Proceedings World Geothermal Congress 2010
Bali, Indonesia, 25-29 April 2010

pH Modification Pilot Plant Trials

Ed Mroczek[a,d], Lew Bacon[a], Duncan Graham[a], Kevin Kotze[b] and Bernd Pummer[c]

[a]GNS Science. PB 2000, Taupo, New Zealand

[b]Armatec Environmental and Engineering Control Ltd, PO Box 3046, New Plymouth, New Zealand

[c]Contact Energy Ltd, PO Box 10-742, Wellington, New Zealand

[d]e.mroczek@gns.cri.nz

Keywords: pH, acidification, scaling, silica, inhibition, pilot plant

ABSTRACT

This work was undertaken for the purpose of designing, testing and optimising a small scale pilot plant process control system for acid dosing of geothermal fluid to mitigate silica deposition in fluid oversaturated with respect to amorphous silica solubility. The pilot plant was based on an approach used for automated laboratory titration. Three acid injection points were included, each upstream of a static mixer. Automated pH measurement was provided at ambient temperature with rapid sampling and cooling to provide pH feedback to the process control.

In the pilot plant the first acid injection was 98% sulfuric acid in sufficient volume to shift the pH to a “set point” near the shoulder of the titration curve. This injection rate was determined by fluid flow rate and a pH trim and controlled through a PLC. The successive second and third acid injections downstream were 20% sulfuric and controlled to a pH set point only (no flow component).

The acid dosing methodology was shown to be highly effective in maintaining the target pH with excellent pH stability over days of operation as well as reasonably quick recovery to target pH conditions after large changes in flow rate.

1. INTRODUCTION

Rothbaum and Rohde (1979) suggested that acidification may be a practical method for minimizing silica scale formation after observing a 100x reduction in the scaling rate at pH 4 in Wairakei and Ohaaki fluids. In subsequent work at Ohaaki, Brown and MacDowell (1983) confirmed the earlier findings in long term trials but also found that aged acidified fluid deposited large quantities of arsenic and antimony sulfide scales. Concurrent corrosion monitoring showed that the corrosion of carbon steel at pH 5 was low so long as a thin adherent continuous layer of silica was first allowed to form (Lichti et al., 2000). Acidification to control silica scaling is used commercially in many countries (Gallup, 2002, 2009). However as far as the authors are aware all acid dosing systems previously installed on geothermal plants had been based on a single acid injection point of either concentrated sulfuric acid or dilute acid produced in a side stream of geothermal fluid. The acid injection rate is usually determined by flow and sometimes includes a pH trim. The difficulty with this arrangement is that the target pH is invariably on a steep section of the titration curve and any variability in the system in terms of flow or fluid chemistry results in substantial pH variability with the consequence that both material corrosion and silica deposition will occur. pH control is normally accomplished either by automated intermittent measurement at high temperature or manual measurement of the fluid pH.

Acid dosing has been proposed for Wairakei as the means by which silica polymerisation can be delayed and deposition of silica in reinjection pipelines and wells minimised.

The purpose of the pilot plant was to trial a dosing system which must be able to maintain pH within close tolerances (± 0.2 pH units) in stable flow and be sufficiently flexible and robust to be able to cope with rapid changes in separated geothermal water (SGW) flow and buffering so that over- and under-dosing is minimised with a rapid return to target pH once conditions stabilize.

2. PILOT PLANT

2.1 Design

To achieve the desired outcomes the proposed design relies on:

- reliable and accurate fluid flow measurement;
- the target pH of 5.5 to 6 being approached slowly.

This is done by a three stage acid injection with approximately 85 to 90% of the acid required being injected at the first injection point. Concentrated (98%) sulfuric acid is injected at the first injection point and dilute (20%) sulfuric acid at the second and third injection points. The bulk of the acid is intended to reduce the pH to just before the rapid steep drop to the equivalence point in the pH titration curve and the dilute acid controls to the final target pH. This methodology was believed to be promising while seeking to minimise the risk of overshooting the target pH and readily providing for changes in buffering capacity of the separated geothermal water. The results from the trial demonstrated the effectiveness of this approach.

A schematic diagram of the plant is shown in Figure 1.

Data from the three pH measurement stations feeds back to a Programmable Logic Controller (PLC) controlling acid injection rates to meet the three selected Set Point (SP’s) pH’s.

