DESIGN AND SUCCESSFUL OPERATION OF A NEW PH MEASUREMENT SYSTEM FOR GEOTHERMAL BRINE

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ABSTRACT

New generation geothermal flash plants generally make use of pH-modification through acid addition to the geothermal brine thereby allowing extraction of energy beyond the brine's silica solubility. The accurate and reliable measurement of the brine pH is important as this is used as a part of the control logic for the acid injection. If too much acid is injected in the geothermal brine this increases risks of corrosion in the brine handling system, whilst if too little acid is injected this heightens the risk of silica polymerization and subsequent deposition either within the injection pipe, injection well or the reservoir formation. Therefore the pH measurement system must provide accurate and reliable pH readings, have a high availability factor and a fast response time.

The previous system installed at one of Mighty River Power's plants resulted in slow response times and provided pH values which at times caused control issues for the acid dosing system. New pH meters were procured, with the ability to make use of ion-sensitive field-effect transistors (ISFET) rather than only glass electrodes. Glass electrodes were found to be prone to deposition from species within the cooled geothermal brines resulting in a slowed response time and drift. Significant design work was conducted to ensure sample conditioning was improved, alongside control and instrumentation work to allow the power plant to communicate more effectively with the pH meters allowing provision of reliable high-availability brine pH values.

Two years of successful operation of the new pH monitoring system has now been achieved. During this time minor refinement of the system design has been made to improve the availability factor. Key learnings are discussed in this paper.

1. INTRODUCTION

1.1 Overview

Mighty River Power owns and operates a number of power plants in which the level of silica in the brine exceeds the amorphous silica solubility limit, thus allowing additional energy extraction than would otherwise be possible if silica was not over-saturated.

Two geothermal flash plants use a process called pH-modification, where acid is added to the geothermal brine to inhibit silica polymerization. 98% sulfuric acid is added to the brine, with pre-dilution occurring prior to entry to the main flow. Controlling the amount of acid added is an acid dosing ratio controller, whereby the amount of acid added to the brine is primarily controlled by the flow of the brine and the ratio, acid flow to brine flow, is trimmed according to the measured pH. Process changes, such as the swapping of production wells or load changes tend to interrupt and change the ratio of the flows. Figure 1 illustrates the acid dosing ratio controller.

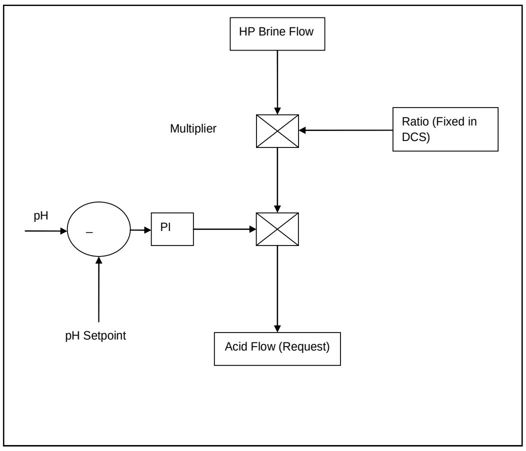

Figure 1: Schematic showing acid dosing ratio controller

If the pH in the geothermal brine is too high, this increases the risk of deposition of silica as there will be an insufficient suppression of pH to inhibit polymerization. Deposition risk exists within the injection pipe, injection well and reservoir formation. This can result in remedial activities being required, such as drilling a new injection well or well acidification (Lim *et al.*, 2011). If no pH adjustment is made, there is also a risk of deposition in the low-pressure two-phase pipe and low-pressure separation plant. A simplified schematic of the plant brine system is shown in Figure 2.

