27
4128180
840 NTIS

UCID-18596

MASTER

**LLL INDUSTRIAL SUPPORT PROGRAM TEST RESULTS
ON SCALE CONTROL, CORROSION, H₂S ABATEMENT,
AND INJECTION AT THE SALTON SEA GEOTHERMAL FIELD
IN FY 79**

**R. Quong
L. B. Owen**

March 1980

The logo for Lawrence Livermore Laboratory, featuring a stylized 'L' symbol and the text 'Lawrence Livermore Laboratory' in a bold, sans-serif font, all contained within a large, stylized 'V' shape.

This is an informal report intended primarily for internal or limited external distribution. The opinions and conclusions stated are those of the author and may or may not be those of the Laboratory.

Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore Laboratory under Contract W-7405-Eng-48.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

CONTENTS

Page

Scaling Rate and Scale Properties

3

S. B. Deutscher, R. Quong, D. M. Ross, and J. E. Harrar

Scale Control Additives

37

J. E. Harrar, F. E. Locke, L. E. Lorensen, R. Quong, C. H. Otto, Jr.,
W. P. Frey, S. B. Deutscher, E. O. Snell, and R. Lim

Evaluation of Tested Metallic Materials for Plant Applications

73

R. D. McCright, A. Goldberg, E. O. Snell, F. E. Locke, R. McLain,
W. P. Frey, W. J. Steele, R. Quong, and G. E. Tardiff

Hydrogen Sulfide Abatement

97

R. Quong, K. G. Knauss, N. D. Stout, L. B. Owen, C. H. Otto, Jr.

Well Casing Materials

115

R. D. McCright, A. Goldberg, E. O. Snell, F. E. Locke, R. McLain,
W. P. Frey, W. J. Steele, R. Quong, and G. E. Tardiff

Injection Studies

137

L. B. Owen, E. Raber, J. E. Harrar, C. H. Otto, Jr., R. Netherton

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

fyg

INTRODUCTION

The Lawrence Livermore Laboratory's Geothermal Project in FY79 included technical assistance to the joint San Diego Gas & Electric/Department of Energy Geothermal Loop Experimental Facility (GLEF) located near Niland in the Imperial Valley, California. LLL's participation consisted of field testing and evaluation of potential solutions to serious operational problems impeding the utilization of the hot, hypersaline brines of the Salton Sea Geothermal Field (SSGF) for electric power production.

A test plan was formulated by the principal industrial participants, DOE/DGE, and LLL for implementation at the GLEF and at the adjacent LLL test facility. The major issues included scale control, corrosion, H₂S abatement, and injection. In addition, other specific engineering concerns such as plant component evaluation, scale removal techniques, and instrument reliability were also to be addressed. The plan was divided into individual tasks to be conducted by the organization with the appropriate expertise. Assigned task priorities were based largely on the potential benefit to progress at the SSGF derived from resolution of that particular issue.

This report summarizes in detail the data and results of the tasks in which LLL had primary responsibility. It also marks the conclusion of LLL's Geothermal Industrial Support activities at the SSGF. The unusual format is based on guidelines established by SDG&E and enables this material to be included with minimal editorial changes in the SDG&E's final report which summarizes all relevant GLEF test activities.

Reference is made to the letter of the 10th of March 1944.

The Commission has received the letter of the 10th of March 1944 and has taken note of the information contained therein. The Commission has also received the letter of the 10th of March 1944 and has taken note of the information contained therein. The Commission has also received the letter of the 10th of March 1944 and has taken note of the information contained therein.

The Commission has also received the letter of the 10th of March 1944 and has taken note of the information contained therein. The Commission has also received the letter of the 10th of March 1944 and has taken note of the information contained therein.

The Commission has also received the letter of the 10th of March 1944 and has taken note of the information contained therein. The Commission has also received the letter of the 10th of March 1944 and has taken note of the information contained therein. The Commission has also received the letter of the 10th of March 1944 and has taken note of the information contained therein.

The Commission has also received the letter of the 10th of March 1944 and has taken note of the information contained therein. The Commission has also received the letter of the 10th of March 1944 and has taken note of the information contained therein. The Commission has also received the letter of the 10th of March 1944 and has taken note of the information contained therein.

The Commission has also received the letter of the 10th of March 1944 and has taken note of the information contained therein.

3.2.2.0 SCALING RATE AND SCALE PROPERTIES

Responsible Organization: LLL

Investigators: Suzanne B. Deutscher, Roland Quong, Donna M. Ross,
Jackson E. Harrar

Priority: 1

3.2.2.1 OBJECTIVES:

The objectives of this test are to measure the amount of scale that forms in various sections of the plant and to evaluate the mineralogical and mechanical properties of that scale in connection with the effort required to remove it. This information will be used to help size piping and vessels, and to indicate the frequency of cleaning for the 50 MWe power plant proposed for the Niland reservoir.

Scaling rates will be measured at the approximate conditions present in each of the following areas:

1. Production line piping;
2. 1st to 2nd stage piping;
3. 2nd stage to atmospheric flash drum piping;
4. Atmospheric receiver drain line;
5. Injection line piping.

Scale samples from each of these areas will be analyzed for mineralogical properties, as well as for mechanical properties such as hardness, adherence to wall, etc. In addition to obtaining scaling rates and conducting scale analyses, various chemical solvents will be tested as a means of enhancing scale removal with possible on-line application.

3.2.2.2 BACKGROUND:

Deposition of scale in separators, piping, and critical components continues unabated at the GLEF as a result of flashing Niland brines. The removal of scale from GLEF piping and components has become a time consuming and costly plant maintenance item. Although acidification of the brine to control scaling has been successfully demonstrated, accompanying effects such as accelerated corrosion characterize this method as too risky for present application. An alternative and promising chemical method for scale control is the use of organic inhibitors. This method will be extensively evaluated in Test 3.0. However, until a scale control method can be successfully demonstrated both technically and operationally, it will be necessary to periodically descale the plant. The chemical and physical properties of the scale and the rate at which it forms will dictate selection of methods and frequency of removal. Methods of removal will be evaluated in Test 1.0. The properties of the scale and the rate of deposition will be evaluated in this section of the test program. Much of the previous work at the GLEF on scaling rate and scale properties remains applicable (1-3). However, the effects of the changeover to a 2 stage flash process and of the use of brine from the reworked Woolsey #1 will need to be determined.

-
- (1) SDG&E/DOE Geothermal Loop Experimental Facility (GLEF). Bimonthly and Quarterly Reports, SAN/1137-1-9, 1976, 1977, 1978.
 - (2) Quong, R., H. K. Bishop, J. H. Hill, Scale and Solids Deposition in the SDG&E/US ERDA GLEF at Niland, California, Geothermal Resources Council, Transactions, 1, May 1977, (249).
 - (3) Quong, R., Scaling Characteristics in the GLEF, Lawrence Livermore Laboratory Report UCRL-52162, November 1976.

3.2.2.3 TEST DESCRIPTION AND PROCEDURE

3.2.2.3.1 Test Materials and Equipment

Testing will be carried out at the GLEF. At the GLEF, 4 feet long scaling spools of the same material and diameter as the lines in which they are located will be the test specimens. Spools will be located in the separator drain lines, the atmospheric flash tank drain line and in an unpigged portion of the injection line downstream of the clarifier-filter system. The spools should be horizontal and easily accessible. If spools are not available, the plant piping by necessity will be used to satisfy the test objectives. No additional plant equipment is required assuming flowrate, temperature, and pressure are being measured and recorded at reasonable frequencies throughout the plant.

Chemical methods of scale removal will be tested using conventional laboratory equipment. If such a chemical is discovered, on-line tests will be conducted at the LLL 2-stage flash system. Figure 1 is a schematic diagram of this system which will include a control channel with scale from testing of scale control additives as described in Test 3. Removal of this scale will be the basis for the on-line scale removal test by chemical methods.

SCALE-CONTROL TEST SYSTEM

FIGURE 1

3.2.2.3.2 Test Prerequisites

In order to conduct an on-line test of a chemical for scale removal, at least one channel of the LLL test system (Fig. 1) will need to have been scaled during conduct of test 3. Otherwise, there are no other tests which need to be performed prior to or in conjunction with this test.

3.2.2.3.3 Test Conditions

1) At the GLEF, constant (and preferably full design) flow and temperature should be maintained in the plant during the operational period between each inspection of the spools. Flow variations of no more than $\pm 10\%$ from the mean is desirable, but $\pm 20\%$ is acceptable if that is the best achievable at the GLEF. Temperature within $\pm 5\%$ of the mean is required. Flashing in liquid drain lines should be minimized. Flow from Magmamax #1 and Woolsey #1 should be restricted to their respective trains. During the test period, scale in the lines upstream and downstream of the spool sections should not be disturbed. If scale removal is necessary, then the spools themselves should also be cleaned.

3.2.2.3.4 Required Data & Observations

Data will be obtained from the scaling spools located in the production line, in the drain lines of each separator stage, in the atmospheric receiver drain line, and in the unpigged portion of the injection line. During each inspection period, scale thickness,

hardness, adherence, and density will be measured/observed and recorded. Scale thickness at different points along the spool perimeter will be measured using simple tools such as rulers and micrometers. Scale hardness will be measured by using an ASTM Shore A, D, & O Hardness apparatus. Adhesion will be defined as the lateral force per unit contact area to dislodge a piece of scale from a surface. Density will be determined by combined gravimetric and volumetric measurements on a sample. Scale mineralogy will be determined by X-ray diffraction analysis. Occasional chemical analysis by X-ray fluorescence, emission spectroscopy, or atomic absorption will be necessary.

Corresponding plant operational data will also be recorded. These include the usual plant data such as flowrate, temperature, and pressure at each and every flash stage, and brine chemical composition and pH.

The type and amount of chemicals used in the scale dissolution/removal tests will be recorded along with a narrative of effectiveness. The on-line tests will require measurement of scale thickness at the start of the test and again at the completion of the test. The rate of chemical usage will be documented.

3.2.2.3.5 Test Duration

A 30-day test period with fluid flowing from Magmamax #1 and Woolsey #1 through their respective trains either simultaneously or separately is required. A second 30 day period should be allowed for

reruns. An additional 30 days should be allowed for data analyses and preparation of results.

The scale removal test at the LLL facility is anticipated to be completed within 2 days.

3.2.2.4 RESULTS

3.2.2.4.1 Expected Results

The data obtained from the GLEF will provide at the minimum scaling rate and scale properties, both chemical and mechanical for a 2-stage flash process utilizing Magmamax #1 and Woolsey #1 brines.

Evaluation of scale removal techniques (Test 1) is an important part of this test program. Knowledge of scale mineralogy, hardness, adherence, and density may influence removal methods. If a chemical for scale dissolution is found, then adopting this for on-line scale removal may be possible.

It is expected that these data will enable designers to make a more accurate estimate of scaling rate and scale properties in a 50 MW plant and hence reduce the risk of having an inadequate scale maintenance program and the associated uncertainty in estimating the cost of such a program.

3.2.2.4.2 Data and Observations

Experimental Procedures:

After the operation of the GLEF with Magmamax No 1 brine for 1351 hours, ending in September 1978, six samples of scale were removed from various points in the plant as shown in Fig. 2. In March 1979, after 904 hours of operation with Woolsey No 1 brine, 5 samples of scale were removed, the locations of which are also shown in Fig. 2.

These samples represent scale deposited during two major periods of GLEF operation. Intermediate shutdowns for scale thickness measurements and sampling were not scheduled because of other higher priority tests and hence are not available. Scaling rates were determined by thickness measurements of scale in pipes at the GLEF and from scale samples. Scale properties measurements and dissolution tests were carried out with the above described samples. Also included in the dissolution experiments was a sample of Magmamax No. 1 wellhead scale obtained early 1978.

The samples designated V11 Top and V11 were taken, respectively, from above and below the brine level of the second stage separator. The appearance of the scales ranged from very wet and soft (V11) to very hard and dry (wellhead). The scales were rinsed, dried in a vacuum desiccator, and ground with a mortar and pestle.

A 1-g sample of the prepared scale was mixed with 100 ml of the solution of interest, using a polyethylene-coated overhead stirrer. Stirring continued throughout the experiment. Solutions run at 80°C were allowed to warm before addition of the scale and were kept warm during the experiment with hot plates. After the allotted time had

Figure 2. Schematic Diagram of the Geothermal Loop Experimental Facility. Scale Sampling Points are Indicated on the Diagram.

elapsed (1, 4, or 24 hrs.) the mixtures were filtered through tared Whatman No. 541 filter paper. The filtrates were collected and the residues rinsed and allowed to dry for 2 days. A blank was run with each set by omitting the addition of the scale. The dried filter papers containing the residues were weighed, the amount of dissolution calculated, and the residues together with the filtrates reserved for further analysis.

Results

The scales can be divided into three general types: from the wellhead (or production line in the case of the Woolsey scales), from the first stage separators, V4 and V1, and from the 2nd stage separators, V11 and V14. The V15 atmospheric receiver scales fit into the 2nd stage separator group. The analyses of these scales are given in Tables 1 and 2. These data indicate that wellhead and production line scales are primarily Pbs with small amounts of SiO_2 and Fe_3O_4 ; V1 and V4 scales are mainly SiO_2 , Fe_3O_4 , and some Pbs; and V11, V14, and V15 scales are mostly SiO_2 . Silica in all the scales is amorphous.

The results of the dissolution experiments are given in Tables 3 and 4. Figures 3-14 are plots of percentage of a specific scale dissolved versus the type of reagent. The reagents selected were based on existing knowledge of the mineralogy of scale deposited at the GLEF. The concentrations used would be considered "safe" in an in-plant situation. In addition to common laboratory solvents, a solution of inhibited acrolein (2-propenal) marketed as Magnatreat M by Magma Corporation was tested on V4 scales. Magnatreat M is used to remove iron sulfide deposited at the formation surface in oil-field injection wells. In all cases the Magnatreat was less effective than water.

Scaling rates were determined by dividing scale thickness by total time. Scaling rates may actually vary considerably from the onset of exposure of a clean surface to brine to a point in time when heavy scaling has occurred. Scaling rates may be very low during an initial

Table 1. Composition of Scales for the GLEF after Operation with
Brine from Woolsey No. 1 and Magmamax No. 1

Concentration, Wt %, in scale from:

904 hours Operation with Woolsey No. 1 brine Sampled in March 1979						1361 hours with Magmamax No. 1 brine Sampled in September 1978						
Element	WPL	W1A-in	W1ADS	W2ADS	WV15OUT	Wellhead	V4	V4D	V11TOP	V11	V11D	V15
SiO ₂ ^b	0.15	33.0	40.4	78.7	52.6	4	25.8	23.6	66.4	57.2	70.3	63.8
Sb	7.1	0.22	0.41	0.15	0.28	12	2.6	2.0	0.32	0.24	0.28	0.86
C1b	0.12	2.6	2.0	1.1	3.4	-	3.5	2.5	0.89	4.8	3.2	3.8
Kb	0.08	1.6	1.1	0.76	2.0	-	1.6	1.7	0.58	1.09	0.96	0.89
Ca ^b	0.20	3.3	1.6	1.1	4.5	0.2	3.6	2.4	1.08	2.9	4.4	1.9
Ti ^b	-	-	-	-	-	0.03	-	-	0.01	0.008	0.07	0.08
Mn ^b	0.41	2.0	2.5	0.33	0.37	0.03	1.2	1.1	0.67	0.16	0.65	0.06
Fe ^b	≥8.2	≥13.	≥14.	2.0	1.8	0.07	17.7	11.6	12.5	0.88	0.68	0.92
Cu ^b	0.25	0.42	0.43	0.08	0.18	0.02	0.28	0.10	0.38	0.05	0.04	0.32
Zn ^b	0.11	0.11	0.13	0.12	0.13	0.70	1.02	0.26	0.17	0.07	0.15	0.06
Rb ^b	0.10	0.02	0.01	0.008	0.01	-	-	-	-	0.004	0.004	0.005
Sr ^b	.00	0.07	0.03	0.05	0.09	trace	0.11	0.07	0.02	0.05	0.04	0.04
Ag ^b	-	-	-	-	-	0.34	0.12	0.09	0.01	0.01	0.01	0.009
Sb ^b	-	-	-	-	-	trace	0.04	0.01	0.12	0.01	0.005	0.006
Ba ^a	0.1	0.15	0.2	0.6	0.4	-	0.1	0.05	0.03	0.02	0.3	0.3
Pb ^b	≥20.0	1.0	2.3	0.12	0.40	~.76	15.1	16.0	3.6	0.50	0.48	0.32
As ^b	0.19	0.09	0.12	0.05	0.02	-	-	-	<0.2	<0.04	<0.01	≤0.01
Na ^a	0.2	5	2	1	.5	-	5	2	2	10	10	10
Al ^a	0.1	0.4	0.5	0.15	0.05	-	1.0	0.05	0.5	0.03	0.05	0.05
Mg ^a	0.04	0.5	0.5	0.04	0.02	-	1.0	0.04	0.3	0.04	0.03	0.01
Ba	0.005	0.04	0.04	0.05	0.04	-	0.03	0.05	0.02	0.05	0.07	0.07
Be ^a	0.001	0.008	0.015	0.015	0.004	-	0.01	0.008	0.005	0.005	0.005	0.005
Mo ^a	0.01	0.01	0.01	nd<.003	nd<.003	-	0.01	0.003	0.003	nd<.003	nd<.003	nd<.003
Zr ^a	nd<.001	0.01	0.01	nd<.001	nd<.001	-	<0.01	<0.005	<0.005	nd<.001	nd<.001	nd<.001
Cr ^a	0.01	<0.003	<0.003	<0.003	<0.003	-	0.003	nd<.003	0.003	nd<.003	nd<.003	nd<.003
Co ^a	0.003	0.001	0.001	nd<.001	nd<.001	-	0.01	0.001	0.001	<0.0003	<0.0003	<0.003
Ni ^a	0.01	0.003	0.005	0.0005	0.0005	-	0.01	0.01	0.01	nd<.0003	0.0003	0.0003
Cd ^a	nd<.01	nd<.01	nd<.01	nd<.01	nd<.01	-	0.005 ^b	nd<.01	nd<.01	nd<.01	nd<.01	nd<.01

Elements not detected in any sample
Bi < 0.003 Sn < 0.003
Nb < 0.003 V < 0.001

^a by emission spectroscopy
^b by x-ray fluorescence
nd = not detected

Table 2. Composition of GLEF scales after operation with brine from Woolsey No. 1 and Magmamax No. 1 as determined by x-ray defraction analysis

Mineral	Woolsey No. 1					Magmamax No. 1						
	WPL	W1AIN	W1ADS	W2ADS	WV15OUT	Wellhead	V4	V4D	V11TOP	V11	V11D	V15
Amorphous Silica, SiO ₂	nd	major	major	major	major	nd	minor	trace	major	major	major	major
Halite, NaCl	nd	major	major	minor	minor	nd	major	major	minor	major	major	major
Barite, BaSO ₄	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Galena, PbS	major	trace	trace	nd	nd	major	major	major	minor	trace	minor	minor
Montmorillonite Complex Al ⁺⁺⁺ Silicate	nd	nd	nd	nd	nd	minor	minor	minor	trace	nd	nd	nd
Fluorite, CaF ₂	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Sylvite, KCl	nd	nd	nd	trace	nd	nd	nd	nd	nd	minor	nd	minor
Magnetite, Fe ₃ O ₄	nd	nd	nd	nd	nd	nd	trace	nd	major	nd	nd	nd
Laurionite, Pb(OH)Cl	trace	nd	nd	nd	nd	trace	nd	trace	trace	nd	nd	nd

nd = none detected

Table 3. Magmamax #1 Scale Dissolution Results

Solvent	Time	Temp. °C	% Scale Dissolved						
			V15D	V4D	V11TOP	V11D	V11	V4	Wellhead
0.2M HNO_3^+ 0.1M HCl	1 hr	23	19.2	35.3	12.3	29.3	22.3	39.4	13.6
	24 hr	23	24.7	58.7	11.5	--	29.4	58.0	10.4
	1 hr	80	20.7	58.8	21.0	28.0	24.3	61.3	11.0
0.05M EDTA^+ 0.5M NaOH	1 hr	23	23.0	10.8	7.9	27.0	26.2	15.9	6.5
	24 hr	23	23.3	19.8	10.6	33.4	24.8	22.2	9.01
	1 hr	80	68.4	17.7	10.9	56.5	29.8	19.0	4.6
0.5M HCl	1 hr	23	19.4	25.1	8.7	29.3	23.8	31.5	4.9
	24 hr	23	21.7	56.3	19.4	32.2	26.7	58.7	9.7
	1 hr	80	53.8	29.6	24.3	30.1	25.5	60.7	10.1
0.5M NaOH	1 hr	23	20.6	8.0	7.9	24.0	24.8	14.8	3.4
	24 hr	23	17.3	9.5	5.4	18.7	18.6	15.6	3.8
	1 hr	80	62.3	10.5	7.9	26.9	22.2	16.3	--
0.1M HF	1 hr	23	33.1	32.5	14.9	31.0	27.5	32.4	7.7
	24 hr	23	34.8	40.5	27.8	38.5	34.2	46.7	11.9
	1 hr	80	31.7	36.0	21.6	29.2	28.3	38.8	12.5
0.1M HF^+ 0.5M HNO_3	1 hr	23	28.5	58.2	22.1	37.6	30.2	49.2	10.5
	1 hr	80	35.6	76.9	33.8	40.2	36.8	77.2	77.4
0.5M HNO_3^+ 0.5M HAc	1 hr	23	22.5	26.0	10.1	29.7	28.6	27.4	4.5
	24 hr	23	23.0	57.8	14.9	32.7	27.5	55.8	52.4
	1 hr	80	20.6	58.2	15.5	31.1	26.2	58.8	75.4
0.13M H_2O_2^+ 0.5M HCl	1 hr	23	21.9	24.8	7.8	29.9	25.6	28.4	9.3
	24 hr	23	21.1	47.6	15.5	30.6	25.1	53.3	20.8
	1 hr	80	21.2	60.3	18.0	28.5	25.1	59.7	50.8
H_2O	1 hr	23	18.3	7.5	4.5	22.1	22.5	14.8	0.9
	24 hr	23	19.7	8.5	3.1	22.1	24.6	15.0	0.8
	1 hr	80	18.6	8.8	11.1	21.6	23.3	15.4	0.8

Table 4. Woolsey #1 Scale Dissolution Results

Solvent	Time	Temp. °C	% Scale Dissolved				
			W-PL	W1AIN	W1ADS	W2ADS	WV15OUT
0.2M HNO_3 + 0.5M NaCl	1 hr	23	11.4	28.9	12.1	14.5	45.3
	24 hr	23	24.6	49.2	32.5	16.2	47.8
	4 hr	80	45.5	57.1	45.6	15.8	50.2
0.05M EDTA + 0.5M NaOH	1 hr	23	9.3	16.9	0.1	11.6	47.0
	24 hr	23	18.2	19.5	4.4	18.0	52.1
	4 hr	80	12.3	23.0	5.4	49.4	85.9
0.5M HCl	1 hr	23	20.6	37.3	19.2	15.2	46.4
	24 hr	23	25.3	53.2	46.3	16.4	47.8
	4 hr	80	38.1	59.4	48.0	17.6	67.1
0.5M NaOH	1 hr	23	11.8	17.2	3.4	14.0	42.6
	24 hr	23	11.0	17.5	3.2	6.2	44.0
	4 hr	80	15.4	20.0	7.7	55.7	58.4
0.1M HF	1 hr	23	15.7	54.4	40.8	25.5	--
	24 hr	23	23.4	57.1	33.5	27.2	62.1
	4 hr	80	24.1	65.0	28.9	29.8	64.0
0.1M HF + 0.5M HNO_3	1 hr	23	23.1	59.5	43.1	24.9	62.2
	24 hr	23	38.7	76.9	63.6	28.4	65.4
	4 hr	80	87.9	--	59.9	26.3	63.9
0.5M HNO_3 + 0.5M HAc	1 hr	23	10.9	27.5	10.2	12.8	46.0
	24 hr	23	21.4	43.5	22.6	12.7	48.8
	4 hr	80	78.4	50.0	37.0	17.7	48.9
0.13M H_2O_2 + 0.5M HCl	1 hr	23	12.5	25.8	10.0	13.3	47.5
	24 hr	23	24.2	42.3	23.6	15.9	48.4
	4 hr	80	41.8	58.2	44.5	19.5	45.4
H_2O	1 hr	23	1.8	12.4	1.8	12.0	44.6
	24 hr	23	2.7	19.3	2.2	11.9	44.3
	4 hr	80	3.8	20.5	3.6	12.6	45.8

Figure 3. Dissolution of WPL Scale (Woolsey, Production Line) by Various Reagents

Figure 4. Dissolution of W-1A-In Scale (Woolsey, 1st Stage) by Various Reagents

Figure 5. Dissolution of W-1A-DS Scale (Woolsey, 1st Stage) by Various Reagents

THE FOLLOWING INFORMATION IS FOR YOUR INFORMATION ONLY. IT IS NOT TO BE USED FOR ANY OTHER PURPOSE. THE INFORMATION IS SUBJECT TO CHANGE WITHOUT NOTICE. THE INFORMATION IS NOT TO BE USED FOR ANY OTHER PURPOSE. THE INFORMATION IS SUBJECT TO CHANGE WITHOUT NOTICE.

Figure 7. Dissolution of W-V15-OUT Scale (Woolsey, Atmospheric Receiver) by Various Reagents

Figure 8. Dissolution of Wellhead Scale (Magmamax) by Various Reagents

Figure 9. Dissolution of V4 Scale (MagmaMax, 1st Stage) by Various Reagents

Figure 10. Dissolution of V4D Scale (MagmaMax, 1st Stage) by Various Reagents

Figure 11. Dissolution of Vllt Scale (MagmaMax, 2nd Stage) by Various Reagents

Figure 12. Dissolution of V11 Scale (Magmamax, 2nd Stage) by Various Reagents

Figure 13. Dissolution of VIID Scale (MagmaMax, 2nd Stage) by Various Reagents

Figure 14. Dissolution of V15D Scale (MagmaMax, Atmospheric Receiver) by Various Reagents

induction period when, for example, a pipe surface is relatively smooth and noncorroded. After the surface is scaled, a constant scaling rate should prevail. However, as the scale layer thickens and the open cross section of the pipe is reduced, the brine flow dynamics began to change significantly toward more turbulence and larger temperature and pressure losses. This results in an accelerated rate of scaling that quickly leads to a required shutdown for cleaning.

