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**SITE SPECIFIC NEEDS AFFECT PROCESS CHOICES
FOR H₂S ABATEMENT IN GEOTHERMAL POWER PLANTS**

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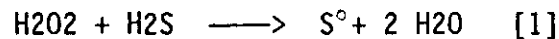
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The abatement of hydrogen sulfide in geothermal power plants has undergone considerable change in recent years. More stringent regulatory requirements for H₂S abatement have increased costs. This paper will review the history of abatement technology, discuss the effect of operating conditions on the requirements for abatement processes, review process choices for both primary and secondary abatement, and provide two case examples of the economics of the Dow Chemical Company's GAS/SPEC RT-2 technology and the SulFerox* Technology (1,2,3).

Early Abatement Methods

When the maintenance of air quality became a problem in the early days of the geothermal power industry, effective technology was not available to abate H₂S in the condensate. To compensate, acceptable practice was to abate H₂S in the non-condensable gas using the Stretford process. To achieve maximum overall H₂S removal without condensate treatment, condenser design shifted to surface condensers which increase the H₂S partition to the non-condensable gas. Even so, H₂S emissions from the condensate continued to be a problem for some sites, and finally, technology to treat the condensate emerged.

An early method for secondary abatement of H₂S in the condensate revolved around the reaction of hydrogen peroxide and H₂S.



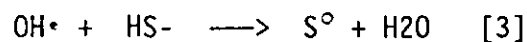
The H₂S is oxidized irreversibly to a variety of sulfur species.

Improvement With Peroxide

Improvements were made in secondary abatement technology by using ferrous sulfate in conjunction with hydrogen peroxide. Divalent iron, Fe⁺², reacts with peroxide to generate a hydroxyl radical, HO•; by the following reaction:



Small amounts of the Fe⁺² substantially accelerate the peroxide decomposition. The hydroxyl radical reacts with the ionized H₂S the condensate. The rate of the overall reaction is reasonably fast.



* Service Mark of Shell Oil

There are draw-backs to this technology. First, chemical costs are high. The hydrogen peroxide abatement reaction, the reaction between sulfide and the hydroxyl radical, is not specific. The hydroxyl radical will also oxidize elemental sulfur to a variety of sulfur compounds. In addition, a portion of the peroxide will decompose to water and oxygen. Iron consumption is also high because the iron catalyst precipitates as both the iron sulfate and the iron sulfide.



Secondly, the iron sulfate/peroxide process results in process problems, the precipitation of ferrous sulfide, ferrous sulfate, and elemental sulfur. These compounds tend to settle in the cooling towers basins of the geothermal power plant which require shutting down the tower periodically for cleaning. The cleaning process usually is manual, involving the use of shovels to do the job. Furthermore, the iron salts will stain the equipment brown or red.

The iron sulfate/peroxide technology was used commercially at the Geysers after 1974. The level of H₂S abatement achievable with the iron/hydrogen peroxide process was an improvement, but still did not provide the air quality desired. To get that last bit of H₂S requires a very large amount of chemical addition which was extremely expensive and generated tremendous amounts of solids in the cooling tower.

The Development of Chelated Iron Technology (4,5,6)

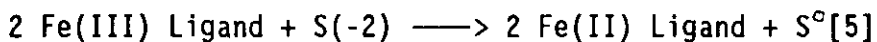
In the burst of growth of geothermal power, there were a number of cooling towers built with a corresponding increase in the pounds of H₂S emitted. In the late 70's it became apparent that the volume of H₂S being released from the Geysers must be curtailed not only to build new plants but to allow the plants that were running to continue. Retrofitting of running plants to better abatement technology would be required.

In searching for suitable alternate processes, Pacific Gas and Electric Company (PG&E) evaluated many primary and secondary abatement technologies. During this period, Dow Chemical talked to PG&E about adding a chelate compound to keep the iron in solution. Preventing iron precipitation would substantially reduce catalyst cost. In fact, it was thought a system could be developed that did not require any hydrogen peroxide. Preliminary tests were conducted. Dow and PG&E conducted a research field trial in January, 1980, which abated 90+% of the H₂S. However, all the sulfur appeared as elemental sulfur in the cooling tower. Since PG&E felt that the solid sulfur problem was unacceptable, Dow and PG&E continued to work together. The low solids technology was developed from this co-operative effort. This technology converts H₂S in the non-condensable gas to sodium sulfite which subsequently is added to the condensate to solubilize the sulfur produced by the chelated iron.

