NGATI TUWHARETOA GEOTHERMAL ASSETS LTD REBOILER PLANT WATER/STEAM CHEMISTRY IMPROVEMENTS TO RESOLVE ONGOING CORROSION ISSUES AND PREVENT FUTURE TUBE FAILURES

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ABSTRACT

The Ngati Tuwharetoa Geothermal Assets Ltd (NTGA) Kawerau reboiler plant has suffered from major corrosion and plant failure issues since commissioning, including the premature complete replacement of the tube bundles. These corrosion related failures have occurred due to water/steam chemistry issues and interactions with plant materials not being fully considered and understood in the design process of the plant.

In 2018 a major root cause analysis was undertaken into the failures that included a detailed chemical and metallurgical investigation and successfully identified the failure mechanisms. A number of simple chemical treatment changes, including hydrogen sulfide neutralization, pH correction and the application of corrosion inhibiting film forming substances (FFS), were carried out to successfully mitigate ongoing corrosion of the plant and to significantly extend asset life.

1. PLANT DESIGN BASIS

1.1 Plant Mechanical Design

The NTGA plant was designed by Dobbie Consulting Mechanical Engineers (Dobbie's) in 2009 with steam and boiler side chemistry advice provided by Quest Integrity Group (Quest). The plant was constructed and commissioned in 2010. The expected design life of the plant was 25 years with carbon steel selected as the main tube bundle materials.

The design basis of the NTGA Clean Steam Plant is an industrial steam generator/reboiler/boiler/heat exchanger (HEX) that takes geothermal steam and then via a steam transformation process, produces and supplies "clean steam" onto an industrial steam customer. The NTGA plant, its design process, early operation and commissioning are described in a 2011 technical paper[1] . The key aspects of the plant are summarised here and also shown in Figure 1. The key details are as follows;

1. The plant takes geothermal steam at approximately 22 bar(g) pressure and 220°C temperature as the primary heating source of the reboiler (one of two units).

2. After providing heating, the geothermal steam subcooled condensate is flashed and the resulting "clean" condensate is then passed through a stripping column to remove the majority of the residual geothermal gases (mainly hydrogen sulfide and carbon dioxide) to form the boiler feedwater. Please note however that this stripping process is not 100% effective and some residual hydrogen sulfide will always be present as condensate exits the stripping column and will enter the reboilers.

3. This feedwater is then deaerated, down to ~30 µg/L of dissolved oxygen, in the feedwater tank and supplied onto the steam generator where it is heated by the geothermal steam and used to produce 16.5 bar(g), 200°C "clean steam" for the end user processes. Some condensate is also returned from these processes and is mixed with fresh boiler feedwater for re-use. The plant has two steam generators with a common feedwater system with both steam generators supplying steam into a common steam main.

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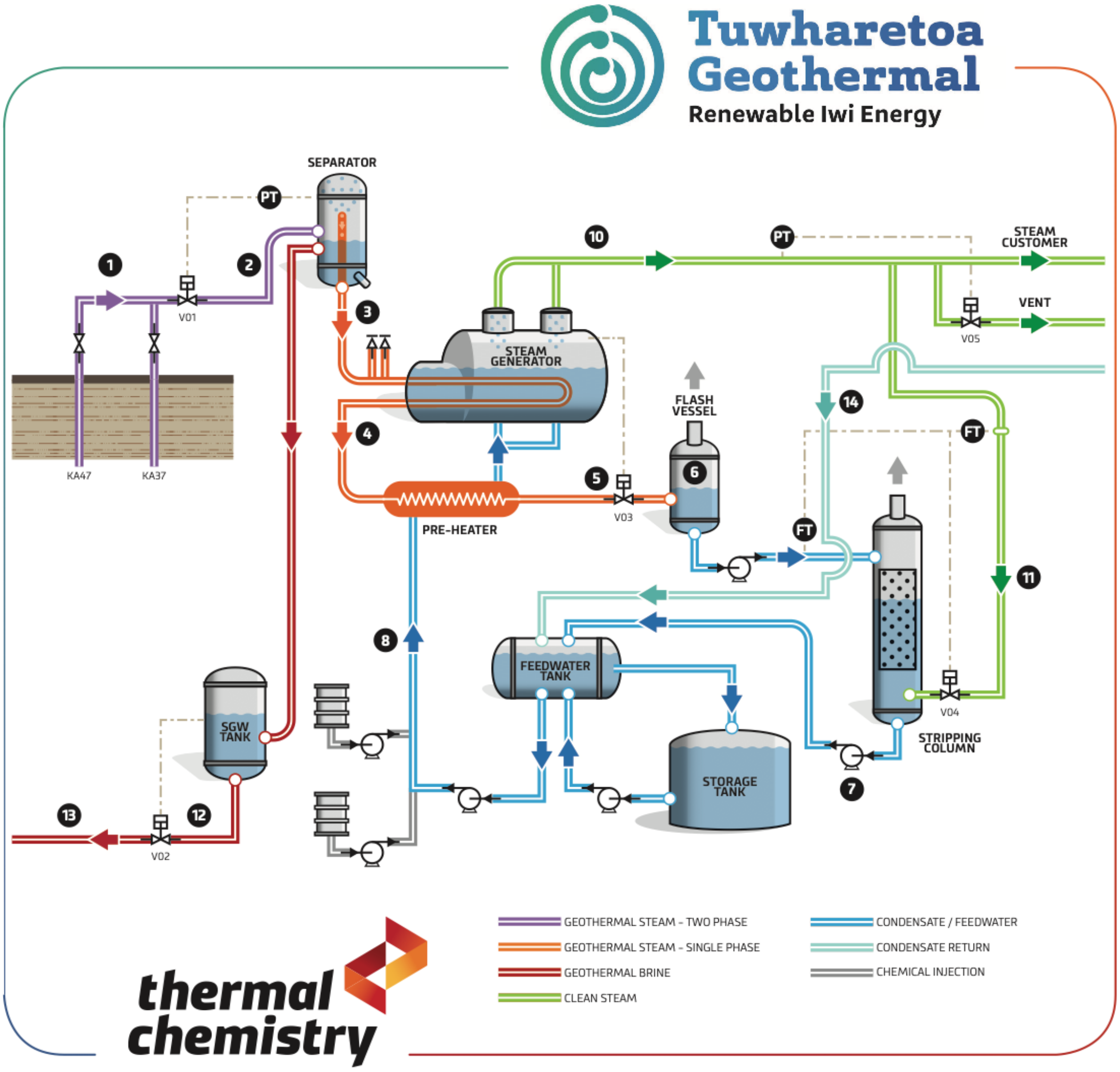

1	2 Phase Geothermal	40 Bar(g) 252°C	310 tonnes/hr
2	2 Phase Geothermal	22 Bar(g) 220°C	310 tonnes/hr
3	Seperated Steam	22 Bar(g) 220°C	35 tonnes/hr
4	Steam/Condensate mixture	22 Bar(g) 200°C	35 tonnes/hr
5	Sub-cooled Condensate	22 Bar(g) 130°C	
6	Flashed Condensate	0 Bar(g) 100°C	
7	Stripped Condensate	0 Bar(g) 100°C	
8	Feedwater	16.5 Bar(g) 95°C	28.5 tonnes/hr
9	Heated Feedwater	16.5 Bar(g) 190°C	28.5 tonnes/hr
10	Clean Steam	16.5 Bar(g) 200°C	28.5 tonnes/hr
11	Stripping Steam	16.5 Bar(g) 200°C	2.5 tonnes/hr
12	Separated Water	22 Bar(g) 220°C	280 tonnes/hr
13	Flashed SGW	12 Bar(g) 192°C	
14	Process Condensate Return	1 Bar(g) 80°C	0-25 tonnes/hr

