Biological Hydrogen Sulfide Abatement in Geysers Geothermal Cooling Towers

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ABSTRACT

Since the early 1980's The Geysers cooling tower hydrogen sulfide (H_2S) emissions control (secondary abatement) has been implemented by the addition of chelated iron to the circulating water. This chelated iron reacts with the $H_2S_{(aq)}$ that has been transported to the cooling tower in the condensate stream. The H_2S is converted to non-volatile sulfur compounds. Over the years this process has been improved by finding ways to reduce condensate H_2S loading to the tower and by increasing the reaction time for H_2S to be oxidized prior to distributing the condensate on the cooling tower deck where "air stripping" occurs as the water falls from the deck to the basin. Another improvement to H_2S abatement efficiency has recently been applied at The Geysers, wherein the naturally occurring sulfur oxidizing bacteria existing in the cooling towers are promoted to oxidize H_2S in the cooling tower.

At The Geysers, cooling tower H_2S abatement efficiency was found to unexpectedly improve during the spring months. Coincidentally, air-borne pollen counts in the forested region around the Geysers increase tremendously. Improved H_2S abatement efficiency also occurs when tertiary treated waste water (containing phosphate) is added to supplement cooling tower makeup. The addition of tertiary treated waste water has the effect of adding nutrients to a system that typically does not have the full complement of nutrients for sustaining bacteriological growth. The additional nutrients promote natural biological H_2S abatement.

Background

Most geothermal cooling towers have dual purposes. They not only perform their traditional design function dissipating heat, but also as H_2S abatement devices. The need for abatement is that steam condensate is the makeup water source in geothermal power plants. H_2S entering the plant "partitions" between the vent gas and the condensate as a function of temperature, pH, condenser type and water flow. Other researchers have described H_2S partitioning (Baducci et al., 1996, Weres, O., 1983).

The result of H_2S partitioning into the condensate dictates the need to monitor H_2S emissions from the cooling towers to meet air quality permit restrictions. Due to a lack of reliable real time monitoring devices, The Geysers manually measures emissions from the cooling tower stacks. This is performed by using California Air Resource Board Method 1 and 2 which measures air velocity for mass flow calculations, and NSCAPCD Method 102 to quantify emissions. The method entails drawing gas samples through a probe from equal area quadrants using a vacuum system and measuring H_2S on a Jerome model 631-X monitor. Total emissions are then calculated from the air flow rate and concentration of H_2S. Calpine's Geysers plants operate with 17 cooling towers and emissions must be measured, according to air permits, at least once per month; some are measured quarterly.

The degree to which H_2S abatement is required is the difference between the amount of H_2S added to the cooling tower in the hot condensate and the emission limit set by the air quality permit. The Geysers steam supply is variable in total gas concentrations ranging from 500 ppmw to 100,000 ppmw (Beall et al 2007). H_2S is therefore also quite variable as H_2S is approximately 5% of the total gas. This results in large differences in H_2S loading rates to cooling towers across The Geysers ranging from less than the emission limit at some plants (e.g. Unit 14, Unit 18 and Unit 20) up to 40 times the emission limit at others (Aidlin Power plant). Power plants having the highest H_2S loading, or the greatest difference between H_2S loading and emission limits, are the most expensive towers to treat with abatement chemicals. Secondary chemical abatement cost for iron chelate can reach nearly $500,000/year in some power plants. The cost makes it imperative to understand all the variables involved in H_2S abatement, and to find ways of reducing those costs.

Traditional Abatement

Iron chelate is the secondary abatement chemical used in cooling towers at the Geysers. The reaction with H_2S is described in equations A and B for the reduction and oxidation of iron respectively.

$$16Fe^{+3} + 8H_2S \rightarrow S_8 + 16Fe^{+2} + 16H^+ \quad (A)$$

$$16H^+ + 16Fe^{+2} + 4O_2 \rightarrow 16Fe^{+3} + 8H_2O \quad (B)$$

The net reaction is pH neutral and the end product is solid elemental sulfur. Power plants with a burner/scrubber system providing primary abatement can eliminate the build up of elemental sulfur by conversion of the solid sulfur to thiosulfate as described in the RT-2 process (Bedall et al. 1996). The end product of the burner/scrubber primary abatement reactions are various forms of sulfites (Na_2SO_3, H_2SO_3 or HSO_3^-). These sulfites react with elemental sulfur to form thiosulfate as described in equation C.

