CAUSTIC CLEANING OF GEOTHERMAL PREHEATER HEAT EXCHANGERS AT THE NGATAMRIKI POWER STATION

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ABSTRACT

The Ngatamariki power station uses OEC units to extract heat from geothermal fluid and drive pentane turbines for power generation. The preheater stage of heat exchangers at this plant experience scaling from antimony and arsenic sulphides as a function of both the temperature and pH of the mixed brine and condensate that supplies them. This type of scaling is well documented in the geothermal industry and caustic cleaning is standard practice at many plants. This paper describes a case study of a recent set of caustic cleans of the preheaters at Ngatamariki and the results from the cleaning.

During each unit's cleaning operation a series of samples of the cleaning fluid were taken and analysed for dissolved sodium, antimony, arsenic, sulphide, total alkalinity and solids. Sodium concentration was used to calculated the total system volume and enable the total mass of each dissolved species to be determined. This data was analysed against the improvements in heat transfer in order to better understand cleaning efficacy.

1. INTRODUCTION

The Ngatamariki power plant has four Ormat Energy Converting (OEC) Units generating 20MW net per unit. Each unit consists of 5 heat exchangers – a super-heater, a vaporiser and three preheaters. The super-heater is a brine fed heat exchanger, the vaporiser is a steam-only heat exchanger while the preheaters are fed from the combined output of the super-heater and vaporiser – a brine/condensate mix (Figure 1).

The preheaters in this plant experience scaling with antimony and arsenic sulphides. In the initial stages of operating this plant, these deposits were water blasted out during the annual shuts downs. This was time consuming and often was on the critical path for the shutdown. Caustic cleaning is another well-established method (Brown and Dorrington, 2001) for removing these deposits in geothermal plants due to their solubility in alkaline solutions. In an effort to reduce the cleaning time at Ngatamariki we successfully trialled this method in 2016.

This paper looks at a recent set of caustic cleans conducted on the units in late 2017, where we conducted a technical investigation to better understand the efficacy of the caustic cleaning process in the Ngatamariki units.

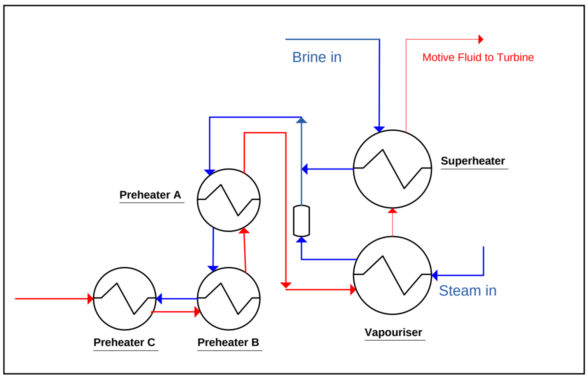

Figure 1: Schematic diagram of the Ngatamariki Ormat Unit Heat exchangers

1.1 Caustic Dissolution of Stibnite

Stibnite (Sb_2S_3) is extremely insoluble. Brown (2011) describes the dissolution of stibnite in water according to this formula:

$$\mathbf{Sb_2S_3 + 6\,H_2O = 2\,Sb(OH)_3 + 3\,H_2S} \qquad \text{----- (1)}$$

To get significant solubility in water, the $Sb(OH)_3$ has to ionise to $H_2SbO_3^-$, which requires very high pH (this being the basis for using caustic to dissolve stibnite). If the hydrogen sulphide product is converted to sodium sulphide, which consumes alkali, then the overall equation should be:

$$\mathbf{Sb_2S_3 + 8\,NaOH = 2\,Sb(OH)_4^- + 3S^{2-} + 8Na^+} \qquad \text{---- (2)}$$

So in round numbers, 1 t of stibnite would react with 1 t NaOH according to this equation.

Stibnite solubility in caustic soda is improved at elevated temperatures, so heat exchanger cleans are typically done at about 80°C.

To determine sodium hydroxide consumption during a caustic clean, it is necessary to separately measure the different alkali species – NaOH, Na_2S, and Na_2CO_3. This can be done using a titration procedure with different indicators to detect different end-points (SCAN-N 2:88).

