CHEMISTRY AND SILICA SCALING POTENTIAL OF MULTIPLE FLASH GEOTHERMAL WATERS

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ABSTRACT

The removal of carbon dioxide and hydrogen sulphide at each successive stage of steam separation from a geothermal discharge leads to pH values in the residual waters which for New Zealand systems fall in the range 7.5 - 8.5. In this pH range the dissociation of silicic acid to form silicate ions becomes significant and the solubility of amorphous silica increases. Recognition of this effect allows that, without the development of significant scaling potential, steam may be separated at pressures substantially lower than has normally been recommended in the past on the basis of the solubility of silica in pure water.

A computer program is described for the routine calculation of water and steam chemistry resulting from primary and secondary steam separation from well discharges. These data may be used in the design of flash plant and the management of geothermal fields to achieve maximum steam recovery while minimising problems due to silica deposition in pipeline systems. Data from Wairakei and the proposed Ohaki (Broadlands) field are given as examples.

INTRODUCTION

Environmental constraints on future developments of geothermal energy have led to a demand for more detailed understanding of the chemistry of flashed geothermal water and steam than has previously been the case. Whereas in the past the disposal of waste waters containing toxic elements has largely been by discharge into inland waterways (Ellis, 1977), current constraints have placed more emphasis on disposal by reinjection. The presence of relatively high concentrations of silica in these waters leads to potential problems of scaling in reinjection pipelines and wells so that in the design of geothermal power development schemes such as on the Broadlands-Ohaki field, New Zealand, reliable chemical data are required for the degree of silica saturation and scaling potential of waste waters, over a range of multiple flash separation conditions, well in advance of the reopening of exploration wells and installation of separator plant.

CHEMISTRY OF DISSOLVED SILICA

Due to the equilibrium between fluid and quartz in the majority of geothermal reservoirs, the silica concentration of the water separated from a discharging geothermal well is a function of the temperature of the reservoir fluid supplying that well (Mahon, 1966). Successive removal of steam at the wellhead leads to simultaneous increase in the silica concentration of the resultant residual liquid. In some cases the incorporation of additional reservoir steam into the well discharge may lead to a proportional increase in the silica concentration of the subsequently Separated water.

The silica dissolved in geothermal waters is present both as silicic acid (H_4SiO_4) and silicate (H_3SiO_4, $H_2SiO_4^{=}$) ions as well as a variety of polymeric species such that

Total dissolved

$$SiO_2 = m_{H_4SiO_4} + m_{H_3SiO_4^-} + m_{H_2SiO_4^=} + m_{polymers} \quad (1)$$

moles/kg

where m is the concentration of the specified species expressed in molal units (moles/kg). The silicate ion forms by the self-dissociation of silicic acid

$$H_4SiO_4 = H_3SiO_4^- + H^+ \quad (2)$$

so that its concentration is a function of both the total concentration of silica and of the pH of the solution ($pH = -\log a_{H^+}$ where a_{H^+} is the concentra- (3) tion of free hydrogen ions corrected for interactions with other dissolved ionic species). For solutions whose pH is less than about 7, silicate ion concentrations are negligible. At higher pH, silicate ions increase in concentration relative to silicic acid, until at pH >8.8 (approx.) in reinjection waters they become the dominant species. At higher pH a divalent silicate ion occurs but its concentration is not significant in the waters discussed here.

The solubility of silica in aqueous solutions is controlled by the temperature dependent reaction

$$SiO_2 + 2H_2O = H_4SiO_4 \quad (4)$$

Solubility data for silica due to this reaction have been determined experimentally (Fournier and Rowe 1977). For high pH solutions the formation of silicate ion from the dissolved silicic acid leads to an increase in the total silica concentration of the solution (Equation 1). This effect of pH, in increasing the solubility of silica, has been recognised for a long time for low temperature natural waters, but until recently has been disregarded for geothermal fluids. Using recent reliable experimental data for reaction (2) (Seward, 1975, Busey and Mesmer, 1977) Henley and Singers (1981a) have shown that, within the pH range of flashed New Zealand geothermal waters, silicate ion may contribute significantly to the solubility of amorphous silica. Fig. 1 shows this effect for flashed water from BR22 at 150°.

