

## **NOTICE CONCERNING COPYRIGHT RESTRICTIONS**

This document may contain copyrighted materials. These materials have been made available for use in research, teaching, and private study, but may not be used for any commercial purpose. Users may not otherwise copy, reproduce, retransmit, distribute, publish, commercially exploit or otherwise transfer any material.

The copyright law of the United States (Title 17, United States Code) governs the making of photocopies or other reproductions of copyrighted material.

Under certain conditions specified in the law, libraries and archives are authorized to furnish a photocopy or other reproduction. One of these specific conditions is that the photocopy or reproduction is not to be "used for any purpose other than private study, scholarship, or research." If a user makes a request for, or later uses, a photocopy or reproduction for purposes in excess of "fair use," that user may be liable for copyright infringement.

This institution reserves the right to refuse to accept a copying order if, in its judgment, fulfillment of the order would involve violation of copyright law.

## UTILIZING THE AMMONIA IN GEOTHERMAL STEAM FOR H<sub>2</sub>S ABATEMENT

Charlotte M. Dorrity

Calpine Corporation  
Aidlin Geothermal Power Plant  
Cloverdale, California

### ABSTRACT

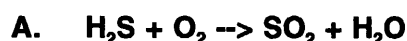
The Aidlin Power Plant was designed to be capable of utilizing steam with high Non-condensable Gas (NCG) concentrations and use an incinerator-scrubber system to abate large amounts of H<sub>2</sub>S. After the first year of operation, Calpine Corporation, acting for Geothermal Energy Partners, initiated a series of tests focused on reducing abatement chemical costs. These tests led to the use of naturally occurring ammonia in the process, which ultimately resulted in improved SO<sub>2</sub> scrubbing, improved control and predictability of secondary H<sub>2</sub>S abatement, reduced ammonia and particulate emissions, and lower commercial chemical usage.

### INTRODUCTION

The Aidlin Geothermal Power Plant, located in the Northwest section of the Geysers Geothermal Field, began producing electricity in May, 1989. The Plant was designed for non-condensable gas concentrations which were high, even relative to the highest NCG areas of The Geysers Field. The Aidlin facility was built with surface condensers which typically result in 80 to 90% partitioning of the H<sub>2</sub>S to the gas phase (Ballantine, 1991). The Aidlin Plant came on line with an incineration process for Primary H<sub>2</sub>S abatement, and a chemical secondary (or liquid) abatement system which utilizes iron chelate to chemically treat the sulfides partitioned into the hot well condensate.

The incineration of H<sub>2</sub>S, at 1900 to 2100° F., with the introduction of excess oxygen, results in the production of sulfur dioxide (A). The gas is cooled in a quench tower where it is sprayed with water to lower the gas temperature to 180° -200° F. It then passes through two packed bed scrubber-absorbers in series, which are designed to remove up to 99.9% of the SO<sub>2</sub>. In the quenching and scrubbing processes, the SO<sub>2</sub>, coming into contact with water, reacts to form sulfurous acid (B), supplying sulfite (and bisulfite) for the secondary abatement process (C). In the liquid phase abatement, chelated iron in the Fe<sub>3</sub><sup>+</sup> form reacts with the sulfides

partitioned into the hotwell condensate and the sulfites from the Primary abatement system to form thiosulfate, a soluble bi-product which can be directly reinjected (D).



The high rate of chemical consumption during the first year of operation made it apparent that chemical costs to maintain pH in the scrubbers and to maintain an effective secondary abatement would represent one of the greatest single operating costs of the Plant. Consequently, tests were designed to improve H<sub>2</sub>S abatement efficiency, and to reduce the need for caustic in the SO<sub>2</sub> scrubbers.

### INITIAL TESTING

In 1990, chemical costs exceeded 1.1 million dollars. With this knowledge, Geothermal Energy Partners (GEP) applied to the Northern Sonoma County Air Pollution Control District (NSCAPCD) in 1991 for permission to run tests on the primary abatement system. These tests, staged from October through December of 1991, culminated in design changes to the scrubber system. One important change made was to implement a single-pass make-up water system in the first scrubber, while maintaining the recirculating water system in the secondary scrubber. The significance of this change was that it involved using high flows of cooling tower basin circulating water as the water source for the primary scrubber, allowing the chemically-rich circulating waters to scrub much of the SO<sub>2</sub>, thereby decreasing demand for added commercial chemicals (Figure 1).

