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THE DIRECT CHLORINATION PROCESS FOR GEOTHERMAL POWER PLANT OFF-GAS - HYDROGEN SULFIDE ABATEMENT

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TABLE OF CONTENTS

Tables

Figures

Appendices

I. ABSTRACT

The Direct Chlorination Process removes hydrogen sulfide from geothermal off-gases by reacting hydrogen sulfide with chlorine in the gas phase. Hydrogen chloride and elemental sulfur are formed by this reaction.

The Direct Chlorination Process has been successfully demonstrated by an on-site operation of a pilot plant at the 3 M We HPG-A geothermal power plant in the Puna District on the island of Hawaii. Over 99.5 percent hydrogen sulfide removal was achieved in a single reaction stage. Chlorine gas did not escape the pilot plant, even when 90 percent excess chlorine gas was used.

A preliminary economic evaluation of the Direct Chlorination Process indicates that it is very competitive with the Stretford Process. Compared to the Stretford Process, the Direct Chlorination Process requires about one-third the initial capital investment and about one-fourth the net daily expenditure.

Because of the higher cost of chemicals and the restricted markets in Hawaii, the economic viability of this process in Hawaii is questionable.

Sulfur recovery from the Direct Chlorination Process was much improved in Phase II of the project. However, additional development work is necessary to define fully this aspect of the process.

II. EXECUTIVE SUMMARY

The Direct Chlorination Process removes hydrogen sulfide from geothermal off-gases by reacting hydrogen sulfide with chlorine in the gas phase. Hydrogen chloride and elemental sulfur are formed by this reaction and are saleable by-products. This process has been successfully demonstrated on a pilot plant scale by on-site operation at the HGP-A geothermal power plant located in the Puna District on the island of Hawaii.

In August, 1982, the Department of Energy contracted with the I. Sheinbaum Co., Inc. to explore the possibility of providing an H_2S abatement process suitable for the geothermal off-gases of the 3 M We power plant on the island of Hawaii. The I. Sheinbaum Co., Inc. thereafter constructed a pilot plant based on its proprietary Direct Chlorination technology and shipped it to Hawaii to be tested directly on the exhaust gases of the geothermal power plant.

This project was carried out in two phases. The skid-mounted unit used in Phase I employed a teflon-lined pipe reactor. A total of seventeen runs were made during this phase of the project, with a wide range of chlorine to hydrogen sulfide molar ratios and at varying feed rates. In some selected and repeated runs, over 99.8 percent removal of the hydrogen sulfide was achieved in a single stage, treating approximately 10 percent of the exhaust gas produces in the geothermal plant.

Hydrogen sulfide exhaust is removed in the Direct Chlorination Process primarily by reacting chlorine and hydrogen sulfide. However, a secondary reaction between sulfur and chlorine in the presence of water produces higher oxidation compounds of sulfur. Sulfur oxides formation requires a higher mole ratio of chlorine to sulfur. For the efficient use of the chlorine gas in removing hydrogen sulfide from the geothermal exhaust gases, it is desired to minimize the formation of oxides of sulfur. SO_x production averaged about 0.2 percent of the input sulfur. At molar ratios of chlorine to H_2S greater than 1.0, the SO_x production increased, reaching 16 percent of imput sulfur at a ratio of 1.9. Sulfur deposited in the equipment made it impracticable to conduct a sulfur balance.

A carbate (impervious graphite) shell and tube exchanger was used as the reactor in Phase II. Unlike the reactor in Phase I, the reaction took place inside the tubes of the heat exchanger at a constant temperature of $300^{o}F$. A total of six runs were made with this unit. Previous results were confirmed at higher feed rates, approaching 50 percent of the geothermal power plant exhaust.gas production. Operation at molar $Cl_2/H_2S + H_2$ ratios of 1.0 made it possible to discontinue the use of the pilot plant's experimental caustic scrubber. Molten sulfur recovery from the reactor-heat exchanger was in the range of 30 to 40 percent of input.

A preliminary economic evaluation of the Direct Chlorination Process on the mainland U.S.A. and in Hawaii was conducted. The Direct Chlorination Process was also compared to the Stretford Process, assuming that the Stretford Process can provide the same level of hydrogen sulfide removal experienced by the Direct Chlorination Process. The result of the preliminary economic evaluation indicates that, while the Direct Chlorination Process is very competitive on the mainland, it may be only marginal in Hawaii. The dependency of the Direct Chlorination Process on the cost of chlorine and on the sale of hydrochloric acid restricts its viability in Hawaii but enhances its economic advantages on the mainland.

III. INTRODUCTION

A. Geothermal Sulfide Removal Processes

Essentially all geothermal fluids contain hydrogen sulfide, although the amountvaries widely from reservoir to reservoir. The presence of hydrogen sulfide is of concern in geothermal power processes primarily because of the potential for air pollution. The severity of the problem depends on the hydrogen sulfide content of the geothermal fluid, the amount and composition of the noncondensible gases and the characteristics of the electric power production process.

The need for hydrogen sulfide removal exists in all geothermal plants where the heat from the geothermal resource is removed and recovered through the steam flashing mechanism. Once the steam is condensed, noncondensibles invariably contain hydrogen as one of the noncondensible components. The concentration of the hydrogen sulfide in the noncondensibles varies widely. While the Hawaii hydrogen sulfide content of noncondensibles may be as high as 50 percent, in East Mesa, the noncondensibles contain only a few parts per million. Similarly, data received from Roosevelt Hot Springs indicates concentration of hydrogen sulfide in the noncondensibles of several parts per million. Nevertheless, regardless of the amount of hydrogen sulfide in the geothermal noncondensibles, the noncondensibles have to be treated. Ambient quality of hydrogen sulfide should not exceed 20 parts per billion, which is considered the odor sensing threshold of hydrogen sulfide.

Existing sulfur removal processes are not very satisfactory. The Stretford Process is effective and can achieve a high degree of hydrogen sulfide removal. However, the process is complex, costly and was never applied to a high CO_2, high H_2S gas containing hydrogen, such as the geothermal off-gas in Hawaii. Non-regenerative scrubbing processes can be effective but high chemical cost and spent chemical disposal problems ususally make such processes unacceptable. There is, therefore, a need for an effective, simple, low cost sulfur removal process that is suitable for use with geothermal power plants.

B. The Direct Chlorination Process

This report presents the results of the pilot plant testing of the Direct Chlorination Process, a proprietary process developed by the I. Sheinbaum Co., Inc.for commercial use in removing hydrogen sulfide from geothermal and other industrial gases.

In the Direct Chlorination Process, gaseous chlorine is reacted with the hydrogen sulfide in the geothermal off-gas, forming elemental sulfur and hydrogen chloride, according to the following reaction:

1. $H_2S + Cl_2 \longrightarrow S + 2\ HCl$

Most of the H_sS is converted to sulfur by reaction #1. Should hydrogen and ammonia be present in the geothermal off-gas, the chlorine will react with these compounds to form hydrogen chloride and amine chloride, as shown in reactions 2 and 3.

2, $H_2 + Cl_2 \longrightarrow 2\ HCl$

3. $NH_3 + Cl_2 \longrightarrow HCl + NH_2Cl$

An important side reaction that was observed both in the laboratory and in the operation of the pilot plant was the formation of sulfur monochloride, as shown in reaction 4.

4. $2S + Cl_2 \longrightarrow S_2Cl_2$

In the presence of water, sulfur monochloride decomposes in a complex reaction to form both SO_2 and SO_3, as simplified in reactions 6 and 7.

6. $2\ S_2Cl_2 + 2\ H_2O \longrightarrow 3\ S + 4\ HCl + SO_2$

7. $3\ S_2Cl_2 + 3\ H_2O \longrightarrow 5\ S + 6\ HCl + SO_3$

Reaction #6 is the major decomposition reaction for the S_2Cl_2. These two side reactions require a higher molecular ratio of chlorine to hydrogen to remove the hydrogen sulfide.

However, the formation fo sulfur monochloride has several distinct and important advantages in the Direct Chlorination Process. When excess chlorine is fed into the system, deliberately or because of a change in acid gas feed composition,the excess chlorine reacts with the sulfur present in the reactor to form sulfur monochloride as shown in reaction 4, above. Because of the great affinity of chlorine to form sulfur monochloride and because sulfur monochloride is an excellent solvent for sulfur, the chlorine, which is in excess of the required stoichiometric amount, is fully trapped in the sulfur-chloride liquid phase. Monitoring the gases coming out of the reactor for the presence of chlorine gas, when excess chlorine used in the reaction, showed no chlorine gas in both the pilot plant and in the laboratory work.

On the other hand, the sulfur monochloride, with its dissolved sulfur, forms the necessary "buffer" in the system needed to react with excess hydrogen sulfide, as shown in reaction #8.

8. $S_2Cl_2 + H_2S \longrightarrow 3\ S + 2\ HCl$

A minor amount of the H_2S is converted to sulfur by reaction #8. Thus, the S_2Cl_2 prevents hydrogen sulfide from exiting the system when insufficient chlorine is available in the feed.

The success of this process is due, in part, to the formation of small amounts of sulfur monochloride and its partial accumulation in the equipment to both adsorb excess chlorine and release it when excess hydrogen sulfide is present.

The I. Sheinbaum Co., Inc. conducted a study of potential hydrogen sulfide abatement processes for geothermal resources (DOE contract number DE-AC05=79ER10092, entitled, "Analysis of the Hypochlorite Process"). In this study, the Stretford Process and the LoCat Processes were compared to a regenerative hypochlorite process for the removal of hydrogen sulfide from geothermal exhaust gases. Details of these processes are available in the final report, issued in April of 1980. The hypochlorite process developed by the I. Sheinbaum Co., Inc. matured into the Direct Chlorination Process.

C. The Geothermal Test Site

The pilot plant testing was done on-site, using exhaust gas from the geothermal HGP-A plant, located in the Puna District on the island of Hawaii. The geothermal power plant is a single stage steam flash plant. The power plant vent gas, removed from the vacuum condensers, has a relatively high hydrogen sulfide content. The following gas analysis was derived by Mr. D. Thomas, "Geochemical Case History of the HGP-A Well, 1976-1982," Hawaii Institute of Geophysics, Honolulu, Hawaii 96822. The hydrogen sulfide content was confirmed by testing gas samples taken during the pilot plant project.

Component	Volume Percent
CO_2	42.6
H_2S	39.4
N_2	7.0
H_2	8.2
H_2O	2.8
	100.0%

The power plant produces 10 to 20 SCFM of vent gas at 10 inches W.C. pressure. Variations in the H_2S content of the geothermal exhaust gases are presented in Table 2.

TABLE I

SUMMARY OF RUNS

RUN	TIME HR.	FEED RATE, SCFM SOUR GAS	Cl_2	RATIO Cl_2/H_2S+H_2	YIELD, % OF INPUT $S^=$	$SO_4^=$
			PHASE I			
1	1.27	1.14	0.71	1.30	1.2	2.3
2	1.57	1.57	0.87	1.16	1.8	0.7
3	1.17	1.28	0.80	1.31	0.6	1.9
4	1.10	1.28	0.74	1.21	0.3	1.8
5	2.00	1.23	0.31	0.52	11.6	0.2
6	0.95	1.51	0.37	0.52	28.3	0.3
7	1.42	1.21	0.28	0.49	37.3	0.1
8	1.05	1.28	0.32	0.52	27.4	0.2
9	0.92	1.28	0.38	0.63	33.4	0.0
10	0.98	1.05	0.37	0.74	19.9	0.0
11	0.27	1.05	0.88	1.76	1.1	22.0
12	1.38	0.95	0.86	1.90	0.2	11.5
13	0.88	0.68	0.29	0.90	0.7	0.4
14	0.78	0.68	0.29	0.90	0.6	0.4
15	0.47	0.82	0.41	1.05	0.4	0.9
16	0.63	0.82	0.26	0.66	10.9	0.0
17	1.25	0.68	0.26	0.79	16.6	0.0
			PHASE II			
A	2.12	1.42	0.62	0.89	0.6	4.6
B	0.72	1.97	0.94	1.00	1.4	9.5
C	1.72	2.84	1.38	1.02	0.5	4.7
D	1.10	4.26	2.62	1.29	0.8	4.4
E	1.00	4.26	2.10	1.04	0.5	3.4
F	2.47	4.99	2.44	1.03	0.9	0.8

TABLE 2

PILOT PLANT FEED GAS ANALYSES

Date	Vol. % H_2S	Analytical Method
Nov. 1982		
8	35.4	P
9	44.1	P
9	41.7	P
11	39.6	P
11	35.3	P
12	37.3	P
12	34.9	P
15	34.9	P
15	38.7	P
18	37.4	P
18	36.5	P
28	49.7	T
28	35.2	P
28	44.0	T
28	35.0	T
28	44.9	T
28	37.6	P
30	49.7	T
30	55.6	T
Dec. 1982		
1	44.2	T
1	33.1	P
1	41.7	T
1	32.3	P
April 1983		
26	49.7	T

Mean=40.35

Standard Deviation=6.21

P=Pomeroy; T=Kitegawa Tube

IV. PILOT PLANT

A. Pilot Plant Experimental Procedure

The pilot plant tests were conducted in two phases. The skid-mounted unit used in Phase I is shown in Figure 1. The overall dimensions of the skid were approximately 10 feet long by 4 feet wide by 10 feet high.

