AN INNOVATIVE APPROACH TO TREATING GEOTHERMAL POWER GENERATING COOLING WATER SYSTEM IN THE PHILIPPINES

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ABSTRACT

Chemistry from geothermal plant is complex relative to both the initial quality, the problems that this produced and the interactions with the chemicals that are normally selected to control these problems. The condensed water is low in total dissolved solids, free from any appreciable amounts of calcium and high sulfur compounds such as hydrogen sulfide as well as ammonia. Carbon dioxide levels is also high and also contributory to the aggressiveness of the water. Oxidation either by chemical processes or biological activity further increases the aggressiveness of the water. Undoubtedly, the most significant mechanism responsible for the rapid increase in acidity in most geothermal cooling systems was the production of hydrogen sulfide within the circuit by anaerobic bacteria and the resultant oxidation to sulfuric acid by aerobic processes as typified by the sulfur cycle organisms.

The absence of hardness within the water and the high levels of contaminants impose limitations upon the agents that may be selected for treatment program. The size of the circuit also limits treatment considerations to low dose additives from an economic point of view. Introduction of the program based on DS767, an amine based corrosion inhibitor, dispersant as well as biocide showed immediate effect in arresting bacteria proliferation. SRB and TBC counts continued to be less than nil and 10e4 respectively at all times. No deposition/fouling was ever a problem here in this plant with amine levels in the circuit being maintained at 5-7 ppm by site and laboratory test.

1. INTRODUCTION

Asia's power industry is expected to grow by up to 12% a year to 2003, providing a rich stream of business for investors, contractors, manufacturers and consultants.[1] This is driven by two trends. The first is that of a larger rural population becoming more urbanized. The second trend is that Independent Power Producers (IPPs), as opposed to municipally owned and operated facilities, are setting up operations to build new power generating capacity. In many sectors, especially in the Philippines and Indonesia, this rate of growth will surge even higher as IPPs assume the role previously held by municipal utilities. At the same time, power companies are keen to diversify their fuel sources. In particular, they want to replace more traditional forms of power plants with geothermal prospects, especially in those countries located within the "ring of fire."[2]

2. GEOTHERMAL POWER GENERATING SYSTEMS

Geothermal energy is heat that is extracted from the earth. Pressurized hot water and steam, is produced when groundwater meets with the molten magma ascending from the earth's core. Hot water flows to the surface through wells. Once pressure is released, the water flashes to steam. The steam is separated from the water and this steam is used to drive a turbine generator.

Conventional cooling towers are used to condense steam on the low-pressure side of the turbine to maximize electrical generation efficiency. Either direct condensers or surface heat exchanger condensers are utilized. In most cases, the condensate is used as makeup for the cooling towers. There is excess condensate available and this means that cooling towers run at low cycles. Low cycle operation results in excessive cooling tower treatment costs unless programs can be employed that are effective at low dosage rates.

Geothermal power plants are designed with corrosion resistant materials of construction such as stainless steel in order to withstand the trace contaminants that enter the cooling systems with the steam. In addition, most cooling towers are designed with high efficiency fills that are susceptible to fouling if improperly treated. Both of these mechanical design features affect the requirements of chemical treatment.

3. WATER CHARACTERISTICS AND PROBLEMS ENCOUNTERED

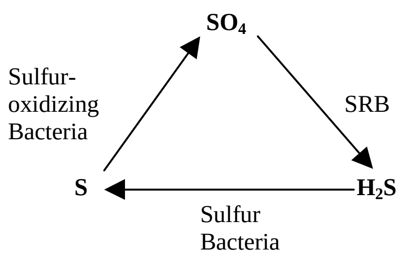
Biofouling and noxious odor problems have challenged geothermal power producers for years, particularly those companies with generating units that depend upon condensed geothermal steam (condensate) for their cooling water source. The demand for a high degree of power reliability at a time of increasing competition means companies cannot afford downtime resulting from water treatment problems. Effective water treatment programs are designed for prevention and control of problems in geothermal plants and are helping energy companies reduce losses and remain competitive.[3]

