THE EFFECT OF COLLOIDAL SILICA ON SILICA SCALING FROM GEOTHERMAL FLUID

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SUMMARY -Silica scaling experiments were undertaken at well BR20 in the Ohaaki geothermal field to determine the effect of colloidal silica on the deposition rate. Fresh geothermal fluid containing only monomeric silica was mixed in known proportions with aged geothermal fluid containing high concentrations of colloidal silica. The fluid was passed through 600 mm long 9 mm I.D. stainless steel tubes at 1 l/min. The total concentration of silica was approximately 730 ppm and the temperature of the mixed fluid ranged between 50 and 75°C. Scaling was found to increase to a maximum on reducing the fraction of monomeric silica to about 0.8 of the total silica concentration. At a fraction of 0.65 the weight of Scale deposited was approximately equal to fresh unpolymerized fluid (but of different morphology) while scaling was negligible at monomeric silica fractions of 0.5 and below. Surprisingly the scale deposited at monomeric silica fraction of 0.8 and below was soft and porous. At the a fraction of 0.85 the scale was compact but non vitreous. Vitreous silica was only deposited from fresh unpolymerized fluid.

1. INTRODUCTION

The deposition of silica from supersaturated geothermal fluid is a complex process. A qualitative understanding of the scaling mechanisms has been obtained by many field and laboratory experiments undertaken over the last 30 years (Kindle et al. 1984). The chemistry of silica in geothermal fluids has been succinctly summarized by Weres and Apps (1982). However being able to predict the extent of scaling in the field under a particular set of process conditions remains an elusive goal. Many factors (such as pH, degree of supersaturation, temperature, catalysis and nucleation site availability) appear to control the kinetics of deposition leading not only to differences in scaling behaviour between fields but also between wells in the same field.

Laboratory experiments by Bohlmann et al. (1980) indicated that there was little tendency for polymeric silica to deposit from solution containing both monomeric and polymeric silica. Weres and Tsao (1981) in a laboratory study concluded that monomeric silica deposition controls the overall scaling rate in polymerizing fluid. As the scaling rates in their experiments were one to two orders of magnitude higher than expected for molecular deposition they concluded that the mechanism involved attachment of colloidal silica to the tube walls followed by molecular deposition between the particles. In contrast Bohlmann et al. (1980) estimated that molecular deposition rates could be changed by one to two order of magnitude simply by changes in specific surface areas and colloidal aggregates were not required to account for the observed silica scaling rates in their experiments. Furthermore they also noted that the interlaced spheroids in a cemented matrix often seen in SEM photos of silica scale occur during deposition of monomeric silica. This implies that the presence of this morphology is not necessarily indicative of colloidal deposition.

Weres and Tsao's conclusions on the control of the scaling by monomeric silica deposition were also supported by recent field silica scaling experiments at Broadlands (Ohaaki) well BR22 (Brown and McDowell, 1983) and Rotokawa well RK4 (Mroczek and McDowell, 1990). In these experiments scaling in pipe runs decreased as the concentration of monomeric silica decreased. There did not appear to be any enhancement of scaling as the concentration of colloidal silica increased even at relatively high concentrations of both monomer and colloidal silica. However in both field experiments obvious colloidal silica deposition did occur where physical conditions allowed. For example in the Rotokawa experiments the impact of a fluid containing high concentrations of polymerized silica with a gravel bed resulted in very soft non adherent silica deposited at .the inlet of the bed. Bohlmann et al. (1981) also observed very rapid scale growth after seeding of heat exchanger pipe surfaces with stagnant brine.

Colloidal silica *can* and does deposit. However as the above few examples indicate the exact role of polymeric/colloidal silica in deposition from fluid where the monomeric silica is rapidly polymerizing is not clear. High scaling rates from fluid in which the monomeric silica had just begun to polymerize, *i.e.* containing low concentrations of colloidal/polymeric silica as in some of the Broadlands BR22 experiments, may simply reflect increased kinetics of monomeric deposition at the prevailing experimental conditions.

