MASTER

EVALUATION OF H₂S CONTROL TECHNOLOGY
FOR GEOTHERMAL ENERGY SOURCES

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ABSTRACT

This study was conducted for the Environmental Control Technology Division of the Department of Energy, to identify processes that are most applicable for control of H_2S from geothermal sources. Both vapor-dominated and liquid-dominated sources were considered within the electric power generation category. The source characteristics, H_2S control requirements, and applicable technologies are discussed for the two geothermal sources. An evaluation of the applicable control technology indicates that there are three major approaches for H_2S removal. These are (a) upstream cleaning (ahead of the power plant), (b) removal of H_2S from condenser vent emissions, and (c) H_2S removal from cooling water, including condensate. The most promising processes for these emission points, based on current information, are as follows: the EIC process for upstream cleaning of liquid-dominated sources. For condenser vent emissions, the Stretford process appears to be most applicable; for cooling tower emissions, the Iron catalyst process, followed by the H_2O_2 process, seems most appropriate.

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SECTION 1

EXECUTIVE SUMMARY

This program was directed toward conducting a state-of-the-art review of H₂S control methods/processes that may be applicable to geothermal energy sources and toward identifying the most promising H₂S removal processes for geothermal applications. Both vapor-dominated systems and liquid-dominated systems were included in the geothermal electric power generating category that was studied.

Vapor-dominated systems, also known as dry-stream systems, are those where steam produced in underground resources is recovered at slightly superheated conditions. In these systems, the major component is steam, as opposed to liquid-dominated systems that are primarily made up of hot water. Electric power is generated from both systems with the help of turbines.

There are numerous sources of H₂S emissions within vapor-dominated and liquid-dominated geothermal systems. These sources include:

- * Well--drilling emissions, standby venting, and bypass venting.
- * Fluid transmission--instrument vents, cyclone vents and temperature equalizer vents.
- * Power plant (process) emissions.

Excluding wellhead and fluid transmission sources, for which relatively little control has been attempted, control of emissions from the conversion

process has centered on two process points: (a) noncondensable (vent) gas emissions from the condenser and (b) dissolved H_2S in steam condensate, the latter of importance because of the high efficiency of cooling towers for dissolved gas removal (approximately 99+%).

There are three available schemes or pathways for H_2S removal from geothermal power plants. These are: (a) upstream cleaning (i.e., H_2S removal ahead of the power plant), (b) control of H_2S in noncondensable vent gases, and (c) H_2S removal from cooling water including condensate. For each of these schemes there are several H_2S control processes that are potentially applicable. All of these processes essentially involve oxidation of the H_2S .

H_2S control options for upstream cleaning include the Dow Oxygenation process, the EIC process, the Solid Sorbent process (Battelle Northwest Laboratory), and the Deuterium process. Of these, the Dow Oxygenation process is used for upstream cleaning of liquid-dominated sources, whereas the other three are primarily designed for vapor-dominated systems. The Dow process is designed to inject oxygen into the geothermal brine at the well-head and is expected to have an H_2S removal efficiency of 90 to 100%. The EIC process uses copper sulfate solution to remove H_2S from geothermal steam; the Solid Sorbent process can use a variety of metal oxides, but zinc oxide is found to be most favorable; the Deuterium process is proprietary with no information being available.

For removal of H_2S from noncondensable vent gases, potentially applicable processes include the Stretford process, the Burner-Scrubber processes, and the Jefferson Lake process. The Stretford process requires direct contact condensers and involves scrubbing of the H_2S -containing gas with an

aqueous solution containing sodium carbonate, sodium metavanadate, and anthraquinone disulfonic acid (ADA). In the Burner-Scrubber processes, the H_2S -containing noncondensable gases are incinerated and the resulting sulfur dioxide is scrubbed with cooling water. One of the two Burner-Scrubber processes uses a catalyst to selectively oxidize H_2S to sulfur dioxide. The Jefferson Lake process is a variation of the Claus process which uses a series of converters to react H_2S and sulfur dioxide to produce sulfur.

To remove H_2S from cooling water and condensate, the Iron Catalyst process, the Hydrogen Peroxide (H_2O_2) process, and the Ozone process are all potentially applicable. The Iron Catalyst process uses ferric sulfate solution to oxidize H_2S contained in the aqueous phase. In the H_2O_2 process, H_2O_2 reacts with H_2S to produce either sulfur or sulfate, depending upon whether the solution is nonalkaline or alkaline. Similarly, Ozone can potentially oxidize H_2S to either elemental sulfur or a sulfate.

Among the processes mentioned above, three appear to be more promising, based on factors such as process availability, potential for H_2S removal, ease of adaptability to subject application, state of development, costs involved, and operating requirements. The promising processes are: (a) the EIC process, (b) the Dow Oxygenation process, and (c) the Stretford process. The Iron Catalyst process is already in commercial use. The EIC process has been field tested and the Stretford process is being designed for installation at the Geysers; the Dow Oxygenation process has been pilot tested in the laboratory.

Anticipated problems with EIC, Stretford, and Dow processes are as follows. In the Dow process, corrosion can be a major problem, since oxygen increases the corrosivity of brine prior to reacting with the H_2S . The Stretford process requires a direct contact condenser, which means conventional geothermal systems need redesigning to include the surface condenser. The EIC process appears most promising, except for potential problems in the regeneration of copper sulfate. Total annual costs for the four processes, based on a 100-MW plant, are reported to be 0.5 mill/kwh for Stretford, 2 mill/kwh for EIC, 0.4 mill/kwh for Iron Catalyst, and 9 mill/kwh for the Dow Oxygenation process.

SECTION 2

INTRODUCTION

Geothermal energy systems have been proposed as relatively clean and environmentally promising forms of energy. At present, there is one commercially operating geothermal power production facility in the United States. This is the 500-MW station at the Geysers in California, which is a vapor-(steam) dominated resource. Efforts are also underway to develop the liquid (hot brine) dominated resource in the Imperial Valley in California. It is estimated that many more geothermal resource areas will be developed in the near future. To ensure that these developing energy systems are environmentally acceptable and that needed pollution control technologies are available, several investigations are being carried out.

One of the pollutants of major concern from geothermal systems is H_2S . The present study was directed toward conducting a state-of-the-art review of available H_2S control technologies, as well as geothermal electric power applications identifying those control processes that are most promising. In order to accomplish these objectives, we have first characterized the emission sources and the control requirements, and then evaluated the available control technology.

This report presents, in sequence, the following discussions:

1. Source characteristics,
2. H₂S control requirements,
3. Available H₂S control technology, and
4. Analysis and evaluation of control technology.

SECTION 3

RECOMMENDATIONS

During the conduct of this study, several needs became obvious. These could be classified into two major categories:

1. Source characteristics, and
2. H₂S control processes.

The needs in each of these areas are summarized below.

SOURCE CHARACTERISTICS

Source characterization for geothermal wells, pilot and demonstration facilities, and production facilities is marginally adequate at best. Additional support is recommended for a systematic, standardized sampling and analysis program to identify H₂S concentrations at various emission points in the geothermal system. The priority areas are points immediately preceding the power plant and emission points within the power plant.

Any sampling and analysis protocol that is developed to characterize H₂S must include prescribed procedures and proper quality assurance techniques so that the data obtained would be meaningful. The present data base has several inconsistencies, making its use extremely limited.

H₂S CONTROL PROCESSES

1. There is an imbalance between the amount of information that exists on process characteristics and the information on cost aspects for any existing technology. This lack of adequate cost data becomes critically important in a comparative evaluation of the various H₂S removal processes. It is, therefore, recommended that a cost evaluation of applicable H₂S removal technologies be undertaken.

2. Processes such as the (a) EIC process, (b) the Dow Oxygenation process, and (c) the Stretford process should be more strongly supported. Specific areas that merit attention within these processes are as follows:

- EIC process - studies to investigate more effective regeneration of CuSO₄.
- Dow process - corrosivity of brine and methods to inhibit corrosion in the presence of oxygen.
- Stretford process - design aspects of surface contact condensers and retrofit problems associated with their use.

3. Investigation of power plant design options to minimize H₂S emissions:

a. Recycle of noncondensable gases--Partial recycle of noncondensable gases would increase the gas-to-liquid ratio at the condenser hotwell, thereby increasing the vapor-to-liquid equilibrium ratio of H₂S. However, this may require larger ejectors. Related concepts are (a) partial or total recycle of noncondensable gases treated to remove H₂S, and (b) air injection. Air injection would serve to oxidize some of the H₂S in the fluid and would also increase the vapor-to-liquid ratio.

b. Dry cooling--The use of either dry cooling or wet/dry cooling technology would eliminate or reduce the emission of H_2S and other pollutants from the cooling tower stack. The cost of such design modifications would be significant, but it appears that the added cost would be more than offset by the savings achieved with the use of a direct contact condenser 1,2/

4. The adaptability of existing H_2S control processes for nonelectric geothermal applications.

SECTION 4

SOURCE CHARACTERISTICS

Potential emission sources associated with geothermal energy utilization include idle; venting wells;* pipeline vents; accidental discharge; and process emissions. Even though the focal point of this study is the energy conversion process (i.e., power plant), the other sources are discussed to enable development of control strategies for points upstream of the power plant and to control H₂S in vent emissions and in cooling water including condensate. This section describes the ranges of emission properties expected for the various sources. This information is useful for evaluating applicable control technologies.

Geothermal reservoirs are characterized by a surprising lack of uniformity, even within the same field, and over distances as short as a few kilometers. The extent of the variation is illustrated in Table 1. Aside from spatial variations, temporal variations are also fairly common; data from the Geysers-Calistoga Known Geothermal Resource Area reflect a two-fold variation over a period of a few months.^{3/} Reference 1 similarly indicates order-of-magnitude variations in H₂S concentration over a 12-month period.^{1/} The

* In the development of a new steam field, new wells are drilled some period of time ahead of power plant construction. This is done because the power plant siting depends to some extent on the locations of successful producing wells. If a well were completely shut off after drilling, the resultant thermal stresses could damage the casing and/or the cement between layers of casing. In order to prevent this, the well is allowed to "bleed" at a reduced flow rate while awaiting power plant construction.

relative proportions of fluid chemical constituents may also differ among different fields; CO₂ is usually the major gas constituent, although in some fields N₂ predominates. Hydrogen and hydrocarbon concentrations are also frequently much higher than shown in Table 1. For these reasons, caution must be exercised in the design of gas cleaning equipment, in order to accommodate concentration changes over time and between different wells.

TABLE 1. RANGE OF GASES AND SOLIDS IN
GEYSERS AREA STEAM^{2/}

Component	Concentration range ^{a/}
CO ₂	216-30,600
H ₂ S	5-1,600
CH ₄	3.6-1,447
NH ₃	9.4-1,060
N ₂	6-638
H ₂	2-218
C ₂ H ₆	0.03-19
C ₃ H ₈	0.06 ^{b/}
HCl	0-10.5 ^{b/}
HF	0.06 ^{b/}
As	0.002-0.05
B	2.1-39
Hg	0.00031-0.018
222Rn	0.32 x 10 ⁻⁸ -3.14 x 10 ⁻⁸ Ci/l

^{a/} Parts per million by weight except as noted.

^{b/} Average for Castle Rock Springs area.