$$S_8 + 8Na_2SO_3 \rightarrow 8Na_2S_2O_3 \quad (C)$$

One method successfully applied to reduce the cost of H_2S abatement has been to reduce the H_2S loading to the cooling tower. This is performed by either decreasing H_2S concentration in the condensate or by diverting some of the H_2S laden condensate directly to injection and bypassing the cooling tower altogether. The concentration of H_2S in the condensate can be reduced by increasing temperature of the coolant flow to the main condenser or after condenser, thereby elevating the temperature of the condensate. H_2S solubility therefore decreases, resulting in significant reductions in H_2S loading. The amount of H_2S loading to a tower can be decreased by as much as 10 to 20% by this method. Elevating the water temperature can have a detrimental effect on power production, as cold water equals better power plant efficiency. The benefit of reduced H_2S loading by higher water temperature must be economically weighed against power output.

Direct re-injection of hot well condensate can result in up to 25% reduction in H_2S loading, depending on the cooling tower water balance. In the summer, when circulation water temperatures and evaporation naturally increase, direct re-injection is often minimized or non existent, to maximize the use of available water. Direct re-injection is more prevalent in winter months when condensate is in large excess of evaporation.

Another process that greatly enhances abatement efficiency is finding ways to prolong the residence time of the condensate before falling through the fill. The Geysers utilizes condensate reroute (Ballantine, Benn, 1993), which is the directing the hotwell H_2S laden condensate to the back of the cooling tower. The condensate then gains valuable time in the basin, ranging from 20 to 40 minutes, before reaching the cooling tower distribution trays on the cross flow cooling towers. Unfortunately, this process is only available in plants utilizing shell and tube condensers. Plants with direct contact condensers result in a circulating water/hot condensate mixture exiting the condenser that provides a short residence time as it travels directly to the distribution trays on top of the cooling tower. These plants are more costly to abate as more iron is required to meet the permitted emission limitations, due to short residence times and greater partitioning of H_2S to the liquid phase. A limited amount of direct contact condenser condensate reroute is possible by routing the inter and after condenser drains to the cooling tower basin, instead of the more traditional route to the main condenser. Up to 25% of the incoming H_2S can be diverted from the cooling tower hot water deck and allowed to oxidize in the cooling tower basin.

What is Biological Abatement?

The process of Biological H_2S oxidation is a fundamental step in the sulfur cycle. The organisms responsible are commonly found wherever H_2S is present. All of these organisms gain energy by the oxidation of H_2S for the synthesis of organic molecules. They are commonly found in waste water treatment, and deep underwater volcanic vents and in geothermal systems, to name a few. Researchers have biologically classified the bacteria in geothermal towers. Culivicchi (2005) found species of sulfolobus and thiobacillus in cooling towers and in surrounding hot springs in Italy. Pryfogle (2005) found various species of thiobaccilus in The Geysers cooling towers.

Many industries rely on bacterial sulfur oxidation. For example, The Geysers sells a great deal of sulfur to farmers for soil amendment. The sulfur oxidizers, present in the soil, convert the sulfur into sulfuric acid to decrease soil pH. Industries that emit H_2S, such as waste water treatment plants, often are required to reduce H_2S odors by installing soil beds or trickling filters containing sulfur oxidizers (Moosavi G.R.et al. 2005). Some geothermal power plants have built large trickling filters for sulfur oxidizers to perform primary H_2S abatement (A Sonneville et al., 2001). The prevalence of biological sulfur oxidation in industry and nature, coupled with the presence of thiobaccilus in The Geysers cooling towers, makes it no surprise that there is some biological component to H_2S oxidation to secondary abatement.

The degree of abatement by sulfur oxidizing organisms is dependent on having a full complement of nutrients. The bacteria require primarily the same basic macronutrients as plants:

- Nitrogen source (supplied by ammonia in geothermal condensate)
- Phosphorus (PO_4)
- Carbon (as carbon dioxide)
- H_2S or S_2O_3

The only requirement not supplied from geothermal steam at The Geysers is PO_4. Pryfogle (2005) showed that spiking geothermal cooling tower water with phosphate increased bacterial metabolism resulting in sulfate formation.