Figure 1: NTGA Clean Steam Flow Diagram and Typical Operating Pressures, Temperatures and Flow Rates

The critical part of the process is the steam generator/reboiler (referred to as Heat Exchanger HEX 1 or HEX 2) unit which contains a carbon steel tube bundle. Geothermal steam flows through the tubes and partially condenses as heat transfer occurs. Water (condensed and stripped geothermal steam or "boiler water") is present on the outside of the tubes. Heat transfer through each tube heats up and nucleate boils the boiler water producing saturated steam which is separated and supplied onto the end user processes. The location of the tube bundle within the reboiler itself is shown in Figure 2 and a bundle under construction is shown in Figure 3.

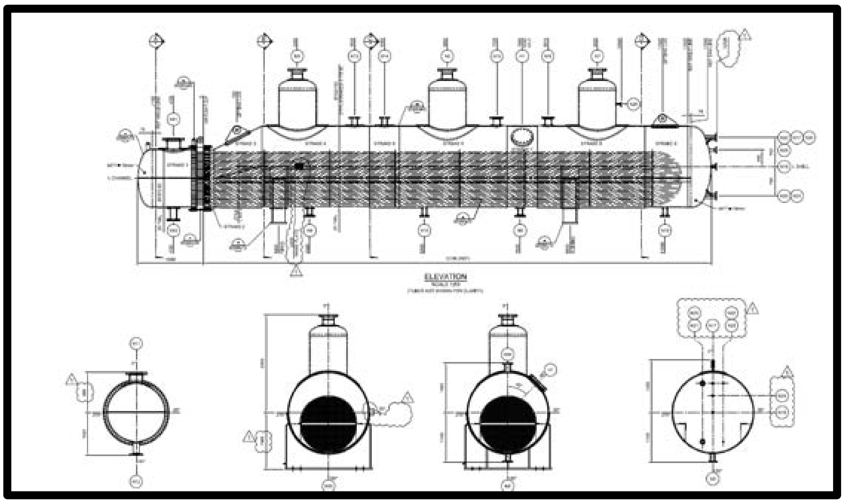

Figure 2: NTGA Reboiler Schematic Showing Bundle and Vessel Arrangements

Figure 3: NTGA Carbon Steel Tube Bundle under Construction

Due to the limited access in the tube bundle, repair of any failures is practically impossible and therefore tube plugging and abandoning via the bundle end (inlet and outlet) is the only option available should a failure and a contaminating leak of geothermal steam into the boiler water occur. If failures continue to occur and additional tubes need to be plugged, the capacity of the reboiler begins to decrease due to the decrease in geothermal steam flow through the tube bundle and available tubes.

1.2 Water/Steam Chemistry Original Design Basis

The design basis of the NTGA plant was partly based on the original Norske Skog reboiler plant[2] but with no provision for any feedwater or boiler water chemical dosing, unlike what has been historically undertaken at the Norske Skog plant with additional solid alkalisation carried out for the boilers. Based on technical discussions[3] with key Norske Skog technical experts, solid alkalisation is utilised on these units to improve the corrosion control via additional pH buffering in the boiler water and was implemented after early life corrosion damage and failures occurred in the plant. This historical information and operating experience was not incorporated into the NTGA plant design process.

The original design basis of the NTGA plant was also to be an in service/standby configuration with one unit in service and the other in wet, hot, oxygen free standby. Limited online chemical sampling and analysis systems were included in the original design with just feedwater conductivity and boiler conductivity provided. A steam pH analyser was added in 2014 to provide additional analysis on the steam supply to the final steam customer. Feedwater dissolved oxygen and HEX pH analysers have also now been installed.

No significant design provisions for offline layup and storage protection was provided for the out-of-service HEX unit other than to be maintained hot. The ability to undertake a cold nitrogen cap/blanket as a means to prevent oxygen ingress to the water side was only installed in late 2018 and used in conjunction with steam sparging on both the water and steam side of the HEX units.

Based on the original geochemistry analysis and modelling of the condensate stripper system, three key assumptions regarding water/steam chemistry were made for the plant during the design process. These were:

1. That dissolved hydrogen sulfide and carbon dioxide would be essentially fully removed in the stripper and;

2. Sufficient ammonia would remain in the condensate after stripping to give a feedwater pH of between 9-10.

3. The ammonia present in the feedwater would provide sufficient alkalisation for the boiler for the minimisation of corrosion of the carbon steel tubes.

4. Feedwater dissolved oxygen levels would be very low.

As will be seen in the following section these design assumptions were not correct.

2. PLANT FAILURES

The plant was initially operated under contract by Mercury NZ (formerly known as Mighty River Power) from 2010 with maintenance services provided by Allied Industrial Engineering with NTGA taking over full operation and maintenance in December 2016. During this time period it was reported that feedwater dissolved oxygen levels may have been elevated for extended periods of time.

In 2014 tube failures started to occur in the tube bundles in the HEX 1 unit. A plant inspection and failure analysis was undertaken by Quest and a summary of their findings is as follows;

- That “oxygen corrosion”* was occurring leading to the tubes failing,
- That this corrosion occurred due to an operational trial/change by Mercury NZ at the end of 2013 that resulted in
  - Higher feedwater demand in the plant and increased feedwater dissolved oxygen levels
  - “Departure from nucleate boiling corrosion” occurring.

*Note that there is no specific corrosion mechanism known as “oxygen corrosion”. It is more likely the reference is meant to be for general electrochemical corrosion of which oxygen is a contributing factor.

The feedwater dissolved oxygen levels then returned to low levels

Tube failures continued to occur in both reboiler units from 2014 and one tube bundle was fully replaced in 2015 (HEX1) with a like for like carbon steel tube bundle at a cost of approximately NZD$1 million. Corrosion continued and by 2018 the need for additional replacement bundles was identified by NTGA with a second replacement bundle to replace HEX2 ordered in late 2018 at a cost of NZD$1.2 million.

3. WATER/STEAM, OPERATING AND INTERFACE ANALYSIS

Due to the ongoing corrosion of the tube bundles and the high cost of replacement, Thermal Chemistry Limited (TCL) was tasked in 2018 by NTGA to undertake a review of the NTGA plant water/steam chemistry to determine the root cause of the corrosion and to provide actions to eliminate/minimise any ongoing corrosion to increase the life span of any replacement tube bundles. This review included the following:

1. A review of the original design basis and water/steam chemistry assumptions;

2. A physical inspection of the plant;

3. Additional water/steam chemistry sampling and analysis;

4. Additional third party metallurgical analysis of tube samples;

5. Corrosion coupon/corrosion studies;

6. Analysis of data collected and the work up of robust, practical and cost effective recommendations to:

    a. Minimize corrosion and deposition within the plant

    b. Optimise the water/steam chemistry and the interface between water and steam and plant surfaces

    c. Improve online water/steam sampling and analysis systems.

