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**Removal of Hydrogen Sulfide
from Simulated Geothermal Brines
by Reaction with Oxygen (II)**

**Final Report
for period
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SUMMARY

This study was a continuation of work done under contract #EY-76-C-D2-2797. This previous work was performed October 6, 1975 through February 4, 1977, and the final report, "Removal of Hydrogen Sulfide From Simulated Geothermal Brines By Reaction With Oxygen", was published in April, 1977.¹ This report concluded that injection of oxygen into simulated geothermal brines in the liquid phase at mole ratios of 1.25-1.5:1, ($O_2:H_2S$), effectively removed the hydrogen sulfide, with reaction times of less than one minute. This was found to be true for sulfide levels up to 100 ppm in the brine.

The work reported here was undertaken to accomplish two major objectives:

1. Air Injection Into Simulated Geothermal Brines

If air could be used as the oxygen source rather than oxygen, the costs and hazards of the hydrogen sulfide oxidation process could be substantially reduced. A system similar to that used for oxygen injection was used, with air in place of the oxygen. Sulfide levels were checked at 1, 3, and 5 minute intervals after air injection. At an initial sulfide level of 11 ppm, a 6.45:1 (O_2 in air: H_2S) mole ratio was required to remove 80% of the sulfide.

Other runs with higher initial sulfide levels also indicated that a high mole ratio would be required to accomplish the removal of the hydrogen sulfide. It was concluded that the noncondensable gas (primarily nitrogen) in the air was interfering with the mass transfer of oxygen to the sulfide. The large volumes of air required for oxidation of the hydrogen sulfide led to the conclusion that air injection would not be preferred over oxygen injection as a means of hydrogen sulfide oxidation in geothermal brine, since the large excess of oxygen would lead to severe corrosion problems.

2. Oxygen Injection Into A Two-Phase Flow Of Simulated Geothermal Brine

The loss of pressure and temperature which occurs when the brine rises to the surface very often causes some flashing to occur. In order for a hydrogen sulfide removal technique to be effective, the sulfide must be removed from both the vapor and liquid phases. This requirement led to consideration of a packed tower in order to maximize the mixing between the oxygen and the two phase flow. The simulated brine was flashed to approximately 5.7% by weight vapor and the two phases were run counter-currently through an eight-foot packed tower.

Oxygen was injected at the point of vapor entry into the packed tower. Mole ratios up to 3:1 ($O_2:H_2S$) were run using this procedure. The sulfide removal was approximately

50% in the vapor phase and 30% in the liquid phase. It was concluded that the presence of noncondensable gases and steam in the vapor phases was preventing the mass transfer of oxygen within the residence time in the tower.

Hydrogen peroxide was then investigated as a possible oxidizing agent. The equipment was modified to permit peroxide injection at the liquid entry to the packed tower. Better than 90% sulfide removal was accomplished at a mole ratio of 3:1 ($\text{H}_2\text{O}_2:\text{H}_2\text{S}$) in both vapor and liquid states. Preliminary cost evaluations of hydrogen peroxide at a 3:1 mole ratio showed 4-8 mils/Kwh, depending upon the sulfide level. This cost is prohibitive, so work was done on sodium hypochlorite as a less expensive oxidizing agent. The sodium hypochlorite was also injected at the liquid entry to the packed tower. Mole ratios of 10:1 ($\text{NaOCl}:\text{H}_2\text{S}$) were attempted, with 70% removal of sulfide from vapor, and 50% removal from the liquid. It was concluded that the brine was too basic after flashing to achieve effective oxidation by the hypochlorite. It is economically infeasible to lower the pH of geothermal brine by acid injection, so work on sodium hypochlorite was discontinued.

Additional oxidizing agents, such as ozone, were considered for possible study, but again economics were prohibitive. Therefore, it is concluded that although oxygen injection into geothermal brine is an effective sulfide removal technique, injection in a two phase flow is an economically unattractive alternative at this time due to the long contact time apparently

required which would necessitate unreasonably large reaction towers. Hydrogen peroxide oxidizes the sulfide without the contact time problems but suffers from excessive material cost. Either method may be desirable at some later date.

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I. INTRODUCTION

1. The Hydrogen Sulfide Problem In Geothermal Waters

Much of the natural sulfur in geothermal brines occurs in the form of hydrogen sulfide (H_2S). Steam from the Gysers in California has been reported to have a hydrogen sulfide content of 208 ppm. Keysuvik, Iceland steam is reported to have a content of 1048 ppm, and values as high as 1600 ppm have been found in various geothermal vapors.³ The Federal OSHA standard for an eight hour average exposure to hydrogen sulfide is 10 ppm, with a 20 ppm maximum. The legal emission limit for hydrogen sulfide in California is 0.03 ppm. There is also a corrosion problem with equipment (turbines, piping, etc.) which is felt to be caused in large part by the presence of hydrogen sulfide. For these reasons, it is desirable to remove the hydrogen sulfide, particularly in those instances where flashing occurs in the production of geothermal brines.

2. Existing Methods of H_2S Removal

There has been investigation into various means to remove the hydrogen sulfide from geothermal sources. Two of the more promising techniques appear to be scrubbing with copper sulfate, developed by the EIC Corporation, and the Stretford Process.

(a) EIC Process

This consists of scrubbing the geothermal steam with a solution of copper sulfate. The copper sulfate reacts with the hydrogen sulfide to form copper sulfide and sulfuric acid. The copper sulfide is separated and regenerated either by roasting or leaching with oxygen.⁵ The cost of this process has been estimated at 3 mils/Kwh for 1000 ppm H₂S in the geothermal steam (300°F, 160 psig), for a 50 MW power plant.⁴

A disadvantage of this process is the pH drop due to formation of sulfuric acid. If ammonia is present, such as in the Geysers in California, the buffering will permit good H₂S removal (>90%). Also, of course, the regeneration process adds to the difficulty of operation. This process has been tested at the Geysers, however, with removal rates of >97% and good servicability. The copper sulfate scrubbing also removed about 80% of both the ammonia and boric acid. There was little degradation of steam quality caused by the scrubbing.⁴

(b) Stretford Process

This process is utilized for scrubbing H₂S from the noncondensable gases emerging from the power plant. The scrubbing is done with a aqueous solution of sodium carbonate, sodium meta vanadate, and anthraquinone disulfonic acid. The reaction mechanism consists of the formation of HS⁻ by the sodium carbonate, followed by oxidation of the HS⁻ by

the vanadate. The reduced vanadate is restored to its original valence state by blowing air through the oxidizer. The cost of this process has been estimated at about 0.45 mils/Kwh for a 117.5 MW plant containing 220 ppm H_2S in geothermal steam (355°F, 114 psi).⁴

An obvious disadvantage of this process is that it does not solve the corrosion problem, as the H_2S is removed downstream of the power plant. The pH must be controlled between 8.5 and 9.5, and a surface condenser is required to minimize H_2S emissions. The advantages are that the H_2S removal is in the order of 90%, commercial quality sulfur is produced, and the steam quality for power production is unaffected.⁴

Other processes which have been investigated, such as iron catalyst scrubbing, the Claus process, solid sorbent processes, and hydrogen peroxide appear less promising due to regeneration problems, corrosion, waste disposal, economics, and/or difficulties with process control.

