THE SILICA PROBLEM IN THE DESIGN
OF GEOTHERMAL POWER PLANTS

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1. Introduction

The precipitation of silica and its subsequent deposition on surfaces is a serious problem in many geothermal power plants. Although the most troublesome situations are associated with flash-steam plants used with high-temperature resources, even lower-temperature systems can encounter problems under certain conditions.

The purpose of this study is to examine the problem from the perspective of the power plant designer and to develop a procedure to enable a quick estimate to be made of the potential seriousness of the silica deposition problem for a wide variety of resources and for selected types of power plant.

The method will employ correlations for the equilibrium solubilities of quartz and amorphous silica and for the saturated liquid enthalpy and the latent heat of water substance. Single- and double-flash plants optimized for highest thermodynamic efficiency will be considered. Binary-type plants will be included generically without mention of cycle specifics. The results will be presented both graphically and in tabular form, and the governing equations will be given in an easily-programmable form.

2. Silica Chemistry

The behavior of silica, SiO_2 , in aqueous solutions has been widely studied and reported [1-5]. The two forms of silica that are relevant to our problem are quartz and amorphous silica. In the geothermal reservoir, we will assume that the geofluid is in equilibrium with quartz at the temperature of the fluid. Over the temperature range of interest, the amount of quartz that dissolves in the fluid increases with temperature, decreases with salinity, and is essentially independent of pH for pH less than about seven. The temperature effect is by far the dominate one, and forms the basis of the commonly-used quartz geothermometer [2].

Upon being cooled, the geofluid with its load of dissolved silica becomes supersaturated with respect to quartz, and if this were the controlling mechanism for precipitation, geothermal plants would be confronted with a gigantic problem of silica scaling. Fortunately, the deposition at the lower temperatures is controlled by the equilibrium of amorphous silica which is much more soluble than quartz at a given temperature. Thus the potential for silica precipitation exists only at temperatures below the appropriate saturation temperature for the solubility of amorphous silica.

It is necessary to have analytic expressions to describe the equilibrium solubility curves for quartz and amorphous silica, both as functions of temperature and salinity, in order to carry out an analytic solution that can be programmed.

2.1 Quartz Equilibirum

The following expression gives the temperature, t (in $^{\circ}\text{C}$) as a function of quartz concentration, q (in mg/kg or ppm) and is due to Fournier and Potter [2]:

$$t = -42.198 + 0.28831 q - 3.6686 \times 10^{-4} q^2 + 3.1665 \times 10^{-7} q^3 + 77.034 \log_{10} q. \quad (1)$$

The equation is valid over the range 20 - 330 $^{\circ}\text{C}$. The correction for salinity is based on the work of Weres et al. [6] as reported in Ref. [5]. The solubility of quartz at any temperature t and at any salinity, expressed as the molality, m , of an equivalent sodium chloride solution, $q(t,m)$, may be found from $q(t,m=0)$ using

$$q(t,m) = q(t,m=0) \times F(t,m), \quad (2)$$

where $F(t,m)$ is a factor given below for $m = 3$ and $m = 5$:

$$F(t,m=3) = 0.5984 t^{0.0762}, \quad (3a)$$

$$F(t,m=5) = 0.3363 t^{0.1644}. \quad (3b)$$

The numerical value for $q(t,m=0)$ may be found by solution of eq. (1), best carried out by an iteration scheme.

To a good approximation (maximum error $\sim 2\%$), one may find F by using a simple linear interpolation between $m = 0$ and $m = 5$, i.e.,

$$F(t,m) = 1 - [1 - F(t,m=5)]x (m/5), \quad (4)$$

which may be used with eqs. (2) and (3b). This scheme was employed for the present study.

