

A-38

Union Oil Company of California
Union Geothermal Division

HYDROGEN SULFIDE EMISSIONS

REDUCTION AND ABATEMENT

WHILE DRILLING A GEOTHERMAL WELL

BY

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June 10, 1977

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INTRODUCTION

This report describes the reduction and abatement of hydrogen sulfide emissions as a result of the current drilling practices used by Union Oil Company while drilling a geothermal steam well at the Geysers Geothermal Project in California. Included also is test data describing the effectiveness of two processes that abate the emissions with use of various chemicals.

The work was carried out by the Geothermal Division of Union Oil Company and the Industrial Chemical Group of F.M.C. Tests were conducted on five wells drilled by Union-Magma-Thermal throughout the Geysers Field from December, 1976 to April, 1977. The processes evaluated were as follows:

1. Reduction in flow rate due to the effective reduction in hole size caused by the drill string being in the well.
2. Air injected into the drill string as the circulating medium.
3. Water injected into the bleed line for particulate emission control.
4. Injection of Ammonium Hydroxide and air into the drill string.
5. Hydrogen Peroxide and Sodium Hydroxide injection into the bleed line.

CONCLUSIONS

Measurements made during the development and testing of various hydrogen sulfide abatement processes applicable to air drilling has shown the hydrogen sulfide emissions to be reduced and abated in a range of 40-68% as a result of the normal drilling practices currently used by Union Oil Company in drilling a geothermal well at the Geysers. This is due in part to the restriction of flow by the drill string in the hole, abatement from oxygen in the air which is pumped down the drill string and water which is injected into the blow line. The hydrogen sulfide emission is reduced from 34 lbs/hr to a range of 11-20 lbs/hr for a typical well (150,000 lbs/hr, hydrogen sulfide content of 225 ppm) at maximum flow rates during normal drilling activity just prior to the completion of the well.

Hydrogen sulfide abatement can be increased to a range between 49 and 73% with the use of ammonium hydroxide injected with air down the drill string. In this case, the hydrogen sulfide emission from a typical well can be reduced from 34 lbs/hr to a range of 9 to 17 lbs/hr during normal drilling operations when air is being used as the circulatory medium. The level of abatement achievable with this process may not be adequate in all cases to meet the concerns of various regulatory agencies.

Higher ranges of abatement can be realized by injecting mixtures of hydrogen peroxide and sodium hydroxide instead of ammonium hydroxide. Abatement levels as high as 98% were measured when using large quantities of these chemicals. This process may be employed independent of normal drilling activities such as air and water injection. It is effective over a wide range of hydrogen sulfide concentrations and produces salts that cannot chemically revert to hydrogen sulfide. The cost of the chemicals

required to abate the hydrogen sulfide to an emission level of 6 lbs/hr is estimated at a range of \$5,000-8,000 for a typical well.

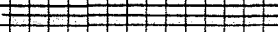
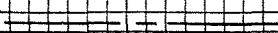

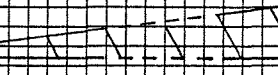
SUMMARY OF RESULTS

The range of reduction and abatement that can be achieved during the air drilling phase of operation by various processes is represented graphically in Figures 1 and 2. They represent a typical well from the Geysers Field capable of producing steam at a rate of 150,000 lbs/hr, with a field average hydrogen sulfide content of 225 ppm by weight. The top solid line represents the unabated hydrogen sulfide emissions under open flow conditions. The emission level would conceivably be zero the first day of drilling and gradually increase to a rate of 34 lbs/hr. The second line shows the effect of the restriction to the flow rate by the drilling assembly in the hole. A 20% reduction was shown on the graph because it was an actual value measured on Well "A". This effect of reduced flow rate could be as high as 58% as calculated on Well "B". The next set of lines (shaded area on Figure 1 and cross hatched area on Figure 2) represents the range of reduction and abatement of sulfide emissions by normal drilling procedures used at The Geysers. Values measured show the range to be 40 to 68% abatement. This is caused by the combination of drill pipe restriction, air injection down the drill pipe and water injection into the blowby line. This combination would lower the sulfides from 34 lbs/hr to a range of between 11 and 20 lbs/hr.

The bottom set of lines on Figure 1 represents the range of additional abatement that can be achieved by injecting ammonium hydroxide with the air into the drill string. The values measured while using ammonium hydroxide show reduction in hydrogen sulfide emissions in the range between 49 and 73%, which will reduce the emissions to a range between 9 and 17 lbs/hr for a typical well.

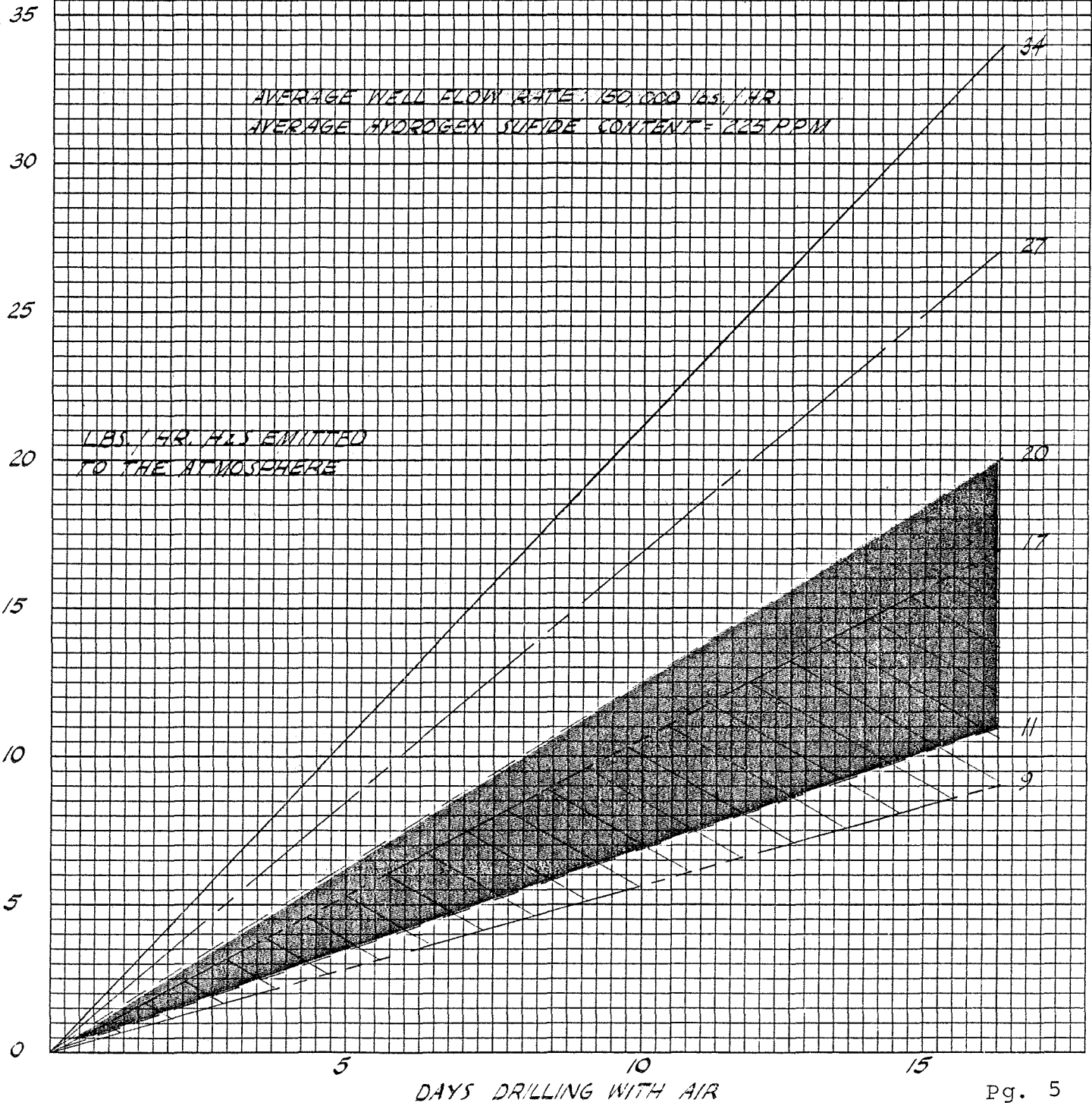
H₂S EMISSIONS DURING DRILLING

LEGEND

- 1.  UNABATED H₂S EMISSIONS UNDER OPEN FLOW CONDITIONS
- 2.  REDUCED H₂S EMISSIONS DUE TO REDUCED FLOW RATE CAUSED BY RESTRICTION OF DRILL PIPE IN HOLE.
- 3.  RANGE OF REDUCED H₂S EMISSIONS DUE TO DRILL PIPE RESTRICTION AND ABATMENT FROM AIR AND WATER INJECTION
- 4.  RANGE OF REDUCED H₂S EMISSIONS DUE TO DRILL PIPE RESTRICTION, AIR AND WATER INJECTION, AND ABATEMENT WITH NHA OR.

AVERAGE WELL FLOW RATE = 150,000 LBS./HR.
 AVERAGE HYDROGEN SULFIDE CONTENT = 225 PPM

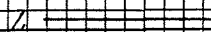
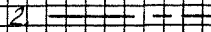
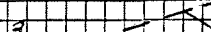
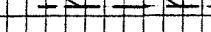
LBS./HR. H₂S EMITTED TO THE ATMOSPHERE



The bottom set of lines on Figure 2 represents the range of additional abatement that can be achieved by injecting an aqueous mixture of hydrogen peroxide and sodium hydroxide into the bleed line. The values measured while using this process show the sulfide emissions can be reduced from 34 to 0.7 lbs/hr, or 98% abatement.

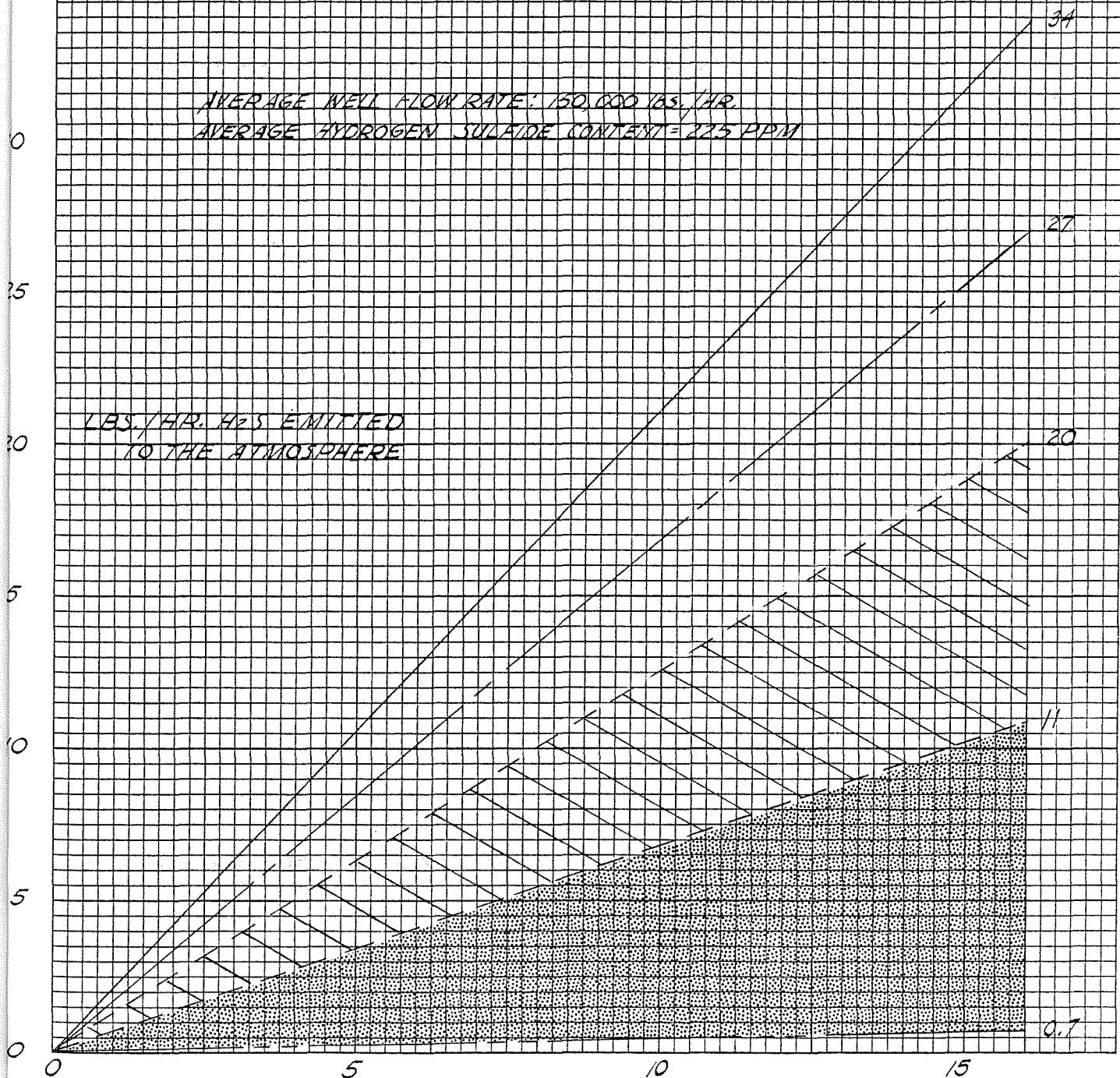
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AVERAGE WELL FLOW RATE: 150,000 LBS./HR.
 AVERAGE HYDROGEN SULFIDE CONTENT = 225 PPM

LBS./HR. H₂S EMITTED TO THE ATMOSPHERE



DISCUSSION

The drilling of a geothermal well in the vapor dominated system at the Geysers Geothermal Project consists of two distinctly different phases. The drilling of the upper portion of the hole is accomplished with conventional drilling muds and is termed the mud drilling phase. The lower portion of the hole, which penetrates the steam reservoir, is drilled without mud and air is used as the circulating medium to remove the drill cuttings from the hole. This is termed the air drilling phase and usually occurs during the last 16 days before the completion of the well. Steam is produced along with the air at increasing rates from "0" at the start of the air phase to essentially full capacity of the well at the time of completion. Hydrogen sulfide is a normal constituent of the steam and is released to the atmosphere during the air drilling phase.

Presented are processes which reduce and abate the hydrogen sulfide emissions.