The hardness of the Woolsey Scales was measured with a Type A durometer, an instrument which conforms to ASTM 2240-75 specifications. Not surprisingly, the hardest scales are the galena based scales deposited in the production line preceding the first flash stage. The hardness of scales decrease progressively further downstream. Beyond the atmospheric receiver, the scales were too soft to be measured on the A-scale durometer. Although these scales have the consistency of mud, they do deposit as a coherent layer in the equipment and piping.

The hardness of the Magmamax Scales were not measured, but they appear to be quite similar to the Woolsey Scales.

The significance of scale hardness is open to interpretation. Hardness may be an important property in assessing the relative ease of scale removal by mechanical techniques. Scale adhesion is another property that may be germane to the ease of scale removal. However, we were unable to adopt a method which we felt would give reproducible data.

Scaling rate and hardness data for Woolsey #1 scales are given in Table 5, and scaling rate data for Magmamax #1 scales are given in Table 6.

Table 5. Woolsey #1 Scale Hardness and Scaling Rates

Sample I.D.	Sample Location	Hardness (Type A durometer)	Scaling rate mils/hr (linear)
W-PL	Production line	97	0.22
W-1A-IN	1st stage inlet	76	0.26
W-1A-DS	1st stage drain	58	1.0
W-2A-DS	2nd stage drain	44	1.7
W-V15-OUT	Atm. receiver drain	0	not measurable from sample

Table 6. Magmamax #1 Scaling Rates

Sample I.D	Sample Location	Scaling Rate mils/hr (linear)
WH	wellhead	nd
--	1st stage inlet	0.1 - .2
V4	1st stage, below liquid level	nd
V4D	1st stage drain	0.2 - .4
V11	2nd stage, below liquid level	nd
V11D	2nd stage drain	0.74 - 1.9
V11T	2nd stage, above liquid level	nd
V15D	Atm. receiver drain	1.5 - 3.0

nd = not determined

Scaling rates are highest in areas downstream of the second flash stage and are about a factor of 10 lower in the production line leading to the first flash stage. Fortunately where the scaling rates are high, the scale is quite soft (when still moist) and presumably the easiest to remove by mechanical means.

3.2.2.4.4 Comparison of Actual and Expected Results

Although some discrepancies in the data exist, there are some general conclusions that can be made with respect to the type of reagent tested best suited for dissolving a particular type of scale.

For scales consisting of predominately amorphous silica, hot NaOH is effective. NaOH in combination with EDTA, a known complexing agent for metals, was even more effective than NaOH alone. At room temperature none of the reagents tested was effective, except perhaps for 0.1 M HF which slightly attacked the scale. A more concentrated HF leach might have been beneficial, but would not be practical from safety considerations in an actual plant application. Not unexpectedly, NaOH or NaOH-EDTA combinations had little or no effect on galena or iron-rich scales.

Hydrochloric acid had some effect on iron-rich scales consisting of in part magnetite or perhaps a complex iron-rich amorphous silica. Temperature seemed to enhance dissolution. Neither HCl nor HNO₃, or combinations had much effect on silica rich scales.

HCl alone was not sufficient to dissolve the galena rich scales. Addition of an oxidant, either H₂O₂ or HNO₃, however, enhanced the effectiveness considerably. The best combinations for dissolving galena rich scales were HNO₃ with HF or acetic acid at 80°C. Apparently sulfide is oxidized, and further dissolution is aided by formation of a lead acetate complex. HF may help overall dissolution by reacting with silica which has been suggested as being the matrix material that cements the high temperature forming scales.

Based on these scale dissolution test results, an in-place scale

cleaning test was conducted in the 1st stage separator (Wellhead conditions and hence PbS scale) at the LLL Niland test facility. Immediately following separator use, combined 0.5 MHNO_3 and 0.5 MHAc (acetic acid) was injected into the lower section of the separator while still hot. After 20 hours of soaking, no appreciable effects were apparent, except for a marginal softening of the scale. Poor results may have been due to cooling of the solvent (we had no means for temperature maintenance) and insufficient solvent to scale ratio.

The results of these in-place tests indicate the problems that will be encountered in an actual application. The foremost difficulty will be slow rate of dissolution owing to the very low surface to mass ratio provided by a thick scale layer. All of the laboratory tests were conducted with scale samples that were finely ground in a constantly agitated solution. Furthermore, maintenance of temperature will require a separate heating system for the reagents or for the plant components. Another concern is the large amount of scale material in a layer deposited on pipe walls compared with the volume available to be occupied by the reagent. Repeated soakings will be necessary.

In conclusion, the laboratory measurements, conducted at near optimum conditions did not reveal an outstanding and fast dissolving reagent that under much less favorable conditions in a plant would seemingly be of some utility. A combination of chemical and mechanical cleaning methods may be most effective. However, the added improvement by use of chemicals may be marginal and greatly overshadowed by their cost, corrosivity, and danger.

3.2.2.5 CONCLUSIONS AND RECOMMENDATIONS

The scaling rates have been determined at critical locations in the GLEF in both the Magmamax #1 and Woolsey #1 trains. The rates are not substantially different from data acquired during earlier 4-stage flash operation. Scale deposition rates particularly downstream of the 2nd stage are sufficiently high (~ 1.5 "/month) to require shutdown and scale removal at frequent intervals of perhaps 1 month. Scaling rates downstream of the 1st stage are approx. 0.5-1.0"/month and would require less frequent maintenance. Wellhead and production line scaling rates are ~ 0.2 "/month and will require much less frequent maintenance, but a greater effort because of the hardness and tenacity of the predominately galena-rich material.

Scale removal based on an in-situ method using chemicals alone would require temperature maintenance of the solvent circulation loops and sufficient time for dissolution of all the scale. In the 3-50% train design, proposed in the feasibility study (Bechtel Nat'l Inc. and The Ben Holt Co., 1978), one train is isolated for a period of time for cleaning and maintenance. If this period is sufficiently long to permit continuous circulation and recirculation of solvent, scale removal without mechanical assistance may be effective. Tests with exposed spool pieces containing the principal types of scales typically deposited at the GLEF and the reagents identified in this study could be useful in final evaluation of the technical and economic merits of scale removal by chemical dissolution.

3.2.3.0 SCALE CONTROL ADDITIVES

Responsible Organization: LLL

Investigators: J. E. Harrar, F. E. Locke, L. E. Lorensen, R. Quong,
C. H. Otto, Jr., W. P. Frey, S. B. Deutscher,
E. O. Snell, and R. Lim

Priority: 1

3.2.3.1 OBJECTIVES:

The objective of this test is to determine the possibility of retarding or eliminating scale formation in a two-stage flash system through the addition of proprietary scale inhibiting chemicals or sludge particles to the brine. If these techniques are shown to have a beneficial effect, the cost per unit mass of brine treated will be estimated. This technique, if successful, may greatly reduce the cost of power from the 50 MWe power plant proposed for the reservoir.

In addition, the consequences of successful scale inhibition on corrosion and erosion of plant components, effluent treatment, injection well lifetime, etc., will be addressed qualitatively through observations and analysis of the treated brine.

3.2.3.2 BACKGROUND:

The deposition of scale from Niland brines continues to be a critical problem in geothermal conversion equipment. Frequent shutdowns for cleaning as required in the GLEF significantly reduce plant availability and contribute to high maintenance costs. Development of a scale control method would have major engineering and cost impact on a 50 MW geothermal power plant. Initial bench tests carried out at 90°C have shown that several compounds are quite promising inhibitors in acidified brine and in initially acidified

brine that subsequently was raised to pH 5.8 by calcite addition (1). Some in-line screening tests at the LLL test facility in which organic additives were injected into the 200°C unmodified brine stream discharged from the wellhead separator indicate scale deposition is indeed inhibited through the use of certain organic compounds (2). However, the brevity and the small number of tests did not permit quantitative conclusions to be made.

Injection of seed particles will also be tested as a means of providing a large and active surface area for scale deposition, thereby minimizing deposition on pipes and components. Tests with effluent brine have demonstrated that silica precipitation can be greatly accelerated by contacting the brine with large quantities of preprecipitated solids.

Additional tests may be necessary should additives prove to be effective in scale inhibition. These are 1) the need to develop methods for destabilizing the brine for effluent treatment and solids removal purposes, and 2) abatement of possible increased corrosion rates from the use of scale control additives themselves. Both of these supplementary tasks are important, will require test and evaluation, but are beyond the scope of this test.

-
- (1) Harrar, J.E., et al., "Effects of Organic Additives on the Formation of Solids from Hypersaline Geothermal Brine", in Trans. Geothermal Resources Council Meeting, Hilo, 1978, pp. 259-262.
 - (2) Harrar, J.E., et al., First On-line Tests of Organic Additives for Scale Control", in LLL Geothermal Energy Development Highlights Report, AHS/ISP-17, Sept., 1978, p. 56.

3.2.3.3 TEST DESCRIPTION AND PROCEDURE

3.2.3.3.1 Test Materials and Equipment

These tests will be conducted at the LLL test facility which operates independently of the GLEF. Figure 1 illustrates schematically the system for scale control testing. In addition to the brine handling equipment necessary to duplicate the GLEF process, analytical chemistry support facilities are also available.

Proprietary scale control additives will be prepared in the appropriate feed concentrations and injected into the high temperature brine stream discharged from the wellhead separator. An additional flash stage will drop the temperature to 125°C.

The effect of the additives on scaling rates will be determined from scaling spools, coupons, screens, and tubing. Several side stream methods designed to shorten the time required to screen the additives will also be tested. These methods include passing the brine through screens in series, capillary tubes, and beds of spherical steel balls to provide high surface area for scale deposition and hence large changes in silica concentration in the brine. The magnitude of this change in silica concentration will be used as a measure of additive effectiveness. Chemical and mechanical properties of the scale will also be determined.

For the seeding tests, precipitated solids (sludge) will be obtained from Magma Power's effluent treatment facility.

For evaluation of stability of the brine, samples of effluent will be collected, held at temperature in sealed bottles, and monitored for changes in dissolved silica concentration and production of particulates.

SCALE-CONTROL TEST SYSTEM

Figure 1

3.2.3.3.2 Test Prerequisites

There are no other tests which need to be performed prior to or in conjunction with this task.

3.2.3.3.3 Test Conditions

At the LLL test facility, fluid is supplied from Magmamax No. 1 via a 2" line. It is highly desirable, but not mandatory, that tests at the LLL facility take place simultaneously with GLEF operation, since salinity, silica concentration, temperatures, and pressures are significantly higher at full wellflow conditions. The primary requirements for conducting these tests are adequate flow of production fluid and the availability of an injection well. When the GLEF is operating steadily, the well fluid properties will normally exceed specified minimal values. However, this is not the case when the LLL facility is operating alone through the 2" line. Under these conditions, the chemistry of the separated wellhead fluid must be such that the Cl^- conc. is ≥ 3.1 moles/liter, and the silica conc. is ≥ 420 mg/Kgm. In addition, the temperature and pressure at the wellhead must be $>200^\circ\text{C}$ and >250 psia, respectively.

These test conditions downstream of the wellhead separator will be adjusted accordingly to meet the test objectives. In general, flowrate variations to the experiment will not exceed $\pm 10\%$ from the set point. Temperature in the two flash stages will be maintained within $\pm 5\%$ of the set point. The variation in flowrate of additive injected into the brine stream will not exceed $\pm 10\%$ from the set point, which will be a function of the additive used, its strength,

and feed concentration. The flowrate in each test channel will be 1.0 ± 0.1 lb/sec; temperature in the wellhead separator $\geq 200^{\circ}\text{C}$; pressure in the wellhead separator ≥ 250 psia; temperature in the flash separator $125 \pm 5^{\circ}\text{C}$. Unless specifically indicated otherwise, the wellhead separator at the LLL test facility is designated as the 1st stage separator.

3.2.3.3.4 Required Data and Observations

Spools located in the discharge lines of each separator stage will be the one source of scale rate data. The spools will be removed following each test and subsequently examined for scale thickness, hardness, adherence, and density - properties which may have a bearing on scale removal techniques. Scale thickness will be measured using micrometers, scale hardness using an ASTM Shore A, D + 0 Hardness apparatus, adhesion by the lateral force per unit contact area to dislodge the scale, and density by combined gravimetric and volumetric measurements on a sample. Scale composition, mineralogy, and morphology will be determined by X-ray fluorescence/emission spectroscopy, X-ray diffraction, and scanning electron microscopy, respectively.

Scaling coupons attached inside the spools will supplement these data. Brine discharged from the final stage will be passed through stainless steel screens as an additional test of scaling potential. A series of screens will also be used in sidestream tests.

Data will also be obtained on the stability of brine effluent from the last flash stage and inside streams by collecting and holding brine at constant effluent temperature and monitoring changes in silica concentration and total particulate content.

Plant conditions such as temperature, pressure, and flowrate at the wellhead and at each stage will be monitored and recorded every hour. Additive flowrates will also be recorded every hour. Brine chemistry will be monitored for pH, salinity, and silica concentration on a daily basis or more frequently as required.

3.2.3.3.5 Test Duration

At least 6 commercially available scale control additives will be tested for a period of 72 hours each to allow sufficient time for a measurable amount of scale to be deposited. The test length could be shortened if one of the rapid methods described in 3.3.1 is successful. Calgon CL-165, Dearborn Geomate 256, and Drew Drewspense 747 will be among the 6 additives tested. The remaining three will be selected after more companies respond. Scale analyses, interpretation of data, and preliminary reporting of results will be available about 1 month after test completion.

3.2.3.4 RESULTS

3.2.3.4.1 Expected Results

The effectiveness of proprietary additives and sludge seeding will be determined.

Scaling rate and scale properties data will be produced at each test condition.

Stability of dissolved silica and production rate of suspended solids in the brine effluent will be determined.

Finally LLL will assist in selecting the chemical additive and in

designing the necessary equipment to conduct a full scale test at the GLEF. This will include preparation of a test plan required for implementation.

3.2.3.4.2. Data and Observations

3.2.3.4.2.1 Observations on Testing Techniques

A major emphasis in our work was to develop and use techniques of scaling rate measurement that would minimize the time required to evaluate a single additive, but still provide useful information for prediction of performance in larger facilities and for longer times. In the tests of the various additives we have made the following observations on the testing techniques:

1. Use of the packed metal-ball column was unsatisfactory, probably because of the difficulty in providing a large surface area for brine contact throughout the columns. However, successful experiments of this type using simulated geothermal brines and other packing materials have been done recently at Oak Ridge (3), and additional work could be done to optimize the metal column used here. However, as discussed below, apparatus such as this, which depends on passing the brine through small orifices with a large surface area of contact, is vulnerable to the suspended solids in the brines that may obscure the "true" scaling rate.

(3) E.G. Bohlmann, R.E. Mesmer, and P. Berlinski, "Kinetics of Silica Deposition from Simulated Geothermal Brines," in Proc. Int. Symp. Oilfield and Geothermal Chem., Houston, 1979, p. 257.

2. Flowing the brine through screens at the high temperature test point ($\sim 200^{\circ}\text{C}$) was unsatisfactory because the usual particulate level in the brine tended to plug the screens and obscure the accumulation of "true" scale. This particulate level was very sensitive to plant upsets (e.g., sudden variations in pressure or flow), and hence so was the screen test. At 200°C it was generally not a reliable indicator of brine scaling tendency. Better results were obtained with screens at 125°C . At this temperature, ~ 24 h were required for a definitive measurement. However, there is still an occasional lack of repeatability in this technique which has not always been explainable in terms of plant operating conditions.

3. Use of the 1-inch-i.d. pipe spools, which were epoxy-potted, sectioned, and polished for microscopic examination, appeared to be a reliable semi-quantitative indicator of brine scaling tendency. At least 60-h exposures were required when these specimens were used. Their disadvantage was the wide variation of scale thickness in a given exposed specimen. In one cross-section, the typical range was a factor of 2 to 4. Longer exposure times would have tended to smooth out this variation. Tubing sections ($\frac{1}{2}$ -in and $\frac{1}{4}$ -in) exposed in sidestreams at 200 and 125°C had the same problem (however, see point 5 below).

4. The most reliable and precise specimens for assessing scaling, at the time of the November/December series, were the pairs of thin, flat coupons. Three materials were used: AISI 1009 mild steel, Teflon TFE, and Hastelloy C-276. The mild steel coupons were mounted on a holder that was held in the flange of the pipe spool. The long dimension of the coupon projected downstream in the 1-inch pipe. The Teflon and Hastelloy specimens were mounted at right angles

to the flow on Petrolite-probe, 2-in pipe plugs in a 2-in section of pipe. Because excessive scaling or plant upsets leading to high suspended solids levels sometimes created severe obstructions at the steel coupon holder, subsequent tests were done with the steel coupons mounted on 2-in pipe plugs in the 2-in line with the Petrolite probes.

5. Another modification to the system that was introduced as experience was gained during the year was the addition of a third, delay stage operating from a 125⁰C sample port. This provided brine at 90⁰C that had been aged ~10 min since flashing to 125⁰C. As expected, specimens placed at the output of the delay stage scaled more heavily than at 125⁰C and this provided a measure of conditions that might be encountered in atmospheric flash and downstream equipment. Tubing ($\frac{1}{4}$ - and $\frac{1}{2}$ -in) installed at the output of the delay collected thicknesses of scale that could be measured accurately by sectioning in 12-24 h exposures. Although this technique was not used for any of the proprietary additives tested, it is unlikely, in the light of subsequent work, that the proprietary additives would have had an effect on the 90⁰C scales, because none functioned as a silica precipitation inhibitor.

6. Scale hardness could not be measured as planned because the amount formed was not thick enough for the penetration test. Longer exposure times would be required to obtain suitable specimens. Adhesion also could not be measured quantitatively because a suitable testing technique was not developed in time.

3.2.3.4.2.2 Results of Proprietary Additive Tests

Most of the tests of the proprietary additives were carried out during November and December of 1978. During that time eight different formulations from eight different companies were tested.

The effects of each of these additives were assessed in 3-day runs, during which the full complement of specimens were in place and the stability of the brine at 90°C was assessed. Experiments were also done during this time to evaluate the more rapid methods for scaling rate measurement that were proposed, i.e., flowing the brine through screens and columns containing small steel balls.

All of the results of the November/December, 1978 test series, with the exception of the chemical analyses of the scale deposits and the results of the examination of the pipe spools, were summarized in a UCID report (4). The test procedures are also described in more detail in that report.

The major characteristics of the effluent brine during that period were as follows:

Chloride concentration: 3.60-4.12 Mol/liter

pH: 5.72-5.96

Density at 25°C: 1.145-1.163 g/cm³

SiO₂ concentration: 425-516 mg/kg

The GLEF operated continuously during this test period, except for November 14th, when the brine concentrations dropped to the lower values noted. Wellhead pressures were in the range of 250-315 psia and temperatures were in the range of 209-220°C.

Table 1 lists the values of scaling rate found during two runs with untreated brine. These served as the controls against which the performance of the proprietary additives were measured. It can be

(4) Harrar, J.E., F.E. Locke, C.H. Otto, Jr., S.B. Deutscher, R. Lim, W.P. Frey, R. Quong, and L.E. Lorensen, Preliminary Results of Tests of Proprietary Chemical Additives, Seeding, and Other Approaches for the Reduction of Scale in Hypersaline Geothermal Systems, Lawrence Livermore Laboratory Rept. UCID-18051 (1979).

Table 1. Scaling rates of untreated brine measured during the November/December test series. (MagmaMax No. 1 well).

Scaling rate at 210°C, mil/h				
	Coupon			
	<u>Steel Pipe Spool</u>	<u>Steel</u>	<u>Hastelloy</u>	<u>Teflon</u>
Nov. 11-17 ^a	0.014-0.042	0.02	0.01	0.05
Dec. 12-15 ^b	0.030-0.061	0.08	0.02	0.03

Scaling rate at 125°C, mil/h				
	Coupon			
	<u>Steel Pipe Spool</u>	<u>Steel</u>	<u>Hastelloy</u>	<u>Teflon</u>
Nov. 11-17 ^a	0.16-0.28	0.21	0.10	0.11
Dec. 12-15 ^b	0.085-0.31	0.38	0.06	0.09

^a Exposure time: 113h

^b Exposure time: 65h

seen that, although the roughness of the scale in the pipe makes its thickness measurement uncertain, there is fairly good agreement between the results of the steel pipe and steel coupon specimens. Also, as has been found to be generally true, the apparent scaling rates found for Hastelloy and Teflon are lower than for steel. We believe this is due to two factors: (a) the combined effects of corrosion and scaling on the steel surface vs. only scaling on Teflon and Hastelloy, and (b) less tenacious adhesion of scale on Teflon and Hastelloy. Longer exposure times and thicker scales tend to reduce the differences of scaling rates among the different surfaces.

Table 2 lists the proprietary additives that were given 3-day tests as antisclalants during the November/December test series. These were selected as a result of an industry-wide solicitation in August of 1978. Table 3 summarizes the results of testing of these additives. For the scaling rates, only the comparison of the rates for mild steel are given here. The data for Teflon and Hastelloy are in general agreement (4).

At 210°C, only the Thermosol APS had a beneficial effect on the scale, but the degree of scale reduction was nearly the same as the experimental uncertainty. As noted, several of the additives increased the deposition of scale, possibly as a result of decomposition of the additive itself. At 125°C, most of the additives appeared to reduce the amount of scale on the coupons, but only two, Drewspers 747 and SC-210, reduced the scale on both the pipe spool and coupons. These two also showed the lowest rates on Teflon and Hastelloy, but they were not lower than the values for untreated brine. Thus the diminished scaling

Table 2. Proprietary Additives Tested in November - December, 1978 Test Series

<u>Product Name</u>	<u>Company, Address</u>	<u>Chemical Type</u>	<u>Concentration Tested, ppm</u>
Geomate 256	Dearborn Chemical Corp., Lake Zurich, IL	Phosphonate + Polymer	35
CL-165	Calgon Corp., Pittsburgh, PA	Polymer mixture	18
Drewspers 747	Drew Chemical Corp., Boonton, NJ	Phosphonate + Polymer	15
Betz 419	Betz Laboratories, Trevose, PA	Phosphonate + acrylic Polymer	20
Thermosol APS	Far-Best Corporation, Los Angeles, CA	Polyalkylphosphonate	20
S-404	C-E Natco, Bakersfield, CA	Organic Polymer	18
SC-210	Southwest Specialty Chemicals, Houston, TX	Low molecular weight carboxylic acid	10
Cortron R-16	Champion Chemicals, Anaheim, CA	Filming amine	120, 20

Table 3. Performance of eight proprietary additives as antiscalants in Magmax No. 1 brine. (See Table 2 for further details of additives).

Additive	% Reduction of scale on mild steel				90°C Silica precipitation test
	210°C		125°C		
	Pipe Spool	Coupon	Pipe Spool	Coupon	
Geomate 256	0	0	0	32	Negative ^b
CL-165	0	0 ^a	0	32	Negative
Drewperse 747	0	0 ^a	30	50	Negative
Betz 419	0	0	0	52	Negative
Thermosol APS	30	30	0	50	Negative
S-404	0	0	0	21	Negative
SC-210	0	0 ^a	80	42	Negative
Cortron R-16	0	0	0	0	Negative

^a Significant increase in the deposit.

^b No effect on the rate of precipitation of silica.

rates shown by Drewspense 747 and SC-210, as well as some of the other additives, as shown in the data of Table 3, may be due only to some action as either a corrosion inhibitor or an agent in preventing the adherence of corrosion product.

An indication of the corrosion rates of mild steel in the brine in the presence of these additives was obtained by measurements using the Petrolite Instruments Company linear-polarization resistance (LPR) equipment. The locations of these LPR probes in the brine streams is shown in Figure 1 .

Table 4 summarizes the data on the corrosion rates of the brines measured by means of the linear polarization resistance technique. The values listed are the levels obtained after about 12-hr of specimen exposure and in all cases these values held nearly steady for the durations of the exposures. It is striking that the corrosion rates at 125°C for the untreated brines, and several of the treated brines, were higher than the rates at 210°C. This must reflect the relative degrees of protection afforded by the corrosion films and scales formed at these temperatures. The higher corrosion rate at 125°C in the brine with the Southwest Chemical SC-210, coupled with its lower scaling rate at this temperature (see Table 3) suggests that it may have exhibited some scale inhibition. The higher corrosion rate in the presence of the Cortron R-16 may be a result of the greater porosity of its scale. It should be realized that complete scale inhibition may result in much higher corrosion rates than are usually observed for scaling brines. In the case of acidification with HCl, it is not only the pH lowering that is responsible for increased corrosion rates, but also the absence of protective silica scale.

Table 4. Corrosion rates of mild steel (AISI 1018) in additive-treated brine measured by the linear polarization resistance technique.

	<u>Corrosion rate, mpy</u>	
	<u>210°C</u>	<u>125°C</u>
Control A	9	14
Control B	7	15
Geomate 256	3	15
CL-165	5	2
Drewperse 747	7	15
Betz 419	7	4
Thermosol APS	7	5
S-404	5	3
SC-210	5	25-60
Cortron R-16	7	25

In our "standard" precipitation test (5), in which the effluent brine, previously treated with the candidate additive in the plant, is held at 90°C to follow the kinetics of the precipitation of silica, we found that none of the proprietary additives had any effect. This was in contrast to the effect of several generic compounds that had been discovered earlier (1). In the November/December test series, one of these compounds, Natrosol 250LR (Hercules hydroxyethyl-cellulose) was included with the proprietary additives for evaluation. In-plant injection revealed that it did inhibit the precipitation of silica at 90°C, but it too failed to significantly retard the formation of scales at higher temperatures.

All of the results of this test series, taken as a whole, led us to the conclusion that none of the proprietary additives, except possibly Southwest Chemical's SC-210, merited further attention as geothermal scale inhibitors.

-
- (5) J.H. Hill, J.E. Harrar, C.H. Otto, Jr., S.B. Deutscher, H.E. Crampton, R.G. Grogan, and V.H. Hendricks, Apparatus and Techniques for the Study of Precipitation of Solids and Silica from Hypersaline Brine, Lawrence Livermore Laboratory Rept. UCRL-52799 (1979).