In order to partially offset the variations in fluid composition, the approach used in this investigation was to express all variables in terms of ranges, wherever possible. Physical and chemical properties expected for vapor-dominated hydrothermal sources at the wellhead are shown in Table 2. Other data for this source category are shown in Table 3. Similar information for liquid-dominated sources is presented in Table 4 and 5.

TABLE 2. RANGE OF SOURCE PARAMETERS FOR VAPOR-DOMINATED
HYDROTHERMAL RESERVOIRS^{a/}

Steam flow, lb/hr	908,000
Pressure, psig	79-114
Temperature, °F	342-355
pH	3.9-9.0
Noncondensibles, by wt	0.1-2%
CO ₂ , by wt	290-30,600
H ₂ S, by wt	5-1,600 ppm
NH ₃ , by wt	9.4-1,060 ppm
CH ₄ , by wt	13-1,447 ppm
H ₂ ,	11-218 ppm
N ₂	6-638 ppm

^{a/} Data based on Geysers power plant.

WELL DRILLING AND TESTING

This emission category is comprised of exploratory drilling, flow testing, well cleanout, and field development operations.

By comparison with H₂S emissions from production sources (wells, vents, and power plants), the H₂S emission potential from well drilling and testing is believed to be relatively small.^{8/}

TABLE 3. VAPOR-DOMINATED GEOTHERMAL ENERGY APPLICATIONS (USA)

System	Developer(s)	Location	Purpose	Unit	Status/Description ^{a/}		H ₂ S emissions ^{b,c,d/}	Additional comments
					Capacity (MWe)	Start-up		
The Geysers	Pacific Gas and Electric Company, Magma Power Company, Thermal Power Company, and Union Oil Company	Sulfur Creek and Cobb Creek areas, Sonoma County, California (Geysers-Calistoga KGRA)	Electric power	1	12	1960	Units 1-12, emission points are:	Units 1-12:
				2	14	1963	• Well head separator ^{2/}	• < 70% of (uncontrolled) H ₂ S emission at cooling tower for discharge ^{1/}
				3	28	1967	• Turbine and turbine controls ^{2/}	• > 30% of H ₂ S emission from steam ejectors, well head emissions, pumps and valves
				4	28	1968	• Condensate system ^{2/}	• Two stage ejectors use geo-thermal steam ^{2/}
				5	55	1971	• Pumps and valves	• Unit 4:
				6	55	1971	• Cooling tower ^{2/}	• "Burner-Scrubber" system controls H ₂ S emissions from condenser ^{2/}
				7	55	1972		
				8	55	1972		
				9	55	1973		
				10	55	1973		• Unit 11:
				11	110	1974	Units 13-15:	• "Iron Catalyst" system controls H ₂ S dissolved in cooling water ($\approx 70\%$) ^{2/}
				12	110	1975	• Cooling tower emissions partially eliminated by use of surface condenser in place of direct contact condenser ^{2/}	• Units 13, 14, and 15:
				13	125	1978		• "Stretford Process" used to control H ₂ S ^{2/}
				14	110	1978		
				15	55	1979		

a/ Capacity projection: PG and E will install about 100 MWe a year as long as the suppliers (Union Oil, Thermal Power, and Magma Power) prove additional reserves for this added capacity 5 years before operation, and as long as the power is economical to PG and E; there are presently plans for installing an additional 900 MWe by 1985.^{2/}

b/ The California Ambient Air Quality Standard for H₂S is 0.03 ppm (42 $\mu\text{g}/\text{m}^3$) (1-hr average).^{2/}

c/ At the Geysers, hydrogen sulfide (H₂S) ranges from 2.0 to 7.0% by weight of the noncondensable gas fraction with a field average of 5.0%. Noncondensable gas fraction ranges from 0.1 to 2.0% by weight of total steam flow with a field average of 0.54%.^{2/}

d/ Steam production ranges from 27,000 to 136,000 kg/hr (60,000 to 300,000 lb/hr). A typical well produces about 90,000 kg/hr (200,000 lb/hr). A 100-MWe unit may require the steam produced from 14 to 16 wells.^{2/} Example: Assuming only 1/2% of the steam flow, on the average, is noncondensable gas, H₂S emissions will be 97,000 lb/day for 1,000 MWe, requiring 430 million pounds per day of steam.^{2/}

e/ Centrifugal separators are installed in steam supply pipes, primarily to remove moisture and particulates.^{2/}

f/ A Yee-type strainer is installed in the main steam line, just ahead of the turbine for particulate removal.^{2/} Between the strainer and the turbine there are numerous stop valves, check valves, and control valves.^{2/} Leakage of H₂S commonly occurs at valve stems and other equipment which may use gland packings.^{2/} Experience has shown it is very difficult to completely eliminate such leaks.^{2/} Leakage through the turbine itself must also be regarded as a potential source of H₂S emissions.

g/ Noncondensable gases are removed from the top of the condenser shell.^{2/} Leakage of H₂S and noncondensable gases is also expected from condensate pumps.^{2/}

h/ Noncondensable gases and H₂S dissolve in condensate and are discharged to the atmosphere when the condensate is evaporated in the cooling tower. (Units 1 to 12.)^{2/} The H₂S solubility is dependent on pH, so H₂S emissions from this source are variable.

i/ The "burner-scrubber" system installed in the Geysers Unit 4 is used to control only the condenser gaseous effluent (about 30% of total H₂S emissions from an uncontrolled direct contact process). Use of this control system resulted in a lower condensate pH, so that a maximum overall H₂S removal efficiency of about 50% could be achieved. This is regarded as an unacceptable level of abatement.

j/ The "iron catalyst" process on Unit 11 is used to control only H₂S dissolved in condensate (less than 70% of total H₂S emissions from an uncontrolled direct contact process). However, an overall removal efficiency of 90 to 92% has been reported.^{2/}

k/ The Stretford Process units designed for Units 13, 14, and 15 are designed for removal of 99% of H₂S in the inlet stream. The power cycle on three units has been modified by use of surface condensers rather than direct contact condensers to reduce cooling tower emissions. The overall H₂S removal efficiency is expected to be between 70 and 92%.^{2/}

l/ Reference 2.

m/ Reference 4.

n/ Because of the necessity of using geothermal fluid as the coolant medium, cooling tower emissions are reduced but not completely eliminated.^{2/}

TABLE 4. RANGES OF SOURCE PARAMETERS FOR LIQUID-DOMINATED
HYDROTHERMAL RESERVOIRS

	Salton Sea KGRA (ppm)	East MESA KGRA (ppm)
CO ₂ , by weight (steam phase)	1,600-4,700	800-2,630
H ₂ S, by weight (steam phase)	1.3-3.9	0.11-1.7
(brine phase)	Not available	0.07-0.33
NH ₃ , by weight (steam phase)	20-41	1-8.1
(brine phase)	394-400	1.4-6.5
CH ₄ , by weight (steam phase)	7.3-14	4-56

TABLE 5. LIQUID-DOMINATED GEOTHERMAL ENERGY APPLICATIONS IN THE UNITED STATES

System	Developer(s)	Location	Purpose	Status/description			H ₂ S emissions	Additional comments
				Unit(s)	Capacity	Start-up		
Binary Cycle Power	Fluor, San Diego Gas & Electric, ERDA ^{2/}	Imperial Valley, California (Heber KGRA)	Electric power	1	45 Mw	1980	Wells, fluid transmission, primary heat exchanger ^{b/}	Control requirements uncertain pending final design ^{b/}
Binary Cycle Power	San Diego Gas & Electric, ERDA	Imperial Valley, California (near Niland, California)	Electric power ^{c/}	1	≤ 10 Mw ^{c/}	1976 ^{c/}	Wells, fluid transmission, primary heat exchanger (condenser vent) ^{d/}	Noncondensable gases are vented to the atmosphere through a 130 ft stack ^{d/}
Binary Cycle Power	San Diego Gas & Electric, Magma Power, ERDA	Imperial Valley, California (Salton Sea KGRA)	Electric Power	1	10 Mw	^{e/}	-	-
Binary Cycle Power	Southern California Edison, ERDA	Imperial Valley, California	Electric power	1	10 Mw	^{f/}	-	-
Binary Cycle Power	DSS Engineers, ERDA	Imperial Valley, California (East Mesa KGRA)	Electric power	1	Unknown	^{h/}	-	-
Binary Cycle Power	Idaho National Engineering Lab, ERDA	Idaho Falls, Idaho	Electric power	1	5 Mw	^{i/}	Wells, fluid transmission, heat exchanger vent, water-from separator vent ^{j/}	Possible "carry through" of secondary fluid with direct contact heat exchanger ^{k/}
Desalination	U.S. Bureau of Reclamation, ERDA	Imperial Valley, California (East Mesa KGRA)	Distilled water	1, ^{2/}	75,000-90,000 liters/day (each) ^{2/}	1976 ^{m/}	Wells, flash system, cyclone separator, condenser vent ^{n/}	-

^{2/} Fluor design; ERDA participation probable.^{2/}

^{b/} For liquid-dominated systems, controlled flashing of noncondensable gases may be required at pumping stations in order to facilitate fluid transmission. Uncontrollable discharges from pump glands, valve stems, etc., may also occur.^{2/} Since noncondensable gases will affect the heat transfer coefficient adversely,^{2/} it is anticipated that most binary cycle designs will include a flash system ahead of the primary heat exchanger.

^{c/} Only the equipment required to evaluate well flow and heat exchanger process characteristics have been installed and tested. Equipment needed to generate electric power may be installed at a later date.^{10/}

^{d/} Brine is flashed initially in a four-stage unit. The separated steam is scrubbed and subsequently used to heat the secondary fluid.^{11/} The H₂S concentration varies from 1,500 to 4,900 ppm (by volume) in the noncondensable fraction.^{11/}

^{e/} Ambient concentrations of H₂S near this facility generally average about 0.005 ppm, the lower limit of detection, with periodic excursions of 0.02 to 0.03 ppm (1-hr average).^{11/}

^{f/} Proposed facility.^{12/} The primary interest is in the development of a binary power system for power generation.

^{g/} Proposed facility.^{12/}

^{h/} Component testing of direct contact heat exchanger under way.^{13/}

^{i/} System design work on the first 5-Mw unit was initiated during the period January 1 to March 31, 1976.^{14/} Laboratory and field studies of heat transfer components are under way.^{10,14/}

^{j/} Emission points determined from flowsheet used for experimental system (March 31, 1976).^{14/}

^{k/} No data were found on H₂S concentrations in brine at Idaho Falls. A comprehensive environmental program is being performed in a parallel effort in support of this program.^{10/}

^{l/} Both are flashed steam units with the geothermal fluid used for water supply and heat input. One unit employs a vertical tube evaporator (distillation column), the other a multiple flash.^{15,16/}

^{m/} Data from Reference 15.

^{n/} Based on a "typical" flow diagram presented in Reference 16. Typical well analysis reportedly contains 11 to 14 ppm H₂S, 0.1 to 0.5 ppm NH₃, 180 to 205 ppm CO₂.^{16/} ReInjection of gases has been proposed for pollution control.^{16/}

However, the discharge occurs at low level and frequently contains high concentrations of H_2S . Therefore, the potential exists for violations of air quality standards. The discharge may be enriched in H_2S relative to the fluid itself, whenever the fluid flow is restricted. Characterization of individual emission sources within this category is discussed next.

