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Field Application of Calcite Antiscalant in New Zealand: Screening Process, Performance Evaluation and Management of Operational Issues

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ABSTRACT

Calcite scaling is a major problem encountered in several geothermal fields in New Zealand. Production from a geothermal well can decline by as much as 50% in one year depending on the fluid oversaturation with respect to calcite and the rate of scale deposition. Mechanical clean-out and acidising are two commonly used options to recover loss in productivity due to calcite deposition inside the wellbore. These options however are not considered cost-effective as these require periodic application, in addition to the high cost of doing the job and business interruption with wells needing to be taken off-line.

Scaling inside the wellbore can be proactively managed with the use of antiscalant chemical, if the potential for calcite scaling can be accurately determined based on fluid chemistry and downhole investigation. The antiscalant is normally dosed below the flashpoint using a capillary tubing, and this has been proven to be effective in controlling calcite blockage formation inside the wellbore.

The screening process for a suitable antiscalant chemical requires careful consideration of the chemistry of the fluid produced and the downhole temperature-pressure condition of the geothermal reservoir. Moreover, evaluating the performance of the selected antiscalant will require conducting a series of field trials that monitor the fluid chemistry and well massflow, including addressing any operational problems in downhole delivery system or detrimental side effects on geothermal power plant operation.

This paper will discuss the screening process for antiscalant chemicals available in the market including the required laboratory testing before deciding on a short-term field trial. This paper will also discuss the long-term monitoring activities necessary to evaluate the overall performance of the antiscalant, the management of the antiscalant delivery system and any observed effect on power plant operation.

1. INTRODUCTION

Calcite scaling in production wellbores is one of the major operational problems encountered by many geothermal field operators. This process normally occurs just above the flash point inside the wellbore and in theory, is governed by the chemical reaction below (Arnórsson, 1989):

$$Ca^{2+} + 2HCO_3^- \rightleftharpoons CaCO_3\downarrow + H_2O + CO_2\uparrow \qquad \textit{Equation 1}$$

Flashing leads to a loss of CO_2 and increase in the reaction activity of Ca^{2+} in the residual liquid. The degassing also increases fluid pH causing bicarbonate to be converted into CO_3^{2-}. This causes the oversaturation of the residual liquid with respect to calcite, and the subsequent scale nucleation/deposition process is responsible for the calcite blockage inside the wellbores of production wells.

The rate of scale deposition in the wellbore is influenced by the level of fluid saturation with respect to a certain mineral in addition to the production massflow rate. For fluid saturation with respect to calcite, this is measured in terms of calcite saturation index (CSI) as plotted in Figure 1 against boiling temperatures.

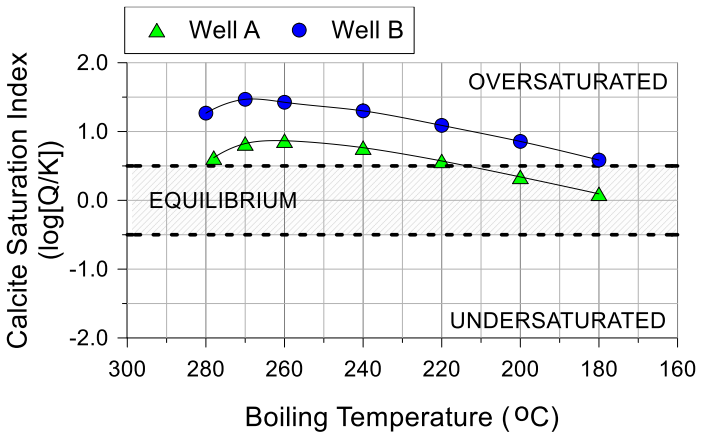

Figure 1: Fluid saturation with respect to calcite mineral at different temperatures.

A CSI above the equilibrium saturation level suggests high potential for calcite scaling in the wellbore as the fluid boils due to changes in pressure-temperature condition. The highest potential for scaling is usually within the flash temperature range of 240-280°C. This scaling potential decreases below 220°C due to the retrograde solubility of calcite with temperature (Arnórsson, 1982). There are special cases of scaling observed in production wells even if the calcite saturation level is close to equilibrium (Quinao et al., 2017). It is expected that scaling would occur at a rapid rate if both high massflow production and high calcite saturation levels are present.