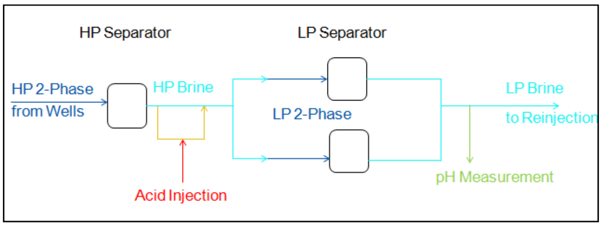

Figure 2: Schematic showing the location of acid injection and pH measurement relative to two-phase and brine flow

If the pH is too low, this increases the potential for corrosion of the pipework to which the brine is exposed. After more than two years of operation of the plant, metal loss was found to be generally localized and most extreme in areas of low pH, high velocity, turbulent and two-phase flow. Examples of such damage are shown in Figure 3 and Figure 4. The solubility of iron increases with a decreasing pH, therefore acid dosing for silica control results in an increased likelihood of corrosion. Moving to high grade alloys reduces corrosion, however this comes with significant extra expense. Equipment that is built out of expensive alloys must be very vulnerable to corrosion if not built out of alloy to justify the expense.

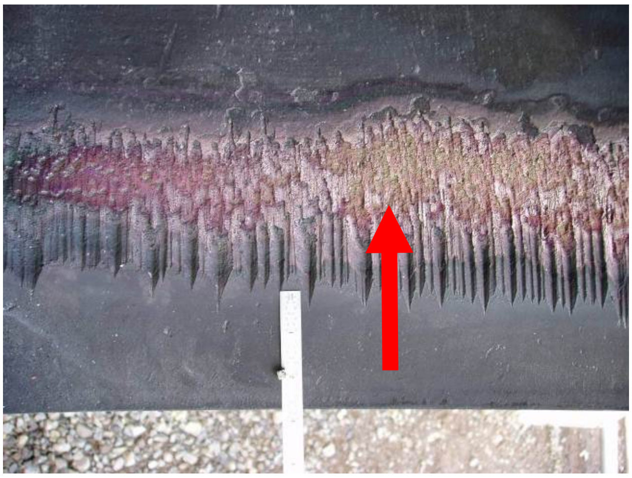

Figure 3: Example of localized metal loss on the welded connection between a weld neck flange and adjoining pipe. Flow is indicated with the red arrow (Amend and Yee, 2012)

Figure 4: Example of localized metal loss inside elbow. Approximate dimensions are 20x30cm. Flow is indicated with the red arrow (Amend and Yee, 2012)

Finding the balance between controlling deposition and corrosion risk can be difficult. Therefore Mighty River Power initiated a number of process-improvement initiatives, one of which was a material change-out as discussed by Amend and Yee (2012) and another was the improvement of the acid dosing system, of which the pH measurement system upgrade formed a part. These improvements were done alongside a number of other projects, including changing the pH set-point and operating methods such as plant and acid dosing system startup and shutdown.

This paper describes the project to install a new pH measurement system using ISFET probes and the challenges this presented.

2. DESIGN BASIS

A cross-disciplinary project team was established at Mighty River Power, comprising chemistry, control and instrumentation, mechanical and electrical engineering disciplines. This team established early on the following key design features for the new pH measurement system:

- A two pH meter system, allowing traditional duty-standby operation;
- Each pH meter must be able to read consistently while the other pH meter is on probe duty changeover;
- The system must be able to characterize the representative pH value of the bulk flow from which the sample was taken from as quickly as possible;
- The system must be able to be operated and maintained safely;
- As much control as practical should be conducted in the Distributed Control System (DCS) rather than the instruments themselves, allowing the operator to see and control the system;
- The system must have the ability to measure and record pH at all times;
- Meters must have the ability to be self-calibrated;
- The system must have the ability to operate with only one meter, allowing for maintenance of the other sample conditioner and instrument.

Two self-calibrating Endress+Hauser Topcal S CPC310 instruments, making use of retractable 225mm ISFET probes were procured. The probe housing is shown in

Figure 5. These instruments were to be installed and new sample conditioning units were designed and installed at the same time. Each pH meter was supplied in a large stainless steel cabinet, with an umbilical cord for buffer reagent lines, a cleaning agent line, along with supply and return air lines. Pneumatic switches provided feedback air pressure from the probe housing back to the Topcal controller, providing information on the probe position.

