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COST EFFECTIVE AIR POLLUTION CONTROL
FOR GEOTHERMAL POWERPLANTS

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March 1985



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**Cost Effective Air Pollution Control
for Geothermal Powerplants**

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COST EFFECTIVE AIR POLLUTION CONTROL FOR GEOTHERMAL POWERPLANTS

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ABSTRACT

Air pollution control technology developed and demonstrated at The Geysers by the Pacific Gas and Electric Company includes two different, but equally effective methods to reduce the emissions of hydrogen sulfide from geothermal power plants. These technologies may be used in other geothermal areas as well. Cost saving modifications and adaptations needed to apply these technologies in other geothermal areas with different steam composition are described. Cost estimates are presented for some typical cases.

If a surface condenser gives poor H_2S partitioning with ammonia rich steam, neutralizing the ammonia with SO_2 is a cost effective alternative to secondary abatement with hydrogen peroxide. Nickel is a cost effective alternative to $FeHEDTA$ when an oxidation catalyst is added to the cooling water of a power plant equipped with a contact condenser.

INTRODUCTION

The very large size of The Geysers geothermal field and its proximity to populated areas forced the air pollution problem to be addressed early on. Of necessity, the Pacific Gas and Electric Company and other companies involved with The Geysers developed, tested, and implemented the technology needed to control emissions of hydrogen sulfide from geothermal power plants.

It is commonly presumed that The Geysers is unique because superheated steam comes out of the wells, not hot brine. In fact, this distinction is largely irrelevant to the design and operation of a steam cycle geothermal power plant. Consequently, much of the powerplant technology developed at The Geysers may be effectively applied in other geothermal areas.

In regard to hydrogen sulfide content and total noncondensable gases, The Geysers resembles many other geothermal areas. The Geysers steam does differ from most other geothermal steam in that it contains more ammonia and boric acid. The concentration of ammonia is an important distinction. Elsewhere (e.g. Cerro Prieto) geothermal steam also contains ammonia, but less relative to H_2S than at The Geysers. Some geothermal steam contains very little ammonia. Historically, the ammonia in The Geysers steam has profoundly influenced the evolution of air pollution abatement technology.

I will outline the two major H_2S abatement technologies developed at The Geysers, and describe simple improvements that decrease chemical costs and qualify these technologies for service in other geothermal fields. A broader review of the subject is presented in Ref. [1].

SURFACE CONDENSER AND STRETTFORD UNIT

The first effective and economically attractive technology for reducing hydrogen sulfide emissions at The Geysers combines a surface condenser with a Stretford Unit. Because the ratio of liquid to vapor in a surface condenser is relatively small, most of the H_2S that enters the plant with the steam leaves the condenser with the condenser vent gas. The Stretford Unit scrubs the H_2S from the vent gas and converts it to elemental sulfur. If desired, the Stretford Unit can be configured to produce sulfur of marketable quality.

Ammonia controls H_2S partitioning. I have used computer modelling to interpret and predict H_2S partitioning and condensate chemistry in a variety of geothermal condensers [2, 3, 4, 5]. Once a model of a particular condenser has been formulated and reconciled with field data, the model may be used to predict accurately the effect of changing steam composition or added chemicals.

I found that the mole ratio of $NH_3:H_2S$ in the steam is the main factor which determines H_2S partitioning in a surface condenser. Ammonia increases the solubility of hydrogen sulfide in the condensate by reacting with it as a base:



If there is no ammonia in the steam, a properly vented surface condenser will direct over 99% of the H_2S in the steam to the vent gas [2, 3]. In this case, emissions of hydrogen sulfide from the cooling tower will be negligible, and practically the only solutes in the condensate will be carbon dioxide and boric acid. A few ppm ammonia in the steam (the case in many geothermal areas) will not significantly increase the amount of H_2S that dissolves in the condensate. With low ammonia steam a surface condenser and Stretford Unit should provide 98+% H_2S emission abatement.

In the case of The Geysers Unit 15, the mole ratio $NH_3:H_2S$ is about 1, a typical value for The Geysers. About 20% of the H_2S dissolves in the condensate and may be emitted to the atmosphere [2]. Similar partitioning will be obtained from other well-vented condensers of conservative design, if supplied with steam of a similar composition. The condenser design that is common to Units 16 and beyond is an example [3].

