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pH CONTROL OF SILICA SCALING

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ABSTRACT

The effect of pH changes on the rate of silica scaling has been studied at BR22 well. In a series of four long term experiments, it was found that the pH needed to be reduced to pH_T = 5 at 100°C before scaling was reduced. As well, we found that the pH needed to be raised to pH_T = 9.0 before scaling was avoided, when alkali was added. 'Ageing' of the separated water reduced scaling and when the pH was lowered, very large amounts of arsenic and antimony sulphides were deposited. Aeration of aged water had no effect on scaling rates at neutral pH values.

INTRODUCTION

The deposition of silica has always presented problems for the disposal of geothermal discharge waters, and has largely inhibited the use of the waste heat contained in these waters. After separation of steam, geothermal discharge waters are greatly supersaturated with silica, and a number of methods have been employed to prevent the formation of silica scales. One method that has been proposed is the adjustment of the pH of the brine. In a series of experiments at Wairakei and Broadlands, Rothbaum (1979) has shown that there was up to 100 fold reduction in scale formation when the pH was lowered to 4.0.' Likewise, Harrer et al (1979) found a reduction of between 2.6 and 21 fold in the scaling rate when the pH of Salton Sea brines was lowered from 6 to 4.5.

The effect of acidification on the polymerisation rate of monomeric silica has been well recognised and documented. Between pH 3 and 6, the polymerisation rate depends on the concentration of OH^-, being ~100 times faster at pH6 than pH4. Between pH 7 and 10, the results are somewhat more confused, with reported rate orders varying between 1 (Coudourier et al 1971) and 3 (Okamoto et al 1957). The effect of degree of polymerisation on silica scalinq also seems to vary from field to field. Rothbaum (1979) found that polymerisation had little effect on the quantity of scale produced whereas Yanagase et al (1970) describe a method of ponding (allowing polymerisation) to reduce scaling. Aeration of separated waters has often been considered to cause enhanced silica scaling, either by direct effect on the polymerisation kinetics, or by enhancing the formation of nucleii for the flocculation process. Previous experiments with unaged waters (Brown and McDowell 1982) showed that aeration had no effect on silica deposition.

The addition of alkali to prevent silica scaling has not received much attention. The solubility of amorphous silica must increase with increasing pH, due to the formation of the soluble silicate anion.

$$H_4SiO_4 + OH^- \rightleftharpoons H_3SiO_4^- + H_2O$$

For a typical Broadlands discharge water. increasing the pH_T to 9 at 100°C will increase amorphous silica solubility by a factor of 2.2.

The present paper describes a series of four field tests at intermediate acidic pH values (pH = 5 to 8) and alkali pHs (pH 8 to 10).

EXPERIMENTAL

The experiment was arranged so that doubly-flashed 100°C separated water at BR22 was held unaerated for varying periods. It was then acidified with sulphuric acid, or the pH raised with caustic soda, and then fed through pipes where the corrosion and scaling could be studied. The test pipes consisted of 4 lines, each of three 6.3 m lengths of 25 mm steel pipe arranged at an incline to prevent accumulation of gas. All lines were insulated. A constant flow of 3 l/min in each line was maintained throughout the experiment. The arrangement of the experimental plant is shown in Fig. 1.

Four experiments were conducted over a period of 8 months. The experimental canditiohs are summarised in Table 1. The first experiment used unaged water, with H_2SO_4 injection to give final pH_T values of 8.12 (control), 5, 6 and 7. Experiment 2 was identical except the water was aged for ~38 minutes prior to acid dosing.

During the first two experiments, it became obvious that the pH_T needed to be reduced to 5.0 before significant retardation of scale was noticed. The third experiment was designed to test the effect of aeration on polymerised waters. Consequently, the first two lines tested the effect of aeration at normal pHs and lines 3 and 4 tested this effect at pH = 5.

The fourth experiment tested the effect of alkali dosing. The water was unaged and pHs were adjusted to 8.5, 9.0 and 10.0 using caustic soda.