The reactor section consisted of two 4-inch diameter teflon-lined pipes in series, each 6 feet long. The reactors were packed with intalox packing made from Kynar plastic for the first ten runs and were empty for the remainder of the runs. Vent gas from the reactor section was cooled in a 1-inch diameter lead coil contained in a water-filled 50 gallon drum. Cooled vent gas flowed into a 100 gallon fiber reinforced plastic tank that served as a reservoir for the water scrubber, mounted directly on the tank. The water scrubber column was constructed from a 6-foot section of a 4-inch diameter PVC pipe, packed with ceramic intalox saddles. Circulation of the water scrubbing liquid was provided by a centrifugal pump. Vent gas from the water scrubber flowed into a caustic scrubber of similar construction, but smaller. The caustic scrubber tank had a 30 gallon capacity and the packed column was 2 inches in diameter.

Operation for a typical run consisted of first loading the respective scrubbers with water and caustic solution and establishing the scrubbers' liquid flows. Sour gas flow to the unit was then set by rotometer, followed by setting the chlorine flow for a 150-pound chlorine cylinder, again using a rotometer. Hydrogen chloride was removed from the reactor vent gas in the water scrubber and carbon dioxide and any unreacted hydrogen sulfide removed in the caustic scrubber. Vent gas flow from the caustic scrubber was negligible and consisted mostly of the nitrogen in the feed gas. Runs were terminated by shutting off the flow of chlorine and sour gas and then shutting off the scrubber circulating pumps.

During a typical run, sulfur would accumulate in the system. An accumulation of elemental sulfur was observed on the packing inside the teflon-lined pipes, in the lead pipe cooler, and in the hydrochloric acid scrubber. Sulfur formation in the reaction zone appeared to be in colloidal form, part of which was settled on solid surfaces and part of it was carried into the water scrubber for final removal. There was no sulfur mist exiting the hydrochloric acid scrubber. No attempt was made during the run to remove sulfur from the system. At the end of each run, the pilot plant was steamed out and molten sulfur was collected. Elemental sulfur in the hydrochloric acid was removed by overnight settling. Because the collection of sulfur was relatively inaccurate, no sulfur balance could be achieved with this procedure of sulfur collection.

A separate skid was constructed and piped into the existing skid for the Phase II runs. The teflon-lined pipe reactor was replaced by a Karbate (impervious graphite) shell and tube heat exchanger with about 90 square feet of heat exchange surface. The resulting test unit is shown in the sketch in Figure 2. Additional equipment included a gas blower that was used to stabilize the feed gas flow into the pilot plant and a water vessel and pump used to circulate hot water to the heat exchanger-reactor. The caustic scrubber was not used, since for the Phase II runs, chlorine to hydrogen sulfide ratios were adjusted to achieve high sulfide removal efficiency.

As a result of the higher pilot plant feed gas flow rates made

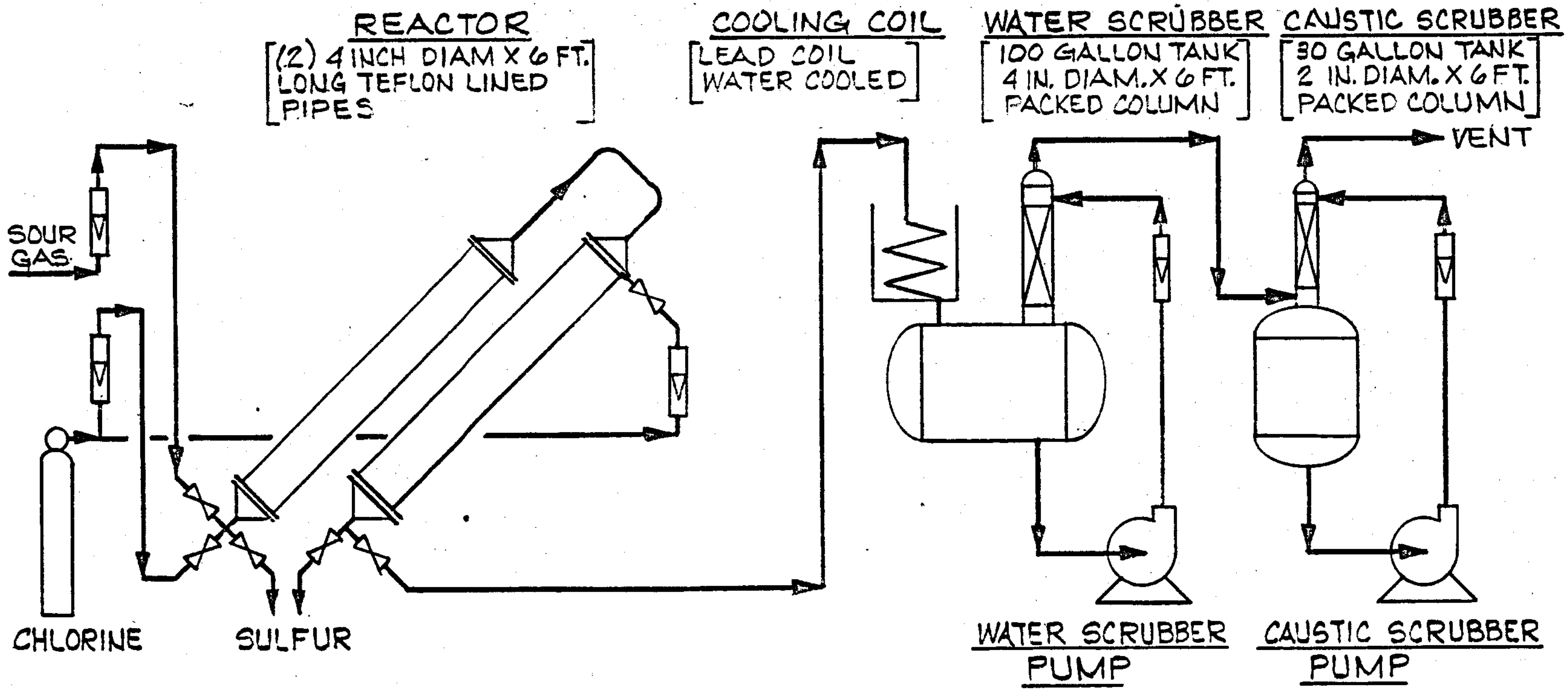
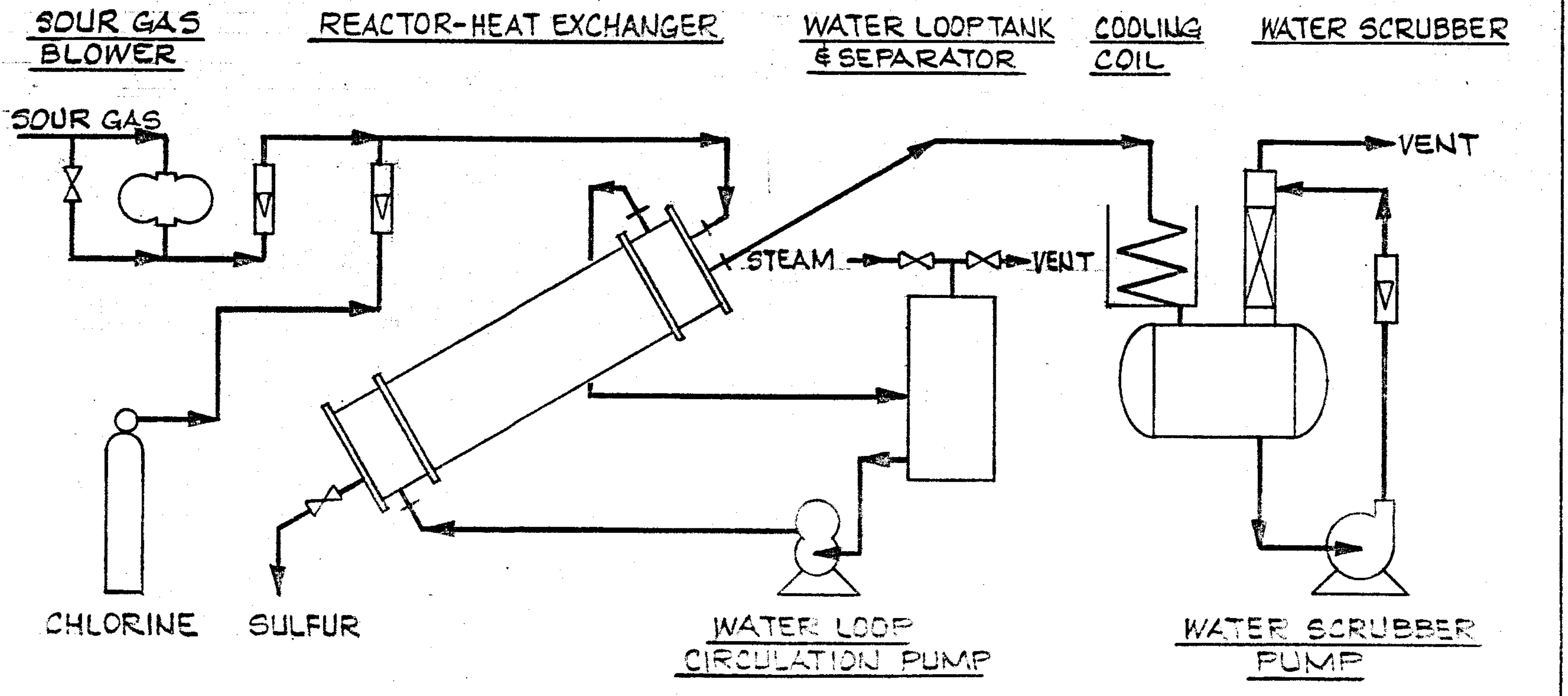


FIGURE 1
TEST UNITS-PHASE 1

FIGURE 2
TEST UNIT- PHASE II



possible with the added gas blower, a manifold system with three chlorine cylinders was needed to supply the chlorine gas requirement. Operation during the Phase II runs was similar to that for Phase I, except that steam was used to bring the reactor-heat exchanger to the approximate operating temperature of 300°F before starting the runs.

To overcome the difficulty encountered in the first phase of the work due to sulfur settling in the various sections of the pilot plant, the heated heat exchanger-reactor utilized in Phase I was designed to continuously drain liquid sulfur as it was formed. Thus, in a typical run, liquid sulfur accumulated in the bottom of the heat exchanger was intermittently drained. Operating the pilot plant with the hot heat exchanger-reactor resulted in approximately 30 to 50 percent of the sulfur being recovered in a liquid form. Additional sulfur was observed exiting the top of the heat exchanger-reactor in colloidal form and settling elsewhere in the pilot plant. When the project was terminated, the piping of the pilot plant was dismantled and large accumulations of sulfur were observed in the entire piping system. Molten sulfur that was removed in Phase II of the project also contained a small amount of sulfur monochloride dissolved in it. Typically, draining sulfur from the heat exchanger-reactor and dripping water on the molten sulfur created hydrochloric acid vapor. An analysis of the concentration of sulfur monochloride in the molten sulfur was not conducted. A full description of all the runs detailing operating procedures and experimental activity is attached as Appendix 1.