Drill String Restriction to Flow

The effect of drill string restriction to flow can be easily understood by visualizing the cross-sectional flow area of the wellbore with and without drill pipe. Normally an 8-3/4" hole is drilled out from below the production casing point. The cross-sectional area of this hole is 60 square inches. The drill collars on the bottom of the drill string are usually 6" O.D., so the resultant cross-sectional flow area when the drill string is in the hole is 28 square inches, or the flow area is reduced by 47%. The actual reduction in flow rate is dependent on several factors including well depth, steam entry depth and total flow potential. A well which is capable of producing 150,000 lbs/hr from open hole may only be capable of producing 75,000 lbs/hr when the flow is restricted by the drill string. Measurements on Well "A" indicated an open hole flow rate of 170,000 lbs/hr and a flow rate

of 127,000 lbs/hr with the drill string in the hole. The measured reduction of flow rate in this case was 25%. The hydrogen sulfide measurements indicated a slightly higher concentration at the lower flow rate so the resultant reduction in H₂S emissions was 20%, as shown in Table I.

TABLE I

<u>WELL</u>	<u>DRILL STRING POSITION</u>	<u>H₂S CONC. (PPM)</u>	<u>FLOW RATE (1000 lbs/hr)</u>	<u>H₂S TO ATM. (lbs/hr)</u>	<u>PERCENT REDUCTION</u>
A	Out of Hole	83	170.0	14.1	20%
A	In Hole	89	127.2	11.3	

Had the measured sulfide content remained at the same level (83 ppm) with the drill pipe in the hole, the percent reduction would have been the same as the flow rate reduction, 25%.

Combined Effect of Reduced Flow Rate, Air and Water Injection

Several factors interact during the normal drilling activity to produce a significant reduction in hydrogen sulfide emissions. These factors include drill string restriction to flow, air injection into the drill string and water injection into the blowie line. All of these factors combined were measured on Well "B" as shown in Table II.

TABLE II

<u>WELL</u>	<u>AIR INJ. RATE (CFM)</u>	<u>WATER INJ. RATE (GPM)</u>	<u>H₂S CONC. (PPM)</u>	<u>FLOW RATE (1000 lbs/hr)</u>	<u>H₂S TO ATM. (lbs/hr)</u>	<u>PERCENT REDUCTION</u>
B	NONE	NONE	23.6	260.0	2.60	68
B	2450	50	7.5	110.3	0.83	

Effect of Air and Water Injection

Other measurements were taken to determine the effect on emissions of just the air and water injection used during the normal drilling operation. The hydrogen sulfide emission reduction measured on Well "A" was in a range of 25-34% as shown in Table III.

TABLE III

<u>WELL</u>	<u>AIR INJ. RATE (CFM)</u>	<u>WATER INJ. RATE (GPM)</u>	<u>H₂S CONC. (PPM)</u>	<u>FLOW RATE (1000 lbs/hr)</u>	<u>H₂S TO ATM. (lbs/hr)</u>	<u>PERCENT REDUCTION</u>
A	NONE	NONE	82	93.6	7.7	25
A	2570	50	62	93.6	5.8	
A	NONE	50*	93	117.5	10.9	34
A	2620	50	61	117.5	7.2	

*H₂S sample was taken from blooie line upstream of water injection.

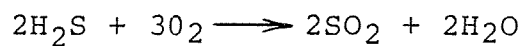
Effect of Air Injection

The abatement of hydrogen sulfide emissions attributable to just the air injected into the drill string as the circulating medium ranged from 17-44%, with the average being 24%. Measurements were made during the drilling of Well "A" and Well "C" are shown in Table IV.

TABLE IV

<u>AIR INJ.</u> <u>RATE (CFM)</u>	<u>WATER INJ.</u> <u>RATE (GPM)</u>	<u>H₂S CONC.</u> <u>(PPM)</u>	<u>FLOW RATE</u> <u>(1000 lbs/hr)</u>	<u>H₂S TO</u> <u>ATM.</u> <u>(lbs/hr)</u>	<u>PERCENT</u> <u>REDUCTION</u>
<u>WELL A</u>					
NONE	NONE	82	93.6	7.7	
2570	NONE	63	93.6	5.9	24
2570	NONE	62	93.6	5.8	
NONE	50	73	114.0	8.3	
2570	50	60.5	114.0	6.9	17
NONE	50	82	114.0	9.4	
2570	50	68	114.0	7.8	17
NONE	50	93	117.5	10.9	
2620	50	67	117.5	7.9	28
NONE	50	100	127.2	12.7	
2412	50	79	127.2	10.0	21
NONE	50	89.5	127.2	11.4	
2486	50	74	127.2	9.4	18
<u>WELL C</u>					
NONE	NONE	163	48.9	8.0	
2400	NONE	92	48.9	4.5	44

This abatement process consists of exposing the air to the hydrogen sulfide downhole in the wellbore under high temperatures and pressure. Hydrogen sulfide can be oxidized with air under these conditions as follows:



The sulfide may have been oxidized to elemental sulfur, but there was no evidence of the reaction.

Effect of Water Injection

Water injected into the blooie line for particulate control showed a low value of sulfide reduction of 9%, as shown in Table V.

TABLE V

<u>AIR INJ.</u> <u>RATE (CFM)</u>	<u>WATER INJ.</u> <u>RATE (GPM)</u>	<u>H₂S CONC.</u> <u>(PPM)</u>	<u>FLOW RATE</u> <u>(1000 lbs/hr)</u>	<u>H₂S TO</u> <u>ATM.</u> <u>(lbs/hr)</u>	<u>PERCENT</u> <u>REDUCTION</u>
<u>WELL A</u>					
2620	50*	67	117.5	7.9	9
2620	50	61	117.5	7.2	
<u>WELL C</u>					
2477	NONE	105	43.3	4.6	9
2477	10	97.5	43.3	4.2	

*Sample taken upstream of water injection point.

Part of the hydrogen sulfide physically dissolves in the water injected into the blooie line and is dropped out the bottom of the atmospheric separator to the settling sump.

The combined values of abatement from air only and water only correlates well with the combined measurements for both air and water in the range of 25-34%, as shown previously in Table III.

Rate of Water Injection Into Blooie Line

The rate of water injection into the blooie line has little effect on the hydrogen sulfide emission level. The injection rate was increased from 50 GPM to 150 GPM with no measurable decrease in sulfide emissions during a test on Well "A".

pH Modification of Water Injected
Into the Blooie Line

Increasing the pH of the injected water had no measurable effect on the sulfide emission level. The pH of the injected water was raised from 8.0 to 10.4 with no apparent effect during a test on Well "A". Sodium hydroxide was added to the blooie line injection water reservoir to obtain the desired pH increase. The molarity of this injected water was 1/100 the value of molarity of the sodium hydroxide used with hydrogen peroxide in another process discussed later.

Effect of Ammonium Hydroxide

Ammonium hydroxide is known to be effective in combating hydrogen sulfide emissions and has been used on occasions by other geothermal operators in the Geysers area. It was therefore tested by Union Oil Company by pumping various concentrations down the drill string with the air. The ammonium hydroxide was effective in reducing the hydrogen sulfide emissions below the levels normally obtained with air and water by 7 to 16% as shown in Table VI.

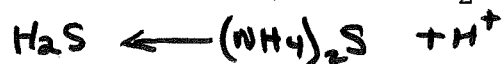
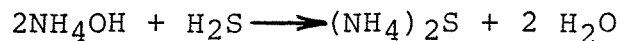
TABLE VI

<u>NH₄OH INJ.</u> <u>(lb-mole/hr)</u>	<u>H₂S CONC.</u> <u>(PPM)</u>	<u>FLOW RATE</u> <u>(1000 lbs/hr)</u>	<u>H₂S TO</u> <u>ATM.</u> <u>(lbs/hr)</u>	<u>PERCENT</u> <u>ABATEMENT</u>
<u>WELL A</u>				
NONE	74	127.2	9.4	---
0.008	69	127.2	8.7	7
0.041	62	127.2	7.9	16
0.073	63	127.2	8.0	15

Various quantities of ammonium hydroxide were mixed with a solution of water and Unisteam (a corrosion inhibitor). The solution was mixed with the air and injected down the drill pipe at high

pressures. Increasing amounts of ammonium hydroxide were used on each test until it appeared that a maximum level of abatement had been reached. This is shown in Table VI with a comparison of the third and fourth tests.

This abatement process consists of exposing the ammonium hydroxide to the hydrogen sulfide downhole in the well. Hydrogen sulfide will react with ammonium hydroxide as follows:




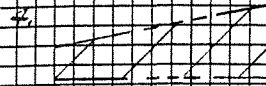



The combined effect of reduced flow rate, injection of ammonium hydroxide with air, and water injection would be in the range of 49-73% reduction in sulfide emissions (Figure 1). This level of abatement is achieved only during normal drilling operations in which air is being used as the circulatory medium. This abatement level may not be adequate to meet air pollution concerns for wells to be drilled near populated areas. The use of ammonium hydroxide may convert an atmospheric hydrogen sulfide problem to a wastewater sulfide problem. The product ammonium sulfide will regenerate hydrogen sulfide if the pH of the disposal pond is allowed to drop below 9.3.

The use of ammonium hydroxide would only be required during the last ten days of the air drilling phase of operation to maintain a minimum emission level of 6 lbs/hr or the lowest level attainable for a typical well as shown in Figure 3. The total reduction of hydrogen sulfide emissions attributable to the ammonium hydroxide in this case is 650 pounds. The cost of the chemical required to abate the hydrogen sulfide to this level is estimated to be less than \$100 for a typical well.

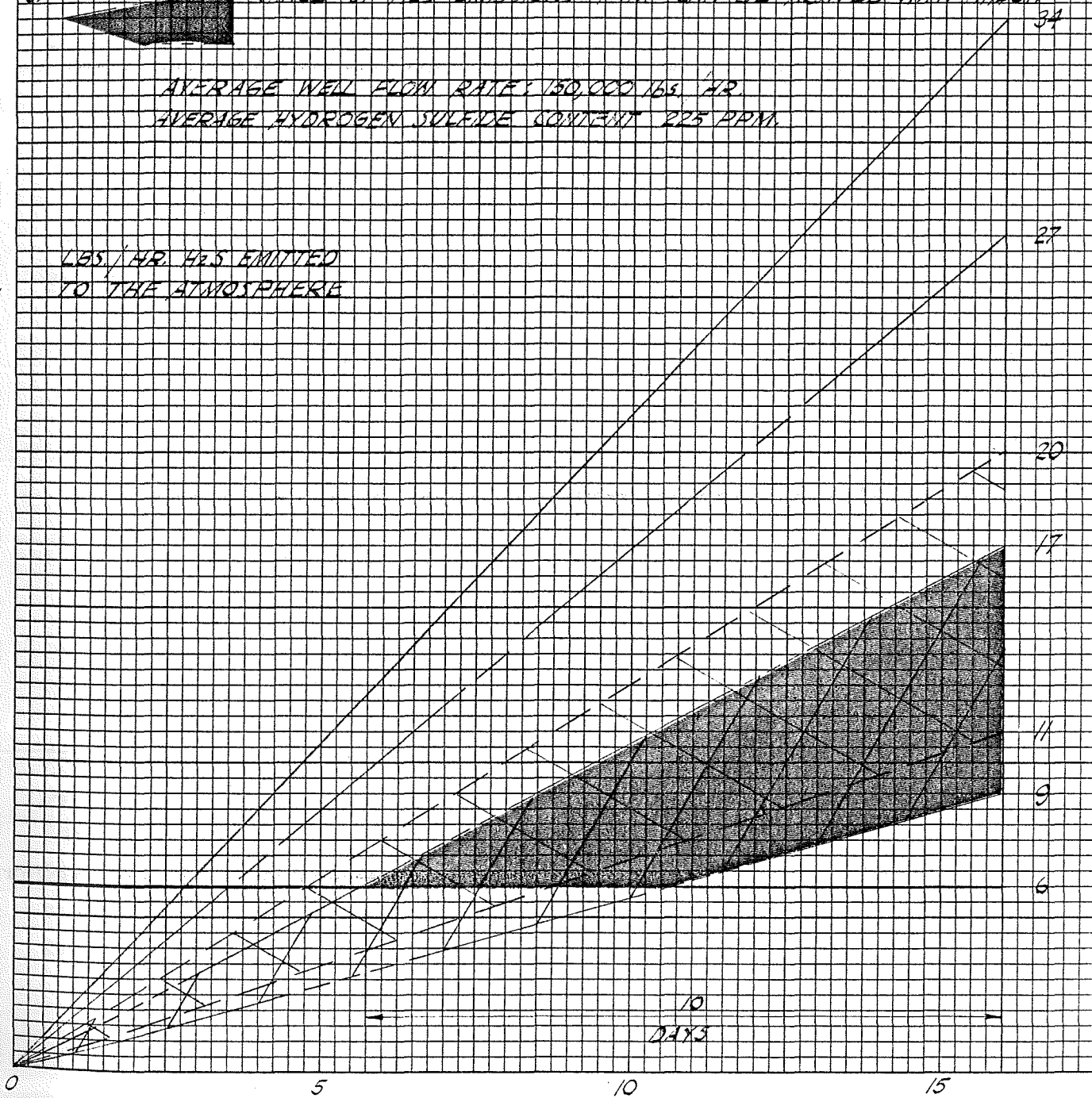
H₂S EMISSIONS DURING DRILLING

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- 4.  RANGE OF REDUCED H₂S EMISSIONS DUE TO DRILL PIPE RESTRICTION, AIR AND WATER INJECTION, AND ABATEMENT WITH NH₄OH.
- 5.  RANGE OF H₂S EMISSIONS THAT CAN BE ABATED WITH NH₄OH.

AVERAGE WELL FLOW RATE: 150,000 LBS. /HR.
 AVERAGE HYDROGEN SULFIDE CONTENT: 225 PPM.

LBS. / HR. H₂S EMITTED TO THE ATMOSPHERE



Sodium Hydroxide and Hydrogen Peroxide Injection

The use of an aqueous solution of sodium hydroxide and hydrogen peroxide to abate hydrogen sulfide was successfully demonstrated during a pilot test in August, 1976. It has since been tested successfully on a full scale basis on three wells. Various concentrations of aqueous sodium hydroxide and hydrogen peroxide were injected into the blooie line.

