THE EFFECT OF AERATION ON SILICA SCALING

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ABSTRACT

Silica scaling rates have been measured for separated water at Ohaaki BR22 well. Injection of oxygen into separated water streams of differing temperatures has no effect on the rate of silica deposition, because the silica present has not polymerised. For 115°C separated water, we observed a silica scaling rate of 0.42 mm/year for a supersaturation level of 1.92 at pH_{20} of 8.9. The mechanism of silica scale formation probably involves cementation of preformed colloid particles onto the walls of the pipes. The rate of polymerisation of monomeric silica has been measured at three different temperatures and no induction period has been observed.

INTRODUCTION

During operation of a sampling unit at Wairakei well WK207, it was noticed (Mahon, Klyen, McDowell, 1972) that ingress of air into the discharge pipe seemed to accelerate the deposition of silica. Rothbaum (1979) and McDowell (1976) also noticed the effect of aeration on silica scaling. As a result of these qualitative observations, concern has often been expressed in the design of geothermal plant by ensuring freedom from oxygen. It was therefore decided to attempt to quantitatively test the problem under controlled field experimental conditions.

EXPERIMENTAL CONDITIONS

Preliminary field tests (McDowell, 1976) had shown that the effect of air was only noticeable above an air injection rate of 3 volume %, so we decided to use just above this mount of OXYGEN injection. It was thought that the effect was due to oxygen in the air, however the possible physical effect of a gas bubble was investigated by including one line of nitrogen injection. The experimental plant consisted of 6 lines, each of two lengths of standard black steel 1" steam pipe, fed from a common manifold of separated water at 115°C. Three different temperatures of separated water were considered and for each temperature there was a control line and a gas injection line. The experimental conditions are given in Table 1.

TABLE 1: Experimental Conditions

Line	Inlet Temp °C	Outlet Temp °C	Gas Injected	Conditions
1	115	112	-	insulated
2	115	112	O_2	insulated
3	115	102	N_2	non-insulated
4	115	102	O_2	non-insulated
5	115	52		water cooled
6	115	52	O_2	water cooled

The plant was located at Ohaaki BR22 well and a chemical analysis of the separated water used for the experiment is given in Table 2.

TABLE 2: Water Analysis (at 115°C)

pH(20°C)	8.90		Cl^-	1628 mg/kg
Li	13.53	mg/kg	$SO_4^=$	12 "
Na	974	"	B	46.8 "
K	214	"	SiO_2	830 "
Ca	2.8	"	HCO_3^-	61 "
Mg	0.007	"	H_2S	7.25 "

The rate of silica polymerisation was measured at the inlet temperature and the outlet temperature of the three different conditions, using a constant temperature hold-up vessel. The experiment was run continuously for 48 days. Flow rates were set at 10 litres/min in each line, corresponding to a residence time of approximately 0.6 minutes.

RESULTS

The outlet temperatures given in Table 1 are average values: for the unlagged lines in particular, these depend on ambient temperature. However outlet temperature variation was less than ±2°C for the unlagged lines and ±4°C for the water cooled lines. The insulated lines remained at constant temperature. The flow rates were somewhat more variable. Silica build up on the control valves may have affected flow rates, particularly on the insulated lines where flashing was occurring across the valve seat.

After 48 days, approximately 10 cm lengths of pipe were cut from the test sections (a) at the beginning of each line, (b) at the centre, and (c) just before the control valve of each line.

The samples were dried and then cut in half lengthwise. The amount of silica deposition was measured by weighing the pipe sections before and after removal. As there was up to 0.5 mm of corrosion product present underneath the scale, the scrapings of each pipe were then analysed for total silica. These silica analyses ranged from 55 to 81 weight percent reflecting corrosion in the pipes before the experiment was started. From these analyses the total silica deposited on the test sections may be calculated and are given in Table 3.

TABLE 3: Wt gains mgms(SiO_2)/cm^2

Line		Initial	Middle	Rear	Temp
1	-	10.4	13.4	9.5	115–112
2	O_2	12.0	8.5	8.7	115–112
3	N_2	10.3	15.8	16.0	115–102
4	O_2	14.3	20.6	15.4	115–102
5		19.2	21.8	9.9	115–52
6	O_2	17.6	16.5	15.6	115–52

The only conclusion that can reasonably be drawn from this data is that there is a trend towards greater deposition as the temperature is lowered. There seems to be no difference in the deposition between the control lines and the oxygen dosed lines, nor between nitrogen and oxygen dosing. Rothbaum (1979) and Mahon, et al. (1972) had suggested a very large increase in scaling rates and this has not been confirmed.

In all cases, the scale formed was of the vitreous silica type, having a high density and hardness. The density of one fragment was measured as 2.13 gms/ml which would given average scaling rates of 0.42 mm/year for the 112°C constant temperature lines. The deposit thickness was rather uneven in all lines and may be linked to the initial corrosion condition of the pipes.