3.2.3.4.2.3 Precipitation Tests of Additional Proprietary Additives

Work subsequent to the November/December, 1978 test period was devoted mostly to investigations of compounds whose identities were known, i.e., generic compounds. However, the state of the art in water treatment was still advancing, and periodically other proprietary additives and mixtures came to our attention that appeared to be worthwhile evaluating. None of these was subjected to a complete scale-abatement test, but a number were subjected to plant injection and measurement by the precipitation-inhibition test. These additional compounds, together with other pertinent information, are listed in Table 5. None of these compounds showed any activity toward silica at 90°C.

Polysperse Plus was of particular interest because experiments conducted at the GLEF by Paul Henry of the NUS Corporation indicated that it inhibited silica precipitation. It failed in two trials at our facility and, although his experimental approach was somewhat different than ours, it has never been determined why these results were in disagreement.

As can be seen from the identities of the proprietary compounds in Tables 2 and 5, most of the materials are the anionic-type polymers traditionally used in various water treatment applications. Although they represent the industry's best guess as to effective antiscalants for hypersaline geothermal brine, in our tests they have certainly not appeared promising. In contrast, as discussed below, cationic polymers have emerged from our generic chemical testing as definite economic possibilities for scale control.

Table 5. Additional proprietary additives tested as silica precipitation inhibitors.

<u>Additive</u>	<u>Company, Address</u>	<u>Chemical type</u>	<u>Concentration tested, ppm</u>
Polysperse Plus	Betz Laboratories Trevose, PA	?	20
Geomate 259	Dearborn Chemical Lake Zurich, IL.	?	40
XFS-43075	Dow Chemical Midland, Mich.	?	40
XD-30469.00	Dow Chemical Midland, Mich.	copolymer of acrylic acid & hydroxyethylacrylate	20
Darex 41s	W.R. Grace Lexington, Mass.	carboxylated polyelectrolyte	20
Visco 3744	Nalco Chemical Houston, Tex.	acrylic polymer + surfactant	20
Belclene 200	Ciba-Geigy Ardsley, N.Y.	low M.W. carboxylic acid	20
Pyronate 40	Witco Chemical New York, N.Y.	low M.W. alkyl aryl sulfonate	20

3.2.3.4.2.4. Experiment With Sludge Seeding to Retard Scale Formation

Another approach to scale control that has been attempted by other investigators for other geothermal brines (see for example, Ref. 6) is to add to the fluid a finely divided solid upon which the scale-forming compound deposits in preference to the plant surfaces. The rationale is similar to the addition of seed crystals to promote precipitation in crystallization processes. Although the scale with which we are dealing is predominantly amorphous silica, by providing a large ratio of seed-to-plant-surface area, reduction of the degree of supersaturation and hence the scaling tendency of the brine should be attainable. Also, to be a viable technique, the seed substance must remain fluidized and pass through the plant equipment with minimal holdup.

For Salton Sea geothermal brines the ideal seed material would be colloidal silica. Closely approaching such material is the wet sludge obtained from the sedimentation of the effluent brine from the GLEF prior to injection. This sludge is of mud-like consistency and is a finely divided precipitate composed primarily of silica, with lesser amounts of iron compounds and metal sulfides, i.e., all of the usual ingredients of geothermal scale. Using sludge as a seed material appeared promising because earlier work (7,8) on developing an effluent process for this brine demonstrated the effectiveness of

(6) T.E. Lindemuth, E.H. Soule, S.H. Suemoto, and V.G. Van Der Mast, Proceedings of Int. Symp. on Oilfield and Geothermal Chemistry, San Diego, 1977, pp. 173-186.

(7) R. Quong, F. Schoepflin, N.D. Stout, G.E. Tardiff, and F.R. McLain, "Processing of Geothermal Brine Effluents for Injection," in Transactions of the Geothermal Resources Council Meeting, Hilo, Hawaii, 1978, pp. 551-554.

(8) Van Note, R. H., J. L. Featherstone, B. S. Pawlowski, "A Cost Effective Treatment System for the Stabilization of Spent Geothermal Brines," 2nd Invitational Well-Testing Symposium Proceedings, Berkeley, CA., 1978, pp.29-33, Report #LBL-8883.

pre-precipitation solids contact as a means of rapidly promoting the precipitation of silica.

A short experiment of seeding for scale control was conducted during the November/December series as a prelude to a longer-duration, more extensive test. In this experiment a suspension of wet sludge containing 20% by weight solids was metered into the 210°C brine in the same manner as the chemical additives. This sludge contained, in addition to the compounds mentioned above, small amounts of BaSO_4 and CaSO_4 ; these were present because of the addition of Salton Sea water in the pilot clarifier tests conducted by the Imperial Magma Company. After an initial short period without additive flow to establish brine silica levels, the sludge feed rate was controlled for one hour at 0.30 gpm and then for 22 h at 0.15 gpm. At 0.15 gpm, assuming 10 μm spherical seed particles and a 1-in. i.d. pipe diameter, a 10:1 particle-to-pipe surface area ratio is obtained.

Since the usual chemical feed pumps cannot be used for slurries, a Moyno progressive-cavity type pump was used for pumping the sludge, and for this short test no difficulties were experienced. Sludge flow rate was measured manually by a volume displacement technique.

In the measurement of scaling rate it was found that screens could not be used because they were rapidly plugged by the accumulation of the suspended sludge. A screen at the 125°C brine sample port plugged in less than an hour. Similarly, there was an accumulation of sludge on the test coupons, especially at corners and attachment points, making it difficult to distinguish scale from sludge deposits. The Petrolite probe in 125°C brine was so heavily

covered with sludge that no estimates of either scale thickness or possible erosion on the Teflon or Hastelloy coupons could be made. The apparent amount of scale accumulated on the mild steel coupons was estimated (4), but the values are very inaccurate because of the accumulation of sludge and the short duration of the run.

Perhaps a better indicator of the potential of the technique was the lack of scale on the pipe spools. On examination of these specimens, only corrosion product was seen, although the shortness of the run mitigates the conclusions somewhat.

A superior measurement method for detecting the effect of seeding may lie in our measurements of the levels of silica in the brine during the experiment. These data, shown in Table 6, were obtained, with one exception, as follows. The test brine (quite dark colored in appearance) was flowed dropwise onto a filter crucible connected to a vacuum flask in such a manner that a minimum time of contact with the sludge filter cake was obtained. Hydrochloric acid was placed in the filter flask to immediately acidify the filtrate and prevent further precipitation of the silica. The silica in the filtrate was determined by atomic absorption spectrophotometry. Using this technique it was found that (see Table 6) seeding reduced the level of dissolved (particle size $<1\ \mu\text{m}$) silica from 453 to 431 and 416 mg/kg at 210°C , which is probably not a significant change, but from 516 to 306 mg/kg at 125°C , which is a substantial reduction in the degree of supersaturation.

This measurement technique, however, may not be completely valid. Because of the extremely rapid reaction of dissolved silica

Table 6. Measurements of concentration of "Dissolved Silica"
in brine during seeding experiment.
(Concentrations of SiO₂ in mg/kg)

210°C			
<u>Before Sludge Addition</u>	<u>After Sludge Addition</u>		
	<u>0.3 gpm</u>	<u>0.15 gpm</u>	
453	431	416	
125°C			
<u>Before Sludge Addition</u>	<u>After Sludge Addition</u>		
	<u>0.3 gpm</u>	<u>0.15 gpm</u>	<u>0.15 gpm^a</u>
516	306	306	396

^a Immediate acidification of sludge-containing brine.

with the seed silica at low temperatures, it is possible that some of the decrease in the concentration of silica occurred as the brine was being filtered. Thus an additional experiment was tried in which the brine at 125°C was captured first in acid and then filtered. This yielded the value of 396 mg/kg, higher than before, but still significantly lower than the starting value of 516 mg/kg.

Corrosion rates estimated by the LPR technique during the seeding experiment yielded values of 10 and 14 mpy and 210 and 125°C, respectively, which are not significantly different from the rates found for untreated brine.

From these limited data it appeared that (a) the reduction in dissolved silica at low temperature (125°C) is sufficient to warrant further tests, (b) a still lower concentration of sludge than used here might be just as effective, and (c) different test surface configurations will have to be devised to measure scaling rates in the presence of sludge.

In this relatively short duration experiment, several inches of sludge accumulated in the bottom of the second stage separator, indicating that process equipment may require special design features to accommodate sludge injection as a means of scale control.

3.2.3.4.2.5 Test of Austral-Erwin Process for Scale Control

The results of the short test of sludge seeding indicated that it would be very difficult to carry out a longer duration test in the LLL facility, without appreciable modification, which would be definitive in terms of an accurate evaluation of scale abatement. Another

proprietary scale control process, devised by R.W. Erwin of the Austral-Erwin Company, had been proposed to us and had shown promise at the Cerro Prieto and Brawley fields. Thus, because the Austral-Erwin process was technically different from those we had previously tested, and further tests of the seeding technique were not easily implemented, we decided to evaluate the Austral-Erwin process instead.

The Austral-Erwin process involves injecting into the brine a water emulsion of a proprietary mixture of cottonseed oil with small amounts of tall oil and other additives which aid in emulsifying the oils. As carried out in the test of the process at our facility, water was metered at 2 gal/h and the oil-additive mixture at ~0.3 gal/day to form a fine spray at the entrance to the brine (see Figure 1). The resulting concentration of the oil-additive mixture in the brine was 40 ppm.

In theory, the process is said to involve a reaction of the fatty acids in the oils with the calcium of the brine to form a soap. In addition, the surface active compounds thus formed, or present in the emulsion, are supposed to coat the metal of the plant and render it hydrophobic. This surface then would have a tendency to repel colloidal silica, which is hydrophilic in nature, thus retarding its adherence and the formation of scale.

The test of the Austral-Erwin additive was performed from March 9-12, 1979, during which time the GLEF was not operating. The effluent brine characteristics during this period were as follows:

Chloride concentration: 3.52-3.67 Mo/l

pH: 5.83-5.95

Density at 25°C: 1.141-1.149

SiO₂ concentration: 461-479 mg/kg

Magmamax No. 1 wellhead pressures and temperatures were 254-309 psia and 203-215°C, respectively. As is usual when LLL is the sole user of the well, the brine is less concentrated and scaling rates are lower than when the well is at full flow into the GLEF.

The results of the scaling test are summarized in Table 7. Comparing the results in Table 7 for the untreated brine with those in Table 1, the effect of the lower brine salinity in producing lower scaling rates at 125°C is quite evident.

Except for one feature of its performance, the effect of the Austral-Erwin process in general was not very satisfactory. As can be seen in Table 7, only at 210°C in the pipe spool was the scaling rate lower for the Austral-Erwin treated brine. Also, in the pipe spool exposed at 125°C, there was an indication that the scale formed from the treated brine was considerably less adherent--it had flaked off in many places before the specimen could be carefully examined. On the other hand, where the scale was still adhering to the pipe wall, it was quite thick. Scale formed on the flat coupons more rapidly from the treated brine, and the scale at 125°C obviously incorporated a considerable amount of the additive. It was quite oily to touch, and samples lost 50-75% by weight on ignition prior to x-ray analysis. A similar oily scale was formed on perforated disks exposed at 125°C. The delay stage was also operated during these tests, and it was found that there was no decrease in the amount of scale formed at 90°C from the Austral-Erwin treated brine compared to the controls. The additive also had no effect on the precipitation rate of silica in the 90°C effluent brine.

Table 7. Scaling rates of untreated brine and brine treated by the Austral-Erwin process. (Magmamax No. 1 well).

<u>Scaling rates at 210°C, mil/h</u>				
	<u>Steel Pipe Spool</u>	<u>Coupon</u>		
		<u>Steel</u>	<u>Hastelloy</u>	<u>Teflon</u>
Untreated ^a	0.07	0.05	0.02	0.02
Austral-Erwin ^b	0.02	0.08	0.10	0.08

<u>Scaling rates at 125°C, mil/h</u>				
	<u>Steel Pipe Spool</u>	<u>Coupon</u>		
		<u>Steel</u>	<u>Hastelloy</u>	<u>Teflon</u>
Untreated ^a	0.11-0.16	0.10	0.03	0.04
Austral-Erwin ^b	0-0.96 ^c	0.60	0.10	0.12

^a Exposure time: 88h

^b Exposure time: 65 h

^c See text

Thus it appears that the Austral-Erwin process may decrease the adherence of the scale on surfaces such as the pipe spools where there is a high velocity flow without excessive eddies. At points where the flow velocity is lower (e.g., in the 2-in pipe), and where there is turbulent flow such as around our specimen coupons, the accumulation of solids is increased. In this respect it resembles the sludge seeding process.

A difficulty with this additive may be that one of its components such as the cottonseed oil (which is a mixture of palmitic, oleic, and linoleic fatty acids) may adsorb on the silica particles rendering them hydrophobic. They then should have a greater than normal tendency to aggregate and form a precipitate. It is also questionable (but it may not be necessary) that the fatty acids form a salt in our naturally acidic brine. An intermittent treatment scheme was proposed in which the additive would be injected periodically -- just long enough to coat the pipe walls, but not so long as to affect all of the nucleating silica -- but funding limitations precluded testing this idea.

3.2.3.4.2.6 Chemical Analyses of Scales

The scales that were deposited on the coupons were analyzed by x-ray fluorescence and emission spectroscopy to provide additional information on the effects of the brine treatment. Most of the samples that were analyzed were taken from the Teflon coupons so that the effects of substrate corrosion would not be included in the measurements. Scale samples from all three types of coupons were analyzed for the control experiments with untreated brine.

The compositions of the scales are given in Tables 8 and 9. Here it can be seen that even the high temperature scale (formed at

210°C; see Table 8) contains over 50% silica, and the 125°C scales (see Table 9) are 80-95% silica. This lends weight to the contention that control of silica deposition is the key to the control of scale in virtually all portions of a geothermal system downstream of the first steam separation.

Few correlations can be made between the elemental analysis data and the quantities and visual appearances of the scales formed as a result of the brine treatments. One ever-present complication is that the concentrations of the constituents of the brine are not monitored all the time, thus an unusual result for the composition of a scale deposited during these short-term tests may represent merely a transient condition in the brine. At 210°C (see Table 8), the most striking feature of the scales that formed is the high concentrations of copper when additives were present compared to when the brine was untreated. The Cortron R-16 scale also contained large amounts of nickel. This scale and several others had a distinctly greenish tint.

Table 8. Elemental analyses of scales deposited on Teflon TFE coupons at 210°C from brine treated with various additives (Magmamax No. 1 brine, 4.1 Mol/l chloride)

Element	Composition in wt. %										
	Controls		Geomate 256	CL-165	Drewperse 747	Betz 419	Thermosol APS	Natco S-404	SW Chem SC-210	Cortron R-16	Sludge
	7-B	12-A	8-A	8-B	9-A	9-B	10-A	10-B	11-A	11-B	12-B
Si as SiO ₂	60	54	49	60	41	54	51	51	51	30	58
Fe	24	18	23	20	17	19	22	21	21	18	24
Ca	1.4	2.2	1.9	1.7	4.2	1.0	1.0	5.4	1.7	5.2	1.4
Cu	0.3	0.3	3.5	1.2	2.1	4.3	3.6	2.3	4.3	9.2	1.9
Ni	<0.01	<0.01	0.01	0.7	0.01	1.4	0.01	0.01	0.01	4.8	1.9
Pb	0.3	7.6	0.2	0.05	0.95	0.4	0.1	0.4	0.05	0.8	0.2
Mn	1.6	1.0	1.1	1.4	0.9	0.8	0.9	1.0	0.9	0.7	1.0
Na	0.9	0.3	0.14	0.14	2.5	0.4	0.07	0.56	0.4	1.2	1.5
K	0.1	0.3	0.2	0.1	1.2	0.2	<0.05	0.3	0.2	0.1	0.1
Zn	0.2	0.2	0.2	0.2	0.2	0.1	0.2	0.2	0.1	0.2	0.07
Cl	<0.2	<0.2	<0.2	<0.2	5.5	<0.2	<0.2	0.6	<0.2	0.4	<0.2
S	<0.1	0.9	2.6	0.9	2.2	2.7	3.4	1.3	2.6	5.6	0.2
Al	0.5	0.4	0.5	0.3	0.4	0.5	0.15	0.3	0.4	0.2	0.1
Ag	0.03	0.04									

Ba, Sr, P, B, Rb, Sb

Cr, Mg, As all <0.1 except 9-A was 5% Mg and 11-B was 0.1% As.

Table 9. Elemental analyses of scales deposited on Teflon TFE coupons
at 125°C from brine treated with various additives
(Magmamax No. 1 brine; 4.1 Mol/l chloride)

Composition in wt. %												
Element	Controls		Geomate 256	CL-165	Drewperse 747	Betz 419	Thermosol APS	Natco S-404	SW Chem SC-210	Cortron R-16	Sludge	Natrosol 250LR
	7-B	12-A	8-A	8-B	9-A	9-B	10-A	10-B	11-A	11-B	12-B	7-A
Si as SiO ₂	83	94	88	83	98	90	96	96	94	77	47	60
Fe	1.1	1.5	0.56	1.2	0.7	0.9	1.3	0.45	1.0	6.7	2.0	5.5
Ca	0.45	0.5	0.80	0.56	0.3	1.0	0.3	0.4	0.5	2.5	5.9	0.56
Cu	0.59	1.2	0.04	0.25	<0.02	0.05	0.2	0.01	1.6	<0.02	1.1	0.57
Pb	0.21	0.06	0.02	0.16	0.1	0.1	0.1	0.02	0.1	0.01	0.33	0.33
Mn	0.20	0.2	0.16	0.17	0.2	0.28	0.2	0.15	0.2	1.4	0.41	1.2
Na	0.5	0.4	0.14	0.3	0.3	0.6	0.3	0.2	0.4	0.2	10	0.3
K	0.8	0.4	0.3	0.4	0.2	1.1	0.4	0.3	0.3	0.3	2.0	0.8
Zn	0.13	<0.02	0.08	0.14	0.07	0.12	0.06	0.09	0.3	0.2	0.13	0.21
Cl	0.08	<0.2	1.1	0.4	<0.2	0.6	<0.2	0.1	<0.2	1.4	14	0.4
S	0.3	<0.1	0.0	0.2	<0.1	0.38	<0.1	0.03	0.08	<0.1	0.24	0.3
Al	0.5	1.0	0.18	0.32	0.6	0.24	0.6	0.24	0.55	0.3	0.03	0.5

Ba, Sr, P, B, Rb

Cr, Mg, As all <0.1

These scales were not analyzed by x-ray diffraction analysis, however, the large amounts of iron, copper, and sulfide suggests that the compounds Cu_2S and CuFeS_2 , previously identified in similar scales,^{9,10} are present in these samples. The high sodium, potassium, calcium, and chloride levels, together with the lower silica level in the Drewspere 747 scale show that this scale incorporated some of the brine, and this may be the reason for the observed increase in scaling rate compared to the controls. The additive CL-165 caused the greatest increase in scaling rate at 210°C , but there is no clue in the analysis to indicate why this occurred. High calcium levels for some of the scales may be due to precipitation of the sparingly soluble calcium phosphonate, since many of these additives are phosphonates.

Among the scales formed at 125°C (see Table 9), the Cortron R-16 scale is again quite different from the others. This additive was a mixture containing a filming amine that was designed for corrosion inhibition. A plant upset occurred during its testing, to which we attributed the large accumulation of scale that occurred on the 125°C specimens⁴. However, the reverse could be true, i.e., the upset may have occurred because of the high rate of deposition of scale. In any event, the scale was very soft, powdery, easy to remove, and green in appearance. It had higher concentrations of iron, manganese, and chloride than the others.

(9) A. L. Austin, A. W. Lundberg, L. B. Owen, and G. E. Tardiff, The LLL Geothermal Energy Program Status Report, January 1976-January 1977, Lawrence Livermore Laboratory Rept. UCRL-50046-76 (1977), pp. 58-65, 69-73, 81-83, 100-102.

(10) B. J. Skinner, D. E. White, H. J. Rose, and R. E. Mays, Econ. Geology, **62**, 316 (1967).

The Geomate 256 scale was snow white in appearance, as borne out by its low concentration of the metal sulfides.

The analysis of the scale accumulated on the Teflon coupon during the sludge seeding experiment is also shown in Table 9. The high levels of sodium, potassium, calcium, and chloride show that large amounts of brine were occluded, and the solids probably include much of the sludge itself.

As noted, none of these additives inhibited the precipitation of silica from homogeneous solution. One substance that did was Natrosol 250LR, a Hercules Company hydroxyethylcellulose, and the results of the analysis of its 125°C scale are also shown in Table 9. It appears to be characteristic of such inhibitors that the solids precipitated in their presence contain less silica and more iron than solids formed from untreated brine. The balance of the composition of the solids in such cases has not been established.

3.2.3.5 CONCLUSIONS AND RECOMMENDATIONS

1. From the results of the tests of proprietary additives, i.e., the chemical mixtures and the Austral-Erwin process, we conclude that none of these brine treatments have a very beneficial effect on the rates of scaling from the brine of Magmamax No. 1 well. Among the chemical additives, Southwest Chemical's SC-210 shows marginal promise, and a modification of the method of addition of the Austral-Erwin additive might be more effective than the one we tested. Its principal effect is in altering the consistency and adherence of the scale.

2. The addition of sludge as a seeding material for accelerating silica precipitation and lowering the levels of silica super-saturation appears to be viable, but the degree of scale abatement brought about by this treatment could not be assessed. If proper equipment can be used to handle the suspended solids levels that exist with this technique, it should be a fairly successful approach to scale control.

3. Although not detailed here, our parallel studies of generic chemical compounds for geothermal scale control have led to a number types of compounds that inhibit the precipitation of silica and scale formation at the lower temperatures (1, 11-13). Cationic polymers and surfactants, and compounds containing large amounts of ethylene oxide are the most promising. Further experiments will be carried out to discover the optimum compounds within the active classes, and other approaches such as combinations of active compounds and combinations of inhibitors with pH adjustment (up or down) will be pursued.

(11) J.E. Harrar, F.E. Locke, L.E. Lorensen, C.H. Otto, Jr., S.B. Deutscher, W.P. Frey, and R. Lim, On-line Tests of Organic Additives for the Inhibition of the Precipitation of Silica from Hypersaline Geothermal Brine, Lawrence Livermore Laboratory Rept. UCID-18091 (1979).

(12) J.E. Harrar, F.E. Locke, C.H. Otto, Jr., L.E. Lorensen, and W.P. Frey, On-line Tests of Organic Additives for the Inhibition of the Precipitation of Silica from Hypersaline Geothermal Brine II. Tests of Nitrogen-Containing Compounds, Silanes, and Additional Ethoxylated Compounds, Lawrence Livermore Laboratory Rept. UCID-18195 (1979).

(13) J.E. Harrar, F.E. Locke, C.H. Otto, Jr., L.E. Lorensen, W.P. Frey, and E.O. Snell, On-line Tests of Organic Additives for the Inhibition of the Precipitation of Silica from Hypersaline Geothermal Brine III. Scaling Measurements and Tests of Other Methods of Brine Modification, Lawrence Livermore Laboratory Rept. UCID-18238.

3.2.5.0 Evaluation of Tested Metallic Materials for Plant Applications

Responsible Organization: LLL

Investigators: R. D. McCright, A. Goldberg, E. O. Snell,
F. E. Locke, R. McLain, W. P. Frey, W. J. Steele,
R. Quong, and G. E. Tardiff*

Priority 2

3.2.5.1 OBJECTIVES

Measure and document the corrosion and stress corrosion of twenty four ferrous (including different conditions of heat treatment) and eleven non-ferrous materials which were exposed in reduced pH Magmax No. 1 brine and flashed steam at two temperatures for a one-month test period completed by LLL during 1978. An additional objective is to compare these results to corrosion and stress corrosion data obtained by the U. S. Bureau of Mines and LLL using unmodified Magmax No. 1 brine. Taken together, these results should delineate those materials which would have a high probability of failure in times short compared with desired plant lifetime and those materials which could reasonably be expected to perform well for the 20 to 30 year periods desired. These evaluations would also permit identification of additional work needed to more fully qualify promising materials for geothermal service in Magmax No. 1-type environments.

* Private Consultant

3.2.5.2 BACKGROUND

Inspection of a section of pipe taken from the GLEF surface piping near the wellhead in mid-1978 suggests that at least the higher temperature carbon steel vessel and piping lifetimes will be limited to well below the desired thirty years. Corrosion and stress corrosion data are needed to identify other materials with adequate resistance to perforating forms of corrosion and resistance to environmentally induced delayed failure. Three bodies of information exist from which such data can be obtained:

- (1): One month corrosion test in reduced pH brine (LLL): these results were obtained in an aggressive low pH environment and can be taken as conservative relative to unmodified brine. This is useful because: a) materials with a tendency toward stress corrosion cracking can be more certainly identified in the relatively short times of exposure in corrosion tests, and b) high performance materials can be identified for application in critical plant components.
- (2): United States Bureau of Mines Tests - the USBM conducted corrosion and stress corrosion tests in unmodified Magmamax No. 1 brine and flashed steam for periods of up to 45 days. These corrosion coupons are currently being analyzed and results will be reported by the USBM. Certain of the already available USBM results will be cited below.
- (3): Timed Interval Corrosion Tests (LLL): - LLL is conducting timed interval (up to 6 months exposure) corrosion testing in unmodified Magmamax 1 production brine to: a) determine the time dependence of the localized corrosion rate for carbon and low to

intermediate alloy steels, and b) determine the level of corrosion resistance possible with Cr-Mo alloy steels. This work is being funded by the Geothermal Technology Development Program of the DOE and results are expected to be available in late 1980. Certain preliminary results will be cited below.

The present task is mainly oriented toward analysis and presentation of the results of the LLL - one month reduced pH brine corrosion test (item 1 above). These results will be presented in the context of materials selections for plant vessels and piping for a plant utilizing unmodified Magmax No. 1-type brine. Results from the USBM (item 2 above) and other LLL (item 3 above) will be cited where appropriate.