Chemistry from geothermal plants is complex. This is related to both the initial condensate quality, problems that this produces and the interactions with chemicals that are normally selected to control these problems. **Table-1** contains a typical chemical composition of geothermal power plant steam and condensate. As can be seen, the condensate contains low dissolved solids, is free from any appreciable amounts of calcium and alkalinity, and contains high sulfur compounds such as hydrogen sulfide and ammonia. Carbon dioxide levels are also high and contribute to the aggressiveness of the water. Depending on the type of condenser design, water chemistries in the cooling systems can be dramatically affected. All of these factors promote the growth of microorganisms that can deleteriously affect geothermal plant operation.

An accumulation of non-condensable gases (NCGs) occurs in the condenser. This accumulation can cause an increase of contaminants in the cooling water. These gases, typically CO_2,N_2,H_2S, other sulfur compounds, CH_4, H_2, NH_3, are usually controlled by purging to the atmosphere or removing via scrubbers.

4. POTENTIAL FOULING PROBLEMS IN COOLING WATER CIRCUITS

The presence of trace amounts of NCGs in the cooling water is inevitable. Oxidation, either by chemical process or biological activity, further increases the aggressiveness of the water. If allowed to proceed without preventative treatment, particularly where H_2S is present, pH levels within the circuit may drop drastically. This can increase caustic consumption dramatically. The most significant mechanism responsible for the rapid increase in acidity is the production of hydrogen sulfide within the circuit by anaerobic bacteria. This species forms sulfuric acid in the presence of water and the cycle is depicted below.[4]



Another water treatment challenge has emanated from the introduction of higher efficiency fills to improve the thermal performance.[5] Given the presence of H_2S, oxidation of sulfur will initiate in the cooling tower environment and, unless driven to completion (SO_4), the opportunity for growth of both sulfate-oxidizing and sulfate-reducing bacteria exists. Examining this further, sulfur-specific bacteria are highly specialized and are of several genera, including desulfovibrio and desulfotomalculum. A number of these species may act as components in a “microbial consortia” creating growth of substantial foulants in cooling towers. At the same time, the presence of ammonia and nitrogen may produce nitrifying bacteria species, as well as other common aerobic bacterial growth. The extensive accumulation of microorganisms can contribute to the clogging of these high efficiency fills. Geothermal cooling water systems can foul at a high rate unless proper treatment is applied. In more severe circumstances, high fouling rates can result in a reduction in the overall cooling efficiency and an increase in operating cost.

5. CORROSION PROBLEMS

Slime-forming bacteria are attracted to and colonize at low water velocity sites.[6] The growing biodeposits trap suspended solids (scrubbed from the atmosphere as well as from the steam lines) rich in iron, which harbor and sustain growth of filamentous iron bacteria. These aerobes consume oxygen and leave anaerobic conditions beneath the deposit. This can sustain the growth of sulfate-reducing bacteria. The resultant biomass can promote localized low pH conditions and other acid-forming bacteria. Additionally, a concentration cell is formed which promotes under-deposit corrosion. Both of these mechanisms can cause pitting corrosion to occur. Carbon steel, stainless steel, and copper-bearing alloys can be severely corroded by H2S formed. Corrosion resulting from microbial attack is termed microbiological induced corrosion (MIC). In addition, further oxidation to sulfuric acid will cause localized pH depression, thus causing a general thinning of any carbon steel metallurgy. Pitting corrosion can also occur in mild steel and stainless steel metallurgy as a result of MIC.

