COMPARISON OF AMORPHOUS SILICA DEPOSITION RATES MEASURED USING PACKED PIPES AND A FLUIDISED BED AT FPlO, WAIRAKEI

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SUMMARY – At Wairakei Flash Plant 10 a quartz sand fluidized bed and pipes packed with zirconia beads were used to measure amorphous silica scaling rates at temperatures between 70°C and 130°C. The residence times in the bed and pipes were shorter than the induction period required for silica polymerisation from solution. The rates measured in the fluidized bed were comparable to the rates measured in the packed pipes (12 to 20 mg cm^{-2} year^{-1}) except that scaling in the packed pipes at the highest temperature of 129 °C was unexpected. At this temperature the dissolved silica was calculated to be undersaturated with respect to amorphous silica. The precipitation of a less soluble scale enriched in aluminium may be the reason for this apparently anomalous result.

1. INTRODUCTION

Predicting the rate of silica scaling in geothermal reinjection wells and aquifers can extend their life by optimising fluid flows and temperature to achieve minimum precipitation compatible with the hydrogeological properties of the aquifer. Unfortunately predicting scaling rates in aquifers is difficult and with the present level of understanding experimental determination of deposition rates in individual fields are required to determine the scaling potential of a given geothermal fluid. This is because of unknown field-specific factors and power station operational requirements, which may influence the scaling rate.

In response to these difficulties we recently developed a field method for measuring deposition rates using a fluidized sand bed (Carroll et al., 1998). This technique allows measurements of amorphous silica precipitation rates to be made simply, rapidly and reliably. However, applying deposition rates measured in the fluidized bed to deposition in aquifers is difficult because of the complexity of modelling fluid transport simultaneously with reacting chemicals, in this case, dissolved silica (Weir and White, 1995, 1996; White, 1995). The aim of the present research was to compare the silica deposition rates in pipes packed with beads, which serve as model aquifers, with fluidized bed rates.

2. EXPERIMENTS

All the experiments were undertaken at Flash Plant 10, Wairakei Geothermal Field. A representative water analysis is given in Table 1. Separated water from the flash plant at 1.8 bg (approx. 130 "C) was cooled to the required temperature by passing through a heat exchanger and fed to the pipes or to the fluidized bed.

Table 1: Representative Wairakei **FPlO** Water Analysis (mg L^{-1}, except pH).

pH(@20°C)	8.61	Li	12.6
Na	1279	K	190
Ca	18.7	Mg	0.010
Rb	2.55	Cs	2.29
Al	0.33	Fe	<0.1
Cl	2068	SO_4	29
B	25.3	SiO_2	533
tNH_3	0.3	F	8
$tHCO_3$	<5	tH_2S	<1

Initially a shell and tube heat exchanger was used but this resulted in rapid blocking of the packed pipes in less than 1 week. The shell and tube's inner pipe was coated in a thick deposit of amorphous silica, which had built up over years of use. It is likely that small scale particles eroding from the heat exchanger wall were physically blocking the pipes and were also accelerating the direct deposition of silica because of the large surface area of the trapped scale. In subsequent experiments a compact plate heat exchanger was used which eliminated the problem.

The piping arrangement, methodology and preliminary results (using the shell and tube heat exchanger) of the packed pipe experiments were presented by Mroczek et al., (1997). Stainless steel pipes 25 mm in diameter, between 1 and 6 m in length, were packed with 1.2-1.4 mm diameter

Table 2. Summary of experimental conditions, t - inlet temperature, m_f - initial mass flow, d - pipe diameter, l - pipe length, M_t - total mass of fluid through the pipe, S_d - total weight of silica deposited in the pipes, S_d/M_t average amount of silica deposited per kg of fluid.

Pipe	t±sd/°C	m_f/ (kg min^{-1})	d/mm	l/m	M_t/kg	S_d/g	(S_d/M_t)/ (mg kg^{-1})
Experiment A, **33.5** days duration							
1	81±2	0.50	25	1	18724	10.8	0.56
2	79±2	0.27	25	1	5454	11.6	2.12
3	81±2	0.31	25	1	13031	10.5	0.80
4	130±2	0.30	25	1	12939	8.8	0.68
Experiment B, **30.8** days duration							
1	71±3	1.21	25	1	47725	19.7	0.41
2	71±3	0.53	25	1	21823	14.0	0.64
3	71±3	0.35	25	1	14483	12.5	0.86
4	129±1	0.31	25	1	12437	7.8	0.63
Experiment C, **28** days duration							
1	97±1	1.10	25	1	45138	8.5	0.19
2	96±1	0.48	25	1	19039	7.9	0.42
3	96±1	0.48	25	2	18921	15.2	0.80
4	129±1	0.36	25	1	15347	6.9	0.45

