

AN INNOVATIVE APPROACH TO CONTROLLING DISSOLVED OXYGEN AND CORROSION IN CORROSIVE GEOTHERMAL REINJECTION LINES

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ABSTRACT

Two major companies in the Philippines do geothermal energy exploration and drilling. Each has its own geothermal fields to explore and develop. The development of geothermal fields includes the wells, lines and steam cleaning facilities. Steam produced is sent to power generators.

Contracts are written that specify the quality and quantity of steam to be produced and the quantity and quality of condensate to be reinjected. The power generators dictate the quality of steam and the steam producers dictate the quality of the bleed-off to be reinjected into non-producing wells. Heavy penalties are instituted if either producers or generators deviate from specifications in the contract.

CalEnergy's Malitbog Station in Leyte is required to reduce dissolved oxygen (DO) in the reinjection condensate to below 70 ppb. They were encountering difficulties in meeting these requirements in an economical fashion. Global Commercial Trading and Drew Industrial embarked on a project with Malitbog personnel to consistently meet the <10 ppb DO limit at a reasonable cost.

1.0 INTRODUCTION

Cat-En's Malitbog power generating system consists of three 77.5 MW Fuji turbines with cooling towers, each having its own bleed-off line leading to a common header. The header leads to a common line, owned by the power generator. This common line is connected to the steam reinjection lines, made of carbon steel, owned by the steam producer. The boundary of these lines is the perimeter fence of the power generator. Discharge of this steam condensate is tested at the boundary, within the property of the power producer.

The turbines are housed in one building. The main condensers are of the direct contact type wherein exhaust steam mixes with the circulating cooling water serving as make-up. Exhaust steam is greater than the evaporation and windage loss. The excess has to be bled. Power plant equipment and lines are made of non-corrosive materials, stainless steel and fiberglass reinforced plastic, respectively. Beyond the boundary of the power generator, the receiving pipelines of the steam producer are of carbon steel and subject to corrosion.

The Malitbog Station is required to protect the reinjection lines against corrosion or else penalties will be levied. These penalties can either be in the form of a monetary payment or a requirement to repair and replace corroded reinjection lines. The contract stipulates that geothermal wastewater must maintain dissolved oxygen levels at or below 10 ppb before being discharged. This requirement is very difficult to achieve economically. In addition, variables such as variations in flows, steam quality, non-condensable gas concentrations, etc. must be considered.

2.0 DISCHARGE CONDENSATE CHARACTERISTICS

The complex chemistry of geothermal water (i.e., low TDS, calcium and alkalinity; high sulfur-as H_2S --; carbon dioxide; and the presence of NH_3) makes it very aggressive. Biocides used in the cooling towers and the presence of toxic elements such as cadmium, boron and arsenic all affect water chemistry. Accumulation of gases depends upon the efficiency of the non-condensable gas (NCG) ejector system. Scrubbers remove gases such as H_2S , CO_2 , and NH_3 . Scrubber fluid also discharges into the reinjection system.

3.0 POTENTIAL PROBLEMS TO ADDRESS

Corrosion is the main problem that occurs in the carbon steel reinjection pipelines. This is caused by a number of potential conditions:

- a **High velocity** - Erosion occurs from suspended solids scrubbed by cooling towers
- a **Low pH** - Acid attack results from the hydrolyzation of H₂S
- a **Dissolved oxygen** - This results in pitting corrosion
- a **Biological deposits** - Bacterial slimes and biomass promote microbially induced corrosion

A complete engineering assessment was performed and it was concluded that pitting corrosion resulting from excessive dissolved oxygen levels was the primary cause of problems. Underdeposit corrosion resulting from tuberculation and fouling was a secondary concern. A decision was made to establish a program to control dissolved oxygen levels in the reinjection lines.

4.0 PRELIMINARY TRIAL

Catalyzed sodium sulfite, provided by a different supplier, was initially used in an attempt to lower the dissolved oxygen to <10 ppb. DO levels were reduced to 9.6 ppb, but 33 kg per day of catalyzed sulfite was consumed to achieve control. Total dissolved solids more than doubled and costs were significantly higher than the plant wanted to spend. Consequently, the trial was discontinued with only moderate success.

5.0 GLOBAL - DREW PHILOSOPHY OF TREATMENT

A proposal was submitted recommending a Drew proprietary product, AMERZINE™ 35, a catalyzed hydrazine material. Its scavenging property is slower than catalyzed sulfite, but it offers a major advantage in that it does not contribute solids. Also, prolonged use will allow passivation of carbon steel, thus reducing corrosion rates.