The H_2S oxidation reaction requires oxygen and produces sulfuric acid (equations D and E). The rates of H_2S oxidation seen in the cooling towers is too fast to be attributed to merely the affects of oxygen. Hill (1973) determined the residence of H_2S in air is between 1 and 42 days. Millero (1991) determined the half life of hydrogen sulfide in surface waters of the Framvaren Fjord, low in iron and manganese and in the absence of biological activity, to be over 900 minutes. Since oxidation of H_2S in The Geysers cooling towers must occur in the short time period (less than 60 minutes) before the water reaches or falls from the distribution decks, the contribution of H_2S oxidation by oxygen alone is probably insignificant. The accumulation of the reaction products (H_2SO_4) in The Geysers cooling towers is probably a result of biological activity.

$$H_2S + \tfrac{1}{2} O_2 \rightarrow S + H_2O \quad (D)$$

$$2S + 3O_2 + 2H_2O \rightarrow 2H_2SO_4 \quad (E)$$

Indication of Biological Abatement

The realization that biological organisms contribute to H_2S abatement in cooling towers started at The Geysers by trying to explain changes in abatement efficiencies noted in spring months. During the spring, the area around The Geysers surges with life after enduring a relatively dormant winter. Pollen counts rise dramatically and insects multiply. As cooling towers are often described as air scrubbers, the pollen and insects are collected in the tower water and breakdown serving as food for bacteria.

The clearest examples of improved spring abatement are found in power plants not utilizing iron chelate for secondary abatement. The Geysers Socrates-Unit 18 plant is a good example. The cooling tower H_2S loading for this plant, with the help of direct injection, is usually less than 10 lb/hr with an emission limit 11.4 lb/hr. No abatement is necessary at this plant because emissions are less than the limit. The Socrates-Unit 18 graphs (below) show H_2S emissions measured monthly and cooling tower H_2S loading trends from 2006 through 2009. H_2S emissions drop each spring. The month abatement starts to improve varies between April and May depending on weather patterns. All cooling towers at The Geysers have a similar emission trends. The improved abatement continues through July and sometimes into August or September.

Another power plant example of improved H_2S abatement at The Geysers is Grant-Unit 20. This plant is a sister to Unit 18, both having similar design, H_2S loading rates, and emission limits. The difference between them is that Unit 20 has a water balance deficit during the heat of summer. To make up for this

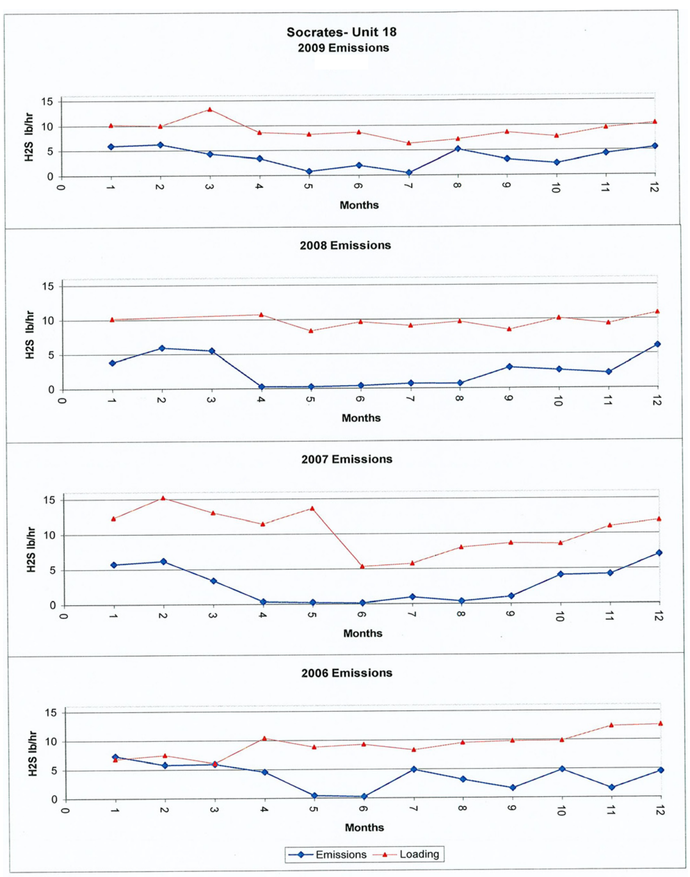

Figure 1.

