LAWRENCE LIVERMORE LABORATORY
University of California/Livermore, California/94550

UCRL-51944

**THE EFFECT OF ELECTRICAL POTENTIAL ON
SCALE FORMATION IN SALTON SEA BRINE**

R. N. Schock and A. Duba

MS. date: November 5, 1975

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Abstract

Field experiments were carried out at a flowing well in the Salton Sea Geothermal Field to study the influence of electrical potential on scale deposition. The scale is composed mainly of silicon, iron, copper, silver, and aluminum. Significantly more scale formed on negative than on either positive or neutral electrodes. The scale on the cathode contained up to 1000 times more lead than the scale on the other electrodes. It may also

contain slightly increased amounts of copper. Although the amount of scale on positive and neutral electrodes appeared to be the same, the scale on the positive electrodes was richer in iron and zinc. X-ray powder diffraction reveals the presence of lead as Pb(OH)Cl and of iron as FeOOH . No crystalline silicon forms were detected. Collectively, the results suggest that both iron and lead are present in complex ionic forms in solution.

Introduction

This report summarizes the results of a series of field experiments designed to determine the effect of electrical potential on the formation of scale in a system exposed to flowing brine from a well in the Salton Sea Geothermal Field. The effect of electrical charge on the precipitation of silica scale might be more quantitatively investigated in the laboratory with experiments on solutions containing controlled amounts of specific solutes. Such experiments would separate the effects of chemical interactions between aqueous species.

However, the operation of the Sinclair No. 4 well by LLL in April of this year provided a unique opportunity to qualitatively investigate the problem on a flowing geothermal well.

The experiment was designed as follows: Six spherical, stainless steel electrodes (9.53 mm diam) were exposed to the fluid for periods of up to 2 h. The configuration is shown in Fig. 1. A 6° nozzle expanded the fluid from a 51-mm-diam pipe past the spheres, which were positioned 80 mm from the throat of the nozzle. The centers of the spheres were placed

Fig. 1. Cross-sectional line drawing of apparatus used in this study.

14 mm from the inner surface of the expansion pipe. They were insulated from the pipe by a Teflon* sleeve through which a stainless steel rod

was passed to allow the sphere to act as an electrode. Four experiments were run; the experimental conditions are described in Table 1.

*"Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Energy Research & Development Administration to the exclusion of others that may be suitable."

In all experiments the spheres remained intact and exhibited scale formation. There was no evidence of corrosion. All surfaces of all spheres were scaled, although not to the same degree in all cases. There were

Table 1. Experimental Conditions.

Experiment No.	Sphere No.	Potential (V)	Duration (h)
1 (PS negative ground) ^a	1	+5	2
	2	0	
	3	+5	
	4	0	
	5	+5	
	6	0	
2 (PS positive ground)	1	-5	2
	2	0	
	3	-5	
	4	0	
	5	-5	
	6	0	
3 (PS floating above ground)	1	0	2
	2	-5	
	3	+5	
	4	0	
	5	-5	
	6	+5	
4 (PS negative ground)	1	+30	0.5
	2	0	
	3	+30	
	4	0	
	5	+30	
	6	0	

^aPS = power supply.

significant, observed differences among +5 V, -5 V, and neutral electrodes. The scale formed on all anodes was black when compared to a brownish-black scale observed on neutral electrodes. Visual observation indicated no significant difference in the amount of scale between positive and neutral electrodes. Subsequently more oxidation was observed for the material on the anodes. Conversely, the cathodes exhibit considerably more scale (brownish-black) than either positive or neutral electrodes. This is illustrated in Fig. 2, where differently charged electrodes

are shown for Experiment No. 2. This scale flowed around the ball under impact from the high-velocity stream, indicating that this type of scale was not brittle while in the environment immediately downstream from the nozzle.

The fourth experiment consisted of three electrodes charged at +30 V and three neutral electrodes. This experiment was curtailed when the electrodes shorted out in 0.5 h. The positive electrodes were bridged with large quantities of salt as if the electrochemical potential of the brine had been exceeded.

Fig. 2. Photograph of apparatus, looking toward nozzle and with pipe cut just below electrode section. Taken after experiment No. 2.