3. Technical Approach

This work was undertaken to accomplish the following objectives:

- a. To evaluate the possibility of hydrogen sulfide oxidation in liquid flow by injection of air. This was done because of the cost and hazards of using O_2 . Air was injected in controlled quantities into

simulated geothermal brine. A reactor with a five minute residence time was provided with sampling points at one minute intervals to follow the course of the reaction. Corrosivity and hydrogen sulfide content of the simulated brine were measured before and after air injection.

b. Evaluate oxygen injection into a two phase simulated geothermal brine. The brine was prepared the same as in objective A. The difference was that the brine was flashed to 5.7% vapor (by wt.) in a flash chamber. The vapor and liquid were separated and run counter-currently through a packed tower. Oxygen was injected at the vapor entry to the packed tower. Hydrogen sulfide levels were recorded for the vapor and liquid out of the packed tower before and after oxygen injection. The vapor was condensed, and both the condensed vapor and liquid were run through a heat exchanger. The stream was then sent to the Dow wastewater treating system for ultimate release into the Brazos River.

c. After verification of oxygen injection in the simulated brine, a test skid with a 50 gpm capacity was to be built and tested at the East Mesa and Niland test sites in California. The construction

of the test rig was to be based on information obtained from objective B.

4. Scope Of Work

The data obtained was to identify:

- a. The optimum oxygen to hydrogen sulfide mole ratio to remove the H S and still avoid the corrosion problem resulting from excess oxygen.
- b. The effect of varying sulfide levels on the effectiveness of oxygen injection and the optimum mole ratio.
- c. The effect of varying the silica, carbonate, and calcium levels on the effectiveness of the process.

II. GENERAL DESCRIPTION OF PROCESS AND EQUIPMENT

1. Preparation Of Simulated Geothermal Waters

In order to have increased flexibility in controlling the geothermal brine composition and conditions, it was decided to simulate the geothermal brine used in these experiments. The process used was very similar to the process used in the earlier work done on hydrogen sulfide oxidation in one phase flow (contract #EY-76-C-02-2797).

The salt source was "chlorine cell feed", a treated 26% sodium chloride brine from a salt dome solution mining process. This brine contains 1200 to 1800 ppm sulfate, which was reduced by batchwise addition of barium chloride. This permitted the addition of calcium without scaling in the heat exchanger. A typical composition of the Dow salt dome treated brine is given in Table 1. This brine solution was then diluted with steam condensate. Chloride solutions of cations such as calcium, iron, etc. were added, and the diluted brine was deaerated in a vacuum steam deaeration column.

The deaerated brine was then run through a heat exchanger. The desired anions were injected into the hot brine. The primary anion solution contained 5% sodium silicate and 10% sodium bicarbonate. Sulfide was added as a solution of 18% sodium sulfide. Technical grade hydrochloric acid was used

TABLE 1

Composition of
Dow Salt Dome Treated Brine

<u>Gaseous and Cationic</u>		<u>Solid and Anionic</u>	
<u>Constituent</u>	<u>ppm</u>	<u>Constituent</u>	<u>ppm</u>
CO ₂	100	Cl	158,000
H ₂ S	1	Br	10 - 20
		I	1
Na	102,000	SO ₄	1,200 - 1,800
K	350	HCO ₃	100
Li	10		
Ca	3 - 6	SiO ₂	0 - 10
Mg	0 - 1	H ₃ BO ₄	0 - 10
Fe	1 - 3	TDS	260,000

to control the pH. All solutions were deaerated and stored under a nitrogen pad prior to injection.

2. Equipment

In order to accomplish the first task of evaluating air as the oxygen source for H_2S removal from the liquid flow, the system shown in Figure 1 was used. This system is identical to the system used to evaluate O_2 injection into the brine. The oxidation reaction was to take place in the reactor, R-1. This is a five-pass, steam jacketed reactor with a one minute residence time for each pass. Provision was made for sampling between passes. This, plus completion of the fifth pass, gave five sulfide analyses at one minute intervals after the air injection. The tubing and piping were Alloy 20 steel to avoid corrosion and contamination in the brine.

The other items in Figure 1 were constructed to avoid exposure of the brine to corrosive mild steel surfaces. All connecting piping was polytetrafluorocarbon-lined. The heat exchanger, HX-1, was constructed of titanium. The flow into the heat exchanger was provided by a 316 stainless steel, triple piston positive displacement pump, Model 431, manufactured by CAT Pump Corporation. A pulsation dampener was used to give a more uniform flow, and flow rates were controlled by changing pump or motor pulleys.

The anion solution, sodium sulfide, and HCl solutions were added with Model Milroyal D chemical injection pumps.

FIG. 1: HYDROGEN SULFIDE OXIDATION SYSTEM FLOW SHEET.

Pump chambers and tubing were constructed of Hastelloy® C or B to avoid corrosion.

The air injection took place just prior to the reactor, R-1. The metering system consisted of a constant differential flow controller upstream from a needle valve. A constant gas flow was maintained by maintaining a constant pressure drop across the needle valve. Total flow was measured with a flow meter and displayed on a square-root guage.

Two in-line mixers were used in the system. One was placed downstream of the anion and HCl injection points, and the other was placed downstream of the air injection point. Both were Dow designed ISG (Interfacial Surface Generator) mixers, manufactured by Charles Ross & Son Company of Hauppauge, New York. The design consists of a series of mixing elements enclosed in a pipe housing. Each element has four passage holes at oblique angles. The ends of the elements form a tetrahedral chamber. The elements were constructed of polytetraflouroethylene, 5.08 cm in diameter, with six units forming one mixer. The layers emerging can be calculated from the equation $L=N(4)^E$ where N is the number of streams and E is the number of elements. A two layer stream through a six element mixer provides 8192 emerging layers, which should give effective mixing. Pressure drop was calculated at 0.22 psi across each mixer. Operating presssure of the system was 200 psi with a total pressure drop of approximately 50 psi at a flow rate of 3 gpm.

Figure 2: IGS Static In-Line Mixer manufactured By Charles Ross and Son. Six (6) units illustrated divides a two (2) layer stream into 8192 layers.

Samples at the reactor sample points were taken into evacuated, 350 ml., polytetrafluorocarbon-lined, stainless steel bombs. Sample valves were Model M9, 316 stainless steel guage valves, manufactured by Anderson, Greenwood and Company. Corrosion rates were determined by the polarization admittance instantaneous rate method. Three electrodes, reference, test, and auxiliary, were used to give instantaneous corrosion rate readings. Provided that the measurement itself does not change the electrochemical potentials, these potentials can give the corrosion rate. The probes used to accomplish this were supplied by the Petrolite Corporation, Petreco Division, Houston, Texas. A photograph of the probe with electrodes in place is shown in Figure 3.

The remainder of the system is for cooling and discharge of the brine into the Dow Waste Canal. This equipment consists of a flash vessel, D-6, which is pressure and level controlled to drop the temperature to 260°F. The liquid flow then goes to a second flash chamber, D-7, which operates at atmospheric pressure. Steam from the two flash chambers is condensed in heat exchangers HX-2 and HX-3. Condensate and the brine from D-7 is then sent to the Dow Waste Canal.

3. Modifications For Investigation of Two-Phase Flow

In order to accomplish the task of evaluating oxidation of H S in two phase flow, the system just described was modified to include a flash chamber and packed tower. The

Figure 3: Photograph of Standard Petrolite Corrosion Rate Probe with three (3) mild steel electrodes in place.

modified system is shown in Figure 4. The hot brine is prepared in the same fashion as described previously, but the reactor, RX-1, is used as a heat exchanger. The brine is then directed to the flash pot, which was a polytetrafluoroethylene-lined mild steel 10" tee.

The entering brine is at a temperature 345°F and pressure of 150 psi. It is flashed to 304°F and 64 psi (~5.7% vapor by wt.) The vapor and water streams are then separated and run counter-currently through a packed tower. The oxygen was injected at the vapor entrance to the tower in the same fashion as the air injection prior to the reactor in the earlier work. A sketch of this system is provided as Figure 5. The vapor and liquid streams were both sampled separately before and after oxygen injection at the exits from the packed tower for various levels of oxygen injection.