2.2 pH Electrodes

Wedgewood Analytical Model OPF19 electrodes were used in the plant. These electrodes have, amongst other benefits, a triple junction reference cell and “non-fouling” porous Teflon junctions. Performance has been better than anticipated, in part because the sample water is cold (hence minimal silica deposition) and because they are easily cleaned in HF acid. However blocking of the porous junction did occur, caused by precipitation, not of silica, but of metal sulfides (mainly stibnite). The electrode expected life in service would easily be 2 weeks between cleans and possibly 1 month total life expectancy. Trial of different electrode designs and makes is recommended once long term dosing commences. For example pH flow through cells could also be considered in a scaled up design rather than currently where the electrodes sit in small “pots” through which the geothermal fluid flows. The primary considerations are reliability, ease of electrode replacement and in-situ calibration.

2.3 Sampling System

The samples were cooled to ambient temperature via a Spirax Sarco cooling coil. The sample flow also passed through a solenoid valve activated by cooling water availability; this was to avoid the pH electrodes being exposed to high temperature water. The selection of these valves needs particular attention as flow channels can be small and only a little deposition is required for failure of pH electrodes to occur. Needless to say, the responsiveness of the control system was very dependent upon the sample residence time i.e. it had a significant bearing on how far the pH moved outside the target pH range when the flow changes.

2.4 Commissioning

The plant was located at Wairakei utilizing mixed fluid from Flash Plant 12. The fluid at 90°C was taken from an open drain downstream of the Flash Plant and piped about 200 m downhill in a Victaulic pipe. The typical fluid composition is presented in Table 1, and Figure 2 shows the pH titration curve. The tuning parameters for the dosing pumps were set by experimentation to avoid pH oscillation. During the commissioning the flow of fluid to the plant appeared to be highly variable (± 25%) over a time period of minutes. This meant that the tuning parameters for the PLC logic controlling the dosing pumps were conservatively set to avoid oscillation of the pH.

After commissioning it was found that the unstable flow was a consequence of the over sizing of the flow control valve (designed for a flow of 100 t/hr) with respect to the actual flow through the plant, which was typically between 40 and 80 t/hr. Setting the flow to a manual setting reduced the flow variability and dramatically improved the pH control and stability. This meant that the tuning parameters were set too conservatively. The pH target reached equilibrium but with retuning it is considered that the system would have performed even better than was observed.

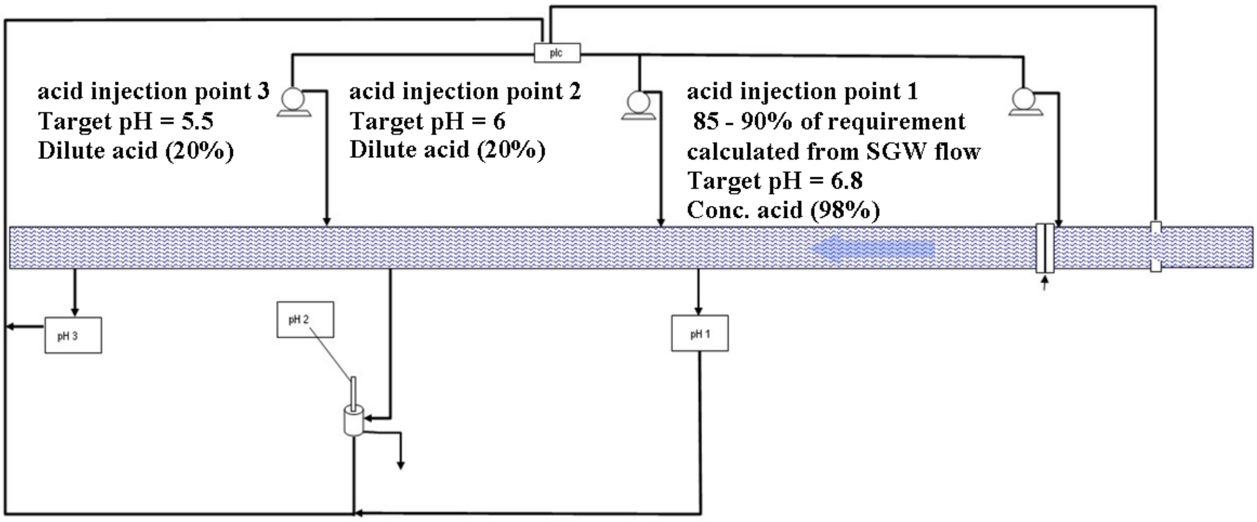

Figure 1: Pilot plant acid dosing schematic.