3.1 Plant Physical Review

The plant was initially inspected in early August 2018 with the HEX2 reboiler out of service and the bundle extracted and visible as per Figure 4.

Figure 4: HEX 2 Tube Bundle Inspection – Late 2018 – Obvious Surface Corrosion Evident

On inspection the following observations where made

1. The bundle surface was extensively corroded, with orange, non-protective oxide or rust present along with pitting clearly visible on the surface of the tubes as per Figure 5. The rusting and pitting was most evident on the top of the bundle.

2. A significant loose crud layer of black corrosion products was present at the bottom of the bundle and inside the HEX vessel as per Figure 6.

3. Some areas of the tubes, located towards the bottom of the bundle showed partially protective oxides flaking off as per Figure 7.

Figure 5: HEX 2 Tube Bundle Inspection – Late 2018 – Rusting and Pitting Present

Figure 6: HEX 2 Tube Bundle Inspection – Late 2018 – HEX Shell Corrosion and Corrosion Products on Bottom

Figure 7: HEX 2 Tube Bundle Inspection – Late 2018 – Flaking Oxides

Based on these observations, in addition to the plant history of tube failures, it was evident that significant corrosion was occurring both when the HEX units were online and when offline that is consistent with general corrosion and pitting corrosion mechanisms.

3.2 Additional Water/Steam Analysis

Water and steam samples were collected and sent to Hills Laboratories for analysis in late 2018/early 2019 and immediately a discrepancy between the online pH analysis and the final laboratory analysis was noted. Sampling and laboratory analysis potential errors were quickly eliminated as the cause of this discrepancy and it was determined to be evidence of an actual chemical process occurring.

Whilst the operating HEX water pH was reported by the calibrated and serviced online pH analyser to be ~9 to 9.5, the laboratory samples consistently were reported back with a pH of ~4 to 5. This observation led to the determination and understanding of the influence of hydrogen sulfide and oxygen present in the HEX water that is discussed later.

Other key observations from the water/steam sampling and analysis included:

- High levels of iron oxide corrosion products consistent with active corrosion activity in the water. Total iron levels of up to 34 mg/L were measured

- High levels of sulphate consistent with the oxidation reactions of hydrogen sulfide and oxygen to form sulphate by-products. Sulphate levels of up to 100 mg/L were measured

3.3 Potential for Departure from Nucleate Boiling

After the initial plant failures in 2014, a tube failures plant inspection and failure analysis was carried out. This analysis identified a phenomenon known as departure from nucleate boiling (DNB) that could have resulted in the observed corrosion. DNB is also known as transition boiling, unstable film boiling, and partial film boiling.

If the heat flux of a boiling system is higher than the critical heat flux (CHF) of the system, the bulk fluid may boil, or in some cases, regions of the bulk fluid may boil where the fluid travels in small channels. Thus large bubbles form, sometimes blocking the passage of the fluid. This results in a departure from nucleate boiling (DNB) in which steam bubbles no longer break away from the solid surface of the channel, bubbles dominate the channel or surface, and the heat flux dramatically decreases. Vapour essentially insulates the bulk liquid from the hot surface.

This situation can lead to aggressive and rapid corrosion of a boiler surface if it was to occur.

Due to the low operating temperatures of the HEX units this mechanism was considered unlikely to be able to occur, but a third party heat flux analysis was undertaken to determine if it was possible. The analysis conclusion was that DNB was not possible, given the low heat flux conditions in the HEX units. DNB was ruled out as a possible corrosion mechanism.

3.4 Design Basis Water/Steam Chemistry Review and Carbon Steel Corrosion Chemistry

The original design basis of the plant was reviewed and compared to what would be carried out for a comparable conventional fossil boiler and also to the Norske Skog reboiler plant. The key critical difference found was that the NTGA plant was not designed with any additional boiler dosing to provide solid alkalization to the boiler water. Also, that the complete removal of hydrogen sulfide from the geothermal steam in the strippers is thermodynamically impossible, with a constant low level of hydrogen sulfide to be expected at all times in the HEX boiler water.

It is almost universally standard for drum type, natural convection boilers operating at a similar pressure range to the NTGA plant to have solid alkalization dosing. The Norske Skog reboiler plant has this capability that was added post commissioning due to corrosion issues with the carbon steel tubes.

The corrosion of carbon steel is heavily influenced by pH as can be seen in Figure 8 and Figure 9, with the optimal water pH for any drum type boiler constructed from carbon steel being 9.8 to 10. This protection is due to the formation of a passive, protective iron oxide layer on carbon steel via reactions between the metal, moisture and oxygen present in the environment. The reaction is self-limiting and results in the formation of a stable oxide film, which is normally comprised of magnetite or Fe_3O_4, and the liberation of a small amount of hydrogen gas. This is demonstrated in the following simplified reaction:

Equation 1: $3\ Fe + 6\ H_2O \rightarrow Fe_3O_4 + 2\ H_2O + 4\ H_2$

The protective oxide film is stable under alkaline pH conditions and prevents the contact of the remaining metal with the water/steam “environment” and any further oxidation reactions. This protective oxide film is pH sensitive and is not stable at low pH where, without the protective layer, reaction of the base metal with the oxidative water/steam continues unabated and produces aqueous or general corrosion.

The corrosion rate of boilers and boiler tube will also be influenced by other characteristics of the operating conditions, including aqueous solution chemistry; heat flux and operating pressure. Of particular relevance for NTGA, minor acidic impurities in the water such as chloride or sulfate can increase corrosion rates.

Natural ammonia pH adjustment, via residual ammonia in the post scrubber steam, has been used in the NTGA boilers since commissioning for providing pH adjustment to try to minimize corrosion. However, the presence of corrosion found during the physical inspections (Section 3.1) and the low pH reported by laboratory analysis (Section 3.2) indicates that the ammonia residual was ineffective. The effectiveness of ammonia on its own for pH control in low pressure boilers is limited by two key issues:

1. Ammonia is a weak alkalizing agent and provides very little pH buffering against strongly acidic species that could enter the boiler or be generated during a contamination event.

2. Ammonia is a fully volatile component and will leave the boiler with the steam. The ratio of ammonia in the

feedwater compared to the boiler water and steam is pressure dependent with low pressure boilers having a lower amount of ammonia remaining in the boiler water at the same feedwater ammonia concentration compared to a higher pressure boiler. In practical terms this means that for a 22 bar(g) boiler, with a feedwater pH of 9.8 buffered by only ammonia, the pH of the boiler water pH may be as low as 9.2 due to a greater percentage of the ammonia partitioning into the steam exiting the boiler.

This issue with a lack of buffering capacity of ammonia and its partitioning into the steam in low pressure boilers may be resolved with the dosing of a non-volatile, solid alkali compound such as sodium hydroxide or tri-sodium phosphate into the boiler water in low mg/L levels to elevate the boiler water pH and provide additional buffering capacity. This is what is undertaken for the Norske Skog reboilers and has been the case for many years.