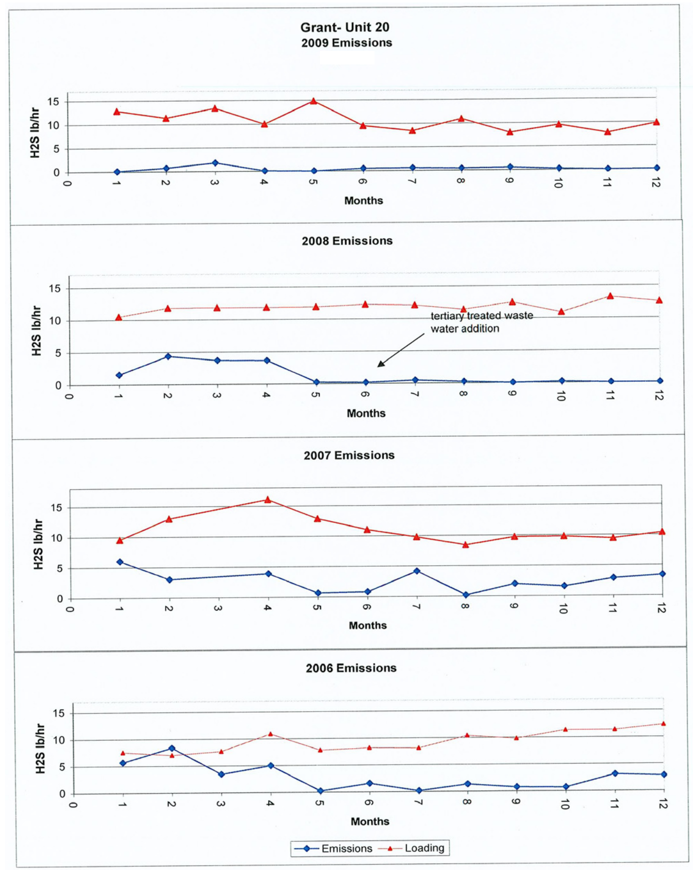

Figure 2.

cooling water deficit during the summer of 2008, additional water was added in the form of tertiary treated waste water. The 4 year trend for Unit 20 shows similar abatement to Unit 18; in 2006 and 2007, prior to any waste water additions. After waste water addition, abatement greatly improved. Interestingly, improved abatement continued throughout the winter of 2008, even without waste water addition. Apparently, the cooling tower was able to store enough nutrients from the waste water to maintain biological abatement through winter. Waste water was again added in the spring of 2009.

A final example of the effects of waste water is observed at The Geysers Lakeview-Unit 17 power plant which has a very high H_2S loading rate to the tower ranging between 40 and 50 lbs/hr (13.2 lb/hr limit). Similar to Unit 20, Unit 17 has a water balance deficit in summer which was solved by the addition of waste water beginning in July 2004. At the same time a condensate reroute system was installed to increase H_2S residence time in the basin. Before the addition of tertiary treated waste water, the U17 plant used iron chelate for secondary abatement, up to 5 mg/l, due to the H_2S loading rate.

The graphs (below) compare H_2S emissions to both iron concentrations and waste water addition flows. The addition of waste water and installation of a condensate reroute system clearly improves abatement in this tower. The drop in iron concentration, after the initial addition of waste water in 2004, appears less dramatic than subsequent years as plant operators were less reluctant to lower iron concentrations in light of these new phenomena. The hot well H_2S concentrations and cooling tower H_2S loading rates have not significantly changed during this time period. Since 2006, iron has no longer been required, even during the winter of 2006 when waste water was discontinued. As in the case of Unit 20 the tower apparently has the ability to store nutrients that sustain H_2S abatement; this probably occurs in the sediments.