7. TREATMENT PHILOSOPHY

The cooling tower evaporates water to remove heat and reject it to the atmosphere. Condensate used for makeup is contaminated with non-volatile chemicals from the steam. Specific contaminants of concern are:

- Ammonia
- Hydrogen sulfide, bisulfide and sulfide
- Silica
- Chloride
- Others (e.g., trace NCGs)

Corrosion-resistant materials of construction are typically used in the design of geothermal plants so generalized corrosion is not normally a problem. The primary problem within the geothermal cooling circuit is the control of microbiological growth due to the high nutrient loading from the ammonia nitrogen and microbiological induced corrosion (MICs). Many of the geothermal plants are located in tropical locations and these climates further exacerbate growth of algae, fungi general bacteria and yeast. Overall microbiological control is essential to prevent slime formation in the fill and on metal surfaces.

Due to the presence of sulfide compounds, use of oxidizing compounds is generally not effective due to very high demand and high usage rates required.[7] Chlorine-based materials, the most common and cost-effective oxidizing biocide, contribute to chloride levels, and this can promote stress corrosion in stainless steels.

An aggressive non-oxidizing biocide program is, therefore, required. The absence of calcium within the water and the high levels of H_2S impose limitations upon the chemicals that may be selected for a treatment program.[8] At the same time, treatment economic concerns become an issue due to the large size of typical geothermal plant cooling systems. Products selected for control are also limited by environmental controls imposed on the condensate being rejected back to the wells.

At the same time, toxicants cannot totally mitigate all microbiological-related problems. These microbiological control agents cannot reach anaerobic bacteria proliferating beneath or around deposits. A three-pronged approach is required to address the following issues:

- Deposit control
- Corrosion control
- Microbiological control

8. DEVELOPMENT OF EFFECTIVE TREATMENT APPROACH

Work commenced to screen potential dispersants, biocides, and corrosion inhibition compounds that would be suitable for geothermal conditions. Numerous products were screened and the vendor finally formulated the program currently in place at one of the Leyte geothermal complex. The low cycles of concentration carried in the system dictated that the program had to be effective at low dosage rates.

The cornerstone of the treatment program is an amine-based material, hereafter called PRODUCT767 cooling water treatment. This compound affords a number of benefits by controlling hydrogen sulfide attack, acting as a microbiocide, providing dispersancy and inhibiting corrosion. Details on each of these functions are provided below.

Mechanisms of PRODUCT 767 Cooling Water Treatment with Hydrogen Sulfide

Reaction with H2S and amine proceeds according to the G-Orbital reaction used in gas purification as follows:[8]

$$2RHN_2 + H_2S \longrightarrow (RNH_3)_2S$$

This reaction is reversible with the amine sulfide being soluble. Reversion is complete at 250F. The amine initially removes H2S by a chemical reaction process and releases it in hot parts of the system as it comes in contact with air. The excess amine residual is available to perform other functions in the circuit.

PRODUCT 767 Cooling Water Treatment as a Biofilm Inhibitor

Another advantage of this program is that residuals between trace and 5 mg/l are effective.[9] In a number of ways, PRODUCT 767 cooling water treatment act as a biofilm inhibitor. It functions by filming the walls of the organism, forming a barrier and inhibiting normal gaseous exchange and the intake of nutrients. It also interferes with enzymes controlling flow through the membranes and organisms resulting in the loss of control of water balance. As the osmotic pressure within the cell is higher than the environment, water rushes into the cell causing rupture of the wall.

With slimes, the filming action of the product onto metal and other materials, such as cooling tower fill, creates a high concentration at the surface, producing an environment unpleasant to the organisms. The surface is also “slippery” so attachment of slime is difficult.

PRODUCT 767 Cooling Water Treatment as a Dispersant

The attraction of the product to organic particles and onto metal surfaces leads to dispersion. First, the attraction to organic particles leads to mobile, light floc, which suspends and removes organic deposits from the circuit. The affinity of the product toward metal surfaces leads to a “scouring” action on the metal that dislodges both organic and inorganic deposits (slimes, loose iron oxide deposit, silt, etc.) that are then removed by water flow.

