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PRECIPITATION AND SCALING IN DYNAMIC GEOTHERMAL SYSTEMS

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SUMMARY

Major additions and modifications to a titanium loop system for conversion to the study of the formation of silica from simulated geothermal brine have been completed. Preliminary pressure and temperature testing with water up to 1000 psig and 200°C, respectively, indicated general operability of the system. A 0.5- to 1.5-gpm side-stream was monitored and cooled under controlled conditions from 190°C to 50°C in a five-section double-tube bypass heat exchanger, then reheated and recycled. Satisfactory performance of the saturator column in providing suitable silica containing brines was also demonstrated. An on-line programmable computer-based data acquisition system was connected to the loop system to read temperature and flow data; to estimate heat transfer coefficients; and to perform additional monitoring, such as limit control and safety functions.

Studies with the Once-Through System showed that seeding by silica polymers formed during shutdowns has been the major factor in promoting scaling in the studies carried out thus far. In a run at pH 6 with 1 M NaCl, no deposits formed during 58 h of continuous operation without seeding, but substantial scale formed in 13 h of continued operation after a 17 h shutdown to allow seeding to take place. Such seeded scales show strong dependence of the amount and nature of the deposit on temperature of deposition. The rate of buildup is also substantially enhanced by raising the sodium chloride concentration from zero to one molar.

DYNAMIC LOOP SYSTEM

Introduction

We have modified a titanium corrosion test loop to provide a dynamic facility for studying the formation of silica precipitates and scale from simulated geothermal brines as a function of composition, temperature, and flow conditions. Since the system has been previously described¹ we will mainly discuss recent additions and preliminary shake-down tests.

Loop Description and Status

The loop is capable of circulating solutions at temperatures up to 300°C and at 2000 psig using a 100 gpm (nominal) titanium canned rotor centrifugal pump at about 100 psi differential pressure. The rear or motor end of the pump requires about a 1 gph bearing-flush solution which is provided by a silica-free brine feed solution. A high-pressure feed pump provides the necessary pressurization while pressure control is maintained with a diaphragm-operated control valve on the loop let-down stream. Cooling sections upstream of the control valve are used to study silica precipitation under low flow rate conditions. The letdown valve is maintained free of scale by an independent concurrent alkali addition stream.

The loop circulating pump discharges into a manifold providing a number of flange connected bypass sections which return the brine to the pump inlet manifold for recirculation. Figure 1 shows a schematic of the system. A bypass side-stream flows at about 1 gpm through an amorphous silica column maintained at the required loop temperature to sustain the desired equilibrium silica concentration in the circulating brine. The inlet of the cooldown-reheat bypass section is connected to the top of the discharge manifold. Via this line, silica saturated geothermal brine passes outside the 1/8-in. steel loop protective shield to a plexiglass enclosure which contains five series-connected double tube heat exchanger sections. It is cooled through the desired

Fig. 1. Schematic of titanium loop for silica precipitation and scaling studies.

temperature range and returned to the loop enclosure. The brine is reheated via a series of heaters and returned to the main loop circulating system. Figure 2 is a photograph of the partially insulated cooldown system. The cooldown-reheat bypass test section is constructed of 1/4-in. schedule 80 titanium pipe with an ID of 0.310 in. and a total length including heater sections of 88 feet. A calibrated 1/2-in. titanium venturi and a titanium throttle valve is used to measure and control brine flow from about 0.5 to 1.5 gpm. The double pipe heat exchangers, each with an effective inside cooling surface area of 0.52 ft.² and a cooled length of 79 in. are provided with 1-in.-OD hard drawn copper cooling jackets. Cooling water flows through the annular passages at rates required to maintain the desired temperature gradients.

Temperatures of process and coolant streams were measured using well type Chromel-Alumel thermocouples; measurements of overall heat transfer coefficients were within design requirements. Thermocouple placement and insulation installation are being completed to improve temperature measurements.

Figure 3 is a photograph of the assembly of heaters installed in series and used to raise the temperature of the cooled silica brine. These heaters have been previously described in detail. Each consists of a 90-in. section of 1/4-in. IPS schedule 80 titanium pipe symmetrically surrounded by four Calrod 1965-W, 240-V Incoloy sheathed heaters providing a power input of ~1 kW per foot of 1/4-in. pipe. Thermon Type 63 Heat Transfer Cement is used to distribute and thermally couple the heaters to the 1/4-in. pipe. The sections are insulated with 2 in. of Fiberfrax insulation. Chromel-Alumel thermocouples are used to monitor pipe and heater temperatures. The heaters are controlled and excessive temperature is limited using a Barber-Coleman proportional controller in conjunction with the Hewlett-Packard 3050B system.

After leaving the heaters, the stream returns to the main loop where it is mixed with the flow from the silica saturation bypass. In the photograph the heaters are the bundle of insulated units on the right, and the silica column is the short vertical unit on the left. The horizontal barrels running from the pump discharge to the pump inlet

Fig. 2. Double pipe heat exchanger bypass.

Fig. 3. Saturator column and electrical reheat section.

manifold are available for the installation of additional experimental bypass units.

