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Silica Scaling in Simulated Geothermal Brines

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Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
NTIS price codes—Printed Copy: A06 Microfiche A01

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ORNL/TM-7681
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CONTRACT W-7405-eng-26

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Chemistry Division

SILICA SCALING IN SIMULATED GEOTHERMAL BRINES

E. G. Bohlmann, A. J. Shor, P. Berlinski and R. E. Mesmer

Date Published: April 1981

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SUMMARY

A 6.3 l/sec (100 GPM) titanium corrosion test loop was modified to provide a dynamic facility for studying the formation of silica deposits, their properties and fates, as a function of brine composition, temperature, and flow conditions. Scale formation was studied in a segmented heat exchanger operating under realistic conditions; the segmented design permitted examination of scale formations in five temperature regimes. Unfortunately, the program was terminated after minimal exploratory operation because of reduced sponsor perceptions of the need for concern with scaling problems.

The runs which were completed dealt cursorily with brine concentration and pH effects. Results of interest were:

Spontaneous nucleation of scale formation was enhanced by increasing brine concentration and pH. At low brine concentration and high pH, nucleation was localized with the formation of ripples transverse to the flow direction. Such sparse nucleation resulted in low accumulation rates. Relic structures observed in some of the heavy deposits produced at higher brine concentrations suggest such formations may often be present during nucleation of deposition.

Rates of scale accumulation increased substantially with brine concentration, perhaps because of "continuous" nucleation. Mixed dependence on supersaturation ratio was observed; in the high pH runs the rate of deposition increased with the supersaturation ratio, the reverse of what was observed in earlier runs at lower pHs.

All deposits had appreciable specific surface areas (≥ 1 or more m^2/g) similar to several field specimens which were examined. These areas enter directly into the growth kinetics and increase the apparent monomer deposition by one or two orders of magnitude.

Electron microscope studies of the deposits frequently showed a framboidal morphology. The assemblages of spheroids were formed in place rather than depositing after having been formed in the brine.

The studies showed that silica deposition is a complex phenomenon with supersaturated but otherwise quite pure brines; additional constituents found in geothermal brines are not necessary adjuncts.

A practical result of this and other studies was the observation that allowing a brine in which silica is polymerizing to remain in stagnant contact with equipment leads to coating surfaces with very active nuclei. Subsequent exposure to supersaturated brine can lead to very rapid scale accumulation. Thus, flushing such brines from systems at shutdowns or other flow interruptions is a desirable preventive measure.

I. INTRODUCTION

The ERDA Definition Report¹ projects that significant utilization of geothermal energy through the year 2000 depends on three resources: Hydrothermal, Geopressured, and Hot Dry Rock. High temperature geothermal waters obtained from such resources will commonly contain appreciable quantities of dissolved silica which will become supersaturated on cooling with resultant precipitation and scaling propensities deleterious to the performance of heat transfer and mechanical equipment (valves, bearings, etc.). A perspective on the magnitude of the problem is supplied by estimates that the silica precipitation potential in various parts of a 100 MWe geothermal plant is approximately one metric ton per hour.²

We modified an existing 6.3 l/s titanium loop to provide a dynamic facility for studying the formation of silica deposits, their properties and fates, as a function of brine composition, temperature, and flow conditions. This loop demonstrated excellent serviceability over a period of years in saline water corrosion studies with and without pollutant additives such as H_2S , NH_3 , and SO_2 and proved equally satisfactory in this application.

The principal function of the modified loop was to provide for circulation of silica saturated solutions of known composition through a heat exchanger-reheat bypass section in order to study silica deposition from the resultant supersaturated solution under conditions like those encountered in geothermal heat transfer equipment. Scaling in the cooldown section was determined by following changes in heat transfer rates and physical examinations. Scales formed were characterized by various techniques: crystallography, electron microscopy, and chemical and physical removal.

Silica saturation of the circulating solution was effected in another bypass section containing a saturator column loaded with powdered silica (amorphous porous Vycor).

The program was terminated by DGE in the light of developed scale removal technology and other shifts in the program for fluid management.

II. LOOP DESCRIPTION

The loop was capable of circulating solutions at temperatures up to 300°C and up to 14 MPa (2000 psi) using a 6.3 l/s (100 GPM) titanium canned rotor centrifugal pump (Fig. 1) at about 0.7 MPa (100 psi) differential pressure. The rear or motor end of the pump required about a 4 l/h bearing-flush purge which was provided by injection of a silica-free brine feed solution with a high-pressure feed pump. This also provided necessary pressurization with control maintained with a diaphragm-operated control valve on the loop letdown stream.

The loop circulating pump discharged into a manifold providing a number of flange connected bypass sections which returned the brine to the pump inlet manifold for recirculation. Figure 2 shows a schematic of the system. A bypass side-stream flowed at about 1 gpm through the amorphous silica column maintained at the temperature required to sustain the desired equilibrium silica concentration in the circulating brine. The inlet of the cooldown-reheat bypass section was connected to the top of the discharge manifold. Via this line, silica saturated geothermal brine passed outside the 3 mm steel loop protective shield to five series-connected double tube heat exchanger sections in a plexiglass enclosure. It was cooled through the desired temperature range and returned to the loop enclosure. The brine was reheated via a series of heaters and returned to the main loop circulating system. The bypass heat exchanger shown in Figs. 3 and 4 was intended to provide realistic flow conditions (i.e., linear flow rates of 1-2 m/s, Reynold's numbers ranging from 10^4 to 10^5 , depending on conditions) for the study of the effects of silica scaling on heat transfer rates at various geothermal brine temperatures and compositions. The brine flowed at a nominal rate of 4 l/min through sections of 1/4 inch schedule 80 titanium pipe. Cooling water flowed in the annulus of a 25 mm nominal ID copper tubular jacket surrounding each cooler section. The annuli were sealed with swaged type heat exchanger tees. Depending on the range of cooldown temperatures and the temperature distributions desired, up to 5 sections, each with an effective length of 2 m could be installed in series permitting the brine temperature to drop,

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Fig. 1. 6.3 l/s (100 GPM) canned rotor, centrifugal circulating pump,

ORNL-DWG. 75-14902AR

Fig. 2. Titanium loop for silica precipitation and scaling studies, schematic.

Fig. 3. Bypass segmented heat exchanger for scaling tests.

Fig. 4. Photograph of segmented heat exchanger.

for example, from 250 to 100°C in five temperature increments. Figure 3 is a diagrammatic sketch of the arrangement of the coolers. Every cooler was identical, permitting ready substitution; each could be inspected in situ by removing blind end-flanges and inserting a borescope into the pipe. Specimens of scale could be removed for examination and the amount of scale formed could be measured by chemical removal and analysis. Well type thermocouples monitored inlet and outlet temperatures of both process fluid and coolant for each double tube section (see Fig. 5). Heat transfer from the process fluid through the inside liquid film, the deposited scale, the titanium pipe wall and into the coolant water could be estimated.

Figure 6 is a photograph of the assembly of heaters installed in series and used to raise the temperature of the cooled brine back to the main loop temperature. 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. Each segment consisted of a 90-in. section of 6.4 mm IPS schedule 80 titanium pipe symmetrically surrounded by four Calrod 1965-w, 240-V Incoloy sheathed heaters providing a power input of 21 kw per foot of 6.4 mm pipe. Thermon Type 63 Heat Transfer Cement was used to distribute and thermally couple the heaters to the 6.4 mm pipe. The sections were insulated with 50 mm of Fiberfrax insulation. Chromel-Alumel thermocouples were used to monitor pipe and heater temperatures. The heaters were controlled and excessive temperature was limited using a Barber-Coleman proportional controller. The heater assembly and construction detail are shown in Figs. 7 and 8.

After leaving the heaters, the stream returned to the main loop where it was mixed with the flow from the silica saturation bypass. The horizontal barrels running from the pump discharge to the pump inlet manifold were available for the installation of additional experimental bypass units.

To simulate various geothermal brines containing silica it was necessary to maintain a controlled level of dissolved silica in the circulating solution. Part of the loop flow was bypassed through a

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Fig. 5. Heat exchanger detail.

Fig. 6. Photograph of saturator column and reheater assembly.

Fig. 7. Schematic of reheater assembly.

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Fig. 8. Reheater detail.

silica column at a nominal rate of 4 l/min where it equilibrated with the amorphous silica powder (+140, -200 mesh porous Vycor) in the column to a concentration corresponding to the column operating temperature. (Exploratory studies with a smaller column showed reasonable agreement with literature data on amorphous silica solubility in water was achieved with a single pass through a similar column.) The silica saturator was piped between flanges in the inlet and outlet manifolds of the loop as shown in Fig. 9. An orifice meter in the outlet flange was used to monitor flow through the saturator while a manual valve was used to control flow through the column. At a solution flow rate of 4 l/min a feed rate of 4 l/h and a loop volume of 23 l, saturation concentrations of silica were reached in less than an hour following the start of the experiment.

The silica saturator consisted of a section of 100 mm (4 in.) IPS schedule 80 (97.2 mm I.D.) pipe, 610 mm long, welded to a conical discharge section which contained a porous tantalum 70 μ m pore size support frit. The top of the saturator was fitted with a 100 mm 6.3 MPa flange and mated with a flange to which was connected a 13 mm solution inlet line and 32 mm silica loading port. Column loading was approximately 3.6 kg of silica for a 4.5 l column volume and density of 0.8 g/cm³. Based on a saturator solution concentration of 1000 mg/kg, corresponding to a 225°C operating temperature with amorphous silica, and a 75% bed depletion approximately 700 hours of operation was feasible before renewal of silica was necessary.