The vapor stream is run through a condenser and the liquid stream through a heat exchanger prior to both streams being sent to the Dow Waste Canal.

4. Packed Tower Design

After the flash pot, the vapor and liquid streams were separated and run counter-currently through the packed tower. Assuming both streams at saturation and the expansion as adiabatic (constant enthalpy), the vapor flow was approximately 5.7% (by weight) of the entering brine. Reference to steam tables gives the vapor density at the given conditions as 0.1624 lb/ft³. Reference to "Calculation of Brine Properties"

HYDROGEN SULFIDE OXIDATION SYSTEM FLOW SHEET

FIGURE 4

FIGURE 5

HYDROGEN SULFIDE REMOVAL

FLASH POT AND PACKED TOWER

by Gerald Dittman, gives the density of the brine as 58.68 lb/ft³, at 3 wt% solids and the given conditions. At the brine pumping rate of 3.5 gpm, this gives a 29.6 lb/min total throughput, using 63.18 lb/ft³ as the brine density at 100°F. The liquid flow rate is then 27.88 lb/min, and the vapor flow rate is 1.68 lb/min.

The L/G ratio is therefore determined by the process conditions. This information, plus the incoming properties of the brine and vapor, can be used to determine the desired diameter of the tower. Reference to Figure 6⁹ shows the relationship between flow rates, pressure drop, geometry of the column, and processing conditions for packed towers. The operating line for the given conditions,

$$\left(\frac{L}{G}\right) \left(\frac{\rho_g}{\rho_L}\right)^{1/2}$$

is shown on the figure.

In order to use Figure 6, the packing factor F, must be known. This is dependent upon the packing used. To maximize the interfacial area between the liquid and vapor, ceramic Intalox saddles were chosen as the packing. Eckert⁹ recommends that the ratio of packing diameter to column diameter be less than 1/15 for saddles. Because of capacity of the system into which the packed tower was placed, 3/8" saddles were chosen initially. This established the minimum recommended column diameter at 5.6". This packing was reported in supplier literature (Norton, Chemical Process Products Division) to give

FIGURE 6

PRESSURE DROP CORRELATION FOR PACKED TOWER DESIGN
(In. H₂O/Ft of Packing)

L = Liquid Rate,
lb/sec. sq ft

G = Gas Rate,
lb/sec. sq ft

ρ_L = Liquid density,
lb/cu ft

ρ_G = Gas density,
lb/cu ft

F = Packing factor

μ = Viscosity of liquid

ψ = Ratio, $\frac{\text{Density of Water}}{\text{Density of Liquid}}$

g_1 = Gravitational constant =
32.2

$$\left(\frac{L}{G}\right)\left(\frac{\rho_G}{\rho_L}\right)^{1/2}$$

a packing factor of 330. Correspondence with equipment suppliers and reference again to Figure 6 indicated that 0.5 inches of water/foot of packing would be a satisfactory pressure drop to obtain good interaction between vapor and liquid, while still maintaining a safe operating margin below the flood point. Using this packing factor and pressure drop, the recommended column diameter is calculated at 7.98", with a vapor flow rate of approximately 0.0806 lb/sec-ft². The column diameter was safely over the recommended minimum, so the 3/8" Intalox packing and an 8" diameter column were chosen for this work.

The length of the column, or height, is determined by the number of transfer units required for completion of the oxidation. In this tower application, the oxygen-vapor mixture is flowing counter-currently to the brine flow. Mass transfer will be occurring, accompanied by a first order reaction. The complexity of this situation, plus the lack of existing data, led to the design of the tower such that the height could be varied in 2 foot increments. The earlier work with one phase flow indicated that the reaction took place in less than one minute. A one minute residence time in the tower would mean that the free space should be 10.34 ft³ for the vapor and 0.475 ft³ for the liquid. The free space of the 3/8" Intalox saddles was reported by the supplier as 0.67, so a one minute residence time would require 15.68 ft³ for the total column tower volume.

Using an 8" diameter, the required height for the one minute residence time would be 45 ft. This height is uneconomical, particularly when scaled to a geothermal well, so the reaction must come to completion in well under one minute, at least for the given liquid and vapor flow rates. The initial height chosen for the column was eight feet, for a residence time of 10-11 seconds.

The column was constructed of 8" ID polytetrafluoroethylene-lined pipe, with a Norton #4666 ceramic orifice distributor plate and a Norton #4808 ceramic support.

III. EXPERIMENTAL PROCEDURES

The experimental procedures followed in this work consisted of the following steps:

1. Preparation and deaeration of the base brine solution.
2. Circulation and heating of the base brine solution.
3. Adjustment of additive levels and pH.
4. Injection of oxidant.
5. Sampling and analysis of samples.
6. Corrosion monitoring.

A more detailed description of each step is contained in the following paragraphs.

1. Preparation and Deaeration Of Base Brine Solution

The brine solution containing 26% dissolved solids is stored in an open tank, where it is treated with barium chloride to precipitate the sulfate. When the desired sulfate level, 25 ppm, is reached, the brine is pumped into the 10,000 gallon tank, D-1. Steam condensate is then added to dilute the brine to the desired concentration. At this point, any ion which will not cause scaling in the heat exchanger may be added. Cations such as calcium,

magnesium, iron, nickel, etc. are added from cation solution tank D-2 prior to deaeration.

Mixing and deaeration are achieved by circulating the solution through the steam-stripping vacuum deaeration column. The typical oxygen levels after deaeration were 15-20 ppb (parts per billion) as measured by a modified Beckman Model 735 Dissolved Oxygen Analyzer and the Winkler method. The operation of the deaerator consisted of pumping into the column at a rate of 150 gpm by way of a steam heat exchanger which raised the temperature of the solution to 110°F. The column operated with steam stripping at 2 in. internal pressure and was level controlled.

2. Circulation and Heating of Base Brine

After deaeration, the brine is stored under a nitrogen pad in tank D-1 until a run is initiated. This is accomplished by pumping the brine through heat exchanger HX-1 with the Cat positive displacement pump (P-3). The heat exchanger raises the brine to a maximum temperature of 350°F. The pressure of the system at this temperature is 150 psi. Brine flow rates are controlled by changing the ratios of the drive and pump pulley diameters. The calculated flow rate for all the runs was 3.8 gpm, which agreed well with the actual flow rates observed after extended time periods.

3. Adjustment of Additive Levels and pH

When the hot base brine flow had been stabilized, injection of the desired anions, including sulfide, was begun. The Milton Roy pumps were adjustable to give the desired injection rates, based on analysis of the brine. The 33% hydrochloric acid solution is also injected at this point in a manner similar to the anion injection. Samples were taken at several points to insure that no deposition was occurring.

4. Injection of Oxygen or Air

a. Air injection into liquid flow: The air was injected just prior to entry into the reactor, R-1. The air source was a cylinder containing compressed breathing air. The flow was controlled by a needle valve and flow indicator as described previously. This flow was set to provide the desired oxygen to sulfide mole ratio based on the % oxygen in the breathing air and the sulfide level as determined by analysis.

b. Two phase flow through the packed tower: The oxygen was injected into the vapor entry to the packed tower using the control procedures described previously. The oxygen to sulfide mole ratio was based on the analysis of the sulfide level in the brine flow prior to flashing. The source of oxygen was medical grade cylinder oxygen.

For the work being done with hydrogen peroxide (H_2O_2), and sodium hypochlorite (NaOCl), the tower was altered to allow injection with the liquid entry into the packed tower. As with the anion solutions, the pump was a Milton Roy injection pump. The mole ratios were based on the sulfide level in the unflashed brine as determined by analysis.

