SOME CURRENT CHALLENGES IN PRODUCTION GEOCHEMISTRY

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ABSTRACT

Power production from geothermal energy could be considered a mature technology. However, some comparatively recent advances have presented new challenges in production geochemistry.

The first is the use of pH modification to handle geothermal brines that are grossly oversaturated with silica. Although pH modification has been used previously with Salton Sea brines, it has only recently become used extensively in low Total Dissolved Solids (TDS) brines, such as those found in New Zealand geothermal systems. This has presented several new challenges in the geochemistry of power station processes and materials and also in the interaction of a pH modified brine with reinjection reservoir formations.

The second challenge is the emerging technology associated with the possible utilisation of supercritical fluids present in areas close to magmatic sources. These fluids present unique problems for the geochemist in modelling and then rendering them suitable for use in standard turbines. Experimental work is just beginning for treatment processes for these fluids.

Thermodynamic geochemical data has not always kept up with the use of geothermal fluids of a more “extreme” chemical nature and geochemical modelling is now suffering from a lack of this available data. The basic experimental work required is often hard to justify to science funding providers and worldwide research in this field is limited. It may fall to geothermal power companies to fund this research, just as the thermodynamic data for ore deposit modelling is funded largely by mining companies.

Other geochemical challenges are involved with the microenvironments that can occur in geothermal power stations. Once again, thermodynamic data is often lacking for some of the ‘exotic’ compounds that are formed.

1. PH TREATMENT OF BRINE

1.1 Introduction

In the last five or so years, there has been a move in new and planned geothermal power stations in New Zealand to operate by producing and reinjecting brines that are oversaturated with silica. The incentive is greatly increased power production, and consequently greater revenue. Previously, at Ohaaki and Wairakei in New Zealand, silica scaling was avoided by separating brine above or close to the silica saturation temperature. As far back as 1979, experiments at Wairakei (Rothbaum et al, 1979) showed that lowering the pH could retard the polymerization of silica. Later experiments at Ohaaki (Lichti, Brown and Ilao, 2000) more rigorously confirmed the concepts of acid and alkali addition to control silica scaling. These later experiments also considered corrosion of mild steel with acid and alkali addition. Acid dosing had been trialed and was first used at Salton Sea, California, USA (Gallup et. al.) in the 1990s, but the first use in lower TDS brines was at Coso in the USA. In New Zealand, Mighty River Power utilises acid dosing at Kawerau and Nga Awa Purua, and Contact Energy is contemplating acid dosing at the Te Mihi station. As of today, there are no geothermal power plants that raise the pH to avoid silica scaling.

1.2 Silica scaling background

Dissolved silica exists in solution as discrete silicic acid molecules H_4SiO_4. In the reservoir, the dissolved silica comes to chemical equilibrium with quartz. The amount of silicic acid in the geothermal water in equilibrium with the quartz (the “solubility”) depends on the temperature, with hotter water able to hold more dissolved silica. Therefore the amount of silica dissolved in the geothermal water in the reservoir is proportional to the temperature of the water in the geothermal reservoir that is tapped by the production well.

When this water is brought to the surface in a geothermal power plant, it is flashed and/or cooled, and steam possibly extracted, and the amount of silicic acid that can now be dissolved in the geothermal water is correspondingly reduced. However, the excess silicic acid does not normally re-precipitate as quartz, but instead forms an amorphous (non-crystalline) colloid called amorphous silica. Colloids are very small particles, nominally < 3μm, that are suspended in the geothermal water and they form the characteristic voluminous silica scale when they are precipitated. Silica colloids are formed by chemically bonding individual silicic acid molecules to each other to produce dimers as in Figure 1.