In both the oxygen injected and control lines, there were nodules of silica. These were 1–2 mm across and generally declined in number along the length of the pipe. When broken open, they revealed a white powder which EDAX analysis showed to be pure silica. There was normally a pit in the metal associated with each nodule. By some unknown mechanism, the nodules seemed to have formed and frozen the silica polymerisation at the time of the formation of the nodule. Scanning electron micrographs of the contents of some of these nodules are shown in Figs 1 to 4 and show the path of silica scale growth. Fig. 1 shows very regularly sized silica particles of about 1.3 µ diameter. (About twice the size of precious opal silica spheres). The reason for the very regular particle size distribution is unknown but no smaller spheres were found in any of the samples. Fig. 2 shows silica spheres that have grown in size (3.2 µ - 12 µ) and are far less regular in their shape and size distribution. Fig. 3 shows clumps of these single particles which have grown by agglomeration and which deposit on the walls and undergo further cementation to give the observed scale shown in Fig. 4.

X-ray diffraction of the deposit showed magnetite as the only crystalline phase. EDAX analysis of some of the SEM samples also showed the presence of small amounts of iron silicates and aluminium iron silicates - particularly associated with the nodules.

POLYMERISATION KINETICS

The rate of disappearance of monomeric silica, as measured by the ammonium molybdate colormetric method, is shown in Fig. 5. For the three different temperatures. As expected, the rate of polymerisation is fastest for the lowest temperature. Also, the concentration of monomeric silica has dropped to $610 ppm during the 0.6 minutes in the water cooled pipe and the sampling tube. We could detect no difference in polymerisation rates between the inlet and outlet of the insulated line. While the 112°C and 102°C samples drop rapidly to their saturation solubility, the 50° sample falls to $300 ppm and stays constant for at least 60 minutes: the saturation solubility at this temperature being ∿180 ppm. (Fournier and Rowe, 1977).

DISCUSSION

Using the discussion of Weres, et al. (1982), the predicted molecular deposition rate of silica at 100° for the conditions of the experiment is ∿0.015 mm/year. This is the calculated rate for direct chemical bonding of dissolved silica on to a solid surface. The observed rate is very much greater than this and therefore some other deposition mechanism must be operating to account for the majority of the scale deposited. This other mechanism (also recognised by Weres) probably involves the initial formation of a colloid by homogeneous nucleation, followed by growth of the colloidal particles by both agglomeration and direct growth. The particles then adhere to the pipe surface and are cemented in place by further direct deposition from solution. The SEM photographs (Fig. 1-4) graphically illustrate this mode of deposition. The deposits from all six lines had a similar appearanceinferring that the mechanism is similar for all three temperatures. The total silica deposited in the 112° line was $170 *gms* of a total of 280 kg of silica available for deposition.

The lack of any effect in these experiments due to aeration, arises because the silica has only just started to polymerise while in the pipes In the previous cases of Rothbaum, et al. and Mahon, et al. the degree of polymerisation was much greater than in the present case, due to longer hold-up times. (e.g. >30 minutes at BR27 and WK207 for Mahon, et al.). These previously observed effects of aeration are probably due to seeding or flocculation of the already formed colloidal silica by particles formed through oxidation by air, e.g. iron hydroxides. It is significant that the scale formed during aeration