5. Sampling Procedures And Analysis of Samples

a. Air injection into liquid flow: As stated previously, the reactor, R-1, was a five pass concentric tube design. Provision was made for sampling at the beginning of each pass and the end of the fifth pass. Each pass was one minute of residence time in the reactor and samples were taken at the end of the first, third, and fifth passes for the work with air injection.

Samples were taken through sample valves into evacuated, 350 ml., polytetrafluoroethylene-lined bombs. Although some flashing probably takes place in the sampling procedure, the final sample is believed to be equilibrated and representative of a true value. Samples were representative of known values, reproducible, and no solid residue appeared over an extended period of time.

The bombs filled very quickly and were immediately drenched with cold water from a hose to stop, or greatly slow, the oxidation reaction. The samples were then immediately analyzed for sulfide level.

The method used for analysis of sulfide is the Methylene Blue Photometric Method. This method is based on the reaction which takes place between paraaminodi-methylaniline, ferric chloride and sulfide ion to form methylene blue. The color formed is measured on a Spectrophotometer at a wave length of 600 mμ.

This was substantiated with frequent checks by the Dow Central Analytical Laboratory using more sophisticated methods. When desired, metal ions such as iron and nickel were determined with adsorption spectrophotometric methods. Silica levels were determined from the molybdate colorimetric procedure with Central Laboratory checks, and calcium was determined by chelation titration.

b. Oxygen injection with two phase flow: The means of obtaining samples was slightly different from the procedures used for air injection. For the vapor stream at the exit from the packed tower, an alloy 20 coiled condenser was used to condense the vapor, which was collected in a purged 125 ml. glass bomb. The condenser was cooled with cold water from a hose. A similar procedure was used to cool the liquid from the liquid exit from the packed tower.

The procedure used for analysis of the samples from the packed tower was identical to the procedures used during the work on air injection.

6. Corrosion Monitoring

Geothermal brines are oxygen-free, and since residual oxygen in the brine is highly corrosive, it is important to regulate the oxygen injection to achieve complete sulfide removal without excess oxygen. Also, since hydrogen sulfide is corrosive, measurement of the corrosivity of the brine flow as the oxygen is injected would give valuable information about the progress of the oxygen reaction. The corrosivity would be lowest when the sulfide has been removed and no excess oxygen added.

As previously described, the Petrolite method was used to measure corrosion rates. The three electrodes were ASTM 101B mild steel. The probe was the M-510 standard industrial probe, and the instantaneous corrosion rate in mils per year (MPY) was displayed and recorded by a Petrolite Corrosion Rate Meter Model M-1000.

IV. EXPERIMENTAL RESULTS

1. Air Injection In Liquid Flow

The earlier work on oxygen injection into simulated geothermal brine indicated that hydrogen sulfide removal was accomplished at mole ratios of 1.25-1.50:1 (Oxygen:H₂S). This indicated that reactions such as:

must occur, as well as the reactions:

Also since the reactions were complete within one minute, the reactions are near first order.

It was found that injection of air into the brine was not nearly as effective as oxygen injection for the removal of hydrogen sulfide. At a mole ratio of 6.45:1 (O₂ in air:H₂S) the removal rate was 80%. This level of removal was for an initial sulfide level of 11 ppm. For two runs with initial sulfide levels of 45 ppm and 38 ppm, the sulfide removal levels were 53% and 32% respectively, for mole ratios of 1.5:1.

An additional run was made to verify the earlier work utilizing oxygen which gave 96% sulfide removal at a mole

ratio of 1.5:1 (pure $O_2:H_2S$). It appears from this work that the presence of inert gas, primarily nitrogen, is inhibiting the mass transfer of oxygen into the liquid phase. Work done by Tamir and Taitel⁷ indicates that the absorption from a binary gas mixture into a liquid accompanied by a first order reaction can lead to a concentration of the inert gas at the gas-liquid interface. This can significantly affect the gas-side resistance of the absorption process. This work was done examining the absorption of C_2S (.01-.1 wt %) in nitrogen into dimethylamine solutions. Work done by Kafarov⁸, et. al., on the absorption of slightly soluble gases indicates that the gas phase resistance has the severest affect on absorption when a pseudo-first order reaction takes place in the liquid phase.

Therefore, it was concluded that the presence of nitrogen was interfering with the mass transfer of oxygen. The 80% removal ratio of 6.45:1 (O_2 in air: H_2S), if it could be achieved at higher sulfide levels, would not be economical. This, plus the fact that the sample taken five minutes after air injection did not show appreciably higher sulfide removal than the one minute sample, indicates that air injection is not desirable over oxygen injection for hydrogen sulfide removal from geothermal brines.

Some additional runs were attempted to further substantiate this, but difficulties occurred with pH control and high pressures. Due to the high volumes of gas required, pressure

shutdowns occurred which stopped the run prematurely. This may have been further aggravated by the presence of CO_2 in the air which could have caused some scaling through the formation of calcium carbonate. Also, in one run, air injection was lost due to malfunctioning of the regulator. The results of the air injection runs are considered in Table 2.

Figure 7 shows the percent removal of sulfide for Run 1, 2, and 3 using air injection. These results are compared to Run 4 using pure oxygen injection. It appears from comparison of Runs 1 and 2 that an increase in pH increases the efficiency of air oxidation, and a comparison of Runs 2 and 3 indicates that an increase in initial sulfide level increases the efficiency of air oxidation. None of the air oxidation runs, however, gave an oxidation efficiency comparable to Run 4, using pure oxygen. All runs were made with the brine at 350°F.

The corrosion measurements are included in Table 2. None of the air oxidation runs indicates an appreciable change in corrosivity. The oxidation run using pure oxygen shows a marked increase in corrosivity at the 1.5:1 ($\text{O}_2:\text{H}_2\text{S}$) mole ratio, indicating the presence of excess oxygen. This is consistent with earlier results.¹

2. Oxidation In Two Phase Flow

a. Oxygen injection: Oxygen injection was the first work done utilizing two phase flow through the packed tower.

TABLE 2

RESULTS OF AIR OXIDATION OF HYDROGEN SULFIDE

Run No.	O ₂ :H ₂ S Mole Ratio	Reaction Time (minutes)	H ₂ S (ppm)	pH of Brine	Corrosivity (mpy)	% Removal
1	0:1	0	45	10.3	18	0
	0.75:1	1	37	10.2	18	17.8
		2	36			20.0
		3	37			17.8
		5	38			15.6
	1:1	1	32	10.1	19	28.9
		2	30			33.3
		3	30			33.3
		5	31			31.1
	1.25:1	1	23	10.2	22	48.9
		3	24			46.7
		5	23			48.9
	1.5:1	1	21	10.2	28	53.3
		3	20			55.6
		5	21			53.3
2	0:1	0	38	6.4	22	0
	0.75:1	1	33	6.2	17	13.2
		3	32			15.8
		5	33			13.2

TABLE 2

RESULTS OF AIR OXIDATION OF HYDROGEN SULFIDE

Run No.	O ₂ :H ₂ S Mole Ratio	Reaction Time (minutes)	H ₂ S (ppm)	pH of Brine	Corrosivity (mpy)	% Removal
2 cont.	1:1	1	29	6.1	14	23.7
		3	29			
		5	29			
	1.25:1	1	27	5.9	17	28.9
		3	26			31.6
		5	27			28.9
	1.5:1	1	26	6.0	18	31.6
		3	26			31.6
		5	27			28.9
	1.87:1	1	26	5.9	16	31.6
		3	24			36.8
		5	26			31.6
3	0:1	0	11	6.1	8	0
	1.25:1	1	9.5	6.1	8	13.6
		3	9.5			13.6
		5	10.0			9.1
	2:1	1	7.5	6.1	7	31.8
		3	8.5			22.7
		5	9.0			18.2
	4:1	1	5	6.1	7	54.5
		3	6			45.5
		5	6			45.5

