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EVALUATION OF CONTROL NEEDS FOR HAZARDOUS AIR EMISSIONS (NON-H<sub>2</sub>S) FROM GEOTHERMAL PROCESSES

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ABSTRACT

Control technology needs for geothermal air emissions other than hydrogen sulfide have not been considered in federal geothermal research programs, nor to a great extent by private developers. This study (sponsored by the U.S. Environmental Protection Agency under EPA Contract 68-03-3025, Work Assignment SDM-04) was designed to identify the potential emission points, resulting concentrations in ambient air, and the impacts on the environment in the vicinity of geothermal operations.

This paper presents the results of the study in which ammonia, arsenic, benzene, boron, fluoride, hydrocarbons (other than benzene), mercury, radon, and sulfur oxide emission information was compiled for over 40 national and international geothermal development sites. The emission points within the geothermal processes, the compounds emitted, and the need for control technology are discussed.

INTRODUCTION

Geothermal energy is usually found in the form of heat contained in steam, hot water, or heated rock located beneath the earth's surface. The first two sources (steam and hot water) contain substances from the surrounding rocks within the geothermal reservoir. These substances include a variety of potentially toxic gases. To date, hydrogen sulfide (H<sub>2</sub>S) has attracted a considerable amount of attention, however, other gases are emitted from geothermal developments. These potential emissions (ammonia, arsenic, benzene, boron, fluorine, hydrocarbons, mercury, radon, and sulfur dioxide/sulfur peroxide) are of concern to the Environmental Control Panel of the Interagency Geothermal Coordinating Council. In 1981, the Panel recognized the need for characterizing these emissions and recommended that control strategies be developed for these emissions, if needed.

Monsanto Research Corporation (MRC), under EPA Contract 68-03-3025, Work Assignment SDM-04, was assigned the task of estimating potential loadings, resulting concentrations in air, and the expected environmental impact of non-H<sub>2</sub>S emissions resulting from the use of geothermal energy.

The objectives of this study were to:

1. Identify and quantify the potential non-H<sub>2</sub>S air emissions from a representative variety of geothermal sites;
2. Describe health and environmental effects of identified contaminants and the associated exposure levels, and
3. Describe control concepts and approaches that are or may be applicable to non-H<sub>2</sub>S emissions which need to be controlled.

PROJECT APPROACH

The three (3) objectives of the project were considered as separate tasks and were performed consecutively. Table 1 gives the specific activities associated with each task.

Task A

Task A involved gathering and evaluating all available published and unpublished information on geothermal site developments, engineering data on the resource, and gaseous emissions characterizations. The data gathering included U.S. and world-wide geothermal developments. The data were obtained from twelve computerized data bases, Department of Energy (DOE) and Environmental Protection Agency (EPA) reports, and geothermal energy developers and experts within DOE, EPA, and the academic community. Information on each development site was collected regarding site name, location, geothermal well information, present activity, past activity, planned future development, environmental controls in place or anticipated, process schematic, and gaseous emission points, characteristics and volumes. The 44 sites on which information was gathered in Task A are listed in Table 2.

Before initiating Task A, the EPA had directed MRC to pay particular attention to gaseous emissions of arsenic, boron, hydrocarbons, mercury, and radon. During the performance of Task A, ammonia, benzene, fluorine, sulfur dioxide, and sulfur peroxide were added, as the data indicated that these compounds were being emitted also.