Figure 5: The Topcal retractable probe assembly. The probe housing is in the retracted state, with only bottom o-rings visible

The new meters have the ability to use glass probes in the event that the ISFET probes showed any interference or issues in geothermal brine service during commissioning. Previous experience with glass probes indicated that the responsiveness of the probes reduced with time, resulting in the probes taking a significant time to read the correct pH upon introduction to the geothermal brine. After probe duty changeover a step-change in control pH would be observed, thereby changing the amount of acid delivered through the acid-dosing logic control. The ISFET probes had a much faster response time, with the only cause of measurement errors being issues with the probe itself or through different sample conditioning, for example the flow rate of sample. To reduce the potential for this to be a problem, each sample leg featured its own cooler, sample flow meter and automated control valve. The sample flow loop was controlled from the DCS, allowing for identification of trends in flow rate and identification of fouling, indicating a need for maintenance to be carried out..

Continuous sampling was delivered from a sample probe making use of a packing gland to allow in-service removal and replacement if needed. The pH measurement system was located physically as close to the sample location as was practical. A small-bore tubular stainless-steel sample line was run. Consideration was made of the risk of both flashing and deposition within this line. A simplified schematic of the sample conditioning arrangement is shown in Figure 6.

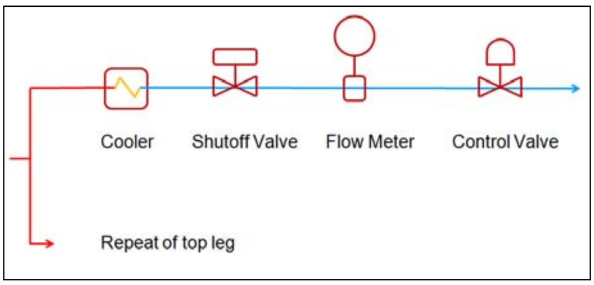

Figure 6: A simplified schematic of each sample conditioning leg. Not all valves are shown.

During design, consideration was made as to the risk of the system being exposed to high sample temperature due to a loss of cooling water event. Whilst the probe was rated to withstand the normal operating temperature of the LP brine, a mechanical thermal shut-off valve was added to the sample conditioning system. The mechanical shut-off valve is designed to function even with a loss of power to the system. In addition to the mechanical shut-off valve, which was set to trigger at 49ºC, upon the probe reading a higher temperature of 60ºC the probe will itself retract and raise an alarm through the DCS. Lighting and insulation was also installed in appropriate places and an external junction box for the power supply was installed away from wetted parts.

Considering how important reliable pH readings are for the stable operation of the brine injection system and minimizing silica deposition, having full information gathering and control through the DCS was a key design feature. As the engineering and geoscience teams are located remotely to the station, having accessible information stored in the DCS allowed for a high level of support to be provided to the station during commissioning and when fault conditions arose. The DCS has a high availability rate with redundancy on many components. Signals are sent through an upgraded C200 fast controller. To improve the interaction between the instruments and the DCS a number of modifications were made and some of these are discussed in section 2.2.

By procuring two pH meters, they can be operated in parallel so that when one is reading and controlling the pH in the acid dosing ratio control, the other is available to undergo program sequences where the probe is either flushed with water, calibrated or cleaned with a cleaning agent. When the two meters are both operating through an automated function of the DCS, they work alongside one another to provide uninterrupted real-time pH measurements, with this being called the Dual Probe Mode within the DCS. However, when one meter experiences a fault or there is maintenance on either one of the pH meters or its sample conditioning equipment, then the DCS automatically sets up the Single Probe Mode where the acid dosing ratio control is held static whilst the pH meter is undergoing its scheduled program of repair or maintenance. Dual and Single Probe Modes within the DCS are discussed in Section 2.3. Along with having automated cycles in the control logic, the operator has the ability to place the meters under manual control and have them work as defined by the operator.

2.1 Instrument and Program Terminology

The probes themselves can sit in either the *Measure* or *Service* positions, as defined by Endress+Hauser. When in the *Measure* position, the probe is extended down into the lower chamber and is in the process fluid. A number of o-rings prevent the cooled brine from feeding through to the upper chamber. When in the *Service* position, the probe is retracted and is in the upper chamber. The upper chamber is supplied by a manifold with a number of non-return valves, where it can be supplied by buffer solutions, water,air or cleaning agent. A number of o-rings prevent the service fluid from feeding through to the lower chamber. The feedback of the probe position is shown in the DCS display in Figure 7 with an orange box.