B. Analysis of Experimental Variables

The streams analyzed for the Phase I runs were the following:

Stream	Analyzed for
sour gas feed	H_2S
water scrubber vent gas	H_2S
caustic scrubber vent gas	H_2S
sulfur	weight
water scrubber liquid	Cl^- H^+ $S^=$ $SO^=$ Cl_2
caustic scrubber liquid	$S^=$ $SO^=$$Cl^-$ Cl_2

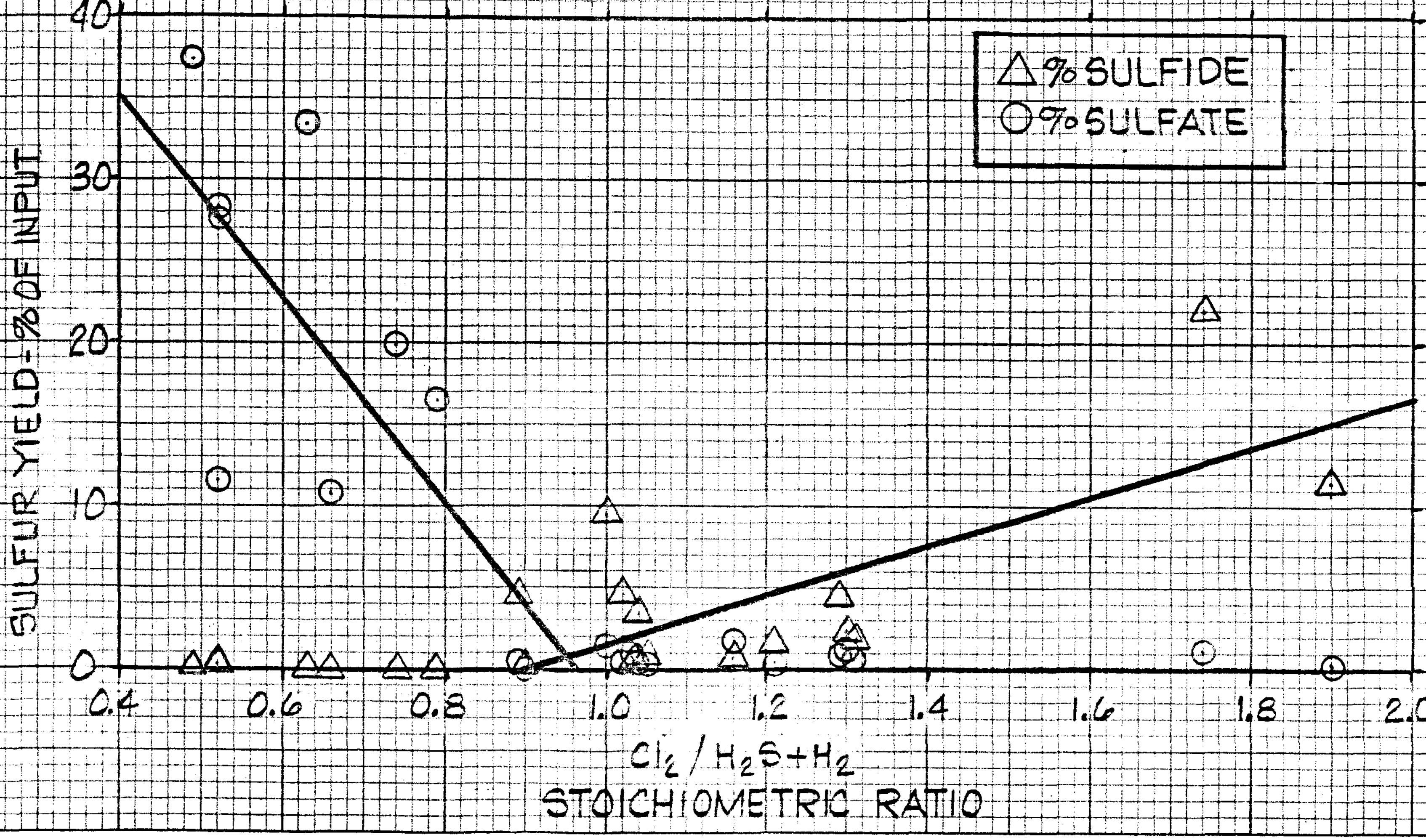
Sour gas feed was analyzed for hydrogen sulfide by absorbing a known volume of gas in a caustic solution and analyzing the solution for sulfide ion by the Pomeroy method and by the use of Kitegawa immersion tubes. Additional information concerning the apparatuses and the experimental procedure used in the analysis of the various compounds mentioned above is attached as Appendix 2.

Water scrubber vent gas was checked for hydrogen sulfide by using lead acetate paper. Although, for some runs, the lead acetate test was negative for short periods, the test generally showed medium to strong color within a few seconds. Attempts to use a GasTech hydrogen sulfide monitor were generally unsuccessful since the sample was over the range of the instrument and once out ranged, the instrument was slow to recover. When operating properly, the caustic scrubber vent gas was free of hydrogen sulfide.

Attempts to drain sulfur from the unit during Phase I runs were only partially successful. Melting the sulfur in the reactor by using steam at 20 to 30 PSIG at the end of a run made it possible to recover some molten sulfur. The amount recovered was generally less than 10 percent however, and the sulfur tended to freeze in the drain valve.

Scrubber liquids were analyzed using wet chemistry methods, as shown in Appendix 2. No trace of elemental chlorine was ever found in either of the scrubber liquids (no color change with a

FIGURE 3
SULFIDE AND SULFATE YIELDS
VS.
STOICHIOMETRIC RATIOS



method using O-toluidene). Chloride ion tests used mercuric chloride as a titrant, as well as Kitegawa immersion tubes. Hydrogen ion concentration in the water scrubber liquid used sodium hydroxide titration to a pH 3.8 end point. Sulfide was determined by the Pomeroy methylene blue method and by the Kitegawa immersion tubes. SO_x was determined by opacity of a barium sulfate percipitate (Hach Test Kit SF-1).

The analytical scheme used in the Phase II tests was similar, except that the caustic scrubber was not used. Vent gas from the water scrubber was analyzed for hydrogen sulfide by two methods. Undiluted vent gas was tested using a length of stain detector tube in a MSA gas sample. In the other method, vent gas was diluted with air using a GasTech HS-80A Detector.

In the Phase II runs, it was possible to drain liquid sulfur from the reactor-heat exchanger during the runs. Sulfur recovery by this method was, however, limited to 30 to 40 percent of total sulfur imput.

C. The Interface Between the Direct Chlorination Pilot Plant and the HPG-A Power Plant

The HPG-A geothermal power plant in Hawaii is a single stage flashed steam power plant. A single well is utilized on-site, producing a two-phase brine-steam flow. At the power plant, the steam is separated from the brine and the steam is utilized to drive the generator-driven turbine. Thereafter, the steam is condensed in the condenser and the noncondensibles are removed in a two-stage vacuum steam jet system. Currently, large quantities of caustic are used to treat the noncondensibles for the removal of the hydrogen sulfide contained therein. Together with the hydrogen sulfide, all the CO_2 is removed which consumed additional caustic.

Recently, there have been several complaints about hydrogen sulfide emission at the geothermal power plant and there is a current litigation in progress concerning hydrogen sulfide emission.

The pilot plant was designed to treat approximately 10 percent of the total noncondensible emissions of this plant in Phase I and in Phase II, the volume to be treated approached 30 to 50 percent of the total amounts of the noncondensibles exiting the power plant. The noncondensible flow from the vacuum jet was pulsating and the content of hydrogen sulfide in the noncondensibles varied by as much as 20 percent in four hours. (See Table 2.) The hydrogen content of the noncondensibles was known to vary similarly. Because of these sharp changes in composition and pulsating flows, the use of the original sulfide incineration system appearedto be difficult.and forced the operators to use the caustic treating method as an alternate. The I. Sheinbaum Co., Inc recognizes the challenge of treating this noncondensible flow with its Direct Chlorination Process. To overcome the noncondensible flow pulsation, a rotary-type blower was installed in Phase II of the project. The composition changes of both the hydrogen sulfide and the hydrogen were fully accepted by the pilot plant and were smoothed out with the help of the sulfur monochloride as indicated elsewhere in this report. Thus, an excellent match was created between the erratic output of noncondensibles and hydrogen sulfide by the power plant and the consistent stable treatment of removing the hydrogen sulfide experienced in the Direct Chlorination Process.

V. RESULTS

A total of 23 runs were made, 17 in Phase I and 6 in Phase II. The results are summarized in Table 1 and Figure 3. The runs in Phase I (1 through 17) cover a wide range of Cl_2 / H_2S + H_2 stoichiometric ratios (.49 to 1.90) and were made using sour gas feed flows of from 0.68 SCFM to 1.57 SCFM. The Phase II runs (A through F) were made with close to stoichiometric ratios of Cl_2 / H_2S + H_2 and with higher sour gas rates (5 SCFM maximum).

Overall, chlorine recovery averaged 87.5 percent, with a standard deviation of 12.5 percent. Much of the loss is attributed to hold-up in the equipment. The equipment was drained and cleaned between runs but difficulties with sulfur plugging made it impractical to attempt complete recovery of the hold-up. These difficulties, combined with carry-over of sulfur into the scrubber, defeated attempts at recovering enough sulfur to achieve an overall sulfur balance. In the Phase II runs, sulfur recovered in the molten form from the reactor-heat exchanger amounted to 30 to 40 percent of input.

As shown in Figure 3, sufide yield (unreacted hydrogen sulfide) is reduced as the Cl_2 / H_2S + H_2 stoichiometric ratio is increased until it is approximately zero, at a ratio of 1.0 (0.96 by linear regression). Above that ratio, the average unreacted sulfide yield is 0.8 percent with a standard deviation of 0.45 percent. This much of the sulfide yield is accounted for by the very brief period at the beginning of each run where sour gas was entering the system before the start of chlorine addition. The entire 0.8 percent unreacted sulfide could be accounted for by assuming that the initial sour gas flow lasted only 15 seconds on the average, before the chlorine gas flow was fed into the reactor. (See pilot plant operating procedure.)

Sulfite/sulfate formation below Cl_2 / H_2S + H_2 stoichiometric ratios of 1.0 is very small, 0.2 percent of input sulfur as hydrogen sulfide with a standard deviation of 0.2 percent. Sulfite/sulfate production increases with excess chlorine, however, reaching as much as 16 percent of input sulfur at a stoichiometric ratio of 1.9. Even at that relatively high ratio, no elemental chlorine is detected in the vent gases, apparently being consumed in the production of oxidized states of sulfur and sulfur chlorine compounds.

The sour gas entering the pilot plant contains approximately 9 volumes percent of hydrogen. The reaction of hydrogen and chlorine in a gas phase to form hydrogen chloride is well established. However, it was of interest to determine whether the affinity of chlorine to hydrogen is as strong as it is to hydrogen sulfide and, if so, if all the hydrogen is consumed in the reactor. The stoichiometric ratios in Table 1 appear to indicate that the full amount of hydrogen is consumed to form hydrogen chloride when the ratio approaches 1.0. However, from an analysis of the data, it appears that at stoichiometric ratios under .7 moles of chlorine to moles of hydrogen sulfide plus hydrogen, the hydrogen sulfide appears to react first.

The rate of the chlorine-hydrogen sulfide reaction appears to be faster than the rate of the chlorine-hydrogen reaction. As the stoichiometric ratio increases above .7, the hydrogen starts to react with the chlorine. At the stoichiometric ratio of 1.0, both the hydrogen and the hydrogen sulfide reactions with chlorine essentially approach completion. In stoichiometric ratios higher than 1.0, the hydrogen sulfide and the hydrogen reaction with chlorine is essentially complete but the formation of sulfite/sulfate becomes significant.