In this study at Ohaaki well BR20 an attempt was made to determine in a controlled manner the effect of colloidal silica on scaling. This was achieved by mixing known proportions of aged and fresh fluid and passing the mixture through test pipes. Residence times were such that there was no change in the fraction of colloidal and monomeric silica between mixing and after passing through the pipes. It was found that addition of colloidal silica had a marked effect on the quantity of scale deposited. The effect may have been exaggerated because the polymerized fluid was highly aged and would have contained large colloidal particles.

2. EXPERIMENTAL

2.1 Equipment

A diagram of the layout of the experimental apparatus at Ohaaki well BR20 is shown in Figure 1. Fluid from Ohaaki well BR20 was fed to a 200 mm diameter mini-separator. Separated water was carried a distance of approximately 10 meters to the mixing manifold in uninsulated 20 and 25 mm diameter schedule 40 steam pipes. The water was cooled in a 4 m long shell and tube heat exchanger (primary) to below 100°C and then if required the fluid could be further cooled in a smaller 1 m long heat exchanger (secondary). The control valve on the outlet of the secondary heat exchanger regulated the amount of fresh unpolymerized fluid reaching the mixing manifold. Excess water was carried from a tap between the heat exchangers to a 3 m^3 galvanized mild steel aging tank. The mixing manifold was a 25 mm diameter stainless steel pipe 150 mm in length. A flow spoiler was inserted in the pipe immediately upstream of the manifold to ensure adequate mixing of fresh and aged fluid.

The test units were connected to the mixing manifold by flexible rubber tubing and were insulated with fibreglass wool covered with aluminum foil. In experiments 1 to 5 two test units were 160 mm long glass tubes (15 mm I.D.) packed with glass beads and steel filings and two were 9 mm I.D. 600 mm long 316 stainless steel seamless polished tubes. In all later experiments the packed glass tubes were eliminated as these units blocked with silica at too fast a rate. The test units were reduced to three stainless steel tubes.

2.2 Method

The control valves on the separator and outlet to the primary heat exchanger were adjusted to obtain a separation pressure of 4 bg. Under optimum conditions the total flow of separated water was between 6 and 8 *l*/min. The required fraction of aged and polymerized fluid was obtained by adjustment of control valves at the tank and secondary heat exchanger outlets. The total flow through each test unit was adjusted and maintained at 1 *l*/min by pinching the flexible rubber connecting hose. The cooling water flow through the heat exchangers was adjusted to obtain final mixed fluid temperature of around 70°C.

Flows, temperatures and pressures were measured and adjusted as required every two days. The first 5 experiments ran for approximately 40 days while the remainder ran for 15 days. The fluid chemistry was measured at least once every 15 days but more in the event of unstable flow or temperature conditions.

The quantity of scale deposited was determined by drying and weighing the tubes.

2.3 Problems

The plan in these experiments was to maintain experimental conditions as uniform as possible within each experiment as well as between experiments. Changes in scaling could be then be directly attributed to the differences in silica chemistry rather than to other operational parameters. The major problem was obtaining sufficient flow of separated water, at times barely above the minimum requirement of 4 *l*/min. This problem was exacerbated by natural well cycling so that adjustments of total flow were soon incorrect. The main consequence of this lack of flow control was difficulty in maintaining steady water temperatures and mixing ratios. Changing the flow rate and temperature of fluid into the aging tank may also have affected the silica particle sizes in the aged fluid. Thirteen experiments were started but four were abandoned due to experimental difficulties.

3. RESULTS

Typical chemistry of the separated fluid is listed in Table 1. There was little difference between fresh and aged fluids except for loss of total dissolved carbonate and sulphide in the latter.