Abatement up to 94% attributable to just sodium hydroxide and hydrogen peroxide injected into the blooie line has been measured, as shown in Table VII.

TABLE VII

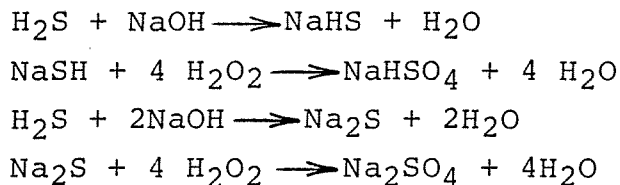
<u>AIR INJ.</u> <u>RATE (CFM)</u>	<u>WATER INJ.</u> <u>RATE (GPM)</u>	<u>H₂O₂ INJ.</u> <u>(lb-mole/hr)</u>	<u>NaOH INJ.</u> <u>(lb-mole/hr)</u>	<u>H₂S TO</u> <u>ATM.</u> <u>(lbs/hr)</u>	<u>PERCENT</u> <u>ABATEMENT</u>
<u>WELL C</u>					
2400	NONE	NONE	NONE	3.9	72
2400	NONE	0.463	0.504	1.1	
2400	NONE	NONE	NONE	4.5	78
2400	NONE	0.695	0.820	1.0	
NONE	NONE	NONE	NONE	9.4	94
NONE	NONE	0.811	0.933	0.56	
2477	10	NONE	NONE	4.2	85
2477	10	0.371	0.404	0.63	

The combined effect of injecting sodium hydroxide and hydrogen peroxide into the blooie line during normal drilling operations (drilling with air and water injection) would be in the range of 68-98% abatement or a reduction from 34 lbs/hr to a range of 11 to 0.7 lbs/hr of hydrogen sulfide (Figure 2). This range correlates well with actual measured values as shown in Table VIII.

TABLE VIII

<u>AIR INJ.</u> <u>RATE (CFM)</u>	<u>WATER INJ.</u> <u>RATE (GPM)</u>	<u>H₂O₂ INJ.</u> <u>(lb-mole/hr)</u>	<u>NaOH INJ.</u> <u>(lb-mole/hr)</u>	<u>H₂S TO</u> <u>ATM.</u> <u>(lbs/hr)</u>	<u>PERCENT</u> <u>ABATEMENT</u>
<u>WELL C</u>					
NONE	NONE	NONE	NONE	8.0	88
2400	NONE	0.695	0.820	1.0	
NONE	NONE	NONE	NONE	9.4	--
2489	NONE	0.811	0.933	0.44	95
2489	NONE	0.695	0.757	0.73	92
2489	NONE	0.579	0.631	0.81	91
2489	NONE	0.463	0.504	1.7	82

The sodium hydroxide used has a high affinity for hydrogen sulfide and the hydrogen peroxide reacts readily with the alkaline sulfide as follows:



The products of the reaction, Na₂SO₄ and NaHSO₄ will not physically revert to hydrogen sulfide. The NaOH can react with the CO₂ present in the steam to form Na₂CO₃ and NaHCO₃. The H₂O₂ can react with H₂S or the sodium sulfides to form trace amounts of S, SO₂, SO₃ and possibly thiosulfate. The H₂O₂ will oxidize the SO₂ to SO₄. It can also decompose to form oxygen and water or react with iron to form Fe₂O₃. Thus it cannot be said that x moles of NaOH and y moles of H₂O₂ reacted with z moles of H₂S in simple stoichiometric proportions.

Measurements on the steam from the atmospheric separator showed no significant pH change as a result of treatment and was free of residual hydrogen peroxide.

The use of sodium hydroxide and hydrogen peroxide would be required during the last ten days of air drilling to limit the hydrogen sulfide emission rate to 6 lbs/hr from a typical well as shown in Figure 4. The cost of chemicals required to maintain this level of abatement is estimated to be in the range of \$5,000 to \$8,000. The total reduction of hydrogen sulfide emissions attributable to the chemicals in this case is 1140 pounds.

This abatement process can be effective any time steam is vented since the sodium hydroxide and hydrogen peroxide can be injected into the blowie line on a continuous basis, independent of other drilling activities.

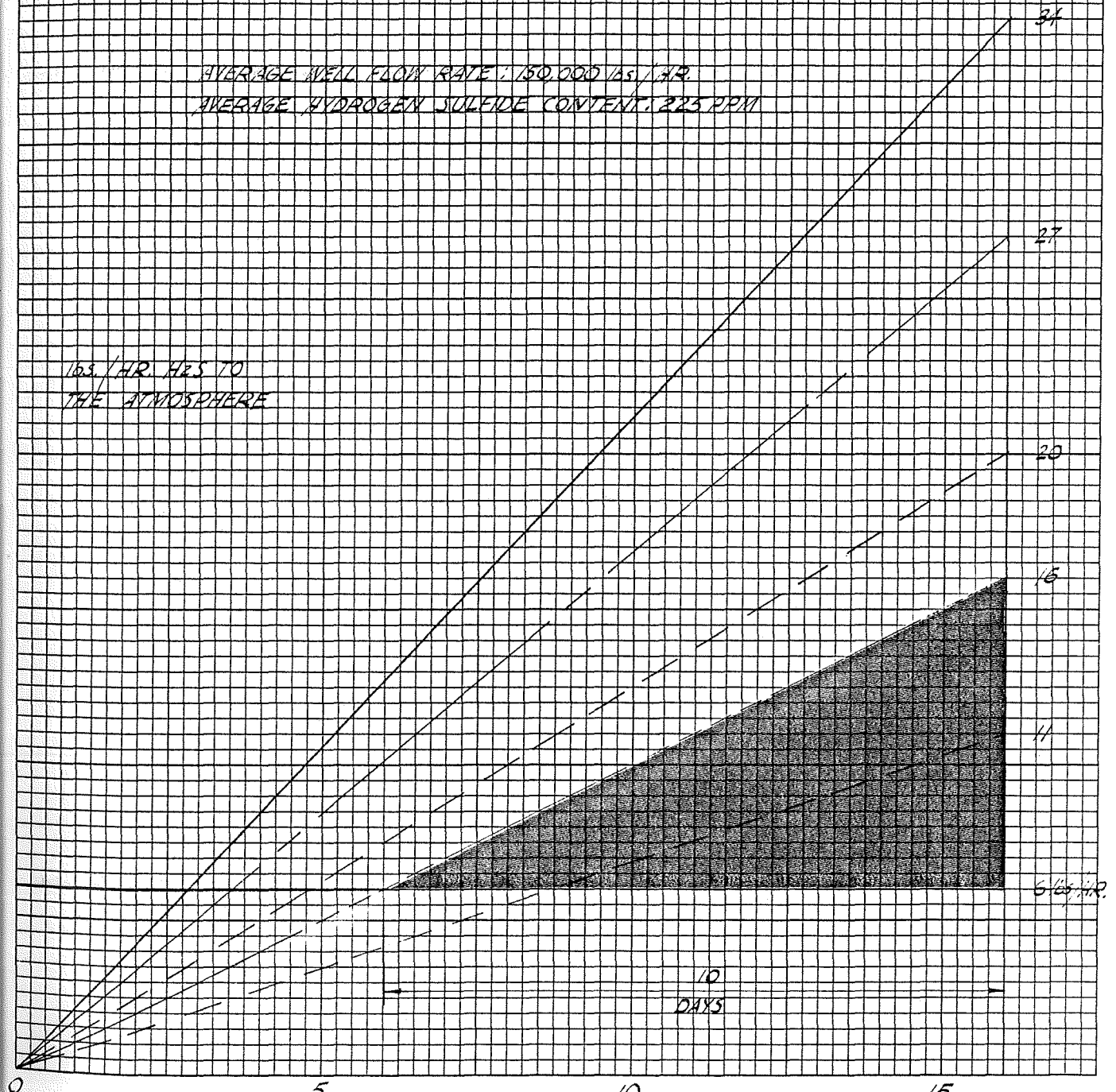
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- 4. [shaded area] RANGE OF H₂S EMISSIONS THAT CAN BE ABATED WITH H₂O₂ AND NaOH.

AVERAGE WELL FLOW RATE: 150,000 GALS/HR.
 AVERAGE HYDROGEN SULFIDE CONTENT: 225 PPM

163. /HR. H₂S TO THE ATMOSPHERE



PROCEDURE

Analytical Techniques

Drager tubes were used to measure the atmospheric hydrogen sulfide emissions in the steam during testing of Wells "C", "D", and "E". The steam was sampled in one of three ways:

1. At the top of the muffler. This yielded quite reproducible results but presented some hazard in that shifting winds occasionally resulted in exhaust steam enveloping the person taking the samples. This method was abandoned early in the test program in favor of the following modification:
2. A new sampling point was provided by a 0.38 inch hole drilled in the side of the muffler at a point seven feet above the platform and nine feet from the top of the muffler. This method and location for sampling was reproducible, convenient and safe. A few spot checks on hydrogen sulfide assays showed no difference between assays taken at the top and side of the muffler.
3. Steam was withdrawn with a peristaltic pump (Cole Parmer Model 7016) through a 0.75 inch I.D. perforated SS tube inserted into the muffler nine feet from the top. The steam was passed through a coil of Tygon tubing immersed in cold water. The tube led to a one-quart bottle where the condensables and noncondensables were separated. The noncondensables gases were passed through a Drager tube for H₂S measurements. Reproducibility required several minutes of operation under any given conditions to insure that gases from the prior test were swept out of the bottle's vapor space. This method was used primarily for spot checking the direct readings from the muffler.

The Drager tube measurements gave very reproducible results, and were used to get a relative measurement of the reduction in sulfide emissions. A Drager tube measurement was taken before any chemicals were added and during chemical injection. The two measurements were then compared to calculate the percent reduction or abatement of hydrogen sulfide.

The well-known iodometric titration method (Appendix B) was used to determine the total sulfide content during testing of Wells "A" and "C". The steam was sampled in one of three ways:

1. A steam sample was withdrawn six inches from the top of the atmospheric separator through a three foot long stainless steel probe. The probe was connected to a 1/4 inch braided stainless steel line connected to a condensing coil located on the ground. The condensing coil was then connected to the gas collection bottle described in Appendix B. This method proved to be very satisfactory because all personnel could remain on the ground, and was used throughout Well "C" testing.
2. Steam was withdrawn through a three foot long stainless steel probe at a point five feet above the platform and eleven feet from the top of the atmospheric separator. The probe was connected in the same manner as described in 1 above. (Appendix C for typical drilling setup) This method also proved to be satisfactory, and was used during some of the testing of Well "A".
3. Another sampling tap was provided about two feet downstream of the banjo box (Appendix C). A 1/4 inch stainless steel line was connected to the tap and the steam sample withdrawn from it. The 1/4 inch line was then connected to the same

condensing coil used in the two previous steps. This method was also used during the testing of Well "A".

Method three was used to acquire a sample upstream of the point on the blooie line where water is injected for particulate control. This was used to determine the effect of water injection emissions. Methods one and two were used throughout all abatement testing to determine the effect of air injection and chemical injection on the sulfide emissions. A sample was taken before there was any air injection and while there was air injection. The two measurements were compared to determine the effect. The same procedure was used to determine the effects of the various chemicals tested.

pH of the condensate from the separator and pond water was tested with pH paper. Residual hydrogen peroxide in the atmospheric steam was tested with EM Quant strips.

The steam flow rate was determined one of two ways:

1. An orifice plate was installed in the blooie line and pressure measurements were then taken upstream. The measurement was then used to calculate the flow rate.
2. Air injection rate to steam produced ratio was also used to determine the flow rate. This was accomplished by drawing a sample of steam from the blooie line and passing it through a condenser. The condensate was collected in a graduated bottle and the noncondensable gas was measured through a wet-test gas meter. It was then possible to calculate the steam flow rate by comparing the measured quantity of gas and condensate to the measured air injection rate.

APPENDIX A

WELL TEST DATA

WELL "A"

AIR INJ. RATE (CFM)	WATER INJ. RATE (GPM)	H ₂ S CONTENT		AVERAGE (PPM)	FLOW RATE (1000 lbs/Hr)	H ₂ S to ATM (lbs/Hr)	OPERATION
		FROM SEPARATOR (PPM)	FROM BLOOIE LINE (PPM)				
2570	50	51					
"	"	54.5		50	93.6	4.7	DRILLING
"	"	44					
2570	NONE	61		63	93.6	5.9	DRILLING
2570	NONE	65					
NONE	NONE	82		82	93.6	7.7	SURVEYING
2570	NONE		61	61	93.6	5.7	DRILLING
2570	59	62		62	93.6	5.8	DRILLING
NONE	50	73		73	114.0	8.3	SURVEYING
NONE	~150	85		85	114.0	9.7	SURVEYING
2570	~150	58		58	114.0	6.6	DRILLING
"	50	58		60.5	114.0	6.9	DRILLING
"	"	63					
"	"		81				
"	"		76	73		8.3	DRILLING
"	"		63				
NONE	50	64		60.5	114.0	6.9	R.I.H.*
NONE	"	57					
2570	"	61		61	114.0	6.9	REAMING
2570	50 (pH=10.4)	68		68	114.0	7.8	DRILLING
NONE	50 (pH=10.4)	76					
NONE	50 (pH=10.4)	88		82	114.0	9.4	P.O.H.*

*R.I.H. = RUNNING IN HOLE

P.O.H. = PULLING OUT OF HOLE

WELL "A"

AIR INJ. RATE (CFM)	WATER INJ. RATE (GPM)	H ₂ S CONTENT		AVERAGE (PPM)	FLOW RATE (1000 lbs/Hr)	H ₂ S to ATM (lbs/Hr)	OPERATION
		FROM SEPARATOR (PPM)	FROM BLOOIE LINE (PPM)				
NONE	50		98	93	117.5	10.9	SURVEYING
"	"		91				
"	"		91				
"	"		91				
"	"		62	67	117.5	7.9	SURVEYING
"	"		69				
"	"		70				
"	"		69				
"	"		67	61	117.5	7.2	DRILLING
"	"	61					
"	"	63					
"	"	60					
2412	50		78	79	127.2	10.0	DRILLING
2412	"		80				
NONE	"		85	100	127.2	12.7	SURVEYING
"	"		97				
"	"		102				
"	"		116				
NONE	50	82		83	170.0	14.1	OPEN HOLE (DRILL PIPE OUT OF HOLE)
"	"	85					
"	"	87					
"	"	75					
"	"	87		89	127.2	11.3	R.I.H.*
"	"	82					
"	"	90					
"	"	94					
NONE	50		94	93	127.2	11.8	P.O.H.*
NONE	50		92				

*R.I.H. = RUNNING IN HOLE

P.O.H. = PULLING OUT OF HOLE

WELL "A"

AIR INJ. RATE (CFM)	WATER INJ. RATE (GPM)	H ₂ S CONTENT			FLOW RATE (1000 lbs/Hr)	H ₂ S to ATM (lbs/Hr)	OPERATION
		FROM SEPARATOR (PPM)	FROM BLOOIE LINE (PPM)	AVERAGE (PPM)			
2486	50		74				
"	"		74	74	127.2	9.4	DRILLING
"	"		75				
"	"		67	69	127.2	8.7	DRLG. (NH ₄ OH@ 0.008 <u>lb-mole</u> Hr
"	"		71				
"	"	68		69	127.2	8.7	DRLG. (NH ₄ OH@ 0.022 <u>lb-mole</u> Hr
"	"	70					
"	"	58		62	127.2	7.9	DRLG. (NH ₄ OH@ 0.041 <u>lb-mole</u> Hr
"	"	63					
"	"	66					
"	"	64		63	127.2	8.0	DRLG. (NH ₄ OH@ 0.073 <u>lb-mole</u> Hr
"	"	63					
NONE	"	88		89.5	127.2	11.4	P.O.H.*
NONE	"	91					(NO NH ₄ OH INJ.)

