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SILICA SCALING FIELD EXPERIMENTS

E.K. Mroczek and G. McDowell

Geothermal Research Centre, Chemistry Division,
D.S.I.R., Wairakei, Private Bag, Taupo, New Zealand.

ABSTRACT

The deposition of silica from geothermal fluid discharged from a high temperature New Zealand geothermal field was investigated at temperatures between 120 and 180°C. At these temperatures the corresponding silica supersaturation ratios were between 2.7 and 1.4. The fluid was passed through 25 mm diameter pipes and 150 mm diameter gravel beds at 3 and 30 l/min.

At 160 and 180°C before the onset of polymerization the deposition rate was uniform across the length of the pipes and beds and there was little difference between the two flows. At the lower temperatures where the silica was rapidly polymerizing there was a large reduction in the deposition rate between the pipe inlet and outlet and in the gravel beds a soft voluminous silica deposited right at the fluid inlet. There appeared to be no substantial enhancement of scaling rate due to the high polymer concentrations at 120°C and the deposition rate in the pipes appeared to be independent of flow rate.

INTRODUCTION

Development of a water dominated geothermal resource for power production may be severely constrained unless the problem of silica deposition from waste production fluid can be avoided or minimised. Deposition may occur in plant equipment, transmission pipelines, injection wells and in the rock formation. Steam separation and reinjection of geothermal fluid at a temperature greater than the amorphous silica saturation temperature will reduce scaling potential but may be wasteful in utilising the available energy.

The behaviour of silica in geothermal environments has been extensively studied but it is still difficult to predict the scaling tendency of any given brine. This is primarily because small traces of contaminants can significantly effect the rate of silica polymerization and deposition (Kindle et al., 1984). In addition quantitative

data on the effect of the many other factors, such as pH, temperature or silica supersaturation, which affect the silica deposition kinetics are only known at temperatures well below that usually encountered in geothermal situations.

These factors dictate that comprehensive site specific field tests need to be undertaken before designing any silica disposal or treatment process.

EXPERIMENTAL

Equipment

Fluid, after separation at the required temperature, was fed to a test manifold which distributed the fluid to two 150 mm diameter, 3.3 m long gravel (8 mm mesh) packed beds and two 25 mm diameter, 45 m long steam pipes. The layout is shown in figure 1.

The flow through each of the test units was controlled by globe valves. The fluid could be individually bypassed to a 350 mm diameter silencer where the flow could be measured by bucket and stopwatch. Each unit and the inlet manifold was lagged with foil covered fibreglass and the lagging joints were sealed by aluminium tape. Thermometer pockets and sampling valves were fitted to the inlet manifold and just prior to the discharge valve on each unit.

Method

Experiments 1, 2, 3 and 4 were nominally at temperatures of 180, 160, 140 and 120°C respectively. Inlet and outlet temperatures and pressures were monitored daily. Inlet temperatures usually varied by 3-4°C from day to day and conductive heat losses at the lower flow rate resulted in temperature differences between inlet and outlet of between 5 and 10°C.

At the conclusion of each experiment the 25 mm pipes were dismantled and 10 cm sections were cut at selected positions (seven in total). The deposited scale