2. METHODOLOGY

2.1 The Caustic Cleaning Method

A caustic cleaning temperature of 80 degrees Celsius was selected due to the prograde solubility of antimony and arsenic sulphides in caustic solution, with the temperature limited by the susceptibility of carbon steel to caustic stress corrosion cracking at elevated temperatures.

To achieve this temperature, the unit was shut down and allowed each preheater allowed to cool from their operating temperatures of 145-95 deg C to 80 deg C. Once set to temperature the circulation tank was set into motion. With circulation established, caustic was dosed into the circulation tank using flow rates to determine a dosing rate to achieve a 10% caustic solution. Surfactants were also dosed to improve wettability and therefore clean efficacy. The system volume for cleaning was approximately 34,000 litres for each OEC unit.

Circulation was maintained for 60 minutes. After the circulation time had elapsed the system was drained of the cleaning solution and all hoses and couplings flushed with a neutralising solution of citric acid.

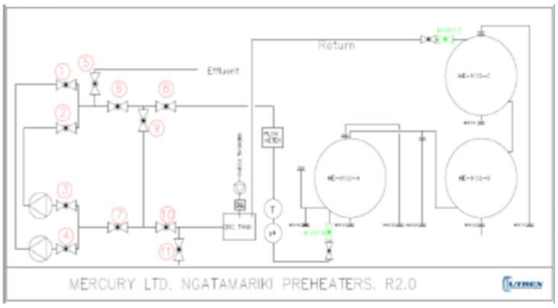

Figure 2: Plant configuration for caustic cleaning

Sampling of cleaning fluids was via a side tapping off of the circulation tank. Based on analytical results over a time series of samples for each clean it appears that the side tapping provides reproducible samples of the cleaning fluid.

2.2 Measuring Heat Transfer Coefficients

The heat transfer coefficient method used was based on an Overall Heat Transfer Coefficient calculation method for each preheater heat exchanger using the mean temperature difference across the overall length of the heat exchanger.

Equation 1: Overall Heat Transfer Coefficient

$$Q = UA\Delta t_{o,lm} = UA\frac{\Delta t_H - \Delta t_L}{\ln\left(\frac{\Delta t_H}{\Delta t_L}\right)}$$

Where:

q = heat transfer rate

U= overall heat transfer coefficient

A = heat exchanger area

$\Delta t_{o,lm}$ = log mean temperature difference

Δt_H = Temperature Hot

Δt_C = Temperature Cold

The assumptions made in this method are constant overall heat transfer coefficient constant mass rates of flow, no change in phase, constant specific heats and negligible heat losses.

2.3 Analytical Methodology

The analytical approach is outlined in Figure 3. Samples were first filtered to separate the suspended solids. The filtrate was then tested for Total Dissolved Solids according to APHA 2540C, alkalinity according to SCAN-N 2:88 (giving separate estimations of NaOH, Na_2S, and Na_2CO_3), and the concentrations of antimony, arsenic, sodium, silica, and calcium were determined by ICP-OES analysis (APHA 3120-B 22nd Edn.) The suspended solids, recovered by filtration, were first quantified (APHA 2540-D 22nd Edn.), then acid digested, and analysed (as above) for the same cations.

2.4 Mass Balance for Dissolved and Suspended Solids

To convert the concentrations of the determined analytes into absolute masses of each material, it was necessary to know the system volume throughout each cleaning operation, since brine ingress could have caused dilution. To estimate system volume the concentration of sodium ions was used, since the mass of caustic solution added to each clean was known with reasonable accuracy (ie. 5 IBC's of 50%w caustic for each OEC).