*P.O.H. = PULLING OUT OF HOLE

HYDROGEN SULFIDE MEASUREMENTS

WELL "B"

AIR INJ. RATE (CFM)	WATER INJ. RATE (GPM)	H ₂ S CONTENT		FLOW RATE (1000 lbs/Hr)	H ₂ S to ATM (lbs/Hr)	OPERATION
		FROM SEPARATOR (PPM)	AVERAGE (PPM)			
2450	50	5.6	7.5	110.3	0.83	DRILLING
"	"	2.3				
"	"	2.0				
"	"	11.0				
"	"	16.7				
NONE	NONE	23.6	23.6	110.3	2.6	OPEN FLOW (Drill Pipe Out of Hole)
"	"	22.5				
"	"	22.3	23.6	260.0	6.14	
"	"	25.9				

WELL "C"

AIR INJ. RATE (CFM)	WATER INJ. RATE (GPM)	H ₂ O ₂ INJ. (lb-mole/Hr)	NaOH INJ. (lb-mole/Hr)	H ₂ S CONTENT		FLOW RATE (1000 lbs/Hr)	H ₂ S to ATM (lbs/Hr)	OPERATION
				FROM SEPARATOR (PPM)	AVERAGE (PPM)			
2400	NONE	NONE	NONE	90				
"	"	NONE	NONE	74	78	48.9	3.9	DRILLING
"	"	NONE	NONE	71				
"	"	0.463	0.504	23				
"	"	0.463	0.504	20	22	48.9	1.1	DRILLING
"	"	0.463	0.504	23				
"	"	0.347	0.441	30				
"	"	0.347	0.441	32	31	48.9	1.5	DRILLING
NONE	"	0.579	0.631	36				
NONE	"	0.579	0.631	46	41	48.9	2.0	SURVEYING
NONE	"	0.579	0.631	41				
2400	"	NONE	NONE	79				
2400	"	NONE	NONE	78	78.5	48.9	3.8	DRILLING
NONE	NONE	NONE	NONE	160	163	48.9	8.0	P.O.H.*
NONE	"	NONE	NONE	166				
2400	"	NONE	NONE	85				
"	"	NONE	NONE	99	92	48.9	4.5	DRILLING
"	"	0.695	0.820	19	19	48.9	1.0	DRILLING
"	"	0.811	0.933	25				
"	"	0.811	0.933	28	26.5	48.9	1.3	DRILLING
NONE	NONE	NONE	NONE	189				
NONE	"	NONE	NONE	194	191.5	48.9	9.4	R.I.H.*
NONE	"	0.811	0.933	10				
NONE	"	0.811	0.933	13	11.5	48.9	0.56	R.I.H.*
2489	"	0.811	0.933	9	9	48.9	0.44	DRILLING
"	"	0.811	0.933	9				
"	"	0.695	0.757	12				
"	"	0.695	0.757	18	15	48.9	0.73	DRILLING
"	"	0.579	0.631	22				
"	"	0.579	0.631	11	16.5	48.9	0.81	DRILLING
"	"	0.463	0.504	38				
"	"	0.463	0.504	32	35	48.9	1.7	DRILLING

*R.I.H. = RUNNING IN HOLE

P.O.H. = PULLING OUT OF HOLE

HYDROGEN SULFIDE MEASUREMENTS

WELL "C"

<u>AIR INJ.</u> <u>RATE (CFM)</u>	<u>WATER INJ.</u> <u>RATE (GPM)</u>	<u>H₂O₂ INJ.</u> <u>(lb-mole/Hr)</u>	<u>NaOH INJ.</u> <u>(lb-mole/Hr)</u>	<u>H₂S CONTENT</u>		<u>FLOW RATE</u> <u>(1000 lbs/Hr)</u>	<u>H₂S to ATM</u> <u>²(lbs/Hr)</u>	<u>OPERATION</u>
				<u>FROM</u> <u>SEPARATOR</u> <u>(PPM)</u>	<u>AVERAGE</u> <u>(PPM)</u>			
2477	NONE	NONE	NONE	105	105	43.3	4.6	DRILLING
"	10	NONE	NONE	96	97.5	43.3	4.3	DRILLING
"	"	NONE	NONE	99				
"	"	0.371	0.404	13	14.5	43.3	0.63	DRILLING
"	"	0.371	0.404	16				
"	"	0.811	0.404	11	15.0	43.3	0.65	DRILLING
"	"	0.811	0.404	19				
"	"	0.371	0.946	13	16.5	43.3	0.71	DRILLING
"	"	0.371	0.946	20				

HYDROGEN SULFIDE MEASUREMENTS

WELL "D"

<u>AIR INJ.</u> <u>RATE (CFM)</u>	<u>WATER INJ.</u> <u>RATE (GPM)</u>	<u>H₂O₂ INJ.</u> <u>(lb. Mole/Hr)</u>	<u>NaOH INJ.</u> <u>(lb. Mole/Hr)</u>	<u>H₂S *</u> <u>CONTENT</u> <u>(PPM)</u>	<u>FLOW RATE</u> <u>(1000 lbs/Hr)</u>	<u>OPERATION</u>
2350	50	NONE	NONE	100-120	80.0	DRILLING
2350	50	3.4	0.62	82-84	80.0	DRILLING

*Measurements Taken With a Drager Tube

HYDROGEN SULFIDE MEASUREMENTS

WELL "E"

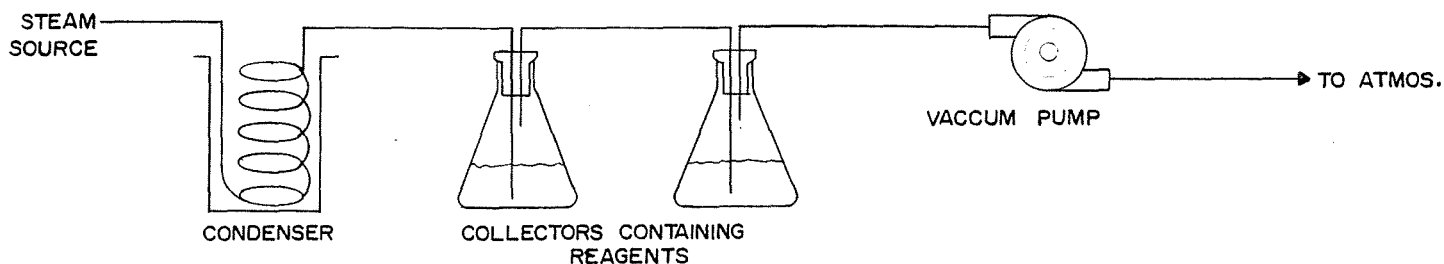
<u>AIR INJ. RATE (CFM)</u>	<u>WATER INJ. RATE (GPM)</u>	<u>H₂O₂ INJ. (lb. Mole/Hr)</u>	<u>NaOH INJ. (lb. Mole/Hr)</u>	<u>H₂S * CONTENT (PPM)</u>	<u>FLOW RATE (1000 lbs/Hr)</u>	<u>OPERATION</u>
NONE	50	NONE	NONE	400	61.6	R.I.H. **
NONE	"	3.31	1.38	40-50	"	R.I.H. **
2419	"	NONE	NONE	220	"	DRILLING
"	"	0	1.04	100	"	"
"	"	0	0.69	180	"	"
"	"	1.26	0.69	50-80	"	"
"	"	2.92	0.69	50-100	"	"
2520	50	NONE	NONE	240	70.8	DRILLING
"	"	3.31	NONE	120	"	"
"	"	0	1.85	100	"	"
"	"	3.31	1.85	10	"	"
"	"	1.66	1.85	40	"	"
"	"	0.53	1.85	50	"	"
"	"	0.53	2.77	10	"	"
"	"	0	2.77	40	"	"
"	"	3.31	0.92	40	"	"
2520	50	NONE	NONE	220	"	"
"	"	0	0.37	170	"	"
"	"	3.31	0.37	100	"	"
"	"	3.31	0.37	140-180	"	"
"	"	0	0.37	200	"	"
"	"	3.31	0.37	100-130	"	"
2450	50	NONE	NONE	205-200	74.7	DRILLING
"	"	1.68	0.37	110	"	"
"	"	1.68	2.10	35	"	"
"	"	6.63	0.37	100	"	"

* MEASUREMENTS TAKEN WITH A DRAGER TUBE

**R.I.H. = RUNNING IN HOLE

APPENDIX B

For the determination of hydrogen sulfide, a 1-quart bottle containing a weighed volume (approximately 100 ml) of 15% neutral cadmium sulfate or cadmium chloride is placed in the sample train shown below. Condensate and gas contact this solution after passing through an immersed glass frit and hydrogen sulfide is quantitatively removed from both phases.



Sampling continues until approximately 100 ml of condensate has been collected. (A second "check flask" of cadmium sulfate or cadmium chloride can be used in a series to make certain there is no H_2S carry-over). The bottles are then removed from the train, weighed, and analyzed. The analysis procedure consists of adding excess standard iodine, acidifying and back titrating with standard thiosulfate. Care must be taken to include any cadmium sulfide adhering to the glass frit in the analysis.

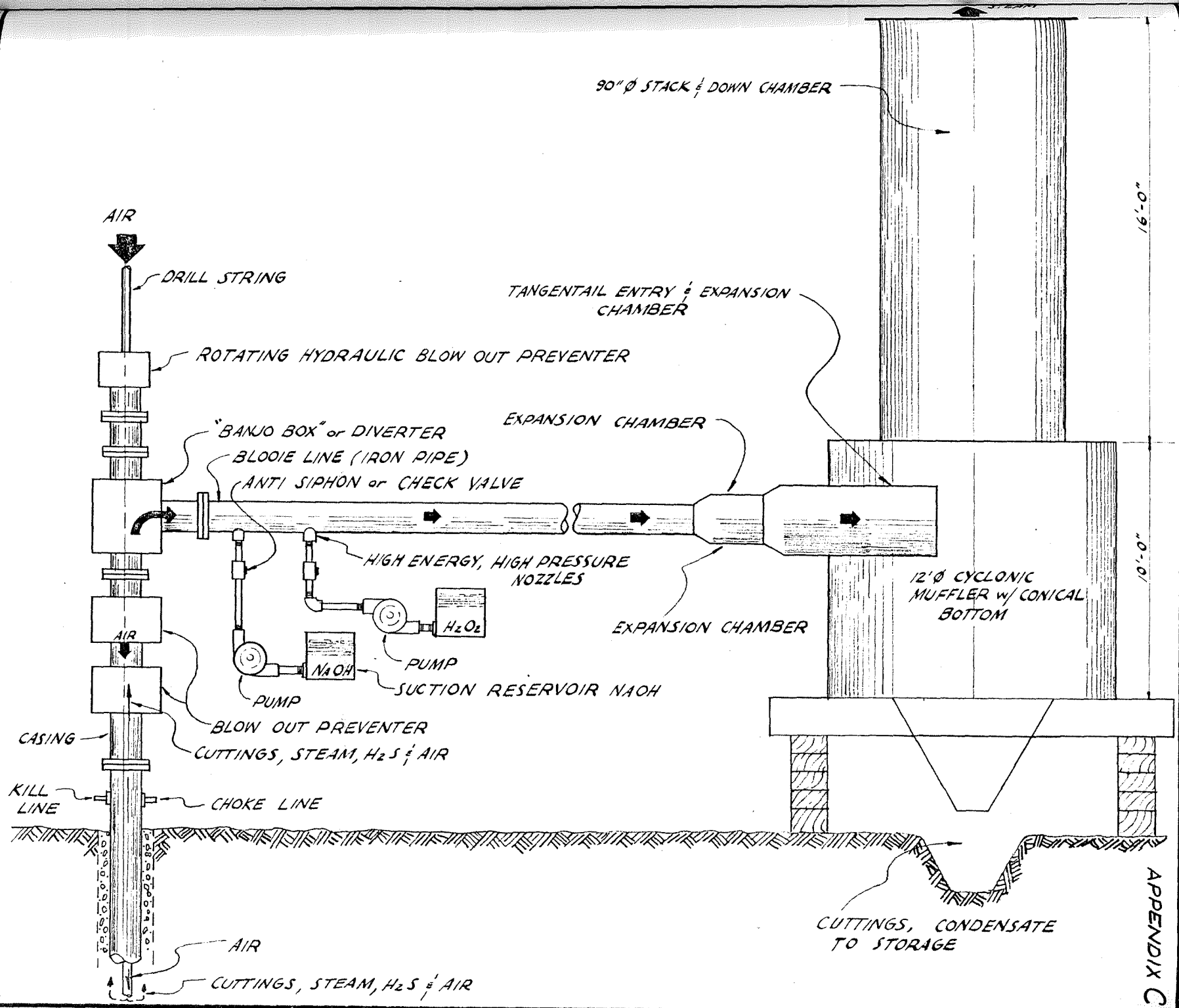
REVISED DATE

UNION OIL COMPANY OF CALIFORNIA - GEOTHERMAL DIVISION
 H₂S ABATEMENT PROCESS TYPICAL EQUIP.
 THE GEYSERS SONOMA CO. CALIF.