A number of different terminologies are applied to cover the specific details of what the pH meters are doing. A number of the terms used were previously used for the old system and therefore were carried across to enable more familiarity for the operations staff. The modes as defined are:

- Duty – The probe is in the *Measure* position reading brine pH and is being actively used for brine pH control through the acid dosing ratio. Only one probe at any time can be in the Duty mode. If no probe is in the Duty mode, the acid dosing ratio is held constant.

- Standby – The probe is in the *Measure* position reading brine pH, however is not used for control of the acid dosing ratio until it is moved into the Duty mode. The main reason for having standby with ISFET probes is to allow for temperature equilibration of the probe to the brine temperature.

- Available – The probe is in the *Service* position and is available to either commence another program sequence (Wash, Calibrate or Clean) or move into the *Measure* position through the Standby mode.

- Wash – The probe is in the *Service* position. A wash sequence consists of water being flushed through the probe chamber.

- Calibrate – The probe is in the *Service* position. A calibration sequence consists of water being flushed through the probe chamber followed by pH buffers being pumped and the probe being recalibrated with a two-point calibration.

- Clean – The probe is in the *Service* position. A clean sequence consists of water being flushed through the probe chamber, a cleaning agent applied and then pH buffers being pumped and the probe being recalibrated with a two-point calibration.

The Clean program sequence was added as a provision but has not been utilized. The relative cost of programming the Clean program was considered very low and worthwhile if this is required in the future. The modes above are exclusive and are shown in the DCS display in Figure 7 with a red box.

The DCS featured an On and Off mode. Due to the large number of interlocks present, the Off mode is there to simply allow a de-latching of control from the DCS, allowing for local operation without any interference from the DCS. This feature is important during periods of commissioning and maintenance. The buttons for control are shown in the DCS display in Figure 7 with a blue box.

The previous system made use of an Auto function where each probe could be washed with water, then would move through a Standby period before heading into Duty. This same philosophy was carried across to the new system, however with the additional complexity and subsequent risk of faults in the new system a number of interlocks had to be designed. Manual control was needed to allow operator override. Each pH meter can be operated in either Auto or Manual. When only one probe is on Auto, it automatically runs in Single Probe Mode, discussed in section 2.3. The buttons for control of mode (Auto/Manual) are shown in the DCS display in Figure 7 with a yellow box.

Wash is the default program sequence when a meter has completed its Duty cycle. Timers were installed in the control logic to allow automatic raising of a flag at set intervals. After the flags are automatically raised then the next time the meter completes its Duty cycle it will conduct a Calibrate or Clean cycle depending on what flag is raised. The clean flag is rated as higher priority than the calibrate flag. At any stage the operator can themselves initiate a flag, and when in Auto mode the pH meter will then initiate the selected program sequence the next time it comes out of the Duty cycle. Upon completion of a Calibrate or Clean cycle, the timer is reset to prevent unnecessary extra use of buffer reagents and cleaning agents. The flags for control are shown in the DCS display in Figure 7 with a green box.

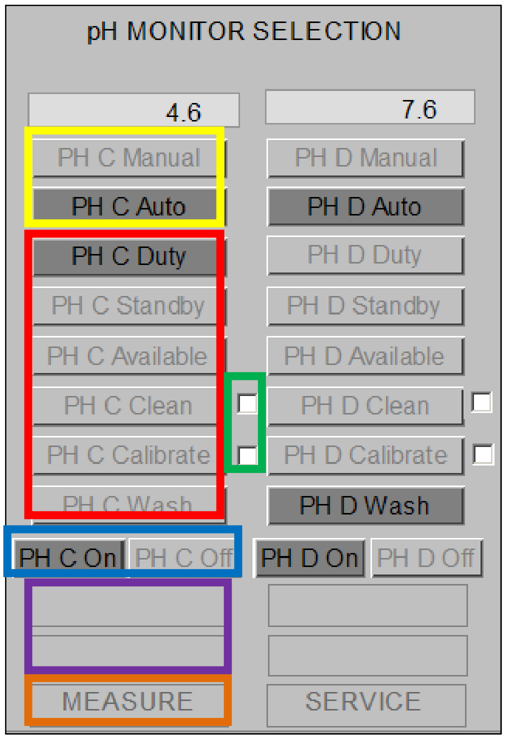

Figure 7: DCS interface showing buttons and display for the Operator. Darker grey indicates the active modes the meters are in.