Results

After exposure to the flashing brine, the cylinders with spheres and their mounts were detached from the nozzle, wrapped in plastic bags and brought back to the laboratory. Small pieces of scale, most of which had begun to exhibit the signs of oxidation evident in Fig. 2, were taken from each electrode in Experiments No. 1 and 2 and analyzed by flame spectroscopy.* Although insensitive to small changes in relative amounts of elements, the data (Table 2)

indicate that there are significant differences among +5 V, -5 V, and neutral electrodes. Specifically, copper and silver are depleted on the anodes relative to neutral electrodes, while iron and chromium were enhanced. However, with

*E. Peck, Lawrence Livermore Laboratory.

Table 2. Spectrochemical Analysis Report (E. Peck). Selected elements were examined for direct comparison of relative amounts in each sample. One sample (indicated by ^b) was selected as a reference for each element, and the values for other samples determined by relative intensity ratios.

Charge	Si	Fe	Cu	Ag	Al	B	Ga	Cr	Be	Ba	Pb ^a
+5 V	26%	14%	7%	0.5%	1 %	0.3%	0.04%	0.06%	0.06%	0.03%	
+5 V	24	17	5 ^b	0.3 ^b	0.8	0.3	0.05	0.08	0.05	0.03	
+5 V	26	16	8	0.5	1	0.2	0.05	0.06	0.05	0.03	
0	22	10	8	2	0.8	0.2	0.04	0.01	0.04	0.01	
0	24	10	10	2	1	0.2	0.05	0.02	0.05	0.02	
0	26	16	8	2	0.8	0.2	0.05	0.03	0.04	0.02	
-5 V	10 ^b	5 ^b	10	1	0.3 ^b	0.1 ^b	0.01 ^b	0.02 ^b	0.01 ^b	0.01 ^b	
-5 V	11	6	9	0.7	0.3	0.1	0.02	0.02	0.01	0.02	
-5 V	16	8	20	2	0.5	0.2	0.03	0.02	0.02	0.01	
Pipe	10	8	6	0.0	0.3	0.1	0.03	0.01	0.01	0.02	
Nozzle	12	6	6	1	0.6	0.09	0.02	0.05	0.01	0.01	

^aDifferences in lead concentrations were too great to apply this method.

the possible exception of copper and iron, these trends do not show an opposite effect on the cathodes. On the other hand, silicon, aluminum, boron, gallium, and beryllium were all depleted and lead enhanced on the cathodes; but again, there was no detectable opposite effect on the anodes. This lack of a definite correlation might indicate that these species are not in solution as simple ions but rather as complexes. This is not unusual considering the number, type of species, and temperatures in these natural solutions. None of the other elements analyzed by flame spectroscopy showed any notable correlation. A complete list of all elements found by flame spectroscopy and their relative abundance is given in Table 3. Note that no analysis could be made for sulfur.

The scale from Experiment No. 3 was analyzed by x-ray fluorescence^{*} for 11 elements, including sulfur. Relative abundances are shown in Table 4, referenced to calcium. There is no recognizable trend in either sulfur or silicon abundance. However, Ryon states that the sulfur numbers are suspect. One might discern a trend toward less silicon on the cathodes. (See previous paragraph.) Chlorine appears concentrated on anodes relative to cathodes. Potassium is depleted on the cathodes. This is

surprising, because one might expect potassium to be in solution as a simple cation and to be attracted to a cathode (if its electrochemical potential were exceeded). Iron appears to be greatly depleted on the cathodes, copper and silver show little trend, zinc is enhanced in the anodes, and lead is greatly enhanced on the cathodes (in agreement with the flame spectroscopic analyses). As with the flame spectroscopic results, there seems to be little correlation for opposite trends in the oppositely charged electrodes, with respect to neutral.

The same scale analyzed by x-ray fluorescence was also analyzed for crystal structure by x-ray powder diffraction in an attempt to determine the chemical state of the elements observed.[†] Three phases were positively identified: Pb(OH)Cl (laurionite) on the cathodes, $\beta\text{-FeOOH}$ (akaganeite) on one of the anodes, and NaCl (halite) on one of the neutral electrodes. This electrode was situated at the bottom of the expansion pipe and it is probable that salt precipitated while flow was being shut

^{*}D. Ryon, Lawrence Livermore Laboratory.

[†]W. Birka, Lawrence Livermore Laboratory.