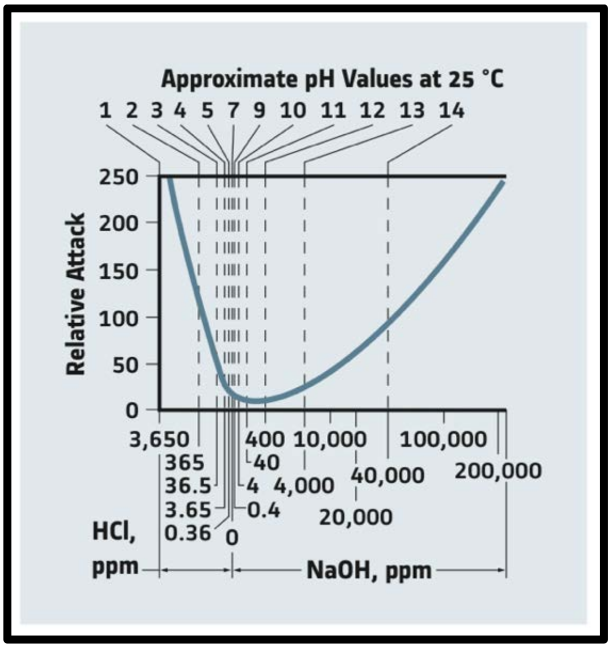

Figure 8: Influence of pH on the Corrosion of Carbon Steel – pH 1 to 14[4]

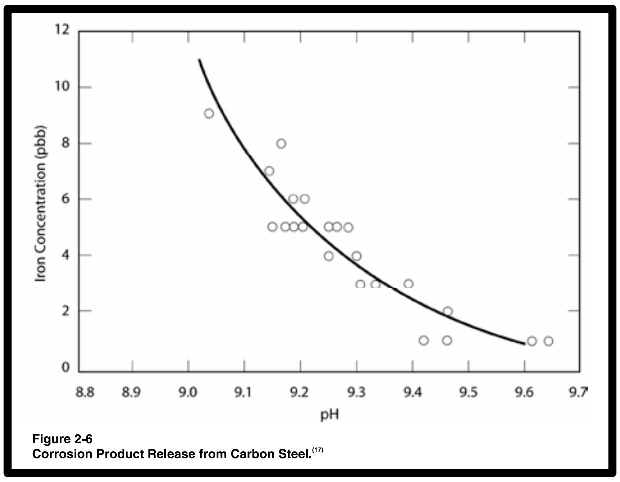

Figure 2-6
Corrosion Product Release from Carbon Steel.[17]

Figure 9: Influence of pH on the Corrosion of Carbon Steel – pH 8.8 to 9.7[5]

3.5 Hydrogen Sulfide Chemistry in a Boiler Water Environment

Whilst the chemistry of hydrogen sulfide (H_2S) is generally well understood in the context of conventional geothermal power plants from a geothermal engineering and emissions perspective[6] it has not been well understood by the geothermal industry in a boiler water perspective even through the fundamental chemical properties of hydrogen sulfide are very well understood[7].

Hydrogen sulfide is slightly soluble in water and acts as a weak acid (pKa = 6.9 in 0.01–0.1 mol/litre solutions at 18°C), giving the hydrosulfide or bisulfide ion HS^- (also written SH^-) as shown in the following reaction,

Equation 2: $$H_2S + OH^- \leftrightarrow HS^- + H_2O$$

The sulfide anion S^{2-} is only formed in aqueous solution at extremely alkaline pH ($pH > 12$). Hydrogen sulfide, bisulfide and their solutions are colourless and are the stable in the absence of oxygen, as would ideally be the case in an, oxygen free, alkaline boiler water environment.

When exposed to oxygen, hydrogen sulfide and bisulfide will oxidize to form, under various conditions, various other sulfur compounds including sulfur dioxide (SO_2), sulfuric acid (H_2SO_4), polysulfides or elemental sulfur (S_0), which is not soluble in water.

Under ideal HEX operating conditions, there will be approximately 30 µg/L dissolved oxygen in the feedwater with the majority of this oxygen immediately leaving the HEX water with the clean steam due to oxygen being volatile in steam. This would leave only 3-5 µg/L that will then be consumed by reactions with the H_2S present in the HEX water. This will produce a small pH drop and leave excess H_2S. If the feedwater dissolved oxygen levels were to increase then all the residual H_2S in the HEX water would be consumed with a larger pH drop occurring. In this situation if there was an increased amount of H_2S in the HEX water due to an active/unplugged tube leak allowing geothermal steam to directly enter the HEX water then an increased reaction rate would occur with localised pH decreases likely leading to higher corrosion rates and further tube failures.

As in the following simplified reactions, hydrogen sulfide or bisulfide can react with oxygen to form water and sulfur dioxide,

Equation 3: $$2\,H_2S + 3\,O_2 \rightarrow 2\,H_2O + 2\,SO_2$$

Equation 4: $$4\,HS^- + 5\,O_2 \rightarrow H_2O + 4\,SO_2$$

Sulfur dioxide can then continue to react with water and oxygen to form sulfuric acid,

Equation 5: $$2\,SO_2 + 2\,H_2O + O_2 \rightarrow 2\,H_2SO_4$$

This formation of acid would rapidly lower the pH of an aqueous solution. Sulfuric acid is classified as a strong acid with a high degree of dissociation and even a small amount of sulfuric acid can make an aqueous solution strongly acidic.

3.6 Hydrogen Sulfide and Corrosion Risk in Boilers Related to Oxygen in the Online and Offline Environments

The corrosion of carbon steel is heavily influence by pH as can be seen in Figure 8 and Figure 9. When hydrogen sulfide is present in a boiler or reboiler water and sufficient oxygen is present, there will be a rapid reaction resulting in the formation of sulfuric acid and an immediate drop in the pH of the solution with the solution becoming acidic.

Under this situation, even if the solution starting pH is alkaline (for example a pH of 9.2-9.3 due to aqueous ammonia being present), sulfuric acid as a strong acid will quickly neutralises this alkalinity and results in an acidic solution with a pH < 7.This would be the case at NTGA if there was a excess of dissolved oxygen in the feedwater or if during a shutdown period of time the water in the HEX units was permitted to become oxygen saturated. This situation was observed during the sampling and analysis program (Section 3.2).

This drop in pH immediately destabilises any protective oxide layers and corrosion then rapidly occurs resulting in the formation of a non-protective iron oxide product known as “rust” or hydrated iron oxides such as $Fe_2O_3{\cdot}nH_2O$, FeO(OH) and $Fe(OH)_3$ all with a distinctive orange coloration.

There will be two different appearances to this corrosion depending on if the plant is in operation (hot, circulating/moving fluid) or offline (cold, no circulation/movement of fluid).

If a low pH situation occurs with the plant in service then there will be a general increase in corrosion rate over the carbon steel surfaces observed as orange rusting on the surface, a general thinning of the corroding material with an increase in iron oxide corrosion products in the bulk fluid or as a crud layer on the bottom of vessels or pipes.

A low pH situation could occur locally in the vessel and not be apparent from any bulk fluid sample or noticeable via online pH analysis.