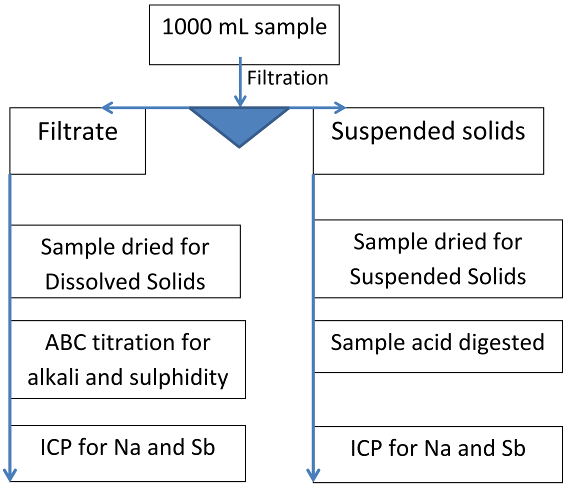

Figure 3: The scheme for analysis of the samples

3. RESULTS AND ANALYSIS

3.1 Chemistry

Table 1 shows the concentrations of the titrated alkaline species and the masses of the dissolved species determined for antimony, arsenic, silica and total dissolved solids. The NaOH concentration determined by titration was about 8% higher than that calculated from the assumed mass of caustic soda added to each unit. In general, there was very close agreement between all four samples collected at 15 minute intervals during each clean (data not shown). Hence, it appears that the dissolution reactions were rapid and were largely complete after the first 15 minutes, following caustic addition. It is also clear that sampling was representative of the dissolved materials in the circulating fluid volume of about 34 m^3 in each OEC unit.

Arsenic sulphide was about 10% of the total mass of arsenic plus antimony sulphides that was dissolved. In terms of the proposed reaction stoichiometry (eqn-2) the concentration of Na_2S determined by titration averaged 43% of that calculated from the dissolved antimony and arsenic concentrations.

An average of 11% of the sodium hydroxide was consumed during each clean, as calculated from the ratio of (Na_2S + Na_2CO_3) to Total Alkalinity. The averages for each OEC varied from 8% for OEC 2 to 14% for OEC4, showing a reasonable correlation with the amounts of stibnite dissolved.

The most surprising result was the large amount of dissolved solids (Figure 5) that are not accounted for. The Total Dissolved Solids (TDS) measurement was corrected for the NaOH originally in the cleaning solution (assumed to be present as its monohydrate). However, on drying these TDS samples to constant weight it was uncertain how much additional sodium carbonate may have formed from reaction with atmospheric carbon dioxide or whether the sodium sulphide had all oxidised to sodium sulphate. Nevertheless, calculating the effects of these scenarios on the measured TDS mass, showed similar results to assuming that all the NaOH was present as its monohydrate. Validation of this assumption is supported by the data plotted in Figure 4, which shows the amounts of stibnite and SiO2 estimated for each OEC versus the measured TDS mass. As both trend lines go close to the origin suggests that the "NaOH correction" is about right.

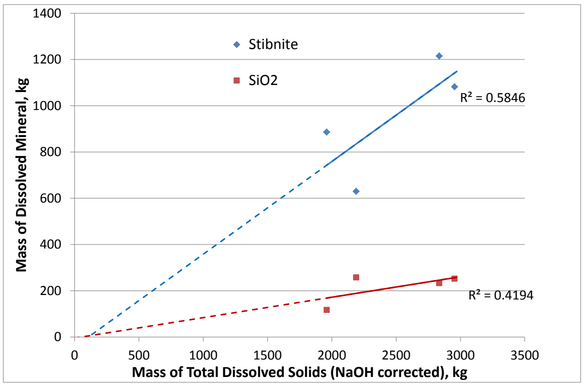

Figure 4: Plot of the amounts and stibnite (Sb_2S_3) and SiO2 estimated for each OEC versus the measured mass of Total Dissolved Solids

Subtracting the masses estimated for arsenic, antimony and silica from the corrected TDS values for each OEC gives the remaining solids 'unaccounted for' of between 856-1500 kg.

The presence of significant amounts of dissolved silica was unexpected and indicates an additional scaling mechanism in the heat exchangers beyond the previously known arsenic and antimony scaling.