Secondary abatement with hydrogen peroxide. Because ammonia degrades H_2S partitioning to this degree, the surface condenser - Stretford Unit technology is directly applicable only with low ammonia steam. The ammonia-rich steam at The Geysers necessitates *secondary abatement* to destroy the H_2S in the condensate before the condensate reaches the cooling tower.

Hydrogen peroxide is added to surface condenser condensate at The Geysers to oxidize the H_2S [6]. A small amount of iron hydroxyacetate is added to catalyze the reaction. With the

In a contact condenser the steam mixes with cooling water and condenses, and there is no real distinction between cooling water and condensate.

In 1980 PG&E tested iron chelated with N-hydroxy EDTA as a catalyst (*FeHEDTA*). Adding *FeHEDTA* to the cooling water stopped H_2S emissions from the cooling tower, but produced colloidal sulfur.

Sulfur dioxide eliminates colloidal sulfur. Nickel ion is the most potent catalyst for this application. Leon Tsao and I studied the reaction catalyzed by nickel. In 1980, we found that adding sodium sulfite to "synthetic cooling water" in the laboratory completely suppressed the formation of colloidal sulfur [8, 9].

The condenser vent gas at The Geysers and most other geothermal fields is weakly flammable. PG&E installed a burner-scrubber at Geysers Unit 1 in mid-1981. This device burns the condenser vent-gas, and the SO_2 in the burner exhaust is transferred to the cooling water by adsorption in a side stream of water. There reaction with ammonia converts SO_2 to sulfite ion. The whole system is schematized in Figure 1, which depicts the computer model that represents Geysers Unit 1 [4].

PG&E demonstrated use of SO_2 to suppress colloidal sulfur at Geysers Unit 1 in October 1981, with *FeHEDTA* for catalyst. This process is now routinely used in several Units at The Geysers [10], and has been patented by the Dow Chemical Company [11]. The *FeHEDTA* - SO_2 process does not aggravate corrosion problems [12].

The required catalyst concentration varies from Unit to Unit. Typically, enough catalyst is added to maintain 30 ppm of iron chelated with *HEDTA* in the cooling water, and 98+% H_2S abatement is achieved. Laboratory work indicates that iron citrate is an equally strong catalyst [9, Chapter 4]. Other iron chelates are less effective.

If the condenser vent gas has insufficient fuel value to burn by itself, propane may be added to support the flame. (At The Geysers, a propane flare is used as a pilot light only, and is extinguished once the vent gas is burning.) Alternatively, a flameless oxidation process that utilizes a solid catalyst may be substituted for the burner part of the burner-scrubber [13].

Nickel is the cheapest catalyst. Nickel ion is a much more powerful catalyst than *FeHEDTA*. Our kinetic data indicate that 0.6 ppm *Ni* in the cooling water will reduce H_2S emissions by 98% [8, 9]. No feed system for a solution of the catalyst would be needed, because the low dosage rate required could handily be provided by electrolytic dissolution of a nickel anode.

The combination of nickel and SO_2 has not been field tested because of lingering concerns about the toxicity of nickel. Because the required nickel concentration is so low, the protective measures already in force to mitigate the hazards associated with arsenic and mercury naturally present in the steam would effectively mitigate the nickel hazard as well.

The *Ni* - SO_2 process is in the public domain. While particular designs for a burner-scrubber may be proprietary, the basic idea of a burner-scrubber is also in the public domain.

Reaction mechanism. We have proposed a mechanism for the nickel catalyzed reaction which is consistent with most of our data [8, 9]. The reaction catalyzed by chelated iron has not been studied in this detail, but probably is much the same. This mechanism is summarized in Table 1.

The condenser steam strips all dissolved oxygen from the cooling water. The oxidation reaction proper (7) occurs between condenser and cooling tower where the cooling water is anoxic, and molecular oxygen plays no role in it. Oxygen containing polysulfido- radical ions actually oxidize the H_2S . The oxidizing agent is regenerated by reaction with atmospheric oxygen in the cooling tower (9). The role of the catalyst is limited to initiating free radical chains (not shown). The catalyst is not directly involved in the oxidation reaction. Therefore, there is no minimum concentration of catalyst needed to completely destroy the H_2S . In particular, 0.6 ppm = 10 μM *Ni* will reduce 100 μM H_2S to 2 μM , given 90 seconds reaction time.