Figure 4 includes a view of the control panels. The one in the foreground is used for the control and monitoring of the main circulating system; the farther panel board contains the circuitry for monitoring the cooldown system temperatures and flow, and controls the nominal 40 kW of power input to the vertical heaters in the reheat section of the bypass, again shown to the right. Also shown is the 1/8-in. steel protective shielding with several sections removed for display.

The loop letdown system, consisting mainly of two small double-pipe heat exchangers in series and a titanium diaphragm operated control valve, is shown behind plexiglass shielding in Fig. 5. The flow control system for the air or water coolant supplied to the annulus side of the small double-pipe heat exchangers is mounted on the loop shielding to the right of the enclosure. Temperatures are monitored throughout the letdown system. The independent flushing system for the letdown valve is not visible in the photograph. The letdown system is designed so that corrosion and scaling tests with various suitable materials may be made by replacing the double-pipe heat exchangers and subjecting materials to various temperature and heat flux levels by adjustment of the air or water coolant supply rates.

Data Acquisition and Control System

Necessary software has been written² for the Hewlett-Packard 3050B Data Acquisition System. The central unit is a 9825 computer with scanners, x-y plotter, printer, tape storage and DVM peripherals on an HP Interface Bus, with provision for additional peripherals as required.

The software is saved on a special two-track high-speed tape cartridge of about 250K byte capacity. An "Executive" program operates 24 programmable tasks. Each task can be paced with a timer-clock/calendar at any period on a selected priority basis, that is task zero, which performs safety monitoring functions, has highest priority. Task one, operating in conjunction with the loop temperature controller by turning on fixed heaters as necessary, has second priority. Other system tasks

Fig. 4. Dynamic loop control panels.

Fig. 5. Brine letdown system.

involve data scanning and analysis. The operator can program the machine with this software "conversationally". The machine asks specific questions and displays acceptable responses which are typed on the 9825 keyboard in assigning tasks and for task activation, task shutdown, clock/calendar reset, scan table generation, and various task status reports. The display indicates which task is running or if the machine is idling. Data are stored in preassigned tracks and files on a data cartridge. Work is continuing in the software on debugging and programming x-y plotter tasks.

Shakedown Operations

a) Silica Column Operation

To check the performance of the silica saturator, tests were made by circulating a water bypass stream from the main loop through the silica column at a nominal rate of 1 gpm at 200°C. The silica-containing solution was then returned to the main loop circulating system and recycled. The entire test was run under isothermal conditions with the necessary exception of the feed and letdown system. Differential pressure was measured and monitored across the silica column and orifice flow meter. Samples were removed at intervals from the main loop and letdown system as well as the rear of the circulating pump to observe the buildup of silica concentration.

An early run indicated that silica powder was passing around or through a porous tantalum frit used to support the silica bed. After flushing all the silica from the system and placing a glass wool layer on the frit no further such problems were observed.

Upon resumption of operation, difficulty in system pressure control and maintenance was experienced as a result of malfunctioning of the titanium letdown pressure-control valve. Replacement of the control valve trim and the operation of an independent concurrent (0.01 M HCl) acid flush injection system immediately upstream of the valve inlet improved loop pressure stability and control.

Following a thorough cleanup of the loop and after a period of steady state operation at 200°C and 1000 psig, part of the loop flow

was bypassed through the preheated silica column at about 1 gpm. With a loop feed of 1 gph and a loop volume of ~6 gal., close to a saturated silica condition in the loop mainstream should be reached in less than an hour. Samples from the loop mainstream were analyzed for dissolved silica soon after flow through the silica column was started. The results are shown plotted in Fig. 6 as ppm SiO_2 dissolved against time. The dotted line shows the calculated or expected increase in silica concentration. Although some scatter is shown, the measured loop silica concentration coincides with and is maintained at the expected levels in about 45 min. following flow startup through the silica saturator bypass. The asymptotic concentration of about 1180 ppm approximately corresponds to equilibrium solubility reported for porous Vycor³ at the column operating temperature. The latter is shown as a function of time in the lower part of Fig. 6 rising to about 220°C at the column effluent. Differential pressure across the silica bed (about 13 psi) was within the expected design range for a 1-gpm column flow.

To determine the efficacy of feed stream injection into the back of the circulating pump in preventing back diffusion and precipitation of silica into the pump rotor bearings, the feed rate was decreased from about 1.4 gpm ($88 \text{ cm}^3/\text{min}$) to 0.38 gpm ($24 \text{ cm}^3/\text{min}$) over the course of 3 hr. Samples removed from the rear of the pump showed negligible dissolved silica concentrations even at the lowest flow rate. However, following complete shutdown of feed injection to the back of the pump (an alternate feed point in the loop mainstream was used to maintain normal loop pressure), 117 ppm silica was detected in the back of the circulating pump in 15 min. Silica concentrations rose to 588 ppm in about 50 min. before the test was terminated indicating the necessity of maintaining at least an 0.4 gpm flow to the rear of the pump.

b) Segmented Heat Exchanger Operation

Initial silica-free runs were made using the original loop heaters at relatively low temperature (100°C) for cleaning, leak checks, and preliminary heat transfer trials. The desired flow range through the

Fig. 6. Approach to steady state (SiO₂) in dynamic loop.

cooldown-reheat bypass of 0.5 to 1.5 gpm was readily obtained. Frequent adjustment to maintain a steady, desired flow rate (1 gpm) was required until after the system was cleaned for several days. Flow stability through the bypass was improved by the inclusion of a fixed orifice so that less frequent manipulation of the manual titanium flow control valve was required. We expect to further improve flow control following delivery and installation of a commercially designed automatic valve activator controlled through a venturi flow-metering system.

