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EVALUATION OF H₂S CONTROL TECHNOLOGY
FOR GEOTHERMAL ENERGY SOURCES

MONTHLY REPORT NO. COO/4255-3
November 1, 1977

ERDA Contract No. EE-77-G-02-4255
MRI Project No. 4412-L

AC02 - 77EV04255

Prepared For

Department of Energy

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PREFACE

This report was prepared for the Environmental Control Technology Division, to summarize work performed under Contract No. EE-77-C-02-4255 during the month of September. The work was performed in the Environmental and Materials Sciences Division of Midwest Research Institute. This report was written by Dr. Jim Galeski.

Approved for:

MIDWEST RESEARCH INSTITUTE

L. J. Shannon, Director
Environmental and Materials
Sciences Division

November 11, 1977

TABLE OF CONTENTS

	<u>Page</u>
Summary	1
Status.	1
Schedule.	3
Budget.	3
Personnel	3
Continuation.	6
Appendix A - Preliminary Summary of Processes Used to Control H ₂ S Emissions From Geothermal Steam.	8
Appendix B - Example Source Parameters.	10
Appendix C - Fraction of Noncondensable Gases (NCG's) at Salton Sea and East MESA Test Facilities	15

SUMMARY

This study is divided into three tasks. The initial task involved an extensive review of the literature to identify ongoing and planned geothermal developments and potentially applicable H₂S control technology. Contacts were also made with individuals and agencies involved with the development of H₂S control technology for geothermal applications.

Task 2 efforts involve review of available experimental and operating data for H₂S control systems which have been applied to geothermal sources and preparation of a state-of-the-art report on H₂S removal systems. In this task, data are also being acquired on ongoing H₂S control development programs.

Task 3 efforts involve the evaluation and development of a listing of candidate clean-up systems which could be used for future geothermal energy development projects. Projects being considered include electric power generation as well as selected nonelectric applications. Source characterization involves identification of process (source) parameters as well as ranges of key emission variables.

STATUS

Task 1. Literature Search

Task 1 efforts are essentially complete. Any additional data acquisition efforts will center on acquisition of data pertinent to specific control technology and planned geothermal development projects.

Task 2. State-of-the-Art Review

A preliminary list of processes currently under evaluation in this task is presented in Appendix Table A-1. Evaluation of each process is being performed according to a systematic procedure using specific data forms for (a) H₂S control technology information and (b) H₂S control applications (see Work Plan , Tables 1 and 2). The former data reduction efforts involved the preparation of a generalized process description for each control technology while the latter involves a summary of available test data. During the month of October, data summaries were prepared for the Copper Sulfate process (EIC), the Dow Process, and several processes being developed by FMC Corporation in cooperation with Union Oil. We are awaiting receipt of additional information from Magcoban Division, Dresser Industries. We have identified a fairly extensive

body of unpublished information related to control evaluations at the Geysers. We will attempt to obtain copies of these reports during the next reporting period.

The list of H₂S removal processes in Table A-1 should be regarded as preliminary. We are awaiting receipt of additional control technology information as a result of contacts made with Electric Power Research Institute and Mexicala I.E.E. It is also likely that the list of processes will be expanded as a result of our visit to the Geysers' field (see planned activities).

Task 3. Selection of Potentially Applicable H₂S Removal Processes for Future Geothermal Development Projects

Source characterization efforts for this task initially involved power production units at the Geysers field. Additional source characterization efforts have been directed toward planned power and desalination units in the East Mesa KGRA and a geothermal power plant planned near Salton Sea KGRA (Niland, California). We have acquired process descriptions for these projects and several other binary power systems (Heber and Raft River) and are awaiting detailed process information for the East Mesa Desalination Project.* Source characterization involves identification of H₂S emission points (sub-sources), and characterization of each source according to thermodynamic properties, range of total noncondensibles, and ranges of compositions. As far as possible, field-wide composition ranges of various components in brine or steam are being used to determine composition ranges or probable composition ranges at emission points.