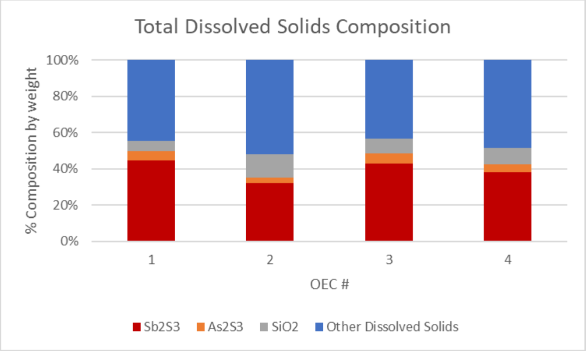

Figure 5 – Percentage Composition of Scaling Compounds

Table 1: Average concentrations of alkaline species and calculated masses of soluble analytes, stibnite, As_2S_3, silica and other dissolved solids

	OEC1	OEC2	OEC3	OEC4
% NaOH consumed	**11**	**8**	**13**	**14**
NaOH, g/L - [Na]^a	**109**	**109**	**101**	**106**
NaOH, g/L – titrn.	**112**	**123**	**108**	**114**
Na_2S, g/L – titrn.	**8**	**8**	**9**	**12**
Stoich.Na_2S, g/L^b	**19**	**15**	**26**	**24**
Na_2CO_3, g/L – titrn.	**5**	**3**	**8**	**7**
Stibnite Sb_2S_3, kg	**886**	**630**	**1215**	**1082**
As_2S_3, kg	**101**	**58**	**157**	**120**
Silica, kg as SiO_2	**117**	**258**	**233**	**252**
Other DS ^{c}	**856**	**1243**	**1230**	**1500**

[a] calculated from the measured sodium concentration
[b] calculated from stoichiometry of equation (2)
[c] calculated as TDS – stibnite – As_2S_3 – SiO_2

Suspended solids concentrations were quite low, at less than 1 g/L and accounted for only about 20 – 30 kg total mass from each OEC. However, the composition of the suspended solids material does provide some complementary evidence about the nature of the heat exchanger scales. Table 2 presents the suspended solids concentrations in the cleaning solutions and the compositional analysis following acid digestion.

By definition, the suspended solids are material that has not dissolved in caustic soda, but may also represent partially dissolved scale. It is apparent from Figure X and Table 2 that the analysed minerals only represent between 10 to 30% of the solids, with average compositions being quite variable between the four OEC units. Hence, from 70 – 90% of the suspended solids are unknown in composition and origin.

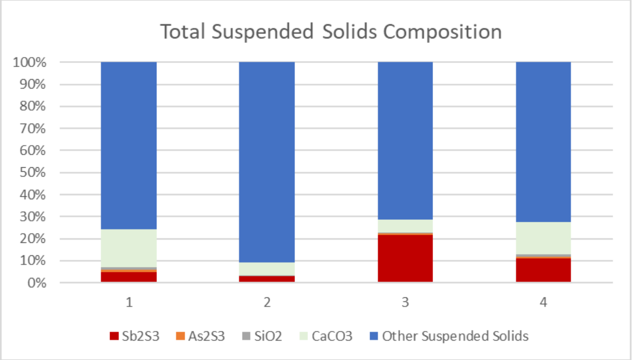

Figure 6 : % Composition of total suspended solids in cleaning solution – with Bal.b representing the balance of materials unaccounted for.

Table 2: Average Total Suspended Solids (TSS) concentrations in the cleaning solutions and the compositional analysis of the acid-digested solids

OEC	TSS	Composition of Suspended Solids[a], g/kg				
	mg/	Sb_2S	As_2S	CaCO	SiO_2	Bal.
1	512	50	10	171	10	760
2	843	28	2	57	4	908
3	787	218	6	60	4	713
4	707	111	8	149	9	723

[a] mineral compositions based on analysis for Sb, As, Ca, and Si (Ca calculated as $CaCO_3$)
[b] the balance of unaccounted material

3.2 Improvements in Heat Transfer

Observations and testing of scale samples collected during previous shut-downs indicated that stibnite scale was most obvious in the C-stage preheaters, which experience the lowest temperature brine. The absolute improvement in HTC in the C-stage preheaters correlates almost linearly with Sb_2S_3 removed (Figure 7).