Samples of the circulating brine were obtained with the arrangement shown in Fig. 10. Key factors are the low holdup capillary tubing and the rapid quench in the ice bath. Many samples were taken with this setup without scaling problems in the tubing or valves in spite of the fact that valves frequently plug rapidly — the letdown valve would plug in an hour without alkali injection. Brines showing very rapid polymerization were collected in a volumetric flask containing an aliquot of hydrochloric acid such that the pH of the mixture was kept in the range 2–3 during sample collection. In this pH range silica polymerization is inhibited for hours even at high silica concentrations (1200 mg/kg) or salinity.

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Fig. 9. Saturator column schematic.

ORNL-DWG 80-19698

Fig. 10. Re-entrant capillary sampler system.

The loop overflow letdown system consisted mainly of two small double-pipe heat exchangers in series and a diaphragm operated titanium control valve as shown in Figs. 11 and 12. The flow control system for the air or water coolant supplied to the annulus side of the small double-pipe heat exchangers was mounted on the loop shielding to the right of the enclosure. Temperatures were monitored throughout the letdown system. The letdown valve was maintained free of scale by an independent concurrent injection of 4.8 molal NaOH at a few percent of the letdown flow just before the valve. The presence of a low flow velocity holdup volume in which particulates could settle out also was useful in promoting smooth letdown valve operation. The letdown system was designed so that corrosion and scaling tests with various suitable materials could 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.

A Hewlett-Packard 3050B System was used for data acquisition and analysis during the extended operations required for the scaling investigations. The central unit was a 9825 computer with scanners, x-y plotter, printer, tape storage, and DVM peripherals on a Hewlett-Packard Interface Bus. Software provided by J. T. Hutton of the Instruments and Controls Division included an "Executive" program which operated 24 programmable tasks which could be paced by a timer-clock/calendar at desired intervals. The system logged data at specified intervals, performed desired calculations and stored the data and results on tape for future manipulation with the "Executive" program as desired by the experimenters.

III. 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 4 l/min at 200°C. The silica-

Fig. 11. Photograph of brine overflow letdown system.

Fig. 12. Schematic of brine overflow letdown system.

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 the porous tantalum frit used to support the silica bed. After flushing all the silica from the system and placing a quartz wool pad on the frit no further such problems were observed.

Upon resumption of operation, difficulty in system pressure control maintenance was experienced as a result of malfunctioning of the titanium letdown pressure-control valve. Replacement of the control valve trim and the introduction of an independent concurrent alkali injection and particle trap 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 7 MPa, part of the loop flow was bypassed through the preheated silica column at about 4 l/min. With a loop feed of 4 l/h and a loop volume of 23 l, 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. 13 as mg/kg SiO₂ 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 mg/kg 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. 13 rising to about 220°C at the column effluent. Differential pressure across the

Fig. 13. Approach to steady state [SiO₂] in dynamic loop.

silica bed (about 90 kPa) was within the expected design range for a 4 l/min 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 88 cm³/min to 24 cm³/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), silica concentration rose to 588 mg/kg in about 50 min indicating the necessity of maintaining at least 25 cm³/min 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 cooldown-reheat bypass of 2-4 l/min was readily obtained. Frequent adjustment to maintain a steady, desired flow rate (4 l/min) was required until after the system was flushed 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. Flow control was improved further by 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 reheater sections, providing an augmented heating capacity for the loop rated at a nominal 40 kW, were made over 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 the nominal input power level of about 1 kW per foot length of 6.3 mm

titanium pipe. The process fluid was cooled through a temperature gradient of 190° to 45°C; a coolant flow of about 20 l/min resulted in a coolant temperature gradient of 10° to 40°C. Only a single-coolant stream (laboratory water) was used in these tests. In subsequent operations two streams and regulator valves were used to try to equalize the temperature drops in the 5 segments.

Heat transfer coefficient calculations were based on the heat transferred from the process stream according to

$$U = \frac{q/A}{\Delta T}$$

where U = overall coefficient

q = BTU transferred/h

A = pipe area, ft²

ΔT = process stream temperature drop, °F

The difference between the reciprocal of the initial or clean tube overall coefficient and the subsequent overall coefficients with conditions held as constant as possible was ascribed to fouling by silica deposition and referred to as a fouling factor.

IV. Characterization of Scales Formed.

During scaling operations, we periodically calculated overall heat transfer coefficients for each heat exchanger section and estimated fouling factors attributed to silica scale formation. It was also noted that the formation of scale in the heat exchanger produced an increased pressure drop and decreased flow. Thus monitoring the position of the operator of the flow control valve as the valve was opened to maintain constant flow through the heat exchanger provided an indication of scaling.

At the end of a run the end flanges were removed from each segment and the deposits on the thermo-couple wells were characterized: photographed, weight determined by weighing before and after chemical cleaning (4M NaOH, 75-90°C).

The deposits at the ends of the segments were examined with an eighteen inch borescope, and in later runs after obtaining required equipment, photographed. Each segment was brushed by passing a test tube brush on a long rod through it until negligible material was removed. Each segment was then individually cleaned by circulating 4.8 molal NaOH solution through it at 80°C. Samples of the cleaning solution were analyzed periodically in an attempt to obtain qualitative data on the "reactivity" of the deposit. Earlier studies on deposits in Pyrex glass pipes from the Once Through System had shown that deposits became appreciably less adherent and coherent but more easily removed as the temperature of deposition decreased.

Samples of deposits physically removed were submitted for scanning electron microscopy and where sufficient material was recovered, surface area determination.

After reassembly, the connectors between heat exchanger segments were cleaned by circulating 4.8 molal NaOH @ 75°C through the entire heat exchanger. The circulating loop was then cleaned with 1 molal Na_2CO_3 ; the heat exchanger and saturator column bypasses were isolated during this operation. After the loop was clean, the amount of deposit in the reheaters was estimated by circulating the carbonate solution through it without feed and letdown streams.

V. Experimental Results

A. Conditions

Conditions for the runs carried out in the Dynamic Loop System are summarized in Tables 1 and 2. Table 1 covers runs principally concerned with the initiation of scale formation from clean brines in a titanium system, 0.1 M^{*} acetate was added as a buffer (pH 6)

^{*}Capital M is used to designate molal concentrations throughout report.

Table 1. Conditions During Higher Brine Concentration Scaling Runs*

Run Number	Scale Formed?	Time (h)		pH	[NaCl] M	[NaAc] M	[SiO ₂] millimolal	Heat Exchanger														
								Section 1			Section 2			Section 3			Section 4			Section 5		
		Operation	"Seeding" ^b					Bulk Fluid ΔT, °C	Ave. wall		Bulk Fluid ΔT, °C	Ave. wall		Bulk Fluid ΔT, °C	Ave. wall		Bulk Fluid ΔT, °C	Ave. wall		Bulk Fluid ΔT, °C	Ave. wall	
									°C	[SiO ₂] ^a millimolal		°C	[SiO ₂] _S millimolal		°C	[SiO ₂] _S millimolal		°C	[SiO ₂] _S millimolal		°C	[SiO ₂] _S millimolal
2DL-A	No	143	30	6.0	1	0.1	15	220-155	150	[5]	155-95	100	[9]	95-65	64	[10]	65-58	50	[12]	58-49	42	[12]
2DL-B	No	46	98	6.0	1	0.1	14	220-160	152	[5]	160-96	102	[8]	96-67	66	[10]	67-58	54	[11]	58-50	43	[11]
2DL-C	No	29	141	6.0	1	0.1	14	215-160	150	[5]	160-106	106	[8]	106-75	73	[10]	75-65	56	[11]	65-57	49	[11]
2DL-D	Yes	29	-	6.0	1	0.1	14	240-170	164	[4]	170-110	112	[7]	110-75	74	[10]	75-60	54	[11]	60-55	46	[11]
3DL	No	48	-	5.9	1	0.1	12	173-138	125	[5]	138-107	98	[6]	107-76	74	[8]	76-51	51	[9]	51-36	35	[10]
4DL	No	51	-	6.9	1	0.1	13	165-134	112	[6.4]	134-100	94	[7.5]	100-72	69	[9.0]	72-49	49	[10]	49-35	34	[11]
5DL	Yes	<29	-	5.9-7.4	4	0.1	11	180-140	128	[5.7]	140-105	98	[7.3]	105-72	71	[8.3]	72-50	49	[9.2]	50-37	35	[9.7]
6DL	Yes	13	-	7.0	4	0.1	11	198-161	134	[5.4]	161-127	114	[6.7]	127-79	87	[7.7]	79-49	56	[8.9]	49-32	40	[9.5]
11DL	Yes	25	-	7.85	1	(0.003 HCO ₃)	9	143-124	102	[3.1]	122-104	91	[3.8]	97-78	71	[4.9]	77-58	54	[5.8]	56-40	41	[6.5]

^aSaturation concentration at wall temperature.
^bTime allowed for polymerization in situ in heat exchangers.
* M = molal