Additional tests raising the system temperature to 200°C and bringing into operation the recently installed reheater sections, providing an augmented heating capacity for the loop rated at a nominal 40 kW, were made for a period of about 8 h. External titanium pipe wall temperatures and associated maximum heater surface temperatures were below maximum design limitations for the Incoloy sheathed Calrod heaters at nominal input power levels of about 1 kW per foot length of 1/4-in. titanium pipe. The process fluid was cooled through a temperature gradient of about 190° to 45°C; a coolant flow of about 5 gpm resulted in a coolant temperature gradient of 10° to 40°C. Only a single-coolant stream (laboratory water) was used in these tests. No attempt was made to adjust coolant rates for individual tubes or groups of tubes or to adjust or manipulate temperature gradients or heat flux. We expect to complete insulation of the system and operate the loop in further shakedown tests through a range of process and coolant flows at higher loop temperatures and various process and coolant temperature gradients to further shake down the system and optimize temperature measurement techniques and heat balances. Following completion of the shakedown period, we expect to begin tests using a silica-saturated brine under conditions similar and comparable to those studied in our once-through experimental system to extend our prior observations to conditions of high linear flow rates (~ 5 ft/sec) and heat fluxes more closely simulating commercially realizable conditions.

ONCE-THROUGH SYSTEM

Introduction

Several additional runs were carried out in the Once-Through System during this report period. Also, since this system is now more a test bed for defining brine parameters for test runs to be carried out in the dynamic system than for development of that system, we have decided to label runs carried out in the (O)nce (T)hrough (S)ystem OTS runs. OTS Run 2, the most recent, shed substantial light on observations made in previous operations with this system as it has evolved, so it will be discussed first.

Run OTS-2

Previous runs with this system were frequently interrupted by silica scale plugs forming in the letdown valves; in fact, several runs were directed at exploring unsuccessful preventatives. Observations during these runs indicated that these shutdowns were a major promoter of scale formation in the cooldown system and OTS-2 was designed to demonstrate this effect. In order to avoid valve plugging we injected 3 M base into the brine stream ahead of the letdown valve as indicated in Fig. 7, the resultant base concentration in the brine was ~ 0.15 M, sufficient to solubilize the silica as the anion. This procedure made it necessary for the letdown valve to be downstream from the Pyrex pipe scaling (cooldown) test section, so we were limited to ~ 180 psi and a saturator column temperature of $\sim 175^{\circ}\text{C}$ and the equivalent ~ 725 ppm silica concentration (solubility). Additional modifications to the cooldown test section for this run are also shown in Fig. 7. The 6-in. long segments (Nos. 1, 3, 5, 7, and 9) shown shaded are fabricated of the same titanium pipe as was used in fabrication of the process piping in the dynamic loop segmented heat exchanger. We plan to use these 6-in. titanium segments for developing methods of recovering representative scale samples from the heat exchanger pipes. They also provide a titanium substrate for comparison with the Pyrex glass. The 6-in. stainless steel sleeves were inserted in an effort to obtain representative

Fig. 7. Once-through system cooldown section, OTS-2.

scale samples in > 100 mg quantities for other studies (surface area, porosity, moisture content, x-ray diffraction). In the OTS runs we also have provided the first three 36-in. Pyrex segments with glass jackets to reduce the rate and variance of temperature reduction; thermocouples were located at the points indicated by T_n .

Conditions for the run were:

725 ppm SiO_2 (saturator column $\sim 175^\circ\text{C}$)

0.1 M sodium acetate

1.0 M sodium chloride

15-20 ppm hydrazine*

~ 30 cc/min flow through cooldown**

The plan was to 1) run the system uninterrupted for ~ 70 h, 2) shut down overnight, 3) run for an additional period, 4) repeat 2) and 3) and observe the resultant scaling. A building power failure terminated the initial operating period 12 h early, fortunately, however, this did not change the overall results.

Table 1 describes the scaling observations in the five 36-in. Pyrex segments during the several periods of operation. Figure 8 shows these segments at the conclusion of the run. To summarize, the results show:

1. Little or no visible scale formed during the first 58 h of continuous operation; the small amounts of deposits could have been ferrous hydroxide from corrosion of the mild steel present as coupons and components between the saturator column and the cooldown section.
2. After the 17 h shutdown, large amounts of scale formed in only 13 h of operation. The descriptions given for 12/20/76 at 1300 h were unchanged from the conditions at the end of the 13 h period except for the hydroxide effect observed at 0900 on 12/20/76.

*To getter oxygen and minimize stress corrosion cracking of stainless steel components.

** ~ 26 cm/min in Pyrex pipe with a cooldown holdup time of ~ 26 min.

Fig. 8. Thirty-six inch Pyrex pipe segments after run OTS-2.