Table 3A. Spectrochemical analysis report (percent by weight)

Element	+5 V	Charge 0	+5 V
	%	%	%
Fe	≥ 10	≥ 10	≥ 20
Si	≥ 10	≥ 10	≥ 10
Cu	4	3	3
Ca	2	3	4
Ag	1	2	0.5
Na	1	1	1
Al	1	1	0.5
B	0.4	0.4	0.5
Mn	0.4	0.4	0.5
Sb	0.2	0.2	0.2
Cr	0.1	0.02	0.2
Be	0.1	0.1	0.1
As	0.1	0.1	0.1
Pb	0.1	0.1	0.1
Ga	0.04	0.04	0.1
Sr	0.04	0.04	0.05
Ba	0.04	0.03	0.05
Zn	0.03	0.04	0.04
Mo	0.03	0.02	0.05
Mg	0.03	0.02	0.03
Ge	≤ 0.03	≤ 0.02	≤ 0.03
In	≤ 0.03	≤ 0.02	≤ 0.03
Ni	0.03	0.01	< 0.03
Zr	nd $<0.01^a$	0.01	0.01

^and = not detected.

The following elements were not detected in these samples:

<0.1 Nb, V
 <0.03 Bi, Cd, Sn
 <0.01 Co, Ti

Table 3B. Spectrochemical analysis report (percent by weight).

Element	0 (%)	+5 V (%)	0 (%)	Pipe (%)	Nozzle (%)
Si	≥ 10	≥ 10	≥ 10	≥ 10	≥ 10
Cu	≥ 10	≥ 3	≥ 4	≥ 10	≥ 15
Fe	≥ 5	≥ 8	≥ 8	≥ 5	≥ 5
Ca	1	1	1	1	1
Ag	0.7	0.9	0.9	0.5	0.5
Al	0.7	0.9	0.9	0.5	0.5
Na	0.6	0.7	0.7	2	0.1
Mn	0.4	0.5	0.7	0.3	0.3
B	0.3	0.3	0.4	0.1	0.05
Pb	0.1	0.2	0.2	>0.5	0.1
Sb	0.1	0.2	0.2	0.5	0.05
As	0.1	0.2	0.2	0.1	0.01
Zn	0.08	0.1	0.1	0.06	0.04
Be	0.07	0.09	0.04	0.005	0.01
Ga	0.07	0.09	0.1	0.05	0.03
In	0.04	0.05	0.06	0.01	0.01
Cr	0.03	0.09	0.02	nd<0.003 ^a	0.05
Ba	0.01	0.05	0.04	0.03	0.01
Sr	0.01	0.02	0.02	0.03	0.02
Ge	0.007	0.02	0.009	0.002	0.003
Mo	0.007	0.02	0.009	0.005	0.01
Ni	0.004	0.009	0.007	nd<0.0003 ^a	0.03
Sn	nd<0.003 ^a	0.05	0.02	nd<0.003 ^a	nd<0.003 ^a
Mg	0.004	0.005	0.006	0.01	0.03

^and = not detected.

The following elements were not detected in these samples:

<0.01 Cd
 <0.003 Bi, Nb
 <0.001 V, Zr
 <0.0003 Co, Ti

Table 3C. Spectrochemical analysis report (percent by weight).^a

Element	-5 V (%)	-5 V (%)	-5 V (%)
Cu	≥5	≥5	≥5
Fe	5	4	7
Si	≥5	≥5	≥5
Na	1	2	1
Ag	0.5	0.5	0.7
Ca	0.5	1	0.7
K	<0.5	≤0.5	≤0.5
Mn	≥0.5	0.3	0.4
Pb	>0.5	>0.5	>0.7
Sb	>0.5	>0.5	>0.7
Al	0.3	0.3	0.4
Ga	0.3	0.3	0.4
As	0.1	0.1	0.1
B	0.1	0.1	0.1
Mo	0.03	0.03	0.04
Zn	0.03	0.03	0.1
Ba	0.01	0.01	0.01
Be	0.01	0.01	0.01
Cr	0.01	0.01	0.01
Mg	0.01	0.01	0.4
Ni	0.01	0.005	0.001
Sr	0.01	0.03	0.01

^aThe following elements were not detected in these samples:

<0.003 Bi, Nb, Sn
 <0.01 Cd
 <0.001 V, Zr
 <0.0003 Co, Ti

Table 4. X-ray fluorescence analysis report (D. Ryon).