zirconia beads of geometric surface area **5.45** cm^2/g. The beads are chemically inert and stable in hot water to above **180 °C** over a wide pH range (**1** to **14**) and are low in silica (**<0.01** mg g^{-1} beads) so that the amount deposited from the geothermal fluid is easily determined. Geothermal fluid and heat exchanger cooling water flowrates were adjusted to achieve the required temperature while minimising the residence time in the pipes and bed. The quantity of silica deposited was determined by dissolving the silica in dilute hydrofluoric acid and analysing the washings using a UV spectrophotometer and the **yellow-β** silicomolybdate method (Iler, **1979**).

A fluidized sand bed reactor was also used to measure the deposition rate of silica. The reactor, which was based on a design by Axtmann and Grant-Taylor (**1986**), was previously used to measure amorphous silica deposition rates at FP10 using the same shell and tube heat exchanger which caused the blockages in the pipes (Carroll et al., **1998**). The reactor was loaded with **5.1** kg of quartz sand with a geometric surface area of **113** cm^2 g^{-1}. The technique and procedures followed were as described by Carroll et al., (**1998**) except that in these experiments the geothermal fluid was cooled using the plate heat exchanger.

3. RESULTS

3.1 Packed Pipes

A summary of the experimental conditions, mass flowrate and mass of amorphous silica deposited down in each of pipes is given in Tables **2** and **3**. The results of the fluidized bed are given in Table **4**.

In the packed pipes the deposition rate was slow and the silica did not significantly change the permeability of the packing over the duration of the experiments. In a few of the pipes there were abrupt drops in flow due to scale fragments and other fines blocking the inlet. Pressure drop measurements down the pipes (not shown) indicated that these fines, which originated upstream of the test pipes and which caused these flow reductions, penetrated less than **4** cm into the pipes.

The average amount of silica removed from solution in the pipes in these experiments is small, generally < 1 mg kg^{-1} **of** fluid (see Table 2), so that the concentration of dissolved silica is essentially constant between the inlet and outlet of the pipes. The amount of scale deposited in the pipes at **81 °C,** 96 "C and **130 "C** appears to be independent of pipe

Table 3. Amount of silica deposited down the pipes in experiments A-C and the amount of aluminium deposited in Experiment *C*; l - distance from the pipe inlet, d - silica deposited per gram of beads, a - aluminium deposited per gram of beads, wt%Al - weight percent aluminium, Blank – dried clean beads after being rinsed in geothermal fluid.

Experiment A

Pipe	Vcm	d/ (mg g^{-1})
1	4	6.12
1	35	5.77
1	65	5.91
1	95	6.64
2	4	6.37
2	35	6.39
2	65	6.54
2	98	6.94
3	7.5	6.23
3	34	5.81
3	64	5.81
3	93	5.87
4	4	5.83
4	34.5	5.08
4	64.5	4.56
4	95.5	4.30
Blank		0.10

Experiment B

pipe	l/cm	d/ (mg g^{-1})
1	3	17.03
1	5	15.14
1	19.5	11.88
1	35.5	10.72
1	50	9.42
1	65.5	8.32
1	80	7.98
1	95.5	8.48
2	5	11.54
2	20	82 1
2	35.5	7.48
2	50	7.04
2	65.5	6.94
2	80	7.04
2	95.5	7.25
3	5	7.83
3	21	7.06
3	35	6.91
3	51	6.85
3	65	6.88
3	81	6.86
3	95.5	7.04
4	5	5.82
4	*20*	4.85
4	35	4.43
4	50	4.21
4	65	3.95
4	80	3.79
4	96	3.82

Experiment C

pipe	Vcm	d/ (mg g^{-1})	a/ (mg g^{-1})	wt%Al
1	3.5	5.56		
1	18.5	4.99	0.30	5.6
1	34	4.75		
1	49	4.61		
1	64.8	4.69		
1	79.8	4.56	0.27	**5.5**
1	95.5	4.61		
2	3.5	5.16		
2	18.5	4.63	0.27	5.5
2	34	4.37		
2	49	4.38		
2	64.9	4.44		
2	79.9	4.38	0.26	**5.5**
2	95.5	4.50		
3	3.5	5.21		
3	22.5	5.04		
3	42.3	4.49		
3	61.3	4.36		
3	80.9	4.30		
3	119.2	4.08		
3	138.2	3.99		
3	158	4.05		
3	177	4.03		
3	196	4.19		
4	3.5	4.66		
4	18.5	4.23	0.34	7.5
4	34	4.01		
4	49	3.80		
4	64.9	3.65		
4	79.9	3.52	0.29	7.5
4	95.5	3.70		
Blank		0.12	0.007	