PRODUCT 767 Cooling Water Treatment as a Corrosion Inhibitor

PRODUCT 767 cooling water treatment is a surface-acting agent and has a characteristic molecular structure consisting of a group that has little attraction for the solvent (water) – the lyphobic group – together with a group that has a strong affinity for the surface.[10] This amphipathic structure and reduction of the surface tension of the solvent, leads to a surface moiety having a positive charge and, thus, it absorbs strongly onto most solids surface (which are usually negatively charged) such as metal and microorganisms. When contacting any new surface, 767 lays down an impervious, non-wettable film that acts as a barrier between the surface and water. This film is of monomolecular layer thickness and does not increase with continued treatment. This absorbed film on the surface is very durable.

Complete Treatment Program

Since PRODUCT 767 cooling water treatment is not an algaecide/fungicide, non-oxidizing biocides are required to complement the treatment program. Two programs found to be effective were glutaraldehyde/quarternary ammonium chloride combination and methylene-bis-thiocyanate, hereafter called BS227 and BS284B, respectively. These are added alternatively on a monthly basis to provide a synergistic effect on the overall treatment. Prior to implementation of the above program at the trial site in Leyte, product samples were submitted to their headquarters for evaluation.

9. PROGRAMS RESULTS

Upon testing and approval, full implementation commenced in 1996. The program, based on PRODUCT 767 cooling water treatment and BS227 and BS284B microbiocides, showed immediate effect in arresting bacteria proliferation. Sulfate-reducing bacteria and Total Bacterial Counts typically continue to be nil and less than 10^5 colonies/ml, respectively. No deposition/fouling has occurred, and this has never posed a problem.

Graphical representations of key parameters monitored in the cooling tower circuit are attached. For three consecutive years, the overall program has been found to be very effective in keeping the surfaces clean and free of foulants, especially in the high efficiency cooling tower fills, condensers and auxillary equipment. Total bacterial counts are consistently controlled below 10^5 colonies/ml with values contained at 10^3 colonies/ml most of the time. The pH of the recirculating water is typically maintained at 6.0 or above, which is indicative of good bacterial control. High ammonia and sulfate ions, as is shown in **Figures-3** and **4,** contribute to difficulty in controlling system pH. It is also interesting to note that the pH of the system is directly related to bacterial count. **Figures-1** and **2** show that occasional low pH excursions were experienced when bacterial counts became out of control. These excursions were quickly brought back into control once microbiological control was reestablished.

During normal operation, the vendor’s service engineer visits the plant to perform and document the results of the following services:

- Perform water testing.
- Review water-testing logs and review statistical process control (SPC) logs for water treatment since last visit.
- Confirm the proper operation of all chemical feed systems.
- Verify chemical feed dosages.
- Review Key Performance Indicators (KPIs):
    1. Corrosion rates
    2. Total bacterial counts (TBC) – via plate counts
    3. SRB results
    4. Tower fill weights and fill inspections – ensure fills remain clean
    5. Heat exchanger thermal efficiency
    6. Cooling tower approach temperatures – indicates cooling tower efficiencies
    7. General fouling – measured using a VCFM (Visual Corrosion and Fouling Monitor)
    8. Biofouling
- Monitoring Key Control Parameters (KCPs)
    1. Total Dissolved Solids
    2. pH
    3. Cycles of concentration
    4. Inventory analysis – monitor actual usage rates versus theoretical
    5. Sulfide
    6. Ammonia
    7. TBC/SRB
    8. Iron
    9. Chloride
    10. Sulfates

10. PROGRAM ECONOMICS

An analysis was performed of the actual cost of the existing vendor's program versus competitively recommended programs. Results after three years have shown cost to be approximately one-third less than the competitively recommended programs. In addition, costs have consistently been reduced each year as a result of optimization efforts.