TABLE 1. PROJECT ACTIVITIES BY TASK

<b>TASK A:</b> Identification and Quantification of Air Emissions	
A.1	Compilation of Existing Site Location Data
A.1.1	Determination of U.S. site locations, process types and current and past activities
A.1.2	Determination of major foreign sites and activities
A.2	Compilation of Existing Engineering Data by Process Type (including end use type)
A.3	Compilation of Existing Emission Data by Process Type
A.3.1	Determination of emission points for each process and end use type
A.3.2	Determination of volumetric (mass) flow rates and physical parameters at each emission point
A.3.3	Determination of emission composition
<b>TASK B:</b> Description of Potential Health and Environmental Effects of Emissions	
B.1	Evaluation of Effects of Emissions from Zero Concentration to Expected Concentration
B.1.1	Description of worker effects
B.1.2	Description of general population effects
B.1.3	Description of plant life effects
B.1.4	Description of animal life effects
B.2	Determination of Emission Fate Pathways
B.2.1	Description of emission decay and daughter molecules
B.2.2	Description of emission dispersion
B.2.3	Description of emission decomposition
B.2.4	Description of synergistic effects
B.3	Determination of Candidate Emission Sources Needing Control
<b>TASK C:</b> Description of Emission Control Concepts	
C.1	Evaluation of Emissions Control Options for Primary and Secondary Applications
C.1.1	Identification of industries with similar emission characteristics
C.1.2	Determination of the most feasible candidate industries
C.1.3	Identification and evaluation of the applicability of analogous control schemes
C.2	Integration of Control Unit Operations
C.2.1	Description of process
C.2.2	Description of chemical and physical reactions
C.2.3	Description of hazardous nature of treated gases
C.2.4	Description of hazardous residues generated by control
C.2.5	Estimation of capital and O&M costs
C.3	Recommendations for Research on New Treatment Methods
C.4	Recommendations for Further Development of Current Control Technology

**Task B**

In Task B, existing toxicological and environmental effects data and publications on geothermal energy toxic effects were evaluated for each of the above compounds to evaluate the potential impacts on human health and the environment. The pollutant concentrations determined in Task A were compared to concentration levels reported in the literature which had previously produced a toxic effect. In addition to toxic effects data, Threshold Limit Values (TLVs) and published emission standards were also used. The order of preference of health effects data to compare the emissions to was as follows:

- Published Standards (EPA)
- Proposed Standards (EPA)
- Other Standards (OSHA, etc)
- TLV Values
- Toxicity Data
- Industry Practices

TABLE 2. GEOTHERMAL SITES INVESTIGATED IN TASK A

<u>U.S. LOCATIONS</u>	
<u>Electric Power Production</u>	
Baca	Baca Ranch, New Mexico
Beowawe	Beowawe, Nevada
Brawley	Imperial County, CA
Fenton Hill	LaCueva, New Mexico
Geo Loop Exp Facility (GLEF)	Niland, CA
The Geysers	Sonoma & Lake Counties, CA
Heber	Heber, CA
Magma Max	East Mesa, CA
Mono-Long Valley	Casa Diablo, CA
Puna	Puna, Hawaii
Raft River	Burley, Idaho
Republic Geothermal	East Mesa, CA
Republic Geothermal	Westmorland, CA
Roosevelt Hot Springs	Milford, Utah
Salton Sea	Salton Sea, CA
<u>Industrial/Residential Uses</u>	
Boise	Boise, Idaho
Brady Hot Springs	Fernley, Nevada
Gulf Coast	Texas and Louisiana
Klamath Falls	Klamath Falls, Oregon
Madison Aquifer	Phillip, South Dakota
North Bonneville	Bonneville, Washington
Susanville	Susanville, CA
<u>FOREIGN LOCATIONS</u>	
<u>Electric Power Production</u>	
Ahuachapan	Ahuachapan, El Salvador
Cerro Prieto	Cerro Prieto, Mexico
China	China
El Tatio	El Tatio, Chile
Hatchobaru	Hatchobaru, Japan
Krafla	Krafla, Iceland
Larderello	Larderello, Italy
Matsukawa	Matsukawa, Japan
Monte Amiata	Monte Amiata, Italy
Ohaki	North Island, New Zealand
Otake	Otake, Japan
The Philippines	The Philippines
Svartsengi	Svartsengi, Iceland
Travale	Travale, Italy
Wairakei	Wairakei, New Zealand
<u>Industrial/Residential Uses</u>	
Carwynnen and Rosmanowas	Cornwall, England
Kodari	Nepal
Low Temperature Areas	Iceland
Mayangdi Khola	Nepal
Namafjall	Namafjall, Iceland
Rear Thermal Spring	Nepal
Surai Khola	Nepal

The rationale for this order is that currently enforceable emission standards will have the greatest impact on the selection of control technology.

