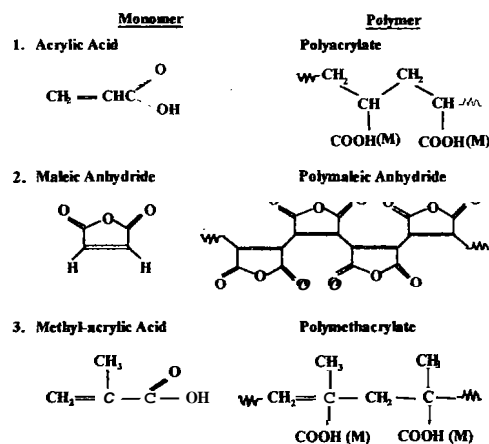


Figure 1. Chemical structures of common base units and their corresponding polymeric chains. In some formulations the COOH group is neutralized with the H^+ replaced by a metal (M) usually from NaOH.

Comparative thermal stability tests of Na-polyacrylate and polymethacrylate show no chemical degradation up to 315°C (Denman and Salutsky, 1969). **Similar** thermal stability tests for polymaleic anhydride show that it is stable up to 300°C (J. C. Shia, pers. com., 1998). Wet tests made with the polyacrylate in dilute solutions with some free NaOH and heated to 900 psig (6.2 MPag) for 2 hours indicated no chemical degradation and little depolymerization.

Table 1 presents typical properties of some commercial formulations. Different commercial products available in the market do not indicate the % composition of the active polymer, but present a mixture of components with water. Similarly, physical and chemical properties are representative for the whole mixture.

Table 1. Chemical and physical properties of some commercial scale inhibitor chemicals.

Product Name	Description	Color	Specific Gravity (kg/l)	pH (Neat)	Viscosity (cps)	% Active Component
1. N9354 Nalco	aqueous soln. of an acrylate polymer a SO ₄ and HSO ₄	clear to pale yellow	1.27-1.32	5.4-8.0	51	trade secret
2. N1340HP Nalco	aqueous soln. of a polyacrylate	clear straw	1.11	4.1	15	trade secret
3. Aquaquest 305 Henkel NZ Ltd	aqueous soln. of a Na-polyacrylate	clear to hazy	1.3	7.5-9.0		trade secret
4. Milperse 815 Drew	polymaleic anhydride	clear straw	1.18	1		trade secret
5. N95 DO-066 Nalw	aqueous soln of a polycarboxylic acid		1.17	<2.0		trade secret
6. DP 3537 FMC	mixture of polycarboxylic acids	amber liquid	1.13	<2.0		trade secret
7. Scaletreat 5818 Clarion	blend of acrylate polymer and dispersant	clear amber liquid	1.12-1.17	6.5-9.5	<30	20%
8. PAS JMC	polyacrylic acid-soda		1.09	9	50	40%

Chemical scale inhibitors come in the form of liquids and solids. The liquids are the more convenient form to use because of the ease in metering by simple inexpensive chemical pumps that can be electric or pneumatic (air driven). Liquid scale inhibitors are seldom marketed in forms greater than 50% by weight. The reasons for this limitation are:

1. Most products, although highly soluble in water, do have solubility limits.
2. Evaporation from chemical pump reservoirs can result in the precipitation of solids from highly concentrated solutions. This in turn can result in plugging of chemical pumps, valves, orifices and tubings resulting in the absence of inhibition.

Since approximately 50% or more by weight of liquid scale inhibitors is water, freezing problems occur. Consequently, some companies provide "anti freeze" or "winter grade" scale inhibitors. This is usually done by adding organic depressants like alcohols, glycols or inorganic salts to decrease the freezing points of scale inhibitor solutions to levels reaching -34°C. These additives should be provided at minimum cost. However, most geothermal consumers in Japan and the USA (Benoit, 1990) have opted to solve the freezing problem by construction of thermal insulation to surface facilities to "winterize" their systems.

Since the liquid scale inhibitors are water based products of highly concentrated electrolytes (charged particles), they can be quite corrosive. Scale inhibitor suppliers try to avoid this problem by pH adjustments, special liners in

drums and tanks, specified materials of **construction** in chemical pump lines and reservoirs, and use of special corrosion inhibitors in the formulation itself. The chemicals **can** be neutralized with NaOH to form Na salts with pH close to neutral or basic, rendering them less corrosive. However, the addition of corrosion inhibitors is specially problematic since scale inhibitors are mostly anionic (negatively charged), while corrosion inhibitors are highly cationic (positively charged) N-derivatives, which **can** result in precipitation or phase separation. If precipitation occurs, it not only nullifies the effect of the two, but also results in severe deposition problems.