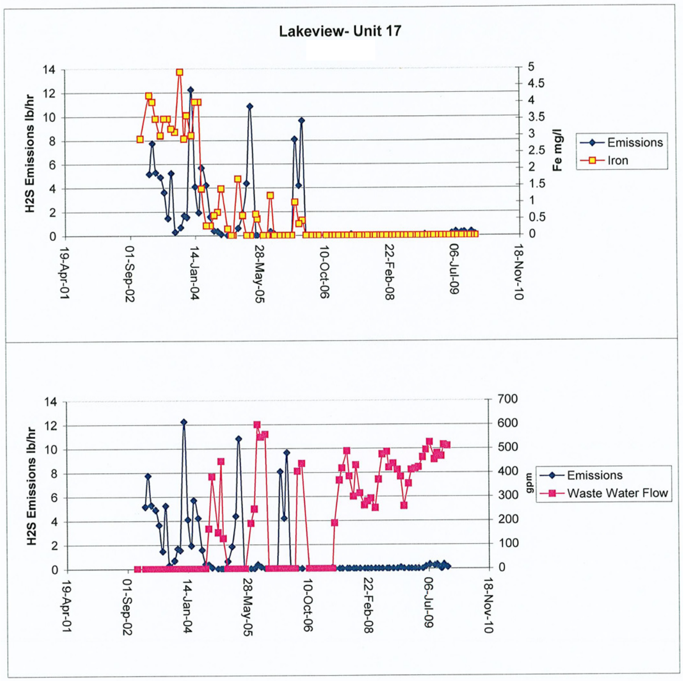

Figure 3.

Negative Affects of Waste Water

When waste water is added to Unit 20 and Unit 17 cooling towers unwanted bacteria flourish along with the helpful sulfur oxidizers. The bloom in bacterial growth is perfectly illustrated in the ATP increase, which rises from 500 relative light units (rlu) (common in most Geysers towers with no waste water), to nearly 50,000 rlu post waste water addition. The primary unwanted growth is from nitrifying and slime forming bacteria that stick to condenser tubes, fouling condensers and depressing circulating water pH. The main condensers at these two power plants have ball cleaning systems to remove this fouling material and maintain condenser performance. However, biocides have to be added to limit overall bacterial growth and keep smaller shell and tube condensers in the plants (without ball cleaning systems) and other surfaces clean and functional.

Significant nitrifying bacterial activity is only found in The Geysers cooling towers where waste water is added as makeup. These bacteria convert ammonia to nitric acid. The nitrification process requires two distinct groups of bacteria: nitrosomonas bacteria that convert ammonia to nitrite (Equation F), and nitrobacter bacteria that convert nitrite to nitrate (Equation G). This two step process is clearly visible in the graph below as initially nitrite accumulates by nitrosomonas activity converting ammonium to NO_2. Then as enough nitrite becomes available nitrobacter populations increases until the rate of nitrate formation is equal to the nitrite formation. The negative aspect of nitrification is the additional acid produced that can lower cooling tower pH.

$$NH_3 + O_2 \rightarrow NO_2 + 3H^+ + 2e^- \qquad \text{(F)}$$

$$NO_2 + H_2O \rightarrow NO_3 + 2H^+ + 2e^- \qquad \text{(G)}$$

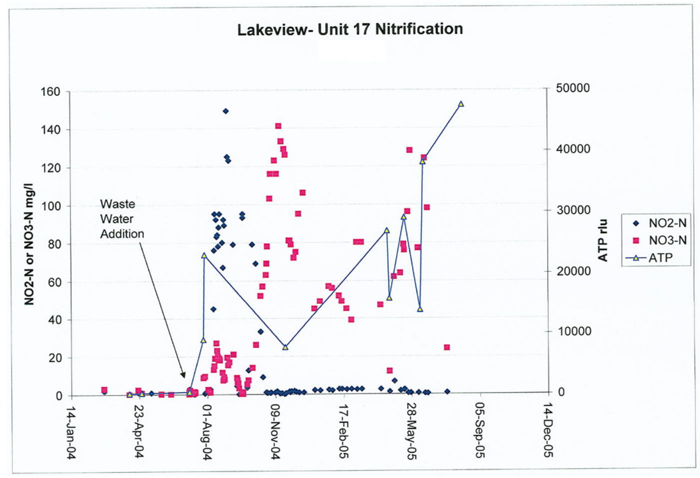

Figure 4.