If a low pH situation occurs combined with a high oxygen environment, such as what would be expected with the plant shutdown but still remaining full of water (i.e. offline, cold, no circulation), then there will be (a) a general increase in corrosion rate over the carbon steel surfaces (observed as orange rusting on the surface);(b) a general thinning of the corroding material with an increase in iron oxide corrosion products in the bulk fluid or as a crud layer on the bottom of vessels or pipes; and (c) the formation of pits on the surface. Pitting corrosion is a more aggressive form of general corrosion that occurs under stagnate conditions

The usage of additional oxygen scavenging chemicals such as hydrazine are ineffective for removing oxygen in an offline environment due to the low temperatures and lack of circulation.

3.7 Corrosion Control Solutions Using Sodium Hydroxide Treatment

Adding sodium hydroxide to boiler water decreases the concentration of both hydrogen sulfide and sulfide dioxide. The reduction in hydrogen sulfide concentration occurs via the reaction of hydrogen sulfide to alkali hydrosulfides such as sodium hydrosulfide (Reaction 6) and sodium sulfide (Reaction 7).

Equation 6: $\mathbf{H_2S + NaOH \rightarrow NaSH + H_2O}$

Equation 7: $\mathbf{NaSH + NaOH \rightarrow Na_2S + H_2O}$

If sulfur dioxide is already present in a solution, then sodium hydroxide reacts with that to form sodium sulphite and water.

Equation 8: $\mathbf{SO_2 + 2\ NaOH \rightarrow Na_2SO_3 + H_2O}$

If sulfuric acid is already present in a solution, then sodium hydroxide reacts with it to form sodium sulphate and water.

Equation 9: $\mathbf{H_2SO_4 + 2\ NaOH \rightarrow Na_2SO_4 + H_2O}$

Interestingly once sodium sulphite is formed this can behave as an oxygen scavenger with the final reaction product being sodium sulphate.

Equation 10: $\mathbf{2\ Na_2SO_3 + O_2 \rightarrow 2\ Na_2SO_4}$

In all cases of sodium hydroxide addition, the pH of the solution will be alkaline provided an excess of sodium hydroxide is present in the water at all times. It can also be expected that dissolved oxygen levels would be maintained at a low level due to the sodium sulphite to sodium sulphate reaction involving dissolved oxygen, provided that there is no hydrogen sulfide present.

4. ONLINE WATER/STEAM CHEMISTRY IMPROVEMENTS TO LOWER CORROSION RISKS

Two improvements were recommended by TCL and undertaken at NTGA plant; (a) sodium hydroxide dosing (Section 4.1) and Film Forming Substance (FFS) dosing (Section 4.2).

4.1 Sodium Hydroxide Water Treatment

The IAPWS boiler water treatment guidelines[8],[9] provide robust, water chemistry guidance to minimise corrosion and deposition of feedwater and boiler water and are utilised by the majority of fossil power plants worldwide.

Whilst not specifically designed for geothermal reboilers, these guidelines are able to be customised quickly and easily to provide specific water/steam chemical treatment guidance. Based on a review of these guidelines and TCL’s extensive water/steam chemistry experience, the following recommendations to improve the water chemistry of the HEX units were made.

1. Commence sodium hydroxide dosing into the feedwater prior to entry to the HEX units to:
    a. Increase the HEX boiler water pH from ~9-9.5 to ~9.9 with 1-5 mg/L of sodium hydroxide during online operation to lower the carbon steel general corrosion rates
    b. Provide neutralization of hydrogen sulfide, sulfur dioxide and sulfuric acid to prevent both local and general area pH depression during online and offline operation leading to increased carbon steel corrosion rates.

2. A slight increase in boiler blowdown levels/lowering of boiler blowdown targets.

Sodium hydroxide dosing was commenced in late 2018 for both HEX units and combined with a preliminary change in blowdown control resulted in the following changes:

1. An increase in HEX water pH, even in the presence of oxygen, from 4 – 5 to 9.6 – 10.6
2. A decrease in HEX water iron oxide corrosion products with total iron levels decreasing to less than 5 µg/L from the previous values of up to 34 mg/L
3. A decrease in HEX water sulphate levels from 100 mg/L to 1 mg/L
4. A decrease in HEX water hydrogen sulfide levels to below detection limits (< 2 µg/L).

The dosing of sodium hydroxide increases the total conductivity of the HEX water and can result in excessive blowdown if blowdown control is based on only total conductivity. Blowdown control is required to prevent the HEX water from becoming over concentrated with contaminate salts, such as sodium chloride, that can result in steam contamination and eventually an increase in corrosion in the HEX units. However, excessive blowdown can result in a shortage of make-up water and restrictions in steam flow and a drop in the overall HEX unit efficiency. Therefore a careful balance of blowdown for chemistry control, make up water availability and maximising HEX efficiency is important.

A second conductivity measurement can be used in place of total conductivity for blowdown control, i.e. Conductivity After Cation Exchange (CACE), that is not influenced by the addition of sodium hydroxide and only responds to increases in anions such as chloride and sulphate. A trial a CACE analyser was undertaken in late 2018 which showed the following;

1. That the measurement would be acceptable for optimizing blowdown control.
2. That the test instrument, that utilises a cation exchange resin system, depleted faster than expected due both the presence of ammonia and hydrogen sulfide. This would result in frequent consumable resin change outs.

Swan Analytical[10] has developed a new type of CACE analyser, as shown in Figure 10 that utilises a self-regenerating resin system based on Continuous Electrical Deionisation (CEDI) technology that does not need manual resin servicing or changing when in operation. This means that the influence of ammonia and sodium hydroxide is negated and minimal maintenance is required.

Figure 10: SWAN AMI CACE Analyser (right) with Geothermal Specific Modifications (left)

This analyser was purchased and installed for each HEX unit to base the HEX blowdown control on CACE rather than just conductivity with the final control values to be determined after further optimisation work. However, there were potential concerns related to hydrogen sulfide impacting on the CEDI regeneration unit. A factory approved field modification to prevent any residual hydrogen sulfide from interfering with the CEDI regeneration was carried out and tested prior to NTGA purchasing the unit. This unit involves air oxidization of any residual hydrogen sulfide and can be seen in Figure 10 to the left of the standard analyser

4.2 Film Forming Substances - Corrosion Inhibitor Bench Testing

One additional potential operational chemistry and layup and storage chemistry option for the NTGA plant is the application of film forming corrosion inhibiting substances either during online operation or during shutdown.

Film forming substances (FFSs) are a class of chemical feedwater/boiler water/steam treatment chemicals that produce a semi-stable, molecular, corrosion inhibiting film on metal surfaces within a plant. These types of products are utilised in some nuclear, fossil and industrial plants worldwide. Whilst effective the products are relatively high cost when compared to tradition feedwater/boiler water treatment chemicals such as ammonia and sodium hydroxide.

The corrosion inhibitor effect is accomplished by the formation and maintenance of a very thin non-wettable film on the surface of the plant equipment. The film acts as a barrier between the metal surface and the water/steam phase and is generally independent of pH and dissolved oxygen levels.

For the NTGA plant, FFS could be applied before extended periods of wet or partially wet storage without nitrogen capping and circulation and still provide corrosion inhibiting properties to the metal surfaces.

They could be utilised in conjunction with sodium hydroxide dosing to provide an additional layer of protection to the NTGA plant via either:

1. Continuous, online dosing; or,
2. Dosing 1-3 hours prior to a plant shutdown.

IAPWS provide specific guidance[11] for the use of FFSs in steam generating plants and their application was extensively studied by TCL regarding potential use at the NTGA plant. It should be noted that there is extremely limited data from any potential chemical suppliers related to the application of FFSs in geothermal type matrices, specifically with hydrogen sulfide present.