Table 2. Conditions for Simulated Roosevelt Hot Springs Brine Runs

Run Number	Scale Formed?	Time (h)	Brine Composition *					Heat Exchanger														
								Section 1			Section 2			Section 3			Section 4			Section 5		
			pH	[NaCl]	[KCl]	[HCO ₃]	[SiO ₂] _S	Bulk Fluid ΔT, °C	Ave. wall		Bulk Fluid ΔT, °C	Ave. wall		Bulk Fluid ΔT, °C	Ave. wall		Bulk Fluid ΔT, °C	Ave. wall		Bulk Fluid ΔT, °C	Ave. wall	
				M	M	M	millimolal		°C	[SiO ₂] _S		°C	[SiO ₂] _S		°C	[SiO ₂] _S		°C	[SiO ₂] _S		°C	[SiO ₂] _S
									millimolal			millimolal			millimolal			millimolal			millimolal	
7	Yes	185	7.9	0.08	0.01	0.003	8	—	94	[1]	119-95	86	[2]	95-72	67	[3]	72-50	49	[4]	50-41	36	[5]
8	Yes	105	7.9	0.08	0.01	0.003	9	—	108	[1]												
9	Yes	95/385	7.9	0.08	0.01	0.003	8	—	112	[<1]												
10	Yes	90	7.9	0.08	0.01	0.003	8	Scale re-dissolved low [SiO ₂]			141-108	100	[1]	108-85	78	[3]	85-58	58	[4]	58-44	41	[5]

*
M = molal

or to maintain uniform conditions. Hydrazine (25-50 mg/kg) was added to getter oxygen and thereby minimize corrosion; this also resulted in a reducing condition similar to natural uncontaminated geothermal brines.

Studies with a Once Through System³ had shown that seeding by silica polymers formed by homogeneous polymerization during shutdowns was a significant factor in promoting silica scaling from clean, one molal brines at pH 6. The first runs, 2DLA-D, were directed at determining whether similar results would be obtained under the flow conditions in the Dynamic Loop System: 90 cm/s, R_e a few times 10^4 , vs 90 cm/min, laminar flow, in the Once Through System. Only after a particularly long shutdown (141 h) between runs 2C and 2D were there indications of scale formation, presumably because there was ample time for the polymers to get cemented to the pipe walls firmly enough to resist removal by the scouring action of renewed flow.

Run 3DL (1M NaCl, pH 6.0) duplicated the conditions of Run 2DL to demonstrate that the cleaning procedures had not left any nuclei which would reinitiate scale formation. No evidence of scaling appeared in 48 h, which, in view of the results in Run 2DL, was considered adequate confirmation. The results of Run 11DL raise some question about this conclusion but we feel the absence of evidence of scale formation in Run 4DL and for the bulk of Run 5DL support the original conclusion.

Runs 4-5DL used increased pH and/or salt concentration in an effort to promote spontaneous nucleation. Increasing the 1M brine pH to 6.9 in 4DL did not produce scaling in 51 h. Inadvertently, Run 5DL involved both an increase in brine concentration and a gradual increase in pH from 5.9 to 7.4. Residual acidity in the amorphous silica freshly loaded into the saturator column at the beginning of the run dropped the pH brine from 7 to 5.9; the feed pH was then increased to 7.4 to accelerate the recovery to pH 7 and did so as shown in Fig. 14. About the time the pH reached 7.2, in the last few hours of operation, a heat exchanger pressure drop increase, and

Fig. 14. pH increase in Run 5DL.

heat transfer decrease in heat exchanger section 1 indicated scale formation; this was confirmed on opening the system after the run. The run was terminated by the loop overpressure safety interlock due to unknown particulate blockage of the pressure control valve.

As suggested by the Run 5DL results, Run 6DL was operated with 4M brine at pH 7, nucleation and scale growth were indicated promptly by heat transfer reduction and pressure drop increase in the heat exchangers.

Runs 7-10DL were conducted at the request of our funder based on a shift of Division of Geothermal Energy emphasis to less aggressive brines like that at Roosevelt Hot Springs, Utah. The molal concentrations chosen (0.08 M NaCl, 0.01 M KCl, 0.003 M NaHCO₃, 8 millimolal SiO₂, pH 7.9) were based on an analysis of a sample from Roosevelt #2 well supplied by the Radian Corporation.⁴ On the basis of the experience with the previous runs, the possibility of spontaneous nucleation appeared to be the major question but the high pH was a favorable factor.

For Run 11DL (Table 1) the brine concentration was raised to 1M with the other conditions of Runs 7-10DL remaining the same to compare the rate of scale buildup with that in Run 2DL as well as that in Runs 7-10DL. An assessment of the increased brine concentration on spontaneous nucleation at the high pH was also to be provided by thoroughly cleaning out segments 4 and 5 of the heat exchanger between Runs 10 and 11DL. Segment 3 was brushed after Run 10DL but not cleaned with 4 M NaOH.

B. Silica Scale Nucleation and Heat Transfer

A primary function of the Hewlett Packard 3050B System was to acquire the data necessary to assess heat transfer (coefficients, fouling factors, see Section III) in the five heat exchanger sections at specified intervals to monitor the formation and growth of silica scales. No indications of effects of silica deposits on heat transfer were observed in runs 2DL-D and 5DL due principally to poor temperature

measurement with the short thermowells. In Run 6DL surprisingly mixed results were obtained as shown by heat transfer and fouling factor plots, Figs. 15 and 16. Fouling was clearly shown in the first two sections of the heat exchanger; but, if anything, somewhat better heat transfer was suggested by the data from sections 3 through 5. Figures 17-23 are borescope photos of scale deposits at various places in the heat exchanger; there was a suggestion that as the scale became sparse, turbulence promotion may actually have increased heat transfer. Results obtained in later runs produced additional evidence that such heat transfer enhancement was produced. Thus the data obtained during Run 8DL, Fig. 24, show what have been characterized as "spoon shaped" fouling factor curves indicative of initially improving heat transfer due to the rippled deposits formed, followed by deterioration as surface coverage increases. Similar rippled deposits and heat transfer effects were observed by Gudmundsson, et al, in simulated heat transfer experiments with geothermal brines at Hveragardi, Iceland, Fig. 25, and by other workers in various water systems. In Run 9DL the fouling factors show general positive trends indicative of decreasing heat transfer with scale buildup, Fig. 26. Variations observed for individual sections appeared reasonably consistent with variations in the buildup of scale observed with the borescope; however, since the borescope examination only included 15% of the area of each section at the ends, this may have been fortuitous. It should be noted that even the heavy scales for which no initial heat exchange enhancement was observed sometimes showed relic ripple structures, see Fig. 17. Rippled deposits also produce anomalously high pressure drops in piping systems; this effect was qualitatively evident in our work also but was often obscured by intermittent unidentified particulate blockage of the heat exchanger flow control valve.

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Fig. 15. Run 6DL silica deposition and heat transfer.

Fig. 16. Fouling during silica deposition.

Fig. 17. Run 6DL silica deposit on bottom of Section 1, 25 cm from inlet (reduced 11%).

Conditions: 4 M NaCl, pH 7.0, 1 m/s, 13 h.

Millimolal $[\text{SiO}_2]$: 11 in brine, 5.1 supersaturation at wall temperature.

Deposit: chalky, $\sim 76 \text{ mg/cm}^2$, (N.D.) m^2/g .

Fig. 18. Run 6DL silica deposit on left side of Section 1, 15 cm from outlet (reduced 15%).

Conditions: 4 M NaCl, pH 7.0, 1 m/s, 13 h.

Millimolal $[\text{SiO}_2]$: 11 in brine, 5.0 supersaturation at wall temperature.

Deposit: chalky, $\sim 65 \text{ mg/cm}^2$, (N.D.) m^2/g .

Fig. 19. Run 6DL silica deposits on bottom of Section 2, 15 cm from inlet

Conditions: 4 M NaCl, pH 7.0, 1 m/s, 13 h.

Millimolal $[\text{SiO}_2]$: 11 in brine, 6.4 supersaturation at wall temperature.

Deposit: chalky, $\sim 62 \text{ mg/cm}^2$, (N.D.) m^2/g .

Fig. 20. Run 6DL silica deposit on bottom of Section 3, 2.5 cm from inlet (reduced 13%).

Conditions: 4 M NaCl, pH 7.0, 1 m/s, 13 h.

Millimolal $[\text{SiO}_2]$: 11 in brine, 7.2 supersaturation at wall temperature.

Deposit: very hard, $\sim 29 \text{ mg/cm}^2$, (N.D.) m^2/g .

Fig. 21. Run 6DL silica deposit on left side of Section 3, 2.5 cm from outlet (reduced 12%).

Conditions: 4 M NaCl, pH 7.0, 1 m/s, 13 h.

Millimolal $[\text{SiO}_2]$: 11 in brine, 8.3 supersaturation at wall temperature.

Deposit: very hard, $\sim 9 \text{ mg/cm}^2$, (N.D.) m^2/g .

Fig. 22. Run 6DL silica deposits on top of Section 4, 25 cm from inlet (reduced 16%).

Conditions: 4 M NaCl, pH 7.0, 1 m/s, 13 h.

Millimolal [SiO_2]: 11 in brine, 8.5 supersaturation at wall temperature.