At the conclusion of each experiment, samples were taken from the pipes in the positions indicated in Figure 1. The total scale was removed and analysed for silica.

RESULTS

The form of silica precipitation in nearly all experiments was of the dense vitreous type. Only in the waste pipe from the discharge manifold did we start to see the porous, less dense silica that is typical of the Wairakei drains for instance

The amount of silica that had deposited on the pipe surfaces are given in Table 2.

Experiment 1 showed that the pH had to be reduced to pH = 5.0 before scaling

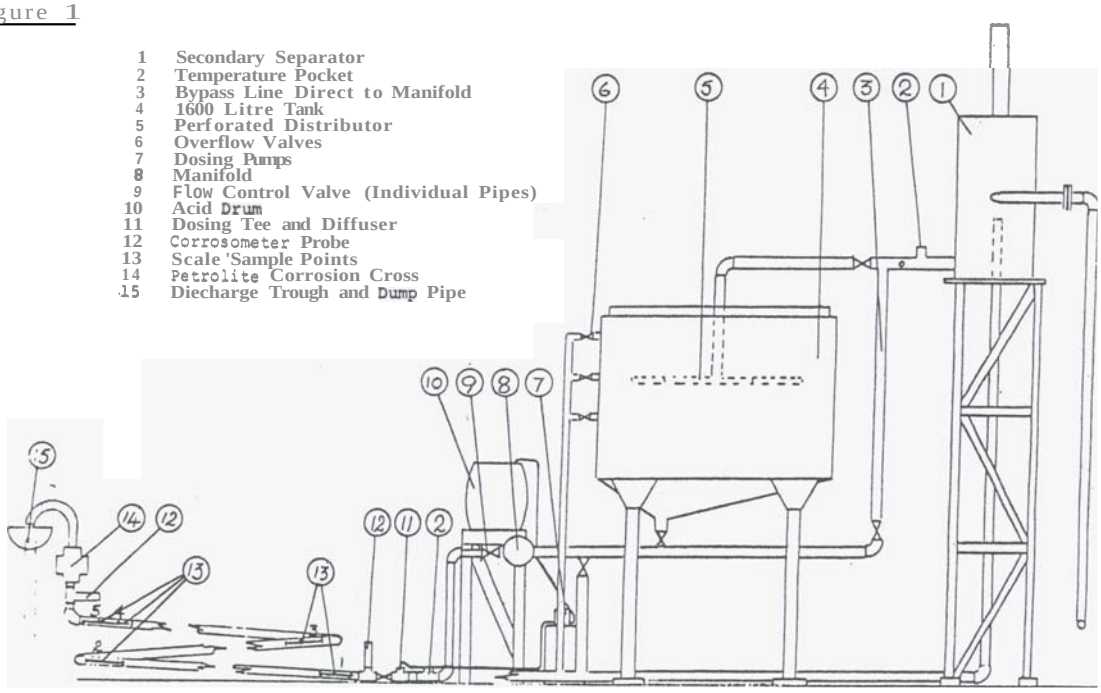
TABLE 1

EXPERIMENTAL CONDITIONS

	Hold up	Aeration	pH	T In °C	T Out °C
EXPERIMENT 1					
Line 1	-		8.29	97	93
2	-		5.23	97	93
3	-		6.65	97	93
4	-		6.95	97	93
EXPERIMENT 2					
Line 1	38 mins		8.19	92	88
2	38 mins		5.01	92	88
3	38 mins		5.76	92	88
4	38 mins		7.07	92	88
EXPERIMENT 3					
Line 1	39 mins		8.14	92	87
2	39 mins	X	8.14	92	84
3	39 mins		4.96	92	87
4	39 mins	X	5.13	92	84
EXPERIMENT 4					
Line 1	-		8.22	96	94
2	-		9.02	96	94
3	-		9.98	96	94
4	-		8.53	96	94