TABLE 2

RESULTS OF AIR OXIDATION OF HYDROGEN SULFIDE

Run No.	O ₂ :H ₂ S Mole Ratio	Reaction Time (minutes)	H ₂ S (ppm)	pH of Brine	Corrosivity (mpy)	% Removal
3 cont.	6.45:1	1	2	6.1	8	81.8
		3	2.4			78.2
		5	2			81.8
4 * pure oxygen	0:1	0	41	5.2	34	0
	1:1	1	13.5	4.5	61	67.1
		3	12			70.7
		5	13.5			67.1
	1.25:1	1	5.5	3.5	90	86.6
		3	4.5			89.0
		5	3.0			92.7
	1.5:1	1	3.3	2.9	155	92.0
		3	2.0			95.1
		5	1.8			95.6
5	0:1	0	25.0	7.3	40	0
	1:1	1	19	8.9	40	24
		3	17			32
		5	20			20
	1.25:1	1	19	10.0	54	24
		3	18			28
		5	17			32

HIGH PRESSURE SHUT DOWN; LOSS OF ACID INJECTION

TABLE 2

RESULTS OF AIR OXIDATION OF HYDROGEN SULFIDE

Run No.	O :H S Mole Ratio	Reaction Time (minutes)	H S (ppm)	pH of Brine	.Corrosivity (mpy)	% Removal
6	0:1	0	32	6.1	32	0
	.75:1	1	28	6.2	37	12.5
		3	29			9.4
		5	30			6.3
		HIGH PRESSURE SHUT DOWN				
7	0:1	0	20	6.4	41	0
	.75:1	1	19	6.1	34	5
		3	20			0
		5	20			0
		HIGH PRESSURE AND MALFUNCTION OF OXYGEN REGULATOR				

FIGURE 7

PERCENT REMOVAL VS. $O_2:H_2S$ MOLE RATIO

Air Oxidation

(Liquid Flow)

Two runs were made using oxygen injection at the vapor stream entrance to the tower, as described previously. The first run utilized an intermediate sulfide level (21 ppm in the unflashed brine), and resulted in a 53% sulfide removal in the vapor phase and no removal in the liquid phase, at a mole ratio of 3:1 ($O_2:H_2S$).

These results were thought to be due to the presence of noncondensable gases in the brine (nitrogen and CO), which are released upon flashing, and to the water vapor itself. These gases probably inhibit the transfer of oxygen into the liquid phase of the brine in the same manner as that described for air injection in one phase flow.

To substantiate this, brine was made up containing no carbonate or SiO_2 , which should reduce the amount of noncondensable gas in the vapor. The same pH and approximately the same initial sulfide level (18 ppm) were used. At a mole ratio of 3:1 ($O_2:H_2S$), sulfide removal was 46% in the liquid phase and 31% in the vapor phase. The higher removal rate in the liquid phase did indicate that noncondensable gas content inhibited oxidation. The results of these two runs (8 and 9) are pictured graphically in Figures 8 and 9, and listed in Table 3.

Corrosion measurements were taken as described earlier on the hot brine flow from the packed tower. These are included in Table 3 and shown graphically in Figure 10. These measurements were consistent with experimental results and the previous work done with one phase flow. Both runs

FIGURE 8

SULFIDE LEVEL IN LIQUID FROM PACKED TOWER

(O₂ Injection)

FIGURE 9

SULFIDE LEVEL IN CONDENSED VAPOR
FROM PACKED TOWER

O₂ Injection

FIGURE 10

CORROSIVITY VS O₂:H₂S MOLE RATIO

Oxygen Injection in Packed Tower

TABLE 3

OXIDATION OF HYDROGEN SULFIDE IN PACKED TOWER

(Oxygen Injection)

Run No.	O ₂ :H ₂ S Mole Ratio	Inlet Brine		Condensed Vapor From Tower			Liquid From Tower			Corrosivity (mpy)
		H ₂ S (ppm)	pH	H ₂ S (ppm)	pH	% Removal	H ₂ S (ppm)	pH	% Removal	
8	0:1	21	6.1	57.5	4.0	0	15	8.5	0	85-100
	1:1			50	3.8	13	15	8.1	0	65
	1.5:1			42.5	4.1	26.1	17	8.5	0	75
	2:1			30	4.1	47.8	17	8.9	0	85
	3:1			27	4.1	53	17	9.0	0	100
9	0:1	18	6.4	128	4.4	0	16	8.8	0	105
	1:1			75	4.1	41.4	12	8.9	25	80
	1.5:1			72	4.3	43.8	11	9.0	31.2	60
	2:1			65	4.2	49.2	10	8.9	37.5	30
	3:1			69	4.5	46.1	11	8.9	31.2	30

(8 and 9) were run with the brine at 350°F and the initial sulfide levels are based upon the ppm in the unflashed brine.

b. Hydrogen Peroxide Injection: If an eight-foot packed tower was not adequate to remove the sulfide with oxygen injection, economics of expanding the tower to a 100 gpm geothermal well could be prohibitive for the tower which would be needed. For this reason, the direction taken with this work was to examine other oxidants. The tower was altered to allow injection into the liquid inlet to the packed tower. Runs 10, 11, 12, 13, 14 and 15 were made using a solution of hydrogen peroxide (H_2O_2) as the oxidizing agent.

The expected reactions were:

The first reaction requires a 4:1 mole ratio ($\text{H}_2\text{O}_2:\text{H}_2\text{S}$) for complete oxidation to sulfate. The second reaction would lead to the reactions mentioned for oxygen. For this reason, it could be expected that the $\text{H}_2\text{O}_2:\text{H}_2\text{S}$ mole ratio required for oxidation should be about twice that required for the oxygen, or 2.5-3.0 ($\text{H}_2\text{O}_2:\text{H}_2\text{S}$). The advantage of the hydrogen peroxide over oxygen is that the oxygen would be in the water. This should avoid the mass transfer problem associated with the oxygen gas. If the level of sulfide in the geothermal liquid is reduced by oxidation, the equilibrium shift would drive

the sulfide in the vapor into the liquid. Also, the low solubility of oxygen in the liquid should give some driving force to move the oxygen into the vapor.

Run 10 was the first run attempted using hydrogen peroxide. The highest mole ratio achieved was 1.5:1 ($\text{H}_2\text{O}_2:\text{H}_2\text{S}$) with a 2% injection solution. Removal levels were 82% in the vapor phase and 53% in the liquid phase. This run did not include carbonate or SiO_2 , and higher mole ratios needed to be investigated. This was attempted in Run 11. However, the acid injection malfunctioned, which gave a low pH in the liquid. This low pH reduced sulfide solubility and drove the sulfide into the vapor. The result was 100% removal in the liquid and 0% removal in the vapor.

Run 12 was with a 2% hydrogen peroxide solution, initial sulfide level of 46 ppm in the unflashed brine, and a pH of 6.4. Removal of sulfide in the liquid was 92.9% and removal of sulfide in the vapor was 96.7% at a mole ratio of 3:1 ($\text{H}_2\text{O}_2:\text{H}_2\text{S}$). Run 13 was shutdown due to a leak in the acid injection line. Runs 14 and 15 were made at identical conditions to Run 11 except the initial sulfide level was lowered. Run 14 had an initial sulfide level of 18 ppm, and removal for liquid and vapor was 93% and 97.6%, respectively. Run 15 was at an initial level of 5.1 ppm, and removal rates for liquid and vapor were 87.1% and 85%. Results of Runs 10 through 15 are contained in Table 4. Figures 11 and 12 show a comparison of removal efficiency for the different initial sulfide levels, for the liquid and vapor phases.