This cost optimization program was achieved by following the vendor's QUALITY PLUS^{SM} process. The basis of this process was the mutual implementation of continuous improvement projects by both the vendor and end-user. The guidelines followed during this optimization effort were:

- Evaluate the total system and monitor critical performance variables.
- Prepare a data collection system that will indicate changes in the Key Performance Indicators (KPIs).
- Initiate step-wise program modifications, collect data and analyze results of these changes.
- Evaluate results of these changes on results (KPIs) and economics.
- Plan next program modification to further achieve continuous improvement goals.

The vendor continues to establish a system to track chemical usage and consumption versus unit performance, focusing on economics (i.e., kg product used/megawatt, kg product used/m3 recirculating rate, overall program cost/megawatt, etc.). To date, the continuous improvements made by practicing the QUALITY PLUS^{SM} process described above have enabled the end-user to realize excellent results and reduce costs for three consecutive years.

11. CONCLUSIONS

The program discussed is now being successfully applied in three cooling towers at the facility. The customer is realizing the following benefits from this program:

- The water treatment program is producing 100% reliability so no unscheduled shutdowns have occurred as a result of water-related problems.
- Microbiological growth is controlled, thus:
    - √ Heat exchanger surfaces remain free from foulants that can impede heat transfer.
    - √ Cleaner equipment reduces cleaning and maintenance costs during turnarounds.
    - √ Microbiologically induced corrosion problems are prevented and equipment life is prolonged.
    - √ Fills remain clean, therefore, promoting efficient cooling efficiencies.
    - √ Control of H2S-forming species reduces the cost of caustic soda.
- PRODUCT 767 cooling water treatment promotes corrosion protection so equipment life expectancy is greater and maintenance costs are minimized.
- The products being applied are environmentally acceptable so condensate can be reinjected into the brine well.
- The program is effective at low dosages rates, thus, minimizing treatment costs.
- Following the vendor's QUALITY PLUSSM process and making continuous improvements have allowed costs to be constantly reduced without sacrificing results.

12. REFERENCES

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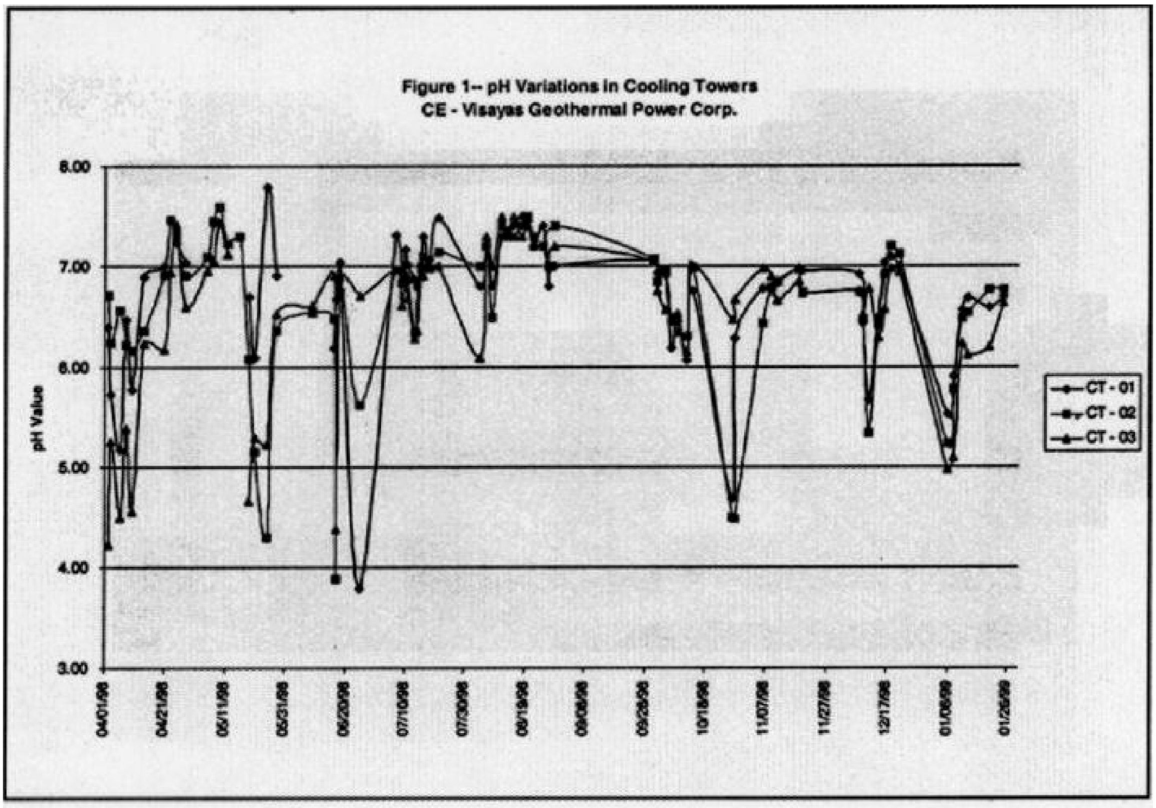