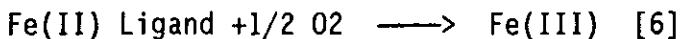
At this time, it appears that the old ferrous sulfate/hydrogen peroxide process is no longer being used commercially. There continues to be residual confusion in the geothermal industry about the role of iron in the various processes. Some are not convinced that the solubility problems in the earlier processes have been conquered.

From the research program of PG&E and Dow, two technologies actually evolved. The first technology (7) was an improvement of the hydrogen peroxide process. The improvement was the addition of a chelating agent to insure the solubility of the iron catalyst. This chelating agent or ligand works to prevent the iron precipitation reactions that occur with ferrous sulfate as the catalytic reagent. Furthermore, the chelated iron is maintained entirely in an ionic form which accelerates the peroxide decomposition reaction. Thus less chelated iron is required to maintain an identical reaction rate. Different chelating agents have different iron solubilizing strengths, and change the speed of the iron reactions. This advancement was patented by PG&E (7) and is commonly used in the geothermal industry.

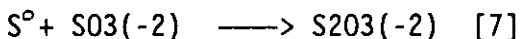
The second technology (8) was the low solids process currently marketed by Dow. This technology uses a ligand to solubilize the iron, but it uses a completely different chemical reaction to abate H₂S. The iron reacts directly with the hydrogen sulfide to form elemental sulfur.



This reaction is spontaneous and specific. The reoxidation of the iron in the cooling tower allows the reuse of the reagent.



These reactions produce sulfur in the cooling tower water, just as the other technologies discussed. However, use of the iron as a direct reduction agent for sulfur allows the use of an additional oxidant for elemental sulfur. The most effective oxidant used to date is sodium or ammonium sulfite.



The reaction product is thiosulfate which is stable, and water soluble. This material is compatible with the myriad of other components in the geothermal condensate of the plants. The sulfite is made in place by burning noncondensable gas and scrubbing the SO₂ formed. This allows the simultaneous abatement of both noncondensable gas and the condensate without solid waste being generated or processed.

Both technologies use iron chelate. In the improved hydrogen peroxide process, the iron chelate is merely a catalyst to decompose the hydrogen peroxide. In the low solids process, the iron is present as ferric (Fe^{+3}), and actually oxidizes the H_2S to elemental sulfur directly.

Both processes are currently installed at the Geysers geothermal power plants. Many units at the Geysers have switched from the hydrogen peroxide based system to the iron chelate based low solids process to reduce costs. Although the iron chelate is more expensive on a per pound basis than hydrogen peroxide, chemical costs are higher in the hydrogen peroxide based process. Unlike the ferric iron chelate, oxidation by hydrogen peroxide is not specific to H_2S , and, therefore, requires more volume of hydrogen peroxide. Moreover, the peroxide is only used in a once-through path while the low solids process is reoxidized in the cooling tower and recycled a number of times. The result is that the cost of the iron chelate in the low solids process is significantly less than that of the peroxide. In addition, the iron chelate does not have the reactive hazard of peroxide, and is safer to handle.

Choosing an Abatement System

Choosing a practical and economical primary and/or secondary H_2S abatement system for a geothermal power plant requires analysis of the factors affecting the individual plant site. Important considerations include: (1) the level of H_2S in the steam and the level of abatement needed, (2) the partition of the H_2S between the non-condensable gases and the condensate, and (3) the volume and quality of sulfur that might be produced. Sites with very low levels of H_2S in the steam may be able to design the plant so that only primary or secondary abatement is needed; but not both. The H_2S partition is profoundly affected by the level of ammonia in the steam. As the ammonia levels increase, the level of H_2S remaining in the condensate increases. Sites with ammonia in the steam will almost always require secondary H_2S abatement. The H_2S partition is also a function of the condenser design. Indirect cooling favoring H_2S partition toward the non-condensable gas. If a process that produces elemental sulfur is chosen, sulfur volume becomes an issue because of the associated disposal costs, particularly if the steam contains heavy metals that may ultimately contaminate the sulfur. Large volumes of sulfur may require additional processing such as re-melters to provide an acceptable form for sale as opposed to landfill disposal.

There are several choices for primary H_2S abatement in the non-condensable gas. These will be discussed in terms of pros and cons.