Exploratory Drilling

Emissions of H_2S may occur whenever air is used as the drilling fluid. This practice is routinely followed at the Geysers field during the final stages of drilling when air is injected to remove cuttings and to cool the drill bit. At this field, the air drilling stage typically lasts from 10 to 20 days with an average duration of 15 days.^{17,18/}

Expected ranges of composition, flow and thermodynamic variables for well drilling are based on data presented in Table 2. There is a flow restriction caused by the drill string,^{17/} but the limited data available do not indicate enrichment of the noncondensable gas fraction relative to full flow. A schematic of the wellhead equipment configuration is shown in Figure 1. The H_2S control equipment used must be compatible with this equipment; i.e., it must not interfere with the basic line configuration. Other requirements are:

- Portability - the equipment used for H_2S control during drilling operations must be portable and must be capable of self-contained operation. Drilling sites at geothermal fields are generally remote, relatively inaccessible, and utilities (gas, water, and electricity) are generally not available. Discussions

Figure 1. Schematic of wellhead equipment configuration used in air drilling.

with drilling personnel indicate that skid- or trailer-mounted equipment would be acceptable for this application.^{19/}

- Flow restriction - it has been suggested that the maximum flow restriction for equipment used to control H₂S emissions during drilling is approximately 120 in. of water.^{19/}

At this point, it is unclear how widely practiced air drilling will become in geothermal operations. It is generally agreed that air is preferable to drilling fluid in that the fluid tends to plug the formation. However, it is currently believed that air drilling would not be practical when thermodynamic properties of the reservoir are such that the producing zone is water saturated.^{1/}

Flow Testing

The purpose of the flow test is to determine production capacity. Flow testing may require from 4 to 24 hr with flows ranging from 25 to 100% of full capacity.^{19/} Flow testing is preceded by an initial cleaning step of from 1 to 2 weeks, required to remove solids ("rock dust") accumulated in the reservoir during drilling.^{20/} The characteristics of the emission during cleaning/flow testing are expected to be as shown in Table 2, except that solid particulates can be much higher than production levels. On the basis of limited test data, it appears that the concentration of insoluble rock dust particulates can range from 0.002 to 0.1% by weight of fluid.^{21/} Other control requirements are the same as for well drilling.

Flow testing is required for all geothermal wells, regardless of the type of fluid, so that the H_2S control problem will exist at virtually all fields. When the fluid is "wet", i.e., when the fluid is not superheated, the fluid discharged during cleaning/testing separates into two phases. The relative proportion of H_2S (and other gaseous pollutants) retained by the fluid is a complex function of temperature, pressure, pH, noncondensable fraction, and liquid fraction; this proportion can vary over rather wide limits corresponding to ranges in fluid properties. However, since the liquid will retain some H_2S which will be released to the atmosphere from ground level, controls for this operation might become necessary.

Standby Venting

After exploratory wells are drilled and before they go into production, they are allowed to vent continuously for periods of from a few months up to several years. The purpose of such "standby" venting is to keep well pipe, casing, and cement hot, thus preventing accidental breakage caused by contraction. Flow from bleeding wells may be from 0.4% to about 10% of full capacity, depending on liquid fraction, the higher figure being representative of "wet" wells.^{8,18/} An "enrichment" of noncondensable gases, including H_2S , is believed to occur when venting at low flow rates, so that the H_2S concentration may be increased by a factor of 4% to 5%.^{22/} An illustration of the potential significance of the standby vent source is the Geysers field, where, as of September 1977, there were 130 production wells, with an additional 70 wells idle and venting.^{20/}

Since each well represents a substantial capital investment (approximately \$250,000 to \$750,000), it is reasonable to consider the application of permanent, rather than portable, control technology to control standby venting emissions. Allowable pressure drop can be high--10 to 15 psig would not seem unreasonable--and other requirements should be less stringent than for control during drilling and testing discussed previously. Estimates of other control requirements for this source are shown in Table 6. As of the date of this report, no test data could be found to substantiate these estimates.

TABLE 6. ESTIMATES OF H₂S CONTROL REQUIREMENTS FOR
STANDBY VENTING (HYDROTHERMAL
RESOURCES)^{a/}

Flow, lb/hr	200-62,500
Pressure, psig	50-58 ^{b/}
Temperature, °F	230-580 ^{b/}
pH	3.9-9.0
Noncondensibles, by wt	0.4-18.0%
CO ₂ , by wt	0.08-15.5%
H ₂ S, by wt	4-8,000 ppm
NH ₃ , by wt	120-5,300 ppm
CH ₄ , by wt	16-7,235 ppm
H ₂ , by wt	8-1,090 ppm
N ₂ , by wt	24-3,190 ppm
Soluble particulate, by wt	1,600-387,000 ppm
Insoluble particulate, by wt	0.002 to 0.1%

^{a/} Estimated from data presented in Tables 1 and 2 and Reference 8.

^{b/} At low flows, temperature and pressure can approach bottomhole conditions.

FLUID TRANSMISSION

Since the fraction of the total H_2S emission potential from pipeline vent sources would be on the order of 4% to 5% of the total H_2S in the geothermal fluid sent to the power plant or conversion process, the H_2S emissions from such sources have been largely overlooked in most previous studies. Vent sources include: (a) instrument vents (two per well), (b) valve temperature equalizer vents (two or more per well), and (c) cyclone vents (one or more per well).

A schematic illustration of the sources of vent emissions at or near the wellhead is shown in Figure 2. There can be more than one cyclone per well in the distribution network. Not shown are temperature equalizer vents which are associated with the pipeline valves. It is believed that control characteristics of pipeline vent sources will be essentially the same as for flow testing (Table 2), with essentially no enrichment of the noncondensibles.

Table 7 presents calculated equilibrium ratios for the distributions of H_2S , ammonia, and carbon dioxide between the vapor and liquid ("condensate") phases for ranges of conditions shown, corresponding to Multistage Flash (MSF) binary and direct contact designs. The calculations were made using a methodology described in Appendix A.

Figure 2. Typical wellhead arrangement showing some of the pipeline vent sources of H₂S (adapted from Reference 3).

TABLE 7. CALCULATED EQUILIBRIUM RATIOS FOR DISTRIBUTION OF H_2S , NH_3 , AND CO_2 BETWEEN VAPOR AND CONDENSATE PHASES^{a/}

	Case I Multistage flash (MSF) binary ^{b/}	Case II MSF direct contact ^{c/}
<u>H_2S in vapor</u> H_2S in condensate	0.005-8.34	0.0024-3.24
<u>NH_3 in vapor</u> NH_3 in condensate	0.012-0.70	0.0033-0.033
<u>CO_2 in vapor</u> CO_2 in condensate	0.04-9.98	0.0014-7.88

^{a/} Based on methodology presented in Appendix A.

^{b/} Range shown corresponds to condenser temperatures of from 72.2-304.4°C and pressures of from 40.1 to 305.3 in. Hg.

^{c/} Range corresponds to a condenser temperature of 48.8°C and a pressure of 4 in. Hg. A cooling water-to-condensate ratio of 20:1 was assumed.

In spite of the fact that there are several flashed steam plants and, binary fluid plants operational and under construction, an extensive literature investigation failed to disclose adequate data on emission properties for source characterization.

ENERGY CONVERSION PROCESSES

This section describes the hydrogen sulfide emission characteristics for geothermal energy conversion processes. General fluid property ranges presented previously in Tables 2 through 5 were chosen to represent the expected

ranges for geothermal energy sources in this country. In this section, we describe, as far as possible, the influence of the conversion process on the properties of emission streams.

In general, the use of geothermal energy involves the conversion of thermal energy contained in the fluid to a more useful energy form. Such conversion can involve either heat transfer or conversion to other energy forms, such as kinetic energy. In either case, the result is that the hot fluid is cooled and its pressure reduced.* The decrease in pressure causes a resultant decrease in solubility of gases, including H_2S , contained in the fluid. The result is that the hot fluid is transformed into two fluid phases, a liquid phase and a mixed phase of vapor plus gas. A portion of the dissolved H_2S is retained by the liquid, depending on fluid properties and the characteristics of the conversion process. Figure 3 presents a conceptual diagram of a geothermal energy conversion process showing three potentially feasible H_2S control points. The emphasis of this study is toward controlling H_2S emissions at these three points, i.e., upstream control, vent control, and condensate control.

Electric Power Generation

State-of-the-art processes for conversion of geothermal energy to electric power have been described previously by Holt.^{23/} These are:

* Total reinjection processes also exist, at least in concept, but are not considered in detail here. Such processes are presently beyond the state of the art.^{1,23/}

Figure 3. Conceptual diagram of geothermal energy conversion process showing potentially feasible H_2S control points.

- Flashed steam process

This is a process in which part of the geothermal fluid is flashed into steam in one or more stages. The steam is then used to produce electric power by means of a turbine and a generator. A schematic flow diagram showing the generalized flashed steam process is given in Figure 4.

- Binary process

This is a process in which the thermal energy in the fluid is transferred into a secondary working fluid such as isobutane. The secondary fluid is then used to turn a turbine while the primary geothermal fluid is returned to the reservoir (Figure 5).

- Hybrid process

The hybrid process employs a combination of the flashed steam and binary fluid processes. In this process, part of the fluid is flashed into steam, which is then used to drive a steam turbine. The residual heat in the fluid is next transferred to an intermediate fluid which is used to drive a secondary turbine.

In addition to the processes just described which are considered technologically feasible with today's process equipment, there are also a number of processes under development which would convert both thermal and kinetic energy of the geothermal fluid directly into shaft work. These are referred to in the literature as "total flow processes." None have yet been demonstrated on a commercial scale.

Several large commercial power plants employing the flashed steam principle, depicted in Figure 4, are in operation throughout the world. Notable

* Note: In some designs, multiple flash stages are integrated into a single unit.

Figure 4. Generalized flashed steam process ("multistage flash direct contact").

* Note: In some designs, multiple flash stages are integrated into a single unit.

Figure 5. Generalized binary fluid process ("flashed steam binary").

examples of successful flashed steam plants include installations in New Zealand, Mexico, and Japan. None are yet operational in this country. There are also a number of binary process plants in operation and several planned for this country in the near future.

Power Plant "Bypassing"

Even though this is not a common occurrence, during the time the plant is down, the fluid and contained pollutants are vented directly to the atmosphere through a relief valve at the wellhead. Physical data for this emission are the same as for the uncontrolled well emission (Table 2).

Although there is virtually no flow limitation or process-related restriction imposed by the source (i.e., all of the energy in the fluid stream could be dissipated in attempts to control it), there has been no attempt made to control this emission source by means of add-on control technology.

If a reasonable level of control required to achieve a given ambient H_2S standard is 90%,* then it is clear that some degree of control of the bypassing emission is required.

Desalination

Desalination to produce water for irrigation, possibly in conjunction with electric power generation, may be the key to the development of western arid regions if the potential environmental problems can be successfully solved. The small-scale project for the Imperial Valley would affect the development of six, 70-Mw plants and about 100,000 acre-ft of fresh water annually from 72 wells. A large-scale plan for regional development includes 1,800 production

* The subject of level of control required in relation to the ambient air quality standard is discussed in Section 4.

wells to produce 10,500 MW and 2.5 million acre-feet annually of fresh water.^{16/} Both pilot desalination processes currently being evaluated at East Mesa KGRA involve venting of noncondensibles. Although reinjection of noncondensibles has been proposed, this could prove difficult in practice.

The most common desalination process proposed would incorporate a cycle for the joint production of electricity and water. A generalized flow diagram is shown in Figure 6.