Table 1. Reaction mechanism.

Combustion in the burner-scrubber:



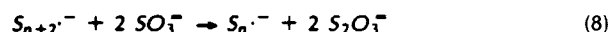
SO_2 converted to sulfite in the condensate:



Oxidation of H_2S in condensate:



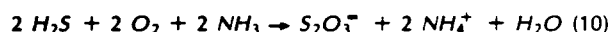
Zero valent sulfur converted to thiosulfate:



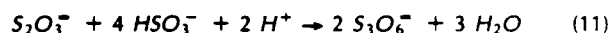
Oxidizing agent regenerated in cooling tower:



Net reaction:



Excess sulfite produces trithionate:



and sulfate:



The rate of H_2S oxidation varies as the square root of catalyst concentration, and catalyst concentration may be traded-off for reaction time.

If cooling water pH drops below about 5.5, the polysulfido-radical ions will decompose, and the oxidation reaction will stop. This consideration imposes a strict lower limit on cooling water pH.

Ammonia limits pH drop. At The Geysers, enough ammonia is present in the steam to neutralize the thiosulfuric acid (and other sulfur acids) produced by the reactions in Table 1. The amount of ammonia present also controls the partitioning of H_2S between the burner-scrubber and the cooling water. When cooling water pH is near 7 the partitioning is near 50:50, and the ratio of H_2S burned to H_2S oxidized in the condensate = 1. If cooling water pH drops and more H_2S goes to the burner-scrubber, more SO_2 will be produced than is needed to consume the colloidal sulfur. Within limits, this shift is acceptable, because most of the excess SO_2 will react with thiosulfate to produce trithionate (11). In practice, cooling water pH is typically 6.5 and about 60% of the total H_2S goes to the burner-scrubber, giving a mole ratio $SO_2:H_2S = 1.5$ in the cooling water.

All told, the mole ratio $NH_3:H_2S = 1$ provides adequate pH control. In fact, approximately this much ammonia is present in the steam supply of most of Geysers Units 1 to 12, and the resulting cooling water pH stays above 6 without adding base.

With low ammonia steam, base would have to be added to neutralize the acids produced and maintain acceptable cooling water pH. Sodium hydroxide has traditionally been used in similar situations at The Geysers, but ammonia would be much cheaper.

Table 2. Common basis for cost estimates.

Steam composition:

Gas	High NH_3 steam (ppmw)	mg-moles per kg	Low NH_3 steam (ppmw)
H_2S	163	4.8	163
NH_3	88	5.2	0
CO_2	1530	35	1530
H_2	38	19	38
CH_4	118	7.4	118
N_2	60	2.1	60

Steam supply = 1 million lbs/hour

Net power = 53 MW

Capacity factor = 90%

Overall H_2S abatement is 98% or better in all cases.

Chemical prices:

50% H_2O_2	\$0.32/lb
100% NH_3	\$200/ton
FeHEDTA sol'n	\$5/gallon
Ni anodes	\$3.50/lb

The specific gravity of the FeHEDTA solution is 11.5 lbs/gallon, and the iron content is 4.5w%.

COST ESTIMATES

I have estimated the savings that may be expected from the process modifications described in this paper. The common basis for my cost estimates is summarized in Table 2.

While I have been unable to estimate the costs associated with operating a geothermal Stretford Unit, these costs probably exceed 1.5 mil/kw-hr. For a surface condenser equipped Unit, I have estimated only the cost of secondary abatement, which is summarized in Table 3. Case (1) represents current practice at The Geysers. The cost of secondary abatement will be approximately proportional to the concentration of H_2S in the condensate.

I did receive approximate cost figures for putting in and operating a burner-scrubber, and I was able to estimate the complete cost of H_2S abatement with a contact condenser. These cost estimates are summarized in Table 4. Cases (4) and (5) represent current practice at The Geysers.

The cost of primary abatement with H_2O_2 (Case 4) is approximately proportional to the concentration of H_2S in the steam. The concentration of H_2S has little effect upon abatement cost in Cases (5) and (6). In Case (7), the amount of ammonia required will vary in proportion to the concentration of H_2S of the steam; other costs do not depend on H_2S concentration.