TABLE 4

OXIDATION OF HYDROGEN SULFIDE IN PACKED TOWER

(Hydrogen Peroxide Injection)

Run No.	H ₂ O ₂ :H ₂ S Mole Ratio	Inlet Brine		Condensed Vapor From Tower			Liquid From Tower			Corrosivity (mpy)
		H ₂ S (ppm)	pH	H ₂ S (ppm)	pH	% Removal	H ₂ S (ppm)	pH	% Removal	
10	0:1	18	6.5	110	4.4	0	15	8.9	0	95
	.5:1			77	4.2	30	8	8.2	46.7	65
	.625:1			75	4.3	31.8	7.5	8.4	50	75
	.75:1			75	4.1	31.8	8	8.5	46.7	42
	1:1			45	4.4	59.1	8	8.6	46.7	31
	1.5:1			20	4.1	81.8	7	8.7	53.3	36
11	0:1	18	6.4	135	4.4	0	15	8.8	0	85
	1:1			70	4.3	48.1	11	8.9	26.7	90
	1.5:1			64	6.1	52.6	5.5	7.8	63.3	60
	2:1			112	4.0	17.0	0.4	7.7	97.3	250
	2.25:1			150	4.0	0	0	3.9	100	450
	2.5:1			155	3.9	0	0	3.5	100	950

TABLE 4

OXIDATION OF HYDROGEN SULFIDE IN PACKED TOWER

(Hydrogen Peroxide Injection)

Run No.	H ₂ O ₂ :H ₂ S Mole Ratio	Inlet Brine		Condensed Vapor From Tower			Liquid From Tower			Corrosivity (mpy)
		H ₂ S (ppm)	pH	H ₂ S (ppm)	pH	% Removal	H ₂ S (ppm)	pH	% Removal	
12	0:1	46	6.4	180	4.1	0	42	8.9	0	80
	1:1			75	4.1	58.3	22	8.7	47.6	40
	1.5:1			40	4.0	77.8	16	8.7	61.9	50
	2:1			14	4.0	92.2	12	8.7	71.4	55
	2.5:1			12	3.9	93.3	11	8.5	73.8	50
	3:1			6	4.0	96.7	3	8.5	92.9	65
13	0:1	51	6.9	70	4.1	0	29	9.1	0	60
	1:1			32	4.5	54.3	26	9.6	10.3	--
	* LEAK IN HCl LINE CAUSED SHUTDOWN									
14	0:1	18	6.4	85	3.9	0	16	8.5	0	25
	1:1			72	3.9	15.3	10.5	7.9	34.4	18
	1.5:1			22	4.1	74.1	11	8.6	31.2	24

TABLE 4

OXIDATION OF HYDROGEN SULFIDE IN PACKED TOWER

(Hydrogen Peroxide Injection)

Run No.	H ₂ O ₂ :H ₂ S Mole Ratio	Inlet Brine		Condensed Vapor From Tower			Liquid From Tower			Corrosivity (mpy)
		H ₂ S (ppm)	pH	H ₂ S (ppm)	pH	% Removal	H ₂ S (ppm)	pH	% Removal	
14 cont.	2:1			8	4.4	90.6	6.5	8.8	59.4	26
	2.5:1			4	4.6	95.3	4	9.0	75	29
	3:1			2	4.0	97.6	1	8.9	93.8	49
15	0:1	5.1	6.7	14	3.8	0	6.2	8.9	0-	32
	1:1			10	3.9	28.6	4.0	8.9	35.5	25
	1.5:1			9.5	3.7	32.1	4.6	8.6	25.8	32
	2:1			5.0	4.2	64.3	3.0	8.9	51.6	28
	2.5:1			4.6	3.8	67.1	1.8	8.6	71.0	33
	3:1			2.1	3.7	85	0.8	8.6	87.1	40

FIGURE 11

REMOVAL VS $H_2O_2:H_2S$ MOLE RATIO
(Varying Initial Sulfide Levels)

VAPOR PHASE

FIGURE 12

REMOVAL VS $H_2O_2:H_2S$ MOLE RATIO
(For Varying Initial Sulfide Levels)

Figure 11 indicates that removal efficiency is not sensitive to initial sulfide level except at the low initial level of 5.1 ppm. Figure 12 indicates that below the 3:1 mole ratio ($\text{H}_2\text{O}_2:\text{H}_2\text{S}$), the oxidation process is somewhat more affected by initial sulfide levels. The actual ppm of sulfide versus mole ratio is shown in Figure 13 and 14 for both liquid and vapor phase.

This data indicates that the hydrogen peroxide is an effective means of sulfide removal from two phase flow in a packed tower for initial sulfide levels in the unflashed brine from 5 ppm to 46 ppm. The mole ratios required for effective removal is 3:1 ($\text{H}_2\text{O}_2:\text{H}_2\text{S}$), which is in agreement with what would be expected, based on the earlier work with O_2 injection in one phase flow.

The corrosion rates, as measured on the hot brine emerging from the packed tower, were not severely affected by the hydrogen peroxide injection. At the 1:1 mole ratio, where the sulfide level has been reduced drastically from the initial level, corrosivity of the brine decreases slightly for all three runs (12,14,15). It then increases to approximately the initial level at a mole ratio of 3:1 ($\text{H}_2\text{O}_2:\text{H}_2\text{S}$). The corrosivity level versus mole ratio is graphed in Figure 15, for Runs 12, 14 and 15.

c. NaOCl injection: Although the hydrogen peroxide injection adequately removed the sulfide in two phase

FIGURE 13

H₂S (PPM) VS H₂O₂:H₂S MOLE RATIO
(Varying Initial Sulfide Levels)

LIQUID PHASE

FIGURE 14

H₂S (PPM) VS H₂O₂:H₂S MOLE RATIO
(For Varying Initial Sulfide Levels)

FIGURE 15

CORROSIVITY VS $H_2O_2:H_2S$ MOLE RATIO
LIQUID FROM PACKED TOWER

H_2O_2 INJECTION

flow, preliminary cost considerations, described later in this report, indicated that a less expensive oxidizing agent would be desirable. Sodium Hypochlorite (NaOCl) was chosen as an inexpensive material to examine. The hoped for reactions were the following:

Therefore, the required mole ratio ($^-\text{OCl}:\text{H}_2\text{S}$) should be between 1 and 4, depending on the relative formation of sulfur and sulfate.

Run 16 was the first attempt to oxidize the hydrogen sulfide with sodium hypochlorite. The hypochlorite was injected as a 2% solution in the same fashion as was the hydrogen sulfide. The initial sulfide level in the unflashed brine was 30 ppm and the pH was adjusted to 6.8. The mole ratio of $\text{OCl}:\text{H}_2\text{S}$ was increased to 4:1 during this run, with 50.8% removal in the vapor phase and 28.6% removal in the liquid phase. Run 17 was a further attempt to evaluate the hypochlorite. In this run, the mole ratio ($^-\text{OCl}:\text{H}_2\text{S}$) was increased to 10:1. The initial sulfide level was 13.5 ppm in the unflashed brine. The removal at the 10:1 ratio was 72.7% in the vapor and 52.9% in the liquid. The results of Runs 16 and 17 are in Table 5 and graphed in Figures 16 through 19. The sodium hypochlorite was not an effective

TABLE 5

OXIDATION OF HYDROGEN SULFIDE IN PACKED TOWER

(Sodium Hypochlorite Injection)