Most commercial products are proprietary and do not declare the % active component, nor adequately describe the components of the formulation. (See Table 1). For instance, N9354 is described as “an aqueous solution of an acrylate polymer” with pH of 5.4-8.0 suggestive of neutralization with NaOH. Confirmatory FT-IR spectra of the dried powder shows an extra peak at 1050cm^{-1} , not present in the pure spectra of Na-polyacrylate (Fig. 2). This is suggestive of other additives or impurities in the formulation. Technical claims in product bulletins and in Material Safety Data Sheets (MSDS) should be factual and must withstand close scrutiny of the buying public. Since not all marketed scale inhibitors have the same performance levels (some better than others), various formulations should accurately identify the % active component and all other additives.

Commercial formulations which are marketed with technical data sheets should not be described in vague, misleading terms. For example, a formulation described as “an aqueous solution of a mixture of polycarboxylic acids” is a general term for literally thousands of polymers containing the COOH functional group. It is the responsibility of the chemical supplier to provide accurate technical data of the product and not mislead the consumer by offering “%lackbox” formulations in the guise of trade secret. Based on Table 1 alone, it appears the consumer is made to buy the same active compound (e.g. Na-polyacrylate) from different suppliers (ergo different brand names) with variable additives of water (as seen from the various densities and Viscosities reported) and other inorganic or organic stabilizers and impurities or by-products of the synthesis.

The present cost of commercial scale inhibitors is highly competitive, mostly ranging from US\$2.50/kg (about 40-50% purity) to US\$6.00/kg for high purity products; with discounts offered for bulk shipments in porta feed units to as low as US\$2.00/kg. Chemical suppliers also offer after sales services for on-line Ca and Mg analysis to monitor the effectiveness of the calcite inhibition program.

3.0 LABORATORY TESTS

For geothermal use, initial laboratory tests to determine the thermal stability of the inhibitor under expected downhole pressures and temperatures should be investigated. The chemical supplier can perform thermal stability tests for the client or the end-user can perform their own simulation tests. At PNOC-EDC, a 10% solution of the inhibitor chemical was prepared and placed in a downhole sampler in a calibration bath and exposed to 244°C and 4 MPa for 24 hours (the expected residence time inside the tubing). The sample was then cooled and observed for physical changes (color, precipitation/turbidity and viscosity) to determine if it poses any degradation or caking tendencies during injection which may plug the tubing. The ultimate confirmation would be the FT-IR spectra of the heated product remaining unchanged.

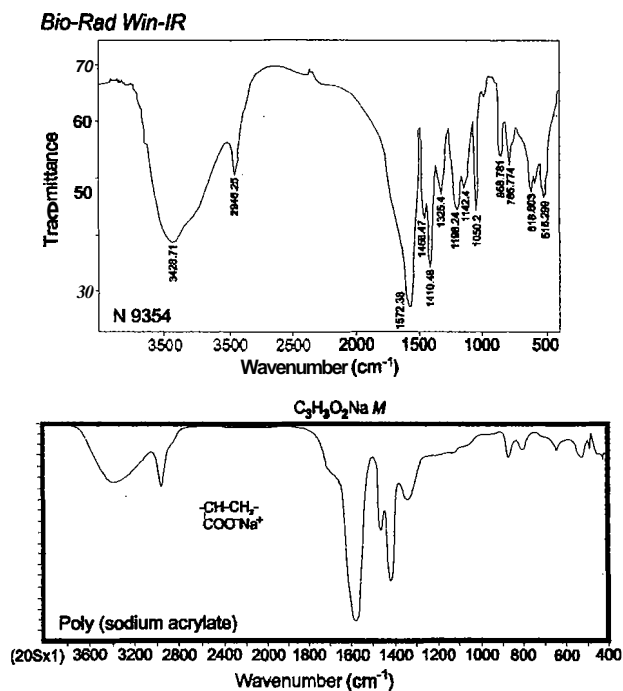


Figure 2. (a) FT-IR spectra of N9354, and (b) pure Na-polyacrylate.