Figure 1-- pH Variations in Cooling Towers
CE - Visayas Geothermal Power Corp.

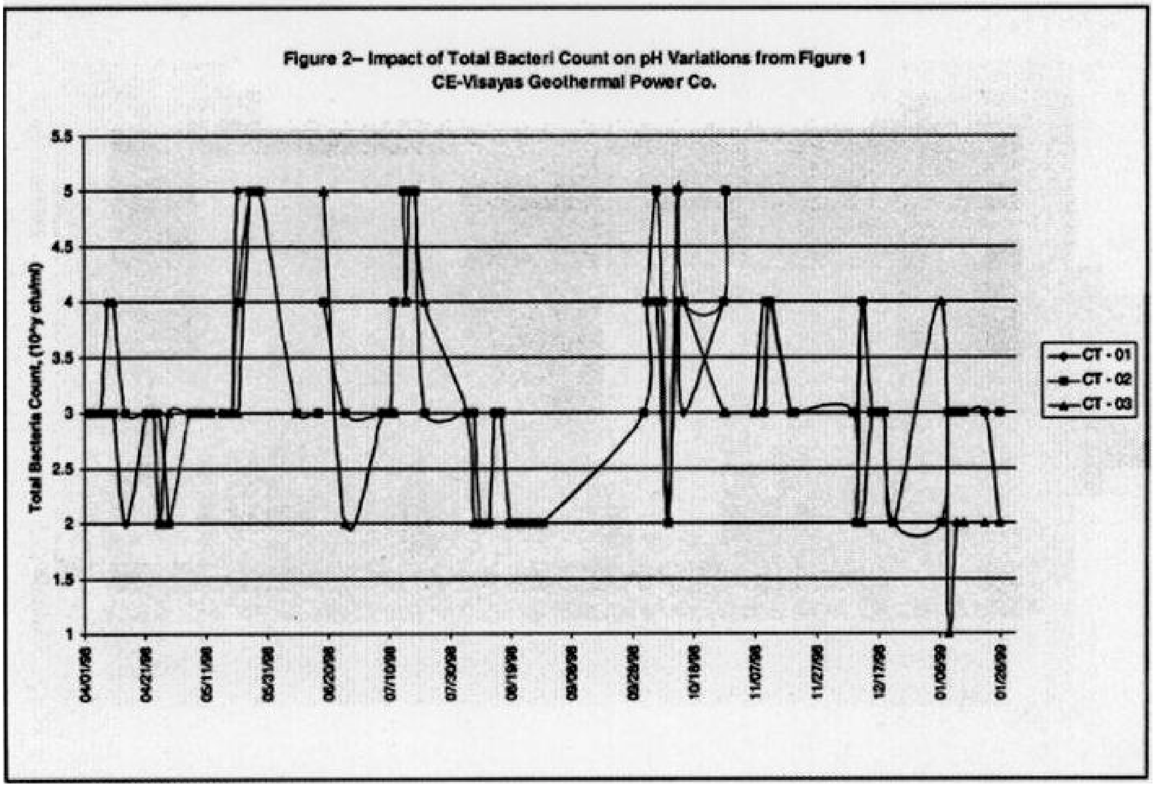

Figure 2-- Impact of Total Bacteri Count on pH Variations from Figure 1
CE-Visayas Geothermal Power Co.