2.2 Amorphous Silica Equilibrium

Fournier and Marshall 1 give the following correlation for amorphous silica solubility, $s(T,m=0)$, (in molal NaCl) as a function of absolute temperature, T (in kelvins):

$$\begin{aligned} \log_{10}s(T,m=0) = & -6.116 + 0.01625T - 1.758 \times 10^{-5}T^2 + \\ & + 5.257 \times 10^{-9}T^3, \end{aligned} \quad (5)$$

where one must multiply s by 58,400 to obtain s in mg/kg or ppm. The effect of salinity on s is obtained from the formula due to Setchenow [7]:

$$s(T,m) = s(T,m=0) \times 10^{-mD(t)}, \quad (6)$$

where $D(t)$ is found from the following to fit the data of Marshall and Chen [8] as shown in Ref. [5]:

$$\log_{10}D(t) = -1.0569 - 1.573 \times 10^{-3}t, \quad (7)$$

in which t is in $^{\circ}\text{C}$.

The range of applicability of eq. (5) is from $90 - 340^{\circ}\text{C}$; eqs. (6) and (7) are valid from $m = 0$ to $m = 5$ and from $t = 25$ to 300°C .

3. Water Enthalpy Correlations

As we will see later, it will be necessary to have at hand simple correlations for the enthalpy of saturated liquid, h_f , and saturated vapor, h_g , plus the latent heat, h_{fg} , for water substance. Since

$$h_g(t) = h_f(t) + h_{fg}(t), \quad (8)$$

we need only correlate h_f and h_{fg} . These can be accurately represented by the following expressions over the range of temperature from $100 - 300^{\circ}\text{C}$ [9]:

$$h_f(t) = 4.218t - 7.98 \times 10^{-4}t^2 + 5.17 \times 10^{-6}t^3, \quad (9)$$

$$h_{fg}(t) = 2501.5 - 2.4335t + 1.8339 \times 10^{-3}t^2 - 1.8616 \times 10^{-5}t^3, \quad (10)$$

where h_f and h_{fg} are in kJ/kg and t is in $^{\circ}\text{C}$. The values for h_f and h_{fg} calculated from eqs. (9) and (10) apply strictly to pure water. They may be used as a good approximation as long as the total amount of dissolved solids does not exceed $20,000$ ppm.

To account properly for the effect of salts in solution would require

detailed knowledge of the types and amounts of impurities in the solution. A simple approach has been reported by Packer et al. [10] and is based on the work of Miller [11]. For the present study, it would be necessary to modify the expression for h_f as follows:

$$h_f(t,c) = a(c) \times t^{b(c)}, \quad (11)$$

where

$$a(c) = 0.2447 + 0.5337c + 1.379c^2 - 6.679c^3 + 9.47c^4, \quad (12a)$$

and

$$b(c) = 1.225 - 0.4617c - 1.002c^2 + 5.58c^3 - 5.371c^4 + \\ - 4.615c^5. \quad (12b)$$

It is important to note that in eq. (11) h_f is in Btu/lbm, t is in $^{\circ}\text{F}$, c is the mass concentration, e.g., $c = 0.05$ represents a concentration of 50,000 ppm.

The latent heat, h_{fg} , for this case is calculated on the assumption that the saturated vapor phase is uncontaminated, i.e.,

$$h_{fg}(t,c) = h_g(t,c=0) - h_f(t,c), \quad (13)$$

where $h_g(t,c=0)$ is found from eq. (8).

The correlations expressed by eqs. (12a) and (12b) were obtained for brines containing potassium chloride, calcium chloride and sodium chloride in the fixed mass ratio of 1.00/1.95/3.55, respectively [10].

4. Thermodynamics of Flash-Steam Plants

The thermodynamic analysis of flash-steam geothermal power plants is well known and has been reported widely in the literature. (See, e.g., Refs. [12-14].) As the geofluid passes through the various components of a flash-steam

plant it undergoes two changes that are conducive to the precipitation of silica: (1) the temperature decreases and (2) the silica concentration in the liquid phase increases due to the removal of the steam fraction.