length and mass of fluid passed through the pipes (flowrate), within the uncertainties of the field experiment. Deposition at 130 °C was surprising. At this temperature the equilibrium solubility of amorphous silica in pure water is 509 ppm (Fournier and Rowe, 1966), but in the geothermal fluid at pH 7.8 the calculated concentration of unionized monomeric silica is 484 ppm (Truesdell and Singers, 1974). This implies that at 130 °C the fluid is undersaturated with respect to amorphous silica and no silica scaling should have been observed. Amorphous silica scaling at temperatures apparently below saturation is not an artefact of the present experiments. Scaling at 120-130 °C was also observed (qualitatively) in year long Wairakei fluid injection trials where fluid was passed through 160 mm diameter pipes packed with pumice gravel.

In experiment B at 71 °C the amount of silica deposited in the pipes (S_d in Table 2) appeared to be dependent on flowrate, which is in contrast to the behaviour observed in experiments A and *C*. We expect that at almost constant silica concentration deposition should be independent of flowrate as was observed in experiments A and **C.** Without further experiments it is not possible to tell from these results whether the other depositing species were colloidal particles formed in the induction period prior to the commencement of rapid polymerisation or silica fines injected into the pipes. There was no difference, within the analytical uncertainties, between the total silica concentration (analysed by atomic absorption) and the dissolved silica (analysed spectrophotometrically).

32 Fluidized Bed

The fluidized bed technique is an elegant method for measuring field deposition rates in the field enabling many measurements to be completed in a day that would have taken months to obtain in the packed pipe experiments. The silica removal rates approach steady state values as soon as thermal equilibrium is reached within the bed (< lhr). In addition the results are more precise and accurate because of the better control of the flowrate and temperature over the short run times compared with the month long packed pipe experiments. Also the silica removed is simply determined from the change in silica concentration between the inlet and outlet. The actual deposition rates are directly measured, avoiding the difficult task of fitting the data to an integrated form of the chosen rate equation.

Table **4.** Silica removal rates in the fluidized bed. Mass of sand was 5.12 kg with a geometrical surface area of 113 cm^2 g^{-1}, f - mass flowrate, t - temperature, d_f - average mg silica removed (3 determinations expect Run 6), R_f - deposition rate.

Run	f/ (kg s^{-1})	t/°C	d_f/mg	R_f/(mg cm^2 $year^{-1}$)
1	0.0068	96.5	28±6	10.4
2	0.0142	83.3	14±2	10.8
3	0.0139	74.4	25±5	18.9
4	0.0136	95.5	6±2	4.5
5	0.0094	95.0	10±4	5.1
6	0.0106	89.6	14±6	8.1

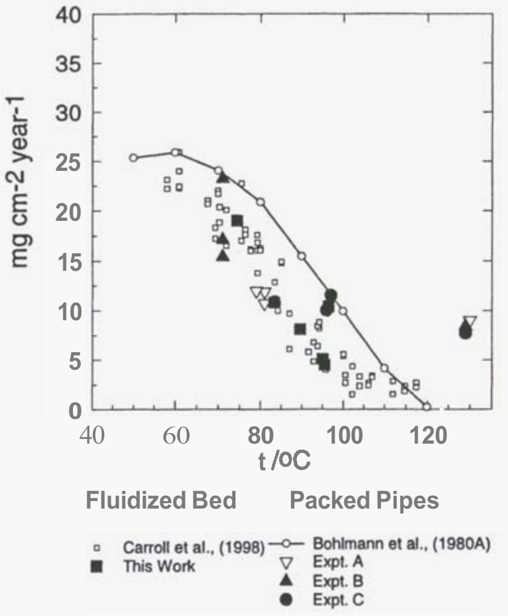

Figure **1.** Silica deposition rates (mg cm^{-1} $year^{-1}$) at FPlO measured using zirconia packed pipes and quartz sand fluidized bed.

The shell and tube heat exchanger was used to cool fluid piped to the fluidized bed reactor in a previous study measuring amorphous deposition rates at FP10 (Carroll et al., 1998). In those experiments soft porous silica, similar to the scale deposited in experiments A and B, was also deposited around the inlet of the reactor immediately before and on the gauze supporting the sand. However only the hard translucent silica was observed on the internal walls of the reactor. Since there was a possibility that the rates previously reported by Carroll et al., (1998) could also be too high, the fluidized bed silica removal measurements were repeated using fluid cooled with the compact plate heat-exchanger. The silica removal rates as well as the calculated deposition rates, normalised with respect to the geometric surface area of sand, are listed in Table 4. These results as well as the previous data (Carroll et al. 1998) are displayed in Fig 1 and show there is essentially no difference between them. The reason is that the overwhelming surface area of sand controls the deposition and amorphous silica fines that may enter the bed are insufficient to significantly alter the rate.