Stretford Process (9)

The Stretford process uses an aqueous solution of sodium carbonate and anthraquinone disulfonic acid (ADA) with an activator of sodium metavanadate. The process takes place in five or more steps. In turn, the H₂S is absorbed by the alkali, the ADA is reduced by a sulfur shifted, elemental sulfur is liberated by dissolved oxygen by air blowing. The process is technically capable of removing up to 99% of the H₂S in the non-condensable gas.

The sulfur is recovered by blowing air into the bottom of the regenerator, or oxidizer, vessel where small particles of sulfur are collected at the top as a froth. The sulfur froth is skimmed from the solution and is filtered or centrifuged to remove the solvent from the sulfur cake. Further sulfur processing may included re-melting.

The chemicals used in the solvent are stable with the exception of the formation of sodium thiosulfate which is not regenerable. The environmental exposure of vanadium through solvent loss and that in the sulfur product present handling and disposal problems.

LoCat Process (10)**

The LoCat process from ARI operates by absorbing H₂S into an aqueous phase where a catalyzed reduction/oxidation reaction converts H₂S to elemental sulfur through the reduction of iron from ferric (Fe⁺³) to ferrous (Fe⁺²). The iron is held in solution by a chelant with the iron concentration in the circulating solution in the range of 500 to 2000 ppm. The circulating solution permits the recovery of solid sulfur and the oxidation of the iron through air blowing.

SulFerox

The SulFerox process is a regenerable iron chelate based process for removing H₂S from gas streams. The H₂S in the gas stream is reacted with the iron chelate solution via a contacting vessel like a spray tower or the proprietary pipeline co-current contactor. The H₂S reacts with the iron in the contactor to form elemental sulfur. The circulating iron chelate is then regenerated using air sparging to oxidize the ferrous (Fe⁺²) to the ferric (Fe⁺³) form and recycled back to the contactor. The sulfur is recovered from the circulating solution by processing a side stream through a filtration /water wash in order to form a salable sulfur cake. The iron chelate is recovered from the sulfur via a water wash and returned to the circulating solution. Typical sulfur cake composition is 25 wt. % moisture. The sulfur cake can be sent to a melter for further processing. The technology is available from the Dow Chemical Company's GAS/SPEC Technology Group.

** Trademark of ARI Technologies, Inc.

Thermal Oxidation

Thermal oxidation of H₂S in the non-condensable gas and subsequent selective scrubbing with caustic results in essentially zero primary H₂S emissions and a solution of sodium sulfite. The sodium sulfite when mixed with the condensate containing elemental sulfur, produces soluble thiosulfate. This method is an attractive primary abatement when used in conjunction with the RT-2 Technology in secondary abatement.

The choices for secondary abatement have been discussed in earlier sections of this paper. The choices include:

1. Ferrous Sulfate - An obsolete technology.
2. Hydrogen Peroxide - Used alone, it provides a process in theory, but is not widely practiced due to high cost.
3. Iron Chelate with Hydrogen Peroxide - Broken into sub-groups
 - a. Iron-hydroxyacetic acid (HAA) - Solubilizes iron, but not to the extent of Fe HEDTA. Minor degradation of the HAA results in precipitation of iron. The reaction rate is not as high as the Fe HEDTA.
 - b. Iron -hydroxyethylethylenediaminetriacetic acid (HEDTA) - The Fe HEDTA solubilizes more iron and reacts faster. It is more resistant to precipitation of iron caused by degradation.

In the above applications, the abatement achieved is over 90% of the H₂S in the condensate. Solubilization of the sulfur depends on the ratio of the sulfur and the peroxide. In general, peroxide is not an effective means of solubilizing sulfur.

- c. GAS/SPEC Iron Chelate - Catalyzed to decreased reaction time while continuing to solubilized high levels of iron. It has the same stability as HEDTA.
4. RT-2 Iron Chelate with Sulfite - Provides over 95% abatement in the condensate and in the non-condensable gas. If sulfite is produced on-site, over 95% of the sulfur in the condensate will be solubilized. Sodium sulfite can be produced from the non-condensable gas by utilizing a burner/scrubber system while achieving primary abatement. Purchased sodium sulfite will achieve the desired solubilization of sulfur, but at a higher cost and without the benefit of primary abatement.

