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THE HYDROGEN SULFIDE EMISSIONS ABATEMENT PROGRAM AT THE GEYSERS GEOTHERMAL POWER PLANT

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This paper describes the scope of the hydrogen sulfide (H_2S) abatement program at The Geysers Geothermal Power Plant and the measures currently under way to reduce these emissions. The Geysers steam averages 223 ppm H₂S by weight and after passing through the turbines leaves the plant both through the gas ejector system and by air-stripping in the cooling towers. The sulfide dissolved in the cooling water is controlled by the use of an oxidation catalyst such as an iron salt. The H₂S in the low Btu ejector off gases may be burned to sulfur dioxide and scrubbed directly into the circulating water and reinjected into the steam field with the excess condensate. Details are included concerning the disposal of the impure sulfur, design requirements for retrofitting existing plants and modified plant operating procedures. Discussion of future research aimed at improving the H₂S abatement system is also included.

I. INTRODUCTION

While geothermal energy has been developed for the production of electric power in several locations throughout the world, the only commercial development in operation in the United States is at The Geysers, about 80 miles north of San Francisco. From Pacific Gas and Electric Company's initial 12 megawatt (MW) unit, which commenced operation in 1960, nine additional units have been constructed. The total capacity is now 396 MW, which makes The Geysers the largest geothermal electric power plant in the world. Design and construction presently under way will increase net output to about 900 MW by the end of 1977. There are plans for continuing expansion as steam reserves are proven and developed. The facilities and operations at The Geysers Power Plant have been well described previously (Refs. 1 through 4). Thus, only those aspects pertinent to the hydrogen sulfide emissions abatement program will be discussed herein.

In contrast to most of the world's geothermal resources, the wells at The Geysers produce slightly superheated steam. This steam contains small amounts, usually less than 1 percent by weight, of noncondensible gases, mostly carbon dioxide. The ranges of concentrations of the noncondensible gases measured at The Geysers are presented in Table 1. These gases are natural components of the atmosphere, and their concentrations that we have measured in ambient air at The Geysers are not considered harmful. However, hydrogen sulfide (H₂S) is an air pollutant that P G and E, or any other user of geothermal steam, is required to control under regulations of the State of California Air Resources Board (ARB) and also the local air pollution control districts (APCD). The APCD regulations applicable at The Geysers generally state that no single emission source shall exceed 1000 parts per million by volume (ppm_v) of any sulfur compound expressed as sulfur dioxide (SO₂). The ARB H₂S standard is 0.030 ppm_v for ambient air. Since this concentration is approximately the odor threshold for H₂S, as a rule of thumb one can say that if one can smell H₂S, the ARB standard is being exceeded.

The generating units at The Geysers use slightly superheated steam at about 100 psig, and after passage through the turbine, the low pressure steam is condensed in direct contact condensers operating at 3-5 inches of mercury, absolute. Figure 1, the power cycle diagram for the proposed Unit 15, is typical of the units of The Geysers. Most of the noncondensible gases in the steam are continuously removed from the condenser by the two-stage gas ejector system and are vented to the atmosphere through stacks from 60-85 feet above ground level, depending on the unit. However, since the steam contacts the cooling waters directly in the condenser, about two-thirds of the H₂S dissolves in the cooling waters and is then carried to the cooling tower.

The cooling waters, in passing through the cooling tower, are partially air-stripped, so the tower exhaust air contains on the order of one ppm_v H₂S. Some of the H₂S (on the order of 30 percent) is naturally oxidized to elemental sulfur in the cooling tower and eventually returns to the steam field with the surplus condensate. Though the emissions from the cooling towers are well within permissible levels, it is still desirable to minimize these emissions from the power generating units to reduce the H₂S concentrations in the ambient air outside of The Geysers Power Plant. Thus, P G and E's H₂S emissions abatement program included the releases from both the gas ejector stacks and the cooling towers.