3.2.5.3 TEST DESCRIPTION AND PROCEDURE

3.2.5.3.1 Test Materials and Equipment

A small scale, four stage brine flash system was constructed to simulate the brine and vapor (flashed steam) environments existing in the Geothermal Loop Experimental Facility (GLEF). The second and third stages (6 ft. height x 14 inch diameter with 1 inch brine lines) were each fitted with racks to permit direct exposure tests of both flat weight loss coupons and bent beam stress corrosion cracking specimens in the brine and vapor environments in each stage. The weight loss coupons were nominally 2 inches x 1 inch x 1/16 to 1/8 inch thick. These coupons were glass bead blasted and bolted onto carbon steel support bars using Teflon washers and sleeves for insulation. The stress corrosion cracking coupons were nominally 3 inch x 1/4 inch x .055 to .080 inch thick. Each of the bent beam specimens contained an electron beam fusion weld (about 40 percent penetration) in its center. No pre

or post heating of the welded specimens was used. The specimens were bent in a four point bending fixture to give an outer fiber stress of 90% of the yield strength. Insulation was provided by using ceramic loading rods. Table 1 gives a listing of the alloys tested together with information on processing and heat treatment.

3.2.5.3.2 Test Prerequisites

Brine flow into the small scale flash system must be taken from a sidestream while the well (MagmaMax No. 1) is flowing at design flowrate (400,000 lb/hr) so that the chemistry of the brine can be as nearly representative of plant operation as possible. In addition, there must be a minimum of flow interruptions or periods of reduced flow operation.

3.2.5.3.3 Test Conditions

Hydrochloric acid to be added to the brine inlet to the 2nd stage to reach a target pH of 4⁺. Flowrate through the system to be targeted at 1 lb/sec to simulate residence time in the GLEF. Target temperature to be 150⁰ and 125⁰C in the second and third stages, respectively.

3.2.5.3.4 Required Data and Observations

Wellhead temperature and pressure and pH in each stage to be determined 12 times daily. Samples for brine chemistry analysis to be taken 4 times over the course of the test period. Corrosion data to be

⁺ One of the test goals was to determine the degree to which scale could be reduced by reduction of pH to 4. Post test examination of the brine lines in the system showed that scale was reduced by factors of 20, 9, and 2.7 at 210⁰C, 150⁰C, and 125⁰C, resp., relative to observed scaling in the GLEF using unmodified brine. Scale inhibition was adversely affected by prolonged test interruptions and pH excursions to as high as pH 5.6.

Table 1. Identification, Compositions, and Heat Treatments of Materials Tested in 720 hr Acidified Brine Corrosion and Stress Corrosion Test.

Carbon and Low to Intermediate Alloy (<11%) Steels

1009, Q+T	: AISI 1009 quenched and tempered (1175°F)
A106B, AR	: ASTM-A106 Grade B, as received
Fe-1/2 Mo, WQ	: ASTM-A204 Grade B, water quenched
Fe-1/2 Mo, WQ+T	: ASTM-A204 Grade B, water quenched and tempered (1175°F)
Fe-1/2 Mo, AC	: ASTM-A204 Grade B, air cooled
Fe-1/2 Mo, FC	: ASTM-A204 Grade B, furnace cooled
4130, Q+T	: AISI 4130 (.95 Cr, .20 Mo), quenched and tempered
S00-90	: (.95 Cr, .30 Mo), quenched and tempered
4130-Mo	: (.95 Cr, .30 Mo), quenched and tempered
Fe-1 Cr-1/2 Mo	: ASTM-A387 Grade 12, quenched and tempered (1175°F)
Fe-2-1/4 Cr-1 Mo	: ASTM-A387 Grade 22, quenched and tempered (1175°F)
Fe-5 Cr-1/2 Mo	: ASTM-A387 Grade 5, quenched and tempered (1175°F)
Fe-9 Cr-1 Mo	: ASTM-A387 Grade 9, quenched and tempered (1175°F)

Ferritic and Martensitic Stainless Steels

403SS, Q+T	: AISI 403SS (12 Cr), quenched and tempered
403SS, AR	: AISI 403SS (12 Cr), as received
410SS, Q+T (1175)	: AISI 410SS (12 Cr), quenched and tempered (1175°F)
410SS, Q+T (1250)	: AISI 410SS (12 Cr), quenched and tempered (1250°F)
410SS, Q+T (1100)	: AISI 410SS (12 Cr), quenched and tempered (1100°F)
422SS, Q+T	: AISI 422SS (12 Cr, 1 Mo, .8 Ni), quenched and tempered (1175°F)
430SS, ANN	: AISI 430SS (16 Cr), 1500°F, 1 hr, water quenched and annealed
439SS, AR	: AISI 439SS (18 Cr, 2 Mo, Ti, stabilized) as received
26-1	: 26 Cr, 1 Mo, as received
26-1, Ti STAB	: 26 Cr, 1 Mo, .3 Ti, as received
29-4	: 29 Cr, 4 Mo, as received
29-4-2	: 29 Cr, 4 Mo, 2 Ni, as received

Table 1 (cont'd)

Austenitic and Duplex Stainless Steels

304SS, AR	:	AISI 304SS (18 Cr, 10 Ni), as received
316L	:	AISI 361L (17 Cr, 2.5 Mo., 12 Ni), 1975 F/20 min/W.Q. & annealed
317LM	:	AISI 317LM (18.5 Cr, 4 Mo, 14.4 Ni, 3 Co), 2000 F, 10 min, oil quench and anneal
α/γSS	:	duplex austenitic/ferritic stainless steel, 23 Cr, .03 Mo, 8 Ni, 1.7 Mn, as received (supplied by Uddeholm Steel, designation MC 20)
18Cr-9Ni-4Si, AR	:	18 Cr, 9 Ni, 4 Si, duplex structure as received (supplied by United States Steel)

High Nickel/Chromium Alloys

Inconel 600	:	76 Ni, 15 Cr, 8 Fe; 1850°F/20 min, water quenched and annealed
Inconel 718	:	52.5 Ni, 19 Cr, 18 Fe, 3 Mo, 5(Nb + Ta), .4 Ti, .5 Al; 25% Cr + Aged
Carpenter 20Cb-3	:	33 Ni, 20 Cr, 40 Fe, 2.5 Mo, 3.5 Cu, 1(Nb + Ta); 1725°F/20 min/water quenched
Incoloy 800	:	32.5 Ni, 21 Cr, 46 Fe, .4 Cu, .9 Al, .4 Ti; as received

High Nickel/Chromium Alloys with >5% Mo

Alloy 6X	:	24 Ni, 20 Cr, 50 Fe, 6.5 Mo; as received (supplied by Allegheny-Ludlum Corp.)
Hastelloy G	:	47 Ni, 22 Cr, 19 Fe, 7 Mo, 2 Cu, 2(Nb + Ta); as received
Hastelloy B	:	62 Ni, 1 Cr, 5 Fe, 28 Mo, 2.5 Co, .3 V; as received
Hastelloy C276	:	56 Ni, 16 Cr, 5 Fe, 16 Mo, 4 W, 2 Co, 40% CR + 95°F/100 hr + 35% CR

Table 1 (cont'd)

Cobalt Containing Alloys

Haynes 25,ANN+A	:	67 Co, 10 Ni, 20 Cr, 3 Fe; annealed + 1100°F/5 hr/air cooled
Haynes 25,CR+A	:	67 Co, 10 Ni, 20 Cr, 3 Fe; 25% cold rolled + 110°F/5 hr/ air cooled
MP35N	:	35 Co, 35 Ni, 20 Cr, 10 Mo; 40% cold rolled + 1425°F/2 hr/air cooled

Q+T - quenched & tempered
AR - as received
WQ - water cooled
AC - air cooled
FC - furnace cooled

determined includes corrosion weight loss on the 2 inch x 1 inch test coupons and pit depth measurements on both types of coupons. Amount of cracking to be determined by microscopic examination of polished sections of the stress corrosion test coupons. Crack propagation mode to be determined.

3.2.5.3.5 Test Duration

Test duration is targeted for 720 hours operation with acidified brine.

3.2.5.4 RESULTS

3.2.5.4.1 Expected Results

Expected results include weight loss, pit depths, and extent of cracking for each of the materials listed in Table 1 after exposure for 720 hours to pH 4 Magmax No. 1 brine.

3.2.5.4.2 Data and Observations

Test Conditions - A short exposure to unacidified brine was necessary for system shakedown. The 720 hour portion of the test was carried out in two segments. A brief review of the operational history of the test is given below:

- 36 hours exposure to unacidified brine.
- 196 hours exposure to acidified brine prevailing pH 4.5 (December, 1977).
- specimens removed from separators, excess scale removed (particularly from 3rd stage bottom specimen rack), stored dry for a month, test resumed.
- 530 hours exposure acidified brine, prevailing pH 4.0 (January and February, 1978).

- specimens removed, dried, scale and corrosion products removed by grit blasting (25-80 um particles).
- specimens weighed, pit depths determined, and selected specimens mounted and polished for optical microscope inspection.

Brine pH varied between 3.5 and 4.5 for the majority of the 720 hours exposure time. Based on daily pH measurements it is estimated that about 110 hours was spent in pH excursions above 4.5 to as high as 5.6 and 90 hours spent in excursions below 3.5 to as low as 2.5. Wellhead pressure ranged between 270 and 370 psia and wellhead temperature ranged between 208 and 228°C over the course of the test period.

After the 720 hour test the specimens in the second and third stages were found to be covered with 0.150 inch of a porous and spongy scale consisting primarily of silica. Many of the stress corrosion specimens were found to have fractured with others remaining in their bent beams fixtures as initially installed. Etch markings on the specimens made prior to test permitted identification.

General Corrosion Results - The weight losses experienced by the various alloys were expressed in terms of the corrosion penetration rate (mpy)⁺ and are reported in the first four columns of Tables 2 through 5. The values were calculated from the weight loss of three different specimens at each location. The precision was within 30%.

⁺ Corrosion and pit penetration rates are based on measurements made after the 720 hour exposure only. It is not known whether or not the results represent steady state rates.

Table 2. Acidified Brine Corrosion and Stress Corrosion Test Results: Carbon and Low to Intermediate Alloy (<11%) Steels.

Material	Measured General Corrosion Rate mpy				Apparent Pitting Corrosion Rate mpy				Stress Corrosion Cracking Results							
									No Cracking Observed				Severe Cracking Observed			
	150B	150V	125B	125V	150B	150V	125V	125V	150B	150V	125B	125V	150B	150V	125B	125V
1009, Q+T	27	31	15	16	67											
A106B, AR	38	51	15	15	66	(160)										
Fe-1/2 Mo, WQ							(24)				W				H,P	
Fe-1/2 Mo, Q+T							(10)		H,P		H,P	H,P	W		W	W
Fe-1/2 Mo, AC	16	8	8	6	139	(72)	(12)	(59)		H,P	H,P	P		W	W	W,H
Fe-1/2 Mo, FC						(59)				W,H,P						
S00-90							(59)	(22)			H,P	H,P			W	W
Fe-1 Cr-1/2 Mo	17	19	8	7	125			(28)	H,P			H,P	W			W
Fe-2-1/4 Cr-1 Mo	13	17	7	4	45			(24)	H,P			H,P	W			W
Fe-5 Cr-1/2 Mo					106	(79)	(19)			H,P	P			W	W,H	
Fe-9 Cr-1 Mo	10	7	7	3	67		(5)	(24)	H,P		H,P	H,P	W		W	W

Test Environments: 150B - Immersed in brine at 150°C
 150V - In wet vapor (flashed steam) at 150°C
 125B - Immersed in brine at 125°C
 125V - In wet vapor (flashed steam) at 125°C

W - indicates weld nugget
 H - indicates heat affected zone
 P - indicates parent metal

Table 3. Acidified Brine Corrosion and Stress Corrosion Test Results: Martensitic and Ferritic Stainless Steels

Material	Measured General Corrosion Rate mpy				Apparent Pitting Corrosion Rate mpy				Stress Corrosion Cracking Results							
									No Cracking Observed				Severe Cracking Observed			
	150B	150V	125B	125V	150B	150V	125V	125V	150B	150V	125B	125V	150B	150V	125B	125V
403SS, Q+T					(54)	(84)			H,P	H,P			W	W		
403SS, AR	6	6	2	4	(54)	(61)			W,P	W,H,P			H			
410SS, Q+T (1175°F)	6	5	4	3	122					W,H,P						
410SS, Q+T (1250°F)						(71)				W,H,P						
410SS, Q+T (1100°F)							(2)	(84)			W,H,P	W,H,P		H,P		
422SS, Q+T						(49)	(2)	(2)			P	H,P			W,H	W
430SS, ANN	3	2	2	2	86	(56)			W,H,P	W,H,P						
439SS, AR					(47)	(19)			W,H,P	W,H,P						
26-1	2	1	1	1	108	(17)			W,H,P	W,H,P						
26-1, Ti STAB					71	(94)			W,H,P	W,H,P						
29-4	1	NIL	1	2	NIL	NIL			W,H,P	W,H,P						
29-4-2					1	12			W,H,P	W,H,P						

See footnotes in Table 2 for meaning of notations.

Table 4. Acidified Brine Corrosion and Stress Corrosion Test Results: Austenitic Stainless Steels

Material	Measured General Corrosion Rate mpy				Apparent Pitting Corrosion Rate mpy				Stress Corrosion Cracking Results							
									No Cracking Observed				Severe Cracking Observed			
	150B	150V	125B	125V	150B	150V	125V	125V	150B	150V	125B	125V	150B	150V	125B	125V
304SS, AR					(59)	(14)		(8)	W,H	W	W,H	W,H,P	P	H,P	P	
18 Cr, 9 Ni, 4 Si, AR	Nil	Nil	Nil	Nil	(12)	(10)	(14)		W,H	W,P	W,H		P*	H	P*	
316L	Nil	Nil	Nil	Nil	(22)	(12)			W,H	W,H,P			P			
317LM	Nil	Nil	Nil	Nil	(14)	(40)			W,H,P	W,H,P						
	Nil	Nil	Nil	Nil	(24)	(19)			W,H	W,H			P*	P*		

See footnotes in Table 2 for meaning of notations.

* Cracking very slight

Table 5. Acidified Brine Corrosion and Stress Corrosion Test Results: High Nickel and High Cobalt Materials

Material	Measured General Corrosion Rate mpy				Apparent Pitting Corrosion Rate mpy				Stress Corrosion Cracking Results							
									No Cracking Observed				Severe Cracking Observed			
	150B	150V	125B	125V	150B	150V	125V	125V	150B	150V	125B	125V	150B	150V	125B	125V
Inconel 600	NIL	NIL	NIL	NIL	(4)	(19)	(5)	NIL	W,H,P	W,H,P	W,H,P	W,H,P				
Inconel 718					(NIL)	(NIL)	(59)	(5)	W,H,P	W,H,P	W,H,P	H,P				W
Carpenter 20Cb-3	NIL	NIL	NIL	NIL	(22)	(19)	(5)	(19)	W,H,P	W,H,P	W,H,P	W,H,P				
Incoloy 800					(11)	(5)	(17)	(4)	H,P	W,H,P	W,H,P	W,H,P	W*			
Alloy 6X	NIL	NIL	NIL	NIL	NIL	(1)	NIL	NIL	W,H,P	W,H,P	W,H,P	W,H,P				
Hastelloy G					(7)	(NIL)	(19)	(130)	W,H,P	W,H,P	W,H,P	W,H,P				
Hastelloy B	NIL	NIL	NIL	NIL	(7)	(4)	(8)	(2)	W,H,P	W,H,P	W,H,P	W,H,P				
Hastelloy C276	NIL	NIL	NIL	NIL	(4)	(NIL)	(NIL)	(2)	W,H,P	W,H,P	W,H,P	W,H,P				
Haynes 25-ANN+A					NIL	NIL			W,H,P	W,H,P						
Haynes 25-CR+A					NIL	(6)			W,H,P	W,H,P						
MP35N	NIL	NIL	NIL	NIL	(2)	(4)	NIL	NIL	W,H,P	W,H,P	W,H,P	W,H,P				

See footnotes in Table 2 for meaning of notations.

* Very slight cracking

Pitting Corrosion - The pitting corrosion results are reported in the second four columns of Tables 2 through 5 in terms of the pit penetration rate (mpy)⁺. The values reported without parentheses were determined from the 1 inch x 2 inch specimens; those with parentheses were determined from the 3 x 1/4 inch specimens. In both cases the results are based on the deepest measured pit.

Stress Corrosion Cracking (SCC) - The SCC results are reported in the third group of four columns (no cracking) and the fourth group of four columns (severe cracking) in Tables 2 through 5. Absence of cracking was determined by microscopic examination of mounted and polished longitudinal sections. The tensile surface of each specimen was examined in the region of the weld nugget (W), the heat affected zone of the weld (H), and the parent metal (P). Crack positions are noted accordingly in Tables 2 through 5.

Metallurgical Structure and Crack Morphology - A large number of the stress corrosion cracking specimens were mounted (longitudinal sections) and polished for evaluation of cracking. These specimens were also used to establish microstructure and crack morphology where appropriate. The results of these inspections are reported in Table 6.

3.2.5.4.3 Calculations

Apparent General Corrosion Rates - the apparent general corrosion rate was calculated from the weight loss of the specimens. The conventional way to express corrosion rates is in mils/year (mpy). The apparent general corrosion rates listed in Tables 2-5 were obtained from the formula:

$$\text{mpy} = 534 \text{ w/DAt}$$

where: w - weight loss in milligrams

D - density of alloy in grams/cm³

A - specimen area in in²

t - exposure time in hours.

The listed rates are averages obtained from three replicate specimens for each test location. The results are based on an assumption of a constant rate of corrosion. The results should, therefore, be used cautiously since corrosion rates may increase or decrease with time.

Apparent Pitting Corrosion Rate - the apparent pitting corrosion rates given in Tables 2-5 were calculated by multiplying the maximum measured pit depth observed after one months exposure (720 hrs) by 12 to give mpy. The results are based on an assumption of a constant rate of corrosion. The results should, therefore, be used cautiously since corrosion rates may increase or decrease with time.

3.2.5.4.4. Comparison of Actual and Expected Results

Carbons Steels - A review of available general and pitting corrosion results leads to the conclusion that simple carbon steels cannot (with reasonable corrosion allowances) provide thirty year plant lifetimes. For example, the USBM* 30 day general corrosion rate results for 1020 steel in untreated Magmamax No. 1 brine indicates rates of 43, 42, and 39 mpy at 229, 207, and 178⁰C, resp. These results are reasonably consistent with LLL results of timed interval tests** in untreated

* Bureau of Mines Report of Investigation/ 1979-RI 8350

** To be discussed (see Table)

wellhead brine which indicate, after the four month exposure interval, rates of 57 and 72 mpy at 220°C for AISI 1010 and ASTM A106B carbon steels, resp. The LLL timed interval tests will be discussed under the section on low to intermediate alloy steels. The present LLL acidified brine results are also consistent with the data cited above giving, for example, corrosion rates of 27 and 38 mpy for AISI 1009 and A106B at 150°C and 15 mpy for both steels at 125°C. These results are in accord with the expectation that the pH 4 brine would not result in corrosion rates dramatically greater than those for untreated brine (pH = 5.7). At pH below 4 however, corrosion rates would be expected to increase exponentially.

Carbon steel could, of course, be considered for brine service on the basis of a periodic replacement program. The data cited above together with pitting corrosion data in BOM Report No. RI 8350 would have to be used to estimate corrosion allowance and replacement frequency.

Low to Intermediate Alloy Steels

The data in Table 2 would indicate the low to intermediate alloy steels would at best offer only marginal (factor of 2) improvement in corrosion life in relation to carbon steels. These results are, however, in very marked contrast to results obtained in LLL timed interval tests conducted in untreated Magmamax No. 1 brine. The LLL Timed Interval Corrosion Task is supported by the Geothermal Technology Development Program of the DOE. The objectives of this task include 1) determination of the time dependence of general and pitting corrosion rate of carbon and low to intermediate alloy steels, and 2) to determine the degree of improvement possible in corrosion life using alloy steels based on chromium and molybdenum. Some preliminary results of this task are given in Table 7. Table 7 indicates that the low

to intermediate alloy steels offer about a factor of 20 improvement in resistance to general corrosion relative to the carbon steels (AISI 1010 and A106B). Also, the alloy steels showed a much reduced tendency to pit in untreated brine/pits 3 mils deep after 4 months). Thus, while low to intermediate alloy steels would have little advantage for handling reduced pH brines, they would offer a large advantage in handling normal pH (5.8) brine. Such low alloy steels, of course, are much less expensive than high alloy steels or nickel base non-ferrous materials. The low to intermediate alloy steels listed in Table 2 are capable of being heat treated to produce a wide range of strength levels and microstructures. Some of these, including untempered martensite and microstructures corresponding to strength levels above $R_c 22$ would be expected to be prone to hydrogen induced stress corrosion cracking. Indeed, the Fe-1/2 Mo, WQ alloy in Table 2 which consisted of an untempered martensitic microstructure was found to be extensively cracked (intergranular) in the parent metal. Thus, the successful use of such materials depends on proper heat treatment to eliminate the tendency toward hydrogen induced delayed cracking.

Reference to Table 2 indicates that welds in the low to intermediate alloy steels can be extremely susceptible to delayed failure due to environmentally promoted cracking. The low pH test conditions aggravate the tendency toward such cracking and tests at low pH are, therefore, useful in delineating the cracking tendency. The welds were made without pre or post heating and resulted in untempered martensite in the weld region (see Table 6). It is, of course, well known that this metallurgical condition is most sensitive to hydrogen induced stress corrosion cracking. Unfortunately,

Table 6 - Observations on Metallurgical Structure and Crack Morphology
for Certain of the Stress Corrosion Tested Specimens

<u>Material</u>	<u>Observations</u>
Fe-1/2 Mo, WQ	Untempered martensite in P* and HAZ*, intergranular cracks in P and HAZ.
Fe-1/2 Mo, Q+T	Untempered martensite in W* and HAZ, cracked thru weld, intergranular crack in HAZ.
Fe-1/2 Mo, FC	Ferritic/pearlitic with decarburized layer (parent metal). No cracks.
500-90	Untempered martensite in W and HAZ. Cracked through weld and HAZ
Fe-2 1/4 Cr-1 Mo	Untempered martensite in W and HAZ. Cracked through weld, Intergranular crack in HAZ.
Fe-5 Cr - 1/2 Mo	Untempered martensite in W and HAZ. Cracked through weld. Intergranular cracks in HAZ.
403SS, Q+T	Untempered martensite in W and HAZ. Cracked through W.
403SS, AR	Untempered martensite in W and HAZ. Cracked through HAZ
410SS, Q+T (1100)	Untempered martensite in W and HAZ, tempered martensite in P. Cracked through weld. Intergranular cracks in P.
439SS, AR	Ferritic in W, HAZ, and P. Equiaxed in HAZ and P. Very shallow crack like corrosion intrusions (.001 inch deep).
26 Cr-1 Mo, Ti STAB	Ferritic Equiaxed grains. Very shallow corrosion intrusions. No cracks.
29-4-2	Ferritic. Equiaxed grains. No cracks.
304SS, AR	Austenitic. Equiaxed grains. Transgranular, branching cracks in P and HAZ.
18 Cr, 9 Ni-4SI, AR	Two phase. Transgranular, branching cracks in P.
316L	Austenitic, no apparent sensitization. Braching transgranular cracks.
317LM	Austenitic. Equiaxed grains. No cracks.

Table 6 (cont'd)

α/γ SS	Austenitic/ferritic. Very small crack-like corrosion intrusions.
Inconel 718	Crack along microstructural discontinuously in weld metal.
Carpenter 20Cb-3	Equiaxed grains. Very fine grained (ASTM9), no cracks.
Incoloy 800	Equiaxed grains. No cracks.
Hastelloy B	Equiaxed grains. No cracks.
Hastelloy C276	Equiaxed grains. No cracks.

* P = parent metal, HAZ - Heat Affected Zone, W - weld metal
WQ = water quenched; Q = quenched; FC = furnace quenched
STAB = stabilized; AR = as received; T = tempered

Table 7. Time-Dependent Corrosion Rates of Steels Exposed to Wellhead Brine (~220°C, ~300 psi)--MagmaMax 1 Well

Material	Corrosion Rate (Mils/Year) After: (4)					Localized Corrosion Tendency
	1 Month	2 Months	3 Months	4 Months	6 Months	
AISI 1010 Carbon Steel	95	73	82	57	65	Heavy mesa-type attack
ASTM A106 B* Carbon Steel	85	56	67	72	53	Mesa-type attack
1/2 Mo Alloy Steel	1.4	4.2	0.7	0.5	0.6	Pits formed, but 2 mils deep
1 Cr-1/2 Mo	1.5	1.9	0.8	0.4	0.6	Pits formed, depth 2 mils
2-1/4 Cr-1 Mo	1.2	2.7	0.7	0.7	0.7	Most pitted of the alloy steels, pit depth 3 mils
5-1/2 Cr-1/2 Mo	1.3	1.3	0.5	0.4	0.5	A few light pits, 1 mil deep
9 Cr-1 Mo	1.5	1.9	0.4	0.4	0.5	Few light pits after 2-mos. exposure 1 mil depth

(1) Construction pipe steel for 10-inch GLEF production line

(2) ASTM A204

(3) ASTM A387

(4) Data obtained from weight loss of duplicate specimens in 6 o'clock position (fully immersed in brine)

stress corrosion type tests have not been carried out on welded coupons for the series of Cr-Mo type steels listed in Table 7 as functions of pre and/or post weld heating designed to optimize resistance to environmental cracking. This type of test program would have to be conducted to properly qualify a weld procedure. Sudden catastrophic failure of pressurized vessels or pipe containing high temperature brines would constitute an enormous hazard. The importance of careful attention to weld procedure and qualification cannot, therefore, be over emphasized.

Martensitic and Ferritic Stainless Steels -

As expected, the martensitic stainless steels (403 to 422) are subject to significant pitting corrosion as well as susceptibility to stress corrosion failure as indicated in Table 3. Such steels would not be suitable for use with brine or vapor (unscrubbed steam). Use of state-of-the-art turbines which are constructed of such materials would depend on reliable delivery of suitably scrubbed steam to the turbine. As indicated in Table 5, the crack path in the case of the martensitic occurs intergranularly along prior austenite grain boundaries as expected for hydrogen-induced stress corrosion cracking.