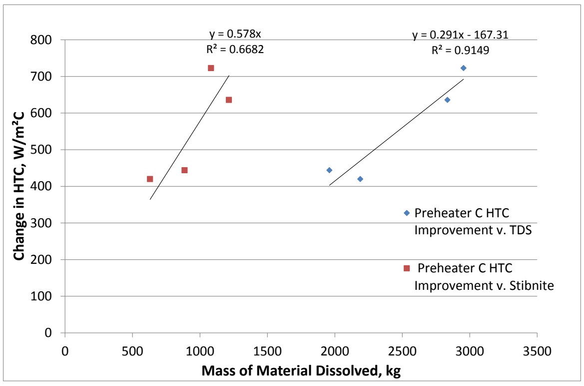

Figure 7: The change in calculated Heat Transfer Coefficients for the four C-Preheaters versus the mass of stibnite dissolved

However, there is far less correlation with the HTC improvements in Preheaters A and B. As Table 3 shows, the relative changes in HTC between the A, B, and C preheaters was not consistent across the four OEC units. Units 2 and 3 gave the largest overall HTC improvements, while the improvements for units 1 and 4 were about 30% lower. These absolute HTC improvements do not appear to be related to the pre-clean HTC values, as was seen for the C-stage preheaters (see Figures 5 - 7). Notably, the A-stage preheaters in OECs 1 and 4 and the B-stage preheater in OEC 4 showed no significant change in HTC after cleaning. By contrast, for OECs 2 and 3 significant HTC increases were seen across all 3 preheaters.

Table 3: Average increase in HTC for each OEC (after cleaning) and the individual changes for each preheater.

OEC	Increase in Avg. HTC, W/m².C	Preheater	Increase in HTC,
1	216	A	0
		B	204
		C	444
2	305	A	374
		B	122
		C	420
3	327	A	225
		B	120
		C	636
4	241	A	0
		B	0
		C	723

3.3 Preheater Stages and Variable Responses in HTC

The improvement in heat transfer coefficient for the preheaters varied depending on the stage of the preheater for all units. Preheater C responded well for all units, with a much more variable response between Preheaters A and B. These results are shown graphically in Figures 8 – 10.

The variable responses in A and B preheaters showed that the units that were most scaled (lowest starting HTC) tended to have the least response to caustic cleaning, versus Preheater C, where the most scaled units had the biggest percentage and absolute increase in HTC after the caustic clean. This suggests that in Preheaters A and B the scale type is significantly different to that fouling the C preheaters, and that the A and B preheaters can reach a level of 'critical scaling' when caustic cleaning is no longer effective.

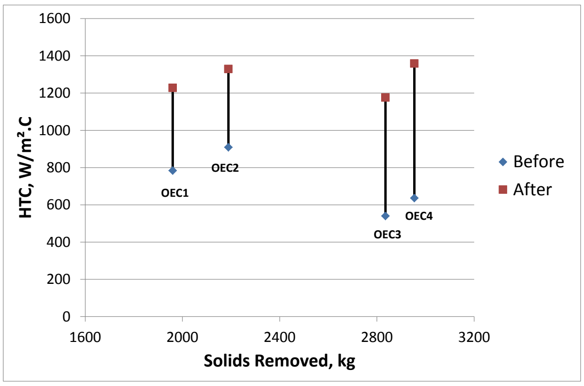

Figure 8: Preheater C heat transfer coefficient response before and after caustic cleaning

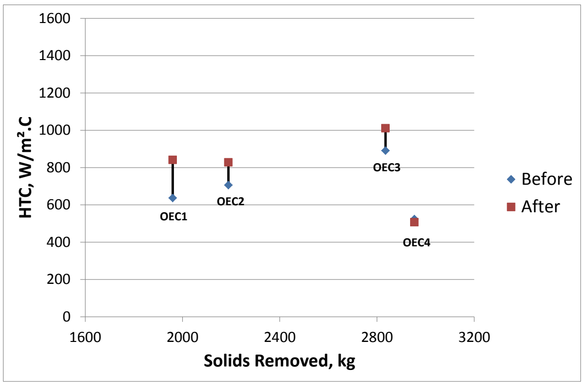

Figure 9: Preheater B heat transfer coefficient responses before and after caustic cleaning