II. DESCRIPTION OF THE ABATEMENT PROGRAM

P G and E began investigating methods to control the H₂S emission from The Geysers Power Plant in 1971. These investigations have included literature searches, parametric evaluations, bench-scale testing (both in the P G and E laboratories at the Department of Engineering Research and at The Geysers), and, at the present time, unit-scale testing at Units 1, 2, and 4.

A. Cooling Tower Emissions

The bench-scale testing at The Geysers investigated four methods to control the emissions from the cooling towers by reacting the H₂S to elemental sulfur (S⁰) in the water phase before it could be air-stripped. These were:

(1) Direct injection of SO₂ into the cooling waters to oxidize the H_2S to S^0 by the Claus reaction

$$2H_2S + SO_2 \rightarrow 3S^0 + 2H_2O$$

- (2) Simultaneous injection of both SO₂ and air.
- (3) Addition of a metal catalyst, iron, to the cooling waters to promote direct oxidation of the H_2S to S^0 by the oxygen dissolved into the circulating cooling waters in the cooling towers:

$$2H_2S + O_2 \rightarrow 2S^0 + 2H_2O$$

(4) Addition of Cataban, a chelated iron compound manufactured by the Rhodia Corporation, to catalyze the direct oxidation of H₂S by the dissolved oxygen.

All four of these methods reduced the H₂S emissions from the bench-scale test apparatus. The third approach, addition of a metal catalyst to the circulating cooling waters, was chosen for unit-scale testing, since this method appears to be best adapted for operations at The Geysers Power Plant. The majority of the tests of methods to control cooling tower H₂S emissions are being made at Units 1 and 2. These two units, of nominal generating capacities of 12.5 and 14 MW, are the oldest and smallest of all the units installed at The Geysers. However, their design and layout are similar to all subsequent units in operation. This permits us to scale up to any desired size with a high degree of confidence. A program to study corrosion by the metal-containing condensate is also underway at Unit 1 (Ref. 5).

Several different metals will catalyze the oxidation of H_2S in the water phase (Ref. 6). Three of these were experimentally investigated at The Geysers: iron, nickel, and copper; copper was the least effective of the three. It was found that iron concentrations of approximately 30 mg/l and nickel concentrations of 1.5 to 2 mg/l could reduce the total H_2S emissions from the cooling towers by 90 percent or more. The choice between these two oxidation catalysts is now a matter of relative economics and their effects, if any, on the long-term operation of the units. Preliminary results from the longterm testing of the iron oxidation catalyst at Unit 1 have shown that there is a definite increase in the corrosion rate for this unit. The overall effect that this may have on equipment service life is still under evaluation. Additional corrosion rate monitoring equipment is being installed to expedite the testing of alternate catalysts and the effectiveness of corrosion inhibitors.

The use of the metal catalysts markedly increases the suspended solid content of the circulating waters, both from the catalyst itself and the elemental sulfur which is produced. Work has been done on minimizing the solids buildup in the cooling tower basin and in removing these solids from the excess condensate that is returned to the steam field. The method of choice at this time is rapid sand filtration. Pilot tests have shown that sand filtration can remove more than 90 percent of the suspended solids and perform consistently with little attention, an important factor in The Geysers' operation.

B. Gas Ejector Emissions

Two methods to control the emissions of the H₂S in the noncondensible gases vented from the gas ejector system are still under evaluation. In one method, the H_2S is burned to SO_2 which is then scrubbed into the cooling waters to maintain the SO₂ concentration in the products of combustion that would be vented to the atmosphere below the 1000 ppm_v regulation. The noncondensible gases will burn since they contain enough methane and hydrogen to sustain combustion (150-200 Btu/cu ft). The SO₂ scrubbed into the circulating waters eventually either is injected into the steam field or it can be neutralized with lime if the waters are too acidic for the reinjection well casing or cooling water system components. The marginal flammability and pulsating nature of the gases from the ejectors posed some challenging engineering designs. However, a full-scale burner/scrubber system has been designed for Unit 4 (26 MW). An oxidation catalyst feeder system and a sand filtration system have also been engineered for the tests at Unit 4, incorporating all the design features to date, and construction has started. The data obtained at this unit will be used in the design of a full-scale abatement system for Unit 11 (106 MW).

