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REMOVAL OF SILICA FROM SPENT GEOTHERMAL BRINE

Richard W. Ryon and John H. Hill

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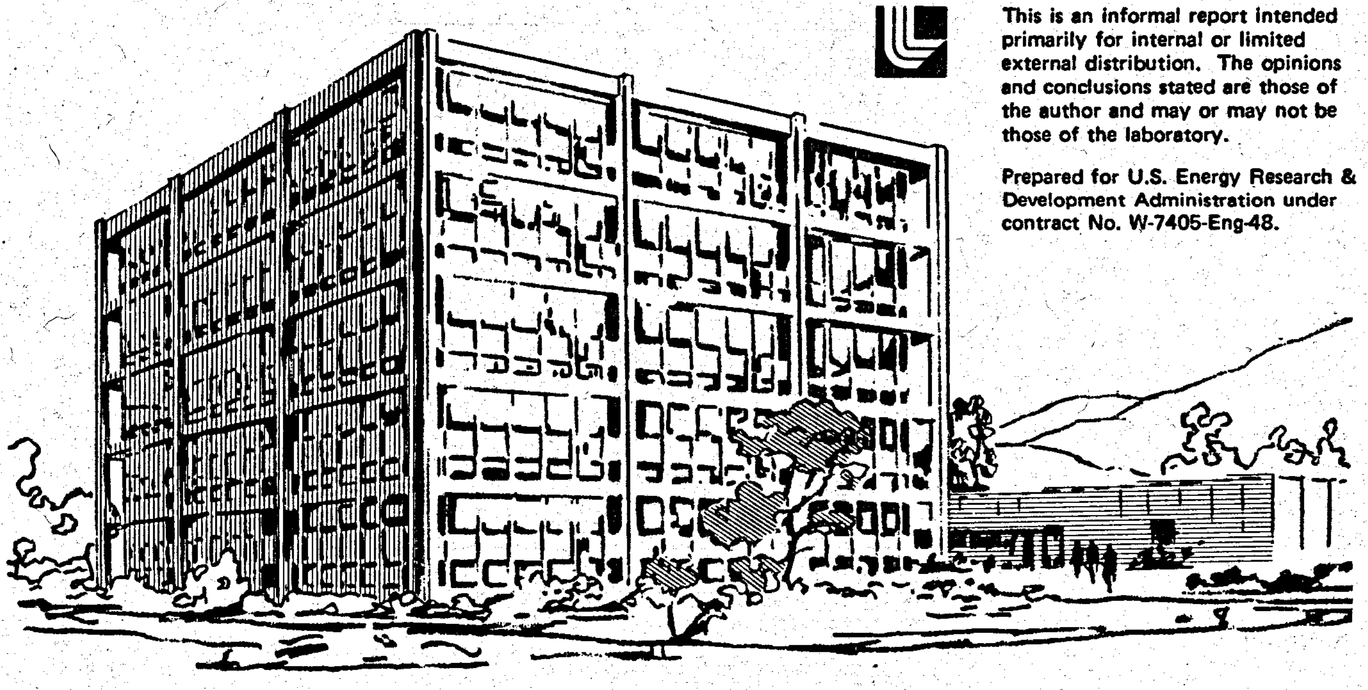

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REMOVAL OF SILICA FROM SPENT GEOTHERMAL BRINE

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ABSTRACT

This report is based on preliminary survey experiments conducted at the LLL Salton Sea Geothermal Test Site in April and May, 1977. The addition of caustic to raise the brine pH to ~6 precipitated silica and other materials. The addition of flocculating agents, such as ferric hydroxide, aids settling and filtration. Small-scale pilot plant studies are recommended.

INTRODUCTION

The large volume of geothermal brine used in test facilities, and ultimately in electrical generating plants, must be disposed of after use. Evaporation ponds would require a large a land area in the agriculturally rich Imperial Valley. There may also be air pollution problems associated with evaporation ponds. Export to the Salton Sea is precluded because that sink is already over-used for agricultural run-off. The most viable alternative available is reinjection into the underground formation. This alternative has the added advantage of maintaining the ground water level, thus alleviating surface subsidence and also maintaining the geothermal resource.

Direct reinjection of spent brine suffers from the fact that precipitation of solids occurs when the temperature and pressure decrease as a result of using the brine. Plugging of the reinjection well at the test site has occurred, and there is concern that the formation itself may become plugged. Precipitates taken from the reinjection line are found to contain large amounts of silica, along with iron and smaller amounts of other minerals.[1] Acidification of the brine to pH <4.5 has previously been shown to slow the precipitation of solids.[2] This may alleviate plugging of the reinjection well. However, reaction with carbonate rocks in the formation may be expected to raise

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[1] Arthur L. Austin, Anders W. Lundberg, Larry B. Owen, and George E. Tardiff, LLL Geothermal Engineering Progress Status Report for January 1976 — January 1977, UCRL 50046-76, April 27, 1977.