For geothermal power production, subsources can be conveniently divided into power plant emissions (venting of noncondensibles, cooling tower emissions, and bypass venting) and drilling/fluid transmission operations which may include a number of separate sources (see Appendix B). This breakdown corresponds to a division of responsibility for H₂S emission abatement between steam producers and power producers. In many cases, as indicated in Appendix A, the same H₂S removal technology could be used for different sources. Data summaries showing example source characterization data for electric power generation from a vapor dominated source (The Geysers) is presented in Appendix B (Tables B-1 and B-2). Two data elements--particulate (rock dust) concentrations and size distribution and average duration of intermittent

* Project status descriptions for these and several other planned projects were included in Monthly Report No. 2 (Table 2).

or occasional emissions were not found in data sources available. It is hoped that most missing data can be obtained during the Geysers site visit, and related meetings, now scheduled for early November.

We have been able to acquire limited source characterization data for geothermal projects in the Salton Sea and East Mesa KGRA's. Appendix C shows noncondensable gas fractionation in flash systems at East Mesa and Niland test facilities. We expect to obtain detailed well test data for these KGRA's from ERDA/RECON data files. Because of the early development status of programs within these KGRA's, it is anticipated that a limited amount of engineering analysis will be needed in order to complete required source characterizations.

SCHEDULE

The schedule shown in Figure 1 depicts the program status as of November 1, 1977. The schedule shows activities completed to date and projected activities. The Geysers site visit and related meetings, originally scheduled for mid-to late November have been delayed slightly and the site visit now is scheduled to begin November 7, 1977.

BUDGET

The project costs as of November 1, 1977, amount to a total of \$31,773. Actual versus projected program costs are shown in Figure 2.

PERSONNEL

Personnel assigned to the program and percent of time spent are as follows:

<u>Individual</u>	<u>% Time Spent</u>
K. P. Ananth	20
J. B. Galeski	60
G. S. Desai	75
L. S. Granger	50
P. G. Gorman	20
M. P. Schrag	2
L. J. Shannon	2

Completed
 Uncompleted

MILESTONES:

- M-1 Submit Draft Work Plan to Project Officer 8/1/77
- *M-2 Meeting with Project Officer 10/14/77
- *M-3 Meeting with Project Officer 1/15/78
(Complete Technical Data Inputs to the State-of-Art Study)
- M-4 Submit Draft of State-of-Art Report 4/1/78
- M-5 Submit Revised Draft of State-of-Art Report 6/1/78
- M-6 Submit Draft Final Report 4/1/78
- M-7 Submit Revised Final Report 6/1/78

*Indicates Tentative Schedule to be Coordinated Through ECT

Figure 1 - Project Schedule and Milestones

Figure 2 - Estimated Cost and Expenditures

CONTINUATION

During the next reporting period, Task 2 (State-of-the-Art) efforts will include the continuation of acquisition and evaluation of test data for H₂S control systems which have been tested on geothermal effluents. During The Geysers site visit, we also plan to meet with representatives from Union Oil, PG&E, Lake County APCD, and Sonoma County APCD. An itinerary for the site visit and related meetings is presented in Table 1.

Planned activities for Task 3 include the completion of source characterization efforts and initiation of H₂S control technology screening activities. It is anticipated that additional details concerning ranges of H₂S concentrations, for the sites within Salton Sea and East Mesa KGRA's, can be obtained during the visit to Lawrence Livermore Laboratory.