In the other method, H_2S emissions from the ejectors are controlled by scrubbing the noncondensible gases with a water solution containing a metal catalyst so that the H_2S is dissolved and oxidized to S^0 . Tests of the H_2S scrubbing method will also be performed at Units 1 and 2 this year.

C. Sulfur Disposal

The solids collected in the rapid sand filter include elemental sulfur with some metal catalyst and fine rock dust carried up the well by the steam. Studies show that it is not economical to refine the recovered sulfur to commercial purity; the cost of the refined sulfur from The Geysers would be higher than that of byproduct sulfur from natural gas desulfurization plants. To date we have not produced large enough quantities of the solids to evaluate their possible direct application to soils or conversion to sulfuric acid for fertilizers. Other practical applications will also be considered. Until a practical application for these solids can be developed, it is planned to dispose of the solids in a landfill. P G and E has retained a consulting firm to evaluate the feasibility of constructing a landfill disposal site at The Geysers for these solids. Should it be necessary to neutralize the cooling waters that have been used to scrub out the SO₂ from burning H₂S in the noncondensibles, the calcium sulfate/ sulfite formed would also be disposed of in the landfill.

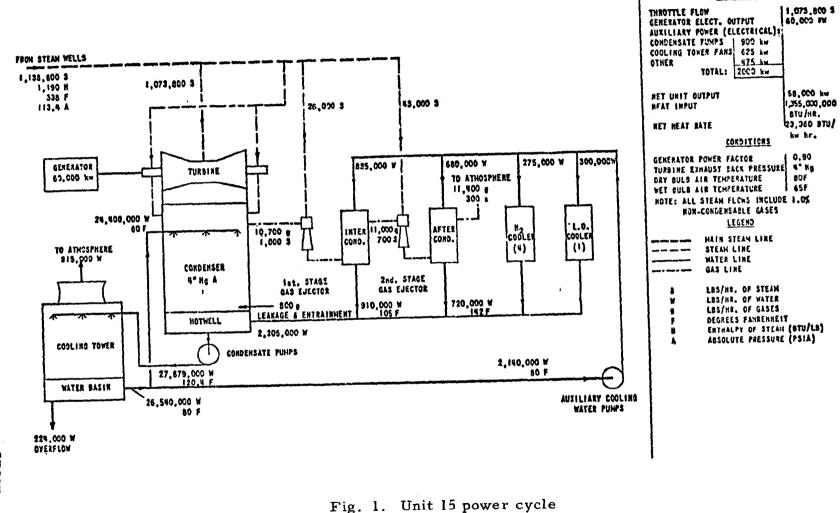
III. CONCLUSIONS

We expect that the control methods described herein will reduce the H₂S emissions from a unit to permissible levels and will control them so that they alone will not exceed the ARB ambient air quality standard for H₂S at ground level beyond a few hundred feet from a unit. In anticipation of a period of successful test operation this year, a program for installing H₂S control equipment on ten existing units, as well as future units, has been proposed to regulatory agencies.

It should be noted that the control methods described above were selected on the basis of our existing knowledge and experience; they are not necessarily the optimum that could ultimately be developed for use at The Geysers. There is considerable effort in progress in the world today on the development of processes and equipment to control emissions of sulfur compounds from industrial equipment. Thus, we anticipate that further research will be performed on H₂S emissions control at The Geysers. One area of interest that we now see is the addition of nonmetallic catalysts to the circulating cooling waters. A second area of interest is the removal of the H₂S from the steam upstream of the turbine. However, the control methods described herein should provide the necessary H₂S emissions control for further development of this important, nonfossil-fueled power generating resource.

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