Biocides

Proof of biological H_2S abatement comes from the use of biocides; when significant doses of biocides are added to the circulating water (killing off or impairing enough sulfur oxidizing bacteria) H_2S emissions increase. The following two examples of biocide additions clearly show these effects. The first is at Eagle Rock-Unit 11, where a 5 ppm dose of a Nalco® quaternary amine was added to the tower. Emissions were measured before and after biocide addition. H_2S emissions doubled from 20 to 40 lbs/hr confirming biological abatement in the cooling tower.

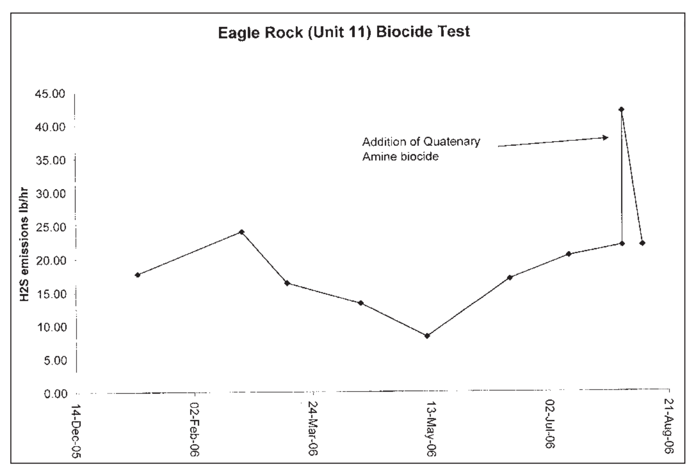

Figure 5.

Another example comes from The Geysers Calistoga power plant. This plant has shell and tube condensers and requires routine maintenance biocide doses of sodium hypochlorite to keep the condensers clean. Hypochlorite has a short life in the circulating water due to elevated oxidant demand from hydrogen sulfide and ammonia. The initial drop in ATP is usually the result of total chlorine residual for that volume of tower water treated. Not all the tower volume is treated so the ATP returns to near normal or

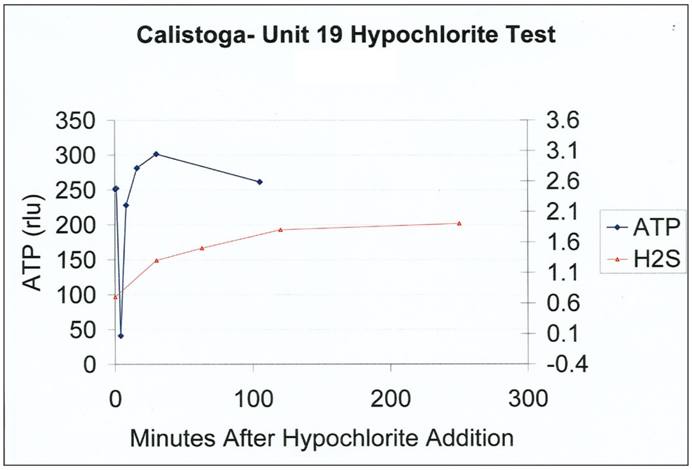

Figure 6.

elevated levels as organisms are knocked off the walls and the treated water mixes with untreated water. The affect of biocide addition is an increase of emissions from 0.6 to 1.6 kg/hr.

Conclusion

Biological secondary abatement is a natural process occurring in The Geysers cooling towers. The degree of unassisted abatement improves annually in spring and early summer with an influx of airborne materials in the tower and can be inhibited with the use of biocides. Activity of the bacteria responsible for abatement can be enhanced by the addition of waste water. These bacteria can contribute significantly to H_2S abatement if managed appropriately.

Unfortunately not all the bacteria enhanced by waste water addition are beneficial. The negative impact of adding extra nutrients to the cooling tower is that other bacteria grow as well. Those may include slime formers, sulfate reducing bacteria and nitrifying bacteria. The proliferation of these unwanted organisms may result in fouling of heat exchangers, microbial induced corrosion and nitrification that can upset the pH balance in the circulating water. These impacts can be mitigated somewhat by having a properly engineered power plant having splash bar fill, direct contact condenser or shell and tube condenser with a ball cleaning system and the use of biocides.

The cost of inorganic H_2S abatement using iron chelate can be expensive and understanding the processes involved in abatement is helpful in managing those costs. Maximizing sulfur oxidizers is one way to reduce H_2S abatement costs if doing so does not jeopardize plant performance

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