The ferritic stainless steels listed in Table 3 (Type 430 and 26-1 through 29-4-2) exhibit low general corrosion rates, various tendencies toward pitting, and no detectible tendency toward stress corrosion cracking in the parent metal or weld region. Of these, the alloy 29-4 shows the least tendency to pit and would be expected to be the best selection among the ferritics for geothermal brine service. It should be noted that pressure sensing tubing fabricated from the 26-1 alloy failed after one month exposure in the Magmamax No. 1 well because of its tendency toward pitting. Also, careful polishing and close inspection of polished specimens taken from this tubing revealed transgranular, sawtooth cracks at the base

of pits indicating a tendency toward transgranular stress corrosion cracking in the 26-1 alloy. The latter observation is consistent with the Bureau of Mines* observations of cracking of 26-1 exposed in Magmax No. 1 environments at 178°C and above. The improved behavior of 29-4 relative to 26-1 is related to the effectiveness of chromium and molybdenum additions in maintaining passivity in chloride containing solutions.

Austenitic Stainless Steels - As expected, the austenitic stainless steels as a class are very susceptible to stress corrosion cracking in the parent metal even in cases where no apparent sensitization is present (see for example 316C in Table 6) - the observed cracking was transgranular (Table 6) as expected for austenitic stainless steels in strong chloride solutions. The apparent greater resistance of 317LM to cracking is related to its higher molybdenum content.

Nickel/Chromium Alloys - Of the nickel/chromium alloys (Inconel 600 through Incoloy 800) in Table 5, Inconel 600 exhibited the least tendency toward pitting and no detectable tendency toward stress corrosion cracking. The high nickel/chromium alloys containing 5% molybdenum (Alloy 6X through Hastelloy C-276) as a group show greater resistance to pitting corrosion than the former alloys containing lesser molybdenum. Alloy 6X and Hastelloy C-276 exhibit the best performance among the nickel/chromium alloys.

*J. P. Carter and S. D. Cramer, Field Stress Corrosion Tests in Brine Environments of the Salton Sea Known Geothermal Resource Area, presented at NACE Corrosion 1980 Meeting, paper No. 203, Chicago, Illinois, March 3-7, 1980.

Hastelloy C-276 pressure sensing tubing has been successfully used for more than three months in the downwell environment of Magmamx 1. No detectible stress corrosion cracking was observed in the high nickel-chromium-molybdenum alloys, as expected.

Cobalt Alloys - The cobalt alloys listed in Table 5 were tested even though the current cost and availability of cobalt would rule out all but the most limited use of these alloys. These materials performed as well as the best of the nickel/chromium alloys.

3.2.5.5 Conclusions and Recommendations

It is clear that low to intermediate chromium/molybdenum alloy steels offer the potential of substantially longer life than conventional carbon steels for handling of high temperature Salton Sea Geothermal Field (SSGF) brine. The large potential factor of improvement in corrosion resistance would more than offset the added cost of such materials. Care must be taken however, to properly qualify the heat treatment and welding procedure of such materials for Salton Sea geothermal brine service to avoid possible sudden catastrophic failures due to stress corrosion cracking. As indicated in the present study, several high nickel chromium/molybdenum alloys did not reveal any significant tendency toward corrosion damage in the Magmamax No. 1 brine environments used in the presented study (29-4, 6X and Hastelloy C-276). Such alloys should be subjected to further qualification testing and considered for critical applications such as vessel cladding, pressure sensing tubing and downwell instrumentation packages.

10. The first of these is the fact that the
the first of these is the fact that the

the first of these is the fact that the

the first of these is the fact that the

the first of these is the fact that the

the first of these is the fact that the

the first of these is the fact that the

the first of these is the fact that the

the first of these is the fact that the

the first of these is the fact that the

the first of these is the fact that the

the first of these is the fact that the

the first of these is the fact that the

the first of these is the fact that the

the first of these is the fact that the

3.2.8.0 H₂S ABATEMENT

Responsible Organization: LLL

Investigators: R. Quong, K.G. Knauss, N.D. Stout, L.B. Owen, and C.H. Otto, Jr.

Priority: 2

3.2.8.1 OBJECTIVES

The objective of this test is to evaluate the technical feasibility and cost benefits of scrubbing H₂S gas contained in the GLEF non-condensable vent gases with brine effluent. The effect on reactor clarifier performance by removal of H₂S with brine effluent will be considered. Technical advantages and disadvantages, and costs of this technique will be compared with the Stretford process.

3.2.8.2 BACKGROUND

Substantial amounts of H₂S are contained in the noncondensable gases when SSGF brines are flashed. It is clear that abatement of H₂S will be necessary to satisfy air quality standards in future power plant installations. A feasibility and risk study of geothermal power plants at the SSKGRA (Bechtel Nat'l Inc., and The Ben Holt Co. 1978) concludes that a 2-stage flash system is the most cost effective process for producing electrical power at the 50 MW level. The studies for plants at the SSGRF included the relatively high costs for H₂S abatement by the Stretford process. However, the above mentioned alternate method looks technically promising and, more importantly, economically attractive.

Niland brine effluents are uniquely suitable for use as a

scrubbing liquid for H_2S . The brines contain relatively high concentrations of metal ions such as lead, zinc, and iron which as sulfides are exceedingly insoluble. Evolution of CO_2 during the flash process results in elevation of the brine pH which also favors heavy metal sulfide precipitation. Preliminary bench tests with Niland effluents and noncondensable gases containing H_2S support calculations based on thermodynamic data indicating reaction of virtually all of the H_2S in the vent gas with heavy metal ions in the effluent brine (LLL, 1978). This alternate method of H_2S abatement appears to be efficient, very simple to operate, and has the potential of providing significant cost savings.

3.2.8.3 TEST DESCRIPTION AND PROCEDURE

3.2.8.3.1 Test Materials and Equipment

Bench scale tests will be carried out at the GLEF utilizing vent gas and brine effluent side streams. Flow rates will be about 0.1-1.0 liter/min brine flow and up to 6 liters/min noncondensable gas flow, too low to affect GLEF operation.

The H_2S -brine contactor will consist of 2" diameter glass pipe without internal packing or baffles (see figure 1). Liquid height will be maintained at approx. 16". Gas flow is in the upward direction in the contactor; liquid flow is downward. Dispersion of gas into fine bubbles is produced by a fritted glass sparger. Most of the plumbing will consist of steel and plastic tubing.

Temperature, pressure, pH, and flow measuring instruments will be required. Use of thermocouples for temperature, standard

EXPERIMENTS CONDUCTED WITH SMALL, SINGLE STAGE, COUNTERCURRENT FLOW CONTACTOR

FIGURE 1.

probes and meters for pH, and rotometers for flow is anticipated. Pressure measurement is not critical, but if necessary, any suitable gauge can be used.

3.2.8.3.2 Test Prerequisites

These tests will be performed in conjunction with operation of the GLEF.

3.2.8.3.3 Test Conditions

A relatively constant flow ($\pm 20\%$) of vent gas through the stack and a continuous source of untreated (upstream of the clarifier) brine effluent are required for these tests. These conditions should be easily provided by normal GLEF operation. The actual location of the test apparatus will be near the base of the GLEF vent gas stack.

3.2.8.3.4 Required Data and Observations

Data will be obtained in the gas and brine effluent streams entering and exiting the test scrubber. Measurements include: concentration of H_2S in the gas stream, concentration of silica, metal ions (Pb, Zn, Fe and others), and particulates in the brine, pH, flow rates, temperature, contact time, and other parameters affecting the process. Samples will be collected and selectively analyzed by atomic absorption spectrometry. The properties of the contacted brine are particularly important in assessing the effect of the H_2S scrubbing process on clarifier effluent treatment performance.

Chemical and mineralogical composition of the precipitated solids in the brine will also be determined as needed. Samples will be analyzed by x-ray fluorescence and x-ray diffraction. These data and observations will also be required in the event of a test where vent gas is injected into the 30 gpm pilot clarifier.

3.2.8.3.5 Test Duration

Each test at a given condition is anticipated to take less than one hour, provided that steady flow conditions have been maintained at the GLEF. Repeat runs at identical conditions will be necessary to assess reproducibility of the data. The number of test conditions will be considerable in order to establish the efficiency of the process over a range of gas/brine ratios, and the effect of effluent temperature. It is anticipated that data acquisition and reduction will be completed in 3-4 months.

3.2.8.4 RESULTS

3.2.8.4.1 Expected Results

The technical feasibility and cost benefits of scrubbing H_2S in the vent gas stream using brine effluent will be established and compared to the Stretford process. The technical and cost impact on the effluent clarification process will also be evaluated.

3.2.8.4.2 Data and Observations

The initial measurements were conducted with cooled second stage effluent as the scrubbing liquid. Data and results are given in Table 1. Noncondensable gas for these measurements was drawn from a tap on the side of the vent stack. Gas temperature was nominally 40°C at the point of entry to the scrubber, dropping instantaneously to the temperature of the scrubbing medium which in this set of experiments ranged from $25\text{--}30^{\circ}\text{C}$. Scrubbing efficiencies, also listed in Table 1, are based on the measured concentration of H_2S in the noncondensable gas stream entering and exiting the scrubber. Runs 1, 5, and 6 were conducted with a gas distribution device which did not produce bubble sizes as fine as the fritted glass sparger used exclusively in the other runs. This apparently was the primary reason for the lower efficiencies.

Table 2 is a summary of results of tests in which brine effluent from the 2-stage at the GLEF was maintained at a temperature of $80 \pm 5^{\circ}\text{C}$. Figure 2 and 3 are plots of H_2S removal efficiency versus noncondensable gas to brine ratios for cold and hot brine, respectively. High efficiencies, $>95\%$, were obtained across a broad range of gas/brine ratios with cooled brine as the scrubbing liquid. At gas/liquid flow ratios corresponding to 0.3 wt. % noncondensable gas in the brine, the present operational characteristics at the GLEF (Jacobson, 1979), $>98\%$ removal of H_2S was obtained.

With brine maintained at $80 \pm 5^{\circ}\text{C}$, $>96\%$ removal of H_2S at 0.3 wt% gas/liquid flow ratios was attained. However, the efficiency of removal begins to decline steeply at a gas/liquid

Table 1. H₂S Scrubbing Data and Efficiencies Using Low Temperature (25-30°C) Brine Effluent (Woolsey Fluid From the GLEF).

Test #	Flowrate liters/min.		Gas/Brine Ratio, wt%	H ₂ S Concentration in noncondensibles ppm (vol)		Efficiency of H ₂ S Removal, %
	Noncondensable gas	Brine		In	Out	
1	.255	.607	.06	1150	216	81.2
2	.200	.265	.11	800	< 1	98.3
3	.315	.265	.12	800	3.3	99.5
4	.290	.320	.13	800	2.9	99.6
5	.280	.242	.17	1250	350.	72.0
6	.280	.242	.17	1140	375.	67.1
7	.315	.265	.17	800	2.	99.7
8	.315	.265	.17	800	3.4	99.6
9	.315	.260	.18	800	4.4	99.5
10	.425	.265	.24	800	7.8	99.0
11	.460	.235	.29	800	10.0	98.8
12	.530	.265	.29	800	9.8	98.8
13	.530	.260	.30	800	9.1	98.9
14	.510	.235	.32	800	9.4	98.8
15	.425	.165 ^a	.38	800	16.5	97.9
16	1.030	.365 ^b	.41	900	13	98.6
17	.770	.265	.43	800	13	98.4
18	1.280	.380	.47	800	14	98.3
19	1.240	.280	.65	800	16.5	97.9
20	1.215	.265	.67	950	16	98.3
21	1.215	.265	.67	800	12.5	98.4
22	1.230	.265	.68	800	15.0	98.1
23	1.215	.180	.99	800	41	94.8
24	1.230	.180	1.00	800	35	95.6
25	1.230	.165	1.10	800	42	94.8
26	1.280	.165	1.14	800	31	96.1

a. pH brine: in 6.0 ; out 4.2

b. pH brine: in 5.6 ; out 4.4

Table 2. H₂S Scrubbing Data and Efficiencies Using Hot (80 ± 5°C) Brine Effluent (Magmamax #1 Fluid from the GLEF)

TEST NO.	BRINE EFFLUENT			NONCONDENSIBLE GAS			GAS/BRINE RATIO Wt %	EFFICIENCY OF H ₂ S REMOVAL %
	Flowrate Liters/Min	pH		Flowrate	H ₂ S Conc. ppm (vol)			
		In	Out		In	Out		
27	.640	-	-	.600	1450	37	.14	97.4
28	.640	-	-	.640	1450	54	.15	96.3
29	.420	-	4.6	.420	2100	14	.15	99.3
30	.640	5.50	4.40	.640	1500	60	.15	96.0
31	.640	-	4.40	.640	1100	35	.15	96.8
32	.320	-	-	.600	1450	46	.28	96.8
33	.240	-	4.30	.700	1100	50	.44	95.4
34	.320	-	-	.960	1400	78	.45	94.4
35	.240	-	4.40	.720	2350	210	.45	91.1
36	.140	5.10	4.48	.490	1450	60	.52	95.9
37	.240	-	4.15	.860	1475	170	.54	88.5
38	.240	-	4.18	.860	1500	220	.54	85.3
39	.320	-	-	1.490	1400	650	.70	53.6
40	.140	5.15	4.30	.700	1500	300	.75	80.0
41	.140	5.40	4.30	.700	2500	700	.75	72.0
42	.140	5.35	4.20	.860	2400	1350	.92	43.8
43	.240	-	4.05	1.490	1200	725	.93	39.6
44	.140	5.05	4.30	.900	1600	825	.96	48.4

RESULTS WITH COOLED EFFLUENT (25°C) INDICATE $\geq 98\%$ SCRUBBING EFFICIENCY AT GAS/LIQUID FLOW RATIOS CORRESPONDING TO 0.3 wt% NONCONDENSIBLE GAS IN BRINE

FIGURE 2.

RESULTS WITH BRINE EFFLUENTS NEAR CLARIFICATION
TEMPERATURES (85°C) INDICATE $\geq 96\%$ SCRUBBING EFFICIENCY
AT GAS/LIQUID FLOW RATIOS CORRESPONDING TO 0.3 wt%
NONCONDENSIBLE GAS IN BRINE

FIGURE 3.

ratio above approximately 0.5 wt%. This drop off may be due to insufficient column height, since the highest gas/liquid ratios used were still well below maximum based on stoichiometric considerations. Gas inlet temperatures were running about 43°C from the stack at the GLEF.

We observed a significant drop in brine pH from pH 5.1-5.5 to pH 4.1-4.6 following contact with the noncondensable gases. This is consistent with the reaction described below and with absorption of CO₂. In plant applications, some adjustment in effluent clarification operation may be necessary to overcome the retardation of silica precipitation as a result of lowered pH. On the other hand, precipitation of metal sulfides could enhance overall clarifier operation by improving solids contact and sludge blanket characteristics.

Samples of the effluent entering and exiting the contactor were collected and analyzed by atomic absorption spectrometry for lead and zinc, the two principal metals available for reaction with H₂S. These data are given in Table 3. The changes in Pb and Zn concentrations were compared with H₂S concentration changes. In most cases much more lead and zinc were consumed than what was indicated by the reduced H₂S concentrations. Apparently Pb and Zn are being removed from solution by precipitation reactions other than by metal sulfide formation. Lead carbonate precipitation is a possibility, but zinc precipitates other than ZnS cannot be identified at these conditions.

Table 3. Lead and Zinc Concentration
in Scrubber Brines

Run No.	Lead, Pb ⁺² ppm		Zinc, Zn ⁺² ppm	
	<u>In</u>	<u>Out</u>	<u>In</u>	<u>Out</u>
27	n.a.	38	n.a.	329
28	65	61	334	302
29	61	17	329	329
32	63	29	329	318
34	n.a.	61	n.a.	307
35	n.a.	55	n.a.	323
36	n.a.	32	n.a.	329
38	65	22	313	307
39	64	62	329	307
40	61	36	329	329
43	n.a.	62	n.a.	313
44	n.a.	42	n.a.	323

n.a. not analyzed

3.2.8.4.3 Calculations

The principal reactions occurring in the scrubber are the absorption of H_2S and dissociation:

followed by precipitation of metal sulfides

where Z is the oxidation number.

The overall Reaction is:

The brines produced at the GLEF contain on the order of 65 ppm Pb, 280 ppm Zn, and 270 ppm Fe, far in excess of the stoichiometric quantity necessary to react with all the H_2S . The reabsorption of H_2S in the spent brine is favorable because of the new equilibrium established between the gas and liquid at lower temperature and higher pH.

The efficiency of H_2S removal in the scrubber test runs were calculated simply from the concentration of H_2S in the noncondensable stream entering, $(H_2S)_i$, and exiting, $(H_2S)_o$, the scrubbing unit:

$$Eff = \left(1 - \frac{(H_2S)_o}{(H_2S)_i} \right) \times 100 \dots$$

3.2.8.4.4 Comparisons of Actual and Expected Results

The results confirm the expectation that scrubbing the vent gas with brine effluent effectively removes gaseous H_2S . This method has been shown to be a technically viable process for abatement of H_2S in geothermal flash processes utilizing brine containing relatively high concentrations of heavy metal ions. Although high efficiency of H_2S removal was demonstrated in a single-stage contactor without internal packing, baffling, or optimization of contactor height, it is clear that some optimization of these options will be desirable should pilot tests ensue.

The adaptation of this technique will impact on the design of the turbine condenser. In order to achieve high overall abatement efficiency, a surface type condenser will be required to minimize the volume of liquid in contact with H_2S in the gas phase and, thereby, maximize the amount of gaseous H_2S to be ultimately scrubbed.

The distribution of H_2S between the gas and liquid phases is not sensitive to the absolute quantity of H_2S , but depends largely on pH and temperature. The distribution is given by Henry's law.

$$\frac{H_2S(ag)}{H_2S(g)} = K = 10^{-1.15} \text{ (@40}^{\circ}\text{C)} \text{ (Helgeson 1969)}$$

where $H_2S(ag)$ is the concentration of dissolved H_2S in moles/liter and $H_2S(g)$ is the partial pressure of H_2S in atmospheres. At a 40°C condensing temperature and a mass ratio of condensate to brine of 0.2, about 98.8% of the H_2S would be partitioned in the noncondensable gas phase. At condensate pH's greater than 6.2, progressively more of the H_2S will be absorbed in

the liquid and less H_2S ejected in the gas phase. Desorption and release of H_2S will then occur should the condensate be used for cooling water makeup. In previous measurements at the GLEF (LLL 1977), the 1st stage condensate pH was approximately 6.2. Lower stage steam condensates had much higher pH's (8.5-9.5) and would readily absorb H_2S . However, only a small fraction of H_2S is retained in the brine after the 1st stage flash. This amount, subsequently desorbed in the lower flash stages and evolved with the low pressure steam, may still pose a problem. For an accurate assessment of specific H_2S abatement requirements, the actual amounts and distribution of H_2S in the various streams need to be precisely determined.

The results and interpretation of these tests also appear in a recently published paper (Quong et al., 1979).

A cost study of geothermal power plants at the SSGF was prepared for SDG&E by Bechtel Nat'l Corp., and The Ben Holt Co. The study was based on plants utilizing the Stretford process as the means for H_2S abatement. The Stretford process is also based on the required use of surface type condensers for the same reasons discussed above. The study estimated the capital costs for the Stretford process alone to be \$1,100,000 for a 50 MWe net power plant. The system consists of a scrubber, absorber, reaction tank, equipment for separation and regenerator of the absorbant liquid, and associated pumps, piping, etc.

By comparison the process utilizing brine effluent would be quite simple. The noncondensibles and brine effluent are passed through a contactor in a countercurrent flow mode. The scrubbed gases are vented as usual, and the effluent pumped to the clarifier for usual

spent brine processing. The capital costs should be significantly less than costs for the Stretford process. Significant operating and maintenance cost savings would also be realized.

The potential for combining the H_2S process with reactor clarification is also very promising. A brief test at the GLEF by Magma and SDG&E using the reaction chamber of a 30 gpm EIMCO clarifier as the contactor indicated scrubbing efficiencies on the order of 97% (Featherstone 1979). This adaptation of the process combines H_2S abatement with preinjection clarification with minimal added plant costs, and with potential beneficial effects with respect to clarifier efficiency and mineral recovery from the sludge.

3.2.8.5 Conclusions and Recommendations

A simple, efficient, and potentially inexpensive method for removal of H_2S from noncondensable gases evolved in geothermal flash processes has been successfully tested on a small scale in the field. The method consists of scrubbing the noncondensable gases of H_2S with brine effluents which contain relatively high concentrations of Pb, Zn, and Fe such as those of the Salton Sea and Brawley Geothermal Fields in the Imperial Valley, California. For plant applications, noncondensibles including H_2S would be ejected from a surface steam condenser (necessary to minimize the volume of liquid in contact with H_2S) and scrubbed with effluent brine just prior to preinjection clarification. The metal sulfide precipitates are removed in the clarification step and the noncondensibles, less H_2S , are vented as usual.

This method eliminates the need for chemical absorbants and the equipment and costs required for absorbant regeneration. The capital costs should be but a small fraction of the estimates for the Stretford process. Further significant reduction in costs can be realized if the scrubber/contactator shells can be eliminated by utilizing the reaction chamber of the clarifier as the contactor. Tests of this application on the 10 MWe clarifier or in a separate scrubber sized for 1 well flow are recommended to provide H₂S abatement efficiency data and to determine what effect the reduced pH effluent may have on clarifier performance.

References

Bechtel National Inc, and The Ben Holt Company, Feasibility and Risk Study of a Geothermal Power Plant at the Salton Sea KGRA, prepared for the San Diego Gas & Electric Co., May 10, 1978.

Featherstone, J.L., GLEF Technical Review Committee Meeting, San Diego, CA, May 1979.

Helgeson, H.C., Thermodynamics of Hydrothermal Systems at Elevated Temperatures and Pressures, American Jour. of Science, 267, 729-804, 1969.

Jacobson, W.O., GLEF Technical Review Committee Meeting, San Diego, CA., May 1979.

Lawrence Livermore Laboratory, LLL Geothermal Energy Development Program, Highlights Report, L.B. Owen & G.E. Tardiff, editors, Report #ATHS/ISP-17, Sept. 1978.

Quong, R, K.G. Knauss, N.D. Stout, and L.B. Owen, An Effective H₂S Abatement Process Using Geothermal Brine Effluents, Geothermal Resources Council Annual Meeting, Sept. 24-27, 1979, Reno, Nev., also LLL Rept. # UCRL-83010.

12.0 WELL CASING MATERIALS

Responsible Organization: LLL

Investigators: R. D. McCright, A. Goldberg, E. O. Snell, F. E. Locke,
R. McLain, W. P. Frey, W. J. Steele, R. Quong, and
G. E. Tardiff*

Priority 1

3.2.12.1 OBJECTIVES:

Determine the API grade of carbon steel best suited for well casing application and the composition-dependent variations within API specifications that influence corrosion lifetime. This will lead to API steel specifications for maximum well casing lifetime.

3.2.12.2 BACKGROUND:

The useful lifetime of carbon steel well casings in the SSGF is expected to be very limited. Downwell corrosion tests of J-55 tubing (State No. 1, Shell Oil Co.), for example, indicate corrosion rates of ~100 mils/yr at the top of the well increasing to 2000 mils/yr at the well bottom. In addition, the carbon steel casing in the Sinclair No. 4 well suffered severe enough corrosion attack by a perforation mechanism after about six months of accumulated operation to cause the operators to abandon the well. No data yet exists on corrosion of carbon steel casing in brine from the upper reservoir in the SSGF. Recent examination of surface piping just downstream of the Magmamax No. 1 wellhead, however, indicated the presence of a perforating mode of attack and a corrosion rate of 120 mils/yr. It is expected that at least the upper portion of the Magmamax #1 well casing is similarly attacked. Present information indicates that carbon steel well casing lifetime will be less than four years even for the upper reservoir.

* Private Consultant

The great expense of new wells and well recasing leads to the conclusion that even nominal improvement in casing life will have a substantial cost benefit. For example, Reference 1 concludes that doubling well casing life will have a greater impact on reduction of busbar energy cost (~10% reduction) than any other R&D initiative.

3.2.12.3 TEST DESCRIPTION AND PROCEDURE

3.2.12.3.1 Test Materials and Equipment

A tubing string consisting of 30' lengths of 1.66" o.d. tubing joined together by threaded couplings will be tested downhole in Woolsey I well. The materials to be tested are API J-55 (baseline) N80 and C-75, all currently available in well casing and tubing string. The string will be designed so that the three materials will be exposed to brine distributed at different depths in the well.

3.2.12.3.2 Test Prerequisites

Appropriate chemical and metallurgical analyses will be performed to characterize each lot of steel before installation.

3.2.12.3.3 Test Conditions

Woolsey I wellflow at design operating conditions is required. Large variations greater than $\pm 10\%$ in wellflow are not desirable, but will not void the tests. The flash point in the well should be maintained above one set of sample tubing lengths to provide constant exposure to a two phase fluid. Again full well flow during as much of the time as possible during the 3 months exposure is desirable.

3.2.12.3.4 Required Data and Observations

Tubing strings containing lengths of J-55 (baseline) N-80 and C-75 will be tested downhole in the Woolsey #1 well. Three lengths of each material will be tested at three different depths in the well as a means of obtaining data on the effect of composition and depth on corrosion. Each lot of material tested will be characterized by chemical and metallurgical analysis. After exposure, the various materials will be analyzed for the various forms of corrosion (general, pitting, crevice, etc.) using metallurgical analysis methods.

Normal well operating data - flowrate, temperature, and pressure will be obtained from the GLEF daily log. Data on fluid properties from other activities in the test program should be sufficient for integrating with the corrosion results.

3.2.12.3.5 Test Duration

The goal is to accumulate 3 months of downwell exposure. Complete analyses and reporting is anticipated to take another 2 months.

3.2.12.4 RESULTS

3.2.12.4.1 Expected Results

The corrosion rate and projected lifetime of 1-3 different API grades of steel exposed to Niland brines at downwell conditions will be determined. The effect of depth will also be determined.

The effect of chemical composition, thermo-mechanical histories, and resulting microstructures within each grade will be evaluated.

Failure mechanism will be evaluated and reported.

3.2.12.4.2 Data and Observations

Test Materials - Three grades of random 30-ft. long x 1-1/4 in. nominal diameter x 0.140 in. nominal wall API steel tubing were obtained for test and evaluation: J55, N80, and C-75. These materials were ordered to API specification 5A (J55 and N80) and 5AC (C75). Table 1 gives the API specification data, the vendor supplied chemical analysis, and the vendor supplied mechanical property data for the three materials.