Table 1. RUN OTS-2. SCALE OBSERVATIONS

	#1 36" Section	#2 36" Section	#3 36" Section	#4 36" Section	#5 36" Section
12/13 - 1100	<u>Start Up</u>				
1615	Slight haze around mild steel tab.				Similar but lesser haze around mild steel tab.
1820	Haze turning yellow (rust?).				No change.
1925	Appears to be accumulating under the horizontal specimen and spreading up the tube wall. Spreading downstream beyond ss specimens.			Only a little deposit where end tabs touch tube wall.	Exit yellow haze for about six inches along tube bottom downstream from mild steel tab.
		Clear with lab lights out.	Ditto	Ditto	
12/14 - 0820	Thin, clear streak on bottom. White deposits at metal tabs. Mild steel corrosion product throughout system.				
1245				May be thin bottom streak in last 12".	Thin bottom streak from entry to middle of 36".
1645	No further changes.	Ditto	Ditto	Ditto	Ditto
12/15 - 0841	No further changes.	Ditto	Ditto	Ditto	Noticeable growth of whitish deposit in entrance area.
1235	<u>Power failure shut system down</u> (58 h operation).				
12/16 - 1345	<u>Start Up</u> (17 h down).				
1500	No change from above.	Clear	Clear	1/8" wide streak on bottom, full length.	Streak along bottom with perhaps some spread up walls.
12/17 - 1420	Slight milky coating compared to 2.			#4 Elbow shows usual pattern.	
1500	<u>Shut system down</u> (13 h operation).				
12/20 0900	As the system cooled down apparently some of the hydroxide solution injected during operation to keep the letdown valve from plugging was sucked back into section 5 and the exit half of section 4 with resultant dissolution of much of the silica deposits which had formed during the previous period of operation.				
12/20 - 1100	<u>Start Up</u> (69 h down).				
1300	Not much change at entrance around metal tabs; heavy deposit on bottom 180° of downstream ~ 18" of this tube.	Speckled deposits all along tube favoring the bottom 180°, also in #2 U bend.	Speckled deposit decreasing along tube.	Sparse speckles at mid-point but heavier around metal tabs.	Fourth U-bend and this tube had substantial deposits which were largely removed by the hydroxide.
12/21 - 1107	<u>Shut system down</u> * (12 h operation).				

* Samples taken at 1529 on 12/20/76 and 0955 on 12/21 (See Table 3) showed 664 and 489 ppm total silica, respectively, indicating the saturator column was running low on silica during this last period of operation. When the column was opened later very little silica remained. See Fig. 2 for condition of these tube segments after the run.

These results show that seeding of surfaces, which results from polymerization of the silica monomer during a shutdown, profoundly enhances scale formation in subsequent operations. The results also indicate that the large percentages of the total scale we have consistently observed on the bottom 120° of the pipe periphery are due to heavier seeding there by gravity settling of polymeric silica. This explains the lack of any substrate effects in our observations.

Figure 9 shows the 6-in. Pyrex segments and U-bends after the run; flow was from left to right at the temperatures shown. Figure 10 shows the amount of silica deposited in the various 6-in. Pyrex and titanium segments. The data show the previously observed pattern of declining amounts deposited with temperature with a minimum at about 50°C and then an increase at the lower temperatures. The data at less than 45°C are artificially low because of the intrusion of the concentrated hydroxide solution during the second shutdown.

Visually the deposits after this run over the entire temperature range appeared more like the low temperature (35°-55°C) scale observed in previous runs rather than showing a transition to hard adherent scale with increasing temperature. This was confirmed during rinsing operations to remove the salt solution prior to drying and weighing the segments. The rinse water had to be applied very gently to avoid washing out the scale. After drying and weighing, the 6-in. sections were brushed with test tube brushes to determine the easily removable scale. The pattern was consistent with previous observations in that less scale was removed the higher the deposition temperature, but, somewhat surprisingly that removable from the titanium segments was substantially less than that from the Pyrex segments, see Table 2 and Fig. 11. The 36-in. segments were brushed while still wet and the loosened scale dried in tared alundum crucibles and weighed. The data for these segments are also summarized in Table 2. The powder removed from each segment was collected and filed for future characterization should that be desirable. Selected samples have been submitted for various examinations.

Brine samples were obtained upstream and downstream of the Pyrex cooldown system to monitor changes in the silica species which occurred

Fig. 9. Six-inch Pyrex pipe segments after run OTS-2.

Fig. 10. Run OTS-2, silica deposition vs. temperature of deposition.