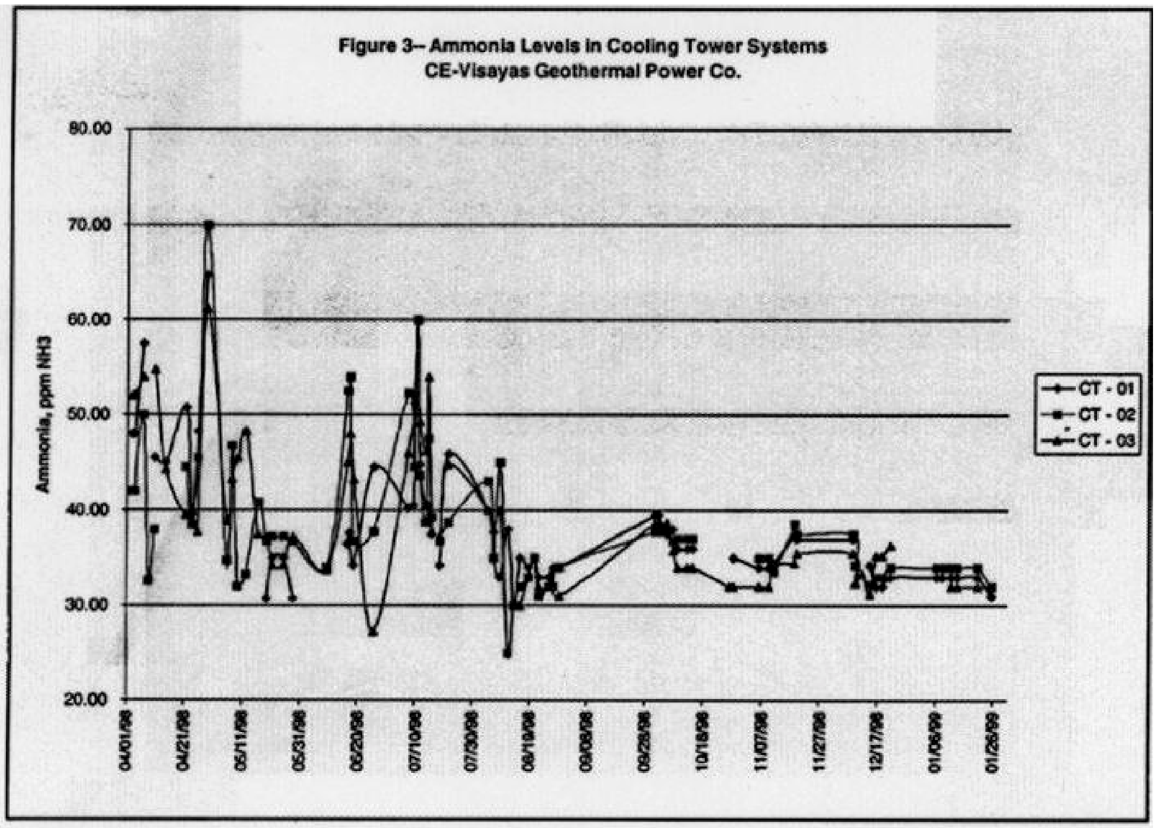

Figure 3-- Ammonia Levels in Cooling Tower Systems
CE-Visayas Geothermal Power Co.