API Test String Makeup - The test string was emplaced in Woolsey No. 1 well according to the scheme shown in Table 2 by coupling individual joint lengths together. The joint number, joint length, depth in well, and material designation are given in the table. The J55 and N80 joints had externally upset and threaded ends and were coupled together using standard couplings. The C75 joints had integral threads and were joined to J55 joints using crossover nipples.

Exposure Duration and Environment - The string was emplaced in Woolsey No. 1 well on January 16, 1979, and removed from the well on March 26, 1979, for a total of 69 days exposure. The well operational history during this test period is summarized in Table 3. Note that the exposure temperature ranged from 260°C (well bottom) to ~190°C (at well head) during those periods when the well was flowing. Brine pH as determined on samples taken at well head conditions and cooled to ambient temperature was 5.8. Downhole pH measurements have not been made, however, brine pH is expected to decrease with increasing depth in the well because of the greater solubility of the acidic gases CO₂ and H₂S at high pressures. Calculations by Jackson², for

Table 1 - Summary of API Material Analysis and Properties

J-55 - Ordered to Following API Specification: tubing, grade J-55, API std. 5A, seamless, 1-1/4" nominal, 2.40 lb/ft., EUE IORD, T & C range 2.

Vendor Supplied Chemical Analysis: .31 C, 1.43 Mn, .011 P, .012 S, .06 Si, .13 Mo, bal Fe.

Vendor Supplied Mechanical Properties: Yield strength - 64,000 and 64,500 psi; ultimate tensile strength - 91,400 and 92,050 psi; elongation in 2" - 34 and 30 percent.

Mechanical Properties Required by J-55 Specification: Minimum field strength - 55,000 psi, maximum yield strength - 80,000 psi. Minimum ultimate strength - 75,000 psi.

N-80 - Ordered to Following API Specification: tubing, grade N-80 API std. 5A, 1-1/4" nominal 2.40 lb/ft. EUE, IORD, T & C, range 2.

Vendor Supplied Chemical Analysis: .44 C, 1.60 Mn, .016 P, .018 S, .023 Si, .20 Mo.

Vendor Supplied Mechanical Properties: Yield Strength - 93,000 and 95,100 psi; ultimate tensile strength - 133,700 and 126,300 psi; elongation in 2" - 28 and 28 percent.

Mechanical Properties Required by API Specification: Minimum Yield Strength - 80,000 psi, maximum yield Strength - 110,000 psi; minimum ultimate tensile strength - 100,000 psi.

C-75 - Ordered to following API Specification: tubing, Grade C-75, API Std. 5AC, 1-1/4" nominal 2.33 lb/ft. IORD 1J, Range 2.

Vendor Supplied Chemical Analysis - Same as for N-80 since C-75 was prepared by heat treatment of N80. Meets API chemical requirements for grade C-75, type 1 material.

Vendor Supplied Mechanical Properties - Not available. Heat treated to produce C-75 properties.

Mechanical Properties Required by API Specification - Minimum yield strength - 75,000 psi, maximum yield strength - 90,000 psi; minimum ultimate tensile strength - 95,000 psi.

Table 2 - Summary of API Test String Makeup

<u>Joint* Number</u>	<u>Material</u>	<u>Length (ft)</u>	<u>Depth in Well (ft)</u>
1	J55	33.8	1728
2	N80	31.6	1694
3	J55	33.2	1662
4	C75	34.5	1629
5	J55	31.1	1595
6	J55	34.5	1563
7	J55	34.2	1529
8	J55	34.2	1495
9	J55	33.2	1461
10	J55	34.5	1427
11	J55	34.4	1393
12	J55	34.1	1359
13	J55	34.4	1324
14	J55	34.4	1290
15	J55	34.4	1256
16	J55	34.5	1221
17	J55	34.4	1187
18	J55	32.7	1152
19	N80	33.5	1119
20	J55	31.5	1086
21	C75	34.3	1055
22	J55	34.4	1020
23	J55	34.4	986
24	J55	34.4	952
25	J55	34.4	917
26	J55	34.4	883
27	J55	33.2	848
28	J55	32.7	815
29	J55	34.5	782
30	J55	34.4	748
31	J55	31.5	713
32	J55	34.5	682
33	J55	31.4	647
34	J55	33.9	616
35	J55	34.5	582
36	J55	34.4	548
37	N80	33.5	513
38	J55	34.4	479
39	C75	34.4	445
40	J55	33.2	411
41	J55	34.4	377
42	J55	34.4	332
43	J55	34.1	298
44	J55	33.8	264
45	J55	34.5	230
46	J55	34.4	195
47	J55	34.5	161
48	J55	34.4	127
49	J55	34.5	92
50	J55	34.4	58
51	J55	34.4	13

* first to go into well - joint #1

**Table 3. Summary of Woolsey #1 Well Operational History
During the API String Test Period from January 16
to March 26, 1979.**

Total number hours with brine flow:	904 hours
Total number hours without brine flow:	752 hours
Total string exposure time:	1656 hours
Downhole temperature:	500°F (260°C)
Wellhead pressure (@ plant boundary):	151 psig
Wellhead temperature (@ plant boundary):	366°F (186°C)
Brine flowrate	500 gpm

example, for a nearby well (Magma No.1) indicate a well bottom pH of 4.5. Flow environment is two phase above the flash point with about 10% quality at the wellhead. Flow velocity increases greatly above the flash point to an estimated maximum of ~100 ft/sec for the Woolsey No. 1 well.

The chemistry of the Woolsey No. 1 brine is given in Table 4. The salient features include the high salinity, mildly acidic pH and the low oxidation-reduction potential as indicated by the sulfide ion concentration.

Scale Deposits - The thickness of scale deposited on various joints are plotted as a function of depth in Figure 1. Scale thickness increased from ~25 mils at the bottom of the string to ~75 mils at the top of the string. The scale consisted of an adherent but somewhat porous layer of PbS in a calcium carbonate and amorphous iron silicate matrix.

Metallurgical Characterization of the Test String Materials - Metallurgical sections which were made for corrosion measurements were also used to characterize the metallurgical microstructure of the materials tested. The metallurgical analysis results are summarized in Table 5. The sections were taken at two locations: an A type located near the upset end of the joint and a B type located in the central region of the joint. Note that the J55 microstructure consisted of two relatively distinct types: fine grained, normalized ferritic/pearlitic and coarse grained, annealed ferritic/pearlitic. The microstructure of both the C75 and N80 consisted of very fine structured tempered martensite.

Table 4 - Woolsey No. 1 Brine Properties* and Composition*.

pH: 5.84 (after flashing and cooling to ambient temperature)

Density, g/cm³ at 25°C: 1.166

Chloride, Mol/l : 4.13

Oxidation - reduction potential: not measured for Woolsey No. 1 brine;
probably similar to Magmamax No. 1 brine at 237 mV vs. SHE.

<u>Element</u>	<u>Concentration, mg/kg</u>	<u>Element</u>	<u>Concentration, mg/kg</u>
Li	138	B	409
Na	42,400	Al	3
K	6,900	Fe	215
		Mn	607
Mg	81		
Ca	21,700	Cu	2.0
Sr	299	Pb	43
Ba	150	Zn	226
Si as SiO ₂	510	Mo	9
Sulfate	108	As	14
Cd	1.6	V	0.6
Ni	0.4	Zr	0.4
Ti	1.4		

* Brine sampled during February, 1979, after depressurization and cooling to ambient conditions. Approximate total evaporation (flashing) was 20% by weight.

Figure 1 - Thickness of Scale on Test String Surface vs. Depth in Well for API Test String Tested in Woolsey No. 1.

Table 5 - Summary of Results of Metallurgical Characterization
of API Test String Materials

<u>Joint Numbers and Section Type *</u>	<u>Metallurgical Microstructure</u>
	<u>J55</u>
3A, 5A, 6A, 7A, 9A, 10B, 12B, 13B, 18B, 27B, 29B, 34B, 40B	Normalized (air cooled) ferritic pearlitic structure with ferrite surrounding prior austenite grain boundaries. Fine grained: 9-10 ASTM grain size number. Slight decarburization up to .003 inch deep.
3B, 6B, 7B, 9B, 11B, 16B, 42B	Annealed (slow cooled) ferritic/pearlitic structure with ferrite surrounding prior austenite grain boundaries. Coarse grained: 2-3 ASTM grain size number. Slight decarburization up to .003 inch deep.
	<u>N80</u>
2A, 2B (19 & 37 assumed to be same)	Very fine structured tempered martensite. Slight decarburization up to .003 inch deep.
	<u>C75</u>
4A, 4B (21 & 39 assumed to be same)	Very fine structured tempered martensite. Slight decarburization up to .003 inch deep.

Corrosion Observations and Data - The surfaces of the joints were visually scanned for the presence of tubercles. These are nodular growths which form because the iron corrosion product has a greater specific volume than iron. The scale was removed from such tubercle areas and the site of the worst pit was established visually. A specimen was cut from this area such that after mounting and polishing the pit would appear in cross section. A total of about 30 such sections were prepared. Every effort was made to select the worst pit area for sectioning. This was based on the premise that the most useful data would be that which would allow an estimate to be made of the least time of exposure required to cause first breaching of a casing wall. The sections were polished and examined at 15 to 25X. The minimum remaining thickness was measured. The results for the sections are recorded in Table 6. Very little corrosion was observed in the cases of the N80 and C75 sections which were examined. In these cases, it was more accurate to measure the maximum pit depth. These results are recorded in Table. 7.

3.2.12.4.3 Calculations

J55: Indicated Penetration Rate - The minimum remaining thickness raw corrosion data listed in Table 6 was converted by calculation to an indicated penetration rate using the following equation:

Table 6 - J55 Corrosion Measurements

<u>Joint No.</u>	<u>Depth (ft.)</u>	<u>Minimum Wall Remaining (mils)</u>	<u>Indicated Rate of Penetration (mils per yr, mpy)</u>
3A	1662	67	428
3B	1662	102	243
5A	1595	106	222
6A	1564	83	344
6B	1564	106	222
7A	1529	87	323
7B	1529	126	116
8A	1495	39	577
9A	1461	55	492
9B	1461	55	492
10B	1427	118	159
11B	1393	126	116
12B	1358	126	116
13B	1324	130	95
16B	1221	130	95
18B	1152	138	53
27B	848	142	32
29B	782	134	74
34B	616	154	32
40B	411	142	32
42B	332	146	11

Table 7 - N80 and C75 Corrosion Measurements

Joint No.	Depth (ft.)	Depth of Penetration (mils)	Calculated Remaining Thickness (mils)	Indicated Rate of Penetration (mils per year, mpy)
2A - N80	1694	3.0	143	16
2B - N80	1694	2.8	143	15
19 - N80	1119	{ Visual Appearance Indicates Similar to 2A and 2B }		
37 - N80	513			
4A - C75	1629	2.8	143	15
4B - C75	1629	2.1	144	11
21 - C75	1055	{ Visual Appearance Indicates Similar to 4A and 4B }		
39 - C75	445			

$$\text{Indicated Penetration Rate (mpy)} = (t_i - t_r) \times \frac{365}{69}$$

where mpy = mils/year

t_i = initial thickness in mils

t_r = remaining thickness in mils

365 = days in year

69 = days exposure

The value of t_i or initial thickness used for the J55 was 148 mils. This was determined by averaging 6 individual micrometer thickness measurements on a length of unexposed J-55 tubing. The results of the above calculation are recorded in Table 6 and plotted as a function of depth of exposure in Figure 2.

N80 and C75: Indicated Penetration Rate - The procedure used above was also applied to the raw data given for the N80 and C75 in Table 7. In the case of N80 and C75, however, the measured pit depth was first used to compute the remaining thickness by taking the difference between the pit depth and the original thickness for N80 and C75. The original thickness for this tubing was determined to be 146 mils (average of 6 individual measurements on unexposed tubing). The calculated indicated penetration rates are given in Table 7 and are also plotted in Figure 2. As indicated in Table 7 and Figure 2, these results correspond to joints which were exposed between 1600 and 1700 ft. depth. No sections were made in the N80 and C75 joints which were exposed at about 500 ft. and 1100 ft. depths. Visual examination

Figure 2. Indicated Penetration Rate vs. Depth for J55, N80, and C75 For API Test String Tested In Woolsey No. 1.

of these joints, however, led to the conclusion that the corrosion experienced by these joints was not as severe as that experienced by the joints exposed between 1600 and 1700 ft. Thus, it has been concluded that the maximum penetration rate for the N80 and C75 is no greater than the maximum rate indicated for the joints exposed at the 1600 - 1700 ft. depth level. The points plotted for the N80 and C75 joints exposed at higher levels in Figure 2 reflects this conclusion. The results in Figure 2 show that neither grain size nor position of the sample (center of joint vs. near the upset) in the J-55 material correlated with the indicated penetration rate.

3.2.12.4.4 Comparison of Actual and Expected Results

The indicated penetration rate results for J-55 given in Figure 2 would rule out J-55 as a reliable material for long life (20 yr) production well casings in the Salton Sea Geothermal Field. For example, the results indicate that first breaching of a 0.5 inch thick casing wall below about 1300 ft. by a small diameter pit would occur in about a year; above 1300 ft. the time required would be about 5 years. While first breach of the wall by a small pit may not constitute failure, it is an occurrence which signals impending major problems. For example, the continued lateral growth of a pit or link up of many pits could lead to a large hole in the casing, which in turn could lead to degradation of the cement and cement bond and also cause in leakage of unwanted waters or escape of brine into non-geothermal aquifers. Also, the link-up of through-the-thickness pits would seriously reduce the structural integrity of the casing and this could lead to serious safety problems. These results were expected on the basis of other published corrosion rate results for J-55 exposed in Salton Sea Geothermal Field Brines³. In this case,

the corrosion of J-55 was observed to be even more severe because of the greater depth of the well and associated higher temperature and more corrosive brines.

Early downwell corrosion testing on specimens of various unalloyed and low alloy steels led to the conclusion that small amounts of Mo and other alloying elements provide a substantial improvement in corrosion resistance. The purpose of the present test in part was to determine the extent to which the small amounts of alloying elements present in the higher grade American Petroleum Institute (API) steels would improve corrosion resistance. Qualitatively an improvement was expected, but it was not possible to quantitatively predict the degree of improvement. Figure 2 shows that beneficial influence of the greater amounts of Mo and Si in the N-80 and C-75 materials is substantial. The present results indicate that the improvement could be as much as a 20 fold increase in the time required for a small pit to just perforate a 500 mil casing wall.

3.2.12.5 CONCLUSIONS AND RECOMMENDATIONS

It is concluded that J-55 is not suitable for well casings requiring long life in the SSGF but that API Grades N80 and C-75 have the potential of providing long life. Of these, it is recommended that C-75 be given priority for further testing and use. The lower maximum yields strength of C-75 (90,000 vs. 110,000 psi for N80) would reduce or eliminate the susceptibility to delayed failure due to H_2S cracking or stress corrosion cracking. In addition, the API specification for C-75 calls for a minimum alloy content, while alloy content is unspecified for the N80 material. A quote obtained from an oil field tubular supply company indicates that the cost premium for N80 and C-75 relative to J55 are 1.35 X and 1.52 X, respectively.

Thus, it does not appear that the cost premium for use of either of these higher API grades is prohibitive.

It is also necessary that confirmatory data be obtained for the better grades of API materials exposed for longer times. The LLL Geothermal Program is being funded by the Geothermal Hydrothermal Technology Group of the DOE to carry out further studies on the use of low alloy steels for SSGF well casing applications. A test string consisting of a variety of low alloy steels including C-75 has been in test in the Magmamax No. 1 well for the last four months. The analysis of the materials in this string should lead to a much greater understanding of the potential benefits and pitfalls associated with the use of these materials for SSGF well casing and brine handling equipment.

References

1. J. G. Leigh, S. M. A. Pond and R. K. Trehan, Cost-benefit analysis of the Federal Geothermal Energy Program: MITRE Corp. Technical Report MTR-7326, 101 pgs.
2. LLL Geothermal Energy Program Status Report, January 1976-January 1977, UCRL-50046-76, April, 1977. See article by D. D. Jackson on page 100.
3. R. S. Treseder and Rita Wieland, Down-Hole Corrosion in a Salton Sea Geothermal Well, paper prepared for the 1977 SPE-AIME International Symposium on Oilfield and Geothermal Chemistry, La Jolla, California, June 27-28, 1977, paper number SPE-6613.

3.2.13.0 INJECTION STUDIES

Responsible Organization: LLL

L. B. Owen, E. Raber, J. Harrar, C. Otto, and R. Netherton

Priority: 1

3.2.13.1 OBJECTIVES:

- a) Establish the injectability of undiluted effluents produced by a pilot size reaction clarifier - gravity filter pre-injection processing system located adjacent to the GLEF.
- b) Evaluate the technical and economic feasibility of utilizing Salton Sea Water, Alamo River Water and New River Water as alternate sources for injection makeup.

3.2.13.2 BACKGROUND:

Previous work by LLL and Magma at the Salton Sea KGRA has demonstrated that an effluent processing system consisting of a reaction clarifier and a final pressure filter is capable of yielding an injectable silica undersaturated effluent containing 2 ppm or less suspended particulates greater than 1 μ m in diameter. By the summer of 1979, all effluents produced by the GLEF were passed through a pilot clarifier-filter system, sized for 2 well flow, prior to injection. However, data are needed to determine the injectability of processed effluents and the expected useful lifetime of a typical injection well receiving processed brine.

The large-scale utilization of geothermal resources in California's Imperial Valley will necessitate a viable supply of cooling water. However, irrigation waters will probably be unavailable

in the quantities ultimately required to satisfy power plant cooling needs. The flash-steam conversion cycle offers a source of clean cooling water in the form of steam condensate. Condensate usage, however, means that a significant mass fraction of produced fluids can not be returned to the production reservoir. In the case of a typical double-flash cycle operating at the Salton Sea Geothermal Field (SSGF), from 20 to 25 percent of the production fluid will be lost as vapor. Since reservoir pressure maintenance may become a vital issue at some Imperial Valley geothermal resources, we have evaluated the feasibility of using local surface waters for injection makeup.

Within the Imperial Valley, there are three potential sources of injection makeup water; the New River, the Alamo River, and the Salton Sea. However, extensive diversion of the waste irrigation waters carried by the New and Alamo Rivers may not be possible in view of the possible detrimental impact on the salinity balance in the Salton Sea. Therefore, our work focused primarily on the utilization of Salton Sea water as source for injection makeup.

The technical feasibility, with respect to injection well and reservoir impairment, of using makeup water is unknown. In the case of partial mixing of makeup water and spent brine, severe problems can be anticipated, because the particulate loading in effluent processing systems may be increased by factors of 2 to 3 times or more as compared to nominal conditions with unmodified production fluids. In addition, the inverse temperature solubility of CaSO_4 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaCO_3 and the possible failure of pre-injection processing to

eliminate supersaturation of dissolved species in residual effluents creates the potential for scaling of the injection system and post-injection reservoir impairment as injected effluents begin reheating. Direct injection of ambient temperature Salton Sea or River water has the disadvantages of necessitating independent effluent processing systems for removal of particulates and control of biological activity, increased rates of thermal degradation in the reservoir, accelerated casing corrosion, and potential reservoir impairment as make-up water reheats or partially mixes with in-situ fluids.

The performance characteristics and efficiency of baseline pre-injection effluent processing, consisting of reaction clarification and final gravity filtration, with makeup water additions is also unknown. Primary uncertainties exist in the areas of sludge contact for removal of dissolved supersaturated species, effects of increased suspended solids concentration on unit performance efficiency and flocculation and settling characteristics of sulfate, carbonate, and oxide particulates. Since the process system may also become the last stage for scrubbing H_2S from vent gas emissions (test 8), effects of heavy metal sulfide particulates on the system performance must also be established.

Required data for optimizing performance of pilot or demonstration brine conditioning systems can best be obtained by bench-scale field tests. This activity will be closely integrated with test 11.

3.2.13.3 Test Description and Procedure

3.2.13.3.1 Test Materials and Equipment

Injectability of effluents with and without makeup water or heavy metal sulfide additions from the pilot pre-injection process systems located adjacent to the GLEF will be assessed with on-line membrane filtration and core flooding tests. An automated apparatus, designed and built by LLL will be located adjacent to the brine processing system¹. A second LLL-designed and built manually operated filtration apparatus will be provided for the use of Magma Power personnel in their evaluation of the 10 MWe sized clarifier². The filtration and core work will be supplemented with anerobic incubation experiments at injection temperature (75-90°C). Effluents will be sealed in nitrogen-pressured glass ampoules and incubated for several days. Periodic measurement of suspended solids will yield data on the potential for reservoir impairment resulting from post-injection precipitation. Sludge contact with and without chemical additives will also be evaluated by means of a "hot" jar testing procedure to establish whether reaction clarification can eliminate supersaturated species of silica, carbonate and sulfate from make-up water-brine mixtures.

No modifications to the GLEF or effluent processing system will be required other than provisions for sidestream brine sampling ports and disposal of small quantities of tested effluent. All bench-scale work will be carried out in the LLL field test facility.

3.2.13.3.2 Test Prerequisites

Not applicable

3.2.13.3.3 Test Conditions

Evaluation of injectability of pilot-system processed effluents will require stable uninterrupted operation of the GLEF and the injection processing system for periods of several days. Operational conditions should be documented carefully. Other task activities can be completed independently of GLEF operations.

3.2.13.3.4 Required Data and Observations

Injectivity tests - An automated on-line apparatus of proven design will be used to obtain filtration and core data in conjunction with Magma's operation of pilot pre-injection processing systems. Filtration data is collected, analyzed and interpreted in accordance with standard methodology.²⁻⁵ Cores and membrane filters are operated with and without prefilters to establish their permeability to processed effluents. Standard procedures for geothermal effluent core tests are described by Tewhey et al.⁶

Makeup Water Evaluation - Processing requirements for makeup water will be established by bench-scale jar and filtration tests.⁷ Necessary supporting analytical data on residual supersaturation levels in processed effluents and composition of precipitated solids will also be obtained.

Anerobic incubation experiments will be carried out to establish chemical stability of makeup water and mixtures of makeup water and brine at temperatures between 70-90°C.⁸ Similar techniques will be employed to establish chemical stability of effluents from Magma's 30 GPM pilot pre-injection processing system.

3.2.13.3.5 Test Duration

Injectivity tests of pre-injection processed effluents are paced by the GLEF operational schedule. Tests are indicated whenever clarifier operating conditions are changed significantly. Therefore, the ability to perform required tests will be maintained until the end of the fourth quarter of FY79. Makeup water processing studies will begin early in FY79 depending upon the availability of brine effluents from the GLEF. Approximately 8 months total field time will be required to complete the assessment of processing requirements for injection of makeup water and to establish the injectivity of processed effluents.

3.2.13.4 RESULTS

3.2.13.4.1 Expected Results

3.2.13.4.1.1 Injectability Tests of Conditioned Brine

The injectivity of processed effluents produced by a pilot reaction clarifier-pressure filter systems located adjacent to the GLEF will be established. Injectivity will be reported as a function of clarifier operating parameters with special attention devoted to the

effects, if any, of chemical additives. Chemical stability of processed effluents will also be determined to establish the potential for injection well impairment resulting from post-processing precipitation of silica and other species. Test results will be used to estimate the useful lifetime of an injection well.

3.2.13.4.1.2 Make-up Water Evaluation

Engineering data describing the effect of make-up water additions to the input fluid of a baseline reaction clarifier-final pressure filter effluent processing system will be generated. The technical feasibility of a full-scale system for pre-injection processing will be assessed. Results of parametric studies will be provided to Magma as a basis for optimization of their brine conditioning evaluation program.

3.2.13.4.2 Data and Observations

3.2.13.4.2.1 Injectability Tests of Conditioned Brine

A Demonstration Reaction Clarifier -- gravity filtration system with a 1600 GPM throughput capability was in operation at the joint DOE-SDG&E-MAGMA test facility located in the Salton Sea Geothermal Field, Southern California during the summer of 1979. The system, which was designed to condition spent effluent from a 10 MWe-size geothermal power plant, removes supersaturated dissolved species and residual suspended solids from brine prior to subsurface brine disposal via injection wells. We established the post-processing chemical stability of conditioned effluents by means of anoxic incubation tests at 90°C. The effect of residual dissolved polymer, that might

be used for the purpose of scale control in upstream power plant components on the efficiency of reaction clarification was also evaluated. Membrane filtration and core tests were used to assess the injectability of processed brine.

We found that the clarifier-filter operational procedures and system design permitted oxygenation of the brine by air intrusion. This resulted in partial stabilization of dissolved silica and precipitation of oxides of iron. As a consequence, conditioned brine injectability was poor. However, elimination of the air intrusion problem would result in a substantial improvement in brine quality.

The clarifier was sized for 1600 GPM throughput, which is adequate to process full flow from two production wells. However, during the evaluation period, it was not possible for the GLEF operators to maintain two well flow because of difficulties with the Woolsey No. 1 production well. As a consequence, the clarifier initially was operated at 50% of its design capacity and, as a result, effluent quality was significantly degraded. The major difficulty was attributed to partial collapse of the sludge blanket.

As an expedient remedial measure, 50 to 60 percent of the clarifier overflow was recycled to boost the average throughput rate in the unit. This procedure resulted in oxygenation of the brine due to air intrusion. Other sources of brine aeration were also subsequently identified. The result of air contamination was precipitation of ferric iron in the form of a hydroxide:

The formation of ferric iron is followed by the hydrolysis reaction:

Table 13.1 Results of Incubation Tests
(August 1, 1979)

Time (Hrs)	CONCENTRATION DISSOLVED SILICA (PPM-WT)				CONCENTRATION SUSPENDED SOLIDS (PPM-WT)		
	Clarifier		Gravity Filter (86-88°C)		Clarifier		Gravity Filter (86-88°C)
	Influent (90°C)	Effluent (86-88°C)			Influent (90°C)	Effluent (86-88°C)	
0	342	202	202		193	80	5.6
0.5	247	200	202		223	81	5.5
1	200	200	200		245	81	5.4
2	200	198	200		283	80	7.8
4	200	198	198		281	82	12.6
8	180	198	198		314	82	19.8
24	157	198	198		346	74	23.3
48	153	198					

Polymer Experiments

The effect of 20 ppm (by weight) of PAE·HCl polymer on dissolved silica in clarifier influent was established by incubation tests at 90°C. A jar testing apparatus was used to study the effect of 20 ppm PAE·HCl polymer on clarifier performance. Brine samples containing the polymer, while maintained at 86-90°C, were mixed at a constant speed of 100 RPM in the presence of 10 volume percent sludge obtained from the clarifier. Aliquots of the mixture were then removed, over a time interval ranging from five minutes to one hour, for subsequent analysis of total dissolved silica by the atomic absorption method described earlier. Experimental data are summarized in Table 13.2 - 13.3.