Case Studies Involving the SulFerox and RT-2 Technologies

The following cases are examples of two different H₂S abatement applications in the geothermal industry. In the first case, only trace amounts of ammonia are present in the steam. In the second case, the H₂S is partitioned between the non-condensable gas and the condensate.

Case 1: The SulFerox Technology

The H₂S partition is such that all the H₂S is in the non-condensable gas. The steam condensate does not require any additional treatment.

The design basis for this case is as follows:

Non-condensable Gas Flow: 4.2 MMSCFD
H₂S in non-condensable gas: 1.2 mole %

The SulFerox process was chosen to abate the H₂S in the non-condensable gas. The SulFerox technology utilizes a proprietary iron chelate solution to abate the H₂S in a continuous loop process. The ferric chelate is contacted with the H₂S (Equation 5) in the gas to form elemental sulfur in the reactor (Figure 1). The abated non-condensable gas exits the contactor into the separator vessel and is vented to the atmosphere. A side stream of the iron chelate solution is further processed to the vacuum filter in order to remove the sulfur solids from the process. This side stream is vacuum filtered and water washed to produce a moist sulfur cake (25 wt. % moisture). The purpose of the water wash is to recover the chelate contained on the sulfur. The water wash stream is then returned to the circulating chelate. The ferrous chelate solution is oxidized to the ferric state by sparging air into the regenerator vessel, thus closing the loop on the SulFerox process (Equation 6).

The material of construction for the SulFerox process is 304L/316L stainless steel. Fiberglass, and lined carbon steel vessels can also be utilized.

The economics for the process are as follows:

Capital Costs: \$883,000

Annual Operating Costs:

Power: \$30,600

Chemicals: \$ 105,000

The capital cost reflects a total stainless steel construction at July 1988 prices. The capital costs includes the license fee for the technology.

In this particular application, the SulFerox unit has been designed to emit 20 ppmv H₂S from the abated non-condensable gas. The unit can be designed to meet more stringent H₂S specifications with minimal costs. The amount of sulfur cake produced in this case is 2 LTPD on a dry basis.

Case 2: RT-2 Technology

In this case, the H₂S in the steam is partitioned between the non-condensable gas and the condensate. Hydrogen sulfide abatement will be required for both phases and will utilize the RT-2 Technology (Figure 2). In this application the non-condensable gas will be burned in a thermal oxidizer which will convert the H₂S into SO₂. The SO₂ from the thermal oxidizer will then be further treated in a two stage caustic scrubber. The scrubber has been designed to run at pH's that allow the SO₂ to react with the caustic to form sodium bisulfite, while the CO₂ present in the gas passes through the scrubbers unreacted. The sodium bisulfite produced from the thermal oxidizer/scrubber unit is sent to the cooling tower circulating water to solubilize the sulfur produced from the iron chelate - H₂S reaction in the condensate (Equation 5 & 6). This technology has been discussed in the secondary abatement section.

The materials of construction are 304/316 stainless steel for the thermal oxidizer and lined carbon steel vessels for the dual caustic scrubber. The iron chelate piping is 304/316 stainless steel. The prices reflect June 1988 costs for stainless steel.

The design basis is as follows:

Non-condensable Gas Flow: 3.5 MMSCFD
H₂S in the Non-condensable Gas: 3.2 mole %

Condensate Flow: 800 GPM
H₂S in the Condensate: 180 ppmw

The economics for the technology are as follows:

Capital Costs: \$1.05 MM

Annual Operating Costs:
Power: \$60,000
Chemicals: \$900,000

The capital cost is for the Thermal oxidizer/scrubber unit and associated piping. The technology fee is not included in the capital cost.

The total sulfur emissions from the RT-2 design unit, including SO₂ emissions from the caustic treaters and the H₂S from the cooling tower drift, is 2 lb/hr.