Initial results of these tests and the preliminary scrubber modifications showed that the alkalinity of the circulating water could be utilized to scrub the SO<sub>2</sub> formed in the incinerator, and that the liquid to gas ratio in the scrubbers was a major factor in the efficiency of the scrubbers.

## Dorrity

Source testing performed at the completion of these tests indicated that caustic consumption could be reduced by more than 50%. An unanticipated benefit of the system using higher make-up water rates was the reduction in stack temperature from 180° to 80°. This resulted in decreased water vapor in the stack emissions, and the consequent reduction of particulate matter emissions from the stack (particulate reductions of 53% by weight were noted). Also, ammonia in the incinerator stack and cooling tower emissions was reduced by up to 98% by weight, indicating retention of the indigenous ammonia in the system, an unanticipated benefit to air quality.

### IMPACT OF DESIGN CHANGES

Over the course of the next three months, time-dependant side reactions of the scrubber design changes became apparent. Sulfur dioxide emissions became more difficult to control at low levels, caustic consumption had risen again and, of most immediate importance, the visible emissions of the plume from the scrubber stack threatened to exceed Air Board standards. Loss of the water vapor in the stack emissions decreased the velocities and dispersion of the plume, making it appear worse, even though the particulate emissions had been reduced. This led to a six-month course of testing which was designed to include mechanical, chemical and industrial hygiene protocols to reduce plume opacity and maintain the chemical benefits of the higher make-up water flow rates to the system.

### SYSTEM WIDE TESTING

One sequence of process tests performed during this test period was designed to determine correlations between type and amount of base in the system, SO<sub>2</sub> concentrations, and plume opacity. The bases which were being compared were commercial caustic (sodium hydroxide) which was added to maintain pH in the circulating water, and ammonia which is naturally occurring in concentrations of up to 500 ppmw in the composite Steam.

It was known that less than stoichiometric amounts of caustic were required to absorb the SO<sub>2</sub> produced in the incinerator. Moreover, source tests indicated that less ammonia was off-gassed when less sodium hydroxide (a stronger base) was added (Equation E).



Sodium hydroxide make-up rates and introduction points in the circulating water system were varied in an effort to optimize the use of both bases in the absorption of SO<sub>2</sub> and the neutralization of the aqueous acids produced in the process. Reduced SO<sub>2</sub> absorption efficiency during these tests led us to test multiple points in the water flow path for any correlation between the caustic addition points, electrical conductivities, and SO<sub>2</sub> controllability.

Analysis of the circulating water, coupled with close review of historical data, did show that a large buildup of sulfates was occurring throughout the system. This was attributable to concentrating SO<sub>2</sub> by-products in one area. Because of diluted scrubber effluents, it was no longer possible to blowdown the sulfates without incurring significant water losses. The measured concentration of sulfates had risen until it was up to one thousand times greater than the concentration of thiosulfate. This indicated two things: 1) the sulfite ions from the incineration and scrubbing process were not reacting with the sulfide ions partitioned into the water phase in the hotwell condensate; 2) greater acidities associated with the presence of sulfur as sulfate rather than as thiosulfate necessitated greater base additions to neutralize the pH, to be available to scrub the SO<sub>2</sub>, and to react with the sulfite ions to form bisulfite (a species necessary for efficient secondary abatement reactions). These findings led to redirected scrubber blowdowns, disposing of those with the greatest concentrations of sulfites and sulfates.

Continuing with the original protocol, further tests were run to determine whether we could effectively utilize the indigenous ammonia in the NCG's. Although the use of naturally occurring ammonia resulted in chemical cost savings, the pH of the circulating water was difficult to maintain and to control. With pHs in the system below 6.0, the efficiency of the secondary abatement was reduced. It soon became apparent that the addition of a base was necessary to control the pH which had been reduced by the presence of acidic sulfur compounds, and to allow the reactions necessary for abatement of the sulfides in the liquid phase to occur.

The first base of choice for pH control in the basin was caustic (sodium hydroxide). Rather than add caustic to the scrubbers as had been done in the past to control SO<sub>2</sub>, it was now attempted to add it to the circulating water system to control the pH. However, adding the caustic to the basin was difficult to control operationally and did not prove to be an efficient means of pH control. The more caustic added, the less ammonium was retained in the circulating water, which in turn required the use of even more caustic.