Screening tests using the standard NACE calcium carbonate method *can* also be used. This test is a standard laboratory screening procedure designed to measure the inhibition efficiencies of various chemicals using a synthetic brine with very high scaling potential at 71°C under static conditions for 24 hours. The synthetic brine prepared has a final Ca concentration of 2,000 ppm, with the inhibitors at 10 ppm in the final mixture. Table 2 shows the results of the NACE test on some commercial products.

The above test suggest that the polyacrylates have higher % inhibition than the other polycarboxylic acids at 10 ppm. Since most geothermal brines have much lower TDS and Ca scaling tendencies than the synthetic brine, we expect an optimum dosage much lesser than 10 ppm to inhibit downhole scaling.

The performance of calcite inhibitor chemicals in preventing calcite deposition *can* also be evaluated using the CaCO₃ shaker test conducted at 90°C, pH=7.8 for 4 hours in a synthetic brine. Test results of some chemical inhibitors are shown on Table 3.

The shaker test attempts to simulate brine chemistry conditions. At much lower dosage concentrations the PMA and phosphino-carboxylic acid based polymers show higher % inhibition. However, *greater* improvement in efficiencies are shown by the polyacrylates at much higher dosage concentrations.

4.0 MECHANISM OF ACTION

The *mechanism* of action of synthetic organic polymers is through crystal *distortion* and *dispersion*. The anionic polymers (due *mainly* to the presence of the polar COO⁻ group) become adsorbed in the *growing* crystal causing *distortion*. The polymer interferes with the ability of the crystal to grow in a precise geometric pattern. This introduces an irregularity which shuts down the growth size or induces a *distortion*. Distortion of the *crystals can* reduce the *hardness* and tenacity of a scale, which allows *scales* to be swept away by fluid flows. In addition the overall *net* negative charge imparted on the micro-crystal results in repulsion or dispersion of the colloidal particles. Crystal distortion *has been* proven in *scanning* electron micrograph studies. The *net effect* is that very small non-adherent micro-crystals are formed, *instead* of the larger adherent crystals present in the absence of inhibition.

5.0 CASE HISTORIES ON COMMERCIAL APPLICATIONS

5.1 USA Geothermal Fields

Coso geothermal field

The inhibition program at the **Coso** geothermal field started since 1988 involves the injection of a **polymaleic anhydride (PMA)** at 30 to 38 L/H (Lovekin, 1990). PMA is the only inhibitor chemical in use at Coso due to the absence of plugging problems. This yields an effective concentration of the liquid phase of 2.5 to 5 ppm. Ca levels in the pre-flash brine is from 20 to 50 ppm at reservoir temperatures of 250°C.

Table 2. NACE test of some commercial formulations

Chemical Inhibitor (10 ppm)	Active component	PH (neat)	% Inhibition
1. Drew 11-598	PMA	<2.0	20.73
2. Bellasol S-20	Polyacrylate	9.0	51.60
3. Nalco 9353	Polyacrylate	3.2	71.01
4. Nalco 9354	Polyacrylate	5.4-8.0	84.48
5. Nalco 95DO-066	polycarboxylic acid	<2.0	44.11
6. Scaletreat 5818	Polyacrylate + dispersant	6.5-9.5	51.77

Table 3. Shaker Test results of some commercial products

Chemical Inhibitor	Active Component	% Inhibition		
		2.5 ppm	5.0 ppm	7.5 ppm
1. Drew 11-598	PMA	72	77	85
2. N9354	polyacrylate	55	73	90
3. N 95DO-066	polycarboxylic acid	66	69	74
4. N9353	polyacrylate	40	70	95
5. BS-20	polyacrylate	54	53	60
6. DP 3537	phosphino-carboxylic acid	64	88	98

The brine water chemistry used for the above test is shown below:

Ca ⁺² : 350 ppm	HCO ₃ ⁻ : 1000 ppm
Mg ⁺² : 56 ppm	Cl ⁻ : 16,058 ppm
Na ⁺ : 10077 ppm	SO ₄ ⁼ : 0 ppm
K ⁺ : 283 ppm	CO ₃ ⁼ : 0 ppm
Ba ⁺² : 50 ppm	TDS : 27,923 ppm
Sr ⁺² : 50 ppm	

A concentric tubing (1/4" capillary tubing inside a 1" carbon steel coiled tubing) is used to inject the chemical 100-150 meters below the flash point depth of the well. The concentric tubing design has grown out of an attempt to solve capillary tubing failures due to high well flow rates. The stainless capillary tubing inside provides a corrosion resistant tubing for the inhibitor, while the carbon steel coiled tubing provides the mechanical strength to withstand well bore turbulence (Lovekin, 1990).