References and Footnotes

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2. Buenger, C.W., Kushner, D.S.; "The SulFerox Process - Plant Design Considerations", Presented at the Gas Processors Association 67th Annual Convention, Dallas, Texas, March 1988.
3. Van Kleeck, D.A.; " The SulFerox Process and Its Application", Presented at the AIChE 1988 Spring Meeting, New Orleans, LA, March 1988.
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5. A compound that can form a complex with a metal ion is known as a ligand. Ligands generally contain a functional group (an electron donor) with a negative charge or a lone pair of electrons. A chelating agent or chelate is a special type of ligand that contains more than one donor group. The formation of a metal-chelant complex (known as a chelate) is thermodynamically favored over a complex formed by ligands containing individual donor groups.
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7. Sharp, S.G.; U.S. Patent 4,363,215.
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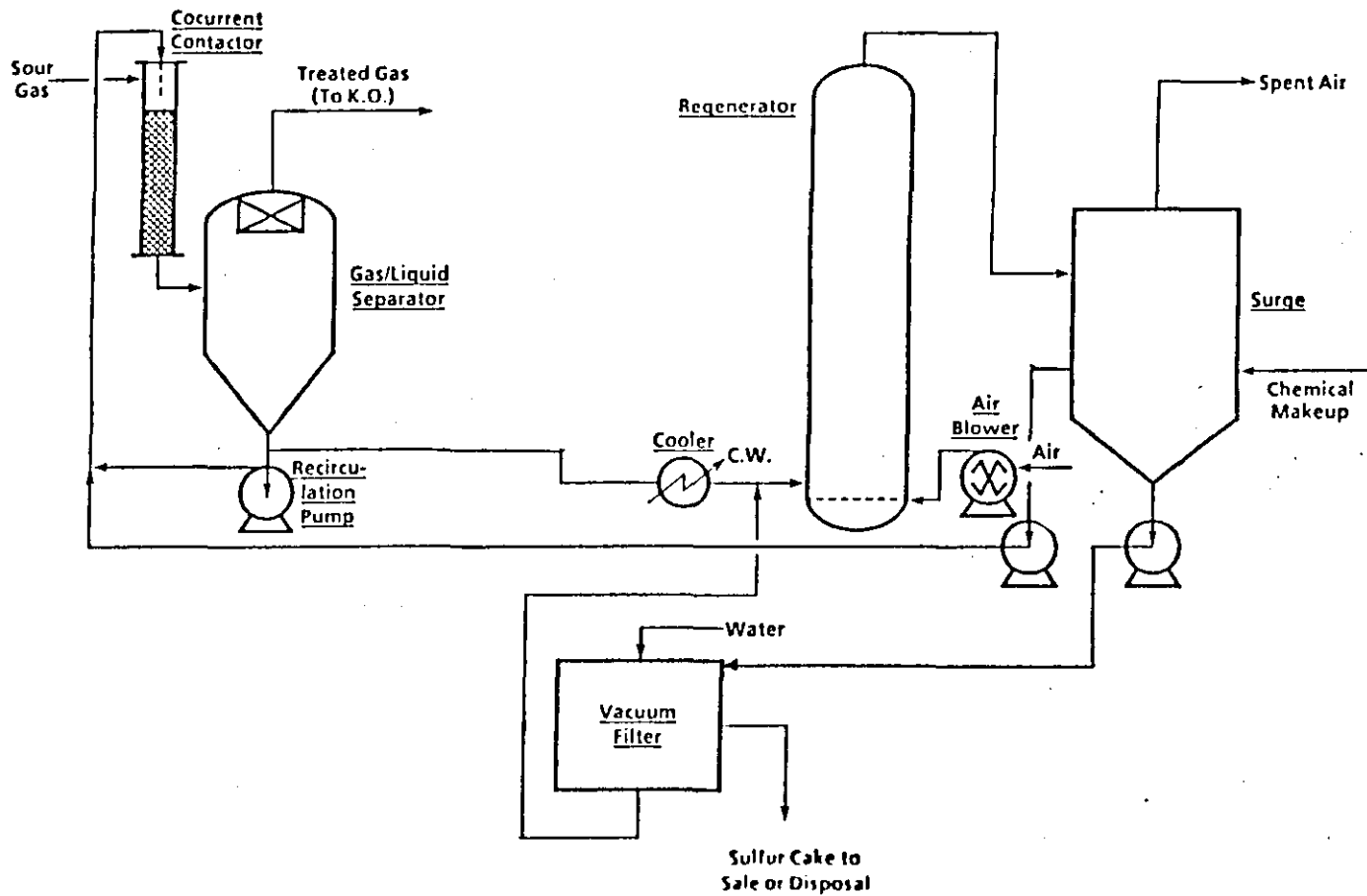


FIGURE 1 - SULFEROX FLOW DIAGRAM

FIGURE 2. GEOTHERMAL POWER PLANT WITH RT-2 ABATEMENT SYSTEM