Membrane Filter and Core Tests - All membrane filter tests were performed with 0.4, 1.0 or 8.0 μ m pore size Nucleopore membrane filters on as received brine effluent from the gravity filtration system. Additional tests using 0.4 and 8.0 μ m membrane filters were also performed with an 1.0 μ m pore size Cuno cartridge filter inserted in the sampling line upstream of the membrane filters. All membrane filter tests were carried out at constant differential pressure. The 0.4 and 1.0 μ m membrane filter were operated at 50 psi differential pressure and the 8 μ m membrane filter tests were run at 10 psi differential pressure. The duration of all filter tests was one-half hour. Membrane filter test results are summarized in Table 13.4 - 13.8.

For the core test, a one-inch (OD) diameter by four-inch long right circular cylinder of Kayenta sandstone was exposed to brine at 101°C and 20 psi differential pressure. Kayenta sandstone is a reasonably good analog of typical upper SSGF reservoir sands. The

Table 13.2 Effect of 20 PPM (wt) PAE-HCL Polymer on Precipitation of Dissolved Silica from Clarifier Influent (90°C) (August 2, 1979)

Time (Hrs)	Concentration • Dissolved Silica
0	391
0.5	324
2	234
4	234

Table 13.3 Effect of 20 PPM (wt) PAE-HCL Polymer on Sludge Contact Removal of Dissolved Silica from Clarifier Influent (90°C) (August 1, 1979)

Time (Hrs)	Concentration Dissolved Silica (PPM-WT)	
	Raw Clarifier Influent	Polymer-Treated Influent
0	391	391
0.08	247	234
0.17	243	216
0.33	184	168
1.00	165	162

Table 13.4

0.4 Micron Membrane Filtration Test Results for Conditioned brine from Magma power's clarifier-filter system. (August 8, 1979)

<u>TIME</u> <u>(Min)</u>	<u>VOLUME</u> <u>(Litres)</u>	<u>FLOWRATE</u> <u>(L/mins)</u>	<u>TIME</u> <u>(Min)</u>	<u>VOLUME</u> <u>(Litres)</u>	<u>FLOWRATE</u> <u>(L/mins)</u>
0.145	0.2	1.379	15.183	7.2	0.292
0.336	0.4	1.047	15.885	7.4	0.285
0.521	0.6	1.081	16.581	7.6	0.287
0.726	0.8	0.976	17.300	7.8	0.278
0.947	1.0	0.905	18.031	8.0	0.274
1.194	1.2	0.810	18.717	8.2	0.292
1.442	1.4	0.807	19.483	8.4	0.261
1.727	1.6	0.702	20.276	8.6	0.252
2.005	1.8	0.719	21.071	8.8	0.252
2.287	2.0	0.709	21.904	9.0	0.240
2.597	2.2	0.645	22.726	9.2	0.243
2.912	2.4	0.635	23.583	9.4	0.233
3.250	2.6	0.592	24.452	9.6	0.230
3.616	2.8	0.547	25.330	9.9	0.228
3.984	3.0	0.543	26.230	10.0	0.222
4.369	3.2	0.520	27.103	10.2	0.229
4.791	3.4	0.474	28.007	10.4	0.221
5.212	3.6	0.475	28.975	10.6	0.207
5.649	3.8	0.458	29.913	10.8	0.213
6.107	4.0	0.437			
6.547	4.2	0.455			
7.007	4.4	0.435			
7.494	4.6	0.411			
8.001	4.8	0.395			
8.520	5.0	0.385			
9.055	5.2	0.374			
9.634	5.4	0.245			
10.190	5.6	0.360			
10.766	5.8	0.347			
11.348	6.0	0.344			
11.940	6.2	0.338			
12.548	6.4	0.329			
13.195	6.6	0.309			
13.837	6.8	0.312			
14.498	7.0	0.303			

Total Volume = 10.890
 Suspended Solids
 ppm (by vol) = 10.64
 ppm (by wt) = 9.09

Table 13.5

1.0 Micron membrane filtration test results for conditioned brine from Magma power's clarifier-filter system (August 8, 1979)

<u>TIME</u> <u>(MIN)</u>	<u>VOLUME</u> <u>(LITRES)</u>	<u>FLOWRATE</u> <u>(L/MIN)</u>	<u>TIME</u> <u>(MIN)</u>	<u>VOLUME</u> <u>(LITRES)</u>	<u>FLOWRATE</u> <u>(L/MIN)</u>
0.132	0.2	1.515	14.395	7.2	0.307
0.268	0.4	1.471	15.057	7.4	0.302
0.424	0.6	1.282	15.736	7.6	0.295
0.601	0.8	1.130	16.428	7.8	0.289
0.802	1.0	0.995	17.124	8.0	0.287
1.020	1.2	0.917	17.783	8.2	0.304
1.249	1.4	0.873	18.501	8.4	0.279
1.507	1.6	0.775	19.245	8.6	0.269
1.772	1.8	0.755	20.008	8.8	0.262
2.060	2.0	0.694	20.772	9.0	0.262
2.330	2.2	0.741	21.541	9.2	0.270
2.642	2.4	0.641	22.321	9.4	0.256
2.971	2.6	0.608	23.082	9.6	0.263
3.305	2.8	0.599	23.898	9.8	0.245
3.665	3.0	0.556	24.772	10.0	0.229
4.051	3.2	0.518	25.527	10.2	0.265
4.439	3.4	0.515	26.399	10.4	0.229
4.854	3.6	0.482	27.262	10.6	0.232
5.282	3.8	0.467	28.138	10.8	0.228
5.727	4.0	0.449	29.071	11.0	0.214
6.172	4.2	0.449	30.002	11.2	0.215
6.621	4.4	0.445			
7.083	4.6	0.433			
7.571	4.8	0.410			
8.067	5.0	0.403			
8.567	5.2	0.400			
9.094	5.4	0.380			
9.621	5.6	0.380			
10.191	5.8	0.351			
10.751	6.0	0.357			
11.268	6.2	0.387			
11.882	6.4	0.326			
12.501	6.6	0.323			
13.121	6.8	0.323			
13.743	7.0	0.322			

Total volume: 11.270

Suspended Solids

ppm (by vol) = 6.09

ppm (by wt) = 5.21

Table 13.6

Prefiltered 0.4 micron membrane filtration test results for conditioned brine from Magma power's clarifier-filter system (August 8, 1979)

<u>TIME</u> <u>(MIN)</u>	<u>VOLUME</u> <u>(LITRES)</u>	<u>FLOWRATE</u> <u>(L/MINS)</u>	<u>TIME</u> <u>(MINS)</u>	<u>VOLUME</u> <u>(LITRES)</u>	<u>FLOWRATE</u> <u>(L/MINS)</u>
0.153	0.5	3.268	20.766	37	1.290
0.670	2.0	2.901	21.595	38	1.206
4.002	3.0	3.012	22.399	39	1.244
1.353	4.	2.849	23.248	40	1.178
1.678	5	3.077	24.076	41	1.208
2.139	6	2.170	24.948	42	1.147
2.545	7	2.463	26.681	44	1.154
2.973	8	2.337	27.500	45	1.221
3.387	9	2.416	28.465	46	1.036
3.828	10	2.268	29.353	47	1.126
4.265	11	2.288	30.281	48.4	1.509
4.721	12	2.193			
5.185	13	2.155			
5.662	14	2.096			
6.142	15	2.083			
6.650	16	1.969			
7.165	17	1.942			
7.712	18	1.828			
8.264	19	1.812			
8.843	20	1.727			
9.443	21	1.667			
9.922	22	2.088			
10.664	23	1.348			
11.341	24	1.477			
11.959	25	1.618			
12.656	26	1.435			
13.328	27	1.488			
14.038	28	1.409			
14.733	29	1.439			
15.461	30	1.374			
16.172	31	1.407			
16.924	32	1.330			
17.655	33	1.368			
18.427	34	1.295			
19.191	35	1.309			
19.991	36	1.250			

Total volume = 48.900

Suspended Solids

ppm (by vol) = 0.035

ppm (by wt) = 0.030

Table 13.7

8 micron membrane filtration test results for conditioned brine from Magma power's clarifier-filter system (August 8, 1979)

<u>TIME</u> <u>(MIN)</u>	<u>CUMULATIVE VOLUME</u> <u>(LITRES)</u>	<u>FLOWRATE</u> <u>(LITRES/MIN)</u>
0.200	0.2	1.000
0.315	0.4	1.739
0.558	1.0	2.469
0.806	1.5	2.016
1.245	2.0	1.139
2.258	2.5	0.494
2.622	2.6	0.275
3.365	2.8	0.269
4.193	3.0	0.242
5.224	3.2	0.194
6.364	3.4	0.175
7.441	3.6	0.186
8.792	3.8	0.148
10.150	4.0	0.147
11.463	4.2	0.152
12.933	4.4	0.136
14.411	4.6	0.135
15.870	4.8	0.137
17.525	5.0	0.121
19.275	5.2	0.114
21.065	5.4	0.112
22.875	5.6	0.111
24.750	5.8	0.107
26.860	6.0	0.095
28.600	6.2	0.115
30.400	6.4	0.111

Total volume: 6.420

Suspended Solids

ppm (by vol) = 9.4

ppm (by wt) = 8.03

p = 1.17 g/cc

Table 13.8

Prefiltered 8 micron membrane filtration test results for conditioned brine from Magma power's clarifier-filter system (August 8, 1979)

Total volume = 78.170

Suspended solids

ppm (by vol) = 0.01

ppm (by wt) = 0.009

<u>TIME</u> <u>(MIN)</u>	<u>VOLUME</u> <u>(LITRES)</u>	<u>FLOWRATE</u> <u>(L/MINS)</u>	<u>TIME</u> <u>(MIN)</u>	<u>VOLUME</u> <u>(LITRES)</u>	<u>FLOWRATE</u> <u>(L/MINS)</u>
1.500	6	4.000	13.289	42	2.404
1.720	7	4.546	13.731	43	2.262
1.931	8	4.739	14.169	44	2.283
2.149	9	4.587	14.603	45	2.304
2.360	10	4.739	15.030	46	2.342
2.579	11	4.566	15.478	47	2.232
2.809	12	4.348	15.922	48	2.252
3.027	13	4.587	16.373	49	2.217
3.281	14	3.937	16.810	50	2.288
3.517	15	4.237	17.269	51	2.179
3.772	16	3.922	17.711	52	2.262
4.037	17	3.774	18.177	53	2.146
4.307	18	3.704	18.620	54	2.257
4.593	19	3.497	19.092	55	2.119
4.900	20	3.257	19.540	56	2.232
5.204	21	3.290	20.008	57	2.137
5.516	22	3.205	20.458	58	2.222
5.847	23	3.021	20.927	59	2.132
6.179	24	3.012	21.376	60	2.227
6.595	25	2.404	21.854	61	2.092
6.868	26	3.663	22.301	62	2.237
7.239	27	2.695	22.777	63	2.101
7.612	28	2.681	23.234	64	2.188
7.986	29	2.674	23.714	65	2.083
8.363	30	2.653	24.178	66	2.155
8.760	31	2.519	24.679	67	1.996
9.154	32	2.538	25.134	68	2.198
9.552	33	2.513	25.626	69	2.033
9.953	34	2.494	26.101	70	2.105
10.365	35	2.427	26.594	71	2.028
10.774	36	2.445	27.070	72	2.101
11.188	37	2.416	27.554	73	2.066
11.597	38	2.445	28.026	74	2.119
12.024	39	2.342	28.521	75	2.020
12.441	40	2.398	29.007	76	2.058
12.873	41	2.315	29.508	77	1.996
			29.994	78	2.058

permeability to brine and porosity of the core were 1050 md and 20 percent, respectively. A confining pressure of 500 psi was applied to the core via a heated (100°C) oil bath. The first 1500 pore volumes (1PV = 10.3 ml) of flow through the core was prefiltered with a 1 µm pore size Cuno cartridge filter. The remainder of the flow to the core was not prefiltered. The core data are summarized in Table 13.9.

In general, our automated membrane filter and core test apparatus control system functioned exceedingly well. All system parameters were maintained within ± 2 percent of their set points.

Incubation Test Results - - As shown in Figure 13.1, clarifier influent is chemically unstable and appreciable amounts of silica precipitate over a period of 48 hours. Quasi-equilibrium solubility of dissolved silica is 153 ppm (by weight). Although the influent temperature was 101°C, we completed the incubation test at 90°C to avoid the need for more complex autoclave-type experimental apparatus. Since the solubility of silica increases with increasing temperature, it would be desirable to correct the 90°C solubility data to yield the actual silica solubility at 101°C. A complication arises, however, because the solubility of silica is also inversely proportional to brine salinity. We attempted to convert the silica solubility value measured at 90°C to the corresponding value at 101°C using data provided by Harrar^{8,10} and methods presented in Subsection 13.4.3.1. Using these procedures, we estimated silica solubility in brine with 4.28 M chloride to be 176 ± 5 ppm at 101°C.

The effect of the clarification process on dissolved silica and on the chemical stability of the effluent is shown in Figure 13.2. A quasi-equilibrium for dissolved silica has been established at 198

Table 13.9

KAYENTA SANDSTONE CORE TEST RESULTS

ITEM	MINS	MLITRES	PORE VOLS	ML/MIN	DARCIES
1	10	680	65.8	68.0	952.0
2	20	1420	137.5	74.0	1036.0
3	30	2180	211.0	76.0	1064.0
4	40	2930	283.6	75.0	1050.0
5	50	3670	355.3	74.0	1036.0
6	60	4420	427.9	75.0	1050.0
7	70	5170	500.5	75.0	1050.0
8	80	5920	573.1	75.0	1050.0
9	90	6700	648.6	78.0	1092.0
10	100	7450	721.2	75.0	1050.0
11	110	8210	794.8	76.0	1064.0
12	120	8975	868.8	76.5	1071.0
13	130	9720	941.0	74.5	1043.0
14	140	10510	1017.4	79.0	1106.0
15	149	11200	1084.2	76.7	1074.0
16	159	11960	1157.8	76.0	1064.0
17	170	12820	1241.1	78.2	1095.0
18	180	13580	1314.6	76.0	1064.0
19	190	14340	1388.2	76.0	1064.0
20	200	15080	1459.8	74.0	1036.0
21	220	17480	1692.2	69.0	966.0
22	230	18130	1755.1	65.0	910.0
23	240	18740	1814.1	61.0	854.0
24	250	19370	1875.1	63.0	882.0
25	260	19960	1932.2	59.0	826.0
26	270	20580	1992.3	62.0	868.0
27	280	21100	2042.6	52.0	728.0
28	290	21600	2091.0	50.0	700.0
29	300	22000	2129.7	40.0	560.0
30	310	22410	2169.4	41.0	574.0
31	320	22790	2206.2	38.0	532.0

Table 13.9 (continued)

KAYENTA SANDSTONE CORE TEST RESULTS

ITEM	MINS	MLITRES	PORE VOLS	ML/MIN	DARCIES
31	320	22790	2206.2	38.0	532.0
32	330	23140	2240.1	35.0	490.0
33	340	23470	2272.0	33.0	462.0
34	350	23770	2301.1	30.0	420.0
35	360	24040	2327.2	27.0	378.0
36	370	24290	2351.4	25.0	350.0
37	380	24520	2373.7	23.0	322.0
38	390	24730	2394.0	21.0	294.0
39	400	24930	2413.4	20.0	280.0
40	410	25120	2431.8	19.0	266.0
41	420	25300	2449.2	18.0	252.0
42	430	25480	2466.6	18.0	252.0
43	440	25640	2482.1	16.0	224.0
44	450	25800	2497.6	16.0	224.0
45	460	25940	2511.1	14.0	196.0
46	470	26080	2524.7	14.0	196.0
47	480	26220	2538.2	14.0	196.0
48	490	26350	2550.8	13.0	182.0
49	500	26480	2563.4	13.0	182.0
50	510	26600	2575.0	12.0	168.0
51	520	26720	2586.6	12.0	168.0
52	530	26840	2598.3	12.0	168.0
53	540	26960	2609.9	12.0	168.0
54	550	27080	2621.5	12.0	168.0
55	560	27200	2633.1	12.0	168.0
56	570	27270	2639.9	7.0	98.0
57	580	27380	2650.5	11.0	154.0
58	590	27880	2698.9	50.0	700.0
59	600	28160	2726.0	28.0	392.0
60	610	28470	2756.1	31.0	434.0
61	620	28750	2783.2	28.0	392.0

Table 13.9 (Continued)

KAYENTA SANDSTONE CORE TEST RESULTS

ITEM	MINS	MLITRES	PORE VOLS	ML/MIN	DARCIES
61	620	28750	2783.2	28.0	392.0
62	625	28860	2793.8	22.0	308.0
63	635	29070	2814.1	21.0	294.0
64	645	29220	2828.7	15.0	210.0
65	655	29400	2846.1	18.0	252.0
66	665	29610	2866.4	21.0	294.0
67	675	29750	2880.0	14.0	196.0
68	685	29890	2893.5	14.0	196.0
69	695	30080	2911.9	19.0	266.0
70	705	30240	2927.4	16.0	224.0
71	715	30370	2940.0	13.0	182.0
72	725	30480	2950.6	11.0	154.0
73	735	30560	2958.4	8.0	112.0
74	765	30755	2977.3	6.5	91.0
75	795	30925	2993.7	5.7	79.0
76	825	31095	3010.2	5.7	79.0
77	855	31335	3033.4	8.0	112.0
78	885	31745	3073.1	13.7	191.8
79	915	31990	3096.8	8.2	114.8
80	945	32100	3107.5	3.7	51.8
81	975	32210	3118.1	3.7	51.8
82	1005	32310	3127.8	3.3	46.2
83	1035	32410	3137.5	3.3	46.2
84	1070	34500	3339.0	59.7	835.8
85	1100	34595	3349.0	3.2	44.8
86	1130	34755	3364.5	5.3	74.2
87	1160	34855	3374.2	3.3	46.2
88	1190	34935	3381.9	2.7	37.8
89	1230	35010	3389.2	1.9	26.6

CLARIFIER INFLUENT INCUBATION TEST RESULTS (90C)
AUGUST 1, 1967

Figure 13.1

CLARIFIER EFFLUENT INCUBATION TEST RESULTS (86-88C)
AUGUST 1, 1979

Figure 13.2

ppm. Suspended solids concentration has also been stabilized at between 70-80 ppm, a value equivalent to the nominal concentration of total particulates in the clarifier overflow. We conclude, based on our previous assessment of silica solubility in clarifier influent, that the clarifier effluent remains slightly supersaturated in silica. The apparent stability of the effluent is an artifact resulting from oxygenation of brine caused by recirculation of 50-60 percent of the clarifier overflow and precipitation of ferric iron.

An assessment of the gravity filter effluent, shown in Figure 13.3, indicates that dissolved silica is still slightly supersaturated (198 ppm). In addition, a new precipitate, consisting primarily of acid soluble iron oxides, forms over a 24-hour period. We were able to detect precipitation of iron because the bulk of the silica-rich particulates were removed by the gravity-filters. Since the brine was weakly acidic, additional precipitation of silica did not contribute significant amounts of suspended solids during the 24-hour incubation period. However, additional silica would eventually precipitate from solution.

Polymer Experiments - A considerable effort has been devoted to an assessment of potential silica scale inhibitors by LLL geothermal project personnel. One concern relative to the use of silica-inhibitors involves the potential for interference with the subsequent brine clarification process. We have already seen how a potent silica antiscalant like hydrochloric acid (in this case produced indirectly by oxidation of ferrous iron) can interfere with

GRAVITY FILTER EFFLUENT INCUBATION TEST RESULTS (86-88C)
AUGUST 1, 1979

FIGURE 13.3

the clarification process. We therefore selected the most potent organic silica antiscalent compound identified to date for evaluation of its effect on sludge-contact removal of silica. Silica precipitation from clarifier influent (at 90°C) treated with 20 ppm of the hydrochloride salt of polyaminoethylene (PAE·HCl) is significantly retarded (Figure 13.4). Results of our bench-scale evaluation of sludge-contact destabilization of dissolved silica (90°) in clarifier influent are summarized in Figure 13.5. Sludge-contact reduces dissolved silica in brine to near equilibrium in one hour while silica in untreated brine requires about 24 hours to reach the same level.

The effect of 20 ppm of the polymer PAE·HCl on the sludge-contact destabilization of silica is summarized in Figure 13.6. Silica in polymer-treated brine is more rapidly removed relative to the nominal rate of silica removal in raw brine contacted with sludge. The accelerating rate of silica precipitation in polymer-treated brine probably results from flocculation of "large" silica particulates by residual dissolved polymer. Thus, we can conclude, at least in the case of PAE·HCl, that polymer treatment of brine for scale control purposes also has the potential for improving the efficiency of the subsequent clarification process.

Brine Injectability Tests - A modified version of a method described by Barkman and Davidson for assessing fluid injectability, based on membrane filtration or core data, was employed to evaluate the injectability of processed effluent.^{2,3} In the Barkman and

EFFECT OF POLYMER ON STABILITY OF CLARIFIER INFLUENT (85-90C)
AUGUST 1-2, 1979

Figure 13.4

SLUDGE CONTACT DESTABILIZATION OF SILICA IN CLARIFIER INFLUENT (85-90C)
AUGUST 1-2, 1979

Figure 13.5

EFFECT OF POLYMER ON SLUDGE CONTACT DESTABILIZATION OF SILICA (85-90C)
AUGUST 1-2, 1979

Figure 13.6

Davidson method, 0.45 μm pore size membrane filters or core samples are exposed to fluid at constant differential pressure. The hydraulic properties of the surface or internal cake formed by deposition of suspended solids or scaling of the porous structure under test are measured and then used to estimate fluid injectability. Analytic models are presented for use in calculating an injection well half-life for various assumed impairment mechanisms. The half-life is defined as the time required for the injection rate to fall to one-half of its initial rate at constant pressure. The most useful impairment models for this geothermal application are wellbore narrowing, which accounts for deposition of solids on the sandface in the injection interval, and invasion which accounts for migration of suspended solids into the injection formation to distances greater than five wellbore radii from the injection well.

In the case of a geothermal reservoir with high porosity ($\geq 20\%$) and primary and secondary permeability, it is obvious that a 0.45 μm membrane filter cannot be used as a realistic analog of an injection interval. We employed a method described by Champlin et al. (see Subsection 13.4.3.2) to estimate the average pore diameter of a porous matrix with 20 percent porosity and 500 md permeability.¹¹ We then selected 8.0 μm membrane filters as conservative analogs of the injection interval. However, additional tests were run with 0.4 μm membrane filters in order to produce comparative data and to obtain data on total suspended solids in the gravity filter effluent. The assumptions used to calculate injection well half-lives are summarized in Table 13.10. The methods used to calculate injection well half-lives, based on membrane filtration and core data are summarized in Subsection 13.4.3.3.

Table 13.10. Basis for Half-life Calculations

Density filter cake	2.0 g/cc
Density brine	1.17 g/cc
Density filter cake/density brine	1.71
X-sectional area of membrane filter.....	9.62 cm ²
X-sectional area of core	5.07 cm ²
Radius well	0.325 ft.
Radius core	0.0417 ft
Brine viscosity	0.5 cp
Injection interval	400 ft
Injection rate	41,143 BLD
Core flow rate	0.679 BLD
Formation permeability	500 MD
Core permeability	1050 MD

Membrane Filtration Test Results - In general, the quality of effluent produced by the large gravity filtration system was poor. It was not possible to pass more than about 10 litres of brine through 0.4, 1.0 or 8.0 μm membrane filters during a 30 minute test interval (Figures 13.7 - 13.8). The 0.4 and 1.0 μm membrane filters performed in essentially identical fashion, but a significantly smaller volume was passed through the 8.0 μm filter. The use of a 1 μm pore size cartridge filter upstream of the membrane filters substantially improved brine quality. Suspended solids data and half-life calculations derived from the membrane filter tests are summarized in Table 13.11.

The quality of brine produced by the gravity filters is poor because of a relatively high concentration of suspended particulates in the filter effluent (5-10 ppm) and a tendency for precipitation of iron from the conditioned brine. The estimated half-life of a typical injection well receiving conditioned brine at a rate of 41,143 BD based on the 8 μm membrane filtration test, is about two months. The use of a cartridge prefilter improves the 8 μm -based half-life estimate by an

MEMBRANE FILTRATION TESTS OF CONDITIONED BRINE
MAGMA POWER CLARIFIER-FILTRATION SYSTEM
AUGUST 8, 1979

BRINE DIRECTLY FROM MAGMA FILTERS

PREFILTERED BRINE FROM MAGMA FILTERS

0.4 MICRON: ---
1.0 MICRON: -O-

0.4 MICRON: -*-

Figure 13.7

8 MICRON MEMBRANE FILTRATION. TEST RESULTS
FOR CONDITIONED BRINE FROM MAGMA POWER'S
CLARIFIER-FILTER SYSTEM
(AUGUST 8, 1979)

Figure 13.8

PERMEABILITY OF KAYENTA SANDSTONE TO CONDITIONED BRINE FROM THE MAGMA POWER CLARIFIER-FILTRATION SYSTEM

Figure 13.9

order of magnitude (2 years). If we assume that the fine particulates passing through the cartridge filter would invade the injection zone to a distance of 10 feet from the wellbore, the half-life estimate increases by another order of magnitude to more than 80 years. As noted earlier, the poor performance of the brine conditioning system is a result of inadvertent oxygenation of the brine. If the conditioning system were operating at its design optimum, the injectability of the brine would be equivalent to the effluent produced by our small 1 μ m pore size cartridge filter.