Dixie Valley geothermal field

The scale inhibition program started in 1988 at Dixie Valley uses Nalco 1340, a copolymer polyacrylate (diluted 3:1) at a dosage of 3 ppm (Benoit, 1990). The chemical is injected using a 1/4" capillary tubing within a larger diameter hang down string (4.8 cm OD). The inhibitor being used however has long term corrosion problem and plugging tendencies. Nalco 1340 has about 8000mg/L S left over as catalyst in the manufacturing process. This S reacts even with stainless steel to produce iron-sulfide (Benoit, 1990).

The Dixie valley brine has 5 to 6 mg/L of Ca at 245°C in the reservoir. Without inhibition, scaling reduces flow to non-commercial levels within 100 days. Low injection flow rates (<10ml/min or 0.6L/hr) have resulted in plugged injection tubings. This is due to the chemical exiting at the bottom of the tubing faster than it is pumped at the surface creating low pressure areas which causes boiling. This can be avoided by higher pumping flow rates (~20ml/min). If the chemical is boiled, it produces a messy residue resembling a black thick tar.

Eleven production wells have been installed identical inhibition systems, which have been in long term operation (about 3 years) before pull-out for inspection. They have also shifted to Nalco 1340HP, a low S product of Nalco 1340 (Benoit, 1998 pers. com.) In July of 1998, they have also field tested a "friendly" chemical N9354, a neutralized polyacrylate for eventual use at Dixie Valley (Benoit, 1998 pers. com.).

More recently, multiple capillary tubings have been strapped on a carbon steel hangdown string. The open hang down string can also accommodate logging with small diameter tools and repeated well kick-offs (Benoit, 1999). This design is the current system at the Dixie Valley geothermal field.

Beowawe

In this field, 3 production wells have flash point depths of 150-300 meters below surface where calcite deposition is actively occurring. A simple 1/4" SS316 tubing delivers diluted (1:15) N9354 downhole at 20ml/min. At the bottom of the tubing are some sinker bars to weight it down and a dispersion head with 4-8 ports for chemical injection to the flow stream. This simple system has worked without any problems even in the biggest well with a TMF of about 133 L/s. Abrasions in the capillary tubing close to the well head has required the pull-out of this tubing every 3 months, to bring the damaged portion to the surface.

Intermountain geothermal field, Roosevelt hot springs, Utah

Prior to chemical treatment, the scaled wells in the field needed to be put off-line every 4 months for acid washing. Well head pressures vary from 240 to 250 psig, with downhole temperatures of 251-268°C. The chemical inhibition was with Millsperse 822 (a maleic based polymer) injected through a 1/4" stainless steel tubing to a depth of 1060 meters. This program has allowed the continuous operation of the well without significant losses in WHP for a whole year.

5.2 Japanese geothermal fields

Nigorikawa geothermal field (Moripower plant)

The Nigorikawa geothermal reservoir fluid is saturated with CaCO₃, resulting to scaling during production. From 1984 to 1985, a scale prevention system was completed which completely solved the deposition problem. A chemical inhibitor of polyacrylic acid-soda (PAS) at pH 9 was injected downhole. This chemical is marketed by Japan Metals and Chemical, Co. The injection tubing is made of Incoloy 825 (OD 3/8", ID 0.249") inside a 7/8" air pipe fitted with a centralizer to protect the tubing (Fig. 3). The air pipe is also used for gas lifting.