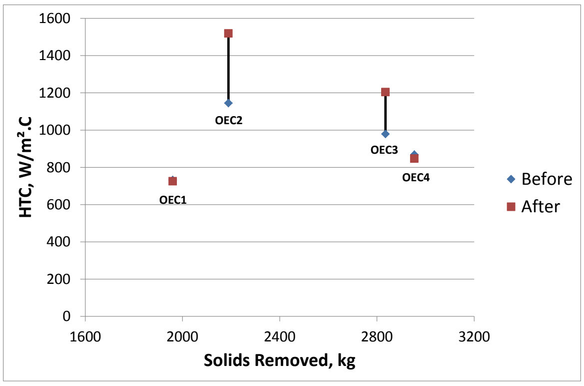

Figure 10: Preheater A heat transfer coefficient response before and after caustic cleaning

3.4 Differential Pressure Improvement

Despite the considerable differences between units on the amount of material removed, the improvement in differential pressure across the units was fairly uniform, with each unit showing a dP reduction, post-cleaning, of between 0.25 to 0.35 bar (Figure 11).

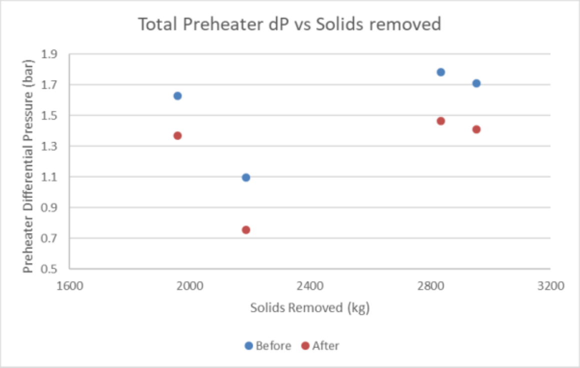

Figure 11: Differential pressure improvement of preheaters in each OEC unit before and after caustic cleaning.

Therefore, it appears that the open cross-sectional areas of the heat exchanger tubes had not shown significant reduction despite the differences in the average HTCs for each unit. Taken together with the relatively uniform dP response between units, indicates that while the amount of deposit present in each preheater was variable, this volume did not play a large role in the differential pressure development. Therefore, it appears that most of the increased dP seen as the units scaled (see Figure 9) was related to increased surface roughness within the heat exchanger tubes rather than a reduction in tube open area.

3.5 Post Clean dP trends

The preheater differential pressure was tracked post caustic clean to determine the approximate time for the unit to return to its pre-clean dP (Figure 12). The trends for all units showed two ‘phases’ of differential pressure increase. For ~1 month directly after the clean, the preheater differential pressure increased at a rate higher than that observed prior to the clean. However in the second month the rate of increase slowed significantly, returning to a similar level to that seen in normal operation prior to the caustic clean. It suggests that either the post clean surfaces were easier for material to deposit on or that shut down released a ‘slug’ of scale material from upstream of the heat exchangers that eventually deposited in the preheaters.