CONCLUSIONS

Contact condensers are by no means obsolete in geothermal service. The combination of a soluble catalyst and SO_2 allows excellent H_2S emission abatement to be achieved. These processes offer a viable alternative to the combination of surface condenser and Stretford Unit currently favored at The Geysers.

Table 3. Costs of secondary abatement.

Case (1):

High NH_3 steam.

Surface condenser is equivalent to Geysers Unit 15.

19% of total H_2S dissolves in the condensate.

Secondary abatement with H_2O_2 .

Annual cost of H_2O_2 = \$313,000/year = 0.75 mil/kw-hr

Case (2):

Surface condenser.

Low ammonia steam.

No secondary abatement is needed.

Case (3):

Surface condenser.

High ammonia steam.

Part of Stretford sulfur is burned to produce SO_2 .

No additional chemicals are required.

Notes to Table 3.

Case (1). Actual costs of secondary abatement will be slightly higher than this, because I have ignored the cost of the catalyst and costs associated with the equipment for storing and metering the chemicals.

Case (3). The cost of the sulfur burner has been ignored, but will probably be smaller than the costs associated with storing and metering H_2O_2 in Case (1).

The Ni - SO_2 process appears to be the least expensive of all the H_2S abatement processes that have been considered for The Geysers. This cost advantage must be balanced against the occupational health hazard associated with nickel. Because the concentrations of H_2S and ammonia in the steam have little effect upon total abatement cost, this conclusion will hold true over a broad range of steam compositions. The only restriction is that the condenser vent gas must be flammable, if a burner-scrubber is to be used. Otherwise, supplementary fuel or a catalytic oxidation process will be required, increasing abatement cost.

In the case of a surface condenser operating with high ammonia steam, H_2S partitioning can always be improved by adding SO_2 , to the point that secondary abatement can be dispensed with. With low ammonia steam, H_2S emissions can be practically eliminated without secondary abatement or SO_2 .

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Table 4. Abatement costs with a contact condenser.

Case (4):

Either steam composition

Abatement with H_2O_2 and caustic

Cost of H_2O_2 = \$1,646,000/year = 3.9 mil/kw-hr

Case (5):

High ammonia steam.

FeHEDTA - SO_2 process is used.

Condenser vent gas is burned in a burner-scrubber.

Six cycles of concentration in the cooling water.

30 ppm chelated iron maintained in the cooling water.

Interest rate = 18%

Amortization period = 15 years

Licensing fees are not included.

Approximate capital invested (\$1,000's):

Engineering and fabrication	1200
Shipping, site prep, installation	100
Total capital invested	1300

Annual operating costs (\$1,000's):

Capital recovery	260
Taxes and insurance	130
Labor and maintenance	100
Cost of FeHEDTA	418
Power and misc.	50

Total abatement cost = \$958,000/year = 2.3 mil/kw-hr

Case (6):

High ammonia steam.

Ni - SO_2 process is used.

0.6 ppm Ni maintained in the cooling water.

No licensing fees.

All else as in Case (5).

Operating costs:

Cost of nickel catalyst = \$5,500/year = 0.013 mil/kw-hr

All other costs as in Case (5).

Total abatement cost = \$545,500/year = 1.3 mil/kw-hr

Case (7):

Low ammonia steam.

Ni - SO_2 process is used.

Ammonia added to control cooling water pH.

Ammonia feed rate = 88 lbs/hour

Operating costs:

Cost of ammonia = \$69,400/year = 0.17 mil/kw-hr

Other costs as in Case (6).

Total abatement cost = \$614,900/year = 1.5 mil/kw-hr

Notes to Table (4):

Case (4). Actual process cost may exceed this estimate, because costs associated with caustic, catalyst, and chemical storage and metering equipment have been ignored.

Case (5). Actual process costs may be higher than this, because possible costs of licensing the technology have been ignored. The capital investment and cost of capital were estimated and provided to me by M.J. Sampson of the Davy McKee Corporation, San Ramon, California.

Case (6). I have assumed that one-half of the nickel purchased is wasted by incomplete utilization of the anodes, and possible precipitation of nickel compounds from the cooling water. The costs associated with the electrolytic nickel feed system have been ignored, but will certainly be smaller than the cost to store and meter FeHEDTA in Case (5).

Case (7). Actual process cost will be slightly higher, as I have ignored the costs associated with storing and metering the ammonia.

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