[2] J. H. Hill, C. H. Otto, and C. J. Morris, Solids Control for High Salinity Geothermal Brine, in "Geothermal: State of the Art," pp. 139-40, Geothermal Resources Council, Transactions, Vol. 1, May 1977.

solution pH, and therefore precipitation and plugging of the formation may occur. The use of sequestering agents or surfactants to hinder precipitation may also suffer from undesireable reactions within the formation.

EXPERIMENTS AND OBSERVATIONS

The approach we chose to survey was to remove silica by the addition of caustic. Crude observations of settling rates and the effect of a ferric hydroxide flocculating agent were made. Precipitates and supernatant solutions were analyzed. Floc was produced by two methods: 1) addition of $FeCl_3$ solution prior to addition of caustic; 2) addition of Clorox bleach (NaOCl) to oxidize ferrous ion in solution to ferric, and then addition of caustic solution. The treated brine was placed in unthermostated 500 ml graduated cylinders, observed visually, and sampled after about 1 1/2 hours.

The treatment of brine by caustic precipitates silica and other materials and decreases the visual cloudiness of the solutions. When ferric hydroxide is present, the solutions are visually clearer than in its absence. Ferric hydroxide also increases the settling rate and makes the suspended precipitates easier to filter with coarse filter media.

Ferric concentrations between 10-100 ppm and pH's between about 5-6 produce rapid settling and easily filterable floc. The bulk of the precipitates settle within 1/2-1 hour.

Table 1 lists the more significant experiments and gives some of the measured brine and precipitate characteristics. Increasing the pH to 7.0 precipitates 90-95% of the Si (~10 mg/l ÷ 155 mg/l); whereas at pH=6.0, about 1/2 the Si precipitates (~80 mg/l ÷ 155 mg/l). Note that less than 500 mg/l (ppm) of total solids are removed at pH = 6.0. Total dissolved solids are about 17% in the brine. The last column gives the percentage of the initial volume occupied by the settled, uncompacted precipitates. These numbers indicate the volume which would have to be disposed of if settling tanks were used.

Table 2 gives the elemental composition of the suspended and settled precipitates as determined by x-ray fluorescence analysis. (No determinations were made for elements below Si.) The last column in the table lists the concentration of the elements found in the as received solution, on a water and NaCl-free basis. Comparison of the concentrations of the elements in the precipitates with the corresponding concentrations of the dissolved solids initially in the brine clearly shows the preferential precipitation of Si at pH=6. It also appears that the fine, suspended solids are somewhat richer in Si and substantially richer in S than the settled solids.

Table 3 lists the percent of the initial concentrations of various elements which precipitate under the given conditions. These data are derived from Tables 1 and 2. Under the given conditions, Si and Fe are the primary elements which precipitate, with some entrainment of other elements.

PRELIMINARY CONCLUSIONS

One might suggest possible schemes for brine treatment prior to reinjection. A flocculating agent such as ferric chloride or alum could be metered into the brine, or ferric ions could be produced by oxidation or electrolysis of the ferrous ions already in solution. Following precipitation with caustic, the brine could either be centrifuged or settled and filtered. Conceptually, centrifugtion seems like the better alternative, since it would require less land area, would not entail cooling of the brine before reinjection, and would avoid the operational requirement of frequent back-washing of the filter bed. Small pilot plant tests of these suggestions are recommended as the next step.

While it is expected that the treated brine will be stable at the equilibrium pH of the geothermal aquifier, this expectation has not been experimentally verified.

TABLE 1. Gross Effects of Brine Treatments.