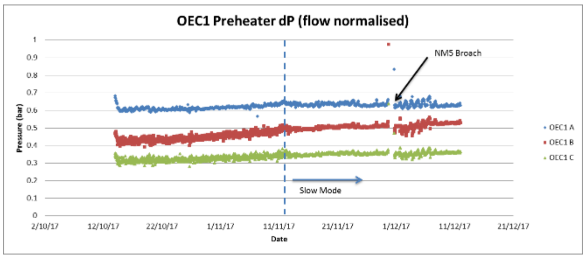

Figure 12: Differential pressure trends post caustic clean

3.4 Power Generation Improvement

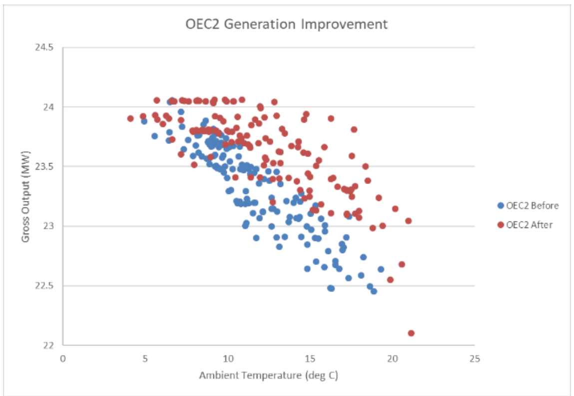

Figure 13: Generation Output of OEC2 before and after caustic clean

Figure 13 illustrates the improvement in gross generation after caustic cleaning of OEC2. It shows a noticeable shift in the output data post clean, with improvement being more significant at higher ambient temperatures where the air cooled condenser does not function as efficiently.

If we examine OEC performance before and after the clean in relation to design conditions it helps to quantify the value of this improvement under constant conditions.

Plant performance correction curves were used to correct 1 hour of data before and after the clean. The raw data was selected to be as close as possible to the design conditions based on ambient temperature, enthalpy and total flow. The correction curves were then applied based on the Ngatamariki Operation and Maintenance Manual. It is important to note that the improvement at design conditions does not necessarily represent the real gains seen at the station as loss of output can be counteracted using a various operation strategies such as increasing the OECs total flow.

The largest improvement in output based on design conditions seems to correspond with HTC improvement in Preheater A for OEC2 and OEC3. However these units also began with the lowest output at design conditions so had greater room for improvement versus OEC 1 and OEC4.

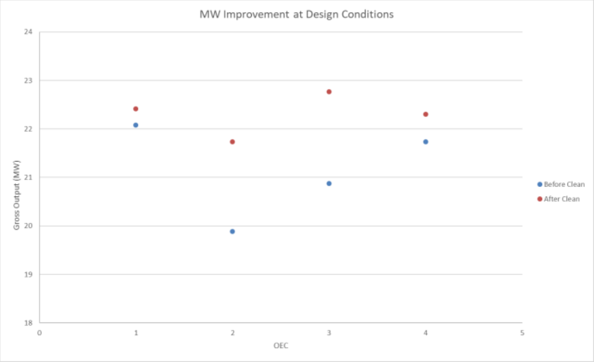

Figure 14: MW improvement at design conditions for OECs before and after caustic cleaning

4. DISCUSSION

4.1 Chemistry

The dissolution of preheater scale was largely complete within the first 15 minutes after caustic soda addition to the cleaning circuit. The compositions of all 4 samples, collected at 15 minute intervals, were essentially the same for all 4 OEC units.

Sodium hydroxide consumption was relatively low, varying from 8 – 14% across the four OECs. The measured concentrations of Na_2S support the dissolution chemistry shown in eqn. 2, although the amounts formed only averaged 43% of that expected based on the amounts of stibnite and As_2S_3 dissolved and the equation stoichiometry.

An objective of this study was to be able to relate the material dissolved with the improvement in heat transfer observed. While a clear relationship was seen for the C-preheaters between stibnite removed and HTC changes, this was much less clear for the A and B preheaters.

The evidence suggests that the scale type predominating in the A and B preheaters was not stibnite. The measurement of significant dissolved silica supports an argument that amorphous silica scales were also present. This is despite the brine pH being about 5, which is considered unfavourable for silica scaling (Lawson et al., 2016). Scale samples collected during station shutdown inspections of the A preheaters have confirmed the presence of amorphous silica.

The significant amount of unidentified material in both the dissolved solids and suspended solids of the cleaning solutions was an interesting find. A possible source of these unidentified dissolved solids could be formation material which had deposited in the preheaters. The Ngatamariki field has a bands of rock formation in its reservoir called the Tahorakuri Formation. There are five units in this formation that span a large depth range. In the heart of the Ngatamariki production area there are three units, spanning from -650mRL to around -1500mRL This is present within the production zones of several Ngatamariki production wells. Sanding of some of these formation units has long been suspected at Ngatamariki with various lines of evidence including superheater deposits and brine accumulator deposits supporting this theory. We hypothesize that the large amount of ‘other material’ found in our chemistry results may be attributable to this sanding mechanism with small particulates being ‘glued’ into preheaters by the active antimony sulphide scaling mechanism.