Charge	Si	S ^b	Cl	K	Ca	Elements ^a		Zn	As	Ag	Pb
						Fe	Cu				
+5V	4	≤0.1	3.7	0.4	1.0	20.	1.2	~0.1	0.15	0.30	0.06
+5V	4	≤0.6	2.5	0.4	1.0	7.3	0.35	0.1	~0.07	0.30	~0.01
0	6	≤0.1	2.4	0.3	1.0	2.63	0.55	-	~0.01	0.30	~0.004
0	7	≤0.4	1.6	0.4	1.0	19.	2.7	-	~0.05	3.19	~0.02
-5V	4	≤0.2	.82	≤0.04	1.0	0.28	0.84	-	c	0.28	2.56
-5V	2	≤0.03	1.6	0.07	1.0	0.84	2.1	-	c	0.10	10.
PIPE	12	~0.6	2.3	2.2	1.0	12.	1.9	-	0.10	1.07	0.05

^aRelative (to Ca) amounts by weight

^bThere is a system background peak of unknown origin that appears at the sulfur wave length. Therefore, S numbers are suspect.

^cAs may be masked by lead.

off. Other possible phases identified from the complex patterns are $\text{Cu}_{1.8}\text{S}$ (digenite) on one and possibly both of the neutral electrodes, and Cu_3FeS_4 (bornite) on one and possibly both of the cathodes. Birka states that it is highly possible that there is at least one unidentified phase on the cathodes. Collectively, the diffraction evidence suggests that the increased iron on the anodes is concentrated as FeOOH , and the increased lead in the cathodes as

Pb(OH)Cl . It is likely that other unidentifiable sulfide phases are present. The state of the apparent increased chlorine and zinc on the anodes is unresolved. All other elements are in sufficiently small quantities so that their phases are undetected by x-ray diffraction. No phases containing silicon, the most abundant element analyzed, could be detected. This implies it is present in either the cryptocrystalline or amorphous state.

Conclusions

In general, it appears that lead is preferentially attracted to the negative electrode. There is some indication that it is followed by copper. On the other hand, iron is concentrated on the anode and is followed by zinc. These observations suggest that lead and copper are present in the brine as cationic species, but that iron and zinc are complexed in solution, perhaps as hydrolysed species. However, the x-ray diffraction results reveal that the lead is present in scale as Pb(OH)Cl . Pb(OH)^+ may therefore be the species in solution. Certainly the presence of FeOOH supports the contention that $(\text{FeOH})^+$ or Fe(OH)^{++} - type complexes exist in the solution. It is possible that FeOOH (with Fe^{+3}) stabilized while the samples were oxidizing enroute to LLL. That iron is enhanced on the anode would seem to indicate that the iron is not present as a simple hydroxide. The lack of a positive correlation between oppositely charged electrodes suggests that species are being precipitated in the presence of an electric field which would remain in solution otherwise.

The form of the large amounts of silicon is unknown and, based on the lack of definitive detection by x-ray

diffraction methods, we might conclude that it is amorphous or cryptocrystalline. The seeming reduction of the amount of silicon that occurs when applying a negative potential is probably related to the presence in suspension of negatively charged colloidal particles of polymeric silicic acid. Polymerization takes place very rapidly in acid solutions.* The pH of the water from Sinclair No. 4 has been measured at $\approx 5.2(25^\circ\text{C})$.† Without more experimental data further discussion would be too speculative.

The results of the preliminary experiments described here are encouraging. Scale formed on the electrodes (as opposed to corrosion) and there were decided differences produced by varying the charge on the electrode. We propose, therefore, that a new series of experiments in the field be conducted in which:

- Runs are made for shorter times ($\leq 1\text{h}$ is sufficient to produce appreciable scale).

* R. K. Iler, private communication, 1975.

† J. Hill, private communication, 1975.

- Precautions are taken to keep samples in an inert atmosphere before analysis so as to avoid oxidation effects.
- An experiment at more negative potentials ($< -5V$) is run which may yield more positive results on depletion of silica scale.
- An experiment at less negative potentials is run to determine if the amount of excess lead being attracted to the cathodes can be reduced while maintaining the smaller amount of silicon present.
- The pH is varied (Eh also altered) and effects noted on scale formed.
- A noble metal or inert electrode is used to prevent possible electrode-brine reactions.

It is conceivable that a system can be designed in which, through control of oxidation and/or acidity, the constituents of scale can either be collected in a separator or kept in suspension, thereby enabling the full potential energy of the brine to be utilized.

Acknowledgment

We are grateful to M. Fulk for critical suggestions.

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