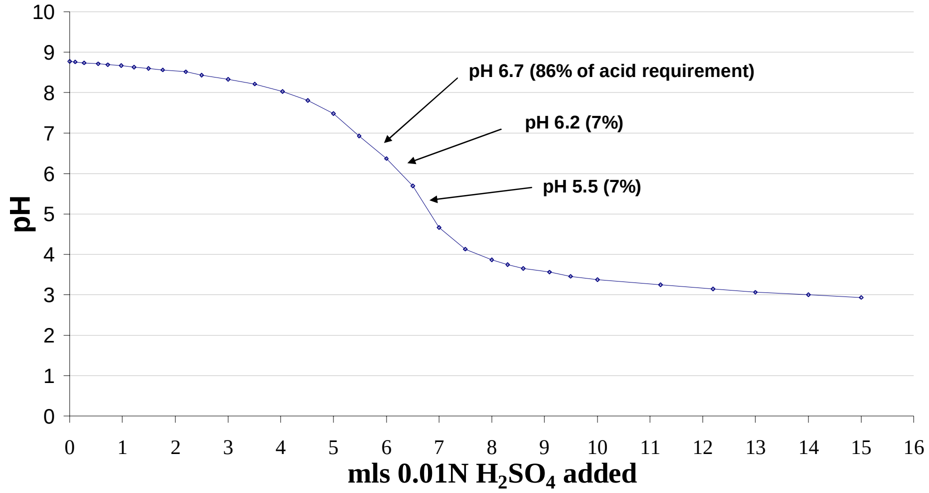

Figure 2: Acid titration curve.

Table 1: FP12 Fluid Weirbox Composition; mg/L except pH and temperature

pH/^oC	8.73/16
HCO_3	<10
B	26
SiO_2	657
Na	1317
K	245
Mg	0.01
Ca	9.8
Cl	2228
SO_4	43

3. RESULTS

3.1 Experiments

Five trials of ~2 weeks duration were held over a 3 month period designed to test the pH dosing methodology. No silica deposition trials were undertaken nor any material corrosion studies. Typical experiments consisted of determining the pH response with flow upsets and to see how the pH control functioned over days of operation. For example Table 2 gives summary statistics for data collected for an experiment where there was a change in both flow (67 t/hr to 43 t/hr) and pH set points (6.8, 6.3, 5.7 -> 6.5, 6, 5.5). Taking into account both the change in flow and set point, 86% of the acid required is injected at pH 1 in the first case and in the second case 89%. Figure 3 shows the pH control and stability were very good under both conditions but perhaps marginally better for the first higher flow case. This may have been because at the higher SGW flow the minimum step size of the dosing pump was better able to control to a given set point. In Figure 4 a scatter plot of the data for the second case pH injection point 2. In this plot the data points are randomly scattered in the vertical direction and the points are densest between at pH 5.99 and pH 6.01 thinning out at either end. The plot shows the pH falling on discrete values which may relate to the minimum step size of the dosing pumps or a measurement artefact with the PLC.

Table 2: Summary statistics for pH 2

Flow 67 t/hr (4 hr of data)			
	pH 1	pH 2	pH 3
Count	961	961	961
Average pH	6.80	6.30	5.70
Standard deviation	0.02	0.02	0.02
Coeff. of variation	0.33%	0.25%	0.29%
Minimum pH	6.72	6.26	5.66
Maximum pH	6.85	6.34	5.74
Range	0.12	0.08	0.08
Flow 43 t/hr (4 hr of data)			
	pH 1	pH 2	pH 3
Count	961	961	961
Average	6.50	6.00	5.50
Standard deviation	0.03	0.03	0.04
Coeff. of variation	0.49%	0.46%	0.66%
Minimum pH	6.30	5.91	5.39
Maximum pH	6.50	6.07	5.60
Range	0.20	0.16	0.21