At the end of Task B, the emission points which (based on their expected toxic effects) had a potential for negative environmental impact were to be defined and candidate emission sources needing control were to be listed.

**Task C**

Task C was originally designed to identify applicable control technology approaches and related costs for the control of non-H<sub>2</sub>S emissions. However, the results of Tasks A and B indicated that non-H<sub>2</sub>S emissions are either not of environmental significance or are controllable with currently available technology and that Task C was not necessary at this time (see conclusions).

**RESULTS****Task A**

The results of Task A on emission locations and their significance are as follows:

- Naturally occurring emissions from fumaroles and hot springs near geothermal developments, in some instances, dwarf emissions from the exploitation of geothermal energy. In those instances, control of non-H<sub>2</sub>S emissions from geothermal developments may have no significant impact on improving environmental quality.
  - Non-electrical uses of geothermal energy (projected to be up to 60,000 times greater users of geothermal energy than electrical users) are "closed loop" with fluid injection and little or no air emissions [1].
  - The emissions from well drilling, testing, clean-out, and stacking (venting of the well during power plant shutdown) are expected to be less than 1 percent of the overall process emissions because: (1) they do not occur often, (2) they are relatively short when they do occur, and (3) the emission rates are reduced by industry practices (throttling back flow from the well if venting is necessary for over two hours, redirection of steam to other users if venting is necessary for more than 24 hours). Thus these emissions should not require controls [2].
  - For liquid-dominated reservoirs using steam flashing for producing electricity, the major air emissions are non-condensable gases from the vent off of the direct contact steam condensers, cooling tower drift, and stripping of volatile compounds in the cooling tower (steam condensate is used as cooling tower make-up). If controls are necessary, these three sources should be considered. Emission control problems are similar for power generating plants using direct steam from vapor-dominated sources as those using steam from flashing of superheated water from liquid-dominated sources.
  - The binary cycle type of power plant, operating with superheated water, and an organic working fluid, should not, in principle have any gaseous emissions to the atmosphere, as the geothermal fluid is in a closed heat exchange system, including injection back to the geothermal reservoir.
- Arsenic concentrations range between 0.002 and 0.2 ppm with a majority of concentrations at 0.02 ppm,  $\pm 0.01$  ppm.
  - Benzene concentrations ranged between 45 ppm and 370 ppm; however benzene was reported to be present in the geothermal fluid at two locations. The existence of benzene in other geothermal fluids and its transfer to ambient air is unknown at this time.
  - Boron concentrations ranged between 2 ppm and 250 ppm with the majority of concentrations at 21 ppm,  $\pm 10$  ppm.
  - Fluorine concentrations ranged between 0 ppm and 0.2 ppm.
  - Hydrocarbon concentrations ranged between 4 ppm and 1,000 ppm with the majority of concentrations at 190 ppm,  $\pm 10$  ppm.
  - Mercury concentrations range from 0.001 ppb to 2 ppb with the majority of the concentrations at 0.005 ppb,  $\pm 0.004$  ppb.
  - Radon concentrations range between 10 pCi/L and 30,000 pCi/L with the majority of concentrations at 480 pCi/L,  $\pm 200$  pCi/L.
  - Sulfur dioxide/sulfur peroxide concentrations are below 50 ppm in nearly all cases.

#### TASK B

The results of Task B can be summarized as follows:

The following results were obtained for individual pollutant concentrations.