Deposit: very hard, $\sim 9 \text{ mg/cm}^2$, (N.D.) m^2/g .

Fig. 23. Run 6DL silica deposit on left side of Section 5 (reduced 13%).

Conditions: 4 M NaCl, pH 7.0, 1 m/s, 13 h.

Millimolal $[\text{SiO}_2]$: 11 in brine, 9.4 supersaturation
at wall temperature.

Deposit: soft, $\sim 9 \text{ mg/cm}^2$, (N.D.) m^2/g .

Fig. 24. Fouling during Run 8DL.

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Fig. 25. Example of rippled silica deposition.

Conditions: geothermal water flow at approx. 80°C.

Reynolds number 44000.

Deposition shown after approx. 2000.

Average ripple height = 0.12 mm.

Average ripple spacing = 0.87 mm.

Fig. 26. Fouling during Run 9DL.

The following should be noted about the data given in connection with the borescope photographs of scale deposits in the exchanger sections:

The silica saturation concentrations at the wall were estimated from graphical interpolations of mid-section calculated wall temperatures, based on average operating conditions.

Where surface areas are given, they were measured on brushed or scraped samples and probably were higher than for underlying, more cohesive materials. Similarly, the amount deposited (mg/cm^2) is the average for the entire section; clearly, the actual amounts at given locations vary widely from this.

Arrows indicate flow direction, $\sim 1\text{m/s}$ in all cases.

N.D. - not determined.

C. Appearance

After Run 2DL (1M NaCl, pH 6) the heat exchanger segments were heavily scaled. The scale was translucent to milky white with random smooth, rippled or granular areas. As in the Once Through System³ the scale often appeared heaviest in the bottom third of the circumference consistent with "seeding" by settled polymeric material. At the end of Run 5DL (4M NaCl, pH 7) equipment for attempting to photograph the scale in situ had been assembled and this was pursued. Several representative photos are shown in Figs. 27-33. Because of the gradually increasing pH and inability to establish the onset of scaling, minimal effort was expended on characterizing the 5DL scales.

The scales formed in Run 6DL (4M NaCl, pH 7) resembled those in 5DL, Figs. 17-23. The very heavy deposits in Section 1 showed more uniform, rippled surfaces with less porosity than after 5DL. Some spheroidal masses in Section 2 were larger, looking like cumulus clouds; but they were more scattered and rifted in the later sections suggestive of initiation as ripples similar to those in Runs 7-11DL.

Fig. 27. Run 5DL silica deposit on top of Section 1, 20 cm from inlet (reduced 11%).

Conditions: 4 M NaCl, pH 5.9-7.4m 1 m/s, <29 h.

Millimolal $[\text{SiO}_2]$: 11 in brine, 4.8 supersaturation
at wall temperature.

Deposits: $\sim 11 \text{ mg/cm}^2$.

Fig. 28. Run 5DL silica deposit on bottom of Section 2, 33 cm from inlet (reduced 10%).

Conditions: 4 M NaCl, pH 5.9-7.4, 1 m/s, <29 h.

Millimolal $[\text{SiO}_2]$: 11 in brine, 7.1 supersaturation at wall temperature.

Deposit: $\sim 11 \text{ mg/cm}^2$.

Fig. 29. Run 5DL silica deposit on top of Section 3, 33 cm from inlet (reduced 17%).

Conditions: 4 M NaCl, pH 5.9-7.4, 1 m/s, <29 h.

Millimolal $[\text{SiO}_2]$: 11 in brine, 8.1 supersaturation at wall temperature.

Deposit: $\sim 10 \text{ mg/cm}^2$.

Fig. 30. Run 5DL silica deposit on bottom of Section 3, 33 cm from inlet (reduced 17%).

Conditions: 4 M NaCl, pH 5.9-7.4, 1 m/s, <29 h.

Millimolal $[\text{SiO}_2]$: 11 in brine, 8.7 supersaturation
at wall temperature.

Deposit: $\sim 8 \text{ mg/cm}^2$.

Fig. 31. Run 5DL silica deposit on bottom of Section 4, 2.5 cm from inlet (reduced 18%).

Conditions: 4 M NaCl, pH 5.9-7.4, 1 m/s, <29 h.

Millimolal $[\text{SiO}_2]$: 11 in brine, 8.8 supersaturation at wall temperature.

Deposit: $\sim 7 \text{ mg/cm}^2$.

Fig. 32. Run 5DL silica deposit on bottom of Section 4, 13 cm from outlet (reduced 18%).

Conditions: 4 M NaCl, pH 5.9-7.4, 1 m/s, <29 h.

Millimolal $[\text{SiO}_2]$: 11 in brine, 9.4 supersaturation at wall temperature.

Deposit: $\sim 3 \text{ mg/cm}^2$.

Fig. 33. Run 5DL silica deposit on bottom of Section 5, 13 cm from inlet (reduced 18%).

Conditions: 4 M NaCl, 5.9-7.4, 1 m/s, <29 h.

Millimolal $[\text{SiO}_2]$: 11 in brine, 9.5 supersaturation
at wall temperature.

Deposit: $\sim 3 \text{ mg/cm}^2$.

Operation with the Simulated Roosevelt Hot Springs brine was continued through four runs -7 through 10DL. Photos were taken after each run, samples were obtained by brushing and total deposits by brushing and chemical cleaning at various times as shown in Table 3. In these low concentration brine runs the scale formed tupples perpendicular to the flow direction with seemingly clear areas between the prominences. Rather than increasing the ripple size with time the frequency or number of such structures seemed to be increasing as indicated in Figs. 34-37. Such deposits are described further in Sect. VI, Thermowells.

It must be recognized, however, that these observations are very subjective as regards the observer's choice of photographs. For example, another area of pipe 3 after Run 7DL is shown in Fig. 38; the scale deposit is many times heavier than further down the pipe as shown in Fig. 34.

Surprisingly a return to higher concentration brine at high pH in Run 11DL (1M NaCl, pH 7.85) produced no greatly accelerated scale accumulation as might have been expected from the 2DL-D experience. Sections 4 and 5, which were thoroughly cleaned prior to Run 11DL, nucleated spontaneously -- or were seeded by material transported from the preceding sections -- and produced scale like that from the low concentration, high pH brine, Figs. 39-41. In the segments which were not cleaned (a drop in silica concentration in the last part of Run 10DL resulted in the scale in Section 1 being partially re-dissolved) the slow increase in scale formation with the same low concentration rippled pattern also continued in spite of the more aggressive conditions, Figs. 42-45. With the pipes already scaled previously it was presumed the rate of growth would be very rapid but this was not the case.

D. Amounts of Silica Deposited

The amounts of silica deposited are tabulated in Table 3 and the average rates of deposition per hour shown in Table 4 and Fig. 46. The amounts per cm^2 and per cm^2 per hr are based on a demonstrably

Fig. 34. Run 7DL silica deposit on left side of Section 3, 15 cm from inlet.

Conditions: 0.08 M NaCl, pH 7.9, 1 m/s, 185 h.

Millimolal $[\text{SiO}_2]$: 8.0 in brine, 3 supersaturation
at wall temperature.

Deposit: friable.

27 X

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Fig. 35. Run 7-8DL silica deposit on left side of Section 3, 25 cm from inlet.

Conditions: 0.08 M NaCl, pH 7.9, 1 m/s, 290 h.

Millimolal $[\text{SiO}_2]$: 8 in brine, 3 supersaturation at wall temperature.

Deposit: friable.

Fig. 36. Run 7-9DL silica deposit on left side of Section 3, 25 cm from inlet.

Conditions: 0.08 M NaCl, pH 7.9, 1 m/s, 385 h.

Millimolal $[\text{SiO}_2]$: 8 in brine, 3 supersaturation at wall temperature.

Deposit: friable, $<1 \text{ mg/cm}^2$.

Fig. 37. Run 7-10DL silica deposit on left side of Section 3, 10 cm from inlet.

Conditions: 0.08 M NaCl, pH 7.9, 1 m/s, 475 h.

Millimolal $[\text{SiO}_2]$; 8 in brine, 3 supersaturation at wall temperature.

Deposit: friable, $\sim 2 \text{ mg/cm}^2$.

Fig. 38. Run 7DL silica deposit on bottom of Section 3, 5 cm from inlet.

Conditions: 0.08 M NaCl, pH 7.9, 1 m/s, 185 h.

Millimolal $[\text{SiO}_2]$: 8.0 in brine, 3 supersaturation
at wall temperature.

Deposit: friable.

Fig. 39. Run 11 DL silica deposit on left side of Section 4, 41 cm from inlet.

Conditions: 1 M NaCl, pH 7.9, 1 m/s, 25 h.

Millimolal $[\text{SiO}_2]$: 8.9 in brine, 5.4 supersaturation at wall temperature.

Deposit: friable, 0.72 mg/cm^2 , $0.8 \text{ m}^2/\text{g}$.

Fig. 40. Run 11DL silica deposit on left side of Section 5, 10 cm from inlet.

Conditions: 1 M NaCl, pH 7.9, 1 m/s, 25 h.

Millimolal $[\text{SiO}_2]$: 8.9 in brine, ~ 6 supersaturation at wall temperature.

Deposit: friable, 0.9 mg/cm^2 , $0.8 \text{ m}^2/\text{g}$.