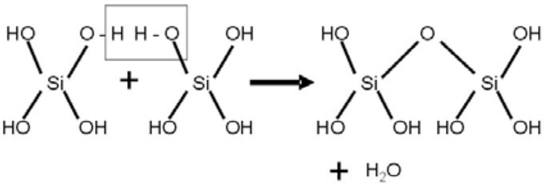

Figure 1: The initial nucleation to start silica polymerisation

This is the initial stage of nucleation of the colloid. The driving force for this nucleation is the degree of saturation of amorphous silica. This is defined by the Silica Saturation Index (SSI), which is the ratio of the silica concentration in the brine divided by the equilibrium amorphous silica solubility at the conditions prevailing. If SSI >1.0 then silica scaling is possible, if SSI <1.0, then generally, silica scaling will not occur. When the SSI is much greater than 1.0, nucleation is very rapid. Further bonding of other silicic acid molecules takes place to form trimers, tetramers, etc. until hundreds to thousands of molecules are bonded to make up a single colloid. This process is called polymerisation. The polymerisation process is catalysed by alkali, and therefore the silica polymerisation can be slowed down for a limited time by adding acid to reduce the pH. Typically at a pH of between 4.5 to 5.5, silica polymerisation can be halted for a few hours – long enough to transport the brine along a reinjection pipeline and reinject it back into the formation. This can avoid the typical voluminous silica scaling found in geothermal brine pipelines.

Silicic acid is so named because it is a weak acid. It can lose a hydrogen ion (H^+) to form a silicate anion ($H_3SiO_4^-$) according to:

$$H_4SiO_4 \Rightarrow H^+ + H_3SiO_4^-$$

This reaction takes place at higher pH, and the effect is to increase the solubility of the dissolved silica at higher pH. Consequently, raising the pH to between 9 and 10 can increase the solubility of silica to the point where it is no longer oversaturated.

Therefore, it is possible to control silica scaling by adding either acid or alkali.

1.3 Acid dosing

The target acid pH of the brine to be reinjected is normally between 4.5 and 5.5 when measured at 25ºC. This is a balance between silica control and limiting corrosion of carbon steel. Most geothermal brines readily precipitate a thin layer if monomeric silica on the surface of carbon steels and this provides a glass-like barrier between the corrosive brine and the carbon steel. These thin silica layers are less effective at low pH in protecting the steel (Braithwaite and Lichti, 1980).

1.3.1 Titration Curves.

The amount of acid that is required to decrease the pH of a brine to a particular low value is different for different wells. This is because the wells have slightly different chemistry. In order to lower the pH of a brine, you need to overcome the effect of chemical buffers. The principal chemical buffer that affects the amount of acid added is the bicarbonate buffer. Bicarbonate (HCO_3^-) is present in nearly all geothermal waters due to the presence of dissolved CO_2 in the water. An example of the titration curve for wells with different bicarbonate concentrations is shown in Figure 2:

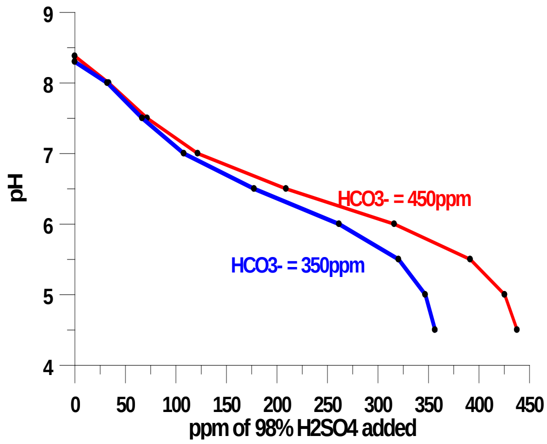

Figure 2: Titration curves for wells with different bicarbonate concentrations

A couple of **geochemical challenges** are hidden in this graph. The first is the steepness of the graph in the area of the target pH. This has the effect of making pH control quite difficult. A few percentage changes in the acid dose rate can have a very large effect on the resulting pH, which can result in possible corrosion if too low or lack of silica inhibition if too high. The second challenge is the difference between wells with different bicarbonate concentrations. When wells with different bicarbonate concentrations are brought on and off line to the power station, there is a change in the amount of acid dosing required. Once again this can result in too high or too low pH, which can have drastic consequences.