In order to determine the effectiveness or otherwise of the application potential of FFSs for the NTGA plant, a bench top corrosion coupon study was undertaken in early 2019 to provide some robust data.

Product selection for the trial was based on the following criteria:

1. Identified active components referenced in the IAPWS Technical Guidance Document with known properties (performance, thermal decomposition etc);
2. Approval for use in New Zealand; and,
3. Availability in New Zealand.

Based on this assessment, the IXOM/Suez product known as Steamate PAS6074 was selected for the trial. Steamate PAS6074 is a mixture of the following components as per what is listed on its Safety Data Sheet:

- CAS 7173-62-8 N-9-Octadecenyl-1,3-Propanediamine (OLDA) ~8.5%
- CAS112-90-3 9-Octadecen-1-Amine (OLA) ~ 1.5%

The OLDA and the OLA are the film forming substance(s) contained within the product. Also present in the product are the following additional components.

- CAS 7173-62-8 Monethanolamine (Ethanolamine) ~ 10%
- CAS 108-91-9 Cyclohexylamine ~ 20%
- CAS 110-91-8 Morpholine ~10%

The rest of the non FFS components are to provide solubility stabilising and pH correction to the FFS component (OLDA and OLA) and are chemically similar to ammonia. The products are all volatile in steam, so if dosed in the feedwater they will transport into the HEX units and also into the steam, and then the condensate return lines and storage tanks. All wetted surfaces will be exposed to these components during dosing.

The trial comprised of carbon steel corrosion coupons exposed to actual plant feedwater, HEX boiler water and steam containing different concentrations of the product. IXOM/Suez advised that the recommended concentrations are 1-2 mg/L as product, dosed to the feedwater. The samples were exposed to oxygen and kept at room temperature. The corrosion coupons were pre-weighed prior to exposure and the corrosion rate is calculated as a function of weight loss over time - the lower the number, the lower the corrosion rate. The coupons were exposed to the solutions for a period of 129 days under the following conditions:

1.	Feedwater (FW) Control	No dosing
2.	Feedwater (FW)	1 mg/L
3.	Feedwater (FW)	2 mg/L
4.	HEX Control	No Dosing
5.	HEX	0.5 mg/L
6.	HEX	1 mg/L
7.	HEX	2 mg/L
8.	Steam Control	No Dosing
9.	Steam	1 mg/L
10.	Steam	2 mg/L

Note that the HEX samples all contained sodium hydroxide for pH adjustment at the time of the trials as this dosing had commenced on the operating plant.

The starting condition of the coupons can be seen in Figure 11. It must also be noted that the Feedwater and Steam control (no dosing) samples immediately started corroding on exposure to oxygen which is only 1 hour after the coupons were placed into the solutions. This was not the case for the HEX control sample that had sodium hydroxide dosed into it. The coupons of 2 mg/Las product dosed immediately showed signs of "cloudiness" in the samples whilst the 0.5 and 1 mg/L samples did not.

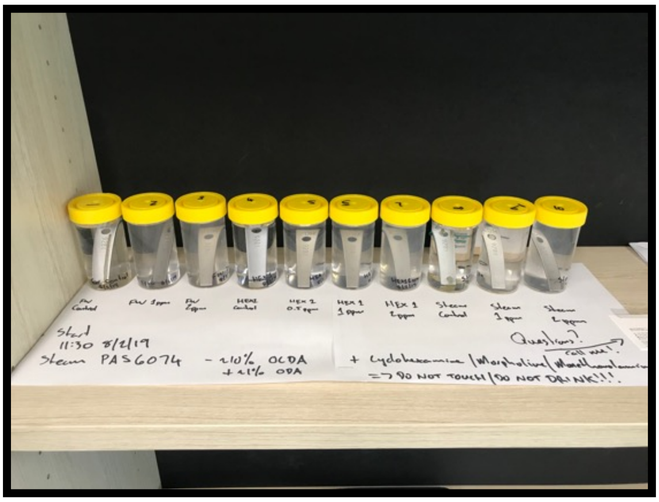

Figure 11: Trial Start – Initial Coupon Exposure

After 10 days exposure all the control (no dosing) coupons showed clear signs of corrosion with the least amount of corrosion in the HEX control sample which had been pH adjusted with sodium hydroxide. All dosed coupons showed no signs of corrosion.

After 129 days of exposure the control coupons for feedwater and steam were showing extensive corrosion with the HEX control sample showing a lower rate. The dosed coupons showed no signs of corrosion as per Figure 12. However the 2 mg/L dosed samples showed significant cloudiness.

The corrosiveness of the feedwater and steam with just ammonia present when exposed to oxygen is shown in Figure 13 and Figure 18 which show significant and extensive corrosion damage. The effectiveness of sodium hydroxide dosing for lowering corrosion rates in the actual HEX water is shown in Figure 15. For the other figures (Figure 14, Figure 16, Figure 17 and Figure 19) the effectiveness of the OLDA and OLA as corrosion inhibitors is clearly evident with full effective corrosion inhibiting shown at just 0.5 mg/L dosage, which is 50% less than the suppliers' recommendation. At concentrations of 1 mg/Lor higher, cloudiness was apparent and this is an indication of the OLDA and OLA starting to come out of solution and form microscopic wax like particles in suspension.