Figure 6. Typical schematic of a desalting cycle (vertical tube evaporation).

There are only limited process data and no emissions data available for two ongoing demonstration projects--one a vertical tube evaporator, the other an MSF evaporator, both located at the East Mesa KGRA.^{24,25/} Process data for both units are within the range of temperatures cited previously for power plants (Table 7).

SECTION 5

H₂S CONTROL REQUIREMENTS

One of the most perplexing problems facing the developers of geothermal energy is that of maintaining existing ambient air quality standards for H₂S. This, in turn, requires the determination of the degree of control needed to meet ambient standards.

Application of detailed analytical models in order to determine the probable concentrations of pollutants at various receptor points can be a very expensive, time-consuming, and frustrating experience, particularly when faced with complex terrain and meteorological conditions. In this section we give some general guidelines which can be used to determine (a) whether a potential pollution problem exists, i.e., whether or not control may be required and (b) the degree of control required. Analytical techniques are then outlined which can be used as a guide for siting individual production facilities.

AMBIENT CONCENTRATION DATA

It is appropriate to present some background data from the extensive body of analysis and measurements made at the Geysers-Calistoga KGRA where there is currently about 500 MW of electric generating capacity. The project has been plagued with air quality problems for H₂S almost since its inception in 1960 when the first power plant was brought on line.

From 1960 through 1977, the steam production at this field has risen from 1.9 to a present level of approximately 35 billion kilograms per year (2.1 to 39.5 million tons per year).^{1/} Since 1970, PG&E, the operating partner at the Geysers, has maintained an ambient sampling network of 37 stations in the vicinity of the Geysers power plants (Figure 7). Although "exceeds" of the California ambient concentration standard of 0.03 ppm by volume* have been numerous, there was little change in the average ambient concentration noted with increasing steam production over the 5-year monitoring period (Table 8).

Since early 1976, an eight-station network has been operated to obtain simultaneous H₂S and meteorological parameter measurement around the periphery of the Geyser area. Using this network, maximum H₂S concentrations were determined when the monitor was downwind from an emission source. Statistical methods were then used to determine the H₂S emission reduction needed to maintain ambient H₂S levels at less than the ambient standard. The results of the statistical analysis are shown in Figure 8. The total H₂S emission rate in pounds per hour is correlated with total number of times the ambient standard has been exceeded at a station downwind of an emission source.

* One-hour averaging time, not to be exceeded more than one time per year.

Figure 7. Location of PG and E sampling stations showing average H_2S concentrations (ppb).^{8/}

TABLE 8. CHANGES IN AMBIENT H₂S CONCENTRATION WITH CHANGES IN
STEAM PRODUCTION AT THE GEYSERS

Year	Total steam production (10 ⁹ kg/yr) ^{a/}	Avg H ₂ S emissions ^{a/}		Area avg H ₂ S concentration (ppb) ^{b/}			
		Plants (kg/hr)	Preplant (kg/hr)	Area 1 ^{c/}	Area 2 ^{d/}	Area 3 ^{e/}	Total
1970	7.71	210	75	20	10	36	20
1971	8.62	235	80	15	9	35	24
1972	16.45	475	65	11	10	37	22
1973	22.28	560	85	7	13	36	22
1974	27.41	620	80	10	7	30	20
1975	31.70	645	85	9	10	32	21

^{a/} Source: Reference 1.

^{b/} Source: Reference 8.

^{c/} Includes sampling Locations 2-6, 15, 23, and 30 (Figure 9).^{8/}

^{d/} Includes sampling Locations 10-14 and 17 (Figure 9).^{8/}

^{e/} Includes sampling Locations 1, 8, 9, 18, 21, 26, and 27 (Figure 7).^{8/}

Figure 8. Statistical correlation between total H₂S emissions and the frequency of ambient air standard violations at the Geysers.^{17/}

The correlation implies that, in order to achieve the ambient air standard, the Geysers emission of hydrogen sulfide must be reduced to a maximum level of between 560 to 620 lb/hr. An emission level of 400 lb/hr was selected on this basis to give a safety factor of 50%.^{26/} This emission level corresponds to approximately 80% control of H₂S emissions from present (1977) generating capacity and to a near-term control level of 90% through about 1985 (Unit 17). The natural abatement level is about 4.5% so that a control level of 85.5% must be achieved in the near term.

The need for more effective H₂S controls is also borne out by the recent rules and regulations of the Northern Sonoma County Air Pollution Control District (NSAPCD).^{27/} These rules are as follows:

Rule 455 - a. No person shall discharge into the atmosphere from any geothermal operation sulfur compounds calculated as sulfur dioxide (SO₂), in excess of 1,000 ppm.

b. No person shall discharge H₂S into the atmosphere at a rate which exceeds those set forth in Tables 9 and 10.

TABLE 9. GEOTHERMAL POWER PLANTS^{a/}

Effective date ^{b/}	<u>In operation before January 1, 1980</u>		Any plant beginning operation after Jan. 1, 1980 (g/hr/GMW)
	With direct contact condenser ^{c/}	With surface condenser (g/hr/GMW)	
Jan. 1, 1979	For Units 3, 4, 5, 6, 11, and 12 emit: no more than 10% of the H ₂ S in the supplied steam at full power plant load or 200 g/hr/GMW average using allocation method ^{h/}	-	-
Jan. 1, 1980	<u>i/</u>	100	100
Jan. 1, 1982	Units 3-6, 11, and 12: 200 g/hr/GMW ^{i/}	-	-
Jan. 1, 1985	<u>i/</u>	-	50
Jan. 1, 1990	-	50	-
Jan. 1, 2000	100 g/hr/GMW ^{i/}	-	-

TABLE 10. STEAM TRANSMISSION LINES^{g/}

Effective date ^{b/}	Existing or permitted systems as of June 1, 1978	New systems	Other geothermal sources	
			Well drilling, reworking, and testing (kg/hr/well)	Small source emissions (kg/hr/source)
June 1, 1979	Upon an unscheduled outage an operator shall within 4 hr or less reduce H ₂ S emissions: (a) by 90% or more for dual units, or (b) by 50% or more for single units or when both units of a dual unit system have a simultaneous outage, or (c) to not more than 15 kg/hr. For scheduled outage the same emission standards shall be met within 1 hr or less.	Upon an unscheduled outage the operator shall within 4 hr or less reduce H ₂ S emissions: (a) by 90% or more, or (b) by 50% or more when both units of a dual unit system have a simultaneous outage, or (c) to not more than 15 kg/hr. For a scheduled outage the same emission standards shall be met within 1 hr or less.	5 ^{e/}	-
Jan. 1, 1980	<u>d/</u>	<u>d/</u>	2.5 ^{e/}	2.0 ^{f/}
Jan. 1, 1982	To be promulgated by A.P.C.O. ^{d/}	To be promulgated by A.P.C.O. ^{d/}	-	1.0 ^{f/}
Jan. 1, 1985	-	-	-	0.5 ^{f/}
Jan. 1, 1990	-	-	-	-
Jan. 1, 2000	-	-	-	-

FOOTNOTES FOR TABLES 9 AND 10

- a/ All geothermal power plants, including new construction, must comply with future emission rate reductions as they become effective.
- b/ H₂S emission limitations for each category of emission source will become effective henceforth on the date indicated at the left of the Table.
- c/ "g/hr/GMW" shall equal "grams per hour per gross megawatt." The rates of emission may be equaled but not exceeded. Compliance shall be verified by the source testing method approved by the District for the applicable emission source.
- d/ The Air Pollution Control Officer shall after proper notice and public hearing promulgate on or before January 1, 1980, the emission standards commencing January 1, 1982, based upon a review of available control technology, air quality, emissions, and extent of development.
- e/ Individual well emissions shall be limited to 5 kg/hr/well (2.5 kg/hr/well after January 1, 1980) unless a higher rate was determined by new source review or unless applicant provides data which subsequently can justify a redetermination of the emission rate by Air Pollution Control Officer.
- f/ Small sources include continuous well and pipeline bleeds. Allowable emissions are those shown in Table 10 unless otherwise determined by the Air Pollution Control Officer.
- g/ "Reduce H₂S by 50%" shall mean emit no more than 50% of the H₂S normally found in the supplied steam at full power plant load. "Dual units" shall refer to those steam transmission lines associated with two power plant units located in the same building and therefore such associated steam transmission lines shall be considered as one source.
- h/ Allocation method: If less than 200 g/hr/GMW is attained at one power plant unit, the reduction (in grams H₂S per hour) can be credited to another power plant unit or apportioned to other power plant units. For instance, a 10-MW plant can be allowed to emit 2,000 g H₂S/hr; but if a credit of 500 g H₂S were allocated, it could emit 2,500 g H₂S per hour or 250 g/hr/GMW. The allocation should be modified no more than quarterly and only if needed based on new data. (The major purpose of the allocation method is for individual power plant unit compliance verification and credit for greater H₂S reduction than 90%.)

(continued)

FOOTNOTES FOR TABLES 9 AND 10 (continued)

- i/ For Units 1, 2, 7, 8, 9, and 10, the Air Pollution Control Officer shall after proper notice and public hearing promulgate on or before January 1, 1980, the emission standards commencing January 1, 1982, and January 1, 1985, based upon a review of available technology, air quality, emissions, and extent of development.
- j/ The Air Pollution Control Officer, 1 year prior to each achievement date, shall, after review of air quality, extent of development, emissions, and available control technology, promulgate a new source emission standard if different than presently set forth after proper notice and public hearing.

RELATIONSHIP BETWEEN SOURCE STRENGTH AND AMBIENT H₂S CONCENTRATIONS

This section briefly describes the methods which are available for predicting the level of control required based on the source strength.

"First-Level" Screening Methodology

The recent multimedia environmental goals developed by the Environmental Protection Agency (EPA)^{28,29/} provide a convenient basis from which to determine the probable health and ecological effects of given pollutant discharge concentrations.

The environmental assessment is a methodology for determining, based on source strength, whether discharge of a given pollutant may constitute a possible environmental or health hazard. The bases of the environmental impact determination are factors termed minimum acute toxicity effluent levels (MATEs). For each substance, there are six MATE values, corresponding to human health and ecological effects and for discharge into the air, into water, or onto the land, such as landfill disposal.^{28/} The pollutant concentration in a given effluent stream is divided by the appropriate MATE value. If the resultant ratio is greater than unity, the effluent may pose a threat either to human health or ecology.^{28/} As an example, the minimum acute effluent toxicity level for H₂S into air is 10 ppm ($1.5 \times 10^4 \mu\text{g}/\text{m}^3$), while for water it is $10 \mu\text{g}/\text{m}^3$. The MATE values are research goals and, as such, provide a conservative measure of potential health and ecological impacts.

Dispersion Estimates

Dispersion of pollutants can be part of the overall control strategy. More importantly, dispersion models can help determine the level of control required at the source. Using the basic Gaussian dispersion model,^{30/} one can compute the maximum ground level concentration from which the desired level of control can be established.