The rate of reaction between chlorine and hydrogen sulfide and chlorine and hydrogen are outside the scope of this project. However, they are believed to be very high. The reaction itself can be viewed as exothermic combustion where the chlorine is the oxidizer. The rate of oxidation is directly related to the level of mixing provided for the oxidizer and the reactant. With the pilot plant sep-up for Phase I, where chlorine was fed through a one-inch valve, opposite a one-inch valve feeding the acid gas, the skin temperature of the reactor was monitored, showing a rapid reaction at the inlet to the reactor, a constant skin temperature along approximately three feet of the reactor and a temperature along approximately three feet of the reactor and a sharp drop in temperature thereafter.

This observation indicates that the reaction (probably with hydrogen sulfide first) takes place instantaneously upon mixing of the gases. The reaction continues in the pipe flow along a distance of another 18 to 24 inches and then the reaction mixture dissipates its heat in the final 6 to 12 inches of the reactor. The reaction temperature was estimated to be between 300°F and 400°F, depending on acid gas flow rate. Inspection of the teflon walls of the reactor indicated no melting of the teflon lining. Thus, is can be assumed that the reaction temperature did not exceed 400°F. Adiabatic calculation of reaction temperature indicates that it can be as high as 2000°F with exothermic heat release of 70,800 BTU/lb. mole of H_2S.

Cooling the hydrogen chloride scrubber should also be considered. The calculated heat of dilution of the hydrogen chloride solution is about 29,000 BTU/lb. mole of HCl.

VI. DISCUSSION-TECHNICAL FEASIBILITY

The Direct Chlorination Process proved its technical feasibility both in the laboratory work and in the two phases of the pilot plant operation. The pilot plant operated on a unique geothermal off-gas, containing about 40 percent hydrogen sulfide. While in Phase I of the work, the pilot plant treated about 10 percent of the HGP-A geothermal plant off-gases. In Phase II, the pilot plant treated approximately 30 to 50 percent of the total geothermal off-gases. The limiting capacity in Phase II was the ability of the chlorine cylinders to vaporize sufficient amounts of chlorine gas needed for the reaction. A one-ton chlorine container was needed; however, it was not readily available on the island.

The chemical reactions governing this process proved to be very fast, with a strong driving force toward completion. In one reaction stage, the concentration of hydrogen sulfide was reduced by a factor of 400 to 1, from approximately 40 volume percent to about 0.1 volume percent. In similar experimental work conducted in a laboratory, starting with approximately 2 volume percent of hydrogen sulfide, the level of hydrogen sulfide in the treated gas (mostly carbon dioxide) was reduced to only a few ppm. These results seem to indicate that a total elimination of the hydrogen sulfide is quite feasible in two stages of reaction, where stoichiometric ratios of about .9 are maintained in the first stage and the balance of the reaction is conducted in the second stage.

One important result obtained in the pilot plant work, improving greatly the feasibility of commercializing this process, is the fact that the off-gases, after being treated in the Direct Chloronation Process, contain no free chlorine. This result was achieved and confirmed with stoichiometric ratios of chlorine to hydrogen sulfide plus H_2 varying between one-half of the required chlorine to approximately twice the chlorine required for the reaction.

The chemistry of the system is such that small amounts of sulfur chlorine compounds present in the system react as a buffer, preventing chlorine gas from leaving the reactor. This insensitivity of the process to the precise amount of chlorine feed also explains the consistent low sulfide concentration in the effluent of the pilot plant, even though the power plant off-gas is known to cycle and pulsate, accompanied with variation in the hydrogen sulfide content of the gas. (See Table 2.)

Hydrogen chloride in the reactor vent gas is easily removed and recovered by a simple water scrubbing column. Although acid strength in the pilot runs did not exceed about 14 percent HCl, the use of a water wash section would make it possible to produce commercial concentrated hydrochloric acid. The acid produced in the pilot unit was frequently cloudly as a result of suspended sulfur particles. Overnight settling invariably produced a water clear product, indicating that the production of acceptable commercial grade acid is feasible.

Complete sulfur recovery was not achieved in any of the pilot plant runs. The use of the reactor-heat exchanger improved recovery and it is possible that relatively simple modification to this unit would provide acceptable recovery. Satisfactory levels of sulfur recovery were not, however, demonstrated and further work is needed in this area.

Process hardware and commercial-sized equipment necessary for commercialization of this process are well within today's state of the art. A hot, continuous process, where the continuous melting of sulfur is achieved or a semi-continuous operation, where the sulfur is recovered in a secondary melt stage, are feasibile. Preference for one operating mode over the other may be determined by the level of hydrogen sulfide in the geothermal off-gas. In the case of the geothermal off-gas in the Hawaii power plant, the continuous melting operation is probably a better choice because of the large amount of sulfur produced. The continuous melting process should include a molten sulfur scrubber to remove colloidal sulfur from the treated gas downstream of the reactor and to ensure that any free chlorine that may escape the system will get absorbed in the sulfur scrubbing.

It is possible to modify the Direct Chlorination Process so that its dependency on both purchased chlorine and on the sale of hydrochloric acid is eliminated. It is feasibile to dissociate hydrochloric acid to hydrogen and chlorine in an electrolytic cell and thus, recycle the chlorine into the process.

The production of chlorine from hydrochloric acid should require considerably less power than the production of chlorine and caustic from sodium chloride. However, additional research may be necessary to develop the proper electrolytic cell to conduct this process. The use of the hydrochloric acid electrolytic cell may be desirable in Hawaii, where the cost of chemicals is high and essentially controlled by a single company. However, the feasibility of the use of this cell is outside the scope of this report.

VII. DISCUSSION-ECONOMIC FEASIBILITY

A. Economic Feasibility of the Direct Chlorination Process in Hawaii

The cost of chemicals and power in Hawaii are significantly different than the cost on the mainland. In Hawaii, a single marketer, Brewer Chemical Company, controls the chlorine and the hydrochloric acid markets. Because the economic feasibility of this process is heavily related to the availability and cost of chemicals, a separate column in Tables 3 and 4 is dedicated to the specific conditions of running the Direct Chlorination Process in Hawaii.

As mentioned elsewhere in this report, the possibility of being self-sufficient in the production of chlorine, whether through the manufacturing of caustic chlorine in a sodium chloride electrolytic cell or through the production of hydrogen and chloride in a hydrochloric acid electrolytic cell, can improve the economic feasibility of the Direct Chlorination Process, especially in Hawaii.

B. Economic Feasibility of the Direct Chlorination Process on the Mainland, U.S.A.

To establish the economic feasibility of the process, it is necessary to introduce realistic chemical costs, such as those available on the West Coast, under competitive conditions. The economic evaluation in Tables 3 and 4 reflects the approximate cost of the chemicals, together with all other charges, for the mainland.

C. The Stretford Process

For the sake of preliminary comparison, cost data for the Stretford

Process is presented herein. The data for the Stretford Process was developed in a previous project conducted by the I. Sheinbaum Co., Inc., for the Department of Energy, Contract Number DE-AC05-79ER10092, entitled, "Analysis of Hypochlorite Process."

D. Cost Items

Plant Cost:

The cost of the Direct Chlorination plant was established by estimating the installed cost of individual processing equipment, based on the pilot plant work done at the Hawaii geothermal power plant. The cost of the Stretford Process was obtained by factoring actual plant costs at the Geysers. The plant costs for the two processes are tabulated in Tables 3 and 4.

Plant Operating Costs:

The operating cost used in this report was calculated in accordance with the following paragraphs:

a. Manpower

It is assumed that each hydrogen sulfide removal plant will require about one-quarter shift operator to operate the plant. On this basis, the labor costs for all plants are identical.. The estimated manpower cost includes supervisory labor necessary to operate each plant. The costs represent operating personnel only and do not include maintenance, labor and overhead personnel.

b. Maintenance

The average annual cost of labor, material and supervision for maintenance is estimated to be 4 percent of the initial capital investment. This is an amount sufficient to keep the plant in good operating condition.

c. Chemicals

The cost alloted under this heading includes chemicals and catalysts required for plant operation. Costs are based on 1983 listed prices for industrial grade chemicals. The sulfur produced in these plants is assumed to be unsaleable. No credit was taken for the production of steam in the Direct Chlorination unit, assuming that the steam will be used internally in the process.

d. Utilities

The power used in the power generation plant should not be subject to transmission charges and should not be expected to make profit for the utility company. It should be available at a cost that is less than the cost for commercial power. Geothermal steam can be produced at a cost of $0.5/1000 lbs. This figure was used for the steam consumed by the Stretford Process.

Fixed Charges

a. Capital Recovery

To establish capital recovery for each of these plants, it was assumed that the funds to build the plants were borrowed at 12 percent interest and are paid in 10 years.

b. Local Taxes and Insurance

The annual cost of local property taxes and insurance is taken to be 2.5 percent of the initial capital investment.

c. General and Administrative

These costs include such items as sales, research and development, governmental relations, legal, accounting and other services in the home office, allocated to this activity. The annual cost is estimated to be 1 percent of the initial capital investment.

d. Overhead

This is the plant burden cost and it is estimated to be 100 percent of the operating cost. It includes all costs associated with the operation of the plant that are not otherwise accounted for.

Other Costs

The cost of land was assumed to be the same for each plant and therefore was not included in the estimated cost. It is assumed that royalties are included in the initial plant cost.

E. Comparison of the Cost of Removing Hydrogen Sulfide by the Stretford Process and the Direct Chlorination Process in Hawaii and the Mainland

Tables 3 and 4 summarize the economic parameters governing the cost of the Direct Chlorination Process and compare it to the Stretford Process. The basis for the calculation is the production of 1,100 lbs./day of sulfur in Hawaii (approximately the reported amount of sulfur in the 3 megawatt plant) and cost data as discussed elsewhere.

It is clear that the cost of chemicals in Hawaii is out of line. The cost of a ton of chlorine on the mainland varies between \$130 to \$150 while Brewer Chemical Company asks for \$580 per ton, delivered to the power plant in Hawaii. Conversely, the cost of hydrochloric acid (22^{o} Be) on the mainland varies between \$90 to \$100 while Brewer offer only about \$50 per ton at the plant. If the cost of shipping a ton of hydrochloric acid from the mainland to Hawaii is about equal to the difference between the mainland cost of chlorine and the cost in Hawaii, the value of hydrochloric acid manufactured locally shouldbe about $400 per ton. Some allowance, of course, has to be madefor marketing and inter-island shipping. But even with this allowance, the prices offered by Brewer Chemical appear to be unreasonable. The economics of operating the Direct Chlorination Process in Hawaii may be much more favorable if either chlorine and caustic can be produced on-site or if the hydrochloric acid can be electrolytically decomposed to hydrogen and chlorine and the chlorine recycled.

The single biggest expense in the present operation of the power plant in Hawaii is the cost of caustic needed to remove the hydrogen sulfide (and the carbon dioxide) in the pollution abatement unit. It was reported that this cost is between $700 and $900 per day. By comparison, even with Brewer Chemical's inflated costs, the cost of chemicals associated with the Direct Chlorination Process is projected to be approximately $650 per day.

In a comparison between the net annual costs of the Stretford Process and the Direct Chlorination Process for the Hawaii 3 megawatt power plant, they appear to be about equal. It should be noted, however, that while the Direct Chlorination Process operated successfully on the Hawaiian off-gases, to the knowledge of the author, no Stretford plant has ever operated on a feed stock containing 40 percent H_2S with the balance being hydrogen and carbon dioxide. In addition, 8 volume percent of hydrogen in the geothermal off-gas may or may not interfere with Stretford's chemical processes.

Using the Direct Chlorination Process on the mainland, with geothermal resources containing significantly less hydrogen sulfide, appears to be economically viable. The daily cost for the production of one-half of a long ton of sulfur appears to be one-fourth of the cost of an equally sized Stretford unit. The production of that much sulfur may correspond to a 50 megawatt power plant on the mainland, where the initial investment of $300,000 in the Direct Chlorination Unit is a very small amount in comparison to the total cost of the plant. In-plant production of chlorine and caustic may also be a viable alternative in the mainland, which may further reduce expenditures associated with air pollution abatement via the Direct Chlorination Process.