Fig. 41. Run 11DL silica deposit on left side of Section 5, 25 cm from inlet.

Conditions: 1 M NaCl, pH 7.9, 1 m/s, 25 h.

Millimolal $[\text{SiO}_2]$: 8.9 in brine, ~ 6 supersaturation at wall temperature.

Deposit: friable, 0.9 mg/cm^2 , $0.81 \text{ m}^2/\text{g}$.

Fig. 42. Run 7-11DL silica deposit on left side of Section 2, 25 cm from inlet.

Conditions: 0.08 m NaCl - 475 h, 1 M NaCl - 25 h, pH 7.9, 1 m/s, brushed after 385 h.

Millimolal $[\text{SiO}_2]$: 8.9 in brine, 1-3 supersaturation at pipe wall.

Deposit: friable, $\sim 0.8 \text{ mg/cm}^2$, $7.6 \text{ m}^2/\text{g}$.

Fig. 43. Run 7-11DL silica deposit on bottom of Section 2, 25 cm from outlet.

Conditions: 0.08 M NaCl - 475 h, 1 M NaCl - 25 h, pH 7.9, 1 m/s, brushed after 385 h.

Millimolal $[\text{SiO}_2]$: 8-9 in brine, 2-1 supersaturation at wall temperature.

Deposit: friable, 0.8 mg/cm^2 , $7.6 \text{ m}^2/\text{g}$.

Fig. 44. Run 7-11DL silica deposit on right side of Section 3, 25 cm from inlet.

Conditions: 0.08 M NaCl - 475 h, 1 M NaCl - 25 h, pH 7.9, 1 m/s, brushed after 475 h.

Millimolal $[\text{SiO}_2]$: 8-9 in brine, 3-5 supersaturation at wall temperature.

Deposit: friable, 0.7 mg/cm^2 , $3.5 \text{ m}^2/\text{g}$.

Fig. 45. Run 7-11DL silica deposit on top of Section 3, 10 cm from outlet.

Conditions: 0.08 M NaCl - 475 h, 1 M NaCl - 25 h, pH 7.9, 1 m/s, brushed after 475 h.

Millimolal $[\text{SiO}_2]$: 8.9 in brine, 3-5 supersaturation at wall temperature.

Deposit: friable, 2.2 mg/cm^2 , $3.5 \text{ m}^2/\text{g}$.

Table 3. Chronology of scale removals from heat exchanger sections after Runs 7-11DL

Run	Section 1	Section 2	Section 3	Section 4	Section 5
7DL	—	—	—	—	—
8DL	—	—	—	—	—
9DL	brushed out	brushed out	—	—	—
10DL	scale redissolved	—	brushed out	cleaned out	cleaned out
11DL	cleaned out	cleaned out	cleaned out	cleaned out	cleaned out

unwarranted assumption of uniform deposition. Thus in 2DL the borescope examination showed the deposition was heaviest on the bottom, consistent with the Once Through System observations.³ This is attributed to gravity enhancement of deposition of polymer "seeds" on the pipe bottoms. Even where the deposit was heaviest it usually was not uniform, see Figs. 17-20. Thermowells provided additional opportunities for obtaining measures of deposition, results are also shown in Fig. 46 and are further described in Sect. VI of this report.

Deposits on thermowells in Run 6DL are shown pictorially in Fig. 61 (Thermowell section). In general, the deposition trends with temperature are comparable to those observed for the pipe deposits, see Fig. 46. For Runs 2 and 6DL the rate of deposition on pipes and thermowells increased substantially with temperature whereas in Runs 7-10 and 11DL the reverse was true. The much lower rate and different trend in 11DL as compared with 2DL was particularly notable since 11DL was at a higher pH-7.9, vs. 6-where even more rapid deposition was expected. Other differences between the runs were: seeding with polymer before 2DL-D versus spontaneous nucleation of deposits in Run 11DL, fifty percent higher silica concentration in 2DL.

A somewhat surprising development was the observation of silica deposition in the reheat piping in spite of the high heat input ~ 3.3 kw/m and, consequently high pipe wall temperatures compared to the brine

Table 4. Silica deposition in dynamic loop runs

		2DL-D				5DL				6DL				7-10DL				11DL			
Heat Exchanger		Brine: 1M NaCl 14 millimolal SiO ₂ pH 6.0 29 hours				Brine: 4M NaCl 12 millimolal SiO ₂ pH 5.9 + 7.4 <29 hours ^g				Brine: 4M NaCl 11 millimolal SiO ₂ pH 7.0 13 hours				Brine: 0.08M NaCl 8 millimolal SiO ₂ pH 7.9 475 hours				Brine: 1M NaCl 9 millimolal SiO ₂ pH 7.9 25 hours			
Section	Thermowell	Surface Temperature °C	SiO ₂ Supersaturation (millimolal)	SiO ₂ Deposition (mg/cm ²)		Surface Temperature °C	SiO ₂ Supersaturation (millimolal)	SiO ₂ Deposition (mg/cm ²)		Surface Temperature °C	SiO ₂ Supersaturation (millimolal)	SiO ₂ Deposition (mg/cm ²)		Surface Temperature °C	SiO ₂ Supersaturation (millimolal)	SiO ₂ Deposition (mg/cm ²)		Surface Temperature °C	SiO ₂ Supersaturation (millimolal)	SiO ₂ Deposition (mg/cm ²)	
				Total	per h ^b			Total	per h ^b			Total	per h ^b			Total	per h ^b			Total	per h ^b
1	1	164	3.5	37.3	1.3	128	7	11	>0.4	198	0.6	negl. ^c	—	146	-2	negl.	—	143	0.4	0.11	.006
	2									144	5.0	76	5.8	109	0.3	.32 ^d	.0008	102	3.4	<0.26 ^f	<.01 ^f
2		112	7.5	31.4	1.1	98	8	10	>0.4	161	3.7	70	5.4	123	0.1	.10 ^d	.0002	123	1.8	0.57 ^f	.02 ^f
	3									115	7.5	53	4.1	92	0.5	.28 ^d	.0007	91	4.0	<0.82 ^f	<.03 ^f
	4									127	5.8	40	3.1	97	1	negl.	—	100	3.4	4.1	.16
3	5	74	10	17.4	0.6	71	9.5	9	>0.3	127	5.8	60	4.6	97	1	0.96	.002	100	3.4	1.27 ^f	.047
	6									82	7.7	9	0.7	70	3	2.3 ^e	.005	71	5.1	<0.70 ^f	<.028 ^f
										79	8.0	10	0.8	74	3	6.10	.013	78	4.6	1.46	.054
4	7	54	11	4.9	0.34	49	10	4	>0.1	79	8.0	6	0.5	74	3	4.05	.008	78	4.6	1.28	.047
										51	9.1	9	0.7	51	4	3.0	.006	54	6.0	0.72	.029
	8									49	9.2	6	0.15	55	4	9.14	.016	57	5.8	1.09	.040
5	9	46	11.5	17.7	0.61	35	11	3	>0.1	49	9.2	2	0.15	55	4	5.54	.011	57	5.8	<0.93	<.034
	10									33	9.7	6.5	0.5	37	5	2.47	.005	41	6.5	0.99	.040
										32	9.8	2	0.15	42	5	4.64	.009	41	6.7	<0.44	.016

^aData are average values for indicated component.
^bAssuming constant, uniform deposition.
^cNegligible
^dEstimated assuming total amount was twice that brushed out after Run 9DL; appeared reasonable from borescope examination and other brushing results.
^eEstimated assuming total amount was twice that brushed out after Run 10DL; appeared reasonable from borescope examination and other brushing results.
^fData include scale built up in earlier runs.
^gTime was probably much less than this, perhaps <5 h.

Fig. 46. Average silica deposition "rate" vs wall temperature.

temperature. Estimated silica deposited in Runs 2, 5, and 6 respectively, were 43g, 24g, and 83g, comparable with total amounts in the heat exchangers. After Run 11DL the reheat piping was dismantled and 5 separate 2.44 m sections were examined with the borescope and brushed out. The first and second sections contained significant amounts of fluffy looking scales not particularly like those in the heat exchanger pipes after Run 11DL. The amount deposited was appreciably smaller at the outlet of section 2 and none was visible in the remaining sections. Brushing removed all the silica deposits indicating they were softer and less adherent than in the heat exchangers where ~35% was removed from the two coolest sections. Borecope photos, Figs. 47 and 48, taken near the inlets to sections 1 and 2, show in situ deposits; amounts removed were 1.35g and 1.11g, respectively, comparable with amounts found in sections 4 and 5 of the heat exchanger.

The deposition patterns in the heat exchanger were not comparable with predictions of the formulation developed in our column kinetic studies probably due to complex and varying influences of the large surface areas of the deposit. Interestingly, the amount of deposit was both positively and negatively related to the degree of supersaturation.

E. Hardness

Physical — samples of deposits were sought after all runs, but retrieval was substantially influenced by the coherence and adherence of the scale. Thus, the scales formed in all heat exchanger sections in Run 2DL-D were so hard that only very small quantities could be scraped out with various probes. The scale formed in 6DL was somewhat more variable. A close fitting drill bit removed 191 mg from the Pipe 1 outlet and 100 mg from the Pipe 2 inlet. The drill was quite ineffective in obtaining samples from Pipe 2 outlet or from pipes 3 and 4. A fluffy, hygroscopic sample was easily obtained from the outlet of pipe 5. Small samples were obtained from the resistant areas by scraping with sharp probes and collecting with a suction tube.