The fact that only 10 – 30% of the suspended solids material was present as identified minerals (Sb, As, Ca, Si) leads support to our hypothesis that much of the unidentified solids have originated from formation material which had deposited in the preheaters.

4.2 Heat Transfer Coefficients

While the C preheaters responded well to caustic cleaning, the response for the A and B preheaters was much more variable. The fact that the A preheaters in OECs 1 and 4 gave no improvement in HTC, while those in OECs 2 and 3 did is difficult to explain based on the data collected in this study. The only conclusion offered is that the nature of the scales must have been different between these OEC units.

The nature of this differential fouling in the A, B and C preheaters and differences between the four OEC units requires further study. This may lead to the development of improved cleaning strategies.

4.2 Differential Pressure

The two ‘phases’ of change in differential pressures across the preheaters (after cleaning) was an unexpected finding.

When we examined overall unit differential pressure it showed that shutting down the OEC for the clean resulted in a drop in the super heater differential pressure also. One potential explanation is that by stopping flow to the unit we allowed material pressed to the inlet face of the super heater to fall off into the end cap. When the unit restarted some of this may have been pulverized by the flow in the end cap and allowed to carry through to the preheaters over a period of time – resulting in a more rapid increased dP rate in the preheaters initially.

4.3 Generation Improvement

As a general rule, activities such as heat exchanger cleaning are usually only undertaken if the heat transfer coefficient and/or differential pressure across the unit is beginning to impact overall MW output from the unit.

The overall output can be limited by a number of factors. The main determining factors of output are often pressure drop across OECs, heat transfer coefficients and fuel supply. At most times during operation, declining heat transfer coefficients can be overcome by simply increasing the flow rate through the unit. This results in less efficient use of fuel, but offset the reduced heat transfer characteristics from scaling. However this is only able to be done within the design dP limitations of the units. Often a plant can maintain output with scaled heat exchangers and significant differential pressure as long as fuel supply is able to counteract the two. A tipping point comes when either fuel supply becomes limited, or differential pressure reaches a level where flow through the unit cannot be increased any further despite further production fluid capacity being available.

Ambient temperature also plays a significant role at Ngatamariki because of its air cooled condensers. Again higher ambient temperatures can sometimes be offset by increased flow rates through the unit, within the dP limitations of the unit. Figure 8 shows that post caustic clean, increased flow rate allows better maintenance of output at higher ambient temperatures.

The overall point of discussion is that the decision to clean is normally based on MW loss or impending MW loss from a unit. However when this occurs is dependent on numerous factors and the ability of a unit to maintain its output with scaled heat exchangers is only relevant as long as fuel supply and differential pressure factors remain unchanged.

4.4 Future Cleaning Considerations

The variable responses to caustic cleaning between Preheaters A, B and C suggests that for preheater A and B, there is a ‘critical scaling’ level where caustic cleaning is no longer effective at restoring heat transfer to its original levels. If this is due to silica scaling occurring in these units, it suggests that in future it may be necessary to consider how a HF clean could be safely utilised in the A and B preheaters to remove the silica scaling layer.

To confirm this we will monitor the efficacy of each clean in each preheater over time to determine whether efficacy in preheaters A and B declines over time.

5. CONCLUSION

In conclusion while the Ngatamariki preheater caustic clean was successful in both recovering heat transfer coefficient and reducing pressure drop in the preheaters, it highlighted that the non-uniformity of scale and the potential contribution of formation material to the scale mass.

The variable response between different preheater stages within an OEC and between the same stage of preheater in the same OEC, highlighted the need to make cleaning decisions based not solely on whether generation is being impacted already but rather on the balance of factors that allow the unit to maintain generation.

On-going monitoring of efficacy of cleans will help to determine if a supplemental hydrofluoric acid clean could be beneficial at some point in the future of the plant’s life.

6. ACKNOWLEGEMENTS

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