The deposition rates onto quartz sand in the fluidized bed tend towards zero as the equilibrium amorphous silica solubility temperature of 125 °C is approached (Carroll et al., 1998). However the rates determined in the packed pipes, although of the same order, follow a different pattern (Fig 1). The packed pipes rates are similar to the fluidized bed results at 71, 81 and 96 °C, but significantly no scaling should have been observed at 130 "C. The simplest explanation for this is that an aluminium rich scale, with a solubility lower than that of amorphous silica is depositing at the higher temperatures. Aluminium has a dramatic effect in reducing the solubility of amorphous silica (Iler, 1979; Gallup, 1997, 1998). Laboratory experiments undertaken by Gallup (1998) showed that at 100 °C an aluminium silicate scale has a solubility of 245 mgkg compared with amorphous silica at 375 mg/kg.

The aluminium content of the scale deposited in experiment *C* for a selected number of pipes is listed in Table 3. At 96 °C the aluminium content in the scale (assumed to contain only SiO_2 + *Al)* is **5.5 wt% and this** figure does not appear to vary down and between the pips. At 129 °C the aluminium content increases **to 7.5%.** The Si/Al scale mole ratios at 96 "C and 129 "C are 7.6 and 5.5 respectively. These concentrations and mole ratios are comparable to the Al-rich silica scales depositing at other geothermal fields (Gallup, 1998).

Carroll et al. (1998) reported about 1-2 wt% Al in the scale deposited on the quartz sand in the fluidized sand bed reactor. That less aluminium was deposited is not surprising as the amount available is limited by the flux through the reactor relative to the total amount of silica depositing. Gallup's (1997, 1998) results suggest that if the fluid contained less aluminium then the solubility of the aluminium rich silica scale would approach that of pure amorphous silica and the 130 °C packed pipe results would agree better with the scaling rates observed in the fluidized sand bed experiments.

4. SUMMARY

In this study we measured the deposition of amorphous silica in pipes packed with zirconia beads. At temperatures less than 100 °C the results agreed with measurements made with a fluidised sand bed using rates normalised with respect to geometrical surface areas of sand and beads. The rates are low as would be expected for the direct molecular deposition of silica which results in a hard compact low surface area scale (Weres and Apps, 1982). Scaling at 129 °C (4 °C above amorphous silica solubility) was unexpected and was most likely due to the precipitation of a AI-rich silica scale with a lower solubility than that of amorphous silica as suggested by Gallup (1998). The influence of aluminium on the deposition rate at the lower temperatures was not as dramatic for reasons that are unclear. Perhaps at the higher temperature a less amorphous, hence less soluble, scale deposits.

It is important to appreciate that the field scaling rates appear to depend on the technique used to measure them, an artefact caused by the effect of aluminium on the deposition rate of amorphous silica. Theoretically the rates measured in the fluidized bed reactor should match the deposition in the packed pipes and indeed they are close at the lower temperatures. However the packed pipe method better approximates the scaling observed in pipelines and aquifers/fractures with low surface to fluid ratios. The opposite would apply to the fluidized bed scaling rates which better approximate deposition in aquifers with high surface area to fluid ratios. In reality the truth will lie somewhere between the two extremes.

For comparison with the present packed pipe results the calculated amorphous deposition rates calculated using Bohlmann's et al. (1980A, 1980B) model but assuming a geometric surface area for the growing scale are drawn in Fig 1. The calculated rates are in good agreement with the measured rates, particularly matching the trend of the fluidized bed results. This suggests that a hard compact dense scale, which is low in surface area, is depositing on the sand in the fluidized bed as well on the beads in the packed pipes.

5. CONCLUSIONS

1. The amorphous silica deposition rates measured in the packed pipes and in the fluidized bed were comparable at temperatures between 70 and 100 °C
2. At 130°C scaling in the packed pipes was unexpected as the dissolved silica was calculated to be undersaturated with respect to amorphous silica.
3. The deposition of a less soluble aluminium enriched scale may be the reason for this anomalous result.

6. ACKNOWLEDGEMENTS

We would like to thank Contact Energy Ltd for access to the borefield and Ian Graham for editorial comments on this paper. This work was funded by the New Zealand Foundation for Research Science and Technology through contract CO5605.

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