Figure 1: Test Unit Layout

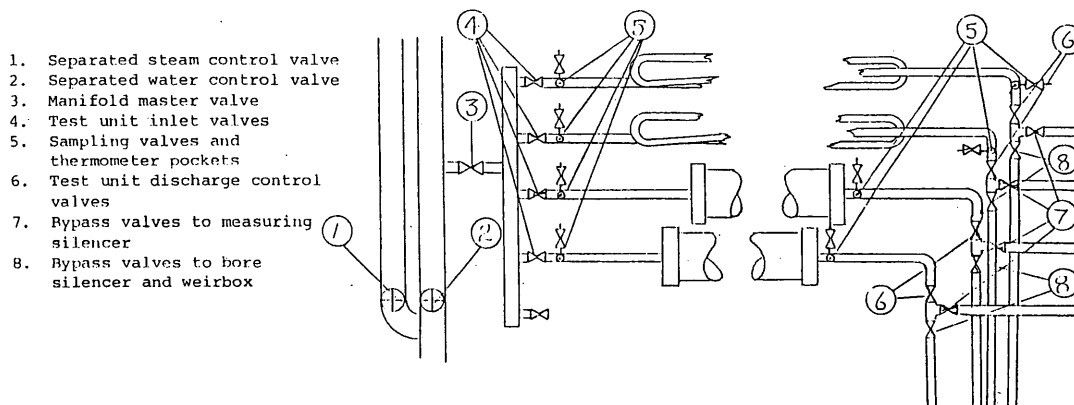
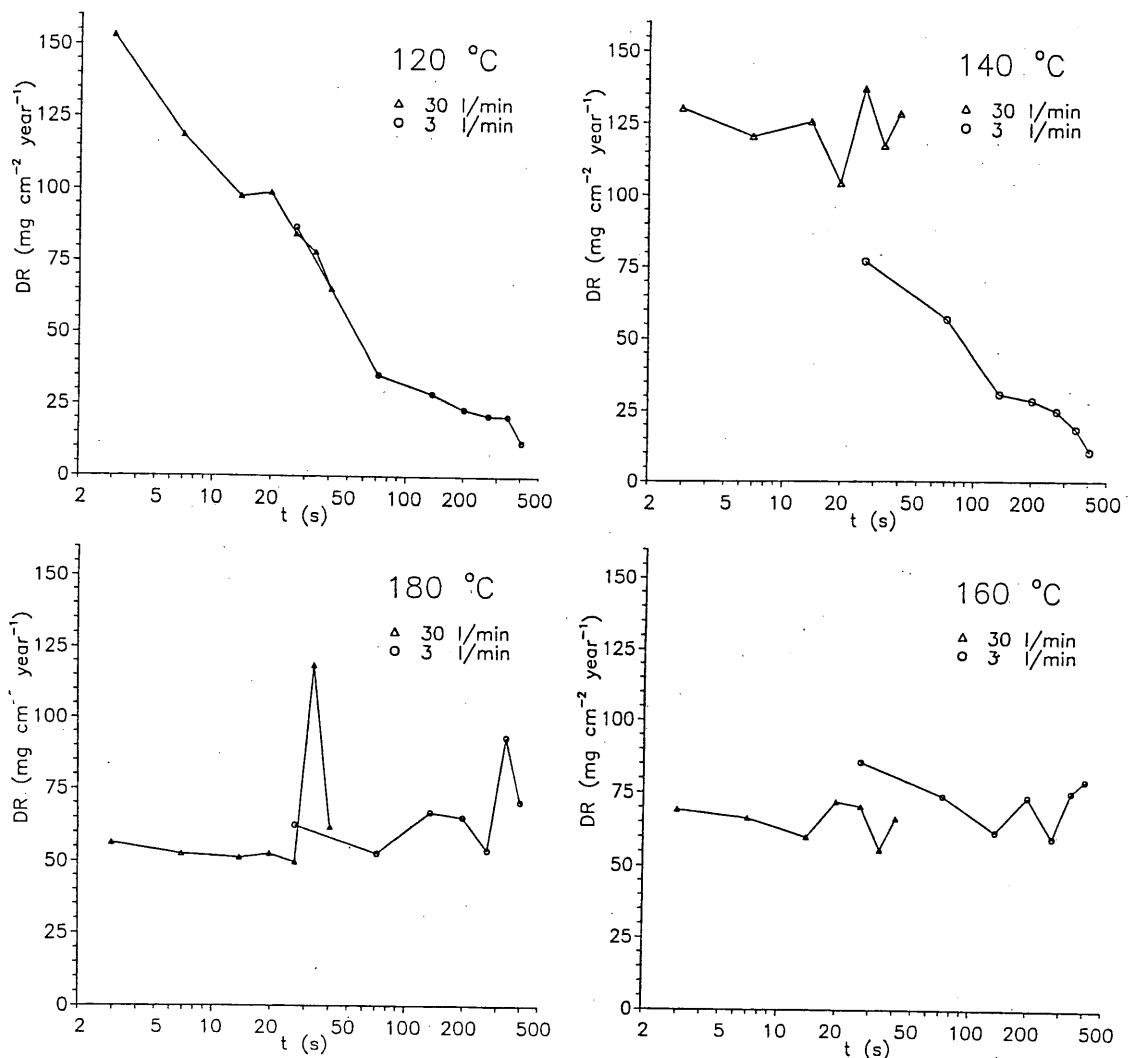


Figure 2: Deposition Rate Plotted against Fluid Residence Time



was scraped off each section and the silica content determined. The amount of silica deposited on the known surface area of the pipe section enabled the silica deposition rate to be calculated.