Experience has shown that for many industrial processes, the ratio of the maximum ground level concentration to the stack concentration is typically on the order of 1/1,000 or less. For power plants with average stack heights and exhaust temperatures, the dilution ratio would be at least 1,000 for atmospheric conditions which exist approximately 99% of the time and would be at least 10,000 for atmospheric conditions which exist approximately 80% of the time.^{31/} Applying this criterion to the Geysers yields a minimum estimate of the H₂S control efficiency required to meet the California ambient standard of 0.03 ppm. Assuming discharge conditions are the same as for conventional power plants, and taking the mean H₂S concentration as 116 ppm,^{3/} a statistical calculation yields a minimum estimate of H₂S control required to meet the California ambient standard of 89.5%.* This value is reasonably close to the value of 85 to 90% obtained by the Northern Sonoma County Air Pollution Control District using a more detailed statistical procedure.^{26/}

* Assuming the dilution ratio is 1,000 or more 99% of the time and a standard deviation of 65 ppm,^{1/} the required control efficiency is computed to be 89.5% to meet the California ambient standard of 0.03 ppm.

Multiple Source Interactions

Although the single source models are useful for estimating required control efficiency, such models fail to take into account the additive effects caused by a number of sources in the same vicinity. Therefore, the control estimate represents a minimum control efficiency. In order to determine the control efficiency needed when a number of plants are in close proximity, more complex models are needed. Such multiple source models are also involved in plant siting.

Multiple source models which take into account the three-dimensional transport of pollutants are referred to as atmospheric dispersion models. Such models can be very complex, and calculations are usually done on a computer. Effects of terrain and buildings are usually taken into account as is the chemical reaction of some pollutants. An example list of data elements used in dispersion modeling is shown in Table 11. One such list is completed for each source in the preparation of an emissions inventory for sources within a given region.

A recent example of the use of three-dimensional dispersion modeling in the prediction of ambient H_2S concentrations resulting from geothermal energy sources is described by Gudiksen et al.^{32/} The reader is referred to more general references for discussions of the detailed treatment of terrain effects, chemical reactions, and other effects on the predicted concentrations.^{30/}

TABLE 11. TYPICAL DATA ELEMENTS USED IN DISPERSION MODELING

I.	Source Type (point/area source)
II.	Source Category
III.	Point Source Characteristics
	Location Coordinates
	Emission Source Characteristics
	Height
	Diameter
	Exit Velocity
	Exit Temperature
	Operating Data (process sources)
	Plant Capacity
	Process Throughput
	Temporal Variations (present and future)
	Emission Rate
IV.	Area Source Characteristics
	Location
	Emission Source Characteristics
	Areal Extent
	Apportioning Factors
	Temporal Variability (present and future)
	Emissions (based on appropriate emission factors)
V.	Meteorological Conditions
	Wind Velocity Profile
	Atmospheric Stability
	Terrain Effects

CONTROL REQUIREMENTS

As discussed in the preceding section, the precise determination of H_2S control efficiency required depends on numerous factors such as source characteristics and location, meteorological conditions, terrain effects and other factors, and is usually site-dependent.

In addition, various equipment design guidelines need to be considered. The Department of Energy (DOE) has provided some guidelines for equipment used at geothermal energy facilities.^{33/} A paper by Finney et al.^{4/} also contains similar information. Site-specific equipment factors are the set of special requirements which the equipment must meet in order to be used at a given location. A number of site-specific factors which may deserve special attention are listed below.

- System reliability - A specific level of reliability may be required by pollution control regulations in some areas. In addition, reliability may impact significantly on the operating and maintenance cost of pollution control equipment.
- Operating safety - This may be an important factor for some processes such as those that handle H_2O_2 . Also, the location of the site itself may be important from the standpoint of moving injured personnel to medical treatment facilities.
- Seismic activity - Seismicity may accompany geothermal activity in some cases and may impact significantly on structural design requirements.

- . Variations in source characteristics - As discussed previously in Section 3, temporal and spatial variations in fluid properties are fairly common. Attempts should be made to determine the extent and rate of the variations in key design parameters.
- . Storage requirements - The quantities of raw materials on hand may need to be relatively long if (a) the location is inaccessible or (b) if the supply is subject to interruption by weather conditions or other factors. The same considerations apply to intermediate storage of sludge or by-products.
- . Process interference - It is important to determine the maximum allowable pressure drop, heat loss, etc., which the process can accommodate. It is particularly important to determine the probable nature of control system malfunctions and the impact on process operations.
- . Process control requirements - Since most geothermal plants are automated, it is important that any emission control process considered have compatible control characteristics. The dynamic response time ("surge capacity") of the control process may be important at some locations.

- . Response to overloads - Since a fairly wide variation in geothermal effluent properties may be expected, it may be important to determine the response of the emission control system to possible overloads, i.e., conditions in which the composition, flow rates, and other properties of the effluent stream exceed design specifications.
- . Location, space requirements - Space requirements for control systems are frequently critical, and this is particularly true for geothermal facilities. As such, it appears that design estimates must be "site-specific" in nearly every case.
- . Other factors - Other factors, such as allowable noise levels, available utilities, construction and zoning requirements, may also differ among different locations.

SECTION 6

AVAILABLE H₂S CONTROL TECHNOLOGY

This section describes the control technology which has been used for H₂S removal from geothermal streams, as well as H₂S removal technology which is potentially available but has never been tried on geothermal streams.

As described in Section 4, there are multiple H₂S emission sources associated with the use of geothermal energy. The following subsections describe available or potentially available control technology, broken down into appropriate categories as follows:

- Upstream controls - This category refers to removal of H₂S ahead of the conversion process. Either vapor or liquid phase treatment may be required, depending on the fluid characteristics.
- Vent controls - This category refers to equipment which can be used for H₂S removal from noncondensable gas streams.
- Condensate/cooling water technology - This category refers to removal of H₂S from liquid streams.
- Power plant design - This category refers to H₂S control by modifying the conversion process itself.

UPSTREAM CONTROL TECHNOLOGY

Upstream control technology refers to controls applied to the entire fluid stream to remove H_2S ahead of the conversion process. A number of techniques have been attempted. Several of these appear promising, but all are in the development stages at this time. Those upstream processes which have been applied to geothermal fluids are listed in Table 12 and described below.

TABLE 12. UPSTREAM CONTROL TECHNOLOGY FOR H_2S REMOVAL

For vapor-dominated systems:

- Steam converters
- EIC process
- Deuterium process^{a/}
- Solid sorbent process^{a/}

For liquid-dominated systems:

- Dow oxygenation process
-
-

^{a/} These processes do not appear attractive at the present time because of low efficiency, proprietary nature of process, or high costs (see Section 7).

Steam Converters

Although not a true H_2S removal process, steam converters have the capability of removing H_2S and other dissolved gases from steam. This allows the use of vent controls to remove H_2S from the separated gases.

A schematic of a typical steam converter is shown in Figure 9. The enthalpy of the geothermal steam fraction is transferred in a heat exchanger to a secondary stream of condensate. The steam loses part of its heat, condenses, and gases are removed in a gas stripping column. The condensate is then re-flashed in the secondary coils of the heat exchanger. The basic underlying

Figure 9. Schematic of a typical steam converter unit.^{1/}

principle of the steam converter is that when steam is condensed by removing heat, the resulting condensate is relatively free of dissolved gases which remain mostly in the residual steam and gas phase.^{1/}

The original steam converters used at Lardarello, Italy, were used to achieve separation of boric acid from the steam. As shown in Figure 9, a small residual condensate stream remains after evaporation and this contains most of the boric acid. The original steam converters which date back to pre-1940 were relatively inefficient, requiring an additional 75% of the steam for operating the converters.^{1/} However, recent design concepts have evolved which offer the promise of relatively high efficiency. Since the steam converter effectively functions as a steam ejector, the efficiency of the converter can be compared to ejectors. For high gas concentrations ($\sim 12\%$), it is projected that steam converters of modern design could be competitive, while at lower gas concentrations of about 5%, the predicted thermal efficiency of a two-stage converter drops to about 80%.^{1/}

EIC Process

Upstream absorption of H_2S by aqueous cupric sulfate ($CuSO_4$) solution has been investigated by the EIC Corporation of Newton, Massachusetts, with funding from both DOE and PG&E.

In the Copper Sulfate Process, the steam is contacted in a scrubber with a recirculating dilute solution of copper sulfate. Copper was selected because its sulfides are sufficiently insoluble, even at high temperature and acidity, to yield favorable equilibria and chemical kinetics. The basic chemical reaction taking place within the scrubber is approximately:

with the formation of small amounts of free sulfur.

A simplified flow diagram of the EIC scrubbing process is shown in Figure 10. The scrubber used is a simple tray-type tower, although Venturi scrubbers and packed towers have also been evaluated.^{34/} The geothermal steam passes through the scrubber where H_2S and other pollutants (NH_3 and boron) are removed. The scrubber solution containing insoluble precipitates is partly recycled to the scrubber, the remainder being sent to the regeneration system. Ammonia is added to the scrubbing solution to maintain the pH at a constant level.^{35,36/} The precipitate is a mixture of cuprous sulfide (Cu_2S), cupric sulfide (CuS), and elemental sulfur. The sulfide fraction has a composition of from $\text{Cu}_{1.8}\text{S}$ to $\text{Cu}_{1.95}\text{S}$.^{37/}

Regeneration techniques are currently in development stages. Two methods have been proposed. Both are adaptations of methods used for production of copper metal from sulfide ores.

One is to use a "sulfating roast," which yields copper sulfate and drives off sulfur dioxide, which would have to be recovered by absorption or conversion to sulfuric acid. The other is acid pressure-leaching in which a slurry of copper sulfide in sulfuric acid solution is treated with air or oxygen under elevated pressure and temperature. Depending on the conditions used, most of the sulfide can be oxidized to elemental sulfur with part being oxidized to sulfate.

Figure 10. Simplified flow chart of copper sulfate emission control process.

The Copper Sulfate Process has been demonstrated using geothermal steam at the Geysers. The pilot test unit used has a capacity of 1,000 lb of steam per hour. In field tests performed thus far, the unit was operated in "open circuit" mode, i.e., without solids regeneration.

Test results thus far have been encouraging. Time on stream was about 50 hr during which more than 50,000 lb of steam were treated with a removal efficiency for H_2S of from 90 to 99+%.^{37/} Steam degradation was negligible. Ammonia removal efficiency ranged from about 70 to 80%.^{38/} Boric acid removal efficiency was in the range of 74 to 84%.^{38/} The greatest concern in the use of $CuSO_4$ as a scrubbing reagent is contamination of steam with copper salts by entrainment. However, analysis of steam condensate from the Geysers tests indicated extremely low levels of copper of about 1 ppb.^{38/} At this time, design specifications have been completed for a 100,000 lb/hr pilot test unit. This would be an integrated facility with closed cycle regeneration of sulfides.^{36/}

Salts other than $CuSO_4$ and various mechanical scrubber designs have also received limited attention as H_2S removal agents during the course of the EIC study. As mentioned previously, both Venturi and packed bed scrubbers appear feasible. A list of other salts which could be used as scrubbing agents is shown in Table 13. These have received limited attention on a theoretical basis for removal of H_2S .^{39/}

A limited feasibility study was performed using bench-scale equipment to determine the feasibility of using zinc sulfate. Although the feasibility of

TABLE 13. CALCULATED H_2S PARTIAL PRESSURES IN EQUILIBRIUM
WITH METAL SULFATE/SULFIDE SLURRIES UNDER
GEOHERMAL STEAM SCRUBBING CONDITIONS^{a/},^{39/}

Sulfate	Sulfide	$\Delta G^\circ_{175^\circ C}(\text{kcal})$ ^{b/}	P_{H_2S} at $175^\circ C$ (atm)
$MnSO_4$	MnS	+38.4	6.1×10^{17}
$FeSO_4$	FeS	+5.4	46
$CoSO_4$	$CoS_{0.89}$	+10.0	8.0×10^3
$NiSO_4$	NiS	+9.7	5.7×10^3
$ZnSO_4$	ZnS (sphalerite)	-2.5	6.1×10^{-3}
$CdSO_4$	CdS	-5.9	1.4×10^{-4}
$PbSO_4$	PbS	-5.5	1.1×10^{-4}
$CuSO_4$	$Cu_2S (+S^\circ)$	-17.1	4.8×10^{-10}
$CuSO_4$	CuS	-18.0	1.7×10^{-10}
$CuSO_4$	$Cu_2S (+SO_4^{2-})$	-22.1	2.3×10^{-13}
Ag_2SO_4	Ag_2S	-30.8	4.9×10^{-15}
$HgSO_4$	HgS	-40.3	2.1×10^{-21}

^{a/} $[M^{2+}]$ or $[M^+] = 0.018$ molal, $[H^+] = 0.043$ molal.