UNION

FOR: L.H.
 BY: L.D.C.
 DATE: 5-16-77
 SCALE: NONE
 DRAWING NUMBER 1338

DRAWN



4'-0"-9/1

4'-0"-0/1

APPENDIX C

HYDROGEN PEROXIDE/SODIUM HYDROXIDE PROCESS
for
HYDROGEN SULFIDE EMISSION
ABATEMENT

BY:

Larry R. Hampshire
Union Oil Company
Geothermal Division
Santa Rosa, California

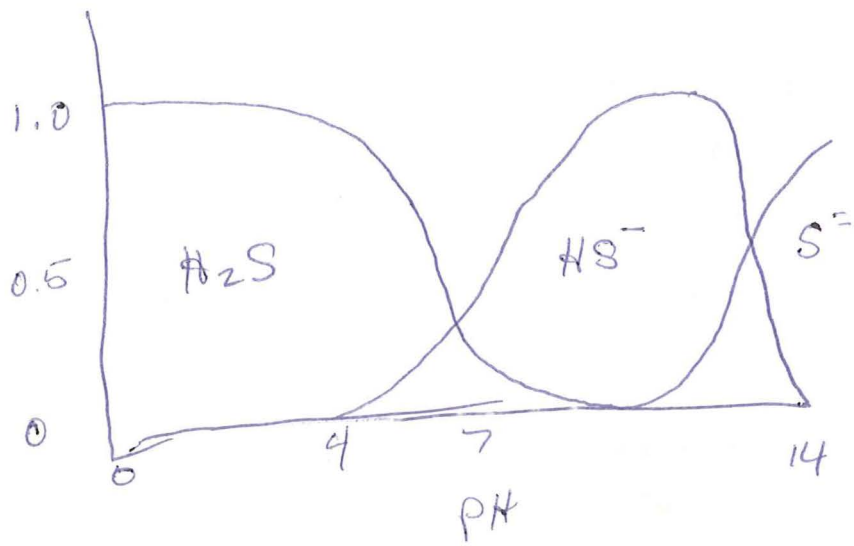
Byron B. Woertz
Union Oil Company
Research
Brea, California

Harry M. Castrantas
F.M.C. Corporation
Industrial Chemical Group
Research and Development
Princeton, New Jersey

August 10, 1977

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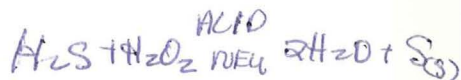
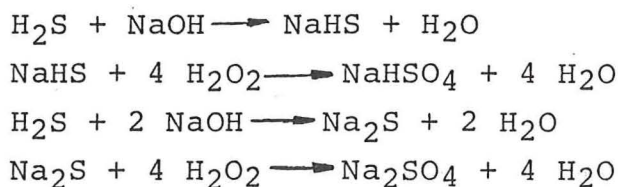
INTRODUCTION

This report describes a process used to abate hydrogen sulfide emissions during geothermal well drilling using aqueous hydrogen peroxide and sodium hydroxide. Abatement levels as high as 94% attributable to just the chemicals were measured during the development and testing of this process. Included also is the physical setup and sampling procedure for hydrogen sulfide emissions during the drilling of a geothermal steam well.

CHEMISTRY OF THE ABATEMENT PROCESS

The abatement process consists of simultaneous injection of aqueous hydrogen peroxide and sodium hydroxide solutions into the blowline through two separate spray nozzles.

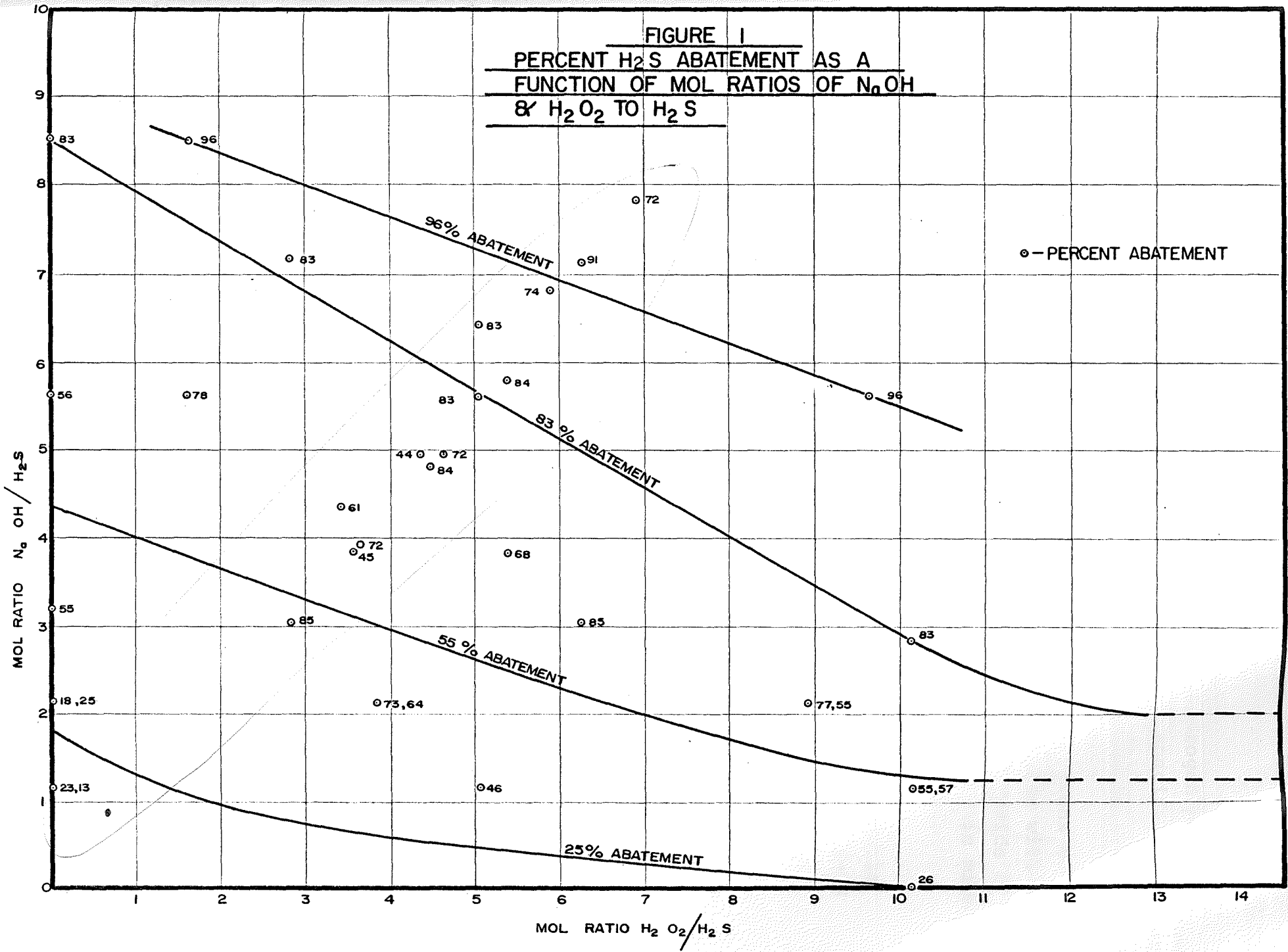
Sodium hydroxide has a high affinity for hydrogen sulfide and the hydrogen peroxide reacts readily with the alkaline sulfide as follows:



The products of the reaction, Na_2SO_4 and NaHSO_4 will not revert to hydrogen sulfide. At less than stoichiometric amounts, the H_2O_2 can react with H_2S or the sodium sulfides to form trace amounts of S , SO_2 ; SO_3 and possibly thiosulfate. It can also decompose to form oxygen and water or react with iron to form Fe_2O_3 . The NaOH can react with the CO_2 present in the steam to form Na_2CO_3 and NaHCO_3 . Thus it cannot be said that x moles of NaOH and y moles of H_2O_2 react with z moles of H_2S in simple stoichiometric proportions.

The steam from the atmospheric separator showed no significant pH change as a result of treatment and it was free of residual hydrogen peroxide.

FIGURE 1
PERCENT H₂S ABATEMENT AS A
FUNCTION OF MOL RATIOS OF N₂O₄
& H₂O₂ TO H₂S



Experimental data indicates that a wide range of hydrogen peroxide to sodium hydroxide ratios can be used to achieve a specific hydrogen sulfide abatement level.

The most efficient mix appears to approach equal proportions of each chemical. Mixes using predominantly hydrogen peroxide will be more expensive. Mixes using predominantly sodium hydroxide are more economical, but hydrogen sulfide absorbed by the caustic might disabsorb in the sump, if not oxidized by hydrogen peroxide.

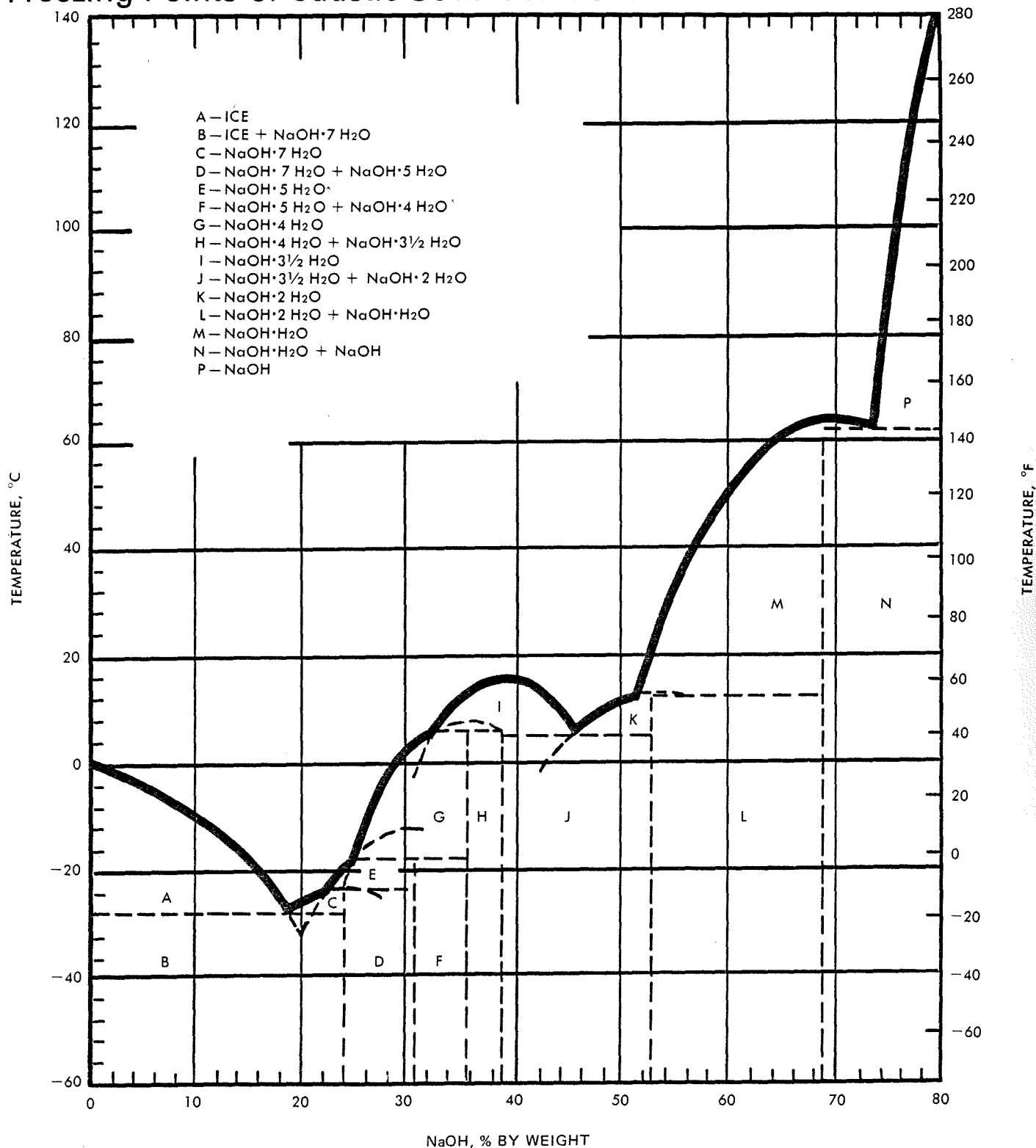
Figure 1 is a graph of actual test measurements on several wells showing percent of abatement as a function of mole ratios of NaOH and H_2O_2 to H_2S . The higher the abatement desired, the greater the chemical consumption.

Mole ratios of 4.75 to 1.00 moles of NaOH to H_2S and 4.50 to 1.00 of H_2O_2 to H_2S are the most practical for purposes of pump sizing and chemical consumption.

During the development of the process, 50% by weight commercial hydrogen peroxide was used and is recommended for full time use. 50% by weight sodium hydroxide was used but is not recommended for full time use because crystals will form in the solution below 50°F (See Figure 2). A concentration of 25-30% is recommended to prevent crystallization. Sodium hydroxide can be purchased in 50% by weight solution and diluted to the desired concentrations.

An example concentration is shown for obtaining the chemical injection rate knowing the hydrogen sulfide emission rate. The calculation is for an average well with an open hole flowrate of 150,000 LB/HR with 225 ppm by weight hydrogen sulfide content. The reduction in sulfide emissions due to the reduced flowrate is 25% and is 30% due to the abatement from air as the circulatory medium (based on actual measured values).

Freezing Points of Caustic Soda Solutions



NOTE:

THE CURVE INDICATES THE POINT AT WHICH CRYSTALS EXIST IN CONTACT WITH SOLUTION.
 From T. P. HOU, Manufacture of Soda Ash, 2nd Ed. N.Y., Reinhold Publishing Corp., 1942.
 From Industrial Engineering Chemistry Vol. 46, #11, p. 2401.

H₂S emission rate during normal drilling conditions:

$$150,000 \text{ LB/HR} \times \frac{225 \text{ PARTS H}_2\text{S}}{10^6 \text{ PARTS}} \times 1-.25 \times 1-.30 = 17.7 \text{ LB/HR}$$

Moles ratios of 4.75 to 1.00 moles of NaOH to H₂S and 4.50 to 1.00 of H₂O₂ to H₂S will reduce this sulfide emission rate of 17.7 LB/HR by 75% or to a value of 4.4 LB/HR.