The 150 mm diameter pipes were filled with washed 8 mm mesh dacite chip which had been saturated by soaking in water for 1-2 weeks. The weight of the pipe and gravel 'full of water' and 'drained' was determined before and after each experiment (except for experiment 1).

Analytical

Inlet and outlet fluid samples were collected a number of times during each experiment and analysed for total silica (preserved by a 1:10 dilution with an NaOH/NaEDTA mixture), monomeric silica and chloride. Chloride concentrations were determined by titration with silver nitrate to a chromate endpoint (Mohr method). Total silica concentrations were determined using atomic absorption spectroscopy (AA) while monomeric silica concentrations were determined spectrophotometrically using the well known molybdate method (Iler, 1979). The concentration of molybdate active silica determined using this test was assumed to be equal to the concentration of monomeric silica. A sample for the monomeric silica analysis was collected at temperature in an insulated stainless steel vessel of about 1 ml capacity. After collection the sample was immediately transferred through a cooling coil into about 50 ml of acid reagent. Simultaneous dilution and acidification effectively suppressed any further polymerization before final analysis.

Problems and Estimated Errors

Reduction in flow rate due to silica fouling in the outlet control valves was the most persistent experimental problem. The valves controlling the 3 l/min flow were barely open and so were affected the most. This at times resulted in a reduced flow usually down to 1-2 l/min but in some instances the flow was completely stopped. Because of this difficulty flow rates were measured and if necessary adjusted once or twice a day during the duration of the experiment.

The estimated error in the total silica analyses, based on quality control standards and known solutions included with the samples on each analytical run, was 2-5%. The variation in the analysed silica concentration of the weirbox samples (with no sample collection problems) was in many cases greater than 5%. Total chloride analyses were performed with the sole function of checking for changes in fluid chemistry which could account for the silica variations. The chloride analyses were, within each experiment, consistent with each other and show the difficulty of obtaining good repeatability in the silica measurements at these high

silica concentrations.

The samples collected for the monomeric silica determination became less gassy with decreasing temperature and this resulted in better repeatability in the results. Each result was averaged over 2 or 3 determinations and the error was estimated to be 5-10%.

The estimated error of 10-15% in the deposition rate in pipes 1 and 2 was based on the actual recovery of silica in the digestion procedure, final analyses by AA, and incomplete scraping. This latter error was estimated from scraping two adjacent pieces.

Weighing of the gravel beds to determine the amount of silica deposited was not as successful as had been anticipated because the absolute amount of silica deposited was small (<0.5 to 5 kg) in relation to the weight of the bed filled with gravel and water (total weight about 230 kg). Even though there was a large uncertainty on the weights obtained by difference, the calculated densities of the deposited silica were all about 2 g/cm³, which is of the same order as that for vitreous amorphous silica (2.2 g/cm³). This agreement gave some confidence in the weighing method.

RESULTS

1. Total Silica Measurements

At all temperatures and flows there was less than a 0.8% change in measured total silica concentration between the inlet and outlet of all the units. The maximum observed difference was greater than that calculated from the greatest amount of deposition but the change was well within the estimated sampling and analytical errors. Table 1 lists typical total and monomer silica concentrations.

Table 1. Typical Total and Monomeric Silica Concentrations

Temp. (°C)	Total Silica* (ppm)	Saturation Ratio†	% polymerized inlet outlet	
180	1104	1.4	0-2	0-2 all units
160	1114	1.6	0-5	0-5 "
140	1186	2.0	30‡	44-48 3 l/min 33-38 30 l/min
120	1250	2.7	29-30	50-53 3 l/min 33-41 30 l/min

* No change (within error) between total inlet and outlet concentrations

† Corrected for ionization, calculated assuming all the silica is present as monomer.

‡ 11% with "normal" level in separator

2. Monomeric Silica Measurements:-

a. At 180 and 160°C

The change in monomeric silica concentrations at 180 and 160°C between the inlet and outlet was within the estimated experimental error (5-10%) for all the units. Although the fluid was supersaturated with silica it appears that at these temperatures the induction time before commencement of polymerization was longer than the maximum residence time in the pipes and gravel beds (407 seconds).

b. At 140°C

The experiment at 140°C ran into severe difficulties. At this temperature the mass of waste water and steam from the separator was greater than the capacity of the pipes carrying the waste fluid to the silencer. As a consequence a normal fluid level in the separator could only be maintained with difficulty. About midway through this experiment the adjustment of the water level was abandoned and the separator was run in a flooded condition.