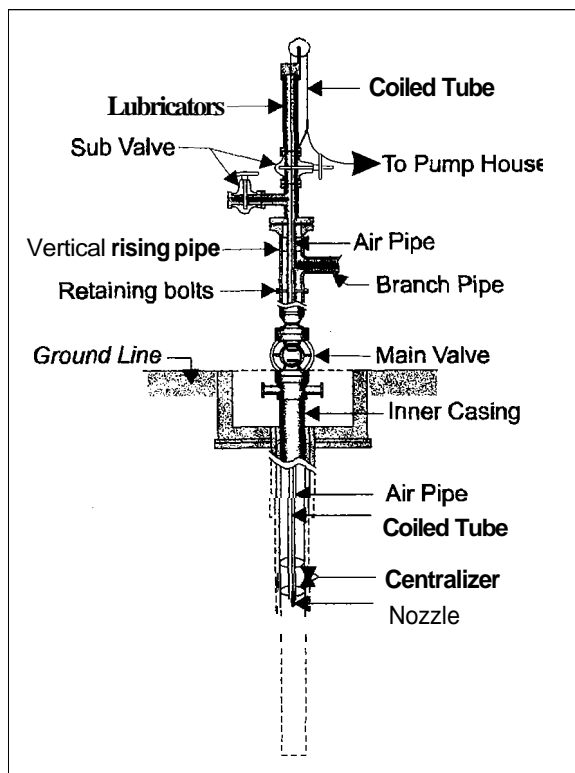


Figure 3. Injection system at Nigorikawa geothermal field

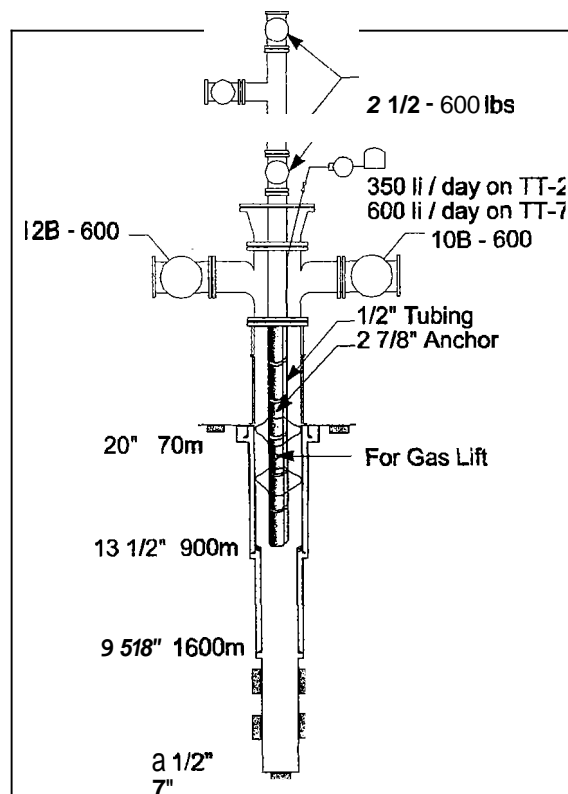


Figure 4. Injection system at Takigami power station.

There are no reported plugging problems with the PAS chemical and a proprietary on-line analysis is claimed to exist. It is however recognized that there is a reduction in output due to the presence of the 2 7/8 pipe inside the well bore.

Takigami geothermal power station

At Takigami, the scale prevention system services two wells TT-2 and TT-7 (Cabel, 1998). The 1/2" injection tubing is bonded on the outside of a 2 7/8" air pipe which also serves as tubing for well stimulation (Fig. 4). Their chemical is supplied by Kurita Chemical Company.

5.3 New Zealand geothermal fields

Kawerau and Ohaaki geothermal fields

Initial inhibition trials were conducted on well KA 35 using an Exxon chemical SURFLO RD 3056 in 1988. A 15% solution of chemical was prepared and injection began at a flow rate of 20L/H to give a dosage concentration of 5 ppm in total mass flow, with a residence time of 16.5 minutes in the tubing. The injection system is made up of a 1/4" OD Incoloy 825 capillary tubing held in place by a weighted injection head attached to the bottom (Fig. 5). At the sinker bar, there is a check valve to stop geothermal fluids from entering the tubing. Prior to the Kawerau trials, no work on calcite inhibition at elevated temperatures (>270°C) has ever been undertaken.

At Ohaaki, a 15% solution of Aquaquest 305, an acrylate polymer is injected using a 1/4" or 3/8" Incoloy 825 tubing with anti-scalant residence times of 1 to 2 hours depending on the injection rate (Bacon, pers.com 1998) For Ohaaki, the reservoir temperatures of wells with scaling tendencies is close to 250°C.