The results for the successfully completed experiments are listed in Table 2. All values listed in the table are average values except for the weight of silica deposited in the stainless steel tubes. The fresh fluid temperatures were adjusted to limit variations to less than 5°C while the flows through the stainless steel test units could only be controlled to between 0.8 and 1 *l*/min. Initial tests showed that the fraction of monomeric silica in the mixed fluid corresponded within analytical error to the flux of monomer measured in both the aged and fresh fluids. Only in one experiment, at 80% aged water, was the fraction of measured monomeric silica less than expected from the mass flows. The cause in this case was thought to be higher pressure from the aged water head lowering the flow of fresh water from the initial setting.

The data in Table 2 has been drawn in Figures 2-4. Figure 2 shows the percentage of silica deposited from the total silica passed through the tubes as a function of the amount of monomeric silica in solution. In Figures 3 and 4 the weight of silica deposited is drawn respectively as a function of the saturation index (monomeric silica concentration divided by equilibrium amorphous silica solubility) and the amount of monomer in solution. As a basis for comparison the weights of silica in Figures 3 and 4 have been normalized to a total mass flow of 20000 kg. Figure 4 also gives a description of the morphology of scale deposited.

On reducing the fraction of monomeric silica the scale morphology changed successively from vitreous → compact and uniform but density much less than vitreous silica → very soft porous uniform coating with striations parallel to fluid flow → very soft granular sparse coating. There was very little scaling at monomer fractions less than about 60%.