1.3.2 Where to add acid?

Silica polymerization can be rapid at high temperatures and silica saturation greater than ~ 1.2. Consequently, in a multi-flash power plant, the high pressure (HP) separation pressure is chosen to be above the silica saturation temperature. Acid is then added to the HP brine before any further pressure reduction. However, it is the pH in the LP brine for reinjection that is required to reach the target pH.

Some further geochemical-operational-metallurgical **challenges** arise here. First, the lower pH causes the gases to be present as CO_2 and H_2S, rather than bicarbonate and bisulfide. Consequently, there is an increased gas concentration in the LP steam. Second, the loss of these acidic gases causes the brine to become more alkaline, therefore extra acid in the HP brine is required to compensate. This means that the pH of the HP brine is lower than that required for the low pressure (LP) brine. This can introduce unplanned scale formation, as well as corrosion problems in the HP pipework at the higher temperatures. Acid demand dictates the volume ratio of acid to brine and high demand raises issues of heat of dilution, corrosion in poorly mixed dilute acid and materials selection for injection quills and in line mixers (Yusoff et al, 2011). Third, with the acid being added in the HP brine, but the pH being measured in the LP brine, there can be a considerable time lag to correct the acid dose rate when a pH offtarget is measured.

1.4 Alkali Dosing

While acid dosing of silica oversaturated brines only delays the onset of possible silica scaling, treatment with alkali will completely dissolve the silica that is in excess of the silica solubility. The dilemma for corrosion is the loss of the normally protective monomeric silica scales, but this is balanced by a reduction in corrosion in moderate alkaline solutions. Control of shutdown chemistry and standby becomes problematic as the bare steel will readily corrode when retained chloriderich waters are aerated.

1.4.1 Target pH

The target pH is set to dissolve all the silica that is excess over the silica solubility for that temperature. It would be prudent to allow a slight excess of caustic to cover excursions in the dosing operation. Unlike acid addition, the required target pH will change with different wells if the silica concentration is different.

1.4.2 Titration Curves

Unlike acid addition, the titration curve for alkali is very easily controlled and is more or less linear in the region of interest, as is shown in Figure 3. The principal chemical buffers to be overcome in raising the pH are the borate and silica buffers. Consequently, wells with high silica concentrations or high boron concentrations or both, will require more caustic to reach SSI = 1.0.

One major advantage of alkali dosing is that you can theoretically decrease the brine to very low temperatures. However, this brings to the forefront the major disadvantage of alkali dosing – it is very expensive. The only real possible alkali that can be used is sodium hydroxide, and it is very expensive and has wild fluctuations in price. Another disadvantage is the possibility of precipitating calcite as the pH is raised. However, if the temperature is low enough, calcite may not precipitate, as it has retrograde solubility. Geochemical calculations (**another challenge**) can confirm or deny!

The good news is that corrosion seems to be less of a problem at the lower temperatures.

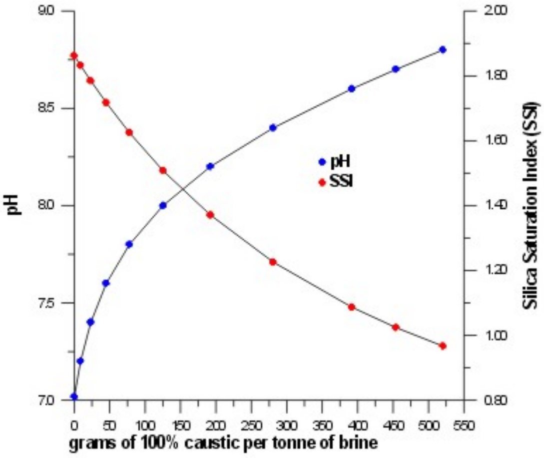

Figure 3: Typical titration curve for alkali dosing

1.5 Binary Plants

Binary plants can also defer silica scaling by mixing hot condensate – at low pH – with brine. This essentially becomes acid dosing. With careful operation, this has the advantage that no additional acid dosing is required. Furthermore, with the added condensate, the mixture can be lowered to considerably lower temperature before reaching silica saturation. A further bonus is that silica polymerization is temperature dependent and can be very slow at the lower re-injection temperatures often found in binary developments.