These effects may be quantified in a straightforward manner by applying a few basic principles of thermodynamics. The processes undergone by the geofluid when used in a single-flash and in a double-flash plant are shown in Figs. 1(a) and 1(b), respectively. The coordinates are temperature and specific entropy. The process from r to 1 represents the flow of geofluid from the reservoir (where the fluid is assumed to be a saturated liquid) to the separator; the process is assumed to be isoenthalpic, i.e., constant enthalpy. At 1 the vapor fraction, x_1 , is given by

$$x_1 = (h_r - h_2) / (h_3 - h_2) \quad (14a)$$

$$= [h_f(t_r) - h_f(t_1)] / h_{fg}(t_1). \quad (14b)$$

Since this fraction of the geofluid is removed for use in the turbine and contains essentially no silica, the concentration of silica in the remaining liquid fraction is increased according to the equation:

$$s(t_1, m_2) = q(t_r, m_r) / (1 - x_1) \quad (15a)$$

$$= q(t_r, m_r) \times h_{fg}(t_1) / [h_g(t_1) - h_f(t_r)]. \quad (15b)$$

In the case of a double-flash plant, the silica concentration in the residual liquid is further increased by the removal of the secondary steam generated by the second flash, process 2-5. The final waste liquid, state 6, will have a silica concentration given by

$$s(t_5, m_5) = q(t_r, m_r) \times C_1 \times C_2, \quad (16)$$

where the concentrating factors C_1 and C_2 are given by

$$C_1 = 1/(1-x_1) \quad (17a)$$

$$= h_{fg}(t_1)/[h_g(t_1) - h_f(t_r)], \quad (17b)$$

and

$$C_2 = 1/(1-x_5) \quad (17c)$$

$$= h_{fg}(t_5)/[h_g(t_5) - h_f(t_1)]. \quad (17d)$$

The extension of these equations to the general case of an N-flash plant is obvious. Only the cases of $N = 1$ and $N = 2$ will be treated here.

The equations above have been written for the case where the effect of salinity on enthalpy can be neglected. If this is not acceptable, then a more elaborate scheme must be followed. Equation (14) now would take the form

$$x_1 = [h_f(t_r, c_r) - h_f(t_1, c_2)]/[h_g(t_1) - h_f(t_1, c_2)], \quad (18)$$

where the salt concentration, c_2 , in the separated liquid is given by

$$c_2 = c_r/(1-x_1). \quad (19)$$

A trial-and-error process must be employed to find that value of x_1 which satisfies both eqs. (18) and (19) for the known value of $h_f(t_r, c_r)$. Equation (8) will be needed for $h_g(t_1)$ and eq. (11) will be needed for the three values of h_f in eq. (18).

For double-flash plants, this procedure must be repeated to obtain the quality x_5 at the end of the second flash process. In this case,

$$x_5 = [h_f(t_1, c_2) - h_f(t_5, c_2)] / [h_g(t_5) - h_f(t_5, c_6)], \quad (20)$$

where

$$c_6 = c_2 / (1 - x_5). \quad (21)$$

The quality after flashing, either x_1 or x_5 , is a small number, typically less than 0.15. Therefore the concentrating effect on c_2 and c_6 through eqs. (19) and (21), respectively, is not large. Check calculations were performed at a high salinity (250,000 ppm) and at two temperatures (250 and 300°C) to examine the effect on the final results of replacing $h_f(t_1, c_2)$ in eq. (18) by $h_f(t_1, c_r)$, thereby rendering the computation straightforward instead of indirect. The error observed in the concentration of amorphous silica in the residual liquid was less than 1%. Under these circumstances, and considering the inherent uncertainty in the several property correlations, it is reasonable and expedient to compute all enthalpy values using the downhole silica concentration, c_r .

Clearly, the final silica concentration depends on the choice of the flash temperatures. For the analysis, we have adopted the rule for determining the optimum flash temperatures reported by Eskesen in Ref. [11], namely that the temperature interval between the reservoir (state r) and the condenser (state 5 or 10) should be divided equally by the flash temperatures. This choice will yield essentially the highest plant output for given reservoir and condenser temperatures. Thus, for a single-flash plant (Fig. 1(a)),

$$t_1 = (t_r + t_5) / 2, \quad (22)$$

and for a double-flash plant (Fig. 1(b)),

$$t_1 = t_r - (t_r - t_{10}) / 3, \quad (23a)$$

and
$$t_5 = t_{10} + (t_r - t_{10})/3. \quad (23b)$$

By adopting this rule, we avoid the calculation of the power output of the plant, greatly simplifying the numerical procedure. Thus there is no need to consider the turbine processes 3-4 and 8-9. If one wished also to calculate the power output, correlations for the entropy of the brine and its saturated water vapor would be required in addition to the enthalpy correlations.