NaOH pump rate required:

$$\left(17.7 \frac{\text{lb. H}_2\text{S}}{\text{HR}} \right) \left(\frac{1 \text{ lb. MOLE H}_2\text{S}}{34.08 \text{ lbs. H}_2\text{S}} \right) \left(\frac{4.75 \text{ lb. MOLE NaOH}}{1 \text{ lb. MOLE H}_2\text{S}} \right) \left(\frac{40 \text{ lb. 100\% NaOH}}{1 \text{ lb. MOLE NaOH}} \right) \left(\frac{1 \text{ GAL 30\% NaOH}}{3.325 \text{ lb. 100\% NaOH}} \right)$$

$$= 29.7 \text{ GAL./HR. OF 30\% NaOH}$$

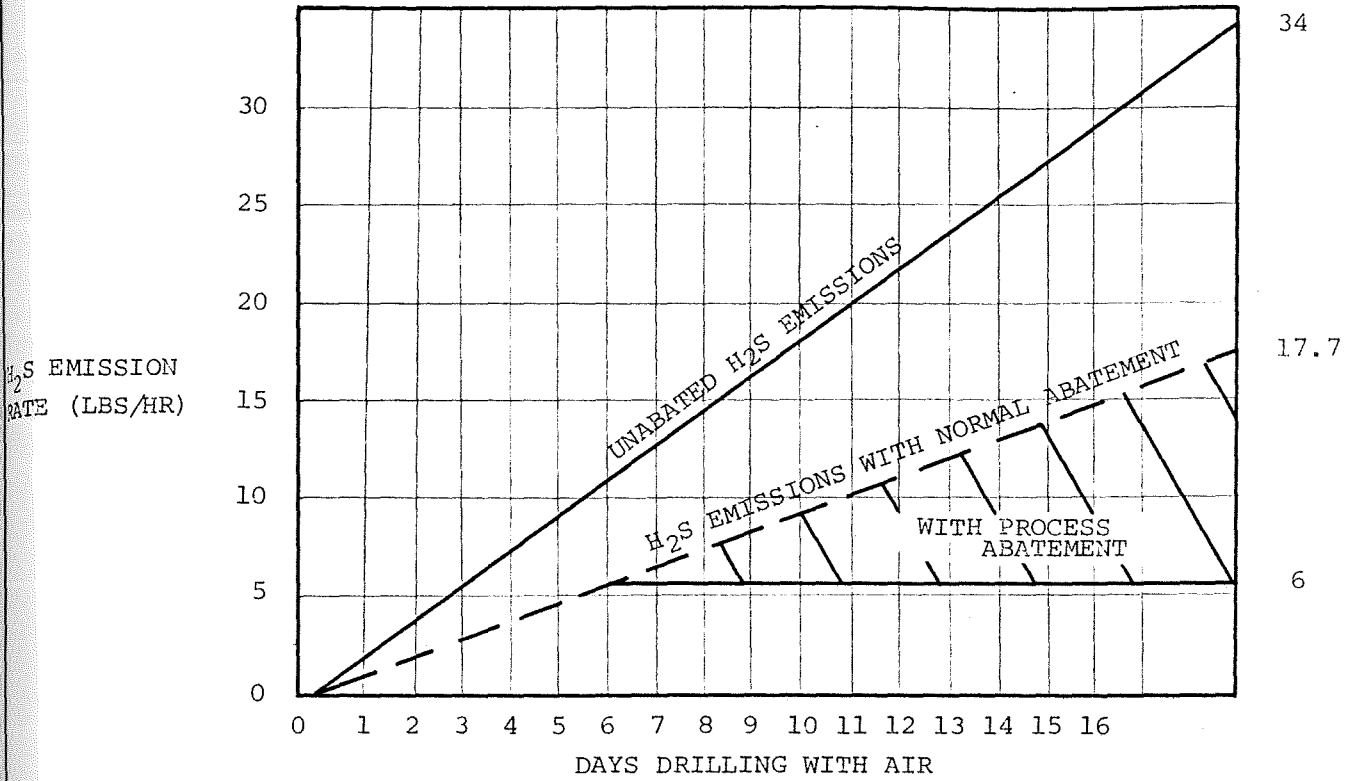
H₂O₂ pump rate required:

$$\left(17.7 \frac{\text{lb. H}_2\text{S}}{\text{HR}} \right) \left(\frac{1 \text{ lb. MOLE H}_2\text{S}}{34.08 \text{ lb. H}_2\text{S}} \right) \left(\frac{4.5 \text{ lb. MOLE H}_2\text{O}_2}{1 \text{ lb. MOLE H}_2\text{S}} \right) \left(\frac{34.02 \text{ lb. 100\% H}_2\text{O}_2}{1 \text{ lb. MOLE H}_2\text{O}_2} \right) \left(\frac{1 \text{ GAL 50\% H}_2\text{O}_2}{5.0 \text{ lb. 100\% H}_2\text{O}_2} \right)$$

$$= 15.9 \text{ GAL./HR. OF 50\% H}_2\text{O}_2$$

The above calculations show the pump rates required the last day of drilling the well when the flowrate is maximum. The pumping rates would be zero the first few days of air drilling and would gradually be increased as more steam is encountered. A hypothetical treating program is shown in the following page. The estimated cost of the chemicals for this hypothetical case is \$14,000. The previously reported abatement chemical cost range was \$5,000-\$8,000 for a well with conditions similar to the hypothetical well above. The difference between the previous range and the \$14,000 shown above is accounted for by the estimated time the well is shut-in for running casing or changing bottom hole assemblies during which there would be no emissions and therefore no need for chemical injection.

H₂S EMISSIONS DURING DRILLING



HYPOTHETICAL WELL TREATING PROGRAM

DAYS ON AIR	STEAM FLOW RATE 1 (1000 LBS/HR)	H ₂ S EMISSIONS (LBS/HR)			CHEMICAL FLOWRATE (GPHr)	
		UNABATED	NORMAL ABATEMENT ₂	PROCESS ABATEMENT	H ₂ O ₂ ₃	NaOH ₄
1	0	0	0	0	0	0
2	10	2.3	1.2	1.2	0	0
3	20	4.6	2.4	2.4	0	0
4	30	6.9	3.6	3.6	0	0
5	40	9.2	4.8	4.8	0	0
6	50	11.5	6.0	6.0	0	0
7	60	13.8	7.3	6.0	1.5	2.6
8	70	16.1	8.5	6.0	2.6	3.9
9	80	18.4	9.7	6.0	3.9	6.8
10	90	20.7	10.9	6.0	4.9	9.6
11	100	23.0	12.1	6.0	6.6	11.7
12	110	25.3	13.4	6.0	8.0	15.4
13	120	27.6	14.5	6.0	9.4	19.2
14	130	29.9	15.7	6.0	11.8	22.2
15	140	32.2	16.9	6.0	12.6	25.3
16	150	34.0	17.7	6.0	15.9	29.7

1. STEAM FLOWRATE UNDER OPEN FLOW CONDITIONS
2. H₂S EMISSION REDUCTION DUE TO DRILL PIPE RESTRUCTION AND ABATEMENT FROM AIR AND WATER
3. H₂O₂ 50% BY WEIGHT
4. NaOH 30% BY WEIGHT

PROCEDURES AND FACILITIES

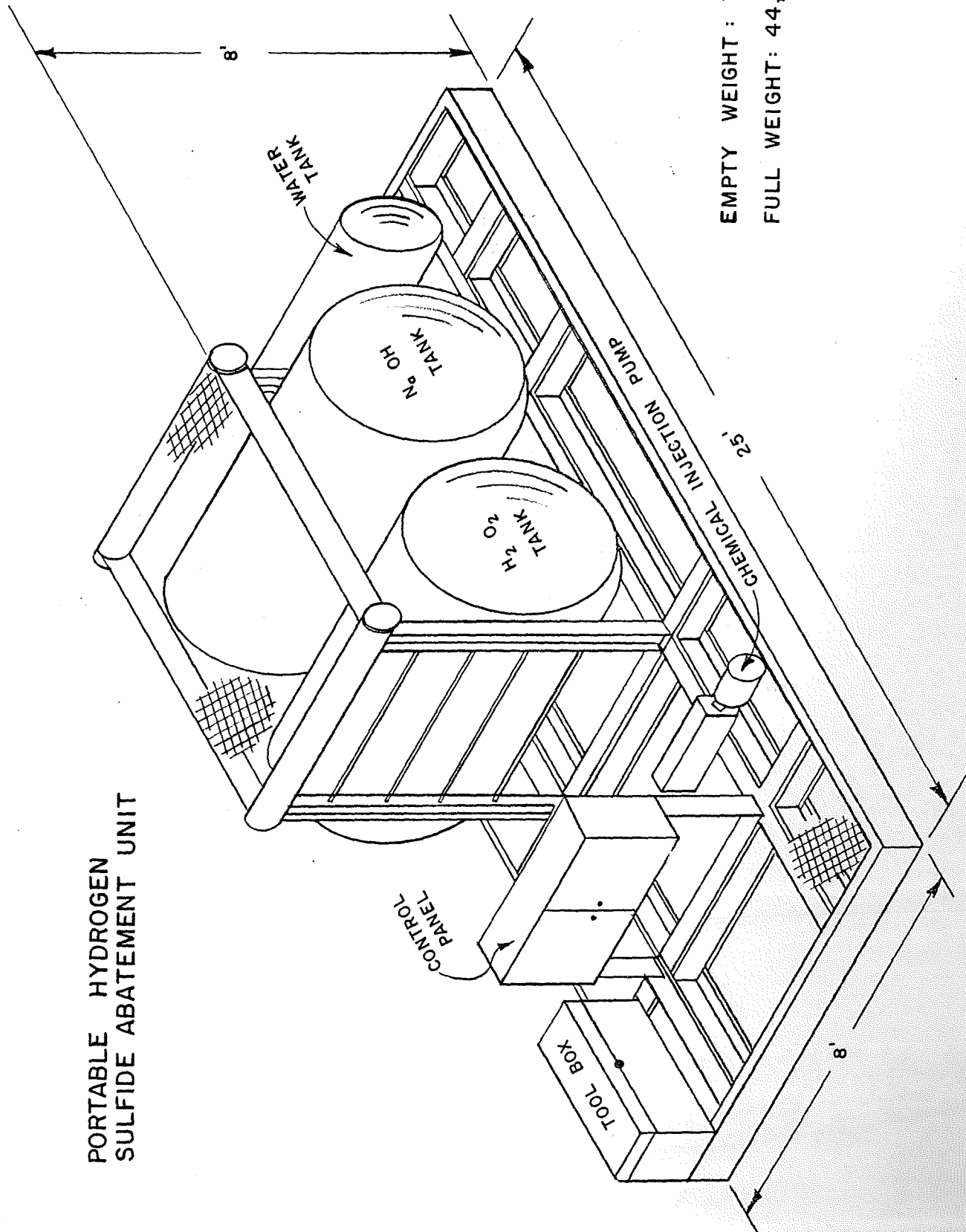
The hydrogen sulfide abatement system consists of chemical storage tanks, chemical injection pumps, spray nozzles, blooie line, blooie line expander tube, atmospheric separator, and the valves and piping necessary to connect the major components. Drawing No. 1350 shows a portable skid with all the chemical handling equipment consolidated into one package. Included on the skid is one 1800 gal hydrogen peroxide storage tank, one 1500 gal sodium hydroxide tank, one 100 gal water storage tank, one sodium hydroxide circulating pump, and two chemical feed pumps. The dimensions of the skid are 8'x25' and the weight full is about 44,000 pounds, empty 7000 pounds. The chemical storage capacity on this skid is sufficient to abate the hydrogen sulfide emissions from a typical geothermal well to a 6#/hr limit throughout the drilling phase. The skid is sized so that it can be easily moved from one drilling location to another, and the chemical storage tank capacity is great enough to accept partial truckload shipments.

The portable skid should be situated at the drill site in an area safe from falling objects and remote from high levels of activity. One suggested area is at the far end of the catwalk and pipe racks. Two injection lines can be run from the skid, under the catwalk to the spray nozzles located in the blooie line near the banjo box. Hookup can be easily facilitated by using sets of flexible stainless steel braided lines at the skid and at the spray nozzles. Figure 3 shows a suggested layout for a typical drilling location.

Figure 4 shows a schematic of a recommended system. The following pages cover a detailed description of each of the components in the system. The abatement injection system consists of two separate injection systems, one for each chemical. The chemicals must be kept separate until injection into the blooie line to avoid rapid decomposition of hydrogen peroxide. A water storage tank is included on the skid so each injection system can be easily flushed when use of the chemicals is terminated.