In such a system, the brine is separated at a pressure above the silica saturation temperature. The latent heat is taken out of the steam in a vaporizer, some of the gases are discharged and then the condensate is mixed with the brine to pass through preheaters. These benefits of mixing brine and acid condensate have generally been implemented in operating plant with a long history of geochemical testing where the fluid conditions have been "measured". An **on-going challenge** is to be able to predict the power station chemistry at the design stage so that these potential process improvements can be implemented on start-up.

1.6 More Geochemical Challenges from pH adjustment

1.6.1 Stibnite and orpiment

At low pH and lower temperatures, and with H_2S present, heavy metals in brines can precipitate. For example, stibnite (Sb_2S_3) and orpiment (As_2S_3) have been found (Brown and Rock, 2005). This is a particular problem in binary plants as they often run at lower temperatures than flash plants and with retained gas in the process fluid. When this low temperature is combined with a low pH, then deposition of these sulfides becomes problematic. Stibnite solubility decreases **very** rapidly with decreasing temperature. For instance, Table 1 shows the calculated solubility of stibnite (as ppb Sb) for a typical geothermal brine with 1 ppm H_2S. The very large temperature and pH effect is obvious.

Table 1: Effect of pH and temperature on Sb (ppb) concentration in brine

pH	5.0	8.0
150ºC	53.4	137260000
130ºC	9.08	28210000
110ºC	1.39	3853000
90ºC	0.21	319287
70ºC	0.03	14396
50ºC	0.004	310

The deposition of stibnite can cause a reduction in heat transfer in the heat exchangers, which reduces the power output of the plant. Current treatment options are to a) mechanically remove the stibnite with a highpressure waterblast, b) chemically dissolve the stibnite with caustic or c) to periodically dissolve the stibnite by changing the on-line process pH conditions as illustrated in Table 1. Research is on-going to try and develop an organic antiscalant that can inhibit stibnite deposition.

Geochemical thermodynamic data is also less than ideal for stibnite. An attempt has been made to massage the best data (Wilson et al, 2007), and this agrees reasonably well with observed scaling, but a more rigorous experimental program is required.

Stibnite can also form in acid-dosed flash plants where the brine is cooled to lower temperatures. A common location for stibnite scaling is in the cooling coils that cool the brine prior to pH measurement.

Although arsenic concentrations are usually greater than antimony concentrations in geothermal brine, the occurrence of orpiment is seen less than stibnite due to the difference in solubility. However, recent pilot plant work (Addison and Brown, 2012) has shown that arsenic sulfide deposition has placed a lower temperature limit on the Ngatamariki binary power station.

1.6.2 Elemental alloy deposition

Gallup, 1995 described precipitation of a silver-antimony alloy in pH adjusted Salton Sea brines. Similar scales have been observed in low TDS brines where the reductive deposition occurs on freely corroding carbon steel. When these deposits are coherent they protect the underlying steel, but when not coherent recent experience has indicated that rapid localized corrosion can result. A significant challenge is in understanding the galvanic effects and enhanced corrosion of carbon steels coupled to the deposited scales. The **research challenge** is to develop geochemical models that can predict when such metals will be deposited and the factors that control deposition rates and that determine the risk of accelerated galvanic or under-deposit corrosion (Solits and Lichti, 2012).