5. Calculations for Flash Plants

The procedure for the calculations begins with the choice of a condenser temperature, t_5 or t_{10} , which was held constant: $t_5 = t_{10} = 50^\circ\text{C}$. Next, the reservoir temperature and geofluid salinity are selected within the ranges 200 - 320°C and 0 - 5 molal, respectively. Quartz concentration at the reservoir conditions is found using eq. (1) and a trial-and-error numerical technique together with eq. (2). Amorphous silica concentration in the residual geoliquid (state 2 for single-flash, state 6 for double-flash) is found from either eq. (15b) or (16). The equilibrium concentration of amorphous silica at the final liquid temperature is then calculated from eq. (6).

The ratio and the difference between the last two quantities are, respectively, the supersaturation, S , and the excess silica, XS , in the waste liquid. The excess silica represents the potential quantity of silica that will precipitate when the fluid reverts to a state of equilibrium from the condition of supersaturation (which is actually a state of metastability). The excess silica concentration when multiplied by the flow rate of the waste liquid will give the total rate of amorphous silica deposition.

The rapidity with which the metastable fluid transforms itself into a state of stable equilibrium depends on the magnitude of S , the temperature level, the pH of the fluid, its salinity, the presence of certain ions, and the

availability of nucleation sites [5]. No attempt is made here to quantify the kinetics of the problem, but only to present the potential deposition that will ultimately occur upon the establishment of stable equilibrium.

The results are shown in Figs. 2-5 and in Table 1. Figures 2 and 3 are similar, the former drawn for $m = 0$ and the latter for $m = 4.28$ (equivalent to 250,000 ppm NaCl solution). With reference to Fig. 2, point r represents a typical reservoir condition at $t_r = 275^\circ\text{C}$. Point 2 represents the state of the waste liquid following separation at the optimum temperature for a single-flash plant, $t_1 = t_2 = 162.5^\circ\text{C}$. Point a is the equilibrium state for the optimum flash temperature. The supersaturation S is equal to

$$S = 768/672.8 = 1.142,$$

and the excess silica is equal to

$$XS = 768 - 672.8 = 95.2 \text{ ppm.}$$

Points 6 and b are the corresponding states for an optimum double-flash plant having a final flash temperature, $t_5 = t_6 = 125^\circ\text{C}$. In this case,

$$S = 827.8/462.7 = 1.789,$$

and

$$XS = 827.8 - 462.7 = 365.1 \text{ ppm.}$$

For a typical double-flash plant producing 50 MW, the excess silica would amount to more than 250 kg/h or more than 6 metric tonnes per operating day.

Results for a high-salinity resource are depicted in Fig. 3. A single-

flash plant with a 300°C, 250,000 ppm geofluid would produce residual brine having $S = 1.577$ and $XS = 273.6$ ppm; the corresponding values for a double-flash plant would be $S = 2.689$ and $XS = 501.4$ ppm.

The supersaturation is shown in Fig. 4 as a function of reservoir temperature for both types of flash plant for $m = 0$ and $m = 4.28$. The excess silica concentration is given in Fig. 5 for the same set of parameters. It is of interest to note that for double-flash plants operating on geofluids at temperatures greater than about 285°C those using essentially non-saline fluids ($m=0$) produce higher excess silica concentrations than those using hypersaline brines ($m=4.28$). This is due mainly to the lower solubility of quartz in the high-salinity brine (593.5 ppm versus 675.1 ppm at, say, 300°C) and to the effect of salinity on the concentrating factors C_1 and C_2 . The supersaturation, however, is considerably greater in the case of the hypersaline brine.