The location of the calcite blockage typically varies between wells, but this usually coincides with the flash point location as illustrated in Figure 2. For Well A, the flash point is located at shallower depth inside the wellbore, and this is the depth where calcite blockage was also tagged. In the case of Well B, calcite blockage was encountered at much greater depth since the flash point location for this well is deeper compared to Well A.

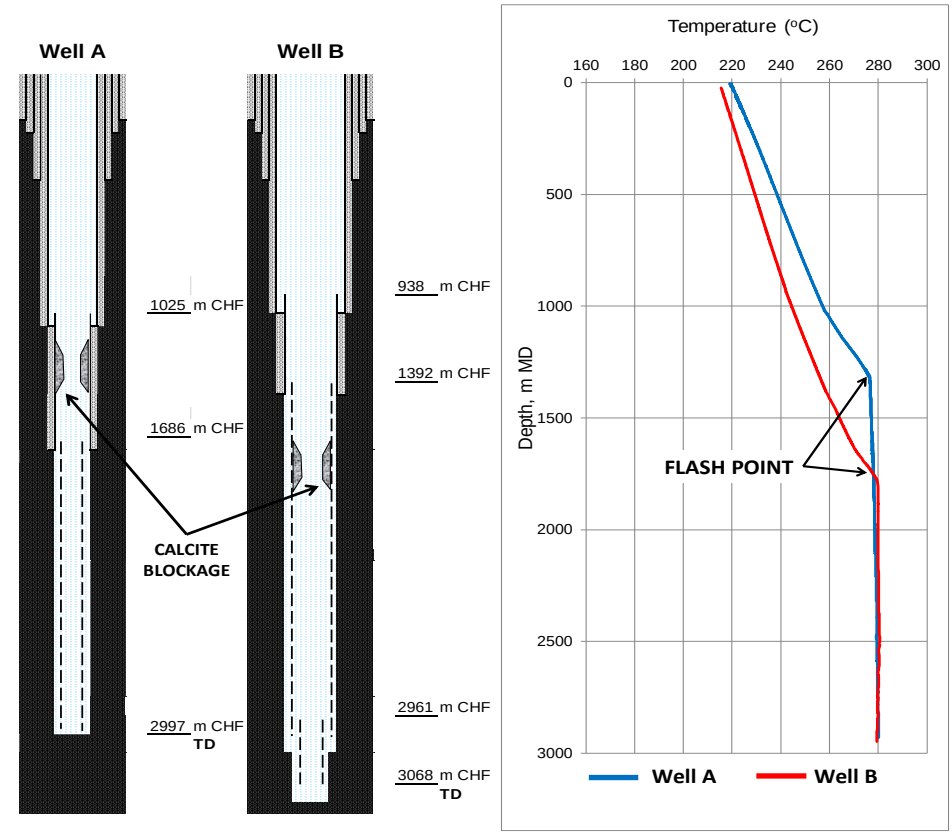

Figure 2: Location of calcite blockage in the wellbore coinciding with the flash point location.

Figure 3 illustrates the effect on massflow of a production well due to scaling. The massflow can decline by as much as 50% in less than a year where scaling rates are particularly severe.

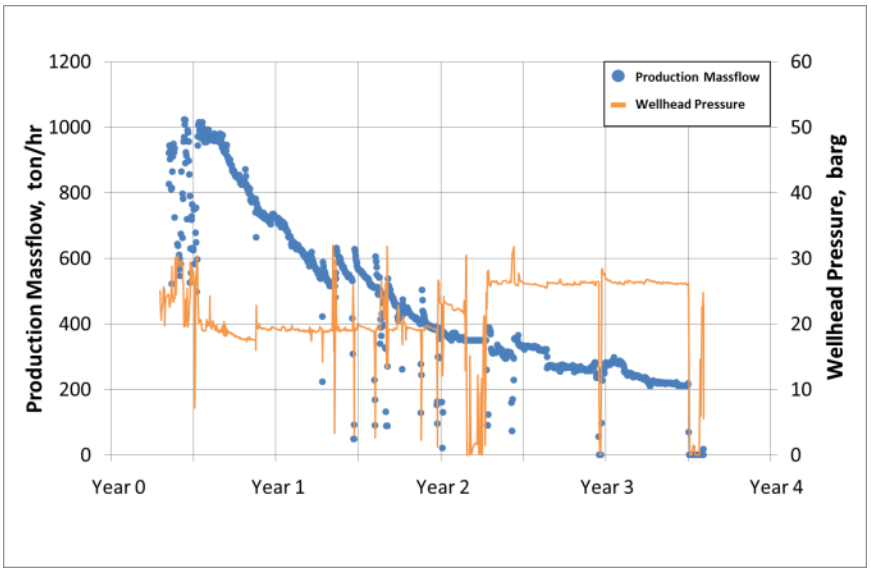

Figure 3: Effect of calcite scaling on well performance.

2. MANAGEMENT OF CALCITE SCALING

Mechanical clean-out and acidising are two commonly used options to recover loss in production from a well affected by calcite deposition inside the wellbore at the flash point location. However, these options are expensive to implement, in addition to the cost of business interruption with wells needing to be taken off-line from the power plant. Clean-out costs can be in the range of $0.5 to $2.0M for a major operation, with a clean-out often required at least every two years. Temporary mechanical broaching (running of different specially-designed gauge tools) may be considered in the short-term. However, as calcite scale can harden over time inside the wellbore this technique can become less effective over time and a full mechanical and/or chemical clean-out becomes necessary to restore well performance.

Calcite scaling inside the wellbore can be proactively managed with the use of antiscalant chemicals. This requires a rigorous process of selecting a suitable antiscalant chemical for the chemistry of the fluid to be treated. As the antiscalant needs to be dosed inside the wellbore at a certain depth and temperature-pressure condition of the geothermal reservoir, a carefully designed surface and downhole delivery system is also required.

The installation costs for a stand-alone system in a well can be between NZ$300-500K, and higher if a centralized mixing system is needed or if there are other wells to be dosed with antiscalant. Annual chemical costs depend on the amount of fluid to be treated and the required dosage rate to effectively control scaling. However, considering less downtime and sustained performance of the production well, proactive management of calcite scaling can be a cost-effective long-term option. The antiscalant chemical is ideally dosed using a capillary tubing set at a depth inside the wellbore of ~100m below the flashpoint (Figure 4). This ensures sufficient mixing of the antiscalant with the well fluids prior to flashing.

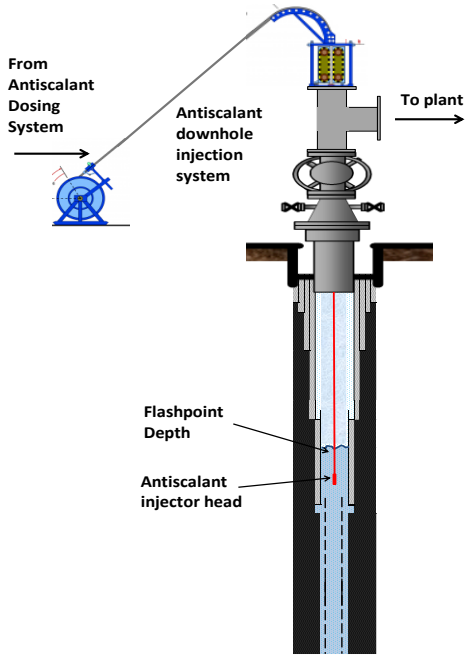

Figure 4: Schematic of antiscalant systems installed in production well.

3. CHEMICAL SCREENING PROCESS

The process of assessing antiscalant chemicals for field application is done in three stages: 1) Market research and laboratory testing; 2) Short-term field trial; and 3) Long-term assessment of well performance. It may take up to 3 months for the first two stages, and between 3-6 months for the last stage of assessment.

The first stage is market research of available chemicals and their validated successful use in other geothermal fields. The short-listed chemicals can then be subjected to a laboratory testing designed specifically for the condition of the field of intended use. Depending on the outcome of the first stage assessment, the chemical that shows the most promising performance is then programmed for a field trial in actual production well downhole conditions. The field trial can consist of frequent brine sampling from the production well two-phase line to monitor calcium levels and monitoring the well massflow trend that is normalised for wellhead pressure. If there is an existing antiscalant chemical being used, this will provide an additional comparative basis in assessing the performance of the new replacement chemical. After the second stage assessment, and if successful control of scaling based on monitored parameters is observed, then final assessment will proceed by using the chemical over a long period of time while monitoring for the production well performance (e.g. massflow).

3.1 Chemicals Available in the Market

The most commonly used calcite antiscalant chemicals available in the market can be categorised into two main classes, as listed in Table 1. The polymers of these antiscalant chemicals behave as both crystal modifiers and dispersants as they develop a negative charge in water and attach themselves to the growing $CaCO_3$ micro-crystals causing distortion and interference with the ability of the crystal to keep growing in a precise geometric pattern. The large negative charge imparted on the aborted micro-crystal will cause it

to repel other like particles. The net effect is that very small non-adherent crystals are formed which can be easily swept away by fluid flow inside the wellbore.

Table 1: Calcite antiscalant chemicals.

Chemical Class	Description
Polyacrylic Acid (PAA)	Straight chain monomer with one carboxylic (COOH) group
Polymaleic Acid (PMA)	Monomer ring with two carboxylic (COOH) groups

Both PAA and PMA are currently being used in several geothermal fields in New Zealand. The short-listing process of antiscalant chemicals in the market involves looking into the following factors:

- Known application in other fields – information around this can be gathered from other operators, conference proceedings, technical papers, or directly from the chemical suppliers
- Temperature application or limitation - thermal stability test results are normally available from the chemical suppliers

Thermal stability is an important factor to consider in the selection process of antiscalant chemicals, especially when the intended use is in a high temperature geothermal reservoir. Degradation of the chemical can happen if it is not stable at the high temperatures reached in its application. This typically results in the less effective calcite inhibition, and subsequent calcite deposition in the wellbore, and in some cases may also result in the degradation products blocking the downhole capillary tubing used to deliver the antiscalant chemical inside the wellbore. A standard method of testing for thermal stability and inhibition effectiveness is discussed in the next section.

Once the above factors can be satisfied, other factors are also evaluated such as supply chain/security and chemical costs.

3.2 Laboratory Testing and Screening

Samples of selected antiscalant chemicals are provided to the GNS Laboratory for thermal stability and NACE testing (NACE International, 2007). These laboratory tests are designed to evaluate the calcite inhibition properties of the chemicals at high temperature, similar to the actual downhole conditions of production wells where these chemicals will be used.

The inhibition performance of the selected chemicals is first measured under no heat treatment condition. For this purpose, a 10% by wt solution is prepared, added to synthetic brine, and assessed following the NACE standard test (TM0374-2007) procedure relative to the blank (untreated control).

Another 10% by wt solution is prepared in a SS316 tubes, capped and blanketed with nitrogen, before being subjected to heat treatment in a forced-draft oven. The target temperature for heat treatment can be as high as 300-320°C and the duration can vary from 2 to 6 hours, with the test temperature and time selected to represent the expected conditions that the antiscalant will be subjected to in the field. The heat-treated solution is then added to synthetic brine and assessed following a similar NACE standard test procedure. The target concentration for the NACE test usually ranges from 5 to 10 ppm based on the chemistry of the fluid to be treated (i.e. calcium concentration) and the dosage recommendation from the chemical supplier.

Typical results from a NACE/thermal stability test are shown in Table 2. From the data, it is evident that without heat treatment, all antiscalant chemicals selected for testing have very high inhibition performance of >95%, based on $CaCO_3$ retained in solution relative to the blank (untreated control). However, after heat treatment all chemicals have shown a decrease in inhibition performance, which varies to a certain degree from one chemical to another.

The antiscalant chemical that shows the highest inhibition performance will either be subjected to further laboratory validation or evaluated in the field using a test rig or in a production well.

Table 2: Results of thermal stability and NACE tests.

No heat treatment	**Calcium Carbonate Retained in Solution (ppm)**	**Inhibition (%)**
Chem 1	4035	98.2
Chem 2	4048	99.0
Chem 3	4025	97.6
After heat treatment	**Calcium Carbonate Retained in Solution (ppm)**	**Inhibition (%)**
Chem 1	3835	85.3
Chem 2	3558	67.5
Chem 3	3255	48.0
Blank	**Calcium Carbonate Retained in Solution (ppm)**	
Before Precipitation	4063	
After Precipitation	2510	

3.3 Short-term Field Trial

Field evaluation of the selected antiscalant chemical can be done through a test rig that simulates the expected downhole conditions and using the actual fluid from a production well. This is usually the method employed before the full commissioning of a new geothermal power plant, with the production wells still on clearing discharge. Bump testing is done by measuring the calcium concentration in the brine that passed through the test rig with and without antiscalant dosing. During the field trial, a series of samples are collected over several days for calcium analysis.

For geothermal fields that have been operating for a certain period, substantial information on calcite scaling is available based on production well history. Hence, it is possible to conduct a field trial to evaluate effectiveness of antiscalant chemical in actual test conditions by using a particular set of production wells.

This is further enhanced if there is already an existing antiscalant system installed as the performance of the antiscalant chemical being used can provide a point of direct comparison. The same method of monitoring calcium concentration can be employed over the field trial period if there is a clear trend observed in calcium concentration during a bump test.

Figure 6 shows the results of the bump test conducted to compare performance of two antiscalant chemicals and the observed massflow trend during the trial for Well B. This well has been known to develop calcite scale previously, so an antiscalant system was installed to mitigate this.

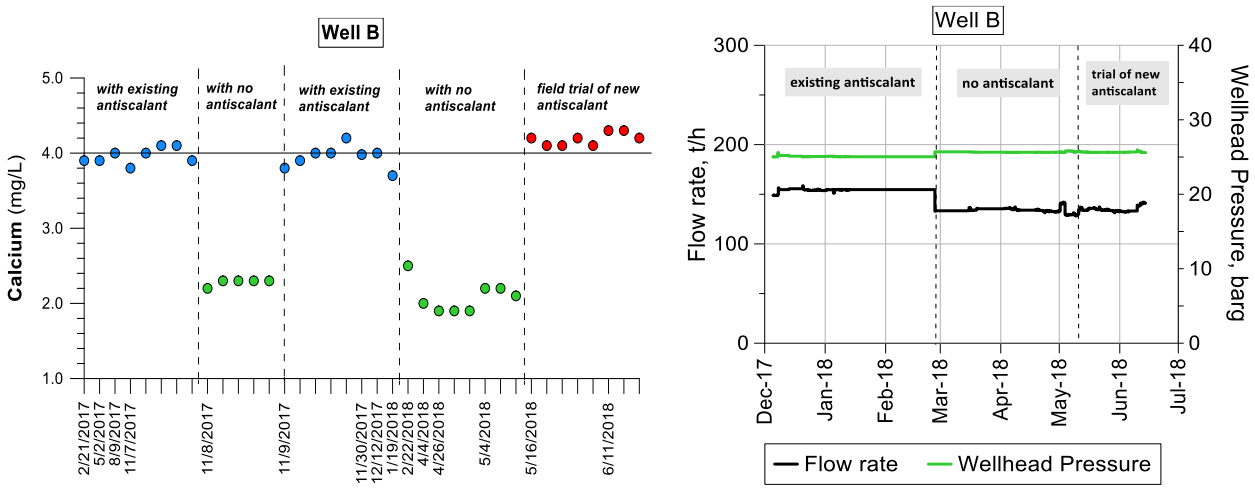

Figure 6: Results of bump tests and well massflow trend.

The first bump test on the existing antiscalant chemical shows the response in calcium concentration when antiscalant dosing was stopped temporarily. From this simple check, it was confirmed that monitoring of calcium concentration can be used to assess the performance of the antiscalant and as an indication of calcite formation and deposition (e.g. calcium loss). This was further confirmed in early 2018 when antiscalant dosing was stopped in production well B due to downhole tubing maintenance. During this period, the calcium concentration dropped again to a level similar to the calcium concentration measured during the first bump test. There are however cases where no calcium response is seen in some wells, and in this instance, it is important to have a close monitoring of the well performance.

After the recommissioning of the antiscalant system, the field trial of a new chemical was started. The results showed that the calcium concentration had increased back to a level even higher than previously measured when using the existing antiscalant chemical. From the trend in calcium concentration, the new chemical appears to be more effective in keeping the calcium in solution and in preventing the calcite from forming.

4. WELL PERFORMANCE MONITORING

Figure 7 below shows the long-term monitoring of production well performance. For about a period of two (2) years, the production flowrate was relatively stable at a constant operating wellhead pressure. Downhole surveys conducted during this period did not tag any indication of a wellbore scale at the flash point. However, due to operational constraints related to a high production requirement, the downhole antiscalant injection system was removed in late 2017 and for a period of over a year antiscalant dosing was stopped. During this period of no antiscalant dosing, production flowrate was observed to continuously decline even as the production well was utilised at fully open condition (i.e. lower wellhead pressure). Subsequent downhole surveys confirmed a restriction at the flashpoint related to calcite scale formation. Antiscalant dosing was resumed after the mechanical clean-out and since then the well performance has been stable.

It is clear that continuous antiscalant use is necessary in this particular production well in order to maintain its production, and that the antiscalant chemical is proven effective in controlling calcite scaling.

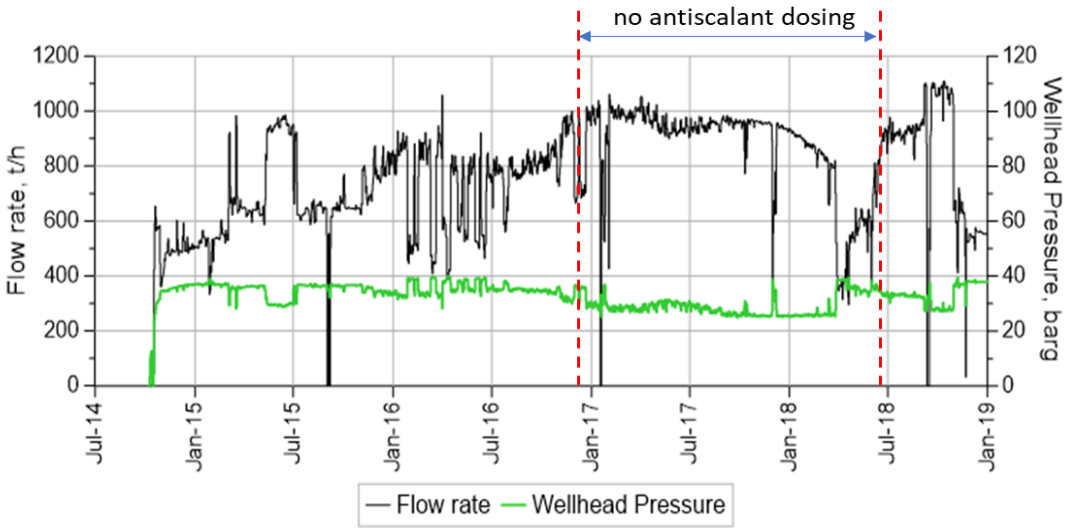

Figure 7: Production flowrate and wellhead pressure trends of a production well.

5. FIELD OPERATIONAL ISSUES

The use of antiscalant chemicals in production wells can present many operational challenges that may need to be addressed to prevent either a reduction in effectiveness of the system, or a system failure that results in a scaled well and/or equipment lost in the well. Key operational challenges may include chemical residence time in the downhole tubing, failure of the installed tubing and fouling of downstream plant equipment; particularly heat exchangers. These challenges are discussed below.

5.1 Residence Time

The residence time of the chemical in the well can have a significant impact on the performance of the antiscalant system, as such it is important that the range of residence times is understood during the system design and taken into account during the antiscalant testing and evaluation described in section 3.2 above. Typically, the vast majority of the residence time will be made up of the time the antiscalant spends in the capillary tubing used to deliver the chemical below the flash depth. While being delivered through the capillary tubing the chemical will be heated up to the well temperature and may start to degrade if it is exposed to well temperatures for an extended period of time. If degradation occurs it could result in a reduction in inhibition effectiveness, and in extreme cases may result in breakdown products depositing within the tubing. This could cause blockages and prevent the delivery of antiscalant to the well. There are several considerations to take into account when designing a chemical delivery system to minimize the retention time including:

- Small delivery tubing size. The advantages of this approach are that it is simple, smaller diameter tubing is generally less costly than larger diameter tubing, and its use results in higher fluid velocities. The disadvantages include the higher pressure drop that may result from the smaller tubing and an increased potential for a tube blockage due to either solids in the antiscalant, or degradation of the solution.
- High antiscalant dilution ratio. The advantages of this approach are its simplicity and an increased solution mass flow, which reduces retention time for a given tubing volume. Increased mass flows and velocities with dilute antiscalants reduce the likelihood of the tubing becoming significantly fouled provided high quality dilution water is used. Disadvantages include an increased pumping capacity requirement (larger dosing pumps), and the (slight) reduction in delivered fluid enthalpy to the plant from injecting a higher quantity of cold fluid into the production well.
- Tube flushing/venting system. A tube flushing/venting system is required to flush the antiscalant from the tubing system in the event that the injection pump is shut down (such as a pump trip or the well being shut in). Leaving the tubing filled with antiscalant at well temperatures can result in tube blockages, rendering the tubing inoperable. Mercury use a flushing system, where clean water (condensate) is pumped through the injection tubing prior to a system shutdown to displace the antiscalant. It is also possible to use a vent line at the surface and utilize the well pressure to push antiscalant from the tubing through to a surface system in case of an injection pump trip.
- Turn down requirements. For wells that operate across a wide range of flow rates, the required turn down ration on the antiscalant delivery will need to be considered such that the system is able to deliver adequate antiscalant at high well flow rates, while still retaining a low antiscalant retention time at low well flow rates. Systems requiring high turn down rates may require higher pressure pumping systems to attain the increased injection pressure required at high flow rates, while retaining the smaller diameter tubing required to minimize retention time during periods of low well flow rates.

5.2 Tubing Failure

Failures of the antiscalant delivery tubing can have a significant impact on well operations, with the potential for reduced well productivity from scaling, and from tubing recovery operations that may be required if the tubing has failed completely and fallen into the well. There are many failure modes for tubing installed into wells, however common failures experienced at Mercury include fatigue at stress points (connection and welds) and rubbing of the tubing on casing and well head components as shown in Figure 8.

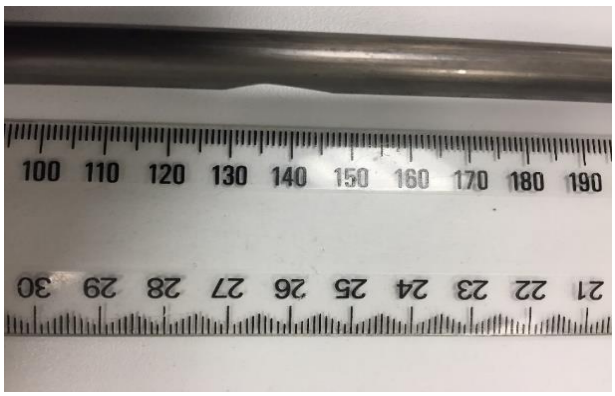

Figure 8: Example of tubing that has experienced rubbing – this damage was identified during routine maintenance and recovered before a complete failure

Maintenance programs have been essential to reducing the failure rate of tubing systems at Mercury. Regular changes in tube setting depth help to reduce tubing failures by changing the sections of tubing exposed to high wear conditions (eg rub points). Regular inspections also help to identify areas of tubing that are experiencing damage and enable these sections of tubing to be removed from the well prior to failure. Full tubing inspections are not always feasible for long tubing strings (up to 2000m), and while pressure tests can be used to detect a failure, it is often not practical to identify tubing sections subject to fatigue prior to failure. As a result, regular replacement of the tubing strings is also undertaken, with the costs of tubing replacement being significantly lower that the costs of tubing recovery should a tube fail completely while in service.

5.3 Heat Exchanger Fouling

The use of antiscalant can cause issues within the power plant, affecting power generation. One such example is the formation of a new type of scale in the heat exchanger of a binary power plant when using a polyacrylate-based antiscalant. The scale has been identified as an alumino-silicate material with a Si:Al ratio of ~2. This scale only forms when the antiscalant dosing system is in operation and has a detrimental effect on the heat transfer properties of the heat exchanger (Figure 9).

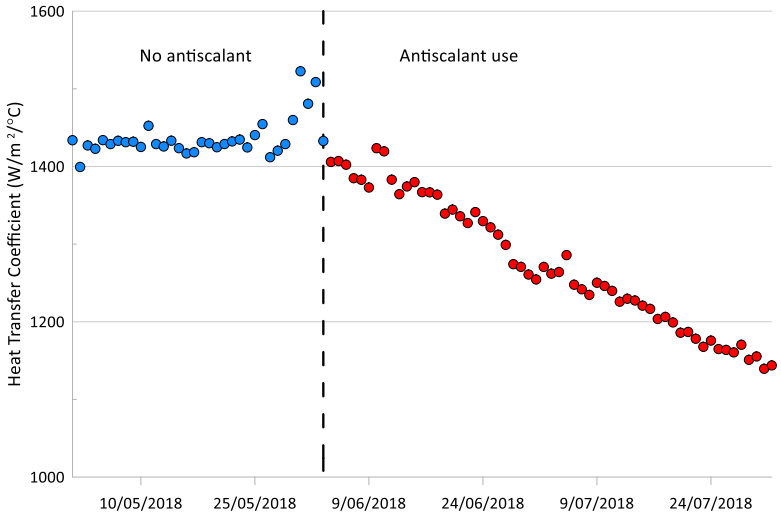

Figure 9: Decline in heat transfer coefficient due to antiscalant use.

This alumino-silicate is thought to form due to the antiscalant chemical carrying aluminium or alumino-silicate colloids through the plant that would normally have been deposited earlier in the process. The scale forms where the pH of the fluid is adjusted through addition of condensate. This modification lowers the pH and therefore makes the antiscalant less effective, releasing aluminium or alumino-silicate colloids and promoting the formation of an alumino-silicate scale with a high aluminium content.

Several options were assessed to find a potential solution to this scaling problem. A trial of a different antiscalant chemical was identified as the logical first step. Alternative chemicals were assessed as detailed in section 3. A key aim was to trial an antiscalant that was chemically and structurally different to the polyacrylate-based chemical currently in use. After a thorough screening process, a phosphino-carboxylic acid polymer was chosen as the preferred chemical to trial, due to its superior performance in the laboratory screening tests and the fact it is chemically and structurally different to the current chemical.

A 3-month field trial of the new chemical was used to assess the impact on plant and production well performance. As the calcium concentration of the wells could not be used to assess the effectiveness of the new chemical, periodic massflow tests of the production

wells was chosen as a key indicator of antiscalant performance in the production wells. In addition, several plant performance indicators were monitored to assess any negative impacts on the plant, including heat transfer coefficient decline in the heat exchanger.

Analysis of the data at the end of the 3-month trial looks promising, with an apparent reduction of the impact on the heat exchanger efficiency (Figure 10) and no negative impact observed in any of the well or plant performance indicators. Following this positive result, the phosphino-carboxylic acid polymer will continue to be assessed over the long-term.

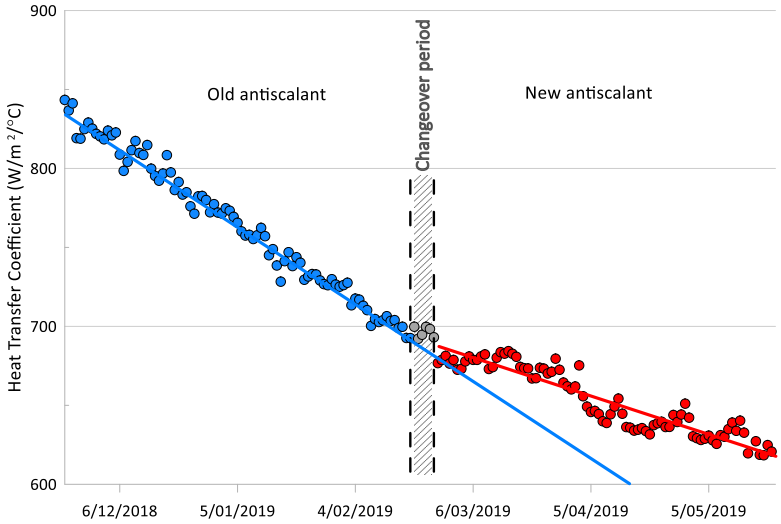

Figure 10: Change in the heat transfer coefficient decline rate, following the switch in antiscalant chemical.

6. CONCLUSION

Calcite scaling in production well is a major problem encountered by several geothermal field operators, both in terms of loss in plant generation as well as the high costs involved in recovering lost well productivity. Therefore, having a good management plan in place to mitigate calcite scaling is critical.

Currently, a cost-effective option to control calcite scaling without requiring long periods of interruption in production well operation is the use of an antiscalant chemical. However, this requires proper identification of a suitable chemical that passes both the laboratory screening process and the field trial. Confirmation of the overall effectiveness of the antiscalant chemical also involves long-term monitoring of well performance, normally over a year period.

In addition to ensuring that the antiscalant is effective, there are other operational challenges that need to be addressed. A good maintenance plan is necessary to make sure that the antiscalant system is running smoothly as any failure can result in a scaled well and/or equipment lost in the well. It is also important to manage any observed issue related to the use of the antiscalant chemical in downstream plant equipment such as fouling in heat exchangers, which may lead to switching to a different chemical.

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