1.6.3 Downhole pH adjustment

New Zealand has been fortunate in not encountering acidic downhole conditions such as those seen in The Philippines and Costa Rica. Geochemical modeling and pH adjustment trials in the Philippines have progressed (Lichti et al 2010), while in Costa Rica caustic injection systems have been in place commercially for some years (Moya et al, 2005). These systems are only viable as the geochemistry of the production wells is relatively well understood. The acid sulfate waters become progressively lower in pH as the waters decrease in temperature while rising up the well, causing the ion pair containing hydrogen to release hydrogen ions. This raises an opportunity for shallow injection of caustic. The balance between caustic induced scaling from anhydrite and continuing acid corrosion is only achieved by continuous monitoring (Moya et al, 2005). A surprising result in some Philippines wells is the precipitation of monomeric silica that protects the casing and wellhead equipment. Although the influence of pH on corrosion product formation has been modeled (Lichti et al, 1998), the ability to predict, using geochemical models, when silica scaling will occur, when anhydrite scaling will occur and when corrosion will occur is a major challenge.

A remaining issue for acidic geothermal fluids is when the acidity is due to the presence of HCl. Dry steam wells have been pHmodified just before the acid dew point to good effect. Wet geothermal systems having HCl acidity downhole are presently unexploitable, as we have no means to control corrosion of cement and bore casing (Sanada et al, 2000). The **challenge** stands.

1.6.4 Reaction of pH modified brines with the formation

This is a major **challenge** at the present time. Geochemical thermodynamics can give indications, but many predicted species are kinetically hindered. Experimental work on a macro basis (“bucket chemistry”) is at its best partially qualitative. More exacting experimental work with high pressure/temperature equipment is more qualitative, but in the meantime, the response in the $3M - $12M pilot plant (called a reinjection well) is the only real information that we have. And it is very difficult to understand the cause and effect in the formation from observations made at the surface.

Some reactions are obvious - maybe. Injection of an acidic brine into a calcite rich formation will rapidly neutralize the acid and polymerise the silica – or not if a layer of protective silica is deposited first? Or maybe the silica will polymerise but not deposit? More work is required in this area. Alkali treated brine could be expected to dissolve more silica above the normal quartz saturation. When this brine reaches a production well, will the silica concentration keep on increasing, or will brine/rock interaction stabilize the system? This is a long term **challenge**.

1.6.5 Understanding silica deposition

We still do not really understand many facets of the mechanism of silica deposition at a fundamental level. We can control the particle size of silica colloids to some extent, and we know that smaller colloid sizes (< 20nm) do not form scale - why not? This is a function of the mechanism that transports silica colloids to a pipe wall, and makes them stick there. Theoretical and experimental work is progressing (Kokhanenko et al, this volume) and hopefully a greater understanding will lead to new methods of controlling silica scaling that don’t necessarily rely on pH modification of the brine.

2 GEOCHEMICAL MODELLING

“All models are wrong, but some are useful” – G.E.P. Box.

Geothermal geochemistry relies heavily on geochemical modelling and geothermal databases. A few computer programs are available publicly to handle calculations such as adding together steam and brine analyses, and then flashing and cooling options for the resulting “reservoir” fluid. More complex calculations are normally performed by people with their own code or spreadsheet. Some of these calculations are definitely a **challenge** to the geothermal geochemist.

There is really only one computer program for geothermal geochemistry that can claim to be “user friendly”. It is a DOS program – which may or may not run on your new computer. And it only handles the basics. And it assumes chemical equilibrium for most of the reactions that are taking place. And the thermodynamic data is different to other geothermal programs. There is a need for a user-friendly modern Windows®-based program for geothermal geochemistry. This will need to replace a series of other programs that are presently used in combination to model the chemistry of the brine and gas phases through a typical power station from downhole to flash plants, binary plants and combinations of these.

An adjunct to the geochemical modelling is thermodynamic and kinetic data. Good high temperature thermodynamic data is difficult to collect. It is expensive and does not necessarily attract the funding and charisma of other forms of experimental science. Consequently, there are few laboratories that are collecting such data. As geothermal development **challenges** new operating boundaries, new problems arise – such as stibnite and other heavy metal deposition – that require good thermodynamic data. Mining companies are recognizing the value of such data and are funding experimental work related to ore deposition. In a similar manner, it will probably fall to geothermal companies to fund experimental high temperature data that is relevant to geothermal. Key amongst this data will be kinetic data for reaction of brines with formation rocks.