2.2 Smartening the Instrument – DCS Interface

The pH meters themselves have three places for cables from the DCS to be connected. To simplify the inside of the cabinet, significant re-cabling was carried out prior to installation, resulting in a single area for cable terminations. A protective Perspex cover was installed over the new cable termination area within the cabinet, protecting the area in the event of a tubing failure on the discharge side of the buffer pumps which are also housed within the cabinet.

Two additional signals were brought back from the instruments through to the DCS, namely: the maintenance required and fault signals. Maintenance required warnings are generated by situations that are not immediately critical to the value provided from the pH meters, and therefore are for information only. An example of a cause of a maintenance required signal is a low buffer reagent level. A fault signal is critical to the value provided from the pH meters, as it indicates that something has gone wrong. In this instance the instrument raises a fault and comes out of Auto into Manual, allowing the operator to investigate. An example of a cause of a fault is if the buffer did run out and a calibration was therefore unsuccessful. Display of the maintenance required and fault signals for control are shown in the DCS display in Figure 7 with a purple box. These are normally empty unless a signal is being received.

Binary code is used to send out details of what program sequence the DCS wants the pH meter to conduct. The instrument itself can only send a busy signal to the DCS when a program sequence is occurring. Therefore, the DCS cannot identify which program sequence has been initiated to ensure the correct program sequence is taking place. The instrument can control two external valves: Valve 1 (V1) and Valve 2 (V2), and therefore these were physically disabled and their signal was used to initiate a switch that was then fed to the DCS. At the beginning of each program sequence V1 and V2 are used to send binary code to the DCS to inform it of which program sequence has been initiated. Due to the availability of only two external valves that can be configured to send an external signal for binary code purposes, a maximum of three program sequences are possible, as this is the maximum number of combinations that can be received from the DCS using only two signals. The feedback from V1 and V2 signals allows successful handshaking between the instruments and the DCS.

Upon each program sequence completion V1 and V2 are both programmed to close, signaling to the DCS that the instrument's program sequence has finished and the instrument is now available to either have another program sequence initiated or to move into the measure position and begin to read brine pH.

Along with V1 and V2 having external relays installed, the Air and Water supplies were also set up to provide feedback to the DCS. These were installed primarily to assist with commissioning and to handshake with the flow switch installed downstream of the service chamber.

2.3 Automatic Operational Modes

When the DCS has the pH meters in Auto mode, the pH meters will work to provide a pH reading as frequently as possible. With two pH meters, when both are in Auto mode the DCS will coordinate the program sequences whilst the other probe is in its Duty cycle. This mode of operation is called Dual Probe Mode.

If one meter is unavailable, or is in Manual, the other meter that is left in Auto will work on its own to read pH as frequently as possible, whilst still undertaking servicing. The acid dosing ratio control is held static during the time when no meter is in a Duty cycle.

2.3.1 Dual Probe Mode

Each meter when in Auto has two timers that operate, namely: a standby timer and a duty timer. Each standby timer is set at 5 minutes, with each duty timer set at 25 minutes. When a pH meter completes its standby phase, the DCS automatically activates its duty timer. At the same time the DCS pushes the other probe out into the *Service* position where a program sequence is initiated. Upon completion of the probe's duty phase, the DCS pushes the other probe into the *Measure* position and the standby timer for this probes is activated. Whilst the duty timer is itself set for only 25 minutes, the Duty cycle that is conducted in dual probe mode is 30 minutes as it includes the standby phase for the other meter. In total the pH meter is in the *Measure* position for 35 minutes because of its own time on Standby. This is shown in Figure 8.