At a normal separator water level the inlet monomer and total silica concentrations were within 10% of each other while in a flooded condition the concentration of monomer was lower by about 30%. Adjustment to a normal water level was accompanied by a rapid change (1-2 minutes) in fluid turbidity from milky to clear, which indicated a substantial alteration in the colloid size. These factors suggest that the difference in fluid residence time between "normal" and "flooded" levels was of the same order as the induction time before rapid polymerization.

The outlet monomer concentrations at 3 l/min were about 650 ppm (silica solubility about 580 ppm at 140°C and pH 7.3) irrespective of the inlet monomer concentrations. At 30 l/min the inlet and outlet monomer concentrations were similar in both units except in the last few measurements before the gravel bed blocked. In the latter case the outlet monomer concentrations were near the calculated silica solubility value at 140°C.

In this experiment the pipe carrying the 3 l/min flow was connected to the far end of the manifold. This configuration may have also affected the results as the increased fluid residence time in the manifold would have been significant in view of the very short induction time (\approx a minute) before commencement of rapid polymerization.

The deposition rates in the pipes and gravel beds at 140°C were difficult to interpret because of the experimental problems experienced at this temperature. The deposition results appeared to be a hybrid between

those observed at the high and that observed at the low temperatures. Whether this was a consequence of the experimental problems or of the pipe configuration could not be ascertained.

c. At 120°C

Modifications to the separator substantially increased the waste fluid mass flow and eliminated the problems experienced at 140°C. At this temperature the silica was substantially prepolymerised (30%) at the inlet manifold and there was little change in inlet monomer concentrations with separator level.

The outlet monomer silica concentrations were about 20% and 3-10% lower after passing through both the pipes and beds at the lower and higher flow rates respectively.

3. Silica Deposition in the 25 mm diameter Pipes

Table 2 lists the deposition rates in the pipes and Figure 2 shows the deposition rate plotted against fluid residence time at the different temperatures.

Table 2. Silica Deposition Rate* in 25 mm pipes (mg cm⁻² year⁻¹)

Expt #	1	2	3	4
Nominal Temperature (°C)	180	160	140	120
duration (days)	35	29	36	35
pH (calculated)	6.8	7.1	7.3	7.4
Pipe #1 3 l/min				
No.	Distance (m)	Time (s)		
0	2.7	27	62	86
1	7.1	72	53	74
2	13.5	137	67	62
3	20.0	202	65	74
4	26.9	272	54	60
5	33.8	343	93	75
6	40.2	407	70	79
Pipe #2 30 l/min				
0	2.6	3	56	69
1	7.0	7	53	66
2	13.4	14	51	60
3	19.8	20	53	72
4	26.7	27	50	70
5	33.7	34	118 [‡]	56
6	40.1	41	62	66

* Experimental Error \pm 15%

† Adjacent test piece 19 mg cm⁻² year⁻¹

‡ Adjacent test piece 100 mg cm⁻² year⁻¹

At 180 and 160°C there was no consistent trend for increasing or decreasing deposition along the length of the pipe and the deposition rate appeared to be about the same at both flow rates. There was no satisfactory explanation for the sharp increase in deposition rate at section number 5 at 180°C which was observed at both flows.

At 140°C and 30 l/min the deposition rate was about double the rate observed at the higher temperatures but also relatively constant along the pipe. However at 3 l/min the deposition rate was significantly lower and decreased exponentially with time. At 120°C there was also an exponential decrease in deposition rate with a good overlap in the data between the two flows at the same residence times. The deposition rates at 3 l/min were similar at both 140 and 120°C.

At all temperatures the deposited scale was hard and vitreous and difficult to remove. Magnetite (Fe_3O_4) was the only crystalline phase present in all the scale samples.

4. Deposition in the Gravel Beds:-

a. At 180 and 160°C

Table 3 lists the deposition rates in the gravel beds.