Fig. 47. Runs 7-11DL silica deposit on bottom of first reheater section
38 cm from inlet.

Conditions: 0.08 M NaCl - 475 h, 1 M NaCl 25 h, pH 7.9,
1 m/s.

Deposit: fluffy and friable, 2.8 mg/cm^2 .

Fig. 48. Runs 7-11DL silica deposit on top of second reheater section
38 cm from entry.

Conditions: 0.08 M NaCl - 475 h, 1 M NaCl - 25 h, pH 7.9,
1 m/s.

Deposit: fluffy and friable, 2.3 mg/cm^2 .

The deposits from the low concentration brine were generally quite friable and appreciable amounts were removed by pushing a test tube brush through the pipes repeatedly. Surprisingly the deposits formed in pipes 4 and 5 during Run 11 also were of this friable type rather than the very hard material as was formed in Run 2DL-D. The soft, friable nature of these deposits is also illustrated in Fig. 49 where the scale is shown to have been crushed and smoothed by the passage of the borescope.

The percentage of the silica deposits removed by brushing are tabulated in Table 5 along with various deposition conditions. No patterns relative to wall temperature, brine concentration, or supersaturation concentration emerge. The data are included principally for record purposes.

Chemical — complete removal of the silica deposits from the heat exchanger section was accomplished by circulating alkali solution through the individual sections with a multihead tubing pump. Initially sodium carbonate solutions were investigated but they proved impractically slow in removing the refractory scales; they were useful as a final cleanup solution at high (200°C) temperatures for the entire loop system-connecting lines, letdown, particulates which got into the main loop system. Four molar sodium hydroxide at 75-80°C was tried next and gave satisfactory removal rates as shown in Fig. 50. Unfortunately, the very slow flows achievable with the tubing pump resulted in the diffusion from the laminar layer at the scale surface to the bulk solution being the limiting rate in the removal process, so information on the refractory character of the scales based on dissolution rates was not obtained.

F. Morphology

During the Once Through System³ studies it was observed that silica deposits formed predominately as spheroidal clusters as shown in Fig. 51. The basic units were approximately 1-2 μm in diameter at the higher

Fig. 49. Runs 7-9DL silica deposition of top of Section 2, 25 cm from outlet, borescope "tracks".

Conditions: 0.08 M NaCl, 385 h, pH 7.9, 1 m/s.

Millimolal $[\text{SiO}_2]$: 8 in brine, 1.5 supersaturation at pipe wall.

Deposit: friable; $\sim 3 \text{ mg/cm}^2$, $7.8 \text{ m}^2/\text{g}$.

Table 5. Percent silica scale removed from heat exchanger pipes by brushing

Run	[Cl ⁻] M	pH	Section 1			Section 2			Section 3			Section 4			Section 5		
			Wall Temp. °C	Silica Supersat'n millimolal	%	Wall Temp. °C	Silica Supersat'n millimolal	%	Wall Temp. °C	Silica Supersat'n millimolal	%	Wall Temp. °C	Silica Supersat'n millimolal	%	Wall Temp. °C	Silica Supersat'n millimolal	%
2DL-D ^a	1	6	150	5	neg. ^b	100	9	neg.	64	10	neg.	50	12	neg.	42	12	neg.
5DL	4	7.1	128	3	neg.	98	5	neg.	71	6	neg.	49	8	neg.	35	9	c
6DL	4	7.0	134	3	neg.	114	4	neg.	87	6	neg.	56	8	neg.	40	9	c
7-9DL	0.09	7.9	—	—	—	86	2	>28 ^e	—	—	N.B. ^d	—	—	N.B.	—	—	N.B.
7-10DL	0.09	7.9	—	—	N.B.	—	—	N.B.	78	3	>75	58	4	60	41	5	38
11DL	1	7.9	—	—	—	91	7	>56	71	5	>61	54	6	33	41	7	42

^aSeeded by homogeneous polymerization.^bNegligible-brushing not tried since other approaches indicated hard, adherent scales; very small amounts might have been removed.^cScale samples removed easily by scraping, so brushing may have been effective also.^dNot brushed at that time.^e> means the operation was continued without chemically cleaning pipe, percent given was calculated using the amount of scale finally removed by chemically cleaning.

Fig. 50. Run 2DL heat exchanger cleanup under various conditions.

Fig. 51. Silica scale formed on Pyrex pipe in Once-Through System Run No. 1.

Conditions: 0.1 M NaAc, 1 M NaCl, pH 6, 12 millimolal SiO_2 (seeded).

(a) Deposition temperature, 146°C - 10,000x.

(b) Deposition temperature, 46°C - 28,000x.

temperatures and decreased to several tenths of a μm at the low temperatures. Initially it seemed surprising that similar structured deposits were formed on a variety of substrates (Pyrex, Ti, carbon steel, stainless steel) but this became reasonable when it was recognized that the deposits formed in those studies stemmed from polymers formed during shutdowns. The deposits found after Run 2DL-D showed similar structures in spite of the much higher flow rates (3 fps vs 3 fpm), see Fig. 52; again, initiation of deposition involved polymer formation during a shutdown. However, similar bulbous structures were also found after the runs involving spontaneous nucleation, see Fig. 53.

Figure 54a shows an area on a thermowell from Run 5DL where more platelike material is present but the relic spheroids present suggest this results from a filling in of the interstices between the spheroids. Figure 54b shows the deposit on the end of the same thermowell which was situated at the downstream end of the heat exchanger section so the flow impinged at this point; note the apparent beginnings of new spheroids on the surfaces of the larger bulbous formations; note also, the magnification required to bring out the structure. The formations in the subsequent lower concentration runs, with spontaneous nucleation, were generally made up of masses of smaller basic spheroidal units with less variation over the temperature range, Fig. 55.

Figure 56 shows the spheroidal deposits formed on thoria microspheres in packed column studies⁶ of silica deposition kinetics in another phase of this program. Photos a and b are head on and grazing shots of the original thoria surfaces and c and d are similar shots after coating with amorphous silica. Note the multiplicity of spheroidal formations in various stages of development. Additional photos of more heavily coated microspheres are shown in Fig. 57. Note the tendency to initiate new spheroids on formations approximately $1\ \mu$ in diameter. Also note the chips in photo in Fig. 53 which shows how the merged spheroids produce continuous deposits.

Where sufficient sample was available, surface areas were determined on the various deposits. These ranged from 0.8 to $32\ \text{m}^2/\text{g}$ as shown in Table 6. The table also shows similar measurements on some natural

Fig. 52. Run 2DL silica deposit in exchanger.

Conditions: 0.1 M NaAc, 1 M NaCl, pH 6, 14 millimolal SiO_2 , 1 m/s.

(a) $\sim 190^\circ\text{C}$, 1 millimolal SiO_2 supersaturation.

(b) $\sim 44^\circ\text{C}$, 11.5 millimolal SiO_2 supersaturation.

Fig. 53. Silica deposit from Run 6DL after spontaneous nucleation.
Conditions: 4 M NaCl, pH 7.0, 1 m/s, 124-100°C, 11
millimolal SiO_2 , 7 millimolal supersaturation.

ORNL-PHOTO 8043-80

Fig. 54. Run 5DL silica deposit on thermowell.

Conditions: 0.1 M NaAc, 4 M NaCl, pH 7.0, ~ 660 mg SiO_2/kg , 72°C .

(a) On body of thermowell.

(b) On end of thermowell.

Fig. 55. Silica deposit from heat exchanger Section 5 brushings.

Conditions: (10DL) 0.08 M Cl^- , pH 7.9, 1 m/s, $58-44^\circ\text{C}$,
8 millimolal SiO_2 , 4 millimolal SiO_2 supersaturation.

PHOTO 5048-79

Fig. 56. Thoria microspheres before and after coating with silica.

Fig. 57. Spheroidal amorphous silica deposits on thorium microspheres.
Conditions: 1 M NaCl, 0.1 M NaAc, 0.01 M NaHCO_3 , pH 7.8,
80→100→121°C.

Table 6. Surface areas (m^2/g) of various scale samples^a

Scale Source	Pipes					Natural ^b Scales
	1	2	3	4	5	
Runs 2DL-D (composite from pipes 1, 3, and 5)	—	—	3.8	—	—	
Runs 7-9DL	31.9	7.8	4.7	—	—	
Runs 7-10DL	—	—	4.7	2.2	2.2	
Run 11DL	—	7.6	3.5	0.8	0.8	
Edge of pond, Sinclair #4						1.0 (1.2) ^c
Fluid exit line of silencer at Cerro Prieto						1.0 (1.0)
Phillips Petroleum Company Well #5						0.8 (3.7)

^aFor the Dynamic Loop Runs the measurements were for brushings from the indicated pipes; in the case of 2DL the combined samples were scrapings.

^bChunks removed from loci indicated.

^cAfter leaching 1 h in distilled water at 100°C to remove salt.

scales before and after leaching in distilled water at 100°C to remove salt, indicated to be present by x-ray analyses in the SEM, with results in the same range as were obtained for our scales. These natural scales did not show the spheroidal morphology as shown in Fig. 58; scale from a reinjection pipeline (60°C) was reminiscent, however, in Fig. 59.