While the Hawaiian geothermal off-gas contains 8 volume percent of hydrogen, the Geysers contain an equal amount of ammonia. As indicated elsewhere, ammonia reacts easily with chlorine to form amine chloride which can then be removed in a water scrubber, together with the hydrochloric acid. Although the Direct Chlorination Process was not tried on Geyser-like geothermal off-gases, it is believed to be quite capable of handling these gases. Unlike all the experimental work at the Geysers, with upstream sulfur abatement processes, the Direct Chlorination Process treats gases downstream of the condenser and thus, any emission from the Direct Chlorination Process has no effect on the delicate parts of the power plant.

TABLE 3

DIRECT CHLORINATION PLANT

Design Basis: Capacity-1,100 lb. sulfur/day; 333 days/oper. yr.

FEED	LBS./DAY	MAINLAND $/LB.	(1) HAWAII $/LB.	MAINLAND $/DAY	HAWAII $/DAY
H_2S	1,169	---	---	---	---
Cl_2	2,950	.0725	0.29	213.9	855.5
H_2	14	---	---	---	---
Water	---	---	---	---	---
				213.9	855.5
ANNUAL COST				$71,200	$285,000
PRODUCT SALES					
(2) HCl 22°Be	8,420	.0475	.025	400.0	210.5
Sulfur	1,100	---	---	---	---
(3) Steam	2,400	---	---	---	---
				400.0	210.5
ANNUAL SALES				$133,200	$70.100
GROSS ANNUAL REALIZATION				$ 62,000	($-214,900)

(1) Based on Brewer Chemical quotation of $580/ton of chlorine and $50/ton of 22°Be HCl delivered to the plant
(2) 22° Be is 36 WT% HCl solution
(3) Heat of reaction 70,800 BTU/Mol H_2S - All steam is assumed to be utilized in internal heating

TABLE 4

COMPARISON BETWEEN THE STRETFORD PROCESS AND THE DIRECT CHLORINATION PROCESS ON HAWAII AND IN THE MAINLAND

	MAINLAND STRETFORD	MAINLAND D.C.U.	HAWAII D.C.U.
CAPITAL COST	$1,100,000	$300,000	$300,000
	ANNUAL COST		
DIRECT COSTS			
Labor Oper.	$ 40,000	$ 40,000	$ 40,000
Maintenance	44,000	12,000	12,000
Chemicals	11,000	71,200	285,000
Utilities	10,500	6,700	6,700
FIXED CHARGES			
Capital Recovery	$ 194,700	$ 53,100	$ 53,100
Taxes & Insurance	27,500	7,500	7,500
G & A	11,000	3,000	3,000
Overhead	40,000	40,000	40,000
TOTAL ANNUAL OPERATIONAL COST	$ 378,700	$233,500	$447,300
PRODUCT SALES	---	133,200	70,100
NET ANNUAL COST	$378,700	$100,300	$377,200
NET DAILY COST	$ 1,137.2	$ 301,2	$ 1,132.7

VIII. CONCLUSIONS

The pilot plant and the laboratory work conducted in the development of the Direct Chlorination Process proved its commercial viability, although additional work is needed to define fully specific unit operations for specific geothermal resources. The operation of the pilot plant was very successful in removing hydrogen sulfide from the Hawaiian geothermal off-gas, which is probably one of the highest in H_2S content available anywhere in the United States. Cleaning up this particular geothermal gas by the Direct Chlorination Process indicates that it may be possible to treat successfully by this method any other geothermal off-gas.

The project can be summarized as follows:

1. The Direct Chlorination Process achieved better than 99 percent hydrogen sulfide reduction in a single stage reaction.
2. A complete reaction between the hydrogen sulfide and the hydrogen in the geothermal off-gases was obtained when the stoichiometric ratio of chlorine to hydrogen sulfide plus hydrogen was approximately 1.0.
3. On-site pilot plant testing with actual geothermal power plant vent gas demonstrated that the reaction is rapid, smooth and easy to control.
4. Chlorine gas did not escape the Direct Chlorination Process, even when 100 percent excess chlorine gas was used.
5. A preliminary economic evaluation of the Direct Chlorination Process indicates that it is very competitive with the Stretford Process (about one-third of the initial capital investment and about one-fourth of the net daily

cost to run the plant on the mainland). Because of the higher cost of chemicals and the restricted markets in Hawaii, the economic viability of this process in Hawaii is questionable.

6. Sulfur recovery from the Direct Chlorination Process was much improved in Phase II of the project. However, additional research and development work is necessary to define fully this aspect of the process.

APPENDIX I

RUN #1 11-1-82 9:03-10:30

1. Chlorine to both reactors.
2. Water pump to first reactor in place, but not used.
3. Water scrubber loaded with 25 gallons of water. Circulation rate 1.5 GPM.
4. Caustic scrubber loaded with 15 gallons of water and 25.5 pounds of 50% sodium hydroxide. Circulation rate 0.8 GPM.
5. First reactor warm over entire length but maximum temperature at mid-point. Second reactor hot at inlet but cool after mid-point. Surface temperature of lead coil inlet was 120°F.
6. Water scrubber liquid cloudy by end of run. Caustic scrubber liquid was clear.
7. Run terminated when water scrubber circulation pump failed. Pump was blocked with sulfur.
8. No sulfur in sulfur drain pots.

RUN #2 11-2-82 10:47-11:54

1. Chlorine to both reactors
2. Sour gas supply pressure at plant was 7 inches of water. Maximum sour gas feed rate obtainable was 1.6 SCFM.
3. Pressure to scrubber was 1 inch water.
4. Reactor #1 hot to mid-point; reactor #2 hot to mid-point (est. 120°F surface), cool at end.
5. Run terminated when sour gas feed rate dropped to 0.75 SCFM with valve wide open. Supply pressure still 7 inches of water at plant gage and pressure to scrubber system still about 1 inch of water.
6. No sulfur in sulfur drain pots.
7. Opened system and found pieces of sulfur in reactor reducers and cross. Steamed reactor section at 32 psig for 30 minutes. Sulfur does not drain to pots. Reducers and valves required mechanical cleaning.

8. Replaced sulfur drain pots with pinch valves.
9. Water scrubber rotometer fouled with sulfur. Dropped water scrubber packing and cleaned system. Packing not plugged but some sulfur coating.

RUN #3 11-4-82 1:40-2:50

1. Chlorine to both reactors.
2. Reactor #1 hot to mid-point, reactor #2 hot along entire length.
3. Opened drain valve of bottom (exit) of reactor #2 for a few seconds during run. Small amount of dark orange liquid drained to bucket, not readily water soluable.
4. Terminated run when liquid entered sour gas rotometer and flow dropped to zero.
5. Steam out and depressure through sulfur drain valves. Some molten sulfur sprayed onto skid.
6. Air line attached to sour gas rotometer. Air flow through system of 1 SCFM requires 4 inches of water pressure at inlet.
7. Replaced ½ inch intalox saddles in water scrubber with 3/4 inch intalox saddles.

RUN #4 11-8-82 11:01-12:07

1. Chlorine to reactor #2 only.
2. Reactor #2 hot for full length.
3. Surface temperature of lead coil inlet was 150°F.
4. Run terminated when water scrubber drain valve cracked and started leaking.
5. Repacked caustic scrubber with 3/4 inch intalox saddles.

RUN #5 11-10-82 9:30

1. Chlorine to reactor #1 only.
2. Insulated piping between reactors #1 and #2 and 1/3 of reactor #2 with fiberglass blanket before run.

3. Reactor #1 hot for 1/2 of length. Reactor #2 at end of insulation was slightly warm.
4. Vent from caustic scrubber shows no H_2S by lead acetate paper or MSA gas sampler.
5. At end of run, less than 0.2 SCFM air (lowest reading) at 11 inches of water.
6. Steamed out reactor section and recovered 1 pound, 2 ounces of sulfur, mostly from reactor #2.

RUN #6 11-12-82 9:55-10:52

1. Insulated reactor #1 top four inches with flange.
2. Chlorine to reactor #1 ibly.
3. Reactor #1 surface temperature at top (exit) estimated at 110°F.
4. Terminated run when sour gas feed rate dropped in spite of fully opened valve.
5. Recovered 11 ounces of clean yellow sulfur from steam out of reactor.
6. Increased size of caustic scrubber column from 2 inches to 3 inches in diameter.

RUN #7 11-15-82 11:15-12:40

1. Added a remote bulb thermometer to reactor system. Bulb was located under insulation of reactor #2, 26 inches from inlet.
2. Chlorine to reactor #1 only.
3. Bulb thermometer 47°C (reactor #2).
4. Pressure drop across scrubber system was less than 1/8 inch of water.
5. Run terminated when sour gas feed rate dropped.
6. Lead cooling coil plugged near inlet. Coil cut and mechanically cleaned, repaired with metal sleeve.

RUN #8 11-18-82 9:17-10:20

1. Chlorine to reactor #1 only.
2. Reactor #1 warm for 3/4 of its length.
3. Reactor #2 inlet temperature was 36°C (maximum).
4. Lead coil inlet temperature 96°F.
5. Run terminated when sour gas feed rate dropped.
6. Sulfur recovered during steam-out amounted to 1/2 pound. Additional sulfur removed mechanically from valves and fittings.

RUN #9 11-19-82 11:02-11:57

1. Chlorine to reactor #1 only.
2. Chlorine cylinder scale repaired and now put into use for the first time. Shows 4 pounds of chlorine to run.
3. Run terminated when sour gas feed rate dropped.

RUN #10 11-22-82 12:13-1;12

1. Chlorine to reactor #1 only.
2. Inlet end of reactor #1 too hot to touch. Mid-point of reactor estimated to be 110°F.
3. Chlorine cylinder scale weight showed 4 pounds of chlorine to run.
4. Run terminated when sour gas feed rate dropped.
5. Reactors taken apart to clear plug. Kynar packing andparts of support plates melted and charred. Packing removed from both reactors.

RUN #11 11-23-82 12:41-1:03

1. Run start delayed since geothermal plant down due to tree falling across power lines.
2. Chlorine to both reactors.
3. Run terminated when water scrubber circulation pump failed. Pump was plugged with sulfur.

RUN #12 11-28-82 8:30-9:53

1. Replaced sour (Calcuflo) rotometer with a Brooks rotometer (R-6-15-B with tantalum float).
2. Chlorine to both reactors.
3. Added water manometer at sour gas feed inlet. Manometer reads 14 inches of water when plant gage shows 7 inches.
4. Vent lead acetate negative. Gas to caustic scrubber showed intermittent positive reaction to lead acetate paper; light tan in 3 to 5 seconds.
5. Run terminated when sour gas feed rate dropped. Valve was full on and inlet pressure was 14 inches of water.
6. Chlorine cylinder scale indicated 14 pounds of chlorine to run.

RUN #13 11-29-82 12:38-1:21

1. Chlorine to reactor#2 only.
2. Reactor #2 inlet hot (est. 120°F) and slightly warm at mid-point. Lead coil inlet surface temperature was 85°F.
3. Supply sour gas pressure varied during run from 7 inches to 13 inches (water manometer at inlet).
4. Sample of liquid from lead coil outlet was dark orange.
5. Run terminated when sour gas feed rate dropped.
6. Chlorine cylinder scale showed 4 pounds of chlorine to run.

RUN #14 11-30-82 10:13-11:00

1. Chlorine to reactor #2 only.
2. Maximum surface temperature of reactor #2 at 2/3 of length; exit end warm.
3. Chlorine cylinder scale showed 3 pounds chlorine to run.
4. Run terminated when sour gas feed rate dropped.

RUN #15 12-1-82 9:30-9:58

1. Chlorine to reactor #2 only.
2. Sour gas supply pressure varied from 11 to 18 inches during run.

Plant gage maximum reading 11 inches of water.