Figure 1

1 Secondary Separator
2 Temperature Pocket
3 Bypass Line Direct to Manifold
4 1600 Litre Tank
5 Perforated Distributor
6 Overflow Valves
7 Dosing Pumps
8 Manifold
9 Flow Control Valve (Individual Pipes)
10 Acid Drum
11 Dosing Tee and Diffuser
12 Corrosometer Probe
13 Scale Sample Points
14 Petrolite Corrosion Cross
15 Diecharge Trough and Dump Pipe



was significantly retarded. All lines except pH = 5.0 deposited a clear vitreous layer of silica that was continuous over the pipe surface. For the pH = 5 line, there was no coherent silica scale present. The pipe scrapings were analysed by semiquantitative arc spectrographic analysis and a selection of the results are shown in Table 3. The deposit is mainly a mixture of silica and magnetite (mill scale from the pipe manufacture).

The polymerisation rate of silica was also measured and results are shown in Fig. 2. It can be seen that at pH = 5, polymerisation is effectively halted for at least 200 mins, while at pH 8.12 and 7.0, polymerisation is so rapid that the residence time in the pipes has not enabled the un-polymerised silica to be detected.

Experiment 2 shows that ageing of separated waters does reduce the amount of silica deposition. The scale deposited in the control line (pH = 8.12) was similar in appearance to that of the first experiment. Scanning electron microscopy showed that the size of the cemented globules was less

Figure 2: Polymerisation rate of silica at acidic pH values.

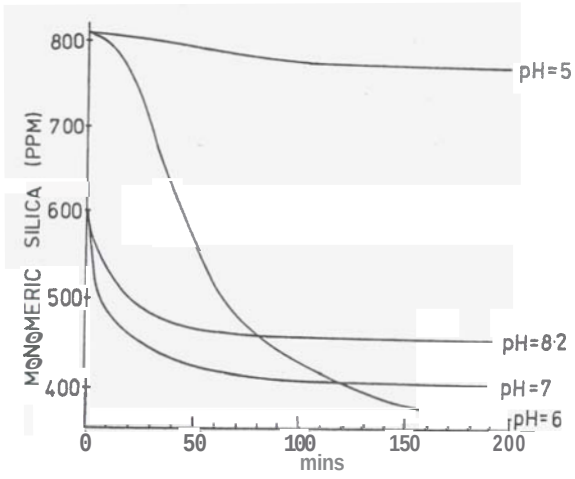


TABLE 2

AMOUNT OF SILICA DEPOSITION IN PIPE SECTIONS
(mgms SiO_2/cm2/year)

Expt 1: No hold up, no aeration

	pH = 8.12	pH = 5	pH = 6	pH = 7
Sample Position 1	153	109	67	197
2	107	17	63	87
3	65	17	56	69
4	56	16	51	52

Expt 2: Hold up = 38 mins, no aeration

	pH = 8.12	pH = 5	pH = 6	pH = 7
Sample Position 1	54	13	19	22
2	22	24	29	17
3	43	22	14	18
4	31	16	23	15

Expt 3: Hold up = 39 mins

	pH = 8.12	pH = 8.12 aerated	pH = 5	pH = 5 aerated
Sample Position 1	50	39	19	32
2	30	34	21	38
3	40	26	11	25
4	22	34	20	15
5	77	122	4	28

Expt 4: No hold up, no aeration

	pH = 8.12	pH = 9	pH = 10	pH = 8.5
Sample Position 1	116	17	1.1	69
2	86	3.7	4.9	48
3	51	5.8	4.3	64
4	35	6.9	2.7	45
5	61	1.0	1.4	58

than in experiment 1. The pH = 5 line had deposited a non-coherent, very porous scale, and this led to severe pitting of the pipe surface. The pH = 6 line had a most distinctive brick-red colour. There were many tubercules growing out of the surface of the pipe and these, as well as the red scale, were composed of amorphous antimony sulphides. All deposits in this experiment showed magnetite as the only crystalline phase identifiable by XRD. The analysis of the deposits (Table 3), show that at pH = 5 and pH = 6, a remarkable amount of antimony and arsenic has been deposited.