Fig. 1. 5500X

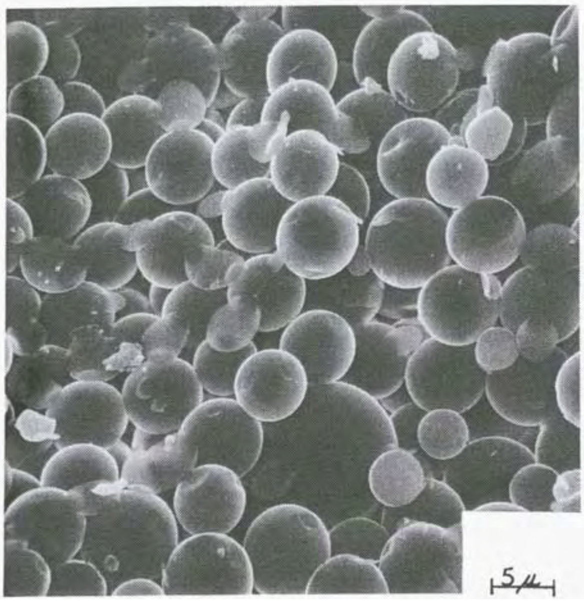


Fig. 2. 2200X

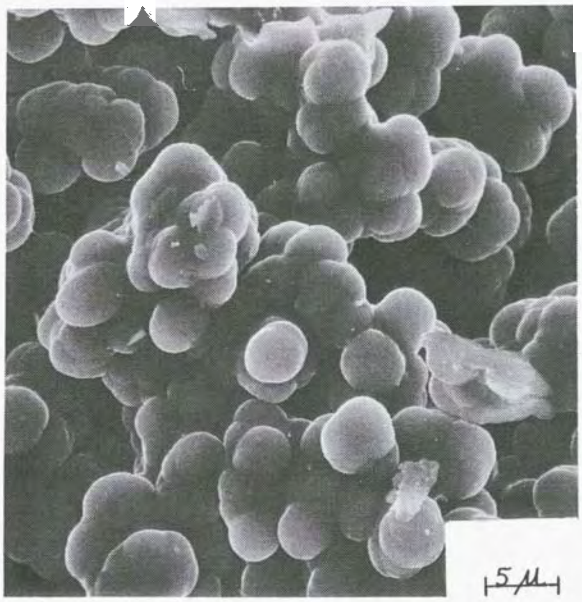


Fig. 3. 2400X

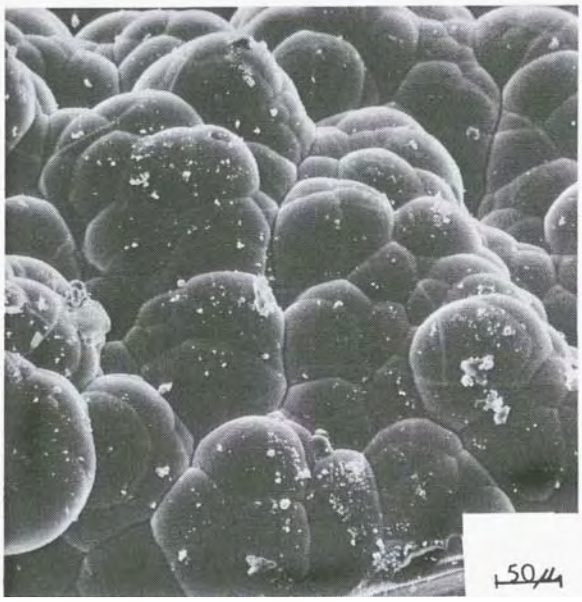


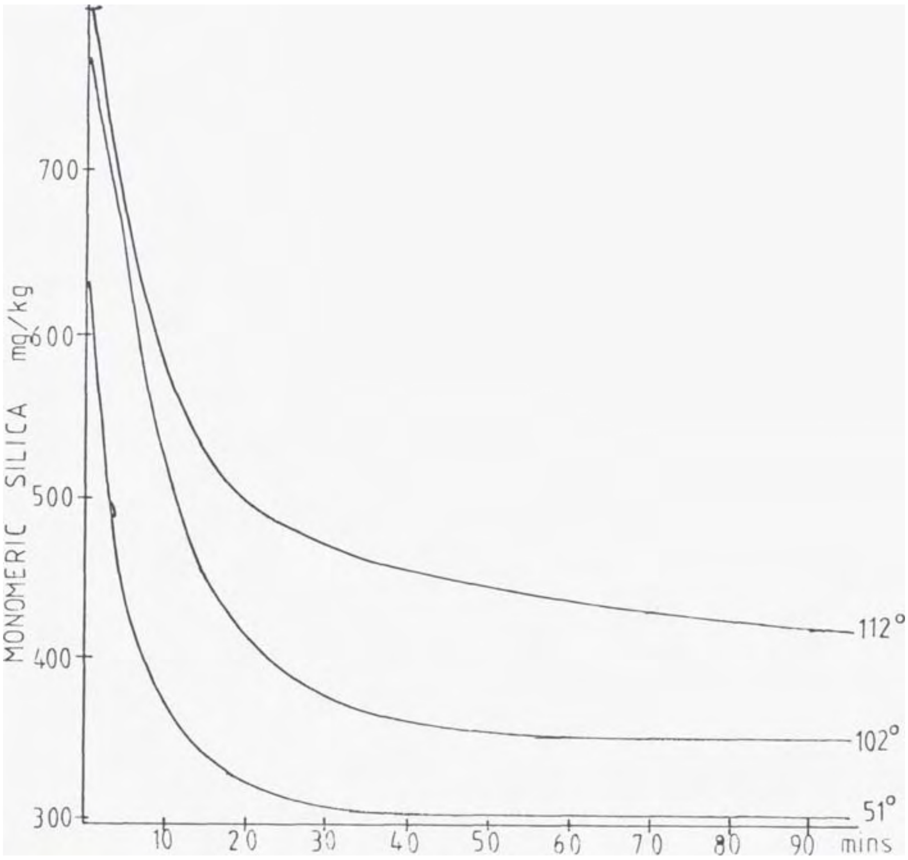
Fig. 4. 240x

Figs 1-4. SEM photographs of the silica scale.

always has a low density and is very porous suggesting a flocculated product, whereas the present experiment produced a vitreous, dense, scale. Fig. 5 shows that the silica is only partially polymerised after 0.6 minutes of residence time: even in the case of the water cooled line. Further experiments with a considerable hold-up time (>30 minutes) will be needed to identify the seeding agent formed by aeration of the separated water.

The observed polymerisation of silica monomers takes place within the order of minutes at Ohaaki. There was no measured evidence of an induction period as discussed by other authors for different conditions. However we estimate a hold-up time of ∿7 minutes at 115°C in the steam separators, water tank and distribution manifold - a value confirmed by experiment. (Henley and Singers, 1982). Any induction time would have to be less than this. Induction times have previously been found to be very short at the pH and silica concentrations at which we were working. (Rothbaum, 1979).

Fig. 5: The Polymerisation Rate of Monomeric Silica.



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