Table 3. Silica deposition in Gravel Beds* ($\text{kg}\cdot\text{year}^{-1}$)

Expt #	2	3	4
Nominal temperature (°C)	160	140	120
3 l/min	38	<9 [†]	11
30 l/min	43	78 [‡]	44 [§]

* total volume 0.06 m^3 , approximate porosity 48%

† below the precision of the weighing method

‡ based on 24.8 days duration

§ based on 16.5 days duration

At both flows a hard silica scale appeared to be uniformly deposited throughout the length of the gravel beds. About the same quantity of silica deposited at both flows at 160°C.

b. At 140°C

At 30 l/min a layer of loosely adhering flocculated amorphous silica deposited in the gravel at the bed inlet. The gravel bed was connected to the manifold by 25 mm steam pipe so that the fluid velocity at this point was much higher than in the main body of the bed. After this initial soft deposit the gravel chips were solidly cemented together throughout the bed to the outlet. At the lower flow rate a soft deposit also formed at the bed inlet. After this layer there was no

obvious silica deposition and the gravel chips were still loose inside the bed at the end of the experiment.

c. At 120°C

At this temperature the behaviour at 30 l/min was similar to that observed at the lower flow rate at 140°C, that is - a soft deposit at the inlet with no obvious silica deposited elsewhere in the bed. At 120°C and 3 l/min there was no silica deposited anywhere in the bed.

DISCUSSION

Previous Laboratory Work and Calculated Deposition Rates

Bohlmann et al.(1980) experimentally studied the deposition of amorphous silica at temperatures up to 120°C. In this study, at 120°C and residence times of 3 and 407 seconds, approximately 80% and 50% respectively of the total silica was present as monomer. Using these monomer concentration values in their equation gave calculated deposition rates of 206 and 18 $\text{mg cm}^{-2}\text{year}^{-1}$ at 3 and 407 seconds respectively. This compares with the experimental values of 153 and 12 $\text{mg cm}^{-2}\text{year}^{-1}$ (Table 2). The rate of molecular deposition at 120°C, calculated using the equations given by Weres et al. (1982) at the same residence times, gave values of 134 and 14 $\text{mg cm}^{-2}\text{year}^{-1}$ respectively.

Weres and Tsao (1981) reported scaling rates for silica deposition from synthetic brines at 95°C. As found in this work, their experimentally determined scaling results were at first high and then dropped off rapidly with time and distance along the tube. They observed that the decrease in scaling rate was roughly parallel to the decrease in molybdate active silica with time. The decrease in colloidal silica was not the cause of the rapid reduction in the deposition rate as only a small fraction of the colloidal silica that was formed in the brine was deposited as scale. They therefore concluded that the rate of molecular deposition must control the overall scaling rate under their conditions. However as the scaling rate was one or two orders of magnitude higher than the rate of molecular deposition they suggested that the mechanism involved the attachment of colloidal silica by electrostatic forces to the tube walls. The deposit was then made solid by molecular deposition of dissolved silica between the particles.

Deposition Behaviour in Present Work

Two different patterns of deposition behaviour were observed in the pipes between the high and low temperature ranges. At 180 and 160°C where the

monomer concentration remained constant, indicating that polymerisation was not occurring, there was no significant change in scaling rate across the pipes and gravel bed. In contrast, at 120°C, where substantial polymerization had occurred between the pipe inlet and outlet, there was a large reduction (92%) in the deposition rate. Although over 50% of the silica was polymerized at the outlet there appeared to be no tendency for substantial colloidal particle deposition.

At the higher temperatures deposition behaviour in the gravel beds was consistent with that observed in the pipes. A hard silica scale deposited uniformly throughout the length of the beds at 180 and 160°C. At the lower temperatures, where the fluid was assumed to contain a large proportion of colloidal particles, the silica deposited as a soft voluminous scale which rapidly blocked the beds. This form of silica deposited only at the bed inlets, the point of maximum velocity and turbulence. The absence of any silica deposit at 120°C and 3 l/min may have been the result of a lower turbulence. However, a soft deposit formed at 140°C at the same flow rate and this suggests that the nature of the depositing particles was also an important factor.

At 140°C at 30 l/min, where there was evidence of rapid silica polymerization, very high scaling rates were observed and there was almost double the amount of hard silica deposited throughout the bed than there was at 160 and 120°C. In addition a flocculated scale deposited at the bed inlet. It was not possible to tell whether two deposition mechanisms were operating concurrently because of the large fluctuations in monomeric silica concentration during this experiment. The high scaling rates were consistent with the presence of high concentrations of excess monomer and colloidal silica particles. In contrast, at 120°C the driving force for direct chemical deposition would have been limited by low monomer concentrations. In addition there would have been less monomer availability for cementing together the colloidal silica particles thus resulting in substantially reduced scaling rates.