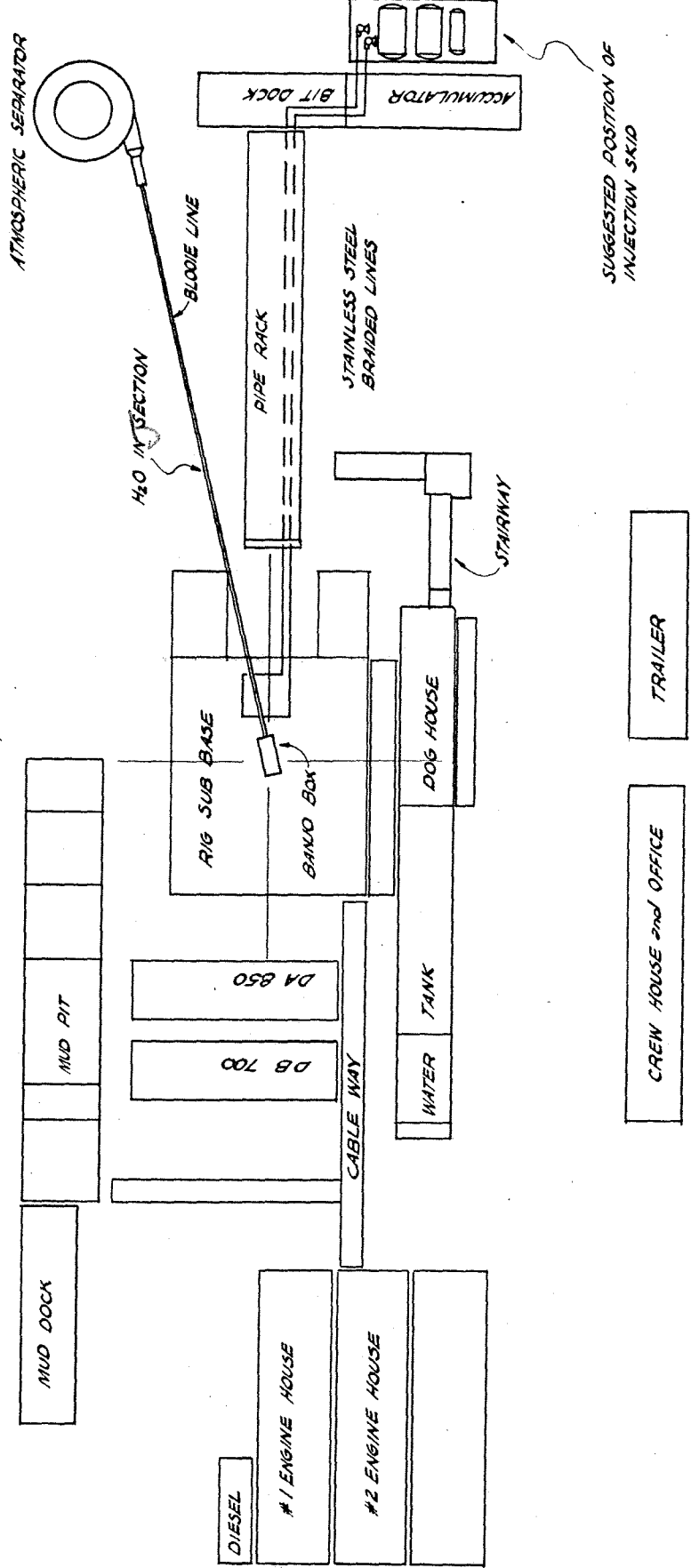
The injection spray nozzles on the blooie line should be located close to the banjo box to ensure adequate contact time between the hydrogen sulfide and the chemicals. They should be located on the top of the blooie line diametrically opposing with a 30° angle between them.

PORTABLE HYDROGEN
SULFIDE ABATEMENT UNIT



EMPTY WEIGHT : 7000 lbs.

FULL WEIGHT: 44,000 lbs.



REVISED	DATE

UNION 76

UNION OIL COMPANY OF CALIFORNIA - GEOTHERMAL DIVISION

TYPICAL RIG LAYOUT-FIGURE 3

DRAWN
FOR: L. H.
BY: L.D.C.
DATE: 7-22-77
SCALE: NONE
DRAWING NUMBER 1354

HYDROGEN PEROXIDE (H₂O₂) SYSTEM:

The hydrogen peroxide storage tank should be made of 5254 aluminum alloy. The tank should be equipped with splash baffles, rupture discs and a vent to the atmosphere fitted with a 50 micron filter. The filter serves to keep contaminants out of the hydrogen peroxide. Stainless steel of the 300 series can be used for the injection system. The injection system must contain a check valve to prevent backflow of hydrogen peroxide into the storage tank. The system should contain a pulsation dampener to obtain a steadier flow to the spray nozzles, a pressure gauge, pressure relief valve, and a sampling port downstream of the chemical pump to check the flowrate.

SODIUM HYDROXIDE (NaOH) SYSTEM:

The sodium hydroxide injection system should contain essentially the same components as the hydrogen peroxide system, except that mild steel may be used in place of aluminum and stainless steel. The line from the sodium hydroxide storage tank to the chemical feeder pump should have an inline filter in it to catch any particles that could plug the spray nozzles or foul the pump check valves. The storage tank should have a circulation pump to keep the sodium hydroxide agitated. The agitation will be needed when diluting the sodium hydroxide from 50% concentration to a range of 25-30%.

WATER INJECTION SYSTEM:

The water storage system should be connected to each chemical injection system in order to flush all lines free of residual chemicals. The line leading from the water storage tank to each chemical feeder pump should contain an inline filter to keep the spray nozzles from plugging.

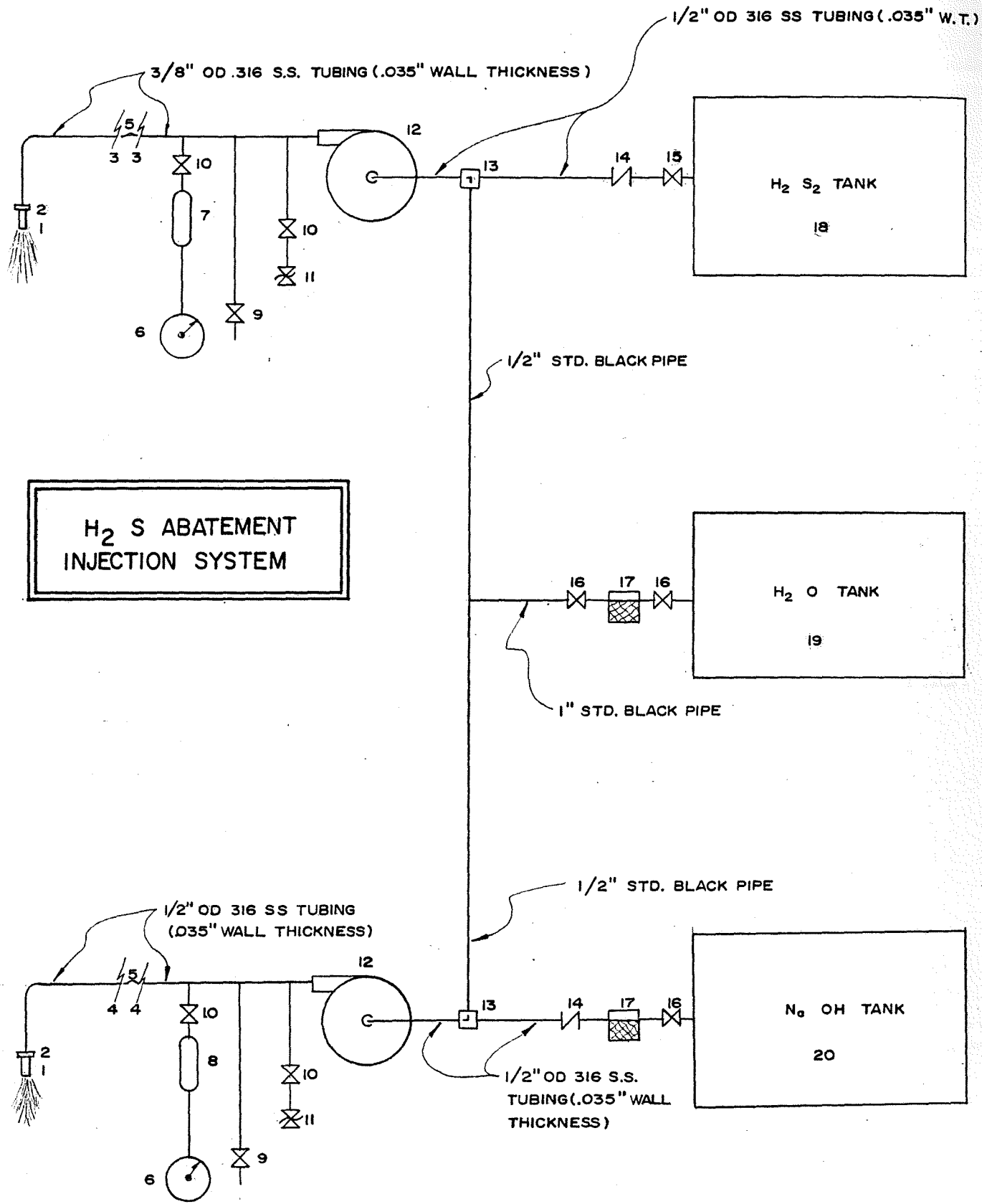


FIGURE 4

systems cost \$218,000

H₂S ABATEMENT INJECTION SYSTEM

1. 1/8 G5 full cone spray pattern spray nozzle available from Spraying Systems Company. Represented by: Thomas G. Kilfoil Co. (415) 583-7242
NOTE: It is recommended that smaller size spray nozzles be avoided to prevent clogging. Using a larger spray nozzle will decrease the effectiveness of the chemicals. The injection pressure should be 20-50 Psig when attainable using reasonable equipment and operating conditions.
2. Converted 1/2" valve bonnet to allow adjustment height of spray nozzle. Spray nozzle should not be located in the mainstream of blooie line because of the severe erosion problem.
3. 3/8" quick connect couplers.
4. 1/2" quick connect couplers.
NOTE: Size of couplers are different to avoid wrong connections.
5. No. 6 stainless steel braided, Teflon coated inside, flexible hose.
6. 0-200 psi oil filled pressure gauge.
7. 316 Stainless steel pulsation dampener 1/3 FT³ size with a Viton or Teflon bag.
8. Pulsation dampener 1/3 FT³ size, can be carbon steel.
9. 316 stainless steel valve. This valve is provided for taking a sample of chemicals and for checking injection flowrate.
10. 316 stainless steel valve.

11. 316 stainless steel pressure relief valve. Set at 165 psi to protect injection pumps and system.
12. Chemical injection pump.
Recommend Pulsa 7120 with stainless steel reagent head, stainless steel valve seats and Teflon diaphragm. Adjustable capacity from 4.2 to 42 G.P.H. Available from Milton S. Frank Co., Inc. (415)391-7650
13. 1/2"-316 stainless steel 3-way ball valve.
14. 1/2"-316 stainless steel check valve.
15. 1/2"-316 stainless steel valve.
16. 1" - carbon steel valve.
17. 1" inline stainless steel strainer. Recommend Sarco Type AT-1" with 40 mesh filter screen.
18. 1800 gallon 6'-6" diameter horizontal 5254 aluminum storage tank for H₂O₂. Available from Schwabel Fabricating Co., Inc., 349 Sawyer Ave., Tonawanda, New York. Additional information and plans for such items as sight glasses available from F.M.C., Industrial Chemical Group.
19. 100 gallon carbon steel water tank. This tank will be used for water storage for flushing the injection systems.
20. 1500 gallon 6'-0" dia. x 8'-0" high carbon steel storage tank for NaOH. Available from Natco Process Equipment (918) 663-9100.

CHEMICAL HANDLING

Hydrogen Peroxide

Shipping - FMC hydrogen peroxide is shipped to customers in drums, tank trucks, and tank cars. It is classified by the D.O.T. as "oxidizer" (yellow label).

The standard drum containers are 15, 30 and 55 gallon sizes. These are polyethylene-lined fiber or steel overpack drums. In the 30 gallon size an aluminum returnable drum is also used. Special drum rockers, bung wrenches, valves and pouring spouts are available. Complete information on drum handling and auxiliary equipment is available on request.

A fleet of FMC owned-and-operated trucks, strategically located throughout the country, provides customers with prompt tank truck deliveries of all concentrations of hydrogen peroxide. The trucks meet MC310 specifications and have a capacity up to 4000 gallons. They are equipped with pumps, hoses and fittings for attachment to customer's storage systems and are unloaded by trained FMC operators. These FMC trucks are equipped to deliver 70% H₂O₂ for subsequent dilution to 35% or 50% concentration with either tap or de-ionized water.

A special fleet of FMC owned aluminum tank cars are used for shipping hydrogen peroxide to large users. These cars range from 4000 to 17,500 gallon capacity. They conform to AAR Specifications. Specific unloading instructions are displayed in a prominent position on the dome. More detailed information is available on request.

It is important that proper unloading and storage facilities be provided at the site of the customer for receiving bulk shipments. Although brief information about the construction of such facilities is included in this manual, it is recommended that the Technical Service Engineering Department of FMC's Industrial Chemical Group

be consulted for specific recommendations. A meeting can be arranged through your local FMC sales representative.

Materials of Construction - The general recommendations that follow are based on long, practical experience in handling hydrogen peroxide. Detailed information is available on request.

For containers used in the storage and handling of H_2O_2 aluminum alloy 5254 is used. Alloy 5652 or 1060 may be substituted.

Pipe lines should be aluminum alloy 1060. Stainless steel of the 300 series may be substituted under certain conditions. Aluminum pipe should be Van-Stone flanged and welded. Screwed fittings should be kept to a minimum. Use schedule 80 (extra heavy) pipe if threads are cut into the pipe. Ordinary pipe thread lubricants or sealants must not be used. Teflon tape is suggested for sealing screwed fittings.

Valves of aluminum alloy 356 are generally used. 300 series stainless steel or porcelain valves may be used under certain conditions. Balltype valves with internal relief seals are preferred. Other type design valves of compatible materials may be used under certain conditions. When diaphragm type valves are used, Kel F or Teflon diaphragms are preferred. Any valve that may trap hydrogen peroxide must be vented in some manner to prevent pressure build-up in the valve body while the valve is closed.

Centrifugal pumps of aluminum alloy 356 or 300 series stainless steel are recommended for most installations. Mechanical seals of glass filled Teflon ceramic and 300 series stainless steel may be used. Other type packing should be Teflon. Common packing materials containing graphite, bronze, copper, lead, etc., must never be used.

Gaskets made of Koroseal 700, Kel F, or Teflon will prove satisfactory.

Hoses for unloading or handling purposes should be of 300 series stainless steel.

Proportioning pumps, flowraters, and other metering devices for delivering accurately measured quantities of hydrogen peroxide solutions will be recommended on request.

Many common engineering materials such as magnesium alloys, iron, brass and bronze, copper, lubricating oils and pipe dope must not be used due to their catalytic action or reactivity with hydrogen peroxide.

These recommendations cover commonly used materials. For information about materials and types of equipment not mentioned, please consult with the FMC Technical Service Engineering Dept.. More complete information on materials of construction and handling of hydrogen peroxide will be found in FMC's Industrial Chemical Group Technical Bulletin No. 104.

Preparation of Equipment - All equipment used in storing and handling hydrogen peroxide solutions must be thoroughly cleaned and passivated before being placed in service to insure maximum peroxide stability. FMC Technical Service Engineers should be consulted about proper passivation techniques since inadequately passivated equipment can cause wasteful and dangerous H_2O_2 decomposition.

Passivation - In general, aluminum and stainless steel should be passivated by:

- A. preliminary detergent wash to remove oil, grease, loose contaminants, etc.;
- B. thorough rinse with clean potable water, followed by draining to remove the contaminated washing medium;
- C. exposure of all parts to an acid solution (preferably nitric);

- D. another thorough rinsing and draining to remove all acid and soluble contaminants.