In July of 1992, the plant began adding commercial aqueous ammonia (ammonium hydroxide) to the circulating water system in place of sodium hydroxide as a supplementary source of hydroxyl ions. This change allowed the utilization of our naturally produced ammonia and reduced the cost for added bases by approximately 50%. The circulating water system pH could be maintained above 6.0. Even though the control of the system still had some operational difficulties, such as maintaining an even pH in all areas in the circulating water system, it was considered viable. Design changes were engineered to enable the plant to use ammonium hydroxide in conjunction with naturally occurring ammonia to control the alkalinity of the circulating water system. In doing so,

ammonia emissions were reduced from the cooling tower and the incinerator stack together by about 416,804 pounds per year (a 98% reduction!) and we significantly reduced our costs by reducing the amount of commercial chemicals used.

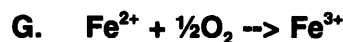
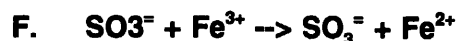
## BALANCING THE ABATEMENT SYSTEMS

Three months after finalizing the transfer to ammonium hydroxide for pH control in the circulating system, the secondary hydrogen sulfide abatement system was showing severe loss of efficiency. This system, based upon chemical abatement of sulfide ions from the hot well condensate, uses iron carried by a chelating ligand. In its oxidized state, the iron reacts to push the production of thiosulfate from a bisulfite in the returns from the incinerator skid and a sulfide ion from the hotwell condensate. The iron is then re-oxidized as it goes across the cooling tower (Equation G). The concentration of iron necessary to be maintained in the system can be calculated based upon dynamic conditions which include the amount of sulfide to be abated (carried in the condensate) and the flow rate of circulating water (as the carrier for the iron product) across the tower. Additions of chelated iron product to maintain a given iron concentration are also calculated, based primarily upon losses due to system blowdown.

During testing of cooling tower emissions, it was discovered that hydrogen sulfide was being emitted in greater than permitted quantities, in spite of the fact that iron concentrations in the circulating water were 33% above the stoichiometric concentrations necessary for complete abatement. Because iron had historically been maintained at 100 to 110 % of stoichiometric, this represented a severe degradation in our abatement efficiency. The three variables which we suspected of influencing the effectiveness of our secondary abatement chemistry were: 1) pH of the circulating water system (low pHs were running lower than historical levels); 2) low circulating water temperature (this occurred during the winter time); 3) condenser partitioning.

Since partitioning in the condensers was, at that time, sending 72 to 75 percent of the H<sub>2</sub>S to the incinerator, it was calculated that approximately 350 pounds per hour of SO<sub>2</sub>, were being produced, most of which was being scrubbed into solution as sulfurous acid/sulfites. The design changes which had been previously made to increase make-up water rates to the scrubbers had resulted in a reduction of the concentration of sulfites in the effluent, which would require greater quantities of water to be blown down to eliminate an equal weight of sulfites. Because it was not operationally feasible to increase blowdown rates proportionately, this left up to 100 pounds per hour of excess sulfite in solution. Sulfites are strong reducing agents, so this presented the possibility that the iron in solution was being reduced (Equation F), before it had time to be utilized in the sulfide to thiosulfate reaction. Because oxygenated sulfur compounds create a much more acidic environment than

thiosulfates do, it became increasingly difficult to maintain the pH of the circulating water system while producing excessive amounts of sulfurous acid and minimal thiosulfate.



Maintaining the pH at 6.0 or above was necessary as a condition of the Air District Permit to Operate. In addition, lower pHs potentially affected reaction times for re-oxidation of the iron; with this occurring, any change in circulating water temperature or cooling tower efficiency could be the final factor necessary to reduce the amount of iron available in the +3 oxidation state to the point that H<sub>2</sub>S abatement was below acceptable limits.