3. Run terminated when sour gas feed rate dropped.

RUN #16 12-2-82 12:55-1:33

1. Chlorine to reactor #2 only.
2. MSA gas tester with color change tubes used to test gas to caustic scrubber.

11:05	0.7% V. H_2S
1:15	4.0% V. H_2S
1:20	15.6% V. H_2S

3. Reactor #2 inlet hot, mid-point warm and exit cold to touch.
4. Run terminated when sour gas feed rate dropped.

RUN #17 12-3-82 9:30-10:45

1. Chlorine to reactor #2 only.
2. MSA gas tester used to test gas to caustic scrubber:

9:47	5.2% V. H_2S
9:55	5.4% V. H_2S

3. Run terminated when sour gas feed rate dropped.
4. End of first series of runs.

RUN A 4-25-83 10:30-12:37

1. First run of series with heat exchanger-reactor and without caustic scrubber.
2. MSA tester on vent gas at 10:50 shows 0.075% V. H_2S (4 strokes gave 0.39% V. H_2S). Vent gas diluted with 1750 CFM air shows 3 ppm H_2S on GasTech analyzer.
3. Water log for heat exchanger 278°F, 38 psig.
4. No sulfur from drain during run.
5. Vent gas samples for H_2S

11:23	1 ppm with 1750 CFM air		H_2S on vent only; MSA=0.005% V.
11:35	5 ppm with 1750 CFM air		
11:37	6 ppm " "		
11:40	5 ppm " "		
11:46	4 " " "		

11:56 8 ppm with 1750 CFM air

12:03 8 " " MSA = 0.43%

12:07 5 " "

12:12 9 ppm with 600 CFM air

12:20 11 " "

12:27 15 " "

12:35 15 " "

6. Run terminated for convenience, not forced.

RUN B 4-27-83 10:00-10:43

1. Sulfur drained during run; few ounces only.
2. Vent gas at 10:11 shows 14 ppm H_2S with 1750 CFM air dilution.
3. At 10:25 manometer showed 3½ feet of water. Vent gas 95-100 ppm H_2S(maximum of range) and vent gas had sulfur dioxide odor.
4. Run terminated when water scrubber column flooded (water crashed in vent gas line.)

RUN C 4-28-83 10:37-12:20

1. Sour gas feed rotometer moved to discharge side of feed gas compressor.
2. A total of 2 pounds 15 ounces of sulfur was drained during the run.
3. Vent gas analyses for H_2S

10:37 35 ppm H_2S with 1750 CFM air dilution

10:41 16 " "

10:47 8 " "

10:52 15 " "

MSA on V. at only 0.4% V. H_2S

11:02 6 ppm H_2S with 1750 CFM air dilution

MSA on vent only = 0.4% V. H_2S

11:10 5 ppm H_2S with 1750 CFM air dilution

11:30 7 " "

11:37 14 ppm H_2S with 1750 CFM air dilution
12:02 6 " "

4. Water loop for heat exchanger at 270°F.
5. Run terminated when water scrubber drain valve broke.
6. Cleaned water scrubber, found lines partially plugged and layers of sulfur in scrubber tank.

RUN D 5-2-83 1:00-2:06

1. Added steam line to sour gas feed just ahead of reactor.
2. Added manifold to increase number of chlorine cylinders from 1 to 3.
3. Steam to reactor not measured; opened ¼ inch needle valve 1/8 turn.
4. Vent gas 19 to 29 ppm H_2S with 1750 CFM air dilution during first part of run. Out of range at end of run and smell of chlorine at very end.
5. Run terminated when water in sour gas rotometer became excessive.

RUN E 5-3-83 11:00-12:00

1. No steam to reactor.
2. A total of 3 pounds 7 ounces of sulfur was drained from reactor during the run.
3. The geothermal plant sour gas pressure dropped from 12 inches to 7 inches of water due to the volume of gas used in the test runs.
4. Vent gas analyses for H_2S

11:00 20 ppm H_2S with 1750 CFM air dilution.
11:05 12 " "
11:20 9 " "
MSA on vent only = 0.35% V. H_2S
11:30 26 ppm ppm H_2S with 1750 CFM air dilution
11:45 40 " "

5. Run terminated due to rapid build up to water scrubber columns

RUN F 5-4-83 9:17-11:45

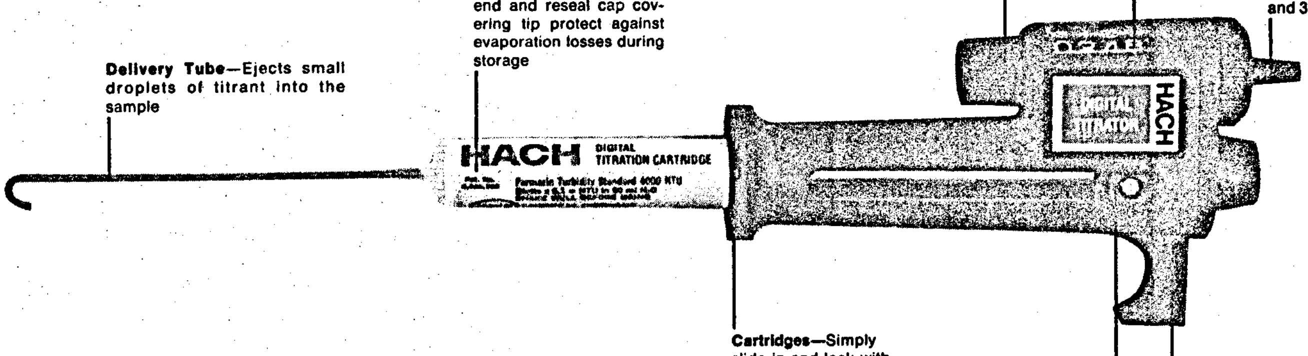
1. Water scrubber column repacked with 18 inches of Kynar packing.
2. A total of 8 pounds of sulfur was drained during the run.
3. Chlorine rate during run kept at maximum available from 3 cylinders.
4. Vent gas analyses for H_2S

   9:30 13 ppm H_2S with 1750 CFM air dilution
   9:43 36 " "
   9:45 45 " "
   10:57 80 " "
5. Water scrubber turbo heated up during run to about 100°F by end of run.
6. Run terminated when water scrubber circulation pump started leaking badly.

GENERAL NOTES

1. No chlorine was detected in any of the scrubber liquid samples.
2. The runs of the first series were generally terminated due to system plugging. Sulfur plugs in the reactor system piping generally required cleaning between runs with both steaming and mechanical cleaning after disassembly.
3. Sulfur carryover to the water scrubber was evident in both series of runs. The use of the heat exchanger-reactor in the second series of runs did, however, substantially reduce sulfur carryover.
4. Final disassembly of the piping between the heat exchanger-reactor and the water scrubber showed sections that were nearly plugged with sulfur.

APPENDIX II



Counter Reset Knob—Resets counter to zero after completion of titration

Digital Counter—You read concentration directly in mg/l

Delivery Knob—Controls titrant flow. Most titrations will take between 10 and 30 turns

Titration Cartridge—Contains high strength, prestandardized titrating solution. Teflon seal at base end and reseal cap covering tip protect against evaporation losses during storage

Delivery Tube—Ejects small droplets of titrant into the sample

Cartridges—Simply slide in and lock with a quarter turn.

Plunger Release Button—Releases plunger from the main threaded drive screw so that it can be manually advanced or retracted to engage the piston with the cartridge

Handgrip—Braces titrator against palm of hand for comfortable hand-held operation

REPLACEMENT PARTS

Cat. No.	Description
16900-08	Methods Manual
17205-00	Delivery tube, straight stem (180°)
17342-00	Delivery tube, 90°-angle bend

SELECTING THE RIGHT TITRANT

To choose the most suitable concentration of titrant for your samples, please *refer to the chart.* Column 2 lists the conventional titrant that corresponds to the concentration of the titration cartridge. For example, if you have been titrating chloride with a 0.0141N $AgNO_3$ solution, you would choose titration cartridge Cat. No. 14397-01, 1.128N $AgNO_3$ as the closest replacement. Likewise 8.00N NaOH, HCl, and H_2SO_4 would replace 0.1N acids and bases in neutralization titrations.

We also offer more dilute solutions for titrating less concentrated samples. In most cases, we recommend a titrant choice that will give an end point within 10-40 turns of the delivery knob. For example, if a 100-ml wastewater sample generally contains between 100-300 mg/L alkalinity, a more concentrated H_2SO_4 titrant (Cat. No. 14389-01) should be chosen. If your sample tends to be less alkaline, or only 40-60 mg/L expressed as $CaCO_3$, use a more dilute titrant such as 0.1600N H_2SO_4 (Cat. No. 14388-01).

SOLUTIONS AVAILABLE IN TITRATION CARTRIDGES

Use	Comparable Conventional Titrant	Hach Titration Cartridge Cat. No.	Description	Cartridge Concentration: Every 10 Turns Equals
Acid-base	0.1N	14390-01	HCl, 8.00±0.04N	1 meq acid
	0.1N	14391-01	H_2SO_4, 8.00±0.04N	1 meq acid
	0.1N	14381-01	NaOH, 8.00±0.04N	1 meq alkali
Acidity	----	14377-01	NaOH, 0.1600±0.0007N	0.02 meq NaOH = 10 mg/L $CaCO_3$ in 100-ml sample
	0.02N	14379-01	NaOH, 1.600±0.008N	0.2 meq NaOH = 100 mg/L $CaCO_3$ in 100-ml sample
Alkalinity	----	14388-01	H_2SO_4, 0.1600±0.0005N	0.02 meq H_2SO_4 = 10 mg/L $CaCO_3$ in 100-ml sample
	0.02N	14389-01	H_2SO_4, 1.600±0.005N	0.2 meq acid H_2SO_4 = 100 mg/L $CaCO_3$ in 100-ml sample
Ca, Mg, Total Hardness	----	14402-01	CDTA, 0.0800±0.0004M	0.01 mmol CDTA = 10 mg/L $CaCO_3$ in 100-ml sample
	0.02N	14403-01	CDTA, 0.800±0.004M	0.1 mmol CDTA = 100 mg/L $CaCO_3$ in 100-ml sample
	----	14364-01	EDTA, 0.0800±0.0004M	0.01 mmol EDTA = 10 mg/L $CaCO_3$ in 100-ml sample
	0.02N	14399-01	EDTA, 0.800±0.004M	0.1 mmol EDTA = 100 mg/L $CaCO_3$ in 100-ml sample
	----	14959-01	EDTA, 0.714±0.003M	1 G.d.h. = 17.85 mg/L $CaCO_3$ in 50-ml sample
	----	14960-01	EDTA, 0.1428±0.0007M	0.1 G.d.h. = 1.785 mg/L $CaCO_3$ in 100-ml sample
Carbon Dioxide	----	14378-01	NaOH, 0.3636±0.002N	0.0454 meq NaOH = 10 mg/L CO_2 in 200-ml sample
	0.0227N	14380-01	NaOH, 3.636±0.02N	0.454 meq NaOH = 100 mg/L CO_2 in 200-ml sample
Chloride	----	14396-01	$AgNO_3$, 0.2256±0.001N	0.0282 meq $AgNO_3$ = 10 mg/L Cl^- in 100-ml sample
	0.0141N	14397-01	$AgNO_3$, 1.128±0.005N	0.141 meq $AgNO_3$ = 50 mg/L Cl^- in 100-ml sample
	----	14393-01	$Hg(NO_3)_2$, 0.2256±0.001N	0.0282 meq $Hg(NO_3)_2$ = 10 mg/L Cl^- in 100-ml sample
	----	921-01	$Hg(NO_3)_2$, 2.256±0.01N	0.282 meq $Hg(NO_3)_2$ = 100 mg/L Cl^- in 100-ml sample
Chlorine	0.00282N	14395-01	PAO,* 0.02256±0.0001N	0.00282 meq PAO = 1.0 mg/L Cl_2 in 100-ml sample
	----	1078-01	PAO,* 0.113±0.0006N	0.0141 meq PAO = 100 mg/L Cl_2 in 5-ml sample
Chromate	----	20600-01	PAO,* 0.2068±0.001N	0.0258 meq PAO = 100 mg/L CrO_4 in 10-ml sample
Dissolved Oxygen	0.0025N	14406-01	PAO,* 0.2000±0.001N	0.025 meq PAO = 1.0 mg/L O_2 in 200-ml sample
	0.025N	14401-01	$Na_2S_2O_3$, 2.00±0.01N	0.25 meq $Na_2S_2O_3$ = 10 mg/L O_2 in 200-ml sample
EDTA	0.0025N	20625-01	$MgCl_2$, 0.0800±0.0004M	0.01 mmol EDTA = 100 mg/L of 38% tetrasodium EDTA in 100-ml sample
Ozone	0.00564N	14395-01	PAO,* 0.02256±0.0001N	0.00282 meq PAO = 0.0845 mg/L O_3 in 800-ml sample
Starch Iodide	0.025N	14401-01	$Na_2S_2O_3$, 2.00±0.01N	0.25 meq $Na_2S_2O_3$ = 0.25 meq I_2
Sulfite	0.0125N	14961-01	KIO_3KI, 0.3998N±0.002	0.04998 meq KIO_3 = 100 mg/L SO_3 in 20 ml sample
Turbidity Standard	----	2461-01	Formazin, 4000 NTU	100 digits = 10 NTU in 50 ml Di H_2O
Volatile Acids	0.9274N	14842-01	NaOH, 0.9274±0.005N	0.1159 meq NaOH = 100 mg/L acetic acid equivalent in 150 ml sample

*PAO is an abbreviation for phenylarsine oxide

TITRATION PROCEDURES

ACIDITY

TEST IMPORTANCE

Acidity is a method of expressing the capacity of water to donate hydrogen ions and gives an indication of the water's corrosiveness. The acidity of natural waters is normally very low unless strongly acidic industrial waters have been introduced.

Acidity can be caused by weak organic acids such as carbonic, acetic or tannic acids, or by strong mineral acids such as sulfuric or hydrochloric acids from industrial wastes. Hydrolyzable inorganic salts such as ferrous and aluminum sulfate also contribute to the acidity of a water.

PRINCIPLE

Acidity of a sample is classified by the pH value of the sodium hydroxide titration end point. In nonpolluted waters the acidity is due primarily to dissolved carbon dioxide which can be analyzed by titrating to its neutralization point at pH 8.3. This value corresponds to the color change of phenolphthalein indicator and is commonly called the phenolphthalein acidity.

For systems that are more complex (such as industrial wastes or buffered solutions), a pH of 3.7 has been arbitrarily chosen to give an estimate of the strong mineral acids present. Methyl orange indicator undergoes a color change from red to orange at pH 3.7 and results are commonly referred to as the methyl orange acidity. Since the methyl orange end point is difficult to see, brom phenol blue indicator solution is recommended as a replacement. Brom phenol blue indicator gives a sharp yellow to pure green end point.

INTERFERENCES

Highly colored or turbid samples may block the color change at the end point.

SAMPLE

Sample sizes will vary depending on the acidity of the water or wastewater.

Acidity depends greatly on dissolved gases, such as carbon dioxide, hydrogen sulfide and ammonia. Care must be taken to avoid aerating or shaking the sample or these gases may be lost. Add a drop of sodium thiosulfate standard solution, 0.1N, to the sample to remove any residual chlorine which may interfere with the indicator. If samples cannot be analyzed immediately upon collection, they can be refrigerated at 4° C up to 24 hours.

ANALYSIS PROCEDURE

Using 1.600N Sodium Hydroxide Titration Cartridge For acidities above 100 mg/L as $CaCO_3$*

1. If performing a hand-held titration, attach a clean, straight-stem delivery tube to a 1.600N Sodium Hydroxide Titration Cartridge. Twist cartridge onto titrator body. If Digital Titrator is to be attached to a laboratory stand, use a clean, 90-degree delivery tube.
2. Flush the delivery tube by turning the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.
3. Take a water sample by filling a clean, 100-ml graduated cylinder to the 100-ml mark. Pour the sample into a clean, 250-ml Erlenmeyer flask.
4. Add contents of one brom phenol blue indicator powder pillow and swirl to mix.
5. Titrate the sample with 1.600N sodium hydroxide standard solution while swirling the flask until the color changes from yellow to pure green. *See Note A.*
6. Read and record the concentration of methyl orange acidity (as $CaCO_3$). *See Note B.*
7. Take another portion of the water sample by filling a clean, 100-ml graduated cylinder to the 100-ml mark. Pour sample into a clean, 250-ml Erlenmeyer flask.
8. Add contents of one phenolphthalein indicator powder pillow and swirl to mix.
9. Continue to titrate with 1.600N sodium hydroxide standard solution until a permanent pink color appears.
10. Read the concentration of total acidity (in mg/L $CaCO_3$) from the digital counter window.

NOTES

A. *Sodium hydroxide standard solution slowly absorbs carbon dioxide when exposed to air, causing a partial loss of strength. The sodium hydroxide titration cartridge should be checked monthly by titrating a 50-ml sample of potassium acid phthalate standard solution using phenolphthalein indicator solution. If the digital counter reading is greater than 240, the sodium hydroxide standard solution should be discarded and replaced with a fresh supply.*

B. A demineralized water solution of the indicator and the correct buffer is strongly recommended for determining the proper indicator color at the titration end point. Mix the contents of one pH 3.7 Buffer Powder Pillow with 50 ml of demineralized water in a 125-ml Erlenmeyer flask and add 6 drops of brom phenol blue indicator solution. Repeat the preparation with one pH 8.3 Buffer Powder Pillow and 6 drops of phenolphthalein indicator solution. Titrate the prepared water samples to the same color as the buffered reference solutions.

REAGENTS AND APPARATUS

Cat. No.	Description	Unit
14550-99	Brom Phenol Blue Indicator Powder Pillows	100
942-99	Phenolphthalein Indicator Powder Pillows	100
14379-01	Sodium Hydroxide Titration Cartridge, 1.600N . . .	each
508-42	Cylinder, graduated, 100 ml	each
505-46	Flask, Erlenmeyer, 250 ml	2

Optional Reagents and Apparatus

Cat. No.	Description	Unit
14551-98	Buffer Powder Pillows, pH 3.7 . . .	25
898-98	Buffer Powder Pillows, pH 8.3 . . .	25
272-17	Demineralized Water	gal
1885-11	Potassium Acid Phthalate Solution, 400 mg/L as CO_2	pt
14377-01	Sodium Hydroxide Titration Cartridge, 0.1600N . .	each
323-13	Sodium Thiosulfate Standard Solution, 0.1N	4-oz DB
620-11	Bottle, wash, poly, 16 oz	each
21145-00	Clamp, extension . .	each
326-00	Clamp Holder	each
17205-00	Delivery Tube, straight	5
17342-00	Delivery Tube 90°	5
563-00	Support Stand . . .	each

*Larger sizes available

Optional Larger Reagent Sizes

Cat. No.	Description	Unit
14552-11	Brom Phenol Blue Indicator Solution .	pt
162-11	Phenolphthalein Indicator Solution .	pt
162-16	. . . .	qt

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*For acidities below 100 mg/L as $CaCO_3$, use a 0.1600N Sodium Hydroxide Titration Cartridge and divide the readings in Steps 6 and 10 by 10 to determine the mg/L acidity as $CaCO_3$.

CHLORIDE

TEST IMPORTANCE

Chlorides are present in all potable water supplies and sewage, usually as a metallic salt. When sodium is present in drinking water. chloride concentrations in excess of 250 mg/L give a salty taste. If the chloride is present as a calcium or magnesium salt, the taste detection level may be as high as 1000 mg/L chloride.

High chloride concentrations in water are not known to have toxic effects on human beings, though large amounts may act corrosively on metal pipes and be harmful to plant life. The maximum allowable chloride concentration of 250 mg/L in drinking water has been established for reasons of taste rather than as a safeguard against physical hazard.

PRINCIPLE

The mercuric nitrate method of chloride analysis has become popular due to the sharp yellow to pinkish-purple end point of diphenylcarbazone, and the absence of a precipitate during the titration. A single, stable powder has been developed combining the color indicator with an appropriate buffer to establish the correct sample pH. Silver nitrate titrating solutions are also available. Although the yellow to red-brown end point is less pronounced than that obtained with the mercuric nitrate titrant, the silver nitrate titrating solutions are suitable for clear water containing lower concentrations of chloride.

INTERFERENCES

Chromate, ferric iron, and sulfite in excess of 10 mg/L interfere with the mercuric nitrate method. Sulfite interference can be eliminated by adding 3 drops of 30% hydrogen peroxide per 100 ml of water sample before running the test. Sulfide interference can be removed by adding the contents of one Sulfide Inhibitor Reagent Powder Pillow to about 125 ml of the sample, mixing for one minute, and filtering through a folded filter paper. Iodide and bromide interfere directly and are titrated as chloride.

SAMPLE

Collect at least 100-200 ml of sample in a clean glass or polyethylene container. Samples may be held up to one week before analysis.

ANALYSIS PROCEDURE
Using 2.256N Mercuric Nitrate Titration Cartridge
For chloride concentrations above 100 mg/L as Cl^-*

1. If performing a hand-held titration, attach a clean, straight-stem delivery tube to a 2.256N Mercuric Nitrate Titration Cartridge. Twist cartridge onto titrator body. If Digital Titrator is to be attached to a laboratory stand, use a clean, 90-degree delivery tube.
2. Flush the delivery tube by turning the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.
3. Take a water sample by filling a clean 100-ml graduated cylinder to the 100-ml mark. Pour the sample into a clean 250-ml Erlenmeyer flask.
4. Add the contents of one Diphenylcarbazone Reagent Powder Pillow and swirl to mix. *See Note A.*
5. Titrate the sample while swirling the flask until the color changes from yellow to light pink.
6. Read the concentration of chloride (in mg/L) directly from the digital counter window. *See Note B.*

---

*For chloride concentrations below 100 mg/L as Cl^-, use a 0.2256N Mercuric Nitrate Titration Cartridge and divide the reading in Step 6 by 10 to determine the mg/L chloride.

NOTES

A. The results will not be affected if a small portion of the diphenylcarbazone reagent powder does not dissolve.

B. The results may be expressed as mg/L sodium chloride by multiplying the mg/L chloride by 1.65.

REAGENTS AND APPARATUS

Cat. No.	Description	Unit
836-99	Diphenylcarbazone Reagent Powder Pillows	100
921-01	Mercuric Nitrate, Titration Cartridge, 2.256N	each
968-00	Clippers, large	each
508-42	Cylinder, graduated, 100 ml	each
505-46	Flask, Erlenmeyer, 250 ml	each

Optional Reagents and Apparatus

Cat. No.	Description	Unit
14393-01	Mercuric Nitrate Titration Cartridge, 0.2256N	each
21145-00	Clamp, extension	each
326-00	Clamp Holder	each
17205-00	Delivery Tube, straight	5
17342-00	Delivery Tube, 90°C	5
563-00	Support Stand	each

ANALYSIS PROCEDURE
Using 1.128N Silver Nitrate Titration Cartridge
For chloride concentrations above 50 mg/L as Cl^-*

1. If performing a hand-held titration, attach a clean, straight-stem delivery tube to a 1.128N Silver Nitrate Titration Cartridge. Twist cartridge onto titrator body. If Digital Titrator is to be attached to a laboratory stand, use a clean, 90-degree delivery tube.
2. Flush the delivery tube by turning the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.
3. Take a water sample by filling a clean 50-ml graduated cylinder to the 50-ml mark. Pour the sample into a clean 125-ml Erlenmeyer flask.
4. Add the contents of one Chloride 2 Indicator Powder Pillow and swirl to mix.
5. Titrate the sample while swirling the flask until the color changes from yellow to red-brown.
6. Read the concentration of chloride (in mg/L) directly from the digital counter window. *See Note.*

---

*For chloride concentrations below 50 mg/L as Cl^-, use a 0.2256N Silver Nitrate Titration Cartridge and divide the reading in Step 6 by 10 to determine the mg/L chloride.

NOTE

The results may be expressed as mg/L sodium chloride by multiplying the mg/L chloride by 1.65.