6. Results for Binary Plants

In the case of binary power plants, the geofluid is normally maintained in the liquid phase under pressure to prevent flashing. The fluid is simply cooled at constant composition as it passes through heat exchangers. A highly simplified cycle diagram is shown in Fig. 6: the geofluid enters the heat exchangers at condition r and is discharged at condition d . The silica problem is much less serious in this case owing to the constant concentration of silica during the process and the generally lower resource temperatures associated with the use of binary plants.

The situation is depicted in Fig. 7. The dashed curve is the line of constant supersaturation, $S = 1.5$. It should be observed that it is unlikely that the geofluid would be cooled to temperatures lower than about 40°C owing to heat exchanger considerations. Thus, for resources at temperatures lower than about 162°C, it is essentially impossible to reach supersaturation conditions for silica.

Table 2 summarizes the findings for the binary case. It can be seen that a temperature drop of about 122°C can be tolerated without fear of silica precipitation over the range of resource temperatures from 150 - 190°C. A drop of 146°C produces a supersaturation no worse than $S = 1.5$. These results were calculated for $m = 0$ NaCl solutions but should be reasonably accurate for relatively low salinity fluids, say, less than 0.34 molal (20,000 ppm).

7. Concluding Remarks

Several methods have been proposed to cope with or otherwise avoid the silica scaling problem. These might be categorized as follows:

Removal of Scale. Mechanical means may be used to scrape the silica from surfaces where it has deposited. A pig, for example, was used periodically to remove scale from the brine discharge pipes at the Salton Sea Geothermal Loop Experimental Facility [15]. Other removal techniques include blasting with high-velocity jets of water, mechanical shock, and flushing with large volumes of water.

Prevention of precipitation. Scale may be discouraged from adhering to surfaces if they are coated with special materials. The fluids may be chemically treated with acids. Two simple steps that may be taken to reduce silica supersaturation are dilution with relatively clean water and/or reheating of the cool brine, perhaps by using a small amount of flashed steam. This approach was discussed by Awerbuch et al. [16]. Although numerous schemes have been proposed [17], only limited success has been achieved in practice.

Controlled precipitation. The recent use of flash crystallizers to control the rate of growth and the nucleation sites of silica particles has been fairly

successful 5 . When combined with a reactor-clarifier, this approach yields waste effluent that is sufficiently stabilized to allow it to be effectively reinjected and at the same time eliminates scale buildup on surfaces where it would be detrimental to the operation of the power plant. The most successful demonstration of this technology is taking place at the 10 MW Salton Sea Power Plant 18

In this study we have presented a method to allow the silica problem to be quantified as soon as a few basic reservoir parameters are known. We have seen that the scale problem is more severe in the case of flash-steam plants, particularly double-flash plants, than in the case of binary plants as currently employed. Although flash-crystallizer/reactor-clarifier technology seems to be technically feasible, simpler and less expensive methods would be welcomed by the operators of geothermal power plants.

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LIST OF SYMBOLS

Letters

a,b	factors, eqs. (12a) and (12b)
C ₁ ,C ₂	concentrating factors, eqs. (17a)-(17d)
c	salt concentration (kg/kg)
D	factor, eq. (7)
F	factor, eqs. (3a) and (3b)
h	enthalpy (kJ/kg)
h _{fg}	latent heat (kJ/kg)
m	molality (1 m = 58,400 ppm NaCl)
N	number of flashes
q	quartz concentration (mg/kg or ppm)
S	supersaturation
s	amorphus silica concentration (molal or ppm)
T	absolute temperature (K)
t	temperature (°C or °F)
XS	excess silica concentration (mg/kg or ppm)
x	quality or dryness fraction

Subscripts

eq	equilibrium
f	saturated liquid
ff	final flash
g	saturated vapor
r	reservoir
1,2 etc.	state points, Fig. 1