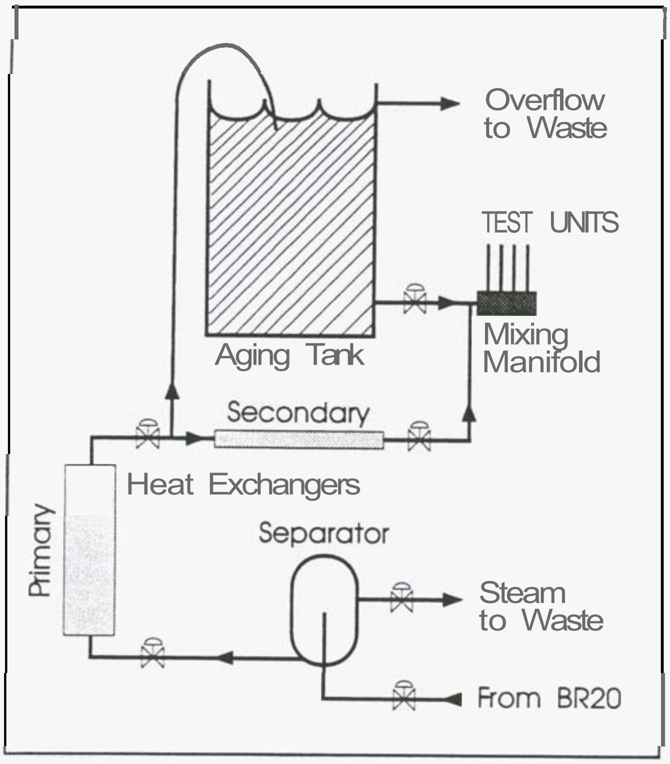

Figure 1 : Layout of Experimental Equipment

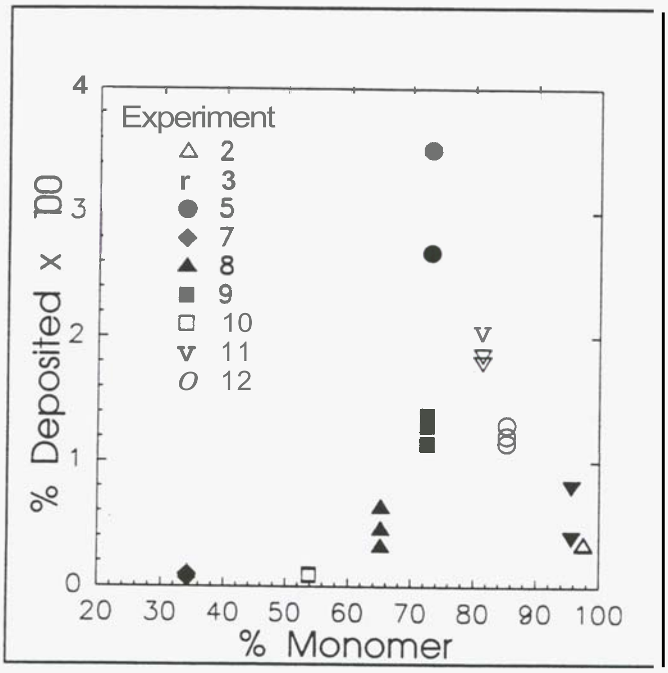

Figure 2 : Percentage of Silica Deposited vs. Amount of Monomeric Silica in Mixed Solution

The scale colour also appeared to change from dark to white on reducing the amount of monomeric silica. This was most likely a consequence of mixing higher ratios of aged fluid containing very little dissolved H_2S.

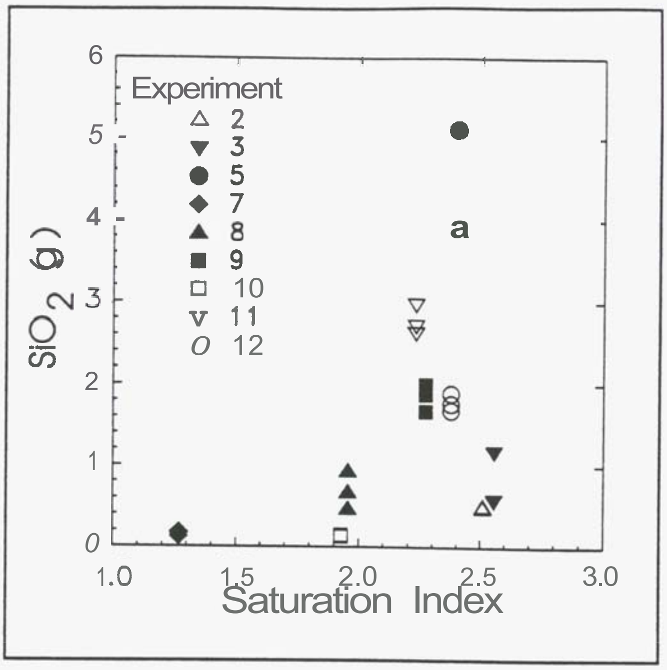

Figure 3 : Weight of Silica Deposited (Normalized) vs. Silica Saturation Index of Mixed Solution