Run No.	OCl:H ₂ S Mole Ratio	Inlet Brine		Condensed Vapor From Tower			Liquid From Tower			Corrosivity (mpy)
		H ₂ S (ppm)	pH	H ₂ S (ppm)	pH	% Removal	H ₂ S (ppm)	pH	% Removal	
16	0:1	30	6.8	65	4.2	0	28	9.0	0	40
	1:1			50	4.7	23.1	26	8.9	7.1	35
	2:1			43	4.5	33.8	24	8.9	14.3	44
	3:1			36	5.0	44.6	23	9.0	17.9	45
	4:1			32	5.0	50.8	20	8.9	28.6	47
17	0:1	13.5	6.3	44	5.1	0	17	5.5	0	30
	2:1			42	4.4	4.5	15	8.5	11.8	20
	3:1			29	5.2	34.1	14	8.5	17.6	15
	4:1			26	4.7	59.1	12	8.6	29.4	8
	5:1			20	5.0	54.5	11	8.6	35.3	7
	6:1			20	4.9	54.5	11	8.6	35.3	7
	7:1			19	4.8	56.8	11	8.6	35.3	8
	8:1			13	4.8	70.5	10	8.5	41.2	12
	10:1			12	4.8	72.7	8	8.5	52.9	18

FIGURE 16

SULFIDE IN LIQUID FROM PACKED TOWER

FIGURE 17

SULFIDE IN CONDENSED VAPOR FROM PACKED TOWER

FIGURE 18

SULFIDE IN LIQUID FROM PACKED TOWER

FIGURE 19

SULFIDE IN CONDENSED VAPOR FROM
PACKED TOWER

oxidizer of the hydrogen sulfide. The oxidation reaction by the sodium hypochlorite takes place best in an acidic medium. The pH of the brine was apparently too high for effective oxidation. Acid injection to lower the brine pH would be undesirable from a standpoint of both economics and corrosivity, so it appears that the sodium hypochlorite is unsatisfactory for removal of the hydrogen sulfide.

V. CONCLUSIONS

1. Air Injection In Liquid Flow

The high mole ratios that are required for effective air oxidation of the hydrogen sulfide in geothermal brines makes this procedure unattractive in comparison to oxygen injection. With an initial sulfide level of 11 ppm, a mole ratio of 6.45:1 (O_2 in air: H_2S) was required for 80% removal. For high initial sulfide levels, the amount of air required would be prohibitive. In addition, although this did not show significantly in the runs performed, the high mole ratios and accompanying excess oxygen would probably result in unacceptable corrosivity of the brine.

The reason such high mole ratios are required is probably due to the large amount of inert gas, primarily nitrogen, which is present. References cited previously have indicated that the absorption of a gas from a binary gas mixture into liquid followed by a first order reaction in the liquid can result in an appreciable increase in the gas side resistance to mass transfer.

A run was made in which medical grade oxygen was injected. This run confirmed earlier work, in that complete sulfide removal was accomplished at a mole ratio of 1.5:1 ($O_2:H_2S$). This indicated that the presence of the inert gases in air is the problem with air injection.

2. Oxidation In Two Phase Flow

a. Oxygen Injection: The injection of oxygen into two phase flow was found to be ineffective as a means of sulfide removal. At a mole ratio of 3:1 ($O_2:H_2S$), 30% removal of sulfide in the liquid and 50% removal in the vapor was achieved. The difficulty is attributed to the same problem encountered with air injection in liquid flow. When the simulated geothermal brine was flashed, some noncondensable gases were formed (nitrogen and carbon dioxide), along with the water vapor. The mass transfer of oxygen into the liquid was apparently inhibited by the vapor and noncondensable gases. The utilization of the packed tower was inadequate to overcome this difficulty.

b. Hydrogen Peroxide Injection: The injection of hydrogen peroxide into the liquid phase of the two phase flow was found to be an effective means of sulfide removal at a mole ratio of 3:1 ($H_2O_2:H_2S$). With initial sulfide levels of 5-46 ppm in the unflashed brine, injection of hydrogen peroxide at the 3:1 mole ratio resulted in greater than 90% removal in both the liquid and vapor phases.

This was attributed to the fact that the hydrogen peroxide could be injected into the liquid phase of the flow. The sulfide in the liquid is rapidly oxidized, and the resulting change in equilibrium causes the sulfide in the vapor to enter

the liquid phase. This process is rapid enough to result in the high sulfide removal within the residence time in the packed tower. The disadvantage of hydrogen peroxide injection is material cost. The cost indicated by preliminary calculations show that hydrogen peroxide is economically unattractive at this point in time.

c. Sodium Hypochlorite Injection: In an attempt to find a less expensive oxidizing agent than hydrogen peroxide, sodium hypochlorite was injected into the liquid entrance to the packed tower. Mole ratios up to 10:1 ($\text{NaOCl}:\text{H}_2\text{S}$) were attempted, with inadequate removal of the sulfide. The oxidation of hydrogen sulfide by sodium hypochlorite is known to take place best in an acidic medium. After flashing, the pH of the simulated brine showed an appreciable increase (to between 8 and 9). It was concluded that the resulting pH of the brine was too high for the effective removal of the sulfide through oxidation by the hypochlorite ion.

Lowering the pH of the brine by acid injection is not feasible, from the standpoint of both cost and resulting corrosivity of the brine. For this reason, it was concluded that the use of sodium hypochlorite for hydrogen sulfide removal from two phase flow is not a viable alternative.

VI. PROCESS DESIGN AND COST ESTIMATE

1. Process Conditions

Based upon data from the pilot plant study, a process applicable to a total flow of 10,000 gpm (10 wells at 1000 gpm each calculated to power a 30 MWe flash plant) was designed for hydrogen peroxide oxidation in two phase flow. A preliminary cost estimate was then completed on the design. The process conditions used were as follows:

- a. 10 wells - 100 gpm each
- b. 375°F brine
- c. 5.7% by wt. vapor
- d. 30 ppm H_2S (unflashed brine)
- e. 3:1 mole ratio ($H_2O_2:H_2S$)

It was assumed that the oxidation process would take place at or near the wellhead to reduce corrosion problems in collection piping. Automatic operation was provided through corrosion rate measurement on the hot brine flow emerging from the packed tower.

2. Process Design

The process was designed based on the parameters established by the 3.5 gpm pilot plant data. A packed tower

providing the same process conditions and residence time was assumed for each 1000 gpm well. The tower was designed using a corrosion resistant alloy (Carpenter 20). The required height was 15 feet, with a diameter of 4 feet. Total capital cost for the entire system was estimated to be \$195,000. A breakdown of these costs is provided in Table 6. These costs were based to a large extent on the estimated costs for the oxygen injection system in liquid flow which is reported as Case II in the earlier report.¹ For this reason, the costs of this process are also listed. Case II was the case in which a packed tower was considered for mixing of the oxygen and brine. The process conditions were identical to those considered here, with the exception of one phase flow. The only change was the replacement of the storage and compressor cost for cryogenic oxygen (\$45,000) with a \$25,000 cost for the storage and pumping equipment required for hydrogen peroxide. These costs were estimated in March, 1977, so a factor of 1.065 was used to estimate 1978 costs.