Table 2. RUN OTS-2 SILICA DEPOSITS IN COOLDOWN SYSTEM

SS = stainless steel, Pyr. = Pyrex, 6U = 6 in. U-bends

No.	Specimen Mat'l.	Lgth. In.	Temp. °C	SiO ₂ Total	Deposits Brushed Out	Residue After Brushing (mg/cm ²)	% SiO ₂ Deposit Brushed Out
0	Pyr.	6	136	1.47	0.43	1.04	29
1	Ti	6	112	1.49	0.09	1.40	6
1	SS	6	110	1.99			
1	Pyr.	36*	112-95	-----	1.40	-----	
2	Pyr.	6	95	1.31	0.36	0.95	28
1	Pyr.	6U	85	1.52	0.44	1.08	29
3	Ti	6	74	1.06	0.21	0.85	20
2	Pyr.	36	74-68	Combined with #3 below			
4	Pyr.	6	68	0.72	0.35	0.37	49
2	Pyr.	6U	65	0.62	0.21	0.41	34
5	Ti	6	61	0.51	0.08	0.43	16
3	Pyr.	36	61-59	-----	0.32	-----	
6	Pyr.	6	59	0.36	0.17	0.19	47
3	Pyr.	6U	54	0.36	0.20	0.16	55
7	Ti	6	49	0.27	0.05	0.22	19
4	Pyr.	36	49-42	-----**	0.42	-----	
8	Pyr.	6	42	0.38**	0.25	0.13	66
4	Pyr.	6U	41	2.15**	1.84	0.31	85
9	Ti	6	39	0.64**	0.31	0.33	48
5	Pyr.	36	39-36				
2	SS	6	37	0.26**			
10	Pyr.	6	36	0.16**	0.12	0.04	75

*14-in. from entrance only, 36-in. tubes kept wet until brushed.

**Obscured by KOH intrusion.

Fig. 11. Run OTS-2, percent of SiO_2 scale removed by brushing.

during the ~26 min. traverse. The data are tabulated in Table 3. The silica concentrations are obtained by a silicomolybdate colorimetric procedure. Three values are given in the table; the first of these, the concentration indicated as "monomer", is that calculated from the color (α silicomolybdate at 390 nm) developed in the first two minutes; the second value termed "monomer and oligomers" is based on the color development in ten minutes. Total silica is measured by making the sample strongly alkaline (~25% NaOH) and digesting for more than one hour before carrying out the colorimetric analysis. Figure 12 is a cross plot of the data and shows the total values grouping around the 45° line as they should since only a very small fraction of the total silica passed through the system is deposited. The "monomer" and "monomer plus oligomer" values show a slight bias to higher upstream values as would be expected as polymerization with time forms unreactive (to the color reagent) higher polymeric species. We believe the polymeric species are less aggressive in scale buildup (as distinct from nucleation) than the more "reactive" monomer and oligomers. We plan to obtain data such as these for future runs to give a measure of scaling "intensity".

Run OTS-1

This run was principally concerned with investigations of procedures for keeping letdown valves from plugging. The procedures investigated were: a) application of heat to the valve body so the surfaces in contact with the brine solution would supply heat rather than be a heat sink, b) reheating the solution after it traversed the Pyrex cooldown system, and c) NaOH injection. Brine conditions used were:

- 0.1 M sodium acetate
- 1.0 M sodium chloride
- 15-25 ppm hydrazine
- ~900 and ~700 ppm silica
- pH 6.0
- 157° to 45°C cooldown ΔT
- 46(40) to 29(25) cc(cm)/min flow rate

The cooldown system was similar to that used in OTS-2 (see Fig. 1)

Table 3. RUN OTS-2 SiO₂ ANALYSES

UPS = Upstream of Pyrex Glass Section
DWS = Downstream of Pyrex Glass Section

<u>No.</u>	<u>Date</u>	<u>Time</u>	SiO ₂ Monomer plus Oligomers <u>ppm</u>		Total (SiO ₂) <u>ppm</u>	<u>pH</u>
<u>Start</u>	12/13	1225				
UPS	"	1315	792	792	799	5.80
DWS	"	1522	762	762	785	5.89
UPS	"	1539	777	777	718	----
UPS	12/14	1021	707	712	748	5.91
DWS	"	1115	724	725	746	5.96
UPS	"	1445	706	712	724	5.89
DWS	"	1521		701	727	
DWS	12/15	0945	664	671	736	5.67
UPS	"	1025	715	715	753	----
<u>Stop</u>		2235				
<u>Start</u>	12/16	1345				
UPS	12/17	0945	703	710	731	6.04
DWS	"	1010	692	697	721	6.02
<u>Stop</u>		1500				
<u>Start</u>	12/20	1100				
UPS	"	1529	683	685	664	6.13
DWS	"	1601	597	597	626	6.15
UPS	12/21	0955	489	489	489	6.03
DWS	"	1046	441	444	469	6.05
<u>Stop</u>						

ORNL-DWG. 77-5094

Fig. 12. Run OTS-2, upstream vs. downstream silica concentration.

except that all the 6-in. segments were of Pyrex, there was no #0 segment, and there was another letdown, control valve between the oil bath cooler and the cooldown system.

The first period of operation was for five hours with the saturator column at $\sim 205^{\circ}\text{C}$ and a silica concentration in the brine of ~ 900 ppm. The upstream control valve plugged tightly by that time and overpressure shut the system down; the valve trim was titanium. A slight milky film appeared in the #1 6-in. Pyrex segment after two hours but the rest of the cooldown section was still clear after 4 h operation. The next morning, 13 h after the system shut down, all parts of the Pyrex glass cooldown system were coated with a milky deposit; the deposit was heaviest at the high temperature entry and appeared to lighten as the temperature dropped. Figures 13 and 14 show the valve stem and seat covered with silica; the SEM analysis showed no other elements were present in the deposits.

For the second period of operation the upstream control valve was equipped with "Stellite" trim and the valve body was kept at a higher temperature (5° to 10°C) than the brine entering it. However, after 2 h operation this valve again showed signs of plugging. Raising the temperature of the valve body to 210° – 225°C , which may have caused flashing in it, appeared to free it. It performed marginally for 2 h longer before excess pressure shut the system down.