Brine Source	Treatment	pH	Suspended precipitates mg/l	Settled precipitates mg/l	Settled Precipitates, corrected for nominal FeO(OH) mg/l	Si in solution mg/l (1.)	Precipitate volume, % of brine volume	
Woosley MX3-L87	As taken	5.2	92	98		155	<1	
	As taken	6.0	78	226			3	
	As taken	7.0	48	1008		10	10	
-L86	Fe = 10 ppm	5		216	200	100/85*	2	
	Fe = 10 ppm	6		296	280	80/75*	4	
	Fe = 20 ppm	5		248	220		3	
	Fe = 20 ppm	6		332	300		4	
	Fe = 50 ppm	5		346	260		3	
-L87	NaClO ≈ 50 ppm	5	50	348	≥220	85	5	Fe^{+3} equiv ~ 75 ppm
	NaClO ≈ 190 ppm	6	52	598	≥140	70		Fe^{+3} equiv ~ 285 ppm
Magma 1 SB-TF 95	As taken	5.9	162	192		110	3	
	As taken	7.0	92	842		15	12	
	Fe = 10 ppm	6.0	116	220	200	110	5	
	Fe = 50 ppm	6.0	48	456	280	105	7	
	NaClO ≈ 50 ppm	6.0	68	292	≥180	110	5	Fe^{+3} equiv ~ 75 ppm
					Settled, less Anal. FeO(OH)			
LM-SB-TF 105	As taken	5.85	120	260	220	70	<1	
	Fe = 50 ppm	6.0	212	234	200	67	8	
	NaClO ≈ 30 ppm	6.0	268	122	60	67	1-2	Fe^{+3} equiv ~ 50 ppm
	NaClO ≈ 100 ppm	6.0	64	376	240	85	8	Fe^{+3} equiv ~ 150 ppm

*Filtered before analysis

1.) Anamet Analysis

TABLE 2. Chemical Analysis of Precipitates.

Brine Sample LM-SB-TF105
Concentrations are Percent by Weight

	As Received pH = 5.85		Fe^{+3} = 50 ppm pH = 6.0		NaClO ~ 30 ppm pH = 6.0		NaClO ~ 100 ppm pH = 6.0		Anal. of Total Solids in Solution[1] - NaCl and water free basis
	Settled	Suspended	Settled	Suspended	Settled	Suspended	Settled	Suspended	
Si	27.	34.	16.	29.	28.	31.	23.	23.	.20
S	.3	2.4	.5	2.	.6	1.0	.4	5.	
K	1.	1.	.8	.8	.8	.7	.7	2.	9.8
Ca	3.5	2.	3.7	3.	2.8	3.	3.5	9.	33.
Mn	.04	≤.1	.11	≤.1	.23	.2	.22	.3	.66
Fe	2.9	4.	20.4	12.	12.6	9.	17.8	22.	.17
Cu	.01	<.01	.01	<.04	≤.01	<.07	.01	.02	<.002
Zn	.35	.4	.89	1.3	1.2	.9	.87	1.	.26
As	~.05	<.06	~1.0	~.8	~3.3	~1.8	~2.3	~3.	
Sr	.04	<.02	.08	<.03	≤.05	≤.02	.07	≤.1	
Ag	.4	<.1	.1	<.1	<.1	.8	.9	<.4	
Sb	.05	<.07	.11	<.06	.10	.06	.05	<.2	
Ba	<.02	<.1	.8	<.1	.1	<.1	.1	<.2	.15
Pb	.2	<.1	1.1	<1.	.9	.7	.9	~2.	.04
Sn									.06

1.) Density = 1.12 g/ml
Total Dissolved Solids = 16.8%
NaCl = 10.2%

TABLE 3. Percent of Dissolved Substances Which Precipitate
Brine Sample LM-SB-TF105*

	As Received pH = 5.85	Fe^{+3} = 50 ppm pH = 6.0	NaClO ~ 30 ppm pH = 6.0	NaClO ~ 100 ppm pH = 6.0
Si	75%	82%	80%	69%
Ca	.05	.08	.05	.08
Fe	10.	55.	30.	64.
Zn	.7	3.	2.	2.
Ba	<.2	3.	.2	.5
Pb	2.	14.	10.	17.

*These data are derived from Tables 1 and 2. To illustrate how the numbers are obtained, consider the case of Si in the "as received" Sample at pH = 5.85:

From Table 1

Settled precipitate = 260 mg/l
Suspended precipitate = 120 mg/l

From Table 2

Si in settled precipitate = .27 × 260 = 70.2 mg/l
Si in suspended precipitate = .34 × 120 = 40.8 mg/l
Total Precipitated Si = 111.0 mg/l

$$\text{Si in Solution} = \frac{.0020\ \text{g Si}}{\text{g(NaCl free solids)}} \times \frac{(.168-.102)\text{g(NaCl free solids)}}{\text{g (solution)}}$$

$$\times \frac{1120\ \text{g(solution)}}{1\ \text{(solution)}} (\times\ 1000\ \text{mg/g}) = 148\ \text{mg Si/l}$$

$$\%\ \text{Si precipitated} = 100\ \frac{111\ \text{mg/l}}{148\ \text{mg/l}} = 75\%$$

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