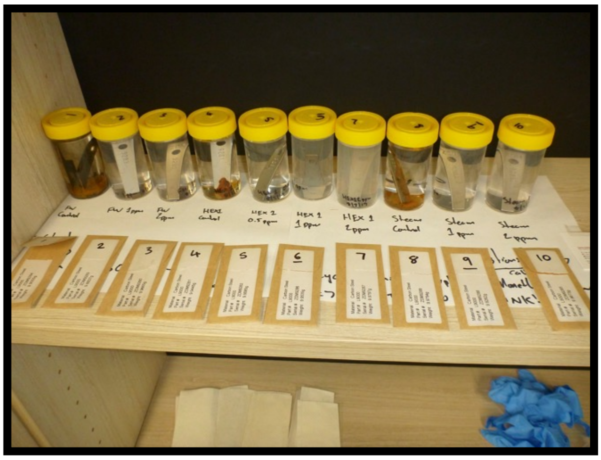

Figure 12: Trial End – Final Coupon Exposure

Figure 13: Trial End – Feedwater Control Coupon

Figure 14: Trial End – Feedwater 1 mg/L Coupon

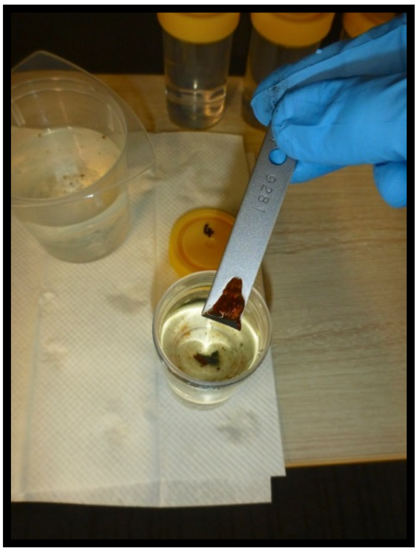

Figure 15: Trial End – HEX Control Coupon

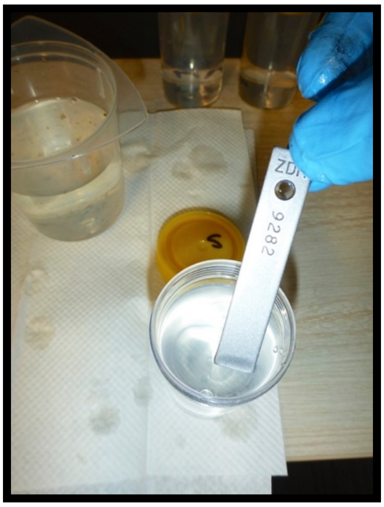

Figure 16: Trial End – HEX 0.5 mg/L Coupon

Figure 17: Trial End – HEX 2 mg/L Coupon

Figure 18: Trial End – Steam Control Coupon

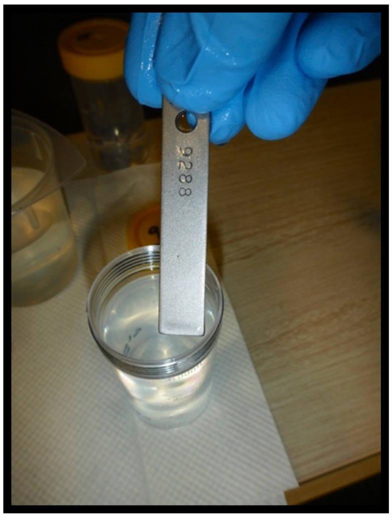

Figure 19: Trial End – Steam 1 mg/L Coupon

The final laboratory corrosion results for the trial are shown in Table 1 with weight loss in grams (g), corrosion rate in millimetres per year (MPY), pitting rate in millimetres per year (MPY) and measured pit depth in micrometres (µm) Table 1 also shows the results for corrosion and pitting rate in millimetres per year (mil/yr or MPY) as bar graphs. These results clearly show the effectiveness of Steamate PAS6074 as a corrosion inhibitor.

These results were extremely positive with the un-dosed control samples showing very high corrosion rates for both millimetres per year, pitting rate and pitting depth, whilst the dosed samples showed almost no corrosion at all or corrosion rates below measurable values.

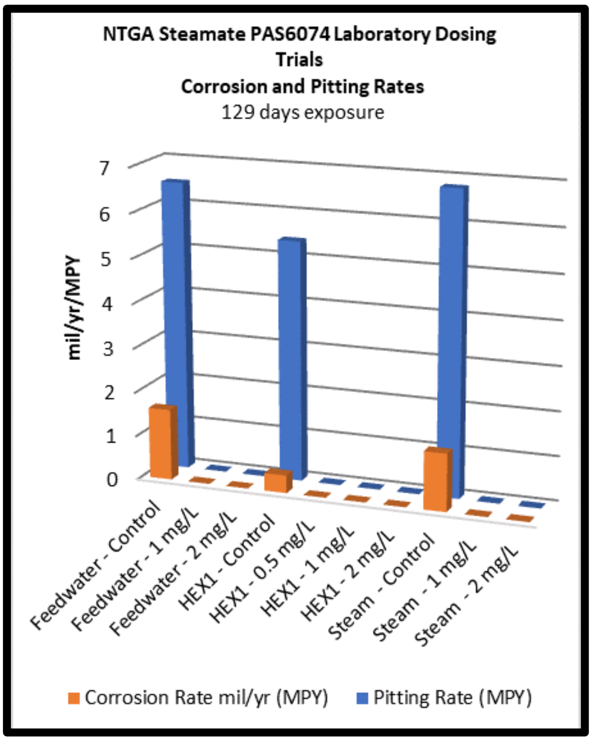

Figure 20: Steamate PAS6074 Trial Corrosion Rate and Pitting Rate Results

Sample	Location	PAS6074 Dosed (mg/L)	Weight Loss after 129 days (mg)	Corrosion Rate mil/yr (MPY)	Pitting Rate (MPY)	Pit Depth (µm)
1	Feedwater - control	0	223.9	1.6	6.5	58
2	Feedwater	1	0.1	<0.1	<2.2	<20
3	Feedwater	2	1.4	<0.1	<2.2	<20
4	HEX1 - control	0	58.6	0.4	5.4	48
5	HEX1	0.5	1.2	<0.1	<2.2	<20
6	HEX1	1	1.2	<0.1	<2.2	<20
7	HEX1	2	1.2	<0.1	<2.2	<20
8	Steam - control	0	179.4	1.3	6.8	61
9	Steam	1	0.3	<0.1	<2.2	<20
10	Steam	2	1.9	<0.1	<2.2	<20

Table 1: Steamate PAS6074 Dosing Corrosion Coupon Results – Coupon Exposure from 8 February to 17 June 2019 (129 days)

The HEX1 un-dosed sample included pH correction with sodium hydroxide which resulted in lower corrosion rate compared to the Feedwater and Steam control samples in terms of MPY corrosion rate, but it still showed relatively high pitting corrosion rates and measured pit depths.

Based on these trials, the application of a FFS at an application rate as low as 0.5 mg/L, has shown to be highly effective in a laboratory environment and would be expected to be as effective in a plant application. This was the proposed dosing concentration that was then applied in the NTGA plant.

4.3 Film Forming Substances - Corrosion Inhibitor Plant Application and Preliminary Results

Based on the extremely positive laboratory testing results dosing of the Steamate PAS6074 product was commenced on the 2nd of August 2019 (still in conjunction with the sodium hydroxide dosing) with a feedwater concentration of ~0.5 mg/L of product. Corrosion coupons were installed at each sample point for additional monitoring. A plant inspection was also undertaken in February 2020.

The plant has reported no operating issues related to the combined dosing of sodium hydroxide and Steamate PAS6074.

The dosing of Steamate PAS6074 is carried out into the feedwater based proportional flow control and tank draw down. There is currently no commercially available online analysis methodology available for checking for residual amounts of Steamate PAS6074. Grab sampling and analysis for FFS residuals is extremely difficult due to the tendency of the residual FFS in the samples to coat the internal surfaces of sample bottles and the low accuracy and repeatability of the most common analytical methods attempted - methyl orange extraction or xanthene dye reaction. At this stage due to these reasons no residual testing has been attempted.

Preliminary corrosion coupons were extracted for analysis after 114 days of exposure with the key results shown in Figure 21. For the feedwater and HEX coupons both the corrosion rate and pitting rates were zero indicating complete corrosion protection compared to the control samples. For the steam coupon the result showed only a 23% decrease in weight loss rates compared to the undosed control samples which indicates a lack of Steamate PAS6074 residual in the steam possibly due to consumption and decomposition in the HEX's.