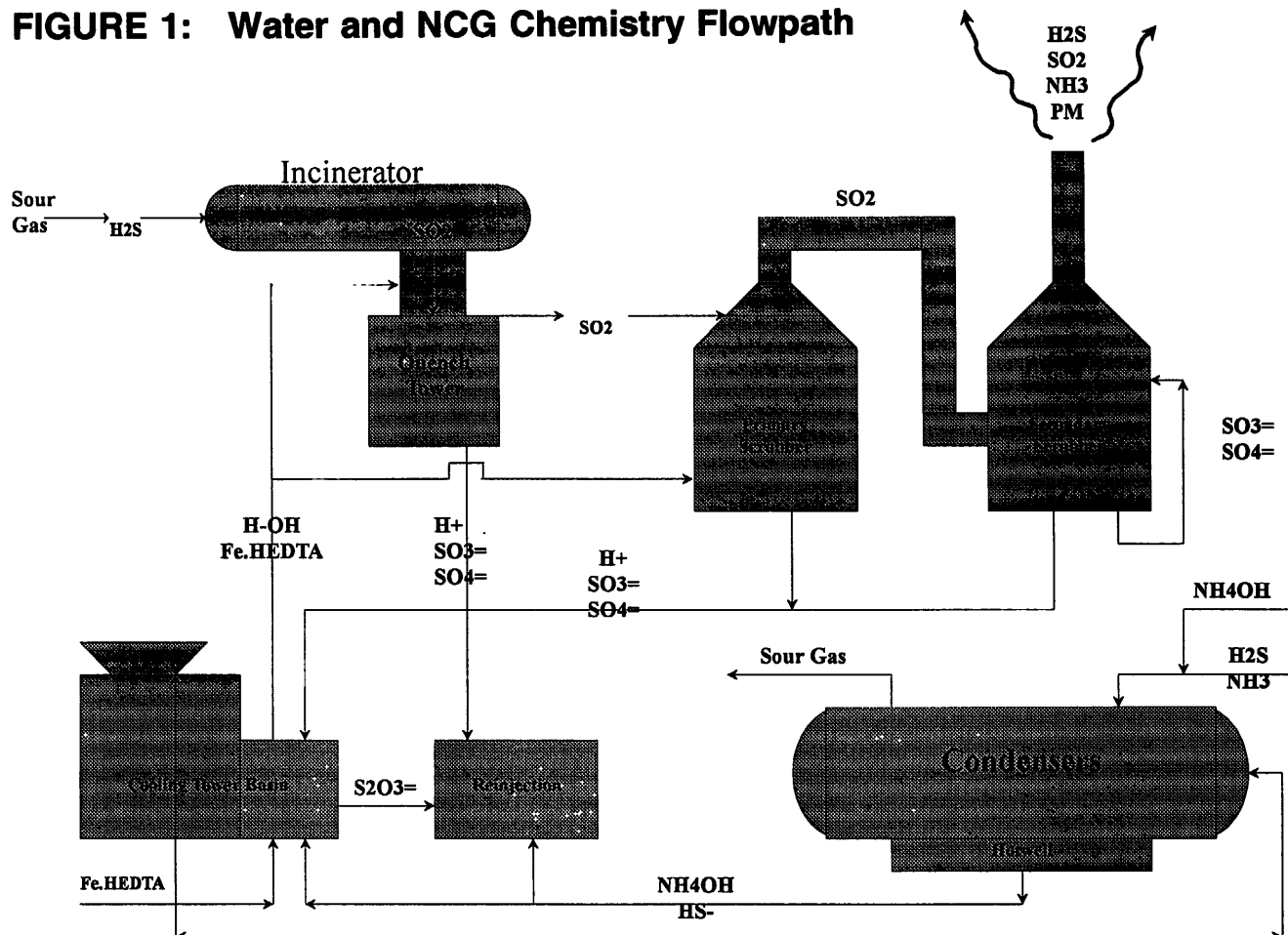
Cooling tower source tests were run under varying conditions, including circulating water temperature swings and pH changes. The testing did confirm that the H<sub>2</sub>S abatement was more complete when the water pH was no less than 6.0, and that increases in the circulating water temperature going into the condensers increased the efficiency of the abatement reactions. Postulating that we could more easily control circulating pH if we controlled acid production in the primary abatement system, we attempted to change the partitioning of H<sub>2</sub>S in the condensers.

## CHANGING PARTITIONING

The initial Partitioning experiments were conducted in the inner and after condensers where ammonium hydroxide could be injected. Ammonium hydroxide was chosen because it was not projected to cause any formation of solids on the outside of the condenser tubes. These initial tests confirmed that using an ammonium hydroxide rich condensate solution on the steam side to raise the pH of the condensate did result in greater partitioning of H<sub>2</sub>S to the water phase.

The next step was to inject ammonium hydroxide into one turbine exhaust, quantifying the changes in H<sub>2</sub>S partitioning vs. pH of the condensate. It was determined that partitioning could be reduced from 72% to 56.6% by raising the hotwell condensate pH by one-half point. The partitioning responded well and almost immediately to the injection of treated condensate, was proportionate and controllable, and reversed with the cessation of ammonia additions. Time dependant trials with the increased partitioning of H<sub>2</sub>S to the liquid phase showed changes in the circulating water chemistry, traceable to the changes in the hotwells. The first indication that the system was changing came with an increase in circulating water pH.