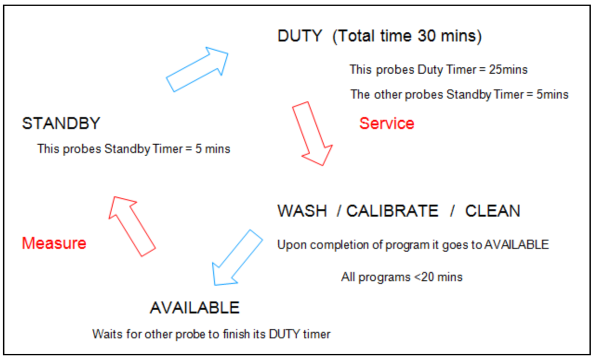

Figure 8: Flow diagram of Dual Probe Mode

At any stage during Dual Probe Mode when one of the instruments is placed into Manual, either due to an interlock or from operator intervention, the DCS automatically moves into Single Probe Mode.

2.3.2 Single Probe Mode

As there is no other meter on Auto, the meter will itself complete its duty phase and the DCS will push the probe into the *Service* position where a program sequence will be initiated. Immediately upon completion of the program sequence the meter's probe will be pushed into the *Measure* position where it will initiate its standby timer. In total the probe is in the *Measure* position for 30 minutes. This is shown in Figure 9.

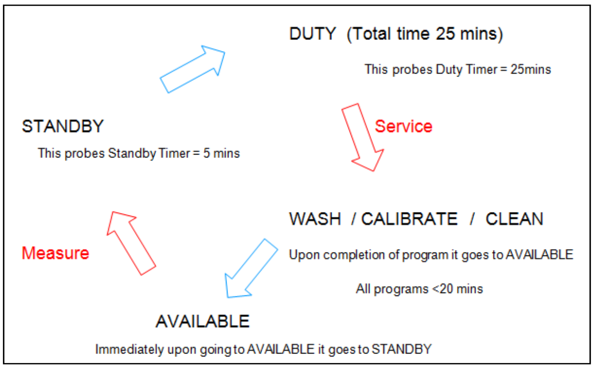

Figure 9: Flow diagram of Single Probe Mode

Whilst in Single Probe Mode if the other meter is in Manual and in Duty, the meter that is in Auto will hold in Standby mode until its duty timer has completed. At any stage during this period if the meter in Manual is removed from Duty, the probe on Auto will immediately switch to Duty. It then will be pushed to the *Service* position where it completes its program sequence before once again moving into the *Measure* position and having its standby timer initiated.