Experiment 3 showed that at normal pHs, aeration has no effect on the rate of silica deposition. At pH = 5, there is only a slight increase in the deposition rate after aeration. Once again, very large amounts of arsenic and antimony had been precipitated. Very small amounts of porous silica were sometimes noticed around the pipe seams which suggests a turbulence factor. Pitting of the steel pipes was very great in the aerated lines especially the line at pH = 5.

Experiment 4 showed that, at 100°C, the pH of these separated waters needed to be raised to 9.0 before silica deposition was halted. The pH = 9 and pH = 10 lines had no recognisable scale at all. Analysis of the pipe scrapings showed that antimony and arsenic no longer precipitate in large quantities. However the alkaline earth metals, Zn, Mg, Ca and Sr are all in increased concentrations, and Ag has also increased in concentration.

DISCUSSION

The expected deposition of the low density porous silica deposit did not occur. At the lower and neutral pH's, the degree of supersaturation was about 2.5 and past experience (Rothbaum, et al. 1979; Weres, 1982) has indicated that a low density silica precipitate could be expected. Certainly the open drain at Wairakei precipitates a voluminous deposit at a saturation ratio of ~2.0. Even when the silica has been prepolymerised and aerated, the only scale we observed in these experiments was a dense vitreous scale. The major factor which has not been allowed for is that of turbulence, and it is this to which we ascribe the lack of a large silica scale. The fluid in the pipes of these experiments, has a Reynolds number of $Re \doteq 9200$. This is barely above what is normally considered to be turbulent flow. For the Wairakei drains, however, $Re \doteq 2{,}800{,}000$. The thickness of the boundary layer (between the pipe walls and the general fluid flow) is reduced at higher Reynolds numbers allowing a higher concentration gradient to exist, and therefore greater deposition. Moreover, above a Reynolds number of $\sim 5 \times 10^5$ the major portion of the boundary layer itself experiences turbulent flow, allowing even greater access to the walls of the pipe from the suspended colloid (Treybal, 1968).

The'deposition of the dense vitreous silica found in these experiments follows a similar mechanism to the deposition of the more porous voluminous scale. The SEM photographs of the vitreous scale show that it is composed of cemented aggregates of colloids, i.e. the mechanism involves a first step of the polymerisation and formation of a colloid and second step involving the aggregation of colloidal particles some of which adhere to the walls and are cemented together by direct deposition of silica (non-polymerised). Thus the only difference between the scale in this experiment and that of the Wairakei drains for instance, is in the rate at which the aggregate scale can penetrate the boundary layer and adhere to the pipe walls. Consequently results obtained in these experiments should correlate with other silica scaling solutions.

Ponding seems to be almost as efficient as pH reduction in decreasing the scale build up. Hold up of discharge waters is practised at Otake and Hatchobaru but very little information is available on scaling problems downstream of the hold up ponds. From the results of experiment 2, it would seem that a small pH reduction combined with the hold up is even more effective, due probably to the lack of cementation availble. We note very small deposition in the hold up tank. Once again low flows were probably responsible for keeping colloidal silica away from the container walls.

Previous experiments had shown that where the silica was not polymerised, there was no difference between aerated and non-aerated water (Brown and McDowell, 1982). In experiment 3, where the water was first polymerised and then aerated, there is no profound increase in silica deposition due to aeration. In the acid treated waters, there is only a slight increase in the deposition with aeration. Therefore any aeration effect must either occur further downstream or be due to some factor which is not present in this experiment (dissolved ferrous ion for instance).