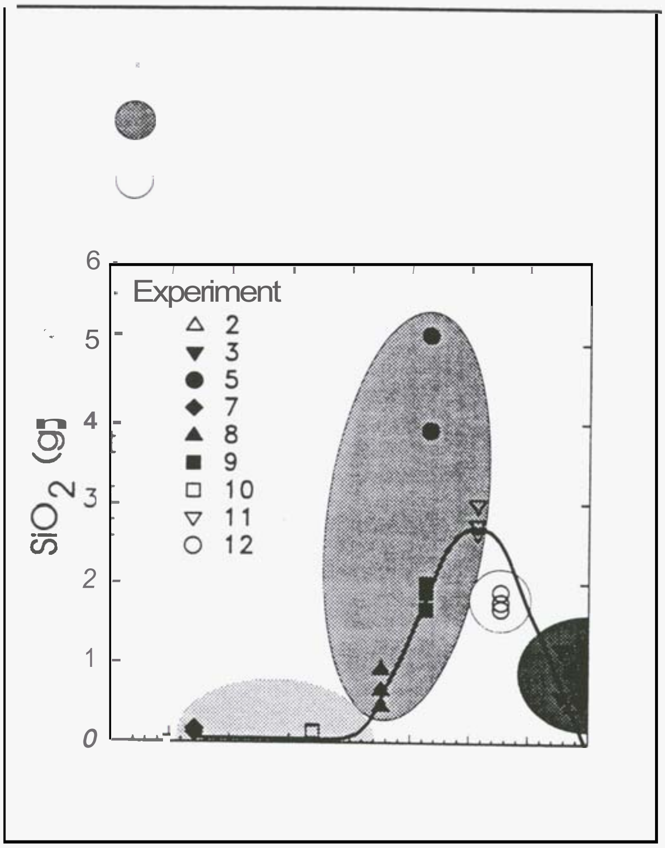

Figure 4 : Weight of Silica Deposited (Normalized) vs. Amount of Monomeric Silica in Mixed Solution

Except in experiments 3 and 5, the amounts of scale deposited in any experiment were reasonably consistent between the three tubes. In some but not all experiments there were slight differences in monomeric silica between the test units indicating inadequate mixing. It could not be

Table 1 : Typical Fresh and Aged Br20 Fluid Chemistry

	pH (at 16°C)	Li	Na	K	Ca	Mg	Cl (ppm)	SO_4	B	SiO_2	NH_3	HCO_3	H_2S
Fresh fluid	8.45	11.1	924	181	0.98	<0.01	1486	20	43.3	730	4.6	245	8.9
Aged Fluid	8.72	11.3	948	185	1.1	0.01	1528	21	43.7	730	3.8	224	1.0

NOTES

1. Except for pH all concentrations are in ppm.
2. SiO_2, NH_3, HCO_3, H_2S are total concentrations of these species

Table 2 : Monomeric Silica Concentrations and Deposition Results

Experiment	t(°C)	C_{Equil}	Mixed	%monomer	%Fresh solution	Saturation Index	Tube #1		Tube #2		Tube #3	
		Monomeric SiO_2 (ppm)					Flow (kg)	Weight (g)	Flow (kg)	Weight (g)	Flow (kg)	Weight (g)
2	72	253	635	98	100	2.5	36834	.9	37329	.9		
3	74	273	698	96	100	2.6	40777	1.2	39012	2.3		
5	59	222	534	73	63	2.4	21311	5.5	22176	4.3		
7	50	197	250	34	0	1.3	17998	.1	17949	.1	18865	.1
8	65	243	476	65	46	2.0	19394	.5	18654	.6	17578	.8
9	62	233	530	73	55	2.3	18462	1.7	18466	1.5	18054	1.8
10	54	204	393	54	13	1.9	18469	.1	18540	.1	17813	.1
11	70	266	594	81	81	2.2	18765	2.8	18632	2.5	18733	2.5
12	69	262	623	85	80	2.4	18293	1.6	18324	1.7	17992	1.5

NOTES

1. All values are averaged except weight of silica deposited.
2. Total silica concentrations were 730 ppm, except for Expt. 2 where the total silica was 651 ppm.
3. The monomeric silica concentration of the fresh fluid was usually about 5% lower than the total concentration.
4. Reynolds numbers for all experiments 4000-6400.
5. C_{Equil} is the equilibrium monomeric silica concentration with respect to amorphous silica.

determined whether this caused the scaling differences between the pipes.

The scaling rate in experiment 5 was much higher than in other corresponding experiments. In this experiment there were 4 test units connected to the manifold so that there would have been different amounts of fluid flowing to and from the aging tank. There were no other unusual experimental factors which could explain the results. The tube in experiment 5 which scaled about 20% more than the other had been previously used in experiment 3. In experiment 3 (only fresh fluid) the higher scaling rate was on a clean tube while the lower rate was onto tube which had been previously used in experiment 2. No repeat experiments were performed so it is not known whether the latter result was an abberation or due to a difference in initial scaling rate between the steel and silica surfaces.

The scaling results are preliminary in that the above interpretations may change when the scale is analysed and the tubes are cut open to better observe the morphology.