3. COMMISSIONING AND OPERATION

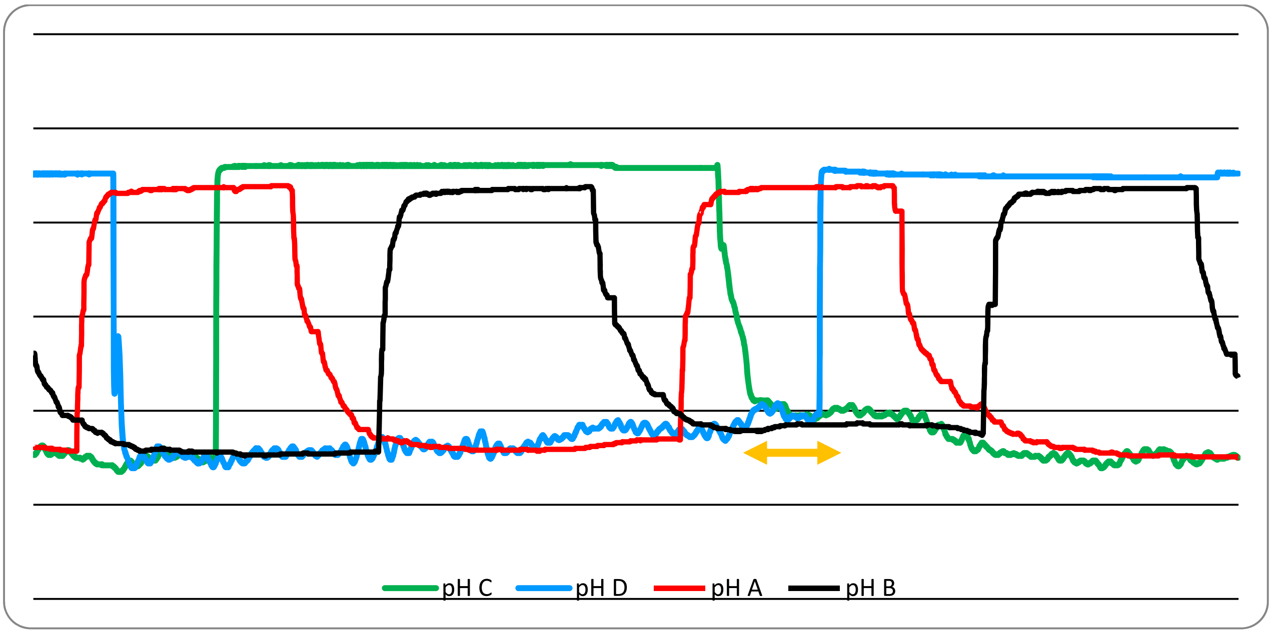

Figure 10: A comparison of new pH measurement system using ISFET pH probes (pH C and pH D) alongside the old pH measurement system using glass pH probes (pH A and pH B). The pH is displayed on the y-axis and time on the x-axis. The orange arrow indicates a time period of 5 minutes.

A multi-staged approach was applied for commissioning. Confirmation was made that no significant pH offset was present between glass and ISFET probes. The end result of the multi-stage approach was confidence that the readings being provided by the system were reliable, that interlocks worked and that the system bugs were significantly reduced when the new system was used for control.

Figure 10 shows a direct comparison between the values provided by the two systems. The new ISFET meters showed a high responsiveness to small pH changes, which were real due to flow variations in the HP brine, whereas the glass probes were very slow to respond. During this direct comparison, meters A and B were used for control of the acid dosing. Due to the large lag times from when the probe is first introduced to brine, a pH value difference was observed on duty changeover in the DCS. This resulted in long-term pH swings of up to 0.50 when the plant was in stable operation.

The slow response of the glass probes in addition to the significant time delays between the bulk flow and the sample being analysed, resulted in significant swings in pH during load changes and acid-dosing plant start-up, with the operator not knowing what the true pH was in the bulk flow. This was not evident until the new fast-response system was installed alongside the old system, with pH excursions seen in the new system as low as pH 3.0 and as high as pH 7.0, whilst the old system read values between pH 4.5 - 5.5. These large swings in pH pose a significant risk of corrosion for the low excursions and of silica deposition in the high excursions.

3.1 Flow Switches

A flow switch was installed downstream from the *Service* position. When water flow was initiated across the probe, the DCS was set to handshake the control of flow of water, or air, with this flow switch. The switch tended to intermittently not work, resulting in the pH meter being pushed by an interlock from Auto into Manual. After a period of having this switch work unreliably, the interlock was removed and instead a transmitter connected to a local pressure gauge was installed on the supply water. This pressure transmitter had alarms installed in the DCS to proactively warn the operator of an impending problem with the water supply, which was the main cause of concern and reason for the installation of the flow switch. Figure 11 shows a simplified schematic with the location of the flow switch.

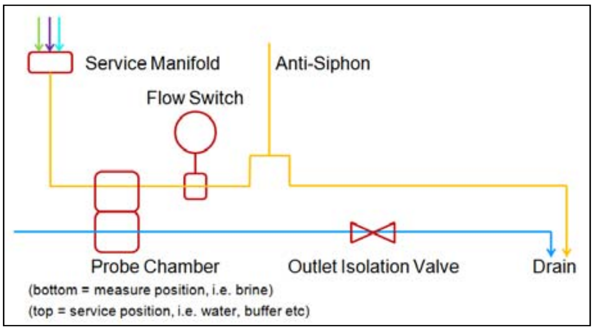

Figure 11: Simplified schematic showing the measurement arrangement. Not all valves are shown.

3.2 Air Pockets

In Figure 10 pH meter C can be seen to have a delayed response when introduced into the geothermal brine. The cause of this problem is an air pocket within the *Measure* chamber. This often was observed when maintenance was conducted, and the probe housing was removed. When the housing was replaced, an air pocket was evident. Therefore an outlet isolation valve was installed, allowing the flowing of the cooled brine sample through the top of the chamber housing to which the probe housing could be attached. This removed the air pocket and the outlet isolation valve was quickly opened once again to allow brine to flow.