VI. Thermowells

Initially 6.4 mm O.D., 51 mm long thermowells, whose tips just reached the center line of the exit/entrance T's of the heat exchangers

PHOTO 8046-80

Fig. 58. Morphology of some natural scales.

(a) Pond edge, Sinclair #4.

(b) Silencer exit, Cerro Prieto.

Fig. 59. Morphology of scale from re-injection pipeline - 60°C, Philips Petroleum Co. Well #5.

were used; but these gave variable temperature responses so they were replaced with 3.2 mm O.D., 152 mm long wells. These wells provided opportunities for further observation of silica deposits, in the following the wells are designated by numbers as shown in Fig. 60. Note that odd numbers are always at heat exchanger section entrances and even numbers are at exits. Figure 61 shows the deposits on several thermowells after Run 6DL. Note the rapid decrease in the amount of deposit on the ends of the wells with decreasing temperature; the amounts on the cylindrical portions, however, remained approximately constant. This surface was in the relatively quiet annulus (0.76 mm thick) between the thermowell and the heat exchanger pipe extending from the T to the blind end flange. The deposits in these areas were usually much thinner than those on the ends and were also softer, Fig. 62. Figures 63-65 are enlargements of three of the heavily coated ends showing the complex coral-like morphology; note that the deposits formed are quite similar whether at the entrance or exit of a heat exchanger. Figure 66 is a further enlargement of the material shown in Fig. 65, again the basic spheroidal morphology is evident. In Table 7 the conditions at the several thermowells sites are summarized along with the gross weights of deposits found on each well. From visual examinations, photos of each well, and the weight pattern as the amount on the tip varied (#1, pipe 1 entrance, had no deposit on the tip) the weight on the cylindrical portion of each well was estimated; subtracting this from the gross weight gave a measure of the amount on the tip for each well. The tip area was roughly 0.5 cm^2 so doubling gave the weight of deposit per cm^2 on the tip, similar numbers are given in the last column of the table for the individual heat exchanger sections.

There is reasonable agreement in the amounts of silica deposited on the well tips and that on the heat exchanger pipes when compared at appropriate wall temperatures as shown in Fig. 46. Similar general agreement for deposition on thermowells and pipe walls was observed for the lower concentration runs (7-11DL) at high pH (see Fig. 46). These thermowell results confirm that the rate of deposition in these runs was higher at the lower temperatures and higher supersaturation ratios, contrary to the observation in the earlier runs.

ORNL-DWG 80-19704

Fig. 60. Heat exchanger reheat bypass-dynamic loop system.

PHOTO 8048-80

Fig. 61. Silica deposits on short thermowellls, Run 6DL.

Conditions: 4 M NaCl, pH 7.0, 11 millimolal SiO_2 .

Fig. 62. Silica deposit on short 6.3 mm O.D. thermowell #2, Run 6DL.

Conditions: 4 M NaCl, pH 7.0, 11 millimolal SiO_2 , 161°C ,
1 m/s in open pipe, supersaturation $[\text{SiO}_2]$: 4 millimolal.

Fig. 63. Silica deposit on end of short, 6.4 mm O.D. thermowell #2,
Run 6DL.

Conditions: 4 M NaCl, pH 7.0, 11 millimolal SiO_2 , 161°C ,
1 m/s in open pipe, supersaturation $[\text{SiO}_2]$: 4 millimolal.

Fig. 64. Silica deposit on end of short, 6.4 mm O.D. thermowell #3, Run 6DL.

Conditions: 4 M NaCl, pH 7.0, 11 millimolal SiO_2 , 161°C,
1 m/s in open pipe, supersaturation $[\text{SiO}_2]$: 4 millimolal.

Fig. 65. Silica deposit on end of short, 6.4 mm thermowell #4, Run 6DL.
Conditions: 1 M NaCl, pH 7.0, 11 millimolal SiO_2 , 127°C ,
1 m/s in open pipe, supersaturation $[\text{SiO}_2]$: 6 millimolal.

Fig. 66. Silica deposit on end of short, 6.4 mm thermowell #4 enlarged to show spheroidal morphology.

Conditions: 4 M NaCl, pH 7.0, 11 millimolal SiO_2 , 127°C, 1 m/s in open pipe, supersaturation $[\text{SiO}_2]$: 6 millimolal.

Table 7. Estimated amounts of silica deposited on ends of thermowells in Run 6DL

Conditions: 4 M NaCl, pH 7, 11 millimolal SiO₂

Thermowell Number	Pipe	Flow	Temp. °C	Sol'y Amorph. SiO ₂ millimolal	Satur'n Ratio	Gross wt. SiO ₂ Deposit mg	Estimated ^a wt. SiO ₂ on end of well		Dep. in Heat Exchanger mg/cm ²
							mg	mg/cm ²	
1	1	Entrance	198	10.2	1.1	19.6	—		76
2	1	Exit	161	7.2	1.5	75.4	110		
3	2	Entrance	161	7.2	1.5	56.3	70		53
4	2	Exit	127	5.2	2.1	39.8	40		
5	3	Entrance	127	5.2	2.1	40.8	60		9
6	3	Exit	79	3.0	3.7	15.8	10		
7	4	Entrance	79	3.0	3.7	15.3	6		9
8	4	Exit	49	1.8	6.1	2.2	2		
9	5	Entrance	49	1.8	6.1	90.1	2		6.5
10	5	Exit	32	1.2	9.2	20.6	2		

^aAmount on cylindrical portion of well estimated from photos and subtracted from gross weights.

Examples of the scales formed in the low concentration runs are given in Figs. 67 and 68 showing several wells after exposure in Runs 7-10DL. The scale formed in ripples transverse to the flow direction along the well barrels at both exits and entrances to the heat exchangers. Elongated craters built up at impingement areas opposite entry pipes (odd numbered wells) but left bare Vs on the bottom of the well opposite the entry. Similar V's were formed on the tops of the wells where the brine exited at the bottom of the pipe (even numbered wells), but on the side of the well facing the exit pipe a bare spot remained. Figures 69 and 70 shows enlarged pictures of such areas at an earlier stage in their development — wells 7 and 10 after Run 8DL.

Figures 71 and 72 show the ripple deposits produced in Run 11DL; quite different than the thick deposits formed with seeding in Run 2DL. As shown in Fig. 46, the rate of deposition was $\sim$ two orders of magnitude less in 11DL than 2DL.

A long well was exposed at position 5 (at entry) in Run 5DL. As shown in Fig. 73, the impingement and opposite areas show patterns similar to those observed in the high pH runs. The deposit along the well, while rippled, is more continuous perhaps accounting for the very much more rapid growth in Runs 5 and 6DL. (The smoothed areas were produced in removal and handling the well.) Some ripples were observed on the pipe surfaces in Run 5 and 6DL (Fig. 21, 22, and perhaps 29-31) but were not evident in heavier deposition areas; again suggesting deposition may initiate as ripples.

VII. Discussion

Simulation of Geothermal Systems (Synthetic Brines and Laboratory Equipment)

The brines in this study were prepared from reagent chemicals with a restricted number of components in an attempt to simulate natural brines and study the dynamics of silica growth from supersaturated brines under controlled conditions of composition, temperature, and hydrodynamics. The apparatus was constructed of titanium because of its corrosion resistance under the conditions of interest.

NO. 7, 72°C [3]*, FLOW —

NO. 8, 50°C [4], FLOW —

NO. 9, 50°C [4], FLOW —

NO. 10, 41°C [5], FLOW —

Fig. 67. Rippled silica deposits on long, 3.2 mm O.D. thermowells, Run 10DL.

Conditions: 0.08 M Cl^- , pH 7.9, 8 millimolal SiO_2 , 1 m/s in open pipe.

[] supersaturation [SiO_2]-millimolal.

Fig. 68. Rippled silica deposits on long, 3.2 mm O.D thermowells, Run 10DL. Wells rotated 180PC compared to Fig. 67.

Fig. 69. Enlargement of impingement area of long, 3.2 mm thermowell #7 from Run 8DL.

Conditions: .09 M Cl^- , pH 7.9, 9 millimolal SiO_2 , 72°C, 1 m/s in open pipe, supersaturation $[\text{SiO}_2]$: 4 millimolal.

ORNL-PHOTO 2681-80

Fig. 70. Enlargement of "impingement" area of thermowell 10 from Run 8DL.

Conditions: 0.09 M Cl^- , pH 7.9, 9 millimolal SiO_2 , 41°C ,
1 m/s in open pipe, supersaturation $[\text{SiO}_2]$: 4 millimolal.

Fig. 71. Rippled silica deposits on long, 3.2 mm thermowell #4, Run 11DL.
Conditions: 1 M NaCl, pH 7.9, 9 millimolal SiO_2 , 104°C,
1 m/s in open pipe, well 3.2 mm O.D., supersaturation
[SiO_2]: 3 millimolal.

Fig. 72. Rippled silica deposit on long 3.2 mm thermowell #8, Run 11DL.
Conditions: 1 M NaCl, pH 7.9, 9 millimolal SiO_2 , 58°C ,
1 m/s in open pipe, well 3.2 mm O.D., supersaturation
[SiO_2]: 5.5 millimolal.