TABLE 1
Summary of Results for Flash Plants

$t_r/^{\circ}\text{C}$	q/ppm	N	$t_{ff}/^{\circ}\text{C}$	$s(t_{ff})$	$s_{eq}(t_{ff})$	S	XS/ppm
(a) $m = 0$ molal NaCl:							
200	261.0	1	125	307.0	462.7	0.663	-
		2	100	321.8	346.2	0.929	-
225	357.2	1	137.5	436.1	528.4	0.825	-
		2	108	461.2	382.8	1.205	78.4
250	467.8	1	150	595.5	598.6	0.995	-
		2	117	635.5	421.6	1.507	213.9
275	575.3	1	162.5	768.0	672.8	1.142	95.3
		2	125	827.8	462.7	1.789	365.1
300	675.1	1	175	952.4	750.4	1.269	202.0
		2	133	1037.5	505.9	2.050	531.5
(b) $m = 0.6$ molal NaCl (35,000 ppm):							
230	370.5	1	140	455.8	503.9	0.905	-
		2	110	482.9	359.9	1.342	123.0
240	413.9	1	145	517.7	530.6	0.976	-
		2	113	550.5	374.5	1.470	176.0
250	458.5	1	150	583.6	557.9	1.046	25.7
		2	117	622.8	389.5	1.599	233.4
275	564.7	1	162.5	753.9	629.0	1.199	124.9
		2	125	812.6	428.4	1.897	384.1
300	663.7	1	175	936.3	703.7	1.331	232.6
		2	133	1019.9	469.6	2.172	550.4
(c) $m = 4.28$ molal NaCl (250,000 ppm):							
225	302.0	1	137.5	349.2	312.4	1.118	36.8
		2	108	364.6	213.5	1.708	151.1
250	401.2	1	150	476.5	362.2	1.316	114.3
		2	117	500.4	239.2	2.092	261.2
275	499.8	1	162.5	610.8	416.3	1.467	194.4
		2	125	646.5	267.0	2.421	379.5
300	593.5	1	175	747.9	474.3	1.577	273.6
		2	133	798.2	296.8	2.689	501.4
320	658.4	1	185	851.8	523.2	1.628	328.6
		2	140	914.7	322.0	2.841	592.7

TABLE 2

Summary of Results for Binary Plants

<u>t_r/°C</u>	<u>t_{eq}/°C</u>	<u>t(S=1.5)/°C</u>	<u>Δt_{eq}</u>	<u>Δt(S=1.5)</u>
150	29	-	121	-
160	39	14	121	146
170	49	24	121	146
180	58	32	122	148
190	68	40	122	150

Figure Captions

- Fig. 1 Flash-steam geothermal plants: Process diagrams for (a) single-flash and (b) double-flash plants.
- Fig. 2 Silica concentration versus temperature for flash plants ($m = 0$).
- Fig. 3 Silica concentration versus temperature for flash plants ($m = 4.28$).
- Fig. 4 Supersaturation versus reservoir temperature for flash plants.
- Fig. 5 Excess silica concentration versus reservoir temperature for flash plants.
- Fig. 6 Binary geothermal plant: Cycle diagram.
- Fig. 7 Silica concentration versus temperature for binary plants ($m = 0$).

FIGURE 1
FLASH-STEAM GEOTHERMAL PLANTS: PROCESS DIAGRAMS FOR
(A) SINGLE-FLASH AND (B) DOUBLE-FLASH PLANTS

FIGURE 2

SILICA CONCENTRATION VERSUS TEMPERATURE FOR FLASH PLANTS ($m = 0$)

FIGURE 3

SILICA CONCENTRATION VERSUS TEMPERATURE FOR FLASH PLANTS ($M = 4.28$)

FIGURE 4
SUPERSATURATION VERSUS RESERVOIR TEMPERATURE FOR FLASH PLANTS

FIGURE 5
EXCESS SILICA CONCENTRATION VERSUS RESERVOIR
TEMPERATURE FOR FLASH PLANTS

FIGURE 6
BINARY GEOTHERMAL PLANT: CYCLE DIAGRAM

FIGURE 7
SILICA CONCENTRATION VERSUS TEMPERATURE FOR BINARY PLANTS ($m = 0$)