For both Ohaaki and Kawerau, in high flow wells (TMF>350TPH) an armored 1/4" Incoloy tubing (OD of armor is 1/2") is used (Fig. 5). On low flow rate wells, a 1/4" or 3/8" Incoloy 825 tubing is used. Presently, the chemical inhibitor being used for both fields is Aquaquest 305, sold by Henkel, NZ. Ltd. There are no reported problems with the present chemical being injected.

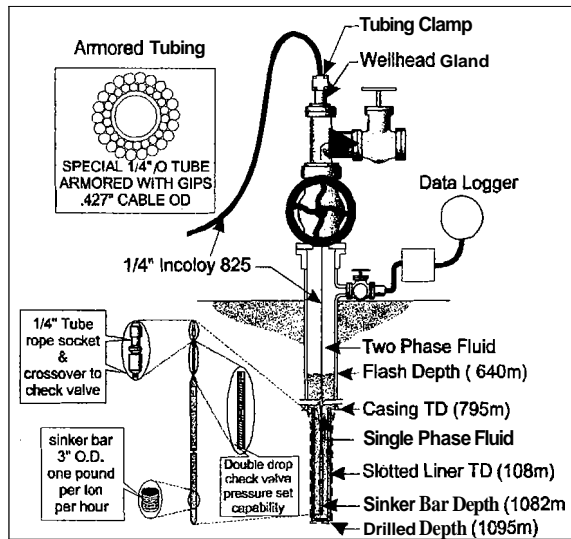


Figure 5. Injection system at the Kawerau geothermal field

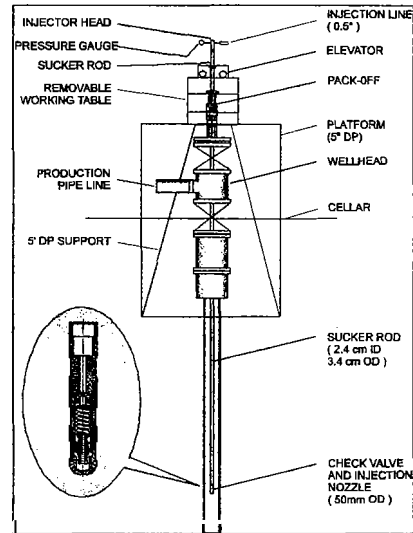


Figure 6. Final set-up of sucker rod during injection.

5.4 Philippine geothermal fields

APO-1D in the Mindanao 1 geothermal production field has a reservoir temperature of 240°C, downhole maximum pressure of 6 MPa and with 80-100 ppm of Ca in the pre-flash brine. The well developed CaCO₃ deposits with 50% reduction in output after 4 months of continuous full bore utilization. Initial field testing in August 1998 of a 10% solution of N9354 in well APO-1D was conducted using 1" ID sucker rod as injection system. The sucker rods reached a depth of 951 meters and was composed of 120 joints fitted with an injection nozzle with 6-8 ports and a non return valve which can be set to open at a given downhole pressure. The injection system is shown in Fig. 6. Due to the presence of the sucker rods, the output of the well decreased from 6.2 MWe (without sucker rods) to 5.1 MWe (with sucker rods).

Injection was at very high pressures ($P_{inj} > P_{whp}$) to maintain a liquid column inside the tubing. Injection flow rate was at 10 L/hr resulting in a dosage concentration of 5 ± 1 ppm in the total mass flow and a residence time in the tubing of around 48 hours. After one month of testing, the tubing was plugged with the chemical inhibitor, corrosion products, clay and rock chips. It is believed that plugging was caused by: 1) boiling and subsequent deposition of the inhibitors due to uncertainties in NRV operation, 2) inherent debris from sucker rods, oxygen induced corrosion pitting of carbon steel rods and diluting water impurities too big to pass the 1/8" nozzle ports, and 3) separation and deposition of the high density polymer from the diluting water during transit due to long residence times.

Water flow monitoring using Na-benzoate as a tracer was conducted on a weekly basis to assess the status of the inhibition program. In the month long test, water flow remained stable. Attempts to analyze the concentration of the polymer in the surface discharge was also undertaken. However, the simple turbidity test recommended by Nalco is beset with interference problems from other brine components (e.g. silica) which precipitate out with the polymer at pH 7. Until now, there is no available working on-line analysis for the polyacrylate. Initial WATCH calculations of the APO-1D fluid show a $Q/K_{CaCO_3} \geq 4$ prior to deposition and a $Q/K_{CaCO_3} \approx 1$ during active deposition. Thus, complete water and steam chemistry analysis is needed to monitor the progress of the inhibition program. Higher $Q/K_{CaCO_3} \geq 4$ are expected with 100% inhibition, while $Q/K_{CaCO_3} \approx 1$ would suggest need for more inhibitor to inhibit deposition.