There are large quantities of antimony and arsenic co-precipitated at lower pHs. For antimony, recent work has shown (Kolpakova, 1982) that there is an order of magnitude decrease in solubility for every pH unit below 7. The solubility of arsenic sulphides also decreases with decreasing pH. It is interesting that the very large arsenic and antimony precipit-

TABLE 3

	Experiment 1				Experiment 2				Experiment 3				Experiment 4			
Nominal pH	8.12	5.0	6.0	7.0	8.12	5.0	6.0	7.0	8.12	8.12	5.0	5.0	8.12	9.0	10.0	8.5
Hold up (mins)					38	38	38	38	39	39	39	39				
Aeration										X	-		X			
Silica (%)	61.4	32.1	44.2	72.7	42.3	24.4	29.5	22.5	42.0	35.0	23.2	21.6	64.8	24.4	11.3	59.3
Iron Flux: (%)																
Iron	20-30	25-35	20-30	20-30	25-35	15-25	15-25	30-40	20-30	20-30	20-30	15-25	na	na	na	na
Arsenic	0.02	0.1	0.1	0.02	c0.02	13-19	3-1	0.3	0.02	-	10-14	10-14		x	x	-
Antimony	0.06	0.4	0.6	0.1	0.04	9-15	9-15	1.0	0.04	0.04	13-18	3-5	0.02	0.03	0.03	0.02
Calcium	0.1	0.02	0.04	0.05	0.004	<0.004	0.005	0.008	0.07	0.06	<0.01	<0.01	0.05	*0.01*	0.4	0.2
Nickel	0.02	0.015	0.1	0.1	0.006	0.02	0.02	0.015	0.015	0.015	0.02	0.025	0.005	0.01	0.008	0.03
Aluminium	0.05	0.05	0.08	0.2	0.02	0.04	0.05	0.2	0.3	0.1	0.05	0.05	0.02	0.2	0.2	0.06
Magnesium	0.002	0.002	0.004	0.007	0.004	0.002	0.004	0.002	0.008	0.005	0.002	0.002	0.004	0.01	0.09	0.02
Manganese	0.09	0.1	*0.08*	0.04	0.1	0.05	0.07	0.1	0.1	0.1-0.15	0.09	*0.01*	*0.01*	0.1	0.15	0.08
Volatiles (ppm)																
Zinc	na	80	60	na	50	25	70	40	100	200	70	200	20	500	150	25
Lead	na	7	7	na	<1	1	<1	<1	2	90	8	35	90	30	100	15
Mercury	na			na									40			<25
Thallium	na	25	20	na	<1	90	>500	15	5	<1	50	35	5	100	200	3
Silver	na	3	2	na	<1	8	5	1	2	∿200	∿100	50	4	>>100	>>100	?
Gold	na	-	2	na	-	3	4			-	3	1	-	10	20	
Tin	na	2	<1	na	<1	3	6	<1	<1	>100	3	40	2	15	>100	15
Boron	na	80	300	na	100	150	70	70	150	100	50	80	150	80	90	*80*
Germanium	na	7	5	na	<1	80	35	1	3	4	8	20	2	6	7	<1

ation only takes place when the water has been held up. This is presumably due to the kinetics of formation of As_2S_3 and Sb_2S_3. It is known that both of these compounds form colloids in a similar manner to silica. The correlation between As_2S_3 precipitation and that of other elements is being investigated.

As expected, addition of alkalitobring the pH of the water up to 9.0, completely inhibited silica deposition. Experiment 4 is useful in providing confirmation of the solubilities of amorphous silica predicted in papers by Henley (1983) and Flemmingand Crerar (1982). At 96°C, pH = 9 they predict a solubility of 750 ppm compared with 730 ppm found. At pH = 8.6 the predicted and found solubilities agree exactly.

The price of alkali is about seven times that of acid (per equivalent). Also, 1½ times as many moles of alkali are required as acid. Consequently, the running costs of alkali addition are very large. For BR22 separated waters, the cost of the alkali alone amounts to 22¢/tonne of separated water, whereas the equivalent cost of the HCl dosing is only 1.75¢/tonne.

Since alkali renders the silica completely soluble, there is no danger of reducing permeability in a reinjection well. Acidification, however, only delays silica deposition, and if the reinjected water is supersaturated with respect to silica, then some silica must precipitate in the well. Consequently, acidification prior to reinjection, as a means of controlling silica deposition cannot be recommended.

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