4. DISCUSSION

The results of these experiments clearly show the effect of monomeric silica on colloidal silica deposition. The maximum scaling rate occurred when 80% of the total silica was unpolymerized and then scaling rapidly reduced to negligible levels at monomeric silica proportions less than 60%. Surprisingly very soft porous silica was deposited at high monomeric silica fractions. Deposition of this type of silica from geothermal fluid is commonly observed where the fluid has been aged to convert excess monomeric silica to colloidal silica (Weres and Apps 1982). In these experiments it had been expected that the deposits should be very hard due to the cementation of colloidal aggregates with the large excess of monomer. At a proportion of 85% monomer a compact but non vitreous scale deposited. This implies that particle size to concentration of monomeric silica concentration is important determining scale morphology. The flow through the tube was not turbulent (Reynolds numbers less than 6400) so it is also possible a more compact Scale could have occurred at higher flow rates as has been observed by Rothbaum et al. (1979).

In the present experiments the factors which can affect the flocculation rate (such as pH, temperature, salinity, hydrodynamics) did not vary significantly between experiments. Therefore the deposition observed could be directly correlated to the concentration of monomeric silica. Mixing fluid containing unpolymerized monomeric silica with fluid containing colloidal silica particles should result in continued particle growth by molecular deposition of fresh silicic acid onto the aged particle surfaces. Homogeneous nucleation in solution would be unlikely under these conditions and nucleation of silica on the pipe Surfaces perhaps only favoured at the highest monomeric silica concentrations. Therefore it is likely that all the Scale is due to flocculation of suspended colloidal particles by the monomeric silica. Differences within analytical error could not be detected between the inlet and outlet total and monomeric silica concentrations because of the very short residence time in the manifold (< 5 seconds) and small amount of silica deposited as a fraction of the total concentration.

Laboratory studies (Fleming 1986 and references therein) show that the growth rate is proportional to surface area and excess monomeric silica above equilibrium solubility of amorphous silica (among other factors as discussed above). The consistent change in scaling on increasing the percentage of monomeric silica (perhaps excluding experiment 5) suggests that surface area is less important than concentration at large colloidal particle sizes. Particle size (and hence Surface area) could not be controlled in these experiments because of changes in flow and temperature of fluid entering the aging tank. Unfortunately particle sizes were not measured except for one set of results taken midway through experiment 8 using a Leeds Northrup Microtrac ultrafine particle size analyser. The measured particle size was 10 nm.

These experiments are qualitatively similar to the scaling experiments at BR22 and RK4 in which the silica was rapidly polymerizing. The same behaviour is observed, *i.e.* the amount of scaling decreases with a decrease in monomeric silica concentration. However in the present experiments the scaling rate first increased to a maximum when the monomeric silica concentration decreased to 80% (Saturation Index about 2.3) of the total silica. Most likely no scaling increase was observed in the Rotokawa study (Mroczek and McDowell, 1990) because at the manifold inlet the Saturation Indexes were 1.9 and 1.4 at 140 and 120°C respectively at a monomer fraction of 0.7. Similarly no increase in scaling was observed in the pipe runs in the Broadlands BR22 scaling work (Brown and McDowell, 1983 and K.L. Brown Pers. Comms.). The silica monomeric concentration in fluid fed directly from the separator was less than 75% of the total (Saturation Index about 2) at the manifold.

Experiments to determine the particle sizes of colloidal silica during polymerization and relating this to silica scaling rates is needed before any further progress can be made in predicting deposition under realistic field operating conditions.

4. CONCLUSIONS

1. The rate of silica deposition is greatly affected by the concentration of monomeric silica. This supports the scaling mechanism of colloidal aggregates adhering to pipe Surfaces rather than changes in molecular deposition kinetics.

2. The maximum deposition rate occurred at and when the monomeric silica concentration was 0.8 of the total silica. The morphology of the scale even at the highest deposition rate (and below) was soft and porous.

3. Particle size may not be as important to scaling as the concentration of monomeric silica.

5. ACKNOWLEDGEMENTS

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