- Ammonia - Although ammonia has been measured in high concentrations in the steam at some sites, the literature published to date does not indicate that ammonia is reaching the atmosphere in significant quantities. The local effects of ammonia emissions should be considered as a part of individual development site pre-operational environmental impact assessments to determine if high concentrations will be emitted and what their impact will be.
  - Arsenic - Concentrations of arsenic in geothermal emissions are generally at least one order of magnitude below toxic threshold concentrations (0.2 mg/m<sup>3</sup> vs. 2.50 mg/m<sup>3</sup> for humans). Therefore, no human health problem is anticipated due to arsenic. However, the very low toxic threshold of honey bees (0.02-0.1  $\mu\text{g}/\text{m}^3$ ) may be of concern in some areas due to the importance of bees to the agricultural industry. The local effects of arsenic emissions on bees should be evaluated during the performance of pre-operational environmental impact assessments.
- Although CO<sub>2</sub> is the major constituent (over 90 percent) of the non-condensable gases, it should not be considered as a pollutant.
  - The concentrations of the nine pollutants investigated varied widely between reservoir locations.
  - Ammonia concentrations range between 0.001 ppm and 1,000 ppm, with a majority of concentrations at 100 ppm,  $\pm 20$  ppm.

- Benzene - In geothermal fluids where benzene is present, it may pose an occupational exposure problem. However, dispersion studies have indicated that benzene will rapidly disperse to levels below the toxic threshold at developments with a flat geography. This may not be the case in mountainous terrain. Benzene should then be investigated further as a part of pre-operational environmental impact assessments if it is present in the geothermal fluid or steam.
- Boron - Although boron air emissions produced toxic effects on vegetation at geothermal developments, these effects are attributed solely to boron contained in cooling tower drift. Cooling tower drift control is a well developed technology, and if implemented, boron air emissions from geothermal developments are not expected to present any hazard to man or the environment.
- Fluorine - Emissions of fluorine are very low (0.2 ppm max.) and are not expected to present any problems to man or the environment with the possible exception of honey bees (toxic threshold of 4 ppm). Although concentrations are expected to be below the threshold, as with arsenic, fluorine effects on bees should be further investigated during the the performance of pre-operational environmental impact assessments.
- Hydrocarbons (other than benzene) - The generally non-toxic nature of C<sub>1</sub> through C<sub>8</sub> emitted hydrocarbons (20,000 ppm toxic threshold), their low level in geothermal emissions, and their rapid atmospheric degradation, indicate that emission controls for these compounds will not be necessary.
- Mercury - The very low concentrations of mercury measured to date at the majority of sites (0.005 ppb), and the lack of any evidence to the contrary, indicate that mercury emissions from geothermal developments are not of environmental significance (this level is 10,000 times lower than observed toxic thresholds).
- Radon - The levels of radon emitted from the majority of sites (480 pCi/L) are similar to natural emissions of radon. Radon is not expected to pose an environmental hazard from geothermal developments. However, the tendency for radiation to amass inside equipment may require some type of maintenance worker protection.
- Sulfur Dioxide/Sulfur Peroxide - Since all new U.S. geothermal developments are expected to employ some type of hydrogen sulfide (H<sub>2</sub>S) control technology, sulfur dioxide and sulfur peroxide are not expected to present an environmental problem because they will be controlled by H<sub>2</sub>S control systems, such as Stretford units, currently planned for the industry.

#### CONCLUSIONS OF THE STUDY

The results of this study indicate that most non-H<sub>2</sub>S emissions are either not of environmental significance or are controllable with currently available technologies. Emission of ammonia, hydrocarbons (other than benzene), mercury, radon, sulfur dioxide, and sulfur peroxide are not viewed as significant problems, while arsenic and fluorine may be a problem where honey bees are an important element in the agricultural industry. Benzene, if present in the fluid may pose an occupational exposure problem. These should be investigated further during the performance of pre-operational environmental impact assessments. Emissions of boron, while significant, can be readily controlled by currently available technology such as cooling tower demisters.

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#### REFERENCES

1. Geothermal Energy Prospects for the Next 50 Years, EPRI Special Report, ER-611-SR, February 1978.
2. Personal communication to S. C. Wilson by M. Scheve, U.S. Department of Energy, November 18, 1981.