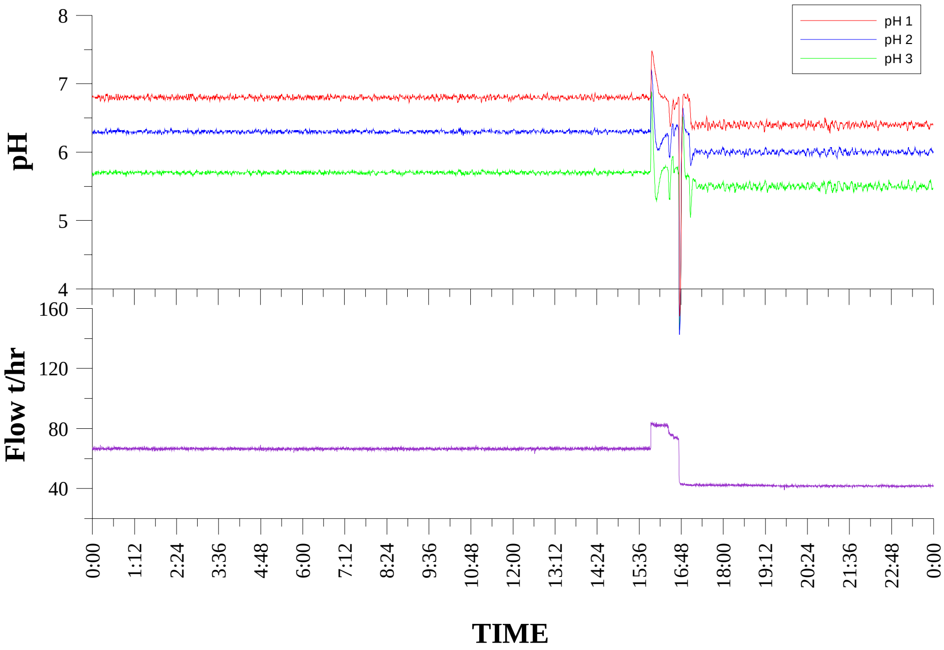

Figure 3: pH stability over a 24 hr period including an example of the flow and set point upset.

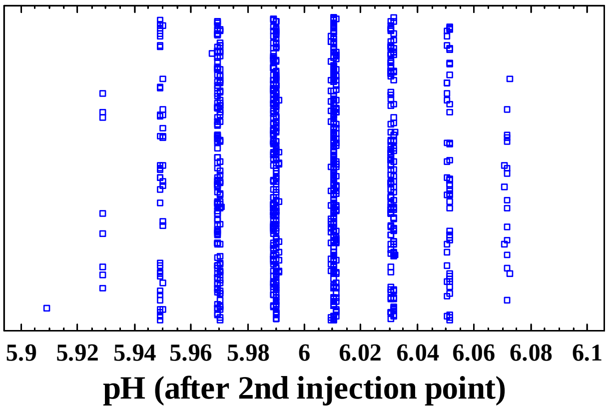

Figure 4: pH scatter plot for injection point 2 at a nominal set point of pH 6.

3.2 Operational Problems

The main problem experienced was the eventual failure of pH electrodes, primarily electrode at pH 1, but even so they lasted over 2 weeks and could be recovered with cleaning. At times the electrodes were coated with a red scale, high in antimony (inferred to be stibnite), which blocked the porous junction leading to poor pH response. The other problem experienced was the blocking of the sampling tube to pH 1 and this was solved by bypassing the solenoid valve and straightening the sampling coil.

3.3 Condition of Plant at the End of Trial

The plant was dismantled and the condition of the static mixers and the acid injection quill was excellent with no observed corrosion, although only three months of intermittent testing had been carried out. There was extensive scaling at the inlet to the plant (~1 cm porous hard scale) and negligible scaling down stream. Fluid flowed through the plant continuously irrespective of whether acid was being dosed. The silica deposition is expected to have provided some protection against low pH conditions.

4. CONCLUSIONS

The objectives of the pilot plant were achieved with acid dosing methodology shown to be highly effective in maintaining the target pH with excellent pH stability over days of operation as well as quick recovery to target conditions after large upsets in flow rate. The results also suggest that the first dosing pump may be best controlled by monitoring only SGW flow as dosing in pumps 2 and 3 can still easily cope with achieving the final target pH of about 5.5. This would avoid the use of the first electrode and sampling lines which were most subject to scaling and blocking by silica and stibnite.

The corrosion by the concentrated acid at 90°C was negligible, however, the corrosion potential at higher temperatures could be significant. This aspect was not investigated in this series of trials.

ACKNOWLEDGEMENT

Contact Energy Ltd for permission to publish this study

REFERENCES

Brown, K.L., McDowell, G.D., 1983. pH control of silica scaling. Proceedings 5th New Zealand Geothermal Workshop, pp. 157–161.

Gallup, D.L. 2002. Investigations of organic inhibitors for silica scale control in geothermal brines, Geothermics, 31, 415-430.

Gallup, D.L. 2009. Production engineering in geothermal technology: A review, Geothermics, 38, 326-334.

Lichti, K.A., Brown, K.L. and Ilao, C.M. 2000. Scaling and Corrosion of pH Adjusted Separated Water, 22nd NZ Geothermal Workshop, 169-176.

Rothbaum, H. P., Anderton, B. H., Harrison, R. F., Rohde, A. G. and Slatter, A. 1979. Effect Of Silica Polymerisation and pH on Geothermal Scaling, Geothermics, 8, 1- 20.