In this work it was not possible to determine how closely the decrease in scaling rate paralleled the decrease in monomer concentration with time. However it is reasonable to suppose that the behaviour was similar to that found by Weres and Tsao (1981). As in their case, the reduction in scaling rate could not have been caused by the decrease in colloidal silica as there was very little change in total silica concentration between the pipe inlet and outlets. This suggests that in these experiments the scaling rate was controlled by the molecular deposition rate. However in contrast to their work the scaling rate was of the same order as the molecular deposition rate. This implies that the most likely scaling mechanism at 120°C was direct molecular deposition onto the pipe walls with only minor contribution from colloidal silica particles adhering to

the pipe walls and then being cemented by excess monomeric silica. The concentration of monomer above the amorphous silica saturation concentration at 120°C was still relatively high at about 43 and 13% of the total silica at 3 and 407 s respectively. It is unclear why the deposition rate was not significantly greater.

Jamieson (1984) rationalised the observed scaling rates in various field tests, where the observed scaling results for steam pipes were close to that predicted for monomeric deposition and did not appear to be greatly enhanced by the presence of a high concentrations of rapidly polymerizing silica, by assuming the formation of large colloidal particles (up to 500 nm). Particles of this size would have low velocity and inertia and in addition may be charge and size stabilised. A direct comparison with Jamieson's model could not be made because the size and number density of the particles was not known.

At the higher temperatures of 180 and 160°C where most of the silica was in monomeric form the deposition mechanism could only have been controlled by the rate of molecular deposition. The concentration of monomer was relatively constant which was reflected in the lack in any significant change in the experimentally determined deposition rates. Bohlmann's et al.(1980) equation although only valid to 120°C gave a calculated deposition rate at 180°C of 58 mg cm⁻²year⁻¹ which is, perhaps fortuitously is in agreement with the experimental data.

Other Field Experiments

A similar drop off in scaling rate was observed by Brown and McDowell (1983) in their investigations at Ohaaki well BR22. The experiments were designed to determine the effect of pH (pH=5 to 8, and 8 to 10) on silica deposition as well as the effect of aeration and ponding. Fluid at 100°C was held unaerated for various times and after the addition of acid or alkali, was passed at 3 l/min through insulated 25 mm steam pipes. At pH 7.0 where the silica deposition was highest and polymerization fastest the deposition rate decayed from 197 to 87, 69 and 52 mg SiO₂/cm²/year between sample positions 1 to 4 across the length of the pipe. After a suitable hold-up time, which allowed polymerization to be substantially complete, the deposition rate was found to be much lower and fairly uniform along the length of the whole pipe (22, 17, 18 and 15 mgms SiO₂/cm²/year between sample positions 1 to 4). The silica deposited as a hard vitreous coherent layer. Jamieson's (1984) analysis of Brown and McDowell's data showed that their scaling rates were also much lower than predicted.

Brown and McDowell's results were in direct contrast to previous work by Rothbaum et al. (1979) at well BR22 where it was found that polymerization had no effect on the quantity of scale formed and appeared

to only effect the character of the scale. Brown and McDowell ascribed the difference to low turbulence in their pipes which limited the rate at which colloidal particles could penetrate the boundary layer and deposit on the pipe walls. Presumably their results correlated with the scaling solutions in this work because turbulence effects were at a minimum.

CONCLUSIONS

1. Deposition in the 25 mm pipe runs at all temperatures was found to be related to the monomeric silica concentration. At 160 and 180°C, where the monomeric silica had not begun polymerizing the deposition rate did not significantly change across the pipes. At 120°C, where the silica was polymerizing the deposition rate rapidly reduced with time and distance across the length of the pipe. The deposition rate was not greatly enhanced at 120°C even with relatively high concentrations of both polymer and monomer. The data at 140°C was difficult to interpret because of the experimental problems experienced at this temperature. The results appeared to be a hybrid between those observed at the high and that observed at the low temperatures.
2. Flocculated colloidal silica deposited in the gravel bed only at the pipe inlet which was the point of maximum velocity and turbulence in the gravel bed.

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