TABLE 1

ITINERARY FOR GEYSERS SITE VISIT
AND RELATED MEETINGS

<u>Date</u>	<u>Location/Purpose</u>	<u>Principal Contacts</u>
11/7/77	Santa Rosa, Ca. Discuss Geothermal Resources Impact Projection (GRIPS) Data Base. Obtain copies of requisite data.	Tom Cordell (Sonoma County APCD, GRIPS Committee)
	Northern Sonoma County APCD, Lake County APCD Obtain emission test data and information on planned control tests.	Mike Tolmasoff Fayne Tucker
11/8/77	Santa Rosa, Ca. Discuss objectives of ETC/ MRI study.	George Frye (Geothermal Environ- mental Committee, Aminail USA)
	Union Oil, Magma Power, Santa Rosa, Ca. Obtain emission and control test data for wells and fluid transmission.	Warren Smith (Union Oil) Ted Wilmsen (Magma)
11/9/77	PG&E/Geysers Site Visit	Gordon Allen
11/10/77	PG&E, Engineering Research San Ramon, Ca. Obtain emission and control test data for power plant operations.	
	PG&E, Engineering Discuss alternative plant designs and add-on technology for H ₂ S abatement.	
11/11/77	ERDA, San Francisco, Ca. Operations Offices Discussion of abatement technology needs for planned developments: review project files.	Art Wilbur Lowell Miller
11/14/77	Lawrence Livermore Laboratory Discussion of Geysers and Imperial Valley projects.	Dave Snieberger John Hill Paul Gudiksen Roy Anstin
11/15/77	Lawrence Berkeley Laboratory, Discuss H ₂ S control technology obtain grid brine chemistry data.	Sid Phillips Olie Weres
11/16/77	LLL/Data Reduction	
11/18/77	Additional contacts	

APPENDIX A

PRELIMINARY SUMMARY OF PROCESSES USED TO
CONTROL H₂S EMISSIONS FROM GEOTHERMAL STEAM

TABLE A-1

PRELIMINARY SUMMARY OF PROCESSES USED TO CONTROL H₂S EMISSIONS FROM GEOTHERMAL STEAM^{a/}

<u>Process</u>	<u>Sources Applied</u>	<u>Vendor</u>	<u>State-of-Development</u>
Ferrifloc "Iron Catalyst"	Cooling water (Direct contact condenser)	Unknown	Commercial ^{b/}
Chemical Oxidizer (a) H ₂ O ₂ /Catalyst (b) Ozone (c) SO ₂ (d) Cl ₂	Condensate Surface condenser wells: drilling emissions	FMC	Development-- PG&E/FMC ^{c/} Shell (H ₂ O ₂ /Catalyst)
Incineration "Burner Scrubber"	Condensate ^{d/} (Direct Contact Condenser) and Negvent Gases	Unknown	Commercial Demonstration ^{e/}
SO ₂ Oxidation "Wackenroder reaction"	Condensate	Unknown	Laboratory - PG&E
Zinc Chelate	Steam Condensate and drilling emissions	Magcobar Div., Dresser Ind.	Conceptual - Union Magcobar ^{f/}
Copper Sulfate	Total steam flow to power plant "upstream treatment"	EIC	Development - PG&E/EIC/ERDA ^{g/}
Stretford	NCG Vent Gases	Ralph M. Parsons, Co.	Commercial ^{h/}
Deuterium	Total Steam flow to power plant "upstream treatment"	The Deuterium Corp.	Development ^{i/} - PG&E/Deuterium Corp.
Couru	Unknown	Couru & Associates, Inc.	Unknown ^{j/}
Jefferson Lake Process	NCG Vent Gases	Unknown	Conceptual - Princeton Univ./IEE Mexicala/Others ^{k/}
Dow Process (oxygen injection)	Brine (or condensate)	Unknown	Development - Dow, Texas Div./ERDA ^{l/}
Battelle (PNL) Process (selective oxidation)	Total Steam Flow	Unknown	Development - Battelle Pacific Northwest Laboratory/ ERDA ^{m/}
H ₂ S Absorption	Drilling Operations	FMC	Development - Union Oil
Hydrogen Peroxide (H ₂ O ₂ /NaOH Injection)	Drilling Operations	FMC	Development - Magma Power/ Republic Geothermal, FMC ^{n/}
Ammonium Hydroxide (NH ₃ /Air Injection)	Drilling Operations	FMC	Development - FMC/Union ^{o/}

^{a/} State-of-Art removal processes (preliminary listing).

^{b/} This is the only abatement process currently in use on a commercial scale to control power plant emissions. It is used only intermittently, for example during adverse climatic conditions. Process related problems associated with the use of the Ferrifloc process are numerous and include plugging and corrosion. Another concern is plugging of reinjection wells.

^{c/} Both pilot test and laboratory tests have been performed.

^{d/} SO₂ generated in combustion of H₂S vent gas was recovered and re-injected into the process at the condenser hot-well. No reaction with H₂S was observed.