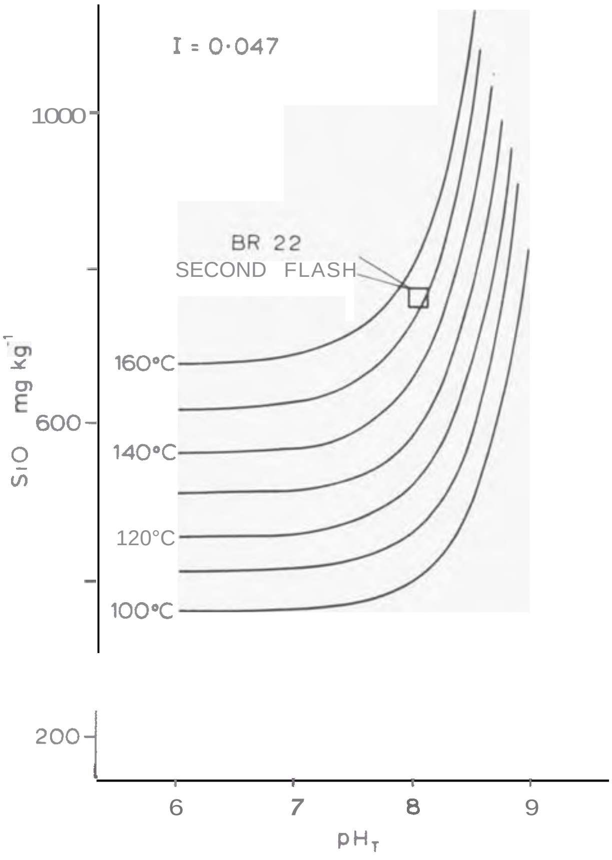


Fig. 1 Isothermal amorphous silica solubility curves as a function of pH and silica content for low salinity New Zealand geothermal waters. The composition of the BR22 waste water after double flash at 183 and 150°C is shown by the square symbol. Solubilities in pure water are represented by the horizontal portion of the curves.

Flashed waters in the temperature range 100-160°C at Wairakei and Broadlands have pH's in the range 7.5-8.5 after double flash steam separation. Cooling of these waters during reticulation leads to minor pH changes of the order ± 0.1 pH units, but the solutility of amorphous silica changes rapidly as shown in Fig. 1. Since pH changes are small the increase in the silica saturation ratio ($S_T = \frac{\text{silica content}}{\text{silica solubility}}$) is approximated by

$$\Delta S_T = 0.013 \quad \Delta T \tag{5}$$

For the high flow rates in reinjection pipelines heat losses are relatively small (5-10°C) but are of obvious significance in designing heat exchange systems with a view to avoidance of scale formation. Clearly for waters whose silica content remains below the amorphous silica solubility ($S_T < 1$) no silica scale can form during reticulation.

Studies of scaling rates are in progress at Broadlands to define the kinetics of silica deposition from flashed waters where $S_T > 1$ as functions of S_T, temperature and pH. For waters flashed to a supersaturated state the maximum amount of silica which may deposit is $S(S_T - 1)$ where S is the amorphous silica solubility. Generally only a small, but cumulatively important percentage of this excess silica actually deposits.

The pH_T of a geothermal water at its separation or reticulation temperature is a function of temperature and solution composition and, as a result of the weak buffering action of the carbonic acid - bicarbonate ion pair, is largely dependent upon the proportion of CO_2 remaining in the liquid following steam separation. This high temperature pH cannot be measured directly but is obtained from water cooled separated water samples by laboratory pH measurement, analysis for major dissolved components and an iterative thermodynamic calculation. While this is possible for operating production wells if suitable sample points are available it is not possible to obtain the high temperature flashed water pH for wells prior to their commissioning for production, unless some practical assumptions may be made concerning the distribution of carbon dioxide and hydrogen sulphide between separated water and steam.

Henley and Singers (1981) have shown that conventional cyclone separators of the type installed at Wairakei (Bangma, 1961) achieve a quasi-single stage equilibrium distribution of gases between the separated water and steam phases. As a result, the chemistry of flash separated waters may be calculated by iterative solution of a set of pH dependent mass balance equations for the major dissolved constituents. The input data are the composition of water and steam determined at the exploration stage and the enthalpy of the total discharge.

The ENTHALPY computer program used at Chemistry Division, D.S.I.R. (Palmer 1976) has been adapted for the routine calculation of these data (Singers et al, in press). The output includes the pH_T of the water resulting from flash separation at any pressure of interest, the concentrations of the principal dissolved species (e.g. bicarbonate, silicate ions) and the gas concentrations in the separated steam. Advanced knowledge of steam chemistry is of value in estimating reduction of plant efficiency due to the presence of gas as well as in assessing the corrosion behaviour of condensates. In addition, the program may be used to calculate these data for successive stages of steam separation from a given well and further, up to 5 well discharges may be processed together to obtain the phase chemistry of steam and water derived from multiple flash plant.

At high flow rates in conventional separators, the rates of steam bubble formation and collapse appear to be too low to achieve the single stage gas equilibrium and a multistage distribution of gases is achieved by the partitioning of gas to each successive steam fraction formed across the pressure drop of the separator. The nett result is the transfer of a higher proportion of the dissolved gas to the steam phase than would be the case for the single stage equilibrium and a concommitant <u>increase</u> in pH of the order of 0.1 pH units.