^{b/} Standard free enthalpy change for the reaction $MSO_4 + H_2S = \underline{MS} + H_2SO_4$.

H₂S removal via a zinc sulfate process appears good, regeneration of the sulfides formed during the scrubbing process remains doubtful.^{35/}

Deuterium Process

The Deuterium Corporation of White Plains, New York, has installed and tested a device to remove H₂S from the geothermal fluid before it reaches the plant. A pilot test unit having an estimated capacity of 1,000 lb/hr (steam) was tested at the Geysers Unit 7. Early test results indicate a removal efficiency of at least 90%.^{1/}

The Deuterium Process is believed to use a liquid absorption scrubber, but process details and the chemical reaction used are considered proprietary. The "GS Process" for heavy water uses H₂S, and the scrubbing process is intended as a component of a heavy water production facility. Development and marketing of the scrubber as a hydrogen sulfide control process appears doubtful.

Solid Sorbent Process

Battelle Pacific Northwest Laboratories has investigated numerous solid sorbents for H₂S removal from geothermal steam. The solids are metal oxides and organic amine sorbents. Among the solids tested, Zinc oxide produced the most favorable results. The zinc oxide-hydrogen sulfide reaction may be represented as follows:

Regeneration is accomplished by reaction with oxygen:

The second regeneration reaction producing zinc sulfate is favored over formation of zinc oxide when zinc sulfide is regenerated at low temperatures with oxygen or air.^{40/} Temperatures in excess of 1200°C are necessary to regenerate zinc oxide directly from zinc sulfide. However, at those temperatures, zinc oxide loses its capacity for adsorbing hydrogen sulfide.^{40/}

A schematic flow diagram of the solid sorbent process is shown in Figure 11. Geothermal steam is introduced from the bottom of a fluidized bed gas-solid contact vessel and hydrogen sulfide is adsorbed by the zinc oxide. The solid sorbent particles suspended in the steam are removed in a cyclonic separator and, if required, a baghouse. The steam is then utilized in the energy conversion system. Solid sorbent is continuously removed from the fluidized bed contactor to the regenerator.^{40/} Regenerated sorbent is returned pneumatically to the top of the contactor vessel for reuse. Sulfur dioxide generated in the regeneration process requires treatment in a separate sulfur recovery process. Battelle's investigation has established that a zinc oxide solid sorbent process is not economically viable for the removal of hydrogen sulfide from geothermal steam and recommends that no further work on solid sorbents be undertaken.^{40/}

Dow Oxygenation Process

The Dow Oxygenation Process is a method of H_2S control by oxidation of the geothermal fluid ahead of the conversion facility. Most experiment work to date has involved the treatment of the liquid phase or "hot brine," which is the most common geothermal energy form. A limited amount of work has also been done on vapor phase treatment. The basic reaction which is believed to take place in the liquid phase is as follows:^{41/}

Figure 11. Schematic illustration of solid sorbent H_2S removal process.

Lesser but significant amounts of sulfite ($\text{SO}_3^{=}$) ion and free sulfur are also formed. The catalytic effect of minerals present in the fluid is suspected but the mechanism(s) involved are still unclear.

Two design concepts have evolved for oxygenation. The simplest concept would involve the injection of gaseous oxygen upstream of a packed tower used to treat the fluid ahead of the conversion facility (Figure 12). An alternative concept would involve the use of liquid oxygen with multiple smaller static mixers.^{41/}

Figure 12. Conceptual design of Dow oxygenation processing using a packed column (design case II).^{41/}

At this time, most work has been done in the laboratory using simulated geothermal fluids. Early results have been encouraging; at a mole ratio of injected oxygen to H_2S of 1.5, essentially all of the H_2S (90 to 100%) is removed within a 1-min reaction time. The biggest problems appear to be corrosion potential and the potential for release of SO_2 to the atmosphere as a secondary pollutant. Release of sulfur (particulate) to the atmosphere must also be given consideration.

Pacific Gas and Electric Company has experimented briefly with injection of oxygen, air, and hydrogen peroxide into geothermal steam.^{1/} Results were not encouraging, although no provision was made to provide a sufficient residence time for the reaction to proceed to completion. Because of the relatively long residence time required (~ 1 min), the use of external mixing equipment (baffled tanks, packed beds, etc.) would be required as was done in the Dow experiments.

VENT CONTROLS

Vent controls refer to technology used to remove H_2S from vented gas streams which have been separated from the geothermal fluid. Some separation occurs naturally in power plant condensers, although a significant fraction of the H_2S can also be retained by the condensate. If the majority of the H_2S can be successfully removed from the fluid with the vent gases, then the control of H_2S becomes relatively simple, since conventional control technology can be used. This is the approach taken in the design of a number of recent geothermal power plants.^{1/} Control processes considered are listed in Table 14 and described below.

TABLE 14. CONTROL TECHNOLOGY FOR H₂S REMOVAL FROM
VENTS/VAPOR STREAMS

-
- Stretford process
 - Jefferson Lake process^{a,b/}
 - Burner-scrubber process^{b/}
 - Ferrox process^{b/}
 - Caustic soda process^{b/}
 - Sodium hypochlorite process^{b/}
 - Potassium permanganate process^{b/}
-

a/ This is a variation of the Claus process.

b/ All of these processes are less attractive
than the Stretford process (see Section 7).

Stretford Process

The Stretford Process has been selected for use on Geysers Units 13, 14, and 15. A modified condenser design is also used to minimize H₂S dissolved in condensate which would be released at the cooling tower stack.

A schematic of the Stretford Process is shown in Figure 13. The process uses a Venturi scrubber to contact a sour gas with a proprietary aqueous solution containing an alkali (sodium carbonate), sodium ammonium polyvanadate, and anthraquinone disulfonic acid. The scrubber solution containing dissolved H₂S is oxidized with air to regenerate the solution. During the oxidation step, the H₂S is oxidized to sulfur. The sulfur rises to the surface of the solution and can be filtered for disposal or treated further to produce by-product sulfur.

Figure 13. Flow diagram for Stretford Process.

There are now between 50 and 60 Stretford units in successful operation in various gas treating applications. Although there are no commercial units yet in commercial operation on geothermal facilities,* contractors reportedly are willing to guarantee performance of commercial units without additional development studies.^{42/}

Reasons cited for selection of the Stretford Process unit for Geysers Units 13 to 15 were (a) demonstrated high reliability with high on-time performance, (b) removal efficiency of greater than 99% with residual H_2S less than 10 ppm, and (c) ability to tolerate and recover rapidly from H_2S overloads.^{43/}

Jefferson Lake Process

The Jefferson Lake Process involves a variation of the Claus Process. Gases containing hydrogen sulfide are reacted with SO_2 in a catalytic reactor to form sulfur and water. Part of the sulfur is oxidized (burned) to form SO_2 which is then recycled back to the reactor inlet.

This process is currently under investigation for use on a geothermal power plant at Cerro Prieto. Economics of the process are believed to be highly dependent on the recovery of by-product sulfur.^{44/}

Burner-Scrubber Process

Noncondensable gases from geothermal fluids can be incinerated fairly easily since they usually contain sufficiently high concentrations of methane, hydrogen, and other flammable gases to support combustion.^{45/} In the Burner-Scrubber Process, the vent gases are incinerated, and the combustion products

* Geysers Units 14 and 15, equipped with Stretford gas cleaning systems, are scheduled for start-up on October 1, 1978.^{1/}

are scrubbed with water. Sulfur dioxide dissolved in the scrubbing liquid is returned to the condensate stream, dropping the pH in the condenser hotwell, thus causing more H_2S to be removed with the vent gases.*

A full-scale prototype of the burner-scrubber concept was tested on the Geysers Unit 4.^{2/} The marginal flammability and pulsating nature of the gases from the ejectors posed some challenging engineering problems; however, these problems were overcome and the system finally became operational. The scrubbed SO_2 proved to have relatively little effect on the condensate pH because of the relatively large volume of cooling water required with the direct contact condenser design--about 20 times the volume of condensate (Figure 1). Therefore, much of the H_2S (40 to 60%) remained in the condensate, rather than being removed with the vent gases to the burner system. For this reason, a maximum efficiency of only about 50% was achieved, based on the inlet concentration of H_2S .^{2/}

In spite of the low overall efficiency of the burner-scrubber, the system was apparently efficient in terms of the H_2S which actually reached the control system. Therefore, incineration should be considered a viable approach for control of H_2S in vent gases and at other emission points where separation of gases from steam and vapor is feasible. The major disadvantage of this process results from possible secondary pollution problems caused by emission of SO_2 , nitrogen oxides, and noncombustible pollutants.

A variation of the Burner-Scrubber process, is the Catalyst-Scrubber process developed by Union Oil Company. This process uses a catalyst to

* The water solubility of hydrogen sulfide decreases with pH.^{46/}

selectively oxidize H_2S to SO_2 . Since oxidation takes place without combustion the system is potentially less complex and safer.^{40/} However, the efficiency of this process is not expected to be much greater than about 50%.

Ferrox Process

In the Ferrox Process, the vent gas is compressed, cooled, then contacted with an aqueous alkaline solution of 3% sodium carbonate with 0.5% iron oxide suspended in the solution. The iron sulfide formed is air oxidized in the regeneration step to form a slurry of sulfur, sulfides, and insoluble oxides. The slurry is filtered to remove solids and then recirculated to the system. The sulfur-containing sludge is disposed of by landfill or other means.

The Ferrox Process was, at one time, widely used in plants designed to sweeten gases containing moderate amounts of H_2S , but most such units have been long since converted to the Stretford Process or shut down. Also, none of these units processed gases containing as much H_2S as is contained in geothermal effluents. Although it is probable that acceptable performance could be achieved by a multistage Ferrox unit, some development work may be required. There are also some serious chemical hazards involved in the handling of the feed and waste products of a Ferrox unit.^{42/}

Caustic Soda Process

The Caustic Soda Process may be used to remove both H_2S and CO_2 from the vent gas stream. The gas is contacted with a solution containing caustic soda ($NaOH$) in a countercurrent packed tower. The spent caustic is then disposed of.

Caustic scrubbing does not appear to be an attractive process for use on most geothermal effluents since it consumes NaOH on a once-through basis in removing both CO₂ and H₂S. Thus, chemical and waste disposal costs are expected to be extremely high. Dow Chemical Company has developed a caustic scrubbing process for removing H₂S selectively from streams containing CO₂, but additional development work would be required to verify the applicability of this technique to the vent gases from any given geothermal facility.^{42/}

Sodium Hypochlorite Process

In the Sodium Hypochlorite Process, the gas is contacted with a 1 to 2% solution of sodium hypochlorite, NaOCl, in a Venturi scrubber to yield solid sulfur, sulfites, and chlorides. Fresh NaOCl is continuously added to the solution which is then recirculated back to the scrubber. There is no attempt to regenerate the solution. The pH is maintained at about 10.5 by the added NaOCl and addition of caustic solution. When the solids content reaches about 15%, the slurry is pumped to disposal, while a fresh NaOCl make-up solution is pumped into the top of the scrubber.

The literature contains very little information regarding the use of sodium hypochlorite to remove large quantities of H₂S from a gas stream. Nor do the manufacturers of hypochlorite have sufficient data to design such a process to treat the type of gas at the Geysers with reasonable confidence of its success. Therefore, before a unit based on this process is built, some development and pilot work would be required.^{42/}

Potassium Permanganate Process

This process involves contacting the vent gas in a packed countercurrent tower with a 1 to 2% aqueous solution of potassium permanganate (KMnO_4). The H_2S is oxidized to sulfite ion with the formation of insoluble MnO_2 . A blow-down stream is continuously withdrawn from the bottom of the packed tower and fresh permanganate solution added at the top.

Potassium permanganate has been used successfully to remove H_2S , mercaptans, unsaturated organic acids, and other sulfur compounds, in low concentration from various gases. Although it has not been used to treat gases with H_2S concentrations as high as that expected for geothermal applications, it is believed that this process would be technically feasible. However, some development and pilot work would be required. There are also some serious chemical hazards associated with handling and use of KMnO_4 . Waste materials would require an appropriate disposal site. No cost information is currently available for this process.

Other Vent Gas Controls

The literature search disclosed a number of other control systems which are capable of achieving greater than 90% removal of H_2S from gas streams. These include Tripotassium Phosphate (Shell),^{47/} Sulfreen Process (Lurgi),^{47-49/} Thylox-Koppers,^{47,48/} Rhodia Cataban,^{50/} and Diethanol Amine (Amoco).^{39,43/} None of these processes have been demonstrated on geothermal effluents, although all are commercially available. Table 15 summarizes available data on these processes.

TABLE 15. CHARACTERISTICS OF OTHER H₂S REMOVAL PROCESSES FOR VENT GAS CONTROL

Process	H ₂ S Removal efficiency (%)	Operating Conditions					State of development	Process availability
		Gas flow	H ₂ S Conc.	Temp. (%)	Pressure	Space velocity		
Tripotassium phosphate (Shell)	91 ^{a/}	Unknown ^{b/}	Unknown ^{b/}	90-130	1-1,000 psi	Unknown ^{b/}	Commercial	Proprietary
Sulfreen process (Lurgi, Ralph M. Parsons)	98.5-99.5 ^{c/}	110 x 10 ⁶ scf ^{c/}	1% by vol.	260-300	Ambient	Unknown ^{b/}	Commercial	Proprietary
Thylox (Koppers Company)	97.99 ^{d/}	5 x 10 ⁶ to 50 x 10 ⁶ ^{d/}	50-1,000 gr/100 scf ^{d/}	73-100 ^{d/}	Ambient ^{d/}	Unknown ^{b/}	Commercial	Proprietary
Cataban (Rhodie, Inc.) ^{e/}	99.9 ^{e/}	Unknown	ppm level	77-106 ^{f/}	Unknown ^{b/}	100-200 hr ⁻¹ ^{f/}	Pilot	Proprietary
Diethanol Amine (SNPA Amoco)	99 ^{g/}	50 x 10 ⁶ scf/absorber	160-180 gr/100 scf ^{g/}	90-130	1,000 psig	Unknown ^{b/}	Commercial	Nonproprietary

^{a/} Typical, 48,51/^{b/} Not listed in literature sources reviewed.^{c/} Typical, 47/^{d/} Typical, 47,48/^{e/} Applicable to both liquid and gas streams.^{f/} Typical, 50/^{g/} Typical, 47,48,52/

H₂S REMOVAL TECHNOLOGY FOR COOLING WATER/CONDENSATE

Processes which have been used or are considered potentially feasible for removal of H₂S from the liquid phase are listed in Table 16 and described below.

TABLE 16. CONTROL TECHNOLOGY FOR H₂S REMOVAL FROM COOLING WATER/CONDENSATE

-
-
- Iron catalyst process
 - Hydrogen peroxide (H₂O₂) process^{a/}
 - Use of ozone^{a/}
 - Wackenroder reaction^{a/}
-
-

^{a/} These processes do not appear attractive at the present time. The H₂O₂ process involves a high temperature environment; the ozone process is economically unattractive; in the Wackenroder process the rate of H₂S reduction is too slow.

Iron Catalyst Process

The iron catalyst (or Ferrifloc) system was developed by PG&E for removal of H₂S from the steam condensate at power plants. In this process, ferric sulfate is added to the cooling water/condensate stream upstream of the cooling tower. Ferric ions thus formed react with dissolved oxygen and hydrogen sulfide, forming elemental sulfur, water and ferrous ions, viz:

In theory, the ferrous ions react with the oxygen encountered in the cooling tower to regenerate the ferric ions, although there have been some problems with incomplete oxidation resulting in the formation of an insoluble FeS sludge. The sludge is pyrophoric, which further complicates storage disposal problems.^{22/}

A simplified flow diagram of this process is shown in Figure 14. Ferric sulfate, in solution, is added to the cooling water, thus oxidizing the hydrogen sulfide contained in the aqueous phase. The noncondensable condenser ejector gases are ducted to the cooling tower and hydrogen sulfide is scrubbed by the falling water containing the ferric sulfate catalyst. The process therefore may be thought of as a scrubbing process in which the cooling tower functions as the scrubber.

The iron catalyst process has been used extensively at the Geysers, where overall H_2S removal efficiency is estimated to be 90 to 92% for the fraction of H_2S which reaches the cooling tower. In addition to a sludge formation problem, operating problems have been numerous. The system causes significant corrosion in the condenser, cooling tower, and associated piping. Plugging has also been a problem in all the equipment which came into contact with the cooling water/condensate. In addition, the sludge generated from the filtration step may cause disposal problems due to its large quantity and toxic nature. An industrial waste disposal site or appropriate landfill disposal site is required. In spite of these problems, the iron catalyst process is the only process which has been successfully used on a commercial scale to remove H_2S from cooling water/condensate streams.

A number of metal salts will catalyze the oxidation of H_2S in the liquid phase.^{53/} Of these, iron, nickel zinc, and copper sulfates were tested in

Figure 14. Iron catalyst hydrogen sulfide removal process.^{60/}

preliminary studies at the Geysers. It was found that iron and nickel salts both were extremely active. Iron concentrations of approximately 30 mg/liter and nickel concentrations of 1.5 to 2 mg/liter could reduce the total H_2S emissions from the cooling towers by 90% or more. The choice between these two oxidation catalysts was a matter of relative economics and their effects, if any, on the long-term operation of the units. Since nickel salts are evidently significantly more active than iron, the question of whether it too causes accelerated corrosion and maintenance problems (plugging) seems appropriate, but there have evidently been insufficient tests made to determine this possibility.

Hydrogen Peroxide Process

Hydrogen peroxide has been used to remove hydrogen sulfide from various wastewater streams. The applicability of H_2O_2 to geothermal cooling water/condensate is somewhat questionable at this time because of the high temperature environment.^{40/} Hydrogen peroxide reacts with hydrogen sulfide in an acidic or neutral aqueous solution to produce elemental sulfur and water:

In alkaline solutions ($pH > 8$), the sulfide ion reacts with hydrogen peroxide to produce sulfate and water:

The FMC Corporation has recently conducted laboratory experiments on oxidation of hydrogen sulfide in samples of cooling water/condensate streams taken from the Geysers power plant. The experiments were conducted with various conditions for the following parameters: hydrogen sulfide solution concentration; pH; temperature; hydrogen peroxide:hydrogen sulfide weight ratio; and ferric sulfide catalyst concentration. The results from the experiments indicate that the hydrogen sulfide oxidation rate increases due to increases in: initial hydrogen sulfide concentration (2.3 to 12.5 ppm); temperature (40 to 51°C); hydrogen peroxide:hydrogen sulfide weight ratio (0.9 to 3.9); and ferric sulfide concentration (0 to 2.0 ppm). An efficiency of 88% was obtained in less than 3 min without the use of a catalyst, a hydrogen peroxide:hydrogen sulfide weight ratio of 1.9, and an initial hydrogen sulfide concentration of 12.5 ppm. The results from the FMC experiments indicate that the use of hydrogen peroxide for oxidation of hydrogen sulfide in geothermal cooling water/condensate is feasible.^{54/}

Ozone

The use of ozone to oxidize hydrogen sulfide in aqueous solutions has not been adequately investigated to evaluate its applicability for controlling emissions from geothermal sources.^{40/} However, ozone has been used to oxidize hydrogen sulfide in the gaseous phase. Elemental sulfur and sulfate are the most likely products of a hydrogen sulfide-ozone aqueous reaction:^{40/}

The feasibility of this process will depend on which of the two reactions dominate since the second reaction requires four times as much ozone as the first one. Therefore the cost of producing ozone will be a major factor in developing this process.

Wackenroder Reaction

The Wackenroder reaction is the liquid phase equivalent of a Claus reaction:

Laboratory experiments were performed at PG&E to determine the feasibility of SO_2 injection for H_2S control in condensate/cooling water. Such experiments evidently were successful in removing part of the H_2S .^{8,45/} No published reports of this work are available.

The Wackenroder reaction was part of the basis from which the "burner-scrubber" concept evolved,^{45,2/} although measured rates of reaction between SO_2 and H_2S were "immeasurably slow."^{55/} No attempt has been made to use catalysts to accelerate the reaction rate.^{55/}

Other Processes

Other approaches which could be used for H_2S removal from the liquid phase include (a) electrolytic oxidation, (b) ion exchange, and (c) reverse osmosis. One other commercial process which could be used is Rhodia Cataban, which uses a water soluble iron chelate as a catalyst.^{50/}

Ion exchange, reverse osmosis, and electrolytic oxidation all were rejected on the basis of economics.^{56/} The addition of Cataban, a chelated iron compound manufactured by Rhodia Corporation, was successful in catalyzing the direct oxidation of H_2S by oxygen dissolved in the cooling tower/condensate stream.^{45/} The reason why the investigation of this process was discontinued is unknown.

POWER PLANT DESIGN ALTERNATIVES

There are at least two process design alternatives which could be used to reduce H_2S emissions from power plants. These are (a) modification of the condenser system, and (b) use of dry or wet/dry cooling. A third alternative, which would involve total reinjection of all fluids, is presently not feasible technically but is described briefly in this section.