The following factors were considered in designing and selecting AMERZINE™ 35:

- scavenging property
- oxygen scavenging time
- solids level contribution
- passivation
- velocity (system not static and minimal retention time)
- temperature
- feeding requirements
- sampling protocol
- testing procedures

It is commonly agreed that the discharge condensate is corrosive and that Cal-En did not want to install non-corrosive pipelines due to their high capital cost. The compromise was to minimize corrosivity by maintaining DO at <10 ppb and raising pH to 5.5 - 6.5 through the use of caustic soda.

6.0 DISCUSSION AND ACTION STEPS

Determining the correct feedrate of AMERZINE™ 35 proved to be tricky, as there were a number of variables to consider. Initial computation considered the volume of reinjection water, flow rate and levels of dissolved oxygen. DO levels, as recorded, ranged from 25 ppb to 75 ppb. An average of 50 ppb was used to compute the theoretical amount of AMERZINE™ 35 to use as starting point.

AMERZINE™ 35 was fed continuously at diluted concentration using a low capacity feed pump. DO levels were lowered but still remained greater than 10 ppb. We continued to increase the dosage/concentration of AMERZINE™ 35 but the results were far from acceptable. The program was not cost effective.

Meanwhile, plant laboratory testing showed that the total scavenging of DO to zero could be achieved within nine (9) minutes, which was faster than expected. This proved to be a breakthrough. By ratio and proportion to the amount of AMERZINE™ 35 and the volume of reinjection water tested, the amount of AMERZINE™ 35 was re-calculated. This amount differed from what laboratory test results showed. Plotting the results showed that it took 3 to 4 minutes to reduce DO to between 5 and 10 ppb. It was surmised that other elements or compounds were consuming the DO. This, in effect, helped the program and generated savings for the plant. Based on the initial and

re-calculated amount, only 1 kilogram per day of AMERZINE™ 35 need be consumed to bring DO to the desired level.

Further data confirmed that it took 3 to 4 minutes for AMERZINE™ 35 to reduce 50 ppb DO level to an average level of 4 to 6 ppb. Knowing this, it became a matter of deciding the optimum distance between the points of feeding and sampling, given the flowrate of reinjection water.

The next step was to determine the optimum feed location. The choices considered were the reinjection header or at the discharge from any of the three cooling towers. Trials showed that feeding at No. 2 and No. 3 Tower discharge created a back-pressure during low loads and this caused difficulty in feed and control of the AMERZINE™ 35. Feeding into the reinjection line from No. 1 Cooling Tower proved to be ideal. It was located the farthest distance from the sampling point, allowing for the greatest reaction time, and was unaffected by back-pressure during low loads.

Further trials revealed that AMERZINE™ 35 fed at various solution concentrations reduced DO to less than 10 ppb but was not sustained. It was reasoned that since the computation was based on the average DO level of 50 ppb, the amount of AMERZINE™ 35 was insufficient to handle the peaks i.e. when DO levels are above 50 ppb. To correct this, the dosage of AMERZINE™ 35 was increased by 50% to 1.5 kilograms.

A number of other observations were made during the time we were optimizing feedrates and results:

- **H₂S** levels, changes in velocity due to fluctuating loads, and contact time all affected the results of the program. Further laboratory experiments revealed that even without feeding AMERZINE™ 35, DO levels dropped after 4 hours in the presence of **H₂S**.
- Sampling protocol was critical. DO readings were easily affected by air leakage during sampling. Stricter sampling procedures were instituted. For example, gas bubbles were allowed to escape, the sampling bottle was shaken to totally eliminate the gas bubbles and then it was immediately cocked.

- Vacuum is created in the pipelines during the on and off flow of sampled fluid. A Dissolved Oxygen Meter was installed to monitor this. The DO meter, however, showed a much higher reading, several times higher than the actual DO levels. It was later discovered that the DO meter was recording **H₂S** gas, as well. To measure DO more accurately, **H₂S** gas was reacted and the remaining DO was analyzed by measuring the liberated iodine, which is proportional to DO. (Refer to Testing Procedures).
- In one instance, DO control became erratic. It was discovered that the AMERZINE™ 35 metering pump had a leak in the suction line, thus causing oxygen to be carried in with the solