ON-LINE SILICA INHIBITION AND DISPERSION BY ORGANIC COPOLYMER DOSING AT WAIRAKEI BINARY PLANT, NEW ZEALAND

Jose (Jun) Seastres Jr.[1], Keith Wigram[1], Christine Siega[1], Abbie Dean[1], Karl Barrie[2] and David Rodman[2]

[1]Contact Energy Limited, Private Bag 2001, Taupo 3352, New Zealand

[2] Ecolab Ltd, 2 Daniel Place, Saint Andrews, Hamilton, New Zealand 3200

jun.seastres@contactenergy.co.nz

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ABSTRACT

A pilot test was conducted at the Wairakei Binary Plant (2 units x 7.5 MWe net rated capacity) to assess the effectiveness of controlling silica deposition by chemical dosing. An acrylic copolymer with non-ionic monomer, NALCO GEO981, was tested at one unit (G16) of the binary plant from July 2014 to January 2015. The test results indicated a reduction in output decline rate for this unit from 70% to 15% per annum.

Following the successful trial results of GEO981, a chemical dosing system was installed at the main reinjection line (X-Line) to dose both units (G15 and G16) of Wairakei Binary Plant in July 2015. Chemical dosing has reduced the total power decline from around 3.2-3.5 MWe to 1.5-3.0 MWe per 200 days production cycle. The variable extent of plant output improvement suggests that silica scaling was not fully controlled and it was still observed within the heat exchanger tubes. Since chemical dosing commenced, there was no decline in reinjection capacity of Otupu wells in which cooled brine from the binary plant was injected.

XRF (X-Ray Fluorescence) analysis of scale samples recovered during testing consist mainly of silica (77%) with significant Al content (≈7%) and minor cation components (Na, K and Ca). Monomeric silica particles can be absorbed on these metal ions reducing the effectiveness of the chemical inhibitor in controlling silica scaling.

A co-dosing trial of GEO981 with another chemical GEO962, anionic acrylic copolymer, is being considered to further reduce the scaling rate at the binary plant by keeping these metal ions including aluminium in soluble state so it will not induce silica deposition.

1. INTRODUCTION

The Wairakei Binary Plant, which was commissioned in 2005, consists of two units (G15 and G16) with each unit at 7.5 MWe net rated output (Figure 1). The plant uses brine from the flash vessels after separating at low to intermediate pressure. It is delivered to the binary plant through the X-Line at an inlet temperature of around 130°C.

The brine is 80% oversaturated with amorphous silica after rapidly cooling to ≤90°C as it exits the binary plant. This condition caused silica scaling within the heat exchanger tubes that resulted to an average decline rate in power generation of ≥70% per annum. A bi-annual hydrofluoric acid clean for each unit has been undertaken to restore the plant to maximum capacity. However, the plant recovery is short term after removal of silica deposits by hydrofluoric acid and the plant output consequently deteriorates as silica is deposited within the heat exchanger tubes.

NALCO GEO981, which is primarily an acrylic copolymer with non-ionic monomer, was initially tested in 2013 using a bypassed line at the Wairakei binary plant. GEO981 functions as an inhibitor that is adsorbed onto silica crystals and blocks active growth size and as a dispersant in which layers of negative charges are developed resulting to repulsion of silica particles and prevent deposition.

A test rig called the "crab cooker" (Gill *et al.*, 2014) which consists of a cylindrical coil immersed in a cooling vessel was used during the pilot testing. The test set-up mimics the temperature profile and the metallurgy and length of the heat exchanger tubes. The test results indicate a 75% reduction in silica scaling compared to the un-dosed coil.

Following this successful pilot testing, the chemical was tested directly on-line at a single binary unit, G16, from July 2014 to January 2015. The testing was also successful as indicated by reduction in the plant output decline rate from 70% to 15% per annum. This result facilitated the installation of a chemical dosing system at the X-Line in July 2015 to fully dose the two binary plant units (G15 and G16) at Wairakei (Figure 1).

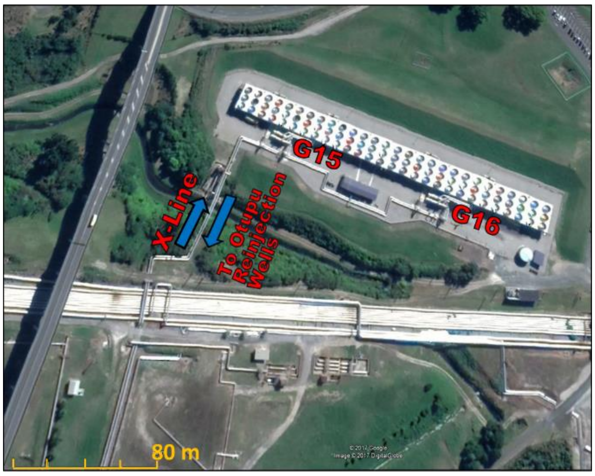

Figure 1: Location of Wairakei Binary Plant showing the brine supply inlet (X-Line) and the binary units (G15 and G16).

Assessment of GEO981 chemical dosing at the X-Line has been conducted to determine its effectiveness in controlling silica scaling within the binary plant and downstream at the reinjection branchlines and wells. This evaluation was mainly based on total and monomeric silica concentration monitoring, the analysis of silica scales within the plant, power generation trends and reinjection capacity of Otupu wells.

2. SILICA MONITORING RESULTS

Chemical dosing was conducted at the X-Line from July 2015 until August 2016 to control silica scaling at G15 and G16 binary plant units. The X-Line brine fluid with mass flow of about 2300 t/h was treated with GEO981 at dosing concentration of 18 ppm.

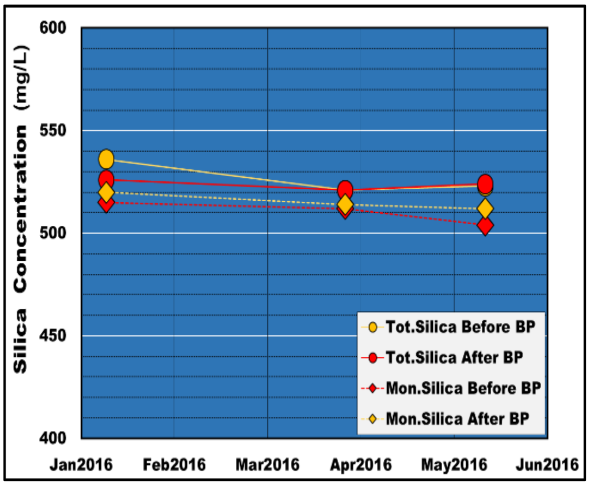

Figure 2: Total silica and monomeric silica concentrations during chemical dosing. Samples were collected before and after the Wairakei Binary Plant.

The total and monomeric silica concentrations were analysed upstream and downstream of the Wairakei Binary Plant. The silica analysis was conducted to determine any loss in total silica concentration due to scaling and to assess the rate of silica polymerisation (monomeric silica) as the brine is cooled during the binary plant heat exchange cycle.

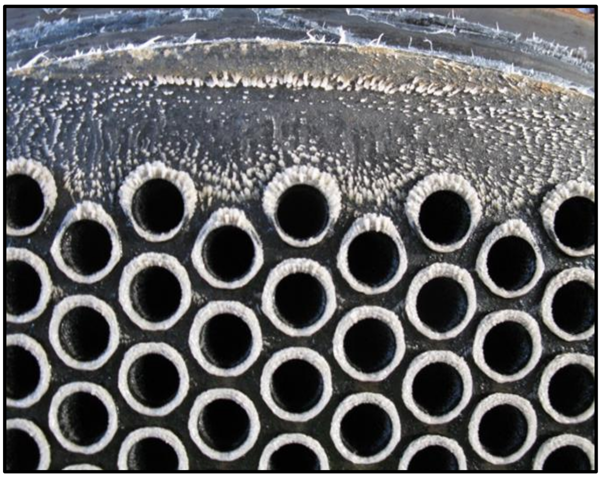

Figure 3: G16 pre-heater end cap tubes coated with silica scales as inspected in May 2016.

The monitoring results indicate that the differences in total and monomeric silica concentrations before and after the binary plant are within the laboratory analytical uncertainty of 3-4% (Figure 2). While there is no large difference in silica concentrations along the line, the brine flow at the X-Line is quite high that even a minimal loss would result to significant silica scaling particularly within relatively small diameter heat exchanger tubes. If the silica lost is within analytical uncertainty of 3%, the maximum total silica that can be precipitated will be around 38 kg/h based on total silica content of 550 mg/L and brine flow of 2300 t/h. However, not all of this silica is deposited as hydrodynamic conditions such as shear stress, particle collision and surface roughness can affect silica scaling (Kokhanenko et al., 2013).

In May 2016, the G16 binary unit was taken out of production for HF chemical line cleaning and the pre-heater tubes were inspected (Figure 3). Silica samples from the tubes were collected for back scattered electron (BSE), secondary electron imaging (SEI) and energy dispersive spectroscopy (EDS) using Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDAX) to characterise the texture, mineralogy and chemical composition of these samples.

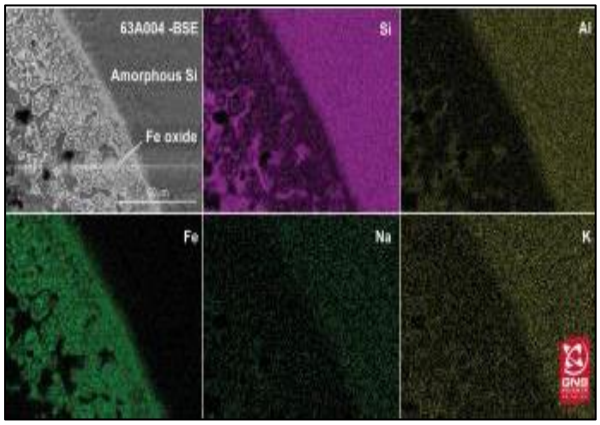

Figure 4 EDS of cross-section of silica spherule. Top left are minerals in BSE image (after Chambefort, 2016).

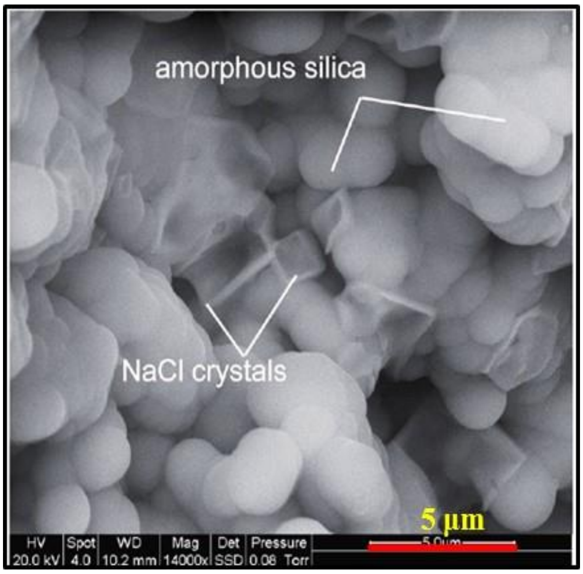

Figure 5: SEI analysis of silica particles (1-5µm dia.). Samples taken from silica scales deposited during GEO981 dosing at the Wairakei Binary Plant.

The analytical results indicated that the samples are primarily colloform amorphous silica with some aluminosilicate (K bearing smectite clay). XRF (X-Ray Fluorescence) analysis showed a silica content of 77% with significant aluminium (7%) and other metal components consisting of K (3%), Na (1%) and Ca (1%). Most of the metals (Al, Na and K) are found within the amorphous silica phase (Figure 4). The absorption of these metals in the amorphous silica structure was also observed in scale samples from Otupu (Wairakei) reinjection pipelines and SP3 (Ohaaki) brine line (Björke *et al.*, 2012).

Secondary Electron Imaging (SEI) of the silica samples (Figure 5) collected at the binary plant showed relatively small silica spherules between 1-5µm dia. The spherules have colloform texture which indicates scale formation by colloidal deposition.

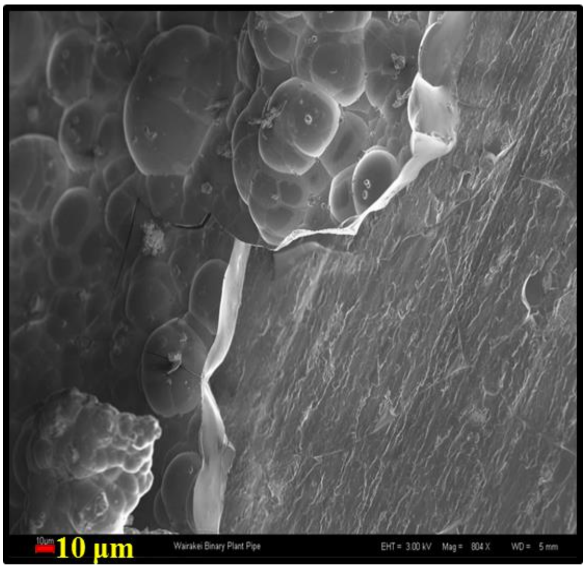

Figure 6: SEI analysis showing coalesced spherules of amorphous silica (40-50 µm dia.) after Zarrouk *et al.* (2014). Samples collected at the Wairakei Binary Plant before GEO981 dosing was conducted.

Prior to chemical dosing, the silica particles deposited are relatively large (40-50 µm) and its' morphology is characterised as dense and vitreous coalesced spherules (Figure 6). The morphology of the silica scale indicates lack of porosity which suggests that it has formed due to molecular deposition rather than by colloidal deposition.

3. IMPLICATIONS TO PLANT GENERATION AND REINJECTION WELL CAPACITY

The Wairakei Binary Plant has a fluid by-pass valve system designed to maintain a maximum pressure difference of 3.5 bars (gauge) between the two binary units (G15 and G16) to prevent flashing of the separated brine and avoid a slug flow.

Silica scaling within the heat exchanger tubes causes an increase in pressure drop particularly due to the rough morphology of the scale which produces flow resistance (Mroczek *et al.*, 2011). In order to prevent a pressure drop above 3.5 bars, the by-pass valves are activated resulting to reduction in power generation as more mass is dumped from the system. A progressive decline in power generation due to increasing silica scaling is encountered each time after the binary plant is cleaned using HF acid.

The gross generation trends of G15 and G16 binary units have been plotted to assess the effectiveness of chemical treatment since GEO981 was dosed in July 2015 (Figure 7 and Figure 8). Each generation plot was relative to the period after HF acid cleaning of the binary units. The data were recalculated at uniform reference temperature of 11^{0}C and at <30% bypassed opening for consistent correlation.

The results indicate that the gross power output of both binary units has improved during GEO981 chemical dosing compared to plant generation without dosing. The total power decline during chemical dosing was reduced from around 3.2-3.5 MWe to 1.5-3.0 MWe per 200 days production cycle. However, the extent of plant output improvement is variable during chemical dosing. This indicates that silica scaling within the binary plant was not fully controlled as the silica inhibition efficiency appears to be inconsistent.

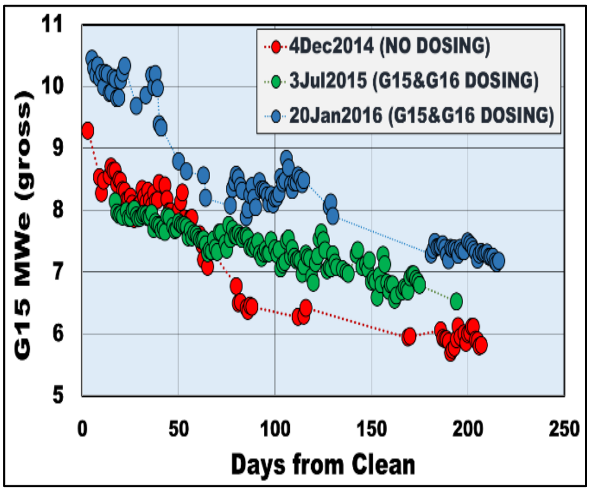

Figure 7: Gross generation trends of binary plant unit G15.

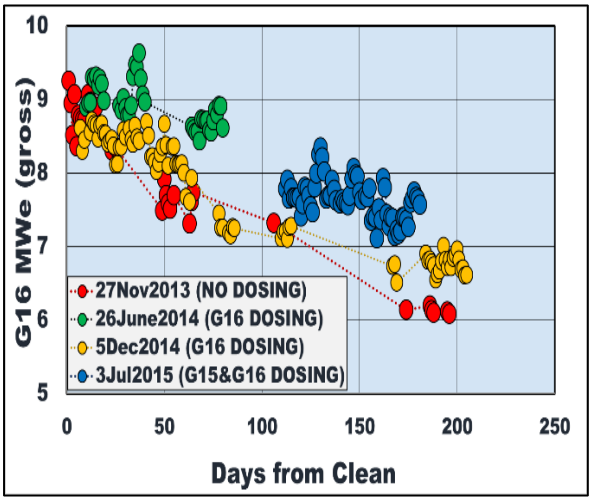

Figure 8: Gross generation trends of binary plant unit G16. Note: Incomplete generation plots are the periods when brine dumping is above 30% bypassed opening.

The brine exiting from the binary plant is injected at Otupu reinjection wells after cooling to ≤90^{0}C and 80% oversaturated with amorphous silica. Despite the increase in the silica scaling potential of the brine, there was no observed decline in reinjection capacity of Otupu wells during chemical dosing.

The reinjection capacity remained generally stable in the Otupu wells after declining prior to GEO981 dosing (e.g.

WK309 in Figure 9). It is likely that the chemical dosing has controlled the rate of nucleation resulting to formation of smaller silica particles. Field experiments conducted at Wairakei geothermal field using carbon steel cylinders flowed with separated brine indicated that smaller particles caused little silica scaling (Brown and Dunstall 2000; Brown, 2011).

Experimental studies by Kokhanenko *et al.* (2014) on silica scaling in mild steel pipes also showed similar results. In this case, the larger colloidal particles that have lower mobility and stability are thought to be trapped in porous formation.

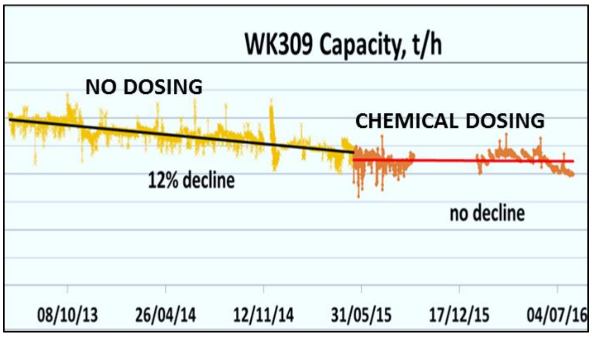

Figure 9: Reinjection well capacity trend of WK309

The smaller particles can be transported farther from the reinjection reservoir where higher temperatures are encountered and particle dissolution is induced; hence, well permeability will be unlikely affected.

4. SILICA INHIBITION EFFICIENCY

The silica samples collected at the pre-heater tube and end cap at the binary plant, which indicated significant aluminium content including minor Na, K and Ca, can enhance silica scaling. Monomeric silica particles could be absorbed on these metals reducing the effectiveness of the chemical inhibitor in controlling silica scaling.

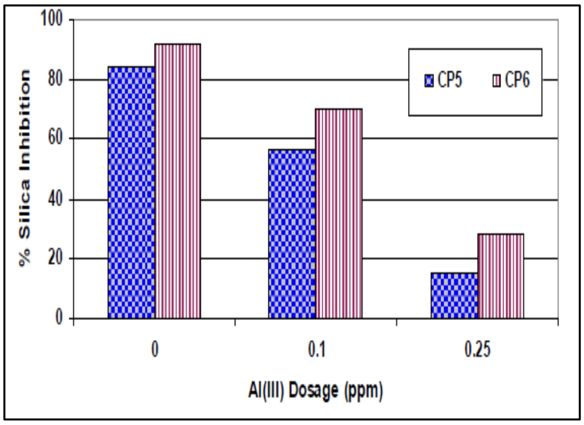

Figure 10: Effect of Al^{3+} concentration on silica inhibition (after Amjad and Zuhl, 2010). NOTE: CP5 and CP6 are proprietary chemicals (copolymer blends).

The negative charge of silica colloids binds metal ions and attracts other colloids to form larger silica particles. Aluminium (Al^{3+}), in particular, has a very high charge and ionic radius similar to Si^{4+}; hence, it can be readily incorporated into the colloid (Brown, 2013). Although the aluminium concentration of the Wairakei reinjection brine is relatively low (<0.40 mg/L), it has a large effect on silica inhibition even at this low concentration (Figure 10).

Additional testing is being considered to further reduce the scaling rate at the binary plant by co-dosing GEO981 with GEO962 (i.e. mainly anionic acrylic polymer) which can interfere in the precipitation of metal hydroxides and control its' particle sizes to <0.2 µm. This essentially keeps the metal ions in an apparent soluble state making less opportunity for monomeric silica to latch on and co-deposit to form large silica particles.

Based on the scale analysis, some aluminosilicate impurities (K bearing smectite clays) are also being deposited. This could be formed by interaction of $Al(OH)_3$ and coprecipitating with silica. The addition of GEO 962, which is a general dispersant can be similarly effective in controlling precipitation of these impurities.

5. CONCLUSIONS

Chemical dosing of the reinjection brine at the X-Line has reduced silica scaling at Wairakei binary units (G15 and G16) which resulted to significant improvement in gross power generation.

The chemical inhibitor, GEO981, appears to have controlled silica particle size to ≤5 µm that is relatively small to cause significant scaling within the reinjection wells.

Silica scaling has not been fully controlled at the binary plant and its' power output can still be maximised by further reducing silica deposition.

Significant metal contents, particularly aluminium, have been detected based on the analysis of silica samples recovered from heat exchanger tubes.

Controlling the precipitation of these metals could reduce absorption of monomeric silica and preventing agglomeration into large particle sizes. This condition would further improve the power generation at the binary plant.

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The testing is in line with the development of technology to enhance power generation by controlling silica scaling at the binary plant and consequently, reduce maintenance costs of reinjection wells.

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