6.0 DISCUSSIONS

There are two class of polymers currently being used for geothermal calcite inhibition control: 1) the polyacrylic acid (PAA's) and 2) the polymaleic anhydride (PMA's). Both have the carboxylic acid (COOH) functional group. The PAA's have a straight chain with one COOH in the monomer, while the PMA's have a ring

for the monomer with 2 COOH groups. The PAA's and PMA's are both acidic in chemical nature and are thus highly corrosive. At present, neutralized PAA's (with the addition of NaOH) are being used in the USA, New Zealand and Japanese fields to minimize corrosion and handling problems. However, PMA applications are limited to the highly acidic ($\text{pH} < 2$) more corrosive form in the USA. Temperature range of applications for both is from 180°C - 280°C , with dosage concentrations of 1-5 ppm in the TMF. Both class of polymers have been used in brines with Ca levels ranging from 2-200 ppm.

Few commercially available scale inhibitors are 100% pure single compounds, but are formulated products. This involves using the same monomer (e.g. acrylic acid, maleic acid, etc.) but with variable MW (1,000-10,000) or chain length and additives (e.g. inorganic catalysts, neutralizers, corrosion inhibitors). These additives to the active polymer are included to stabilize the product or prevent problems during applications. These result in similar products with variable %composition of the active component. Since polymers are highly viscous and dense; formulations with higher viscosities and densities have greater % purity of the active compound. Most chemical companies do not reveal the %composition of their formulations in the guise of trade secrecy, making actual calculations for dosage concentrations difficult on the active component alone. This has led to a number of lapses in the marketing of formulated products, primarily through the scarcity or incomplete technical data which can be verified by the buyer. As the inhibition technology slowly evolves from the "black box" realm to science, room for lapses will be minimized. Greater sophistication in product synthesis is expected due to the great demand as it is unlikely that a single product can solve all the diverse deposition problems in the field.

Also, the Concentration of the chemical inhibitor in the brine matrix collected at the surface is difficult to determine. This is mainly due to the absence of a simple hydrocarbon analysis, with no interference from the other brine component. To date, there is no known existing specific chemical analysis only for the polymer which can be used for routine monitoring of dosage concentration at the surface. Nalco Chemical Company uses the Hyamine method for the semi-quantitative analysis of the polymer solution. However, the methodology which is a simple turbidity test fails in concentrated brines where other brine components precipitate out at the pH of determination. FMC has a rigorous procedure for the analysis of the phosphate group in its scale inhibitors (usually of the phosphino-carboxylic acid kind). This procedure is tedious and prone to error for application to very dilute dosage concentrations expected at the surface. Surface analysis of the polymer is important to check on the fate of the injected inhibitor. This is needed because the success of the inhibition program is hinged on the continuous and consistent dosing of the chemical. Thus, spot checks on the flow and polymer concentration are necessary to adjust dosage.

Since, every field is different in terms of reservoir chemistry and temperature, there is a need to evaluate several inhibitors in the field to determine which works best for a particular application. The key considerations are: 1) thermal stability, 2) residence time in the tubing, 3) reactivity with the dilution water and/or injection tubing. Some anti-scalants breakdown at high temperatures producing insoluble by-products. Some gel in the tubing, if they are there for extended periods due to changes in viscosity at higher temperatures. Some attract bacterial growth upon prolonged exposure in humid environments. Most polymers crystallize into resin-like residue upon removal of the diluting water during boiling inside the tubing. At present, there is no existing single formulation that can solve all the various deposition problems in the different fields. Continued research to formulate more stable chemicals for variable temperatures and chemistries should be actively pursued by the chemical suppliers.

Chemical inhibition is not free from problems. Major problems encountered include: 1) corrosion, and 2) plugging tendencies. For most geothermal applications, the corrosion problem was solved by resorting to corrosion resistant materials like polyethylene, SS316 and Incoloy 825 in surface and injection facilities. However, the metal alloys are quite expensive. Thus, there is a demand for chemical suppliers to devote research efforts to make their products more "friendly" to the end user, at minimum cost. Neutralized PMA applications should also be field tested.