By manual manipulation of the controller we were able to produce some flow through the valve so we tried to clear it by pumping 3 M NaOH through it with a metering pump. This was partially successful in that manual control was adequate, but automatic control could not be restored. The alkaline effluents were diverted to waste ahead of the Pyrex system.

Subsequently, the upstream control valve was bypassed and the entire once-through system was run at a lower temperature ($\sim 175^{\circ}\text{C}$), where the Pyrex system could withstand the resultant pressure, and only the downstream control valve was used. This resulted in a silica concentration of ~ 700 ppm in the brine. The system ran 24 h in this mode without event; depositing silica in the cooldown system. At that time the reheater immediately upstream of the downstream control valve was

Fig. 13. Titanium stem from silica plugged valve.

Fig. 14. Titanium seat from silica plugged valve.

turned on to reheat the brine entering the valve from 45° to 75°C. One hour later the valve showed signs of plugging and the pressure had increased from 150 to 210 psi. Heat was applied to the valve body to try to reverse the deposition, but raising the valve body temperature to 100°C did not help. The pressure continued to rise to 245 psi. Injection of NaOH ahead of the reheater to make the brine 0.1 M in NaOH did not relieve the situation and leaks at Pyrex pipe joints forced a shutdown of the brine pump. The NaOH (1 M) flow was increased from 2 cc/min to 8 cc/min which cleared the control valve in 8 min. so that the brine pump could be restarted. The reheater and heat to the valve body were subsequently turned off and the NaOH flow was stopped after 12 more minutes; no indications of plugging appeared during the next hour.

After that period the above experiment was repeated except that the heat to the valve body was applied before the brine reheater was turned on. After the valve body reached 90°C, the reheater was turned on and the temperatures at the preheater outlet and valve body were adjusted to 75° and 95° respectively. No signs of valve plugging occurred over the next 90 minutes. Over the next hour the valve body temperature was gradually dropped to 57°C without initiating plugging; in the previous experiment the valve body was 65°C when incipient plugging was observed. The system continued to operate at 75°C at the reheater outlet and ~55°C at the valve body for six hours with no indication of valve plugging. At that time the run was terminated. We have found no explanation for the quite different response in these last two experiments, however, we have observed the reheat effect a number of times and plan to investigate it further in future runs because of possible implications for reinjection.

Silica deposits formed in this run are shown in Table 4 and Fig. 15. The same pattern observed in OTS-2 is again apparent. At first the lack of any substrate effect was puzzling, but this is now explained by the overriding seeding effect during shutdowns. The 6-in. Pyrex segments are shown in Fig. 16; the concentration of deposit on the bottoms of the tubes is evident - to the left in the photo. Cross sections of one of the tubes (6-in. Pyrex #6 in Table 4 and Fig. 16) were also mounted in epoxy and examined metallographically. Figure 17 shows the scale at the

Table 4. RUN OTS-1 SILICA DEPOSITION ON SEVERAL SUBSTRATES
VS TEMPERATURE OF DEPOSITION

S = straight tube, H = horizontal, V = vertical, U = u-bend,
SS = stainless steel, CS = mild steel, E = estimated

Specimen Type	No.	Orien- tation	Deposition Temp. °C	Wt. SiO ₂ mg/cm ²	Scale
6" Pyrex	1	S	146	3.0	
SS Tab	1	H	136	5.1	
SS Tab	11	V	136	7.1	
CS Tab	1	H	136	7.0	
CS Tab	4	V	136	2.3	
6" Pyrex	2	S	115	3.5	
SS Tab	2	H	128	5.8	
SS Tab	12	V	128	1.8	
6" Pyrex	1	U	110	---	
6" Pyrex	3	S	100	2.7	
SS Tab	3	H	94	3.8	
SS Tab	13	V	94	1.8	
6" Pyrex	4	S	85	1.7	
SS Tab	4	H	88	3.1	
SS Tab	14	V	88	1.7	
6" Pyrex	2	U	82	---	
6" Pyrex	5	S	79	1.8	
SS Tab	5	H	76	2.7	
SS Tab	15	V	76	1.1	
6" Pyrex	6	S	72	1.2	
SS Tab	6	H	75	2.8	
SS Tab	16	V	75	1.0	
6" Pyrex	3	U	69	---	
6" Pyrex	7	S	66	0.95	
SS Tab	7	H	63	1.1	
SS Tab	17	V	63	0.64	
6" Pyrex	8	S	55	0.62	
SS Tab	8	H	58	0.86	
SS Tab	18	V	58	0.35	
6" Pyrex	4	U	55	---	

Table 4. RUN OTS-1 SILICA DEPOSITION ON SEVERAL SUBSTRATES
VS TEMPERATURE OF DEPOSITION (Cont'd)

S = straight tube, H = horizontal, V = vertical, U = u-bend,
SS = stainless steel, CS = mild steel, E = estimated

Specimen Type	No.	Orien- tation	Deposition Temp. °C	Wt. SiO ₂ Scale mg/cm ²
6" Pyrex	9	S	53	1.1
SS Tab	9	H	50	0.98
SS Tab	9	H	50	0.36
CS Tab	2	H	48	2.0
CS Tab	5	V	48	0.9
CS Tab	3	H	46	2.7
CS Tab	6	V	46	1.3
SS Tab	10	H	45	1.2
SS Tab	20	V	45	1.1
6" Pyrex	6	S	44	3.3

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Fig. 15. Run OTS-1, silica deposition vs. deposition temperature.