Fig. 73. Silica deposit on impingement area of long 3.2 mm thermowell #5, Run 5DL.

Conditions: 4 M NaCl, pH 5.9-7.4, 11 millimolal SiO_2 ,
1 m/s in open pipe, supersaturation $[\text{SiO}_2]$: 7 millimolal.

The validity of our simulation of field operation was demonstrated by two results: the close correspondence between the rippled scales formed in Runs 7-11DL and those observed by Gudmundsson et al⁵ and the associated heat transfer effect, and the surface areas and textures of the deposits consistent with those found for natural scale samples obtained in the field. An interesting sidelight of our results is the demonstration that the ubiquity and complexity of silica scaling is inherently a characteristic of silica supersaturated brines; other constituents like sulfides, calcite, etc., are not necessary adjuncts.

Gudmundsson and coworkers, as a result of a review⁷ of rippled deposition and their own studies, concluded that such deposition was the result of hydrodynamic enhancement of a "deposition driving force that is almost non-existent." This was clearly not the situation in our experiments where supersaturation ratios ranged to 9 in the coolest heat exchanger section. Further, studies of the kinetics of silica deposition in another part of the program⁶ clearly demonstrated that the rate of deposition is not diffusion controlled as is usually the case when hydrodynamic effects are observed.

Silica Surface Area

All the samples obtained from the heat exchangers showed quite high surface areas, as did the natural scales we examined (see Table 6). The kinetic studies⁶ showed that the area enters directly in the growth kinetics and thereby substantially increases the apparent rate of deposition. Thus, if you have a deposit of 1 mg/cm^2 with a surface area of $1 \text{ m}^2/\text{g}$, the potential active surface for silica deposition is $.001 \text{ g} \times 10^4 \text{ cm}^2/\text{g} = 10 \text{ cm}^2$ per cm^2 of pipe wall. In our runs this "enhancement" factor ranged from 8 for section 5 of Run 11DL to 860 for the scale formed in Run 2DL. Such a high value is not likely, however, since as the scale builds the specific surface area of the underlying scale presumably is reduced. On the other hand since diffusion is rapid compared to the deposition process, the accessible surface is all available for continuing silica deposition.

As a result the low molecular deposition growth rates postulated by Iler⁸ and Weres⁹ are increased by factors ranging from one to more than two orders of magnitude, and deposition of colloidal aggregates is not required to account for observed silica scaling rates.

Nucleation

Spontaneous nucleation occurred only under relatively severe conditions from the clean brines used in these studies. Results obtained are summarized in Table 8. They indicated that those factors which promote rapid homogeneous nucleation or polymerization (high pH and/or brine concentration) also favor initiation of deposition on clean exposed surfaces. Curiously, however, the supersaturation ratio, which is a very important parameter in homogeneous nucleation,¹⁰ did not appear similarly significant in our results. Supersaturation ratios for conditions at various locations are shown in Table 9. Note the surprisingly low values, less than 1.1, at which deposition initiated in Runs 7 and 11DL; also note that deposition apparently initiated simultaneously in all parts of the heat exchanger in spite of large variations in the supersaturation ratio. The similar amounts deposited on pipes and thermowells at comparable wall temperatures also indicated that the surface does not have to be a heat sink, that the existence of supersaturation is the significant factor. The formation of deposits at very low supersaturation ratios is surprising in view of the appreciable induction periods observed in polymerization studies,¹¹ but is consistent with the LLL observation¹² of silica deposit formation in their Total Flow nozzle tests with times in microseconds. The formation of deposits in the reheaters in the ORNL loop further substantiates the overriding importance of the simple existence of supersaturation.

The seeding of the heat exchanger surfaces by polymers formed during a shutdown and the subsequent very rapid growth of scale — more than an order of magnitude faster than with spontaneous nucleation — emphasizes the importance of flushing fresh brine out of a plant as part of the shutdown procedure. Such seeding was not always effective

Table 8. Observations of spontaneous nucleation in dynamic loop runs

[NaCl] M	pH		
	6.0	7.0	7.9
0.08	—	—	Yes
1.0	No	No	Yes
4.0	No	Yes	—

Table 9. Silica supersaturation ratios which resulted in spontaneous nucleation in dynamic loop runs

Heat Exchanger Section or Thermowells	Supersaturation Ratios		
	6DL	7DL	11DL
1	—	—	—
1	1.8	1.04	—
2	1.5	1.01	1.3
3	1.5	1.01	1.3
2	3.1	1.2	—
4	2.1	1.1	1.6
5	2.1	1.1	1.6
3	3.3	1.6	—
6	3.7	1.6	2.0
7	3.7	1.6	2.0
4	5.8	2.0	3.0
8	6.1	2.0	2.8
9	6.1	2.0	2.8
5	8.5	2.7	5.6
10	9.2	2.7	6.6

presumably because the polymers were scrubbed off the heat exchanger surfaces by the flowing brine in subsequent operations; however, the varying flow conditions in an operating plant would provide more opportunities for successful seeding. In another system with low (1 m/min) flow rates rapid scale formation was observed after less than an hour of stagnant polymerization.

The deposits formed in the high pH runs were quite unexpected. Based on previous observations very rapid scale formation and growth were expected, particularly in Run 11DL (1M NaCl, pH 7.9). Instead, the deposition rates were more than an order of magnitude less than those observed in 2DL in spite of the fact that the first three heat exchanger sections had been pre-scaled in previous operations. Sections 4 and 5 nucleated and appeared to grow at rates comparable to the first three sections. Also, the rippled character of the deposits was a surprise but provided confirmation of the enhancement of heat transfer which had been hypothesized after the heat transfer observations in Run 6DL. The heat transfer results confirm that lower scale buildup in the high pH runs (7DL-11DL) is due to the sparse nucleation and localized rather than uniform buildup.

Amounts Deposited

A somewhat surprising result was the demonstration of the significant effect of the mode of nucleation on the amount and distribution of silica deposition in the lower brine concentration runs. Thus, nucleation by homogeneous polymerization during a shutdown resulted in much heavier deposits than those obtained with spontaneous nucleation during operation. Also, with polymer seeding the amounts deposited were inversely proportional to the degree of supersaturation whereas the reverse was true with spontaneous nucleation. The very high brine concentration run (6DL) showed the inverse supersaturation dependence and heavy deposition in spite of spontaneous nucleation, perhaps because relatively continuous nucleation comparable to polymer seeding is encountered under these extreme conditions.

The substantial importance of nucleation on deposition suggests the possibility that silica scaling of equipment surfaces might be reduced by nucleation inhibitors which would coat such surface.

Morphology

The many circumstances under which the deposits formed as spheroidal clusters suggested that this morphology is a characteristic growth habit of amorphous silica rather than resulting from the cementing together of deposited spheres formed in solution by homogeneous polymerization. Thus spheroids were formed under a wide variety of solution composition and flow conditions, even at very low supersaturation ratios where polymerization would initiate very slowly. The deposits on thorium microspheres (Figs. 56 and 57) showing spheroids in various stages of development clearly shows such morphology is the result of in situ growth.

The spheroids generally appeared to grow to the order of 1 μm diameter, another spheroid then nucleated at some point on the surface and the process repeated indefinitely. Investigators of silica sphere formation¹³ during polymerization from solution have suggested spheres are formed through retraction of relatively expanded coils by intramolecular reaction between SiOH groups with the formation of the most thermodynamically stable form. It is not clear that a similar mechanism would hold for monomer deposition on a surface. It is also not clear why an amorphous material should show spheroidal morphogenicity; however, similar tendencies have been observed with other polymerizing species.¹⁴

During 185 h in Run 7DL the first heat exchanger section ran at a maximum supersaturation concentration (estimated cool end wall temperature used) of less than two millimolal silica. For 200 additional hours (7-9DL) the supersaturation concentration was less than one millimolal. According to Rothbaum and Rohde¹¹ silica polymerization at such low supersaturations would involve induction periods greater than 10 h whereas solution residence times (or more correctly traverse times) for the first heat exchanger section were less than 3 seconds.

On brushing the first heat exchanger section after Run 9DL appreciable silica deposit was removed in spite of the minimal supersaturation. Sparse deposits were even observed at the entry at appreciably lower supersaturation exposure. These results suggest that silica scale nucleation is possibly independent of the presence of deposited polymers as nucleation sites; that is, that the monomeric species in supersaturation is sufficient. The induction periods described by Rothbaum and Rohde suggest no polymerization in our entire heat exchanger-reheat system arguing that the deposition processes all stem from monomeric species rather than polymer-monomer interactions.

Acknowledgements

We acknowledge the helpful discussions with these colleagues of the Chemistry Division at Oak Ridge National Laboratory (ORNL): F. A. Posey, C. F. Baes, Jr., R. H. Busey, and W. L. Marshall. We also thank Frances L. Ball of the Physiochemical Analysis Group at ORNL for electron microscopy, L. L. Jones of the Y-12 Plant Micromeritics Laboratory for the surface area measurements, and J. T. Hutton of the Instrument and Controls Division for computer software. This research was sponsored by the Division of Engineering, Mathematical and Geosciences, Office of Basic Energy Sciences; and the Division of Geothermal Energy, Office of Resource Applications, U.S. DOE, under Contract W-7405-eng-26 with the Union Carbide Corporation.

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