In contrast, for separator operation at relatively low water level, vortex formation may lead to the carryover of separated steam into the water line flow. After pipeline heat loss downstream of the separator, condensation of this relatively gas rich steam results in <u>decrease</u> in the water pH with respect to the single stage equilibrium pH. Since a pH decrease reduces the solubility of amorphous silica in the flashed water, this effect should be avoided as far as possible by suitable design and operation of flash plant. In particular, the carryover of the gas-rich steam from flash plant primary separators should be prevented.

DISCUSSION

The system of equations used in the modified ENTHALPY computer program described above may be used for the calculation of flashed water pH at any specified sequence of separation pressures using chemical data from exploration or production well discharges. In this way chemical data may be routinely used in the design stage of a geothermal development to minimise or avoid problems of silica scale formation. Similarly during field management, changes in silica concentrations due to enthalpy decreases during the power life of the field may be readily evaluated in order to achieve both optimum steam separation from individual wells or flash plant systems and to control scaling. The Wairakei and Broadlands fields are discussed below to illustrate this approach.

<u>Case Studies</u>

<u>Wairakei</u> Temperatures in the production zone of the Wairakei geothermal field are in the range of 200-260°C. The reservoir fluid is a dilute near-neutral pH chloride water with a relatively low content of dissolved CO_2 and H_2S. For the generation of electric power, multiple steam separation is performed at 159°C (6.2 b.a.) and 124°C (2.3 b.a.) sometimes with a high pressure stage at about 180° (10 b.a.).

Fig. 2 shows the calculated pH and silica contents of waters separated to 140 and 124°C by two stage steam separation at individual wellheads. The wells shown were selected <u>at random</u> but provide a useful illustration of the following:

(a) single flash separation leads to lower pH and higher scaling potential than does double flash e.g. WR215.

(b) calculation of saturation ratios on the basis of amorphous silica solubility in pure water may lead to erroneous conclusions regarding scaling hazards e.g. wells 72, 108 and 206.

(c) combination of high and low silica discharges in flash plants may ensure scale free reticulation for the combined residual water mixture.

At Wairakei, separation to temperatures of the order 130°C (2.7 b.a.) in most cases leads to silica undersaturated waters, quite incapable of depositing silica scale during reticulation. The practice at Wairakei has been to discharge this residual water to an open drain with further steam loss; the associated decrease in solubility due to the lower temperature of the drain water leads to saturation ratios > 1 and inevitably to the deposition of a voluminous silica scale, which requires a costly drain maintenance programme. Pipeline transmission of waste water at the final separation pressure would have obviated the problem of silica deposition. At this stage of the power project the replacement of the existing drain by a pipeline is economically unattractive, but further development of the field in the future will probably involve pipeline reticulation with a consequent avoidance of the silica scaling problem.

<u>Broadlands - Ohaki</u> The reservoir fluid at Broadlands is similar to that at Wairakei but characterised by much higher gas contents (Mahon and Finlayson, 1972). Reservoir temperatures in the proposed production field range from about 240 to 280°C and the discharges of a significant number of wells contain excess reservoir steam. Each of these three factors contribute to the higher pH, broader pH range and higher silica content of Broadlands flashed waters compared to Wairakei. The range of silica contents and pH for the Broadlands wells are shown in Fig. 3 calculated for single and double flash conditions. The separation pressures chosen independently for

Fig. 2 (right) Silica v. pH for a randomly selected set of Wairakei wells, calculated for double flash steam separation to 124°C. The 130°C solubility curve is shown for reference and represents a mean temperature for the avoidance of silica scaling by mixing of flash plant feed wells. The line A shows the solubility of silica in pure water (see text).