Fig. 17. Cross section through 6-in. Pyrex tube segment showing silica distribution.

bottom of the tube (bottom photo) compared with that at the top (top photo); it is apparent that > 90% of the scale is at the bottom of the tube. This was also verified by a crude weight determination obtained by scraping the heavy scale off the bottom of another section of the tube. The bright particles in the scale in the bottom photo were identified as an iron compound, probably a corrosion product oxide. We have observed scattered iron particles regularly without any indication of an interaction between them and the silica deposition.

The effect of brushing out the tubes was first investigated after this run and qualitatively the results appeared consistent with those from after OTS-2. Weight data were not obtainable because the specimens had already been altered for other purposes.

Earlier Once-Through System Experiments

These operations were concerned with development of procedures for satisfactory operation of this system; these included:

1. Means of measuring and characterizing scale formation.
2. Control valve plugging.
3. pH control.
4. Corrosion control.

Significant observations are summarized in this section. The conditions present in control valves apparently are extremely conducive to scale formation. Efforts to eliminate scale formation by partial cooling of the brine with resultant limited supersaturation at the valve were not successful. For example, with the column operating at $\sim 205^{\circ}\text{C}$ (925 ppm amorphous SiO_2 solubility) and the valve at 162°C (700 ppm amorphous SiO_2 solubility) and thereby only 225 ppm of SiO_2 supersaturation, the control valve plugged in 5 hours. This was the result whenever somewhat aggressive scaling conditions were used.

Operation at pH values less than 5 was possible so long as no appreciable salt concentration was present. In the presence of 1 M NaCl, however, vigorous corrosion of carbon steel components resulted in voluminous quantities of ferrous hydroxide which also plugged the valves.

We are converting the system entirely to titanium and 300 series stainless steel with the assumption that oxygen gettering will minimize pitting and stress corrosion cracking.

The use of the 6-in. Pyrex tubes for getting weight data on silica deposition was first tested in an earlier run at pH 6 with 0.1 M sodium acetate present as a buffer. The EIC experience⁴, and also our experience in trying to adequately control the very important pH variable for saturator column effluent, demonstrated the need for the presence of a buffer to fix the pH. In this operation we had planned to first obtain a supply of monomer stock solution in water by operating initially with water feed. A failure of the saturator column support frit terminated the run after 2 h at 180°C; seeding probably resulted during a 5 day shutdown for repairs. The run was restarted on water and the stock solutions were obtained. Streaks of deposit were observed along the bottoms of the last two 36-in. Pyrex tubes after 9 h total operation. Sodium acetate was added to the feed (0.1 M) at 10-1/2 h operation. The reheater upstream of the control valve (Fig. 1) was activated at 9.5 h and the temperature at the control valve raised from 36° to 85°C. The control valve plugged at 26.5 h but was cleared by injecting 6 M NaOH just upstream of it. Plugging indications recurred after the NaOH injection was discontinued, however, so the reheater was turned off. The indications then stopped (at 33.5 h) and the system continued to operate to 68 h without further control valve plugging indications. These results confirmed a previous observation that reheating the solution had a detrimental rather than the expected beneficial effect on control valve performance. The system was again shut down by plugging of an auxiliary shut-off valve at 68 h; the valve was cleared by manually closing and opening a few times. The run was terminated by high pressure drop across the saturator column at 74 h. Subsequent examination showed the high pressure drop resulted from accumulated corrosion product which was generated in the preheater because of the failure of a protective Kanigen nickel plate. The preheater has been replaced with one made of titanium. Silica deposition data are presented in Table 5; the silica concentration during this run was ~825 ppm. The data in the table are corrected for an estimated 5 mg shift in the balance between tare and

Table 5. SILICA DEPOSITS VS DEPOSITION TEMPERATURE

Conditions:

0.1 M sodium acetate

pH 6.1

825 ppm SiO₂

Deposition Temperature °C	Silica Deposit mg/cm ²
98	0.2
94	0.2
88	0.01
80	0.03
72	0.1
65	0.04
58	0.2
50	0.1
40	0.1

final weighings and must thereby be considered approximate, but the difference from the data obtained with 1 M sodium chloride is still substantial. The deposits were also principally along the tube bottoms as in OTS-1 and 2.