If the air pocket was large enough in the *Measure* chamber, possibly due to an o-ring failure feeding through instrument air from the probe position, then the result would be a continuously damped down measurement in addition to a slow initial response.

Any ingress of air to the *Service* chamber, again, is likely to be due to an o-ring failure feeding through instrument air. This problem can result in calibrations being conducted when the probe is not fully inundated with buffer reagent. During the early stages of operation a new procedure was developed to test the o-rings, prior to being placed in service, by making use of spare probe housing units. The ISFET probes are prone to dry-out and therefore air pockets in the *Service* position posing risks of damage to the probes. There are interlocks for a low brine sample flow rate that force the probe to retract to the *Service* position. To ensure there is always water in this location an anti-siphon was installed, thereby ensuring o-ring tightness.

3.3 Supply Air Pressure

The KCl supply to each pH probe requires a pressurized air supply. A single regulator for the two probes was installed and this was set to 3 bar(g).

Each pH meter has its own air pressure regulator within its stainless steel cabinet. Air is used to move the probe between the *Service* and *Measure* positions, along with feeding the pumps that supply buffer reagents or cleaning agent.

The meters procured made use of air switches to detect the location of the probe. Therefore each pH meter had three air pressure switches: one to detect incoming air pressure, one to detect air pressure back from the *Measure* position and one to detect air pressure back from the *Service* position. A number of issues were identified during commissioning with respect to the air pressure and these switches. Setting the air pressure too high resulted in both position air switches reading high, and thus the meter would not know what position its probe was in and would give a fault. Setting the air pressure too low resulted in tripping of the main air pressure switch when the buffer pumps were required to run. Many of the faults found around air pressure were intermittent and required a significant time to resolve.

In the end the air pressure has been set to 6 bar(g) and the pressure switch detecting incoming pressure was deactivated. A common alarm for air pressure is raised on the supply side from a pressure transmitter on the main instrument air supply. In the event of any loss of air pressure, the next time the probe goes to change position an alarm is raised through the system due to a failure of the probe to reach the position ordered.

It is planned to investigate a move to electronic feedback of the probe position.

3.4 Probe Life

Previously glass probes were being replaced approximately once a month per meter in the old system. The responsiveness of the glass probes was noticeably reduced after around two days, and was significantly reduced in the event that acid-dosing was not being applied and the pH meters were still reading brine.

The new ISFET probes are still running well after a period of three months, which is the current frequency of replacement of the probes, which is considered to be conservative. The responsiveness of the probes diminishes slightly with time and this is the main indication that the probe is nearing its time for replacement. No probes are yet to fail a calibration due to long service times. Like the glass probes, responsiveness is reduced in the event that acid-dosing is not operating and the pH meters are still reading brine. Whilst interlocks were attempted to prevent this occurrence as much as possible, it was considered too complicated to distinguish this situation from the situation when acid dosing is restarted following a shut down.

Due to the flow variations in the plant, and the subsequent small pH variations out of the LP separators, monitoring of probe health is considered to be easy as the responsiveness can be measured using the small swings in pH.

3.5 Cleanout of Coolers and Supply Tubing

With time, deposition does occur in the heat exchangers and the tubing downstream. This deposition is primarily antimony sulfides, but also contains some arsenic sulfides and silica. Provision has been made with suitable valving configured to allow for a caustic solution to be flushed through the system to clean this deposition out. At no stage does this flush go through the probe chamber, but only through the sample conditioning equipment. The thermal shutoff valve and control valves benefit significantly from this process.

4. Conclusion

The accurate measurement of pH is an essential part of any acid dosing arrangement for successful pH modification of geothermal brine for silica control. Over two years of successful operation has now been achieved with the new pH measurement system discussed in this paper. The ISFET probes have proven to be robust and reliable for the measurement of the pH of geothermal brine. Whilst the instrumentation that supports these probes has required significant project design to ensure a high reliability and availability, this has been achieved, and the pH values provided from the system can be relied upon. Continuous improvement initiatives are continuing with the new system.

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