Core Test Results - The 8 μ m membrane filter test data suggested that effluent from the gravity filters would impair a core sample by deposition of suspended solids and precipitation of iron and silica. We anticipated additional silica precipitation would occur when the weakly acidic silica supersaturated effluent was partially neutralized by reaction with carbonate-rich minerals in the core sample. The core was, therefore, initially feed 1 μ m cartridge prefiltered brine. As shown in Figure 13.9, core permeability remains constant for the first 1550 litres of throughput. Core permeability then began to rapidly decline. The cartridge prefilter was bypassed after about 2600 pore volumes had been passed. At that time, the system was shut-in for less than an hour while the gravity filters were backwashed. When flow resumed, we observed a partial recovery of core permeability. However, permeability rapidly declined. We observed a similar partial recovery of permeability after the core had been shut-in, (at about 3200 pore volumes) for another gravity filter backwashing cycle. Permeability again declined rapidly with resumption of flow. The reason for the

Figure 13.10. Core Sample Exposed to Conditioned Brine Produced by the 10 MWe Clarifier-Filtration System.

The core was plugged by a deposit of iron and silica-rich solids that formed on its upper surface. The solids did not form scale on the steel perforated disc placed on the upper surface of the core. The disc was used as an analog of a downhole injection well completion liner.

Table 13.11. Results of membrane filtration and core tests of gravity filter effluent

Filter Size (m)	1 μ m Cuno cartridge prefilter	ΔP (PSI)	Suspended solids (mg/l)	Slope ¹ (L/min)	Intercept (L)	W/Kc (ppm/Md)	Kc (Md)	F (yrs)	$G_{1/2}$	$T_{1/2}$ (Yrs)
0.4	no	50	9.09	2.275	-1.636	24.963	0.364	0.274	0.0161	0.004
1.0	no	50	5.21	2.394	-1.902	22.543	0.231	0.478	0.0102	0.005
0.04	yes	50	0.03	11.907	-17.408	0.911	0.033	82.97	0.0015	0.12
8.0	no	10	8.03	1.033	0.673	24.214	0.332	0.310	0.602	0.19
8.0	yes	10	0.10	21.725	-41.008	0.055	0.182	248.90 248.90	0.0081 0.330	2.01 82.1 ²
Kayenta Sandstone core	yes	20	0.03 ³	0.718	10.590	27.816 0.073	0.001 0.410	82.97 82.97	0.0020 0.743	0.17 ⁴ 61.7 ⁵

1 Linear regression "goodness of fit" R^2 factor 1.00 for all runs.

2 Assumes 10 foot invasion radius.

3 Assumed concentration of suspended solids.

4 Half-life based on first 2500 pore volumes through core.

5 Half-life based on first 1500 pore volumes through core.

apparent recovery of permeability after gravity filter backwashing cycles is not known. Possibly, the quality of filtered brine substantially improves immediately following a backwash cycle.

The core test results are summarized in Table 13.11. A pH change was observed across the core. Influent pH was usually about 5.0. The core effluent pH increased to 5.2 - 5.3. For the purposes of half-life calculations, a suspended solids concentration of 0.03 ppm was assumed for the influent. This value for suspended solids was based on results of our 0.4 μ m membrane filtration test of prefiltered brine. The calculated half-life was about two months. A second calculation based on the first 1500 pore volumes of core throughput yield a half-life in excess of 60 years.

Post mortums on the core established that impairment resulted from deposition of iron- and silica-rich solids on the sandface. The deposits did not penetrate more than an inch into the core. As shown in Figure 13.10, no deposits were present on the perforated disc placed on the inlet surface of the core as an analog of a completion liner.

3.2.13.4.2.2 Makeup Water Evaluation

Direct Injection of Ambient Temperature Makeup Water - Chemical analysis of Salton Sea, New River and Alamo River water were determined and are provided in Table 13.12. In general, River water has about 8 times less dissolved sulfate than Salton Sea water. Use of River water for injection makeup will result in a significant reduction in sulfate precipitation. However, the high particulate loading in River water relative to Salton Sea water can significantly increase the sludge processing requirements on a clarifier processing system. Furthermore, seasonal changes in flow rate and particulate loading could cause differences in both the physical and chemical properties of New and Alamo River waters.

Table 13.12

Chemical Analysis of Makeup Water (MG/l)

IONS	New River	Alamo River	Salton Sea*	Salton Sea*	Salton Sea*
Na	880	440	10,000	10,400	11,300
K	39	11	190	302	323
Ca	240	190	940	902	980
Mg	130	97	1,100	1,073	1,147
SO ₄	1,050	840	8,300	8,025	9,016
CO ₃	1.5	1.5	1.3	10	2
HCO ₃	269	180	235	160	187
Cl	1,200	540	14,000	12,719	13,861
Ba				0.1	0.03
TDS	4,000	2,400	37,000	35,860	38,332

* Sampled Between July and November, 1978.

We first evaluated Salton Sea water as a potential source of injection makeup. Sea water samples obtained off Obsidian Butte (Table 13.12) were held at temperatures between 25 and 90°C for periods of 1 to 7 days in nitrogen pressurized and sealed glass ampoules. The sea water was settled overnight and then decanted prior to use in heating experiments. Concentrations of suspended solids were obtained as a function of temperature and incubation time. Relative ease or difficulty of filtration through membrane filters with pore sizes ranging from 0.4 to 5.0 μm was also observed.

Results of the sea water heating experiment are summarized in Table 13.13. Samples heated for 24 hours were all difficult to filter regardless of filter pore size (0.4 to 5.0 μm) or solution temperature. Filters plugged after passage of 200 ml or less of solution. Chemical interaction effects between solutions and filters were not responsible for filtration difficulties because filtrates were highly filterable. One sample incubated at 90°C for 7 days was easy to filter. These results indicate that fine particulates in Salton Sea water readily plug even relatively coarse 5.0 μm pore size filters. Prolonged incubation at 90°C improves filtration properties of sea water either by thermal decomposition of organic particulates or changes in particulate particle size distributions. Ambient temperature Salton Sea water contains 10 ± 5 ppm suspended particulates. Incubation of Salton Sea water at 90°C for 24 hours does not significantly alter particulate concentration. However, incubation at 90°C for 7 days does increase particulates slightly to 19 ppm.

Table 13.13

Salton Sea Water Heating Experimental Results

Membrane Filter Pore Size (μm)	Incubation Temperature (°C)	Incubation Duration (Days)	Particulate Concentration (PPM-MG/KG)	* Filtration Characteristics
0.4	25	1	6.5	Difficult
0.4	50	1	11.3	Difficult
0.4	75	1	4.5	Difficult
0.4	90	1	7.7	Difficult
1.0	25	1	12.3	Difficult
1.0	25	1	15.8	Difficult
1.0	90	7	19.0	Easy
5.0	25	1	4.5	Difficult

* Difficult = Filter Plugging after Passage of ≤ 200 ML of Solution.

Computer calculations assuming Salton Sea water of 'typical' composition are in excellent agreement with results of the reheating experiment.^{12,13} The maximum concentration of particulates after seven days incubation at 90°C was 19 ppm. The computer code predicted 30 to 55 ppm total carbonate solids varying in composition between calcite (CaCO₃) and dolomite (CaMg(CO₃)₂). If Salton Sea water were prefiltered at ambient temperature (25-35°C) prior to reheating, no sulfate solids would precipitate until the brine was reheated to 100°C.

Filtration properties of Salton Sea water, New River, and Alamo River are compared in Table 13.14. All of the waters have extremely poor filtration properties due to suspended particulates. In addition, the high pH and dissolved carbonate and sulfate content (Table 1) of these waters suggests a significant potential exists for post injection precipitation of sulfates and carbonates as makeup waters reheat or mix with typical geothermal brine. We concluded that direct injection of makeup waters is not feasible.

Table 13.14

Makeup Water	Suspended Solids 1.0 μm (ppm)	pH	Filtration Properties (1.0 Nucleopore Membrane Filter Used)
Salton Sea	25.69	8.19	Very poor (filter plugged after 144 gm H ₂ O)
New River	132.00	8.40	Poor (Filter plugged after 200 gm H ₂ O)
Alamo River	557.2	8.25	Very poor (Filter plugged after 200 gm H ₂ O)

* 1.0 μm filtration simulates efficiency attainable by typical pre-injection processing systems consisting of reaction clarification and granular media filtration.

Mixing Experiments - Incubation tests were carried out to establish nominal growth rates of suspended particulates in 1:4 mixtures (by weight) of 1 μm prefiltered makeup water (Salton Sea, New River and Alamo River) and unfiltered brine effluent from the LLL test station (Magmamax No. 1 well). Incubation was done at 90°C for periods ranging from 15 minutes to 30 days in nitrogen-pressurized and sealed glass ampoules.

Our preliminary experiments utilizing 1:4 mixtures of Salton Sea water and brine are summarized in Table 13.15. Samples were incubated at 90°C for 24 hours and then filtered with 1.0 μm membrane filters. All solutions were easy to filter. Normally, 'spent' brine from the LLL test station (Magmamax #1 brine) produces between 300 and 350 ppm suspended solids after 1/2 hour incubation at 90°C. Addition of Salton Sea water to brine increased suspended solids by a factor of at least two. In the absence of excess dissolved sulfate, carbonate and oxygen, the diluting effect of a volume of distilled water significantly retards similar particulate precipitation.

Table 13.15

Salton Sea Water - Brine Mixture Reheating
Experimental Results at 90°C

Solution	* Incubation Duration (Hrs)	Particulate Concentration (Ppm/Mg/Kg)
Brine	0.5	300-350
Brine Plus Distilled Water (4:1 Mixture)	24	230
Brine Plus Salton Sea Water (4:1 Mixture)	24	612

* Particulate concentration reaches Quasi-Equilibrium after 1/2 hour at 90°C.

Additional experimental results for incubation of 1:4 mixtures of Salton Sea water-brine and river water-brine are summarized in Figure 13.11. It is important to note that mixtures of River water and brine attain equilibrium most rapidly. After 1 month, such mixtures produce about the same amount of solids as brine alone. In contrast, 1:4 mixtures of Salton Sea water and brine are still exhibiting large degrees of precipitation after 1 month and at least three times as many solids (primarily sulfates plus silica) were formed in contrast to River water - brine mixtures. According to the chemical analyses in Table 13.16, silica reaches quasi-equilibrium conditions after 4 hours for Salton Sea brine mixtures and after 8 hours for both River water-brine mixtures. Sulfate, however, has not reached equilibrium in either case and is still coming out of solution at 1 months time.

Figure 13.11

Table 13.16

Time	1:4 Salton Sea - Brine *			1:4 New River - Brine *		
	SiO ₂	SO ₄	Suspended Solids	SiO ₂	SO ₄	Suspended Solids
15 min.	326	1482	310	352	296	180
4 hrs.	230	1328	464	286	209	258
8 hrs.	230	1289	510	234	276	234

*Concentrations are ppm by wt.

From these experimental results, it can be concluded that use of Salton Sea water for injection makeup will significantly increase sludge dewatering and disposal requirements. Facilities for removal of at least three times the amount of particulate matter relative to brine alone will be required as part of the pre-injection processing system.

Makup Water Processing Requirement - A series of bench-scale experiments were run to determine the effectiveness of sludge contact on precipitation rates of particulates generated in 1:4 mixtures of Salton Sea water and geothermal brine. A jar testing apparatus was used for these experiments: samples were mixed at a constant speed of 100 RPM at 78-85°C for times varying from 5 minutes to 2 hours. Turbidity, sulfate and silica measurements were made on the 1.0 μ m prefiltered supernatant after allowing approximately two minutes settling time.

Results from the first two experimental runs (see Table 13.17) show that solutions approached quasi-equilibrium within the first 10 minutes. Turbidity also showed a rapid decrease during the first 5 minute interval as suspended particulates settled. On the basis of these experimental results, we concluded that reaction clarification is a viable and efficient means of stabilizing mixtures of makeup water and brine.

Table 13.17

Effect of Sludge Contact on Dissolved Silica and Sulfate
in a 1:4 Mixture of Salton Sea Water-Geothermal Brine

Time (Min)	Turbidity (Ntu)		PPM SiO ₂		PPM SO ₄	
	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
0	70	54	326	332	1482	1482
5	2.0	.8	258	221	927	899
10	1.0	.5	220	196	891	865
20	1.0	.4	216	196	891	855
30	1.1	-	203	-	901	-
45	1.0	-	197	-	881	-
60	.80	-	184	-	889	-
120	.55	-	-	-	-	-

Pilot Test Results - Incubation and injectability tests were run on effluents produced by the Magma Power Company 30 GP, throughput pilot reaction clarifier-granular media preinjection processing system. These tests were performed to establish the isothermal (90°C) chemical stability and injectability of processed 1:4 mixtures of Salton Sea water and geothermal brine. Incubation test results for times up to 24 hours indicated that processed effluents had achieved a quasi-equilibrium condition. Residual dissolved silica and sulfate

concentrations were consistent with results of the bench-scale experiments. Membrane filtration tests (Figure 13.12) indicated that processed effluents containing less than 2 ppm suspended solids are potentially injectable. However, results of the core test (Figure 13.12) indicated that post-injection brine-rock interactions can severely impair injection well performance. The membrane filtration and core test data are provided in Tables 13.18, and 13.19, respectively.

Figure 13.12

Table 13.18 Results of Processed Makeup Water 0.45 μm Membrane Filtration Test

Time (Min)	Cumulative Volume (Litre)	Flowrate (L/Min)
12	6.417	0.535
20	9.149	0.341
30	12.252	0.310
40	15.498	0.325
50	18.344	0.285

Table 13.19 Results of Processed Makeup Water Kayenta Core Test

(Min) Time	Vol (L)	Flowrate (L/min)
5	0.156	0.156
10	0.325	0.034
20	0.548	0.022
30	0.643	0.0095
40	0.704	0.0061
50	0.751	0.0047
60	0.799	0.0048
120	0.981	0.0030
180	1.116	0.0023
240	1.252	0.0023
300	1.373	0.0020
360	1.468	0.0016
420	1.556	0.0015
480	1.650	0.0016
540	1.718	0.0011
600	1.786	0.0011
660	1.840	0.0009
720	1.914	0.0012
780	1.975	0.0010
840	2.022	0.0008
900	2.063	0.0007
960	2.130	0.0011
1020	1.191	0.0010
1080	2.225	0.0006
1140	2.272	0.0008
1200	2.310	0.0008
1260	2.360	0.0007
1320	2.428	0.0006
1380	2.428	0.0006
1440	2.448	0.0003
1500	2.496	0.0008

3.2.13.4.3 Calculations

3.2.13.4.3.1 Temperature Dependence of Silica Solubility

Data from Harrar et al.⁸ for the temperature dependence of silica solubility in Woolsey No. 1 brine (4.10 M Cl; 1.666 g/cm³) over the interval 50 to 90°C was fit by least squares. The best line through six data points is given by:

$$\text{Dissolved Silica (mg/Kg)} = (1.938)(T^{\circ}\text{C}) - 14.79 \quad (1)$$

The regression coefficient (r^2) was 0.96. Application of equation (1) indicates that an increase in brine temperature from 90 to 101°C will cause a corresponding increase in silica solubility from 159.6 to 181 Mg/Kg (12 percent).

Data from Harrar et al.¹⁰ for the salinity dependence of silica solubility in Magmamax No. 1 and Magmamax No. 2 brine were also fit by least squares. The corresponding relationships between dissolved silica, brine density and brine chloride content at 90°C are summarized in equations (2) and (3):

$$\text{Dissolved Silica (mg/Kg)}_{90^{\circ}\text{C}} = (-910.88)(-\text{g/cm}^3) + 1226.62; r^2 = 0.54 \quad (2)$$

$$\text{Dissolved Silica (mg/Kg)}_{90^{\circ}\text{C}} = (-9.97)(\text{Cl-Moles/litre}) + 204.08; r^2 = 0.39 \quad (3)$$

3.2.13.4.3.2 Reservoir Hydraulic Radius Estimates

According to Champlin et al.¹¹, the largest diameter particle capable of passing through a given porous medium is about 25 percent smaller than the average pore size given by:

$$M = 4 \left[\frac{(1-\phi)}{\left(\frac{\phi \times 10^3}{5K} \right)^{1/2}} \right]$$

where M is the mean pore diameter (μm), ϕ is the fractional porosity and K is the permeability (Md). We calculated a mean pore diameter, for the injection zone into which GLEF pretreated brine was injected, of 11.3 μm based on a formation porosity and permeability of ~20 percent and 500 md, respectively. Using the 25 percent criteria, we selected 8.0 μm membrane filters as conservative analogs of the injection zone.

3.2.13.4.3.3. Half-Life Calculations

Half-life Calculations - The half-life is computed as the product:

$$T_{1/2} = F \times G_{1/2} \quad \text{Eq. (5)}$$

where F is proportional to the time required to fill one wellbore volume with solids and $G_{1/2}$ is an adjustment factor related to the impairment mechanism. F is independent of the impairment process and is defined as:

$$F \text{ sec} = \frac{r_w^2 \cdot h \cdot P_c / P_w}{i_o \cdot W} \quad \text{Eq. (6)}$$

where: r_w = radius of wellbore (m)

h = injection interval length (m)

P_c = density of filter cake (g/cm^3)

P_w = density of water (g/cm^3)

i_o = injection rate (m^3/sec)

w = concentration suspended solids (g/g)

A more convenient form of equation 6 is:

$$F \text{ yrs} = \frac{1533 \cdot r_w^2 \cdot h \cdot P_c / P_w}{i_o \cdot W} \quad \text{Eq. (7)}$$

where r and h are in feet and i_0 is in barrels per day.

The permeability of the filter cake formed by deposition of suspended solids or scaling must be known in order to calculate the $G_{1/2}$ -factor. Filter cake permeability is obtained from a measurement of the water quality ratio. The water quality ratio (W/K_c) is defined as:

$$\frac{W}{K_c} = \frac{1.20 \times 10^5}{S^2} \cdot \frac{(P_c/P_w) \cdot A_c^2 \cdot \Delta P_t}{\mu} \quad \text{Eq. (8)}$$

where:

- W = concentration suspended solids ($\mu\text{g/g}$)
- K_c = permeability of filter cake (Md)
- P_c = density of filter cake (g/cm^3)
- P_w = density of water (g/cm^3)
- P_t = Pressure drop across membrane filter or core (Atm)
- A_c = area of membrane filter or core exposed to brine (cm^2)
- S = slope of linear portion of filtration curve ($\text{Ml}/\sqrt{\text{min}}$)
- μ = water viscosity (cp)

S is obtained by regression of the linear portion of the filtration curve plotted in coordinates of cumulative flow (ordinate) vs $(\text{time})^{1/2}$. An example of a typical filtration curve is provided in Figure 13.13. The sign of the intercept formed by extrapolation of the linear portion of the filtration curve indicates whether the porous medium under test has been invaded by fine particulates (positive intercept) or whether solids have formed a surface cake (negative intercept).

We calculated $G_{1/2}$ for the case of wellbore narrowing and invasion:

$$\text{wellbore narrowing: } G_{1/2} = 3 \cdot (K_c/K_f) \cdot \ln(r_e/r_w) \quad \text{Eq.}$$

BARKMAN AND DAVIDSON-TYPE FILTRATION CURVE FOR KAYENTA SANDSTONE SHOWING INVASION

Figure 13.13

(9)

where:

K_f = formation permeability (md)

r_e = radius of effect

r_w = radius of well

$$\text{invasion: } G_{\frac{1}{2}} = 3.2 (K_c/K_f)(r_a/r_w)^2 \left[\ln(r_e/r_w) \right] \quad \text{Eq. (10)}$$

where:

ϕ = fractional formation porosity

r_a = invasion radius

We used the following forms of equations 7-10 to evaluate our experimental data:

$$F_{\text{yrs}} = 2.489/W(\mu\text{g/g}) \quad \text{Eq (11)}$$

$$\frac{W}{K_c} = \frac{2.584 \times 10^6 \cdot \Delta P_t \text{ (PSI)}}{S^2} \quad \text{Eq (12)}$$

$$\frac{W}{K_c} = \frac{7.170 \times 10^5 \cdot \Delta P_t \text{ (PSI)}}{S^2} \quad \text{Eq (13)}$$

$$G_{\frac{1}{2}} \approx 22.13 (K_c/K_f) \quad \text{Eq (14)}$$

$$G_{\frac{1}{2}} \approx 906.6 (K_c/K_f) \quad \text{Eq (15)}$$

3.2.13.4.4 Comparison of Actual and Expected Results

3.2.13.4.4.1 Injectivity Tests

The injectability of conditioned low temperature (101°C) effluent produced by a 10 MWe-capacity demonstration reaction clarification-gravity filtration system was established. Brine processing was accomplished without the use of chemical aids. However, our bench scale experiments illustrated how certain classes of organic polymers which exhibit anti-silica scaling tendency can also improve the efficiency of the clarification process.

Absolute injectability of the conditioned effluent was poor due to clarifier operational procedures and overall system design which permitted oxygenation of brine during the conditioning process. Air contamination resulted in post-processing precipitation of iron and partial stabilization of dissolved silica. Core test results suggested that silica would precipitate in the injection formation as a result of brine-rock interactions leading to a slight increase in brine pH. Half-life calculations based on data obtained from membrane filters and a core sample suggested significant injection well impairment could occur within several months assuming effluents are injected into a porous media with primary permeability. The effect of possible fracture flow would increase well times life.

3.2.13.4.4.2 Makeup Water Evaluation

Direct injection of makeup waters is not feasible owing to high nominal suspended solids loading. The most likely source of injection makeup is Salton Sea water. Performance data describing the effect of makeup water additions to the influent to a baseline reaction clarification-gravity filtration system were established. The processing system is capable of producing an effluent saturated in dissolved sulfate, carbonate and silica species. However, sludge

removal capabilities must be substantially expanded to accommodate the larger-volume of solids (primarily sulfates) produced as a result of 20 percent dilution by makeup water. Membrane filter tests indicated that processed effluent is potentially injectable. However, core test results suggested that post-processing precipitation of silica in the injection interval is possible due to brine-rock interactions which cause a slight increase in brine pH. The pH of influent to the clarification process becomes slightly depressed by addition of oxygen-saturated makeup water and resultant precipitation of ferric iron species.

3.2.13.5 Conclusions and Recommendations

3.2.13.5.1 Injectivity Tests

The quality of brine effluent produced by a 1600 GPM-capacity demonstration reaction clarifier-gravity filtration system was significantly degraded by operational procedures that caused partial oxygenation of the brine. Resulting oxydation of ferrous iron caused a decrease in brine pH and partial stabilization of dissolved silica. The slow formation of flocculant iron-rich precipitates increased the impairment potential of the brine. Our incubation, membrane filtration and core test results suggest that elimination of brine oxygenation would result in production of a highly injectable effluent. The application of organic polymer compounds, such as PAE-HCl, for the purposes of scale inhibition may result in significant improvement in the efficiency of the sludge-contact process for removal of supersaturated silica from brine.

3.2.13.5.2 Makeup Water Evaluation

Salton Sea water is the best source for injection makeup. Although additional experimental work will be required to more completely assess injectability of Salton Sea water-brine mixtures, our preliminary results indicate that the final effluent pH must not be lower than about 5.6 to avoid post-processing silica precipitation induced by interaction of injected effluents and reservoir matrix materials. It can also be anticipated that premature mass breakthrough of injected effluents, diluted by Salton Sea makeup water additions, to production wells has the potential for significantly worsening scaling problems due to deposition of sulfates. Therefore, injection wells receiving makeup water additions should be located with respect to minimizing potential mass breakthrough problems.

3.2.13.6 References

1. Hasbrouck, R. T., Owen, L. B., and Netherton, R., 1979, An automated system for membrane filtration and core tests: Geothermal Resources Council, Transactions, Vol. 3, pgs. 301-304.
2. Owen, L. B., 1979, Evaluating brine injection for DOE's Strategic Petroleum Reserve Program: Energy and Technology Review, (August), pgs. 1-10.
3. Barkman, J. H. and Davidson, D. H., 1972, Measuring water quality and predicting well impairment: Journ. Petroleum Technology, pgs. 865-872.
4. Owen, L. B., Kasameyer, P. W., Netherton, R., and Thorson, L. D., 1977, Predicting the rate by which suspended solids plug geothermal injection wells: Prog. Third Workshop, Geothermal Reservoir Engineering, Stanford University, pgs. 163-171.
5. Netherton, R. and Owen, L. B., 1978, Apparatus for the field evaluation of geothermal effluent injection: Transactions Geothermal Resources Council, Vol. 2, Section 2, pgs. 487-490.
6. Tewhey, J. D., Chan, M. A., Kasameyer, P. W., and Owen, L. B., 1978, Development of Injection Criteria for Geothermal Resources: Trans., Geothermal Resources Council, Vol. 2, Section 1, pgs. 649-652.
7. Quong, R., Schoepflin, F., Stout, N. D., Tardiff, G. E., and McLain, F. R., 1978, Processing of Geothermal Brine Effluents for Injection: Trans. Geothermal Resources Council, Vol. 2, pgs. 551-553.
8. Hill, J. H., Harrar, J. E., Otto, C. H., Jr., Deutscher, S. B., Crampton, H. E., Grogan, R. G., and Hendricks, V. H., 1979, Apparatus and techniques for the study of precipitation of solids and silica from hypersaline geothermal brine: Univ. Calif. LLL Rept., UCRL-52799, 9 pgs.

9. Harrar, J. E., Locke, F. E., Otto, C. H., Jr., Lorensen, L. E., Frey, W. P., and Snell, E. O., 1979, On-line tests of organic additives for the inhibition of the precipitation of silica from hypersaline geothermal brine III. Scaling measurements and tests of other methods of brine modification: Univ. Calif., LLL Rept., UCID-18238, 31 pgs.
10. Harrar, J. E., Otto, C. H., Jr., Deutscher, S. B., Ryon, R. W., and Tardiff, G. E., 1979, Studies of brine chemistry, precipitation of solids and scale formation at the Salton Sea Geothermal Field: Univ. Calif., LLL Rept., UCRL-52640, 17 pgs.
11. Champlin, J. D. F., Thomas, R. D., and Brownlow, A. D., 1967, Laboratory testing and evaluation of porous permeable rock for nuclear waste disposal: U. S. Bureau of Mines, Rept. 6926.
12. Wolery, T. J., 1979, Computer simulation of temperature-dependent equilibrium precipitation: Geothermal Resources Council, Transactions, Vol. 3, pgs. 793-796.
13. Raber, E., Owen, L. B., and Harrar, J. E., 1979, Using surface waters for supplementing injection at the Salton Sea Geothermal Field (SSGF), Southern California: Geothermal Resources Council, Transactions, Vol. 3, pgs. 561-564.