SCALE CHARACTERISTICS

The scales formed in the several runs described above have been examined with a scanning electron microscope to relate morphology to the deposit characteristics: adherence, hardness, quantity. The Pyrex segments are convenient for this since they can be sectioned to provide in situ examination of the deposit. Where deposits are not adherent or are friable, the removable material is examined as brushed out and the residue is examined in situ. Typical deposits at 100°C are shown in Fig. 18; these deposits were produced in the run (described above) with sodium acetate only present at pH 6. Figure 19 shows material deposited at 100°C in Run OTS-1 where 1 M sodium chloride was present in addition. Figure 20 shows typical low temperature deposit, at 46°C, from OTS-1; recall that the low temperature deposits are friable and not adherent. At these magnifications the deposits appear quite different, but Fig. 21 shows that they are morphologically quite similar to high temperature material but that the basic spheroids in a cluster are about one fifth the diameter of those making up higher temperature deposits. Examinations of deposits formed at the intermediate temperatures show mixtures of these two kinds of spheroidal clusters with a gradual transition from predominantly larger spheroids at the high temperatures to smaller at the low. No other characteristics are shown with the large changes in amount and character of the deposit or with the change in feed composition. Specimens from OTS-2 are being examined at this time.

DISCUSSION

The experiments described above demonstrate the substantial effect of nucleation during a shutdown on subsequent scale growth. The lack of growth of small deposits observed in the first 58 h of operation in OTS-2

Fig. 18. SEM pictures of silica scale formed at 100°C from 0.1 M sodium acetate at pH 6, (SiO_2) = 825 ppm.

Fig. 19. SEM pictures of silica scale formed at 100°C from 1 M sodium chloride, 0.1 M sodium acetate, pH 6, (SiO_2) = 725 ppm.

Fig. 20. SEM pictures of silica scale formed at 46°C from 1 M sodium chloride, 0.1 M sodium acetate, pH 6, (SiO_2) = 725 ppm.

Y-144515

Silica Scale Formed on Pyrex Pipe in Once-Through System
Run No. 1
Conditions: 0.1 M NaAc, 1 M NaCl, pH 6, 725 ppm, SiO₂ (seeded)

Deposition Temperature, 146°C - 10,000X

Deposition Temperature, 56°C - 28,000X

Fig. 21. Higher magnification SEM pictures of silica scale formed at 100°C and 46°C showing similar morphology.

suggests these were ferrous hydroxide corrosion products which did not act as suitable nucleation sites, although it is remotely possible they were relatively inactive silica nuclei. OTS-1 operated 45 h after the first shutdown and OTS-2 for 30 h; considering that the exhaustion of the saturator column charge led to declining supersaturation concentrations in the last hours of OTS-2, it seems probable that the differences in the amounts deposited result from the comparative operating times after shutdown. As would be expected from field experience, salt additions resulted in increased silica deposition "rates" after nucleation.

The lack of a marked change in deposit morphology with the considerable changes in amount deposited, temperature of deposition, and deposit adherence and coherence, and solution composition is surprising. It seems unlikely that the original nucleation sets the entire pattern since the apparent successive spheroid growths indicate that many spheroids are formed long after the original nuclei have been covered up. Perhaps the original pattern set up is self perpetuating; other similar mineral framboidal structures observed in nature also suggest this.

The effect of temperature of deposition is also puzzling since the entire Pyrex system cools to room temperature in about 45 minutes and the bulk of the polymerization takes substantially longer than that. Thus the large effect of temperature of deposition must be related to the processes taking place during deposit buildup or growth and not to the nature of the nuclei formed.

MILESTONE CHART

The substantial effect of seeding during a shutdown on scale formation in subsequent operation observed in the Once-Through System studies described above (similar results have also been encountered in the Dynamic Loop) profoundly affects the future program in several ways:

1. A shutdown early in a run followed by relatively rapid scaling requires re-scheduling the run to assess the potential for spontaneous nucleation.
2. Shutdown seeded scaling rates should be evaluated for brines which do not nucleate scale spontaneously to provide a basis for

assessing the need for taking remedial measures during or before a subsequent startup of a geothermal system.

3. The relatively rapid development of scale in the presence of seeds emphasizes the necessity for complete removal of scale formed in a previous run before starting a new one, to avoid quite misleading results.

4. The difficulty in producing spontaneous nucleation from brines which rapidly produce heavy scaling when seeded suggests that seeds are often components of natural brines and that spontaneous nucleation from clean brines is unlikely.

In view of these considerations, the next dynamic loop operation will emphasize stepwise development of conditions expected to increase the likelihood of spontaneous nucleation from clean brines; it is assumed that factors increasing the rate of silica polymerization have a similar effect on nucleation. The run will be carried out as follows:

- A. pH 6, 1 M NaCl, 0.1 M $\text{NaC}_2\text{H}_3\text{O}_2$, 700-800 ppm SiO_2 - operate ~36 h to verify cleanout of scale from previous run.
- B. Raise chloride concentration to 4.0 M - operate ~100 h; if scale forms, continue operation until appreciable. Clean up and characterize scales.
- C. If no evidence of scale formation, raise pH to 7 - operate ~100 h or until appreciable scale forms. Clean up and characterize scales.
- D. If no evidence of scale formation, add 700 ppm Ca^{+2} and operate ~100 h. If no scale forms, shut down for seeding and assess seeded scale formation under these very aggressive conditions. Clean up and characterize scales.

In the event spontaneous nucleation does not occur in these operations, we will investigate methods of introducing seed materials found in natural brines, e.g., silicates, carbonates, sulfates, sulfides, etc. If spontaneous nucleation occurs, we will examine the effect of

clean brine composition on its initiation.

Future plans are so dependent on the results obtained in the next operations that we have not attempted a more detailed milestone chart at this time.

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