^{e/} Process use has been discontinued.

^{f/} Drilling tests are planned by Union/Magcobar for November 1977.

^{g/} Open circuit field tests completed, design completed for 100,000 lb/hr demonstration unit.

^{h/} Proposed for PG&E units 12, 13, 14, 15 Geysers-Calistoga KGRA.

^{i/} Pilot tests performed at PG&E. Process details are proprietary.

^{j/} Development status and process unavailable. May involve steam stripping operation such as used in refinery operations ("sour gas stripping").

^{k/} Under evaluation for Cerro Prieto on a 75 MWe unit. Licensing arrangements have not been decided.

^{l/} Bench scale tests have been performed using simulated brine. Pilot unit designs have been developed involving at least two concepts (a) static mixing, and (b) packed tower

^{m/} Bench scale tests have been performed using simulated geothermal steam and either air or oxygen. A catalyst or absorbent is used to achieve selective oxidation of H₂S to elemental sulfur.

^{n/} Pilot tests completed on geothermal steam.

^{o/} Tests performed under actual drilling operations.

APPENDIX B

EXAMPLE SOURCE PARAMETERS

TABLE B-1

EXAMPLE SOURCE PARAMETERS--WELLS, WELL DRILLING

(Vapor Dominated Source)

Flow (lb/hr)	Range <u>50 - 300 x 10⁶</u>	Avg. <u>100,000 lb/hr</u>
Temperature	Range _____	Avg. _____
Pressure	Range <u>100 - 480 psig</u>	Avg. <u>110 psig</u> (Full Flow)
Noncondensibles portion (wt %)	Range <u>0.1 - 2.0%</u>	Avg. <u>0.54%</u>

Noncondensibles Analysis

<u>Component</u>	<u>Conc. (ppm)</u>
CO ₂	-
H ₂ S	-
NH ₃	-
CH ₄	-
H ₂ , N ₂	-

EMISSION SUB-CATEGORIES

(a) Well Drilling--During final stages of drilling, steam is released through the drill vent at full flow. Average duration of venting is unknown. Accidental discharge of steam may occur in blowouts. Several years may be required to seal blowout wells. Well cleanout and flow testing follows drilling of each well. Twenty-four hours or more may be required for cleanout and flow testing may require from 3 to 4 weeks. When a well is shut in following power plant outage, venting for 2 to 6 hours at full flow may be required for cleanout. Concentrations of rock dust in the steam flow during well drilling, cleanout, and production are not currently available.

(b) Idle Wells--During field development, idle wells are not completely closed but are continuously vented at flows ranging from 3,000 to 4,000 lb/hr. Enrichment of non-condensibles undoubtedly occurs at low flows. Data on enrichment of non-condensibles and particulate size and concentration is not currently available.

(c) Production Wells--3,000 to 4,000 lb/hr of steam is continuously vented at the cyclone separation. An additional 2,700 to 4,000 lb/hr of steam is emitted in the blowdown stream from steam separators in the steam transmission lines.

OTHER CONSIDERATIONS (corrosiveness, solids content, etc.)

a. Corrosiveness--Steam is noncorrosive and carbon steel piping is used in fluid transmission lines.

b. Particulate concentrations--Rock dust concentrations in the steam are probably significant at several emission points. Data regarding the size and concentration of particulates have not yet been obtained.

TABLE B-2

EXAMPLE SOURCE PARAMETERS--ELECTRIC POWER PRODUCTION
(Vapor Dominated Resource)

Flow (lb/hr)	Range <u>0.2 - 2.3 x 10⁶</u>	Avg. <u>0.9 x 10⁶</u>	(11 - 135 MWe)
Temperature	Range <u>342 - 355°F</u>	Avg. <u>350°F</u>	(at power house)
Pressure	Range <u>78.9 - 113.7 psig</u>	Avg. <u>100 psig</u>	(at power house)
Noncondensibles portion (wt %)	Range <u>0.1 - 2.0%</u>	Avg. <u>0.54%</u>	

Noncondensibles Analysis

<u>Component</u>	<u>Conc. (ppm by weight)</u>	
	<u>Range</u>	<u>Average</u>
CO ₂	290-30,600	+ 3,260
H ₂ S	5-1,600	+ 222
NH ₃	9.4-1,060	+ 194
CH ₄	13-1,447	+ 194
H ₂	11-218	+ 56
N ₂	6-638	+ 52

INFORMATION ON VENT GAS AND CONDENSATE

(a) Direct Contact Condenser

1. Condensate

Flow is 20 times amount of steam fed (temp. = 120°F). 20 - 80% of H₂S in steam may be contained in condensate.