3. Operating Cost

The operating cost is the cost of the hydrogen peroxide, plus the cost associated with the equipment (depreciation, maintenance, etc.). These costs are shown in Table 7 for the hydrogen peroxide system. Again, Table 7 compares the cost of the earlier proposed oxygen injection system for liquid only flow. The hydrogen peroxide cost is based upon \$17.00

TABLE 6

CAPITAL COST SUMMARY

(Each 1000 GPM Well)

	<u>OXYGEN INJECTION (Liquid Only)</u>	<u>H₂O₂ INJECTION (Two Phase Flow)</u>
Equipment	67,360	67,360
Piping	18,883	18,883
Instruments	21,750	21,750
Hydrogen Peroxide	---	25,000
Cryogenic O ₂	5,200	---
Electrical	1,800	1,800
Painting	950	950
Insulation	5,500	5,500
Compressor	<u>40,000</u>	<u>---</u>
	161,443	141,243
Engineering (15%)	24,216	21,186
Contingencies (15%)	<u>24,216</u>	<u>21,186</u>
TOTAL	209,875	183,615
TOTAL x 1.065	223,517	195,550

TABLE 7

COST CALCULATIONS

(30 MW Plant)

	OXYGEN INJECTION (Liquid Only)	H ₂ O ₂ INJECTION (Two Phase Flow)
<u>CAPITAL COST:</u> (10 Wells)		
Return on Capital (12.8%)	28,610	25,030
Depreciation (5.0%)	11,176	9,778
Taxes, Ins., Overhead (4.0%)	8,940	7,822
Operating Cost (8.0%)	<u>17,881</u>	<u>15,664</u>
TOTAL ANNUAL COST (WELL)	66,607	58,274
TOTAL ANNUAL COST	<u>\$666,070</u>	<u>\$582,740</u>

HYDROGEN PEROXIDE COST:
(3:1 Mole Ratio)

(3.83×10^6 lb.year x .4864 \$/lb) \$1,863,000

CRYOGENIC OXYGEN COSTS:
(1.5:1 Mole Ratio)

(1.80×10^6 lb/yr x .0348 \$/lb) \$ 62,640

ANNUAL COST/KWH:

Annual Costs	2.72 mils/Kwh	2.38 mils/Kwh
Material Costs	<u>.26 mils/Kwh</u>	<u>7.58 mils/Kwh</u>
Total Costs	2.98 mils/Kwh	9.96 mils/Kwh

COSTS FOR 5, 15 and 30 PPM *H₂S (Mils/Kwh):

5ppm	2.76	3.64
10 ppm	2.85	6.17
30 ppm	2.98	9.96

* In Unflashed Brine

for 100 pounds of a 35% solution, and the oxygen cost is based upon \$0.31 per 100 scf. Both these costs are mid 1978 costs. The amount required is based upon a 3:1 mole ratio ($\text{H}_2\text{O}_2:\text{H}_2\text{S}$) and a 1.5:1 mole ratio ($\text{O}_2:\text{H}_2\text{S}$). The sulfide level in the unflashed brine is assumed to be 30 ppm.

The operating costs are then used to calculate a cost per Kwh for a 30 MWe power plant operating off of ten 1000 gpm wells, each equipped with either the oxygen injection system or the hydrogen peroxide injection system. Both systems are based on the utilization of a packed tower. The power plant is assumed to produce 2.45×10^8 Kwh/year at 90% use. The cost to remove 30 ppm H_2S in the unflashed brine then calculates to be 9.96 mils/Kwh for the hydrogen peroxide system, compared to 2.98 mils/Kwh for oxygen injection in liquid flow. These calculations are summarized in Table 7, along with estimates for costs of both systems for 5, 15 and 30 ppm H_2S in the unflashed brine. Obviously, the relatively high cost of the hydrogen peroxide drastically affects the cost of this system.

4. Comparison To Alternate Methods of H_2S Control

In order for the estimated cost of the hydrogen peroxide system to be meaningful, it should be compared to the cost for sulfide removal using other techniques. The methods chosen for comparison here are the EIC process and the Stretford process, as described briefly earlier in this

report. These costs were obtained from "Preliminary Cost Estimate of Pollution Control Technologies For Geothermal Developments", by R. Sung, et. al.⁴ It is necessary to exercise caution in comparison of each method, due to the fact that existing data used for cost estimates may be based upon different well flow rates, steam or brine temperatures, sulfide levels, and/or power plant size. Also, the Stretford process is downstream of the power plant and does little to decrease the corrosion problem due to H₂S. For these reasons, the process conditions and assumptions used are included for each system.

EIC Process: As described earlier, the EIC process consists of the use of copper sulfate to scrub the H₂S from the steam through the formation of a copper sulfide precipitate. The copper sulfide slurry is concentrated by centrifuging and regenerated to copper sulfate. Some sulfur dioxide and sulfur trioxide is produced during regeneration. This is scrubbed with an ammoniacal solution. The ammonium sulfate is disposed of with waste water.

Information on the projected cost of the EIC process is available using the following process conditions:

Flow Rate: 17,100 Kg/hr steam
53,900 Kg/hr inerts

H₂S: 830 ppm

Steam Conditions: 150°C (300°F)
160 psig

Utilizing these conditions, the estimated capital cost for the EIC installation for a 50 MWe power plant is estimated at \$4,400,000. This is a 1976 estimate. Utilizing a 6.5% per year capital cost increase, this would represent approximately \$5,000,000 in 1978. Using this capital cost, the estimated annual operating costs for the EIC process are listed in Table 8. These costs were adjusted in the reference to 1977 costs. There has been an additional correction of 6.5% to get from 1977 costs to 1978 costs.

It should be noted that the amortization period for annual capital cost was 10 years. Table 8 also contains the estimated cost of the process in mils/Kwh for the 50 MWe plant and given process conditions. This is also adjusted to 1978 costs. Both capital cost and operation cost will vary with H_2S concentration. Annual costs for 2000 ppm H_2S were estimated at \$1,787,800 (1977), and annual cost/Kwh for the 50 MWe plant was estimated at 4 mils/Kwh (1977); adjusted to 1978 this would be approximately 4.3 mils/Kwh.

Stretford Process: As described earlier, the Stretford process is used to scrub noncondensable gases from the power plant, and so is an environmental measure only, and does not affect the corrosivity of the brine in process equipment. The scrubbing process consists of the formation of hydro-sulfide by sodium carbonate, and the subsequent formation of elemental sulfur through oxidation by 5 valent state vanadate. pH control is controlled to between 8.5 and 9.5

TABLE 8

ANNUAL COSTS: EIC PROCESS

(50 MW Power Plant)

Annual Capital	698,320
Maintenance Material	93,720
Maintenance Labor	121,410
Electrical Power	93,720
Water	5,325
Chemicals And Process Materials	106,500
Total O & M Cost	420,675
Total Annual Cost	<u>1,118,995</u>
Annual Cost/Kwh (830 H ₂ S)	<u>2.61 mills/Kwh</u>

by the addition of sodium hydroxide. The scrubbing solution is regenerated by blowing air through the oxidizer. This process is being designed for installation in 1978 at the Pacific Gas and Electric Geysers facility on a 117.5 MWe power plant. This is the basis for the estimates presented here, and the costs are adjusted to 1978 costs. The process conditions are as follows:

Flow Rate: 907,000 kg/hr

Steam Conditions: 180°C (355°F)
114 psia

H₂S: 220 ppm

Using these conditions, the estimated capital cost of the Stretford process for the 117.5 MWe facility was \$2,432,000. Annual operating costs for the 220 ppm H₂S concentration are given in Table 9. These costs were arrived at using a 15 year amortization period for annual capital cost.

Table 9 also contains the estimated annual cost per Kwh for the Stretford process as installed for the 117.5 MWe power plant. This cost was approximately 0.48 mils/Kwh. The Stretford process will also vary with H₂S concentration. The estimated cost/Kwh for a 2000 ppm H₂S concentration is approximately 1.7 mils.

TABLE 9

ANNUAL COSTS: STRETFORD PROCESS

(117.5 MW Plant)

Annual Capital	\$302,670	
Maintenance Material		51,865
Maintenance Labor		53,250
Electrical Power		62,300
Chemicals		47,390
*Sulfur Credit		-27,050
Total O & M Cost	187,755	
Total Annual Cost	<u>490,425</u>	
Annual Cost/Kwh (220 ppm H ₂ S)		<u>0.48 mills/Kwh</u>

* \$20 per long ton

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