REAGENTS AND APPARATUS

Cat. No.	Description	Unit
1057-99	Chloride 2 Indicator Powder Pillows	100
14397-01	Silver Nitrate Titration Cartridge, 1.128N	each
968-00	Clippers, large	each
508-41	Cylinder, graduated, 50 ml	each
505-43	Flask, Erlenmeyer, 125 ml	each

Optional Reagents and Apparatus

Cat. No.	Description	Unit
14396-01	Silver Nitrate Titration Cartridge, 0.2256N	each
21145-00	Clamp, extension	each
326-00	Clamp Holder	each
17205-00	Delivery Tube, straight	5
17342-00	Delivery Tube, 90°	5
563-00	Support Stand	each

SULFATE TEST KIT
0-200 mg/L
MODEL SF-1
CAT. NO. 2251-00

HACH

INSTRUCTIONS

1. Fill the calibrated tube to the top with the water to be tested.
2. Pour the sample into the mixing tube.
3. Use the clippers to open one SulfaVer® Powder Pillow. Add the contents of the pillow to the mixing tube, and mix thoroughly.
4. A white turbidity will appear if sulfate is present.
5. Allow sample to stand 5 minutes.
6. Hold the calibrated tube in such a manner that it can be viewed through the top. Slowly pour the prepared sample into the tube. Continue pouring until the image of a black cross on the bottom of the tube just disappears from view. At this point the bottom of the tube will appear as a uniform field of view.
7. Read the mg/L Sulfate (SO_4) from the scale on the side of the tube.
8. The terms milligram/liter (mg/L) and parts per million (ppm) are essentially interchangeable except at very high concentrations of 7000 mg/L or more.

WARNING: ***The chemicals in this kit may be hazardous to the health and safety of the user if inappropriately handled. Please read all warnings before performing the test(s), and use appropriate safety equipment.***

REPLACEMENTS

12065-66	SulfaVer® IV Powder Pillows	pk/50
2157-00	Calibrated Sulfate Viewing Tube	each
2160-00	Mixing Tube with pouring lip	each
968-00	Clippers	each

® Registered Trademark, Hach Company

3/82
KIT LOT NO. 2173

MADE IN U.S.A. HACH COMPANY, P.O. BOX 389, LOVELAND, COLORADO 80539
TELEPHONE 303-669-3050 TWX 910-930-9038

HIGH RANGE CHLORINE TEST KIT

MODEL CN-21P
CAT. NO. 1447-00

TO INSURE ACCURATE RESULTS PLEASE READ CAREFULLY BEFORE PROCEEDING:
An unusually high content of organic matter may cause uncertainty in the end point of this test.

1. Fill the plastic measuring tube level full of the water to be tested, and pour it into the square mixing bottle.
2. Use the clippers to open one Potassium Iodide Powder Pillow. Add the contents of the pillow to the bottle. Swirl to mix as shown in Figure 1.
3. Use the clippers to open one Sulfamic Acid Powder Pillow. Add to the contents of the bottle. Swirl to mix. If chlorine is present a yellow color will develop.
4. Add the PAO Standard Solution drop by drop to the contents of the bottle. Count each drop as it is added. Swirl the bottle to mix after each drop is added. Continue adding drops until the solution changes from yellow to colorless.
5. The mg/L chlorine (Cl) is equal to 10 times the number of drops of PAO Standard Solution used.

WARNING: ***The chemicals in this kit may be hazardous to the health and safety of the user if inappropriately handled. Please read all warnings before performing the test(s), and use appropriate safety equipment.***

REPLACEMENTS

†1058-37	PAO (Phenylarsine Oxide) Standard Solution 0.0246N for Total Chlorine, High Range (1 drop = 10 mg/L chlorine)	118 mL (4oz DB*)
1058-11		473 mL (pt)
1077-99	Potassium Iodide Powder Pillows	pk/100
1055-99	Sulfamic Acid Powder Pillows	pk/100
439-00	Bottle, square mixing	each
936-00	Clippers	each
438-00	Measuring Tube, plastic 5.83 mL	each

† Direct Replacement
* Dropping Bottle

3/82
KIT LOT NO. 2230

MADE IN U.S.A. HACH COMPANY, P.O. BOX 389, LOVELAND, COLORADO 80539 U.S.A.
TELEPHONE 303-669-3050, TWX 910-930-9038

Kitagawa **No. 120Sh**

HYDROGEN SULFIDE LENGTH-OF-STAIN DETECTOR TUBES
(Type SH)
(Direct Reading Type)

PERFORMANCE :

Measuring Range : 0.1 — 4.0%
Sampling Time : 1minute (1pump stroke)
Color Change : Pale Blue— Black
Sensing Limit * : 0.005%

*The minimum detectable concentration although not precise

*FLOW CONTROL ORIFICE IN THE PUMP SHOULD BE REMOVED BEFORE SAMPLING.

SAMPLING AND MEASUREMENT :

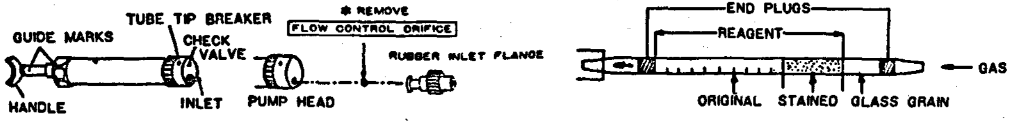

Fig. 1

1. Break tips of a fresh detector tube by bending each tube end in the tube tip breaker, and then insert the tube end marked with braod arrow securely into the pump inlet, as showen in Fig 1.
2. Align the guide marks (red dots) on shaft and back plate of the pump. And pull the handle at a full stroke and lock it with 1/4—turn (90°). Wait 1minute as it is.
3. Remove the detector tube from the pump inlet on the completion of the sampling. The reading can be obtained directly from the scale printed on the detector tube.

SPECIAL NOTE :

When the top of the discolored layer is colored obliquely, read the concentration at the center between the longest and shortest points of the discolored layer. The total stain length should be read regardless of color variations.

TEMPERATURE AND HUMIDITY CORRECTION :

No temperature correction is at the temperatures of 0°C (32°F) to 40°C (104°F).
Up to 100% (25°C=77°F) relative humidity, no need for correction.

INTERFERENCES :

Coexistence of more than 0.5% of Sulfur Dioxide gives lower readings.

HAZARDOUS AND DANGEROUS PROPERTIES OF HYDROGEN SULFIDE :

T. L. V. † : 10ppm
Explosive range in air : 4.3 — 45%

†Threshold Limit Value established by the American Conference of Governmental Industrial Hygienists, 1978.

CHEMICAL REACTION IN THE DETECTOR TUBE :

$H_2S + CuSO_4 \rightarrow CuS$

BEFORE TESTING, THE PUMP SHOULD BE CHECKED FOR PROPER PERFORMANCE.
LEAKAGE OF AIR WILL AFFECT ACCURATE READINGS.
FLOW CONTROL ORIFICE SHOULD BE PLACED BACK TO ITS POSITION AFTER TEST.

No. 201

Kitagawa

CHLORIDE ION DETECTOR TUBE INSTRUCTIONS AND INFORMATION

FUNCTION:

Chloride Ion Detector Tubes provide rapid accurate measurement of Chloride Ion in water in the ranges 50—2,000 PPM (parts per million) by immersion method, or 5—40 PPM by injection method. Sampling and measurement take less than ~~5~~ 3 minutes by immersion method and ~~7~~ 2 minutes by injection method respectively.

DESCRIPTION OF DETECTOR TUBE:

The detector tube is a glass tube filled with reddish-brown granular reagent, which is fixed tightly with cotton stopper (white) at the both ends. The tube is hermetically sealed at the both ends. (Fig. 1)

Instructions for use:

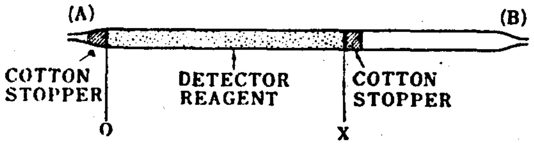

Fig. 1

A) Immersion method:

1. Cut off the tips (A) and (B) of a fresh tube with a file supplied with the tubes
2. Immerse bottom end (A) of the tube into the sample water. (Fig. 2)
3. The sample water goes up gradually through the detector reagent by capillary action and if Chloride Ion exist in the sample a discoloration will occur in the detector reagent layer from its bottom end.

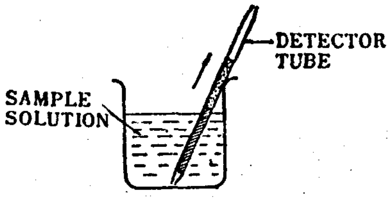

Fig. 2

4. When the sample water ascends to the top of the detector reagent layer, remove the detector tube. Place the tube on the concentration chart in parallel with axis of ordinates so that the boundary line between the detecting reagent and the bottom cotton stopper of the tube will fit the O-O line; and the boundary line between the detecting reagent and the top cotton stopper will fit the X-X line (Fig. 3).
   The graduated reading on the concentration chart, corresponding to the length of the discolored layer, will give the concentration value in PPM. The measurable range–is 50—2,000 PPM. (detecting limit, 20 PPM) If concentration of Chloride Ion in the sample exceeds 2,000 PPM, dilute the sample with distilled water to bring concentration within the measurable range. After measuring the diluted sample, multiply the value obtained by exactly as many times as the ratio of dilution. Depth or angle of immersed tube in sample water will not affect measurements.

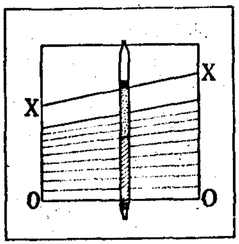

Fig. 3

Interferences:

Measurements by immersion method are not interfered insofar as the PH value and the temperature of sample water are within the ranges PH 4—13 and 40°—180°F (5°—82°C) respectively.

Accurate measurements may be interfered by coexisting Bromide (Br^-) Iodide (I^-) and Cyanide (CN^-) ions, in which case the readings indicate lower concentration than actual concentration. The other ions such as Sulfate (SO_4^{2-}), Nitrite (NO_2^-), Nitrate (NO_3^-), Iron (Fe^{3+}) ions do not interfere with accurate measurements as far as their concentrations are below 1,000 PPM.

B) Injection method:

A glass syrings of 2*ml* capacity is required for measurement by this method. (Fig. 4)

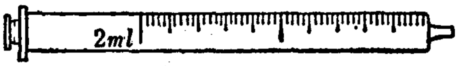

Fig. 4

1. Attach a rubber tubing as supplied to the syringe inlet.
   Collect 2*ml* sample in the syringe by pulling the piston handle.
2. Cut off the tips (A) and (B) of a fresh tube with a file supplied with the tubes.
3. Insert tip (A) of the tube securely into the rubber connecting tube. (Fig. 5)

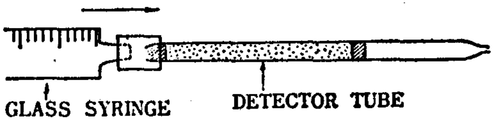

Fig. 5

4. Inject the sample water into the detector tube slowly with a constant speed, so that the 2*ml* sample water will all go through the tube in exactly ~~5~~2 minutes. If Chloride Ion exist in the sample water a discoration will occur in the detector reagent layer from its inlet end.
5. Remove the tube from the syringe and read the Chloride Ion concentration corresponding to the length of the stain in following the instructions given for immersion method. The measurable range by this method is 5—40 PPM (detecting limit, 2 PPM). If concentration of Chloride Ion in the sample exceeds 40 PPM, try again with immersion method.

Interferences:

Messurements by this method are not interfered insofar as the PH value and the temperature of sample water are within the ranges PH 6—10 and 40°—100°F (5°—38°C) respectively.

Accurate measurements may be interfered by coexisting Bromide (Br^-), Iodide (I^-), and Cyanide (CN^-) ions, but the other ions such as Nitrite (NO_2^-), Nitrate (NO_3^-), Sulfate (SO_4^{2-}), Corbonate (CO_3^{2-}), Phosphate (PO_4^{3-}), Iron (Fe^{3+}), Copper (Cu^{2+}), etc. do not interfere with accurate measurements as far as their concentrations are below 100 PPM.

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