2. Noncondensibles in vent gas

Flow is 0.54% of amount of steam fed (temp. = 120°F). Vent gas may contain 30% H₂O. 20 - 80% of H₂S in steam may be contained in vent gas.

(b) Nondirect Contact Condenser

1. Condensate

Flow equals incoming steam (temp. = 120°F). 10 - 20% of H₂S in steam may be contained in condensate.

2. Noncondensibles in vent gas

Flow is 0.5 - 1.0% of amount of steam fed. 80 - 90% of H_2S in steam may be contained in vent gas.

(c) By-Pass Venting

During power unit outages, the entire steam flow is vented to the atmosphere through a pressure relief valve. By-pass venting may occur for periods of from 30 min to 72 hr. A temporary pressure increase of 20 - 40 psig may occur when the steam flow to the turbine is interrupted.

OTHER CONSIDERATIONS

a. Corrosiveness--Steam is noncorrosive. Transmission lines are constructed of carbon steel. As the steam condenses, hydrogen sulfide partially oxidizes to sulfuric acid and corrosiveness increases greatly. Carbon steel, copper-based alloy, and cadmium are unsuitable in this area. Austenitic stainless steels, aluminum, or epoxy-fiber glass are satisfactory. Concrete requires a coal-tar epoxy coating to prevent sulfate deterioration.^{2/}

b. Concentration of "rock dust" particulates can be a factor in some wet treatment processes, and sludge removal capabilities may be required. Currently, there is no published data on rock dust particle size, composition, and concentration ranges at the powerhouses.

c. Concentration of CO_2 in vent gas is currently unknown. Distribution of CO_2 between cooling water and vent gas was apparently not used in sizing Stetford units for Geyser Units Nos. 13 - 15.

d. Powerhouse operation is automated. Surge capacity requirement for stable operation is currently not known.

APPENDIX C

FRACTION OF NONCONDENSIBLE GASES (NCG's) AT SALTON SEA
AND EAST MESA TEST FACILITIES

<u>Substance</u>	Salton Sea KGRA (mg/kg) ^{b,c/} <u>Range (average)</u>	East MESA KGRA (mg/kg) ^{c,d/} <u>Range (average)</u>
H ₂ S Steam Phase	1.3-3.9 (2.6)	0.11-1.7 (1.0)
Brine Phase	Not Available	0.07-0.33
NH ₃ Steam Phase	20-41 (35)	1.0-8.1 (5.1)
Brine Phase	394-400 ^{e/}	1.4-6.5
Hg Steam Phase	1.6 x 10 ⁻³	5.4 x 10 ⁻³
Brine Phase	0.02-0.11	< 10 ⁻³ -3 x 10 ⁻³
CO ₂ Steam Phase	1,600-4,700 (3,000)	800-2,630 (1,920)
CH ₄ Steam Phase	7.3-14 (10.4)	4-56 (30)
Rn Steam Phase	1.1 x 10 ³ pCu/kg	4.2 x 10 ² pCu/kg

a/ Source: Dr. Paul Gudiksen, Lawrence Livermore Laboratory, Private Communication, October 13, 1977.

b/ Determined at first stage flash, Niland test facility.

c/ Data from liquid phase reported as mg/liter.

d/ Determined at flash tank, Magna Electric Company's 10 MWe test facility (single flash).

e/ Based on two data points--for more data see "Imperial Valley Environmental Project: Quarterly Report," (Nyhlon and Anspaugh, Eds.), Lawrence Livermore Laboratory, UCID-17444-1, April 13, 1977.