This procedure is described in FMC Technical Bulletin No. 104. Plastic materials such as gaskets and hoses usually require only a thorough cleaning with a detergent solution.

The size and type of facility will generally determine the specific passivating procedures to follow. In some cases, tanks, piping and other items may be passivated separately before they are installed in the storage and handling system. In other instances, it may be necessary to passivate the storage and handling equipment after installation. Auxiliary attachments, liquid level gauges, manometer type instrument components, etc., must also be thoroughly cleaned and passivated before use.

When constructed of acceptable materials and properly passivated hydrogen peroxide equipment usually does not require repassivation as long as contaminants are not introduced. FMC equipment for "in the field" passivation is available from FMC's Technical Service Engineering Department.

Storage - All concentrations of hydrogen peroxide can be shipped and stored in both drums and bulk.

FMC hydrogen peroxide shipping drums are equipped with a venting device in the drum head, and must always be stored head up, preferably on a concrete floor in a clean, cool, fireproof area away from combustible materials. A source of water should be available to wash down spillage.

Bulk Systems - Since the freezing point of hydrogen peroxide solutions are low and the boiling points are high, storage tanks can be located in the open. Owing to the nature of hydrogen peroxide, the tanks should be made of high purity aluminum alloy.

Care must be exercised during fabrication to prevent undesirable substances from becoming imbedded in the aluminum surface. It is absolutely necessary that the proper welding techniques be employed as well. Additional information on tanks for bulk storage is available in FMC's Industrial Chemical Group Bulletin No. 125.

Like any liquid, hydrogen peroxide can be transferred from one point to another by gravity flow or by pumping. Pressure or vacuum methods of transfer are acceptable but should be used with caution. All equipment used in a transfer must be made of hydrogen peroxide compatible materials. FMC Technical Service Engineers are prepared to make a complete survey of your site and needs, to provide custom design services and make proper material and equipment recommendations for bulk handling systems.

Safety Considerations - A basic understanding of the properties of hydrogen peroxide is the first step in safe handling of this chemical. Remember that solutions containing more than 8% hydrogen peroxide are classified by the D.O.T. as an oxidizer and the chemical is very corrosive. Decomposition liberates oxygen and heat. In dilute solutions the heat evolved is readily absorbed by the water present. In more concentrated solutions the heat raises the temperature of the solution and accelerates the decomposition rate. All handling procedures must be directed towards maintaining a high degree of purity.

Hydrogen peroxide should be stored only in original containers or in containers of compatible materials which have been properly designed and thoroughly passivated. Hydrogen peroxide once removed from the original container should not be returned to it. All containers must be properly vented, and preferably stored away from sources of direct heat and combustible materials. Adequate ventilation and an ample water supply for washing away accidental spillage should be provided. Fires caused by hydrogen peroxide are best controlled by using large quantities of water. The chemical itself will

not burn, but its decomposition liberates oxygen which supports combustion.

Hydrogen peroxide is not considered an explosive. However, when it is mixed with organic substances, hazardous impact-sensitive compounds may result. Small amounts of materials containing catalysts (silver, lead, copper, chromium, mercury and iron oxide rust) can cause immediate decomposition and explosive rupture of the containing vessel if it is not properly vented.

SPECIAL SAFETY NOTES

Safety goggles and plastic or rubber gloves should be worn while taking samples of aqueous effluent from the blooie line or atmospheric separator. They should also be worn while working around the chemical injection system.

Chemical injection should be stopped when the well is shut-in to prevent wastage. The sodium hydroxide injection system should be flushed to prevent clogging if chemical injection is stopped for more than a few minutes to prevent decomposition in the transfer line.

Sodium hydroxide and hydrogen peroxide should not be premixed prior to injection into the blooie line. Premixing will result in very rapid decomposition accompanied by copious oxygen and heat evolution.

NaOH

Safety

Sodium hydroxide (caustic soda) in all forms is a highly corrosive material which can cause serious burns to the eyes and skin. The prime safety consideration is to prevent or minimize bodily contact. Inhalation of sodium hydroxide mist can cause severe damage to the respiratory system. An ample supply of flowing water must be

available at the point of handling for immediate wash-off of any caustic soda that comes in contact with personnel.

Shipping

Sodium hydroxide is available in 50% by weight liquid, or 100% by weight flake or bead form. The liquid form is recommended because it does not pose the health hazards involved when dissolving the flake or bead form. The liquid form is available in 3000 gallon truck shipments or in 55 gallon drums.

Storage and Handling

Sodium hydroxide may be stored and pumped through materials made of mild steel

ANALYTICAL TECHNIQUES

Qualitative Measurement of H₂S

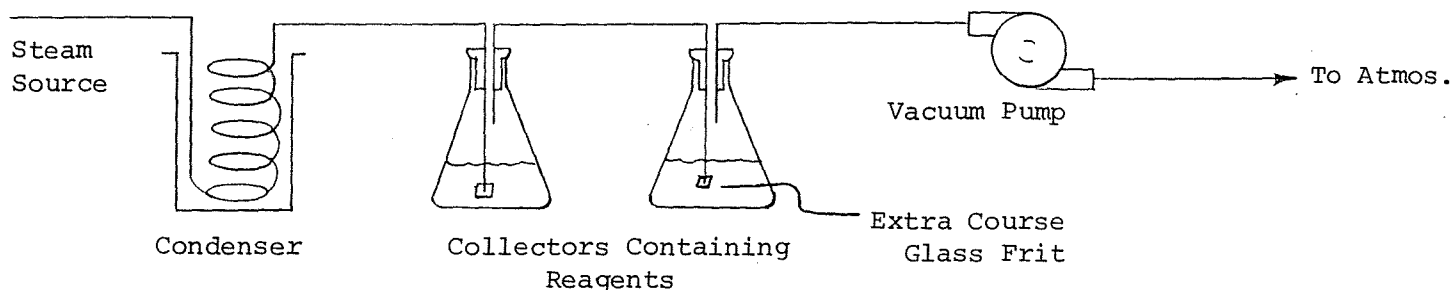
Drager tubes can be readily used to obtain relative measurements of the sulfide content in the steam. The measurements are made with and without chemical injection. The values obtained will provide a relative measurement of abatement, but they should not be construed as an absolute value of sulfide emissions. The steam may be sampled by drilling a sampling port about 3/8 inch in diameter in the side of the muffler at a point about seven feet above the platform.

This method and location for sampling is reproducible, convenient and safe. A few spot checks on hydrogen sulfide assays will show no difference between assays taken at the top and side of the muffler.

Quantitative Measurement of H₂S

To determine quantitatively the sulfide content of steam flow to the atmosphere, a representative sample must be withdrawn from either the blooie line or the atmospheric separator. Because of the required reaction time of the abatement process, it is advisable to withdraw a sample as close to the top of the atmospheric separator as possible taking care not to draw in any air while sampling.

A probe (shown in Figure 5) should be used to obtain a representative sample from the atmospheric separator. The probe is connected by quick connects to a No. 4 stainless steel line attached to a condensing coil located on the ground. The outlet of the condensing coil is connected to the scrubbing train shown below.



The collectors consist of a 1-quart bottle containing a weighed volume (approximately 100 ml) of 15% neutral cadmium sulfate or cadmium chloride. Condensate and gas contact this solution after passing through an immersed glass frit and hydrogen sulfide is quantitatively removed from both phases. Sampling should continue until approximately 100 ml of condensate has been collected. The second "bottle" of cadmium sulfate or cadmium chloride is used to make certain there is not any H_2S carry-over. If the second bottle shows any sign of sulfur by turning yellow in color, it must be titrated also using the procedure which follows. The bottles are removed from the sample train, weighed and analyzed. The analysis procedure consists of adding excess standard iodine, acidifying and back titrating with standard thiosulfate using a starch indicator. Care must be taken to include any cadmium sulfide adhering to the glass frit in the analysis.

The results should be corrected for percent non-condensibles. The percent non-condensibles are sometimes as high as 50% depending on the amount of air being used as the circulatory medium versus the amount of steam the well is producing.

SAMPLING PROBE

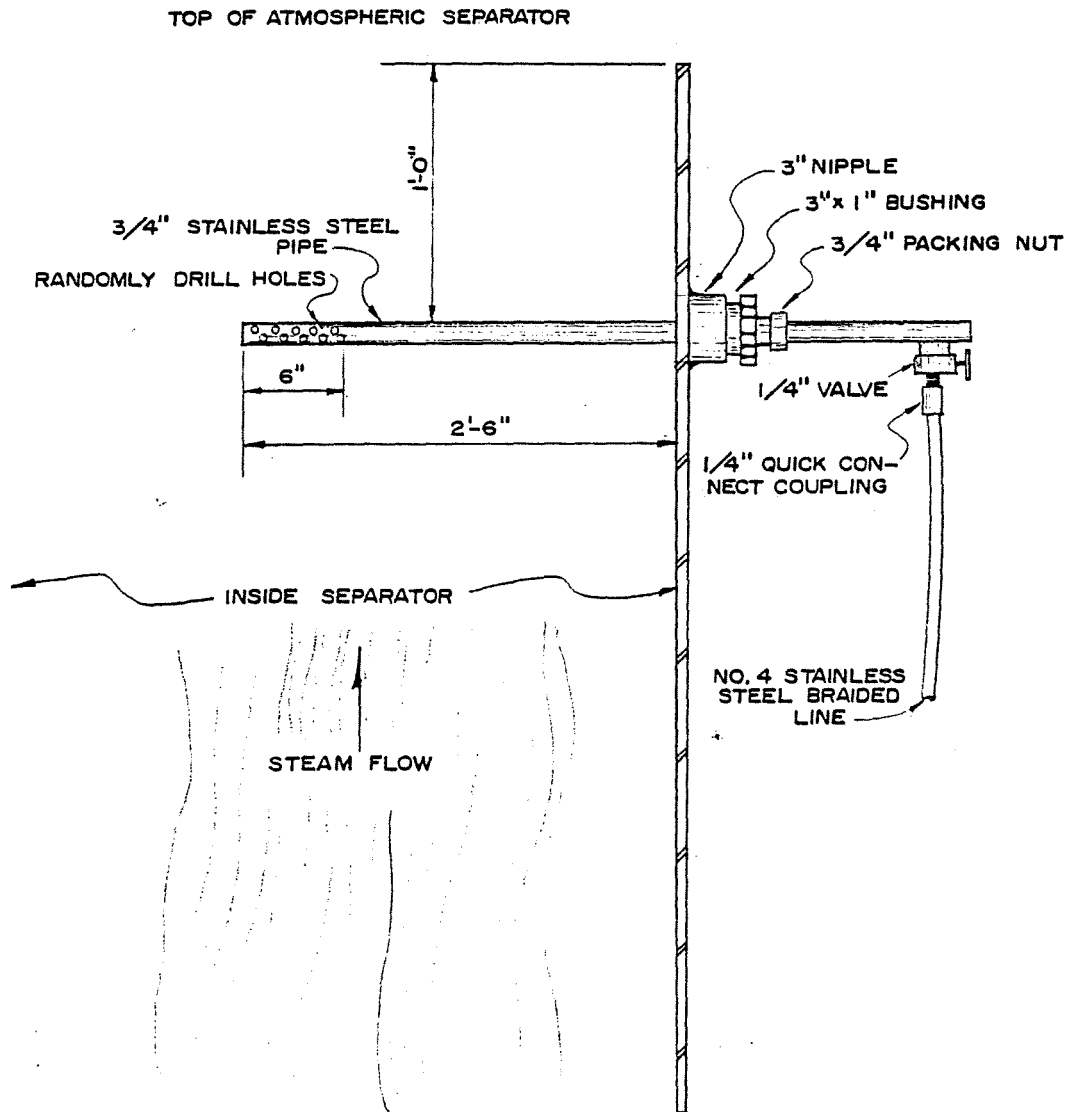
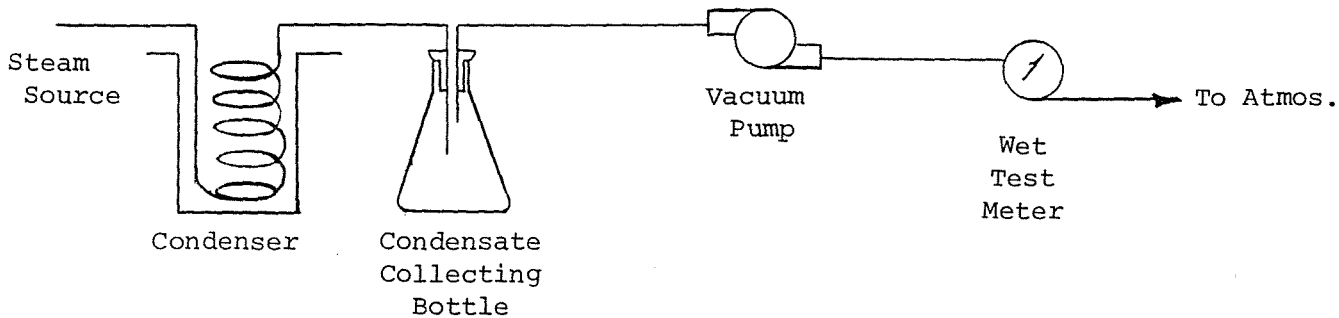


FIGURE 5

Percent Non-Condensable Determination

To determine quantitatively the percent non-condensibles, a representative sample must be taken using the same probe described above. The sample is taken using the sampling train shown below.



The grams of condensate collected is representative of the steam flowrate and the measured cubic feet of gas with the wet test meter is representative of the percent non-condensibles. The wet test meter reading should be corrected for both atmospheric pressure and the water temperature of the meter. This reading is then converted to grams and the percent non-condensibles can be calculated. (During air drilling, the molecular weight of the non-condensibles is essentially that of air, 29).

Determination of the Steam Flowrate

The sample train used for the percent non-condensibles can be used to determine the steam flowrate. The only additional piece of information required is the amount of air being pumped down the drill string as the circulatory medium (in standard cubic feet). The ratio of the amount of condensate collected to the standard cubic feet of non-condensibles measured is proportional to the ratio of the steam flowrate to the amount of air (in standard cubic feet) being pumped down the drill string.

	wt %		
lost %	35	50	70
active O ₂	16.5	23.5	32.9
Sp g.		1.2	
Boil P.		114	
Incey.		- 52	