Modification of the Condenser System

As explained in Appendix A, the ratio of H_2S which remains with the liquid phase is directly proportional to the total liquid flow rate. Therefore, a feasible method of reducing H_2S emissions at the cooling tower is to decrease the quantity of liquid that is present in equilibrium with the vapor at the condenser. This can be done most easily by modifying the condenser design.^{2/} When the geothermal fluid is superheated steam, such as at the Geysers, or where a flashed steam process is involved, the process modification involved is to replace the water spray "direct contact" condenser system with a shell-and-tube heat exchanger, as depicted in Figures 15 and 16. This adds significantly to equipment costs but achieves a 20 to 1 reduction in the total volume of condensate.^{2/}

Use of Alternate Cooling Methods

The efficiency of a Rankine power plant cycle is directly related to the temperature of cooling water available. In addition, a feasible method for reducing the H_2S emitted at the cooling tower is to replace the presently used evaporative cooling methods with either dry cooling or wet/dry cooling. The following heat rejection systems have been considered as candidates for use with large power generation systems.^{57/}

Figure 15. Conventional power plant cycle employing a direct contact condenser.

Figure 16. Modified power plant cycle using shell and tube condenser.^{3/}

- Once-through cooling,
- Cooling ponds,
- Spray ponds,
- Cooling towers (wet and dry),
- Evaporative condensers, and
- Air-cooled condensers.

Of these, dry and wet/dry cooling methods have been proposed^{1/} as a potentially viable solution for elimination of cooling tower emissions of H_2S and other pollutants.

The dry cooling tower is a relatively recent development. Only a few power plants have been built which utilize this cooling technique. Notable examples are a 120-Mw plant at Rugeley, England, and a 15-Mw plant in West Pakistan.

In a dry cooling tower arrangement, the turbine exhaust is condensed in a direct contact spray condenser, as depicted in Figure 15. A part of the condensate is pumped to the cooling tower with the remainder being sent to reinjection.

The dry cooling tower itself consists of an air-cooled heat exchanger mounted inside a cooling tower chimney. The air flow past the heat exchanger may be either forced or natural draft. A dry cooling tower is generally larger and more expensive than a wet tower by about a factor of 2.^{57/} Part or all of the additional cost can be offset by the cost savings of using a direct contact heat exchanger, however. An additional disadvantage of the dry cooling system is that, while it is technically possible to build a dry cooling tower to produce turbine exhaust pressures as low as those obtained with water cooled condensers, this is usually not economically feasible.

Wet/Dry Cooling

A possible compromise between the benefits of wet and dry towers are the so-called wet/dry combination cooling towers.^{1/} These consist of a dry tower-like section with a supplementary wet tower-like section. On cold days the dry section does most of the cooling and little or no cooling water is consumed, while on hot days the wet section takes over most of the cooling load. The split of the cooling load between the two sections may be continually optimized by use of any desired criterion such as minimizing cost or minimizing water consumption.

Total Reinjection^{58,59/}

The concept of total reinjection is based on the use of a binary cycle process (Figure 17) along with a downwell pump. The pump is used to maintain the fluid at high pressure so that gases including H_2S remain dissolved in the fluid. The fluid is pumped from the well to a heat exchanger, where the fluid energy is transferred to a secondary working fluid, such as freon or isobutane. Although the concept of total reinjection may be feasible within the near future, costs associated with equipment may make it unattractive.

Figure 17. Magmamax power cycle ^{60/}

SECTION 7

ANALYSIS AND EVALUATION OF CONTROL TECHNOLOGY

A comparison of the available H₂S control technologies is provided in this section. Based on this comparison, the most promising processes are identified.

Various factors have been taken into account in the comparative analysis of the H₂S control processes. These factors are listed below and briefly explained. Symbols that are represented in these explanations are used in the evaluation grid (see Table 17).

1. Process availability.
2. Ease of adaptability to application.
3. Potential for H₂S removal.
4. State of development.
5. Cross-media impacts (secondary environmental problems).
6. Operating constraints (high pressure/high temperature/high energy requirement).
7. Total annualized cost.

PROCESS AVAILABILITY

As used here, "process availability" denotes whether a particular process has been demonstrated (D) or whether it is feasible merely from a conceptual standpoint (C).

TABLE 17. EVALUATION GRID FOR H₂S CONTROL PROCESSES

H ₂ S Removal process	Process availability	Ease of adaptability (+ or -)	Potential for H ₂ S removal (%)	State of development	Cross-media impacts	Operating constraints	Total annual cost (mills/kwh)
<u>Upstream technology</u>							
Steam converters ^{a/}	D	+	80	CM	None	Needs additional H ₂ S removal from vent gas	Not known
EIC process ^{a/}	D	+	90 - 99+	P	None	None	2
Deuterium process ^{a/}	D	+	90	P	Not known	Not known	Not known
Solid solvent process ^{a/}	D	+	Not known	L	Not known	Not known	Not economically viable (> 10)
Dow oxygenation process ^{b/}	D	+	100	L	SO ₂	Corrosion	9
<u>Vent control</u>							
Stretford process	D	c/	99	P	None	None	0.5
Jefferson Lake process	D	-	Not known	L	Not known	Not known	Not known
Burner-scrubber process	D	+	50	P	SO ₂ , NO _x	None	Not known
Ferrox process	D	Not known ^{d/}	Not known	Not known	Sludge	Not known	Not known
Caustic soda process	D	+	Not known	L	Sludge	Not known	Not known
Sodium hypochlorite process	D	Not known	Not known	Not even lab scale	Wastewater	Not known	Not known
Potassium permanganate process	D	Not known	Not known	Not even lab scale	Waste disposal	Not known	Not known
<u>Cooling water/condensate</u>							
Iron catalyst process	D	+	90 - 92	CM	Sludge disposal	Corrosion	0.4
Hydrogen peroxide	D	+	88	L	Not known	High temperature	Not known
Use of ozone	C	Not known	Not known	Not even lab scale	Not known	Not known	Not known
Wackenroder reaction	D	Not known	Not known	L	Not known	Not known	Not known

Note: D = process has been demonstrated; C = process only a concept.
CM = commercial scale; P = pilot scale; L = lab scale.

^{a/} For vapor-dominated sources.

^{c/} Requires surface contact condensers.

^{b/} For liquid-dominated sources.

^{d/} Process seems to have been abandoned.

EASE OF ADAPTABILITY TO APPLICATION

This criterion is used to determine if an H_2S removal process can be adopted for the geothermal application that is being considered (i.e, technology transfer). A "4" sign indicates it can be adopted.

POTENTIAL FOR H_2S REMOVAL

This denotes H_2S removal efficiency.

STATE OF DEVELOPMENT

This signifies whether a process has been tested in the laboratory (L) or whether it has been demonstrated on a pilot (P) or commercial (CM) scale.

CROSS-MEDIA IMPACTS

Secondary environmental problems such as sludge disposal, release of SO_2 or NO_x , or waste water treatment and disposal are implied in this category.

OPERATING CONSTRAINTS

The need for high temperature, high pressure, or corrosion-resistant environments, and high energy requirements, if any, are considered in this category.

TOTAL ANNUAL COST

The total cost includes capital, operating and maintenance costs, and is obtained from Reference 40 which has reported annual cost versus power generation for various H_2S control processes. The cost values reported here are based on a 100-MW plant.

Using the factors described above, available control technologies were compared as shown in the evaluation grid (Table 17). The following set of selection criteria, which were deemed more important than the others, were then used to evaluate the various control processes:

1. The process had to be demonstrated as being feasible (i.e., "D" rating).
2. H₂S removal efficiency had to be 80% or better.
3. Minimum acceptable state of development was laboratory scale.*
4. Annual costs should be less than 10 mill/kwh, based on 100-MW plant.
5. Cross-media impacts should be minimal.

Application of the above criteria to the processes shown in Table 17 results in the following processes as being most promising.

- For upstream controls -
- Steam converters
 - EIC process
 - Dow Oxygenation process
 - Deuterium process

For vent controls -

- Stretford process

- For cooling water/condensate -
- Iron catalyst
 - H₂O₂

With the exception of steam converters and the Iron catalyst system which are already commercial, development of the other processes should be prioritized as:

* Those processes that have been commercially developed are ranked uppermost among the most promising technologies.

1. EIC,
2. Dow Oxygenation,
3. Stretford,
4. H_2O_2 , and
5. Deuterium.

The rationale for this prioritization is as follows: EIC and Dow Oxygenation processes are ranked high because of the intrinsic advantage of upstream removal of H_2S . The EIC process is also close to commercialization. For the same reason, the Stretford process is ranked last because of the proprietary nature of the process and lack of reliable information.

APPENDIX A

METHODOLOGY USED FOR CALCULATION OF VAPOR-LIQUID EQUILIBRIUM DISTRIBUTION OF NONCONDENSIBLE GASES--H₂S, NH₃, AND CO₂

This appendix presents a summary of methodology used for estimating the fractional distribution of three components--H₂S, NH₃, and CO₂--present in geothermal fluids. The fractional distribution is estimated for the vapor and liquid phases as a function of temperature, pH, vapor fraction, and liquid-to-condensate ratio. The methodology was patterned after a technique suggested by Dankwerts,^{61/} and later implemented by PG and E in design of H₂S removal equipment for their Geysers power plant facility.^{3,62/}

The computational method is outlined schematically in Figure A-1 and is described briefly below.

Step 1. Calculate Fractional Dissociation

The dissociation equilibrium constant for H₂S is determined for a given pH and temperature from information given in Shih et al.^{46/} For a pH less than 9 (Table 2), the second dissociation has only a negligible influence on the equilibrium.^{46/} For CO₂, the dissociation equilibrium constant was determined from information given by Kent and Eisenberg.^{63/} Ammonia was assumed to be 100% associated under the conditions encountered in geothermal brines (Table 1). Following Shih et al.,^{46/} the fractional dissociation (α) of a given species in solution may be expressed in terms of hydrogen ion concentration as follows:

$$1 - \alpha \equiv \frac{[H^+]^2}{[H^+]^2 + K_1 [H^+] + K_1 K_2} \quad (A-1)$$

where $[H^+]$ = hydrogen ion concentration, g-ion/liter

K_1 = the first dissociation equilibrium constant, g-ion/liter

K_2 = the second dissociation equilibrium constant, g-ion/liter

α = the fraction of a given species in solution which is dissociated

Figure A-1. Schematic of computational method used to determine ratio of noncondensable gas components between vapor and liquid phases in two-phase brine flows.

Step 2. Calculate Modified Henry's Law Constant

Following Shih et al.,^{46/} the modified Henry's Law constant may be expressed as:

$$H' \cong H (1 - \alpha) \quad (A-2)$$

where H = Henry's Law constant, mm Hg/g-mole-liter⁻¹

H' = the modified Henry's Law constant, reduced by the fraction dissociated, mm Hg/g-mole-liter⁻¹

α = the fraction of a given species in solution which is dissociated

Henry's Law constants for H₂S and CO₂ were determined from information given in References 46 and 63, respectively. The Henry's Law constant for NH₃ was estimated from data given in References 64 and 65.

Step 3. Calculate Distribution Ratio

Given the fractional dissociation of solute (Eq. (A-1)) and the modified Henry's Law constant (Eq. (A-2)), the distribution of a given component between the two phases can be determined from (a) vapor-to-liquid ratio, (b) liquid-to-condensate ratio, and (c) initial solute concentration using methodology developed by PG and E.^{3,62/} The equilibrium distribution ratio between vapor and liquid is directly proportional to the fraction of total fluid which is vapor. An example of the results obtained for H₂S is presented in Figure A-2, showing the influence of vapor (noncondensable gas) fraction and liquid flow rates.

* Source: Pacific Gas and Electric Company

Figure A-2. Calculated H₂S distribution ratio in vent gas for direct contact and surface condensers.*

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