Because less sulfurous acid was now being produced, and because the hotwell condensate (make up source for the cooling tower basin) was now more alkaline, the pH of the circulating water began to rise. Circulating water pHs

**FIGURE 1: Water and NCG Chemistry Flowpath**

now became more easily controllable above 6.0 than they had been since the initial changes in water flow rates to the primary abatement scrubbers. The results of source testing repeated with the higher pHs indicated that we were now more effectively re-oxidizing and utilizing the chelated iron which was maintained in the system.

After three months of experimentation and temporary lines, a permanent spray ring on each turbine exhaust cross-over duct at the point of entry to the condenser was installed. These rings were engineered for maximum contact between injected condensate, rich in ammonium hydroxide, and the steam prior to entering the condensers. The use of a more effective means of introducing the ammonium was expected to result in further decreased chemical usage.

Since the installation of the spray rings (two years), there have been substantial decreases in ammonium usage, as the ammonia concentrations in the produced steam has risen. This rise in ammonia concentration in the steam is in agreement with observations by Beall (1993), connecting direct reinjection with increased ammonia

production. In the case of the Aidlin plant the increase in the ammonia content of steam is even more pronounced than Beall indicated in his paper. This is because in addition to steam condensate, with up to 500 ppmw ammonium, circulating water is also injected. Due to the solubility of ammonia and the current retention of ammonia, concentrations of up to 6000 ppmw ammonia are found in this water. Consequently, as more ammonium-rich water is put into injection wells which communicate with steam producing wells, ammonium needs are further decreased, and system controllability increases. Indeed, as the concentration of ammonia in the incoming steam has risen from recycling through the steam reservoir, the quantity of commercial ammonium hydroxide additions necessary to shift partitioning has noticeably decreased.

## CONCLUSION

Research and testing, conducted over a course of two years at the Aidlin Geothermal Power Plant, were designed to determine a means to reduce the consumption of chemicals in use for H<sub>2</sub>S abatement. Several

significant changes in operations were made, enabling the use of naturally occurring ammonia, supplemented with use of commercial ammonium hydroxide, to control H<sub>2</sub>S partitioning in the condensers, and circulating water pH.

The introduction of ammonium rich condensate to the steam prior to the condensers has been in use for two years, and continues to be a viable factor in the efficient abatement of Hydrogen Sulfide. The shift in partitioning of more H<sub>2</sub>S to the condensers results in reduced production of excess sulfuric acid, making the circulating water pH easier to maintain. It also results in the formation of fewer excess sulfites (which can reduce chelated iron, making it unavailable for secondary abatement of the liquid phase H<sub>2</sub>S).

In addition, increasing the concentration of the ammonium ion in both hotwell condensate and circulating water, both of which are reinjected to the formation, increases the concentration of produced ammonia in steam. This in turn, maintains a more constant ammonia level and higher pH in the produced steam, requiring less ammonium additions as the steam thus affected is produced. Currently, the base usage rate of ammonium for sulfur abatement and pH control is less than five percent of the volume which was used when testing began in 1991.

#### ACKNOWLEDGEMENTS

The author wishes to thank Geothermal Energy Partners and Calpine Corporation for permission to publish this

paper and the information herein. In addition, thanks to D. Gilles, L. Sessions, T. Netzel and J. Beall for critical review, to J. Jennings for illustration preparation and to J. Hathorn for manuscript preparation.

#### REFERENCES

- Ballantine, D., (1991) Evolution of Power Plant Design at The Geysers. Geothermal Resources Council, Monograph on the Geysers Geothermal Field, Special Report No. 17, pgs. 275-280.
- Beall, J.J., (1993) NH<sub>3</sub> as a Natural Tracer for Injected Condensate. Geothermal Resources Council, Transactions, Vol. 17, pgs. 215-220.
- Bedell, S., A. Hammond, (1987) Chelation Chemistry in Geothermal H<sub>2</sub>S Abatement. Geothermal Resources Council, Bulletin.
- Motekaitis, R., D. Hayes, A. Martell, W. Frenier, (1979) Hydrolysis and Ammonolysis of EDTA in Aqueous Solution. Canadian Journal of Chemistry, Vol. 57, pgs. 1018-1024.
- Motekaitis, R., D. Hayes, A. Martell, W. Frenier (1979) The Iron(III)-Catalyzed Oxidation of EDTA in Aqueous Solution. National Research Council of Canada. Canadian Journal of Chemistry, Vol. 58, No. 19, pgs. 1999-2005.