3 SUPERCRITICAL FLUIDS AND SUPERHEATED GASES

As available subcritical geothermal systems are increasingly exploited, there is increasing interest in development of geothermal sources that tap directly into a magmatic source, such that supercritical temperatures are encountered. There are currently a few examples that have encountered these much higher temperatures.

Supercritical water has physical and chemical properties that can be quite different to subcritical water. Depending on the initial temperature of the supercritical fluid, a number of different phases are possible as the fluid is depressurized. In the supercritical fluid, only a single phase exists. However, depending on the initial temperature and pressure (*i.e.* enthalpy), depressurization of a supercritical fluid can result in either a single phase of superheated steam or two phase liquid and steam. If the fluid is initially above ~450ºC, then adiabatic depressurization, results in a superheated steam phase, with no liquid water present. This is represented as the path from F to C in Figure 4.

Supercritical water can dissolve small amounts of minerals such as silica. When it passes through the critical point and becomes superheated steam, these minerals can come out of solution and appear as a solid aerosol in the flow. Obviously, these will need to be removed before use in a turbine.

At very high temperatures, acid gases such as HCl, HF, H_3BO_3 as well as sulfur gases are present in steam derived from supercritical fluid. Once again, these will need to be removed. The study of natural volcanic environments provides a strong indication that these contaminant gases can have low corrosivity when dry, but at the dew point very low pH and high chloride concentrations mean that even high alloy materials will readily corrode (Lichti et al, 1997). The geochemical **challenge** will be to be calculate the expected chemistry in proposed energy extraction systems to allow prediction of the performance of construction materials across the range of temperatures required. These processes might for example need to include a wash of the cooled steam or condensing the steam in a controlled manner.

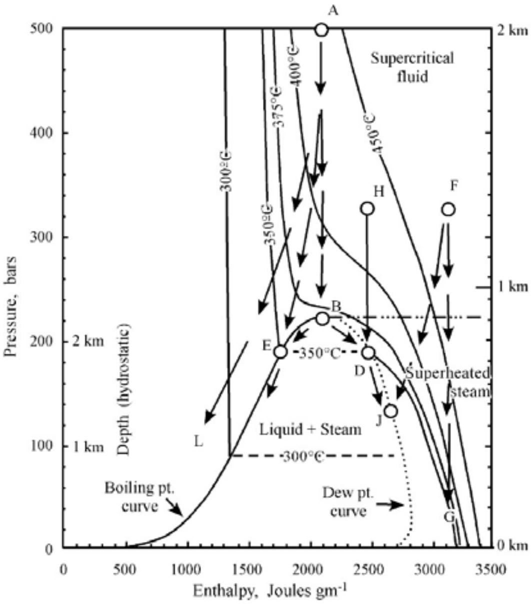

Figure 4: Pressure/Enthalpy diagram for water (after Fournier, 1999)

A further **challenge** lies in the geochemical thermodynamic data for these supercritical systems. There are currently physical modelling programs available (eg Supercritical TOUGH2 and HYDROTHERM) that can correctly model supercritical properties such as pressure, temperature and flow. etc., but there are no corresponding chemistry modelling programs. There is very little geochemical data available for this modelling. Once again, it is a **challenge** to collect this data.

4 MICRO ENVIRONMENTS

A final comment is in order on the geochemistry of geothermal power plants where the bulk chemistry that is readily calculated seldom causes severe corrosion. However, many of the problems that arise are due to geochemical reactions taking place in microenvironments that are difficult or impossible to sample and analyse. These reactions often involve rapidly changing conditions and non-equilibrium. In many situations, the geochemistry must be inferred for example by an analysis of the corrosion damage or the deposit composition. This lack of understanding of the chemistry often results in extended testing, monitoring and inspection programs before a materials or altered chemistry solution can be found. The solutions to these problems will require a combination of novel sampling and analysis methods in combination with process and chemical engineering modelling as well as materials expertise. The new teams will be **challenged** to work together to develop a better understanding that will lead to better and faster resolution of these corrosion problems.

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