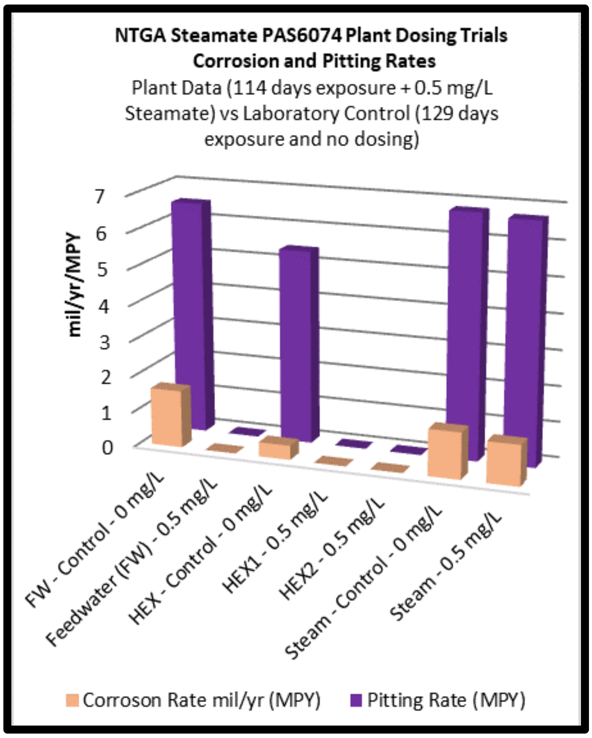

Figure 21: 114 Days Steamate PAS6074 and Sodium Hydroxide Dosing Corrosion and Pitting Rate Compared to Undosed/Dosed Lab Controls

The visual appearance of one of the HEX coupons after 114 days of exposure to a flowing HEX water sample can be seen in Figure 22. Note the extremely clean and uncorroded appearance of the HEX coupons was the same for both HEX units and is consistent with the very low corrosion and pitting rate results obtained.

Figure 22: HEX1 Corrosion Coupon after 114 Days in Service Exposure with Sodium Hydroxide and Steamate PAS6074 Dosing

The visual appearance of the feedwater coupon can be seen in Figure 23. Whilst the corrosion and pitting rates were extremely low, the coupon shows a change in appearance which appears to be a fine, stable surface oxide layer. Further investigations are underway to determine the composition of this surface layer.

Figure 23: Feedwater Corrosion Coupon after 114 Days In Service Exposure with Sodium Hydroxide and Steamate PAS6074 Dosing

The visual appearance of the clean steam coupon can be seen in Figure 24. Active corrosion is evident on the coupon which is consistent with the slightly decreased corrosion and pitting rate compared to the control sample. Further optimisation of the dosing to impart improved protection to the steam system is required and being investigated.

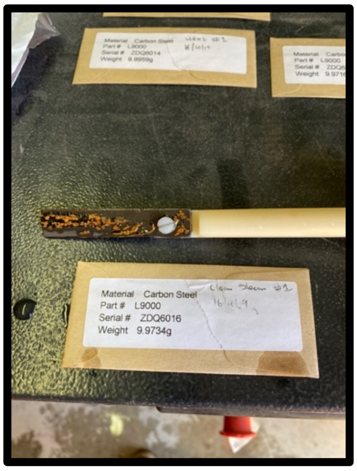

Figure 24: Clean Steam Corrosion Coupon after 114 Days in Service Exposure with Sodium Hydroxide and Steamate PAS6074 Dosing

HEX1 was able to be inspected in February 2020 with the bundle extracted for routine maintenance work. The bundle was considerably different in appearance from the previous inspection in 2018 as shown in Figure 4, Figure 5, Figure 6 and Figure 7 with no active corrosion observed as rusting or pitting; a smooth, passive protective oxide layer present on the tube surfaces; and a lack of corrosion products and crud in the bottom of the HEX unit unlike what was reported for this unit at its previous inspection. Note that this bundle was replaced in 2015 with an all new bundle whilst HEX2 was the original bundle.

Figure 25: HEX1 Full Bundle with No Active Corrosion Present

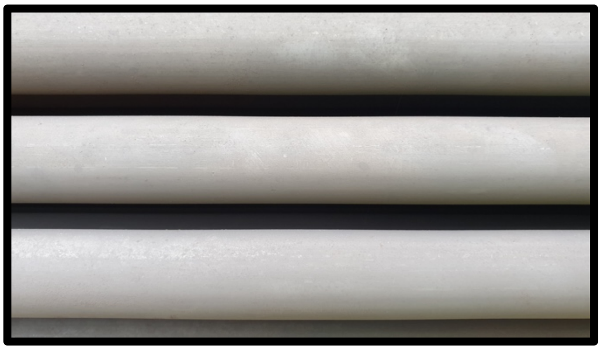

Figure 26: HEX1 Tubes with No Active Corrosion

Combined with the corrosion coupon results, the physical plant inspections show that the previously active corrosion and degradation of the bundle has been halted with the change in chemical dosing to include sodium hydroxide for pH control and hydrogen sulfide neutralisation and with Steamate PAS6074 for additional corrosion inhabitation.

Additional investigations are currently underway to assess the viability of Steamate PAS6074 directly into the geothermal steam to provide additional corrosion protection to the geothermal steam side of the plant. The impact on the scrubbers and feedwater is being investigated currently.

5. WATER/STEAM CHEMISTRY IMPROVEMENT PROGRAM COSTS

The costs to implement the revised water/steam chemistry program to minimise the previously aggressive corrosion in the plant is not excessive. Additional online chemical analysers including feedwater dissolved oxygen, HEX water pH and CACE have been installed for a cost of approximately ~NZD$100k.

The physical hardware to enable sodium hydroxide and Steamate PAS6074 dosing has been installed for a cost of approximately ~NZD$30k

The annual Steamate PAS6074 dosing cost is also extremely low, around ~NZD$1k per annum if both HEX units were in operation on a continuous basis. The annual sodium hydroxide dosing costs under the same conditions are also extremely low, around ~NZD$10k

6. CONCLUSION

The original design basis of the NTGA plant did not fully take into account the possibility of both an online and offline environment with low pH conditions produced by the oxidation of hydrogen sulfide naturally present in the geothermal steam that would remain, at low concentrations, in the feedwater after steam scrubbing. Failure to plan for the effects of hydrogen sulfide and low levels of dissolved oxygen in the HEX water appears to have contributed to high corrosion rates of carbon steel in the heat exchangers and premature failure of the tube bundles. The cost of these failures has been high, with a loss of plant reliability and the premature replacement of the tube bundles being carried out with replacement bundles now costing over NZD$1 million.

The application of sodium hydroxide dosing to the HEX units provides a simple and highly effective means of (a) neutralising any residual hydrogen sulfide in the feedwater through the formation of sodium sulfides and hydrosulfides before any unwanted reactions occur with dissolved oxygen and (b) increasing the pH of the HEX water to lower carbon steel corrosion rates.

The additional use of a Film Forming Substance, in this case Steamate PAS6074 with N-9-Octadecenyl-1,3-Propanediamine (OLDA) and 9-Octadecen-1-Amine (OLA) as the active film forming compounds, provides additional, highly effective corrosion protection of the feedwater and HEX surfaces for both online plant operation and offline storage under wet, oxygenated conditions.

The annual cost of both these chemicals for the NTGA plant is low, around NZD$11k, making their application even more attractive.

Additional work is underway to optimise the water/steam chemistry program and further reduce the clean steam corrosion rates. Investigations are also underway in regards to FFS dosing of the geothermal steam side of the HEX units to lower corrosion rates in that system.

7. ACKNOWLEDGEMENTS

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