Crystallization of concentrated inhibitors is another problem. This is most severe if the chemical solution is boiled off and the diluting water is removed. The common solution is to dilute the chemical with fresh drinking quality water. The highly viscous chemical inhibitors should not be injected pure but diluted at least with 80% water. Scale inhibitors can react with certain water components such as Ca and Fe and end up as scales. In the field, available dilution or make-up water is usually mineralized and with high TSS contents making it problematic for use requiring fine mesh filters. Most suppliers offer diluted versions of their standard inhibitors in porta-feed

units (1200-1600 liters) to avoid these problems. Although the dilution is convenient, the end user is made to pay for the bulk shipment of a solution mostly (about 80%) made up of water.

delivery remains

technology. The original simple 1/4" injection tubing is prone to abrasion, fatiguing, plugging and long term corrosion problem. Attempts to solve these problems have been varied: 1) use of 1.9" hang down strings to protect the tubing (Benoit, 1990), 2)

OD of Tubing (inch)	ID of Production Casing (in)	% Reduction in output
1	9 5/8	10
1	7 5/8	13
2 7/8	13 3/8	22

of the master valve, 3) use of a protective 1-1.25" coiled tubing (Lovekin, 1990), 4) use of 2 7/8 " air pipe to protect the injection tubing 5) bonding the capillary tubing on the outside of a 2 7/8 air pipe, and 6) armored tubing. The main drawback of these protective tubing installations is the reduction in well output due to: 1) decrease in production area, 2) increase in frictional resistance to two-phase flow. Decrease in output has been estimated to be from 10-22% of the original depending on the fraction of the production casing occupied by the tubing. The armored and concentric tubing designs offer greater flexibility and reliability and could prove to be more cost effective in the long term.

7.0 CONCLUSIONS

The chemical inhibition technology has been here for more than a decade and has continued to evolve to address the various calcite scaling problems in geothermal wells. Several chemicals have already been tested for their anti-scalant properties (chelating agents like EDTA, organic phosphonates, polymers with carboxylic or sulfonic functional groups). However in more recent years the polymers with carboxylic acid functionality have been widely used, the more popular being the PAA's and PMA's. Since they contain the COOH functional group, these polymers are highly corrosive. This problem has been initially solved by corrosion resistant materials in the surface and injection facilities. However, new generation polymers have been neutralized with NaOH to make them more 'friendly' and easier to handle. Neutral Na-polyacrylate commercial applications have been known in Japan, USA, Indonesia and New Zealand, while PMA applications remain in the acid form. At present there is no existing single formulation that can solve the various deposition problems in the different geothermal fields. Continued research to formulate stable chemicals for variable temperatures and chemistries should be actively pursued.

Successful chemical inhibition is hinged on the consistent injection and fast flows (short residence times) afforded by the use of small diameter capillary tubing. Various improvements of the original unprotected 1/4" capillary injection tubing in the different fields have led to long term reliability of these systems. These improvements include: 1) sheathing the 1/4" capillary tubing with a coiled tubing of 1-1.25 inch mild steel, 2) use of short 3" hang down string to protect the capillary tubing close to the well head, 3) armoring with GIPS, 4) use of 1.9" hang down string or a 2 7/8" air pipe. More recently, capillary tubings have been strapped or bonded on the outside of carbon steel tubing, with the latter having the dual purpose of lending mechanical strength and for gas lifting. At Dixie Valley, multiple capillary systems have been used for back-up and to piggy back downhole temperature and pressure logging equipment needed for more frequent monitoring purposes (Benoit, 1999 this volume).

Problems related with the entry of geothermal fluids in the injection tubings have also been addressed by: 1) use of non-return valves at the injection head in Ohaaki and Kawerau (Bacon, 1998 pers. com.) and 2) capping the bottom of the injection head at Dixie Valley (Benoit, 1999 this volume).

Even with the drawback of reduced output with the protected tubing designs currently in use, chemical inhibition still remains as the most widely accepted, cost effective and reliable solution to the calcite scaling problems in geothermal production wells. It is expected to be in greater demand in the future as new low enthalpy fields are exploited for power generation.

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