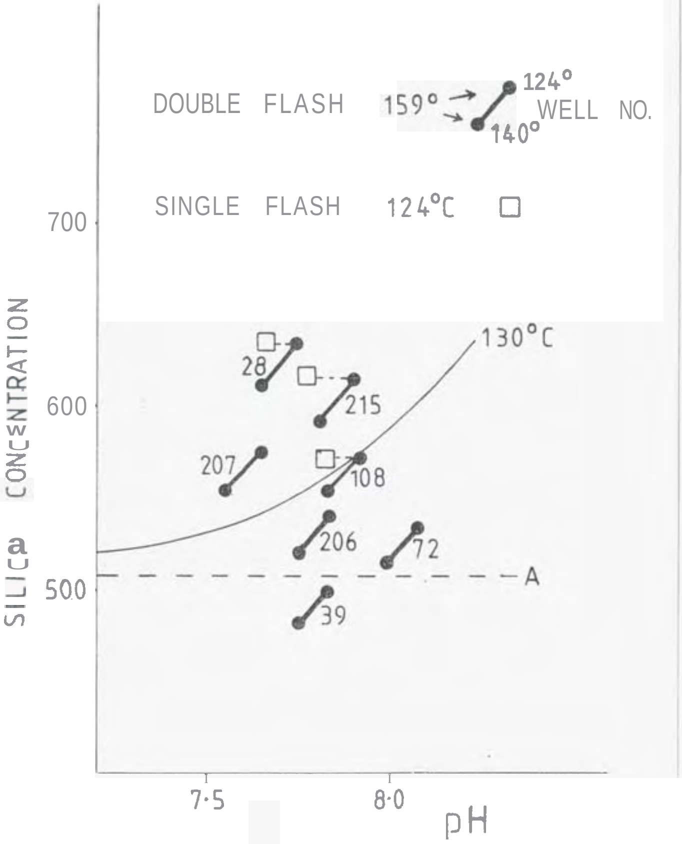
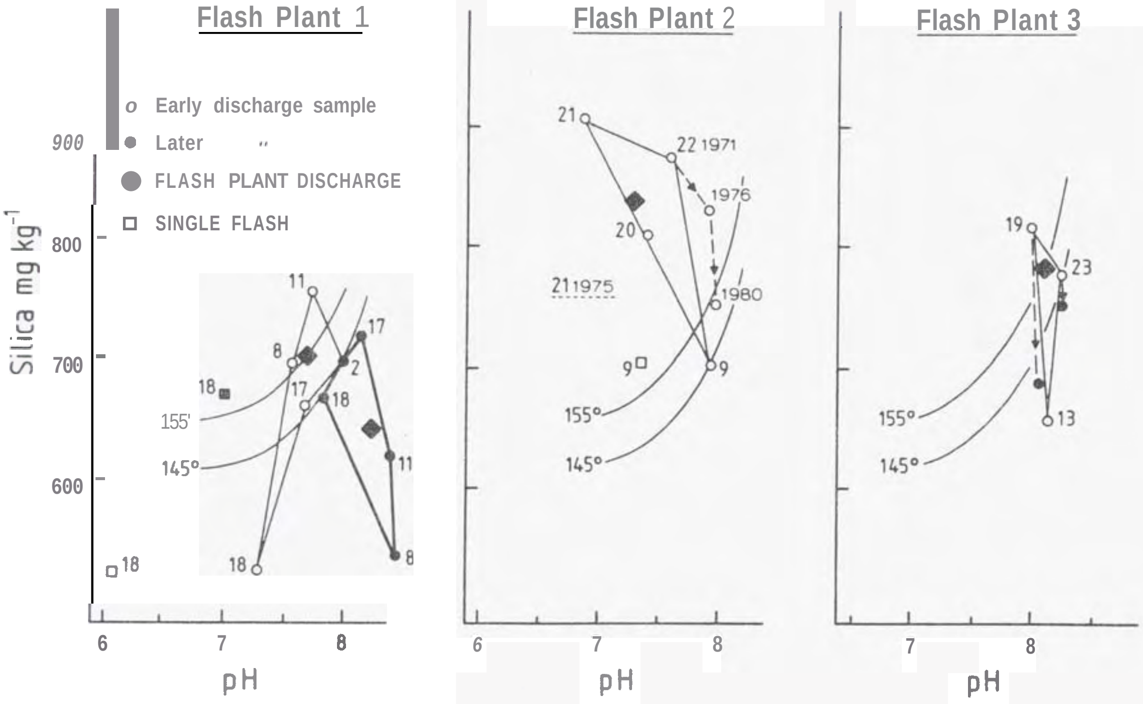


Fig. 3 (below) Silica v. pH for individual well discharges separated at the well head for Broadlands West Bank wells. The flash plant well feeds are selected on the basis of proximity of wells, whereas alternative groupings may resolve the high silica combination of Flash Plant 2.



power production are compatible with the optimum temperature difference required to maximise water pH and amorphous silica solubility. From the figure it is clear that the majority of wells are undersaturated with respect to silica following double flash separation to 155°C (4.5 b.g.) but cooling during reticulation to reinjection wells may lead to the waters from some flash plants becoming just supersaturated. A few wells, such as BR21, are characterised by high source temperatures and gas contents and, as a result, have relatively high saturation ratios at the final flash temperature of 155°C. The possible affect of reduction in field enthalpies are also shown by the silica - pH vectors in Fig. 3.

In fields such as this where steam is to be separated at flash plants, proximity is a principal factor in selecting the feed wells and the site of the plant. In some cases adoption of only this criterion may lead to the choice of well combinations which optimise the pH and amorphous silica solubility of the flashed waters, while other combinations result in flashed water with unnecessarily high saturation ratios. The chemistry discussed above may be used as an additional criterion to avoid or minimise potential problems of silica scaling in pipelines. Fig. 3 shows such a test case for well combinations at Broadlands.

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