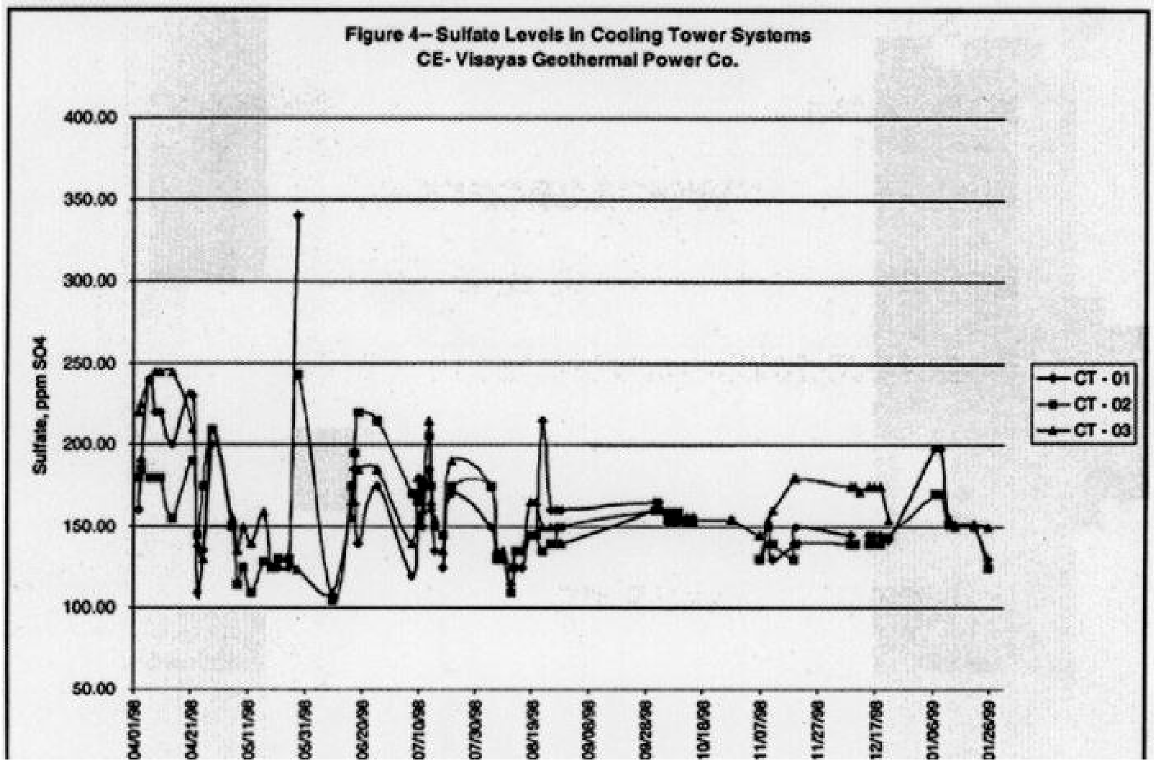

Figure 4-- Sulfate Levels in Cooling Tower Systems
CE- Visayas Geothermal Power Co.

Table-1
CE-Malitbog Steam/Condensate Composition

Total NCG* in steam,%	2.50
Carbon Dioxide in steam,%	2.45
Hydrogen sulfide in steam,%	0.033
Ammonia in steam,%	0.004
Inert gases in steam,%	0.003
NCG Composition:	
Carbon Dioxide, CO_2,%	98.4
Hydrogen Sulfide,%	1.31
Ammonia,%	0.148
Methane,%	0.0028
Nitrogen,%	0.008
Hydrogen,%	0.004
Condensate Composition:	
Unit of pH	5.15
Conductivity, mS/ml	59.2
Total dissolved solids, ppm	28
Chlorides, ppm	0.085
Silica, ppm	0.269
Iron, ppm	0.530
Boron, ppm	0.32
Sodium, ppm	0.056
Sulfide, ppm	3-5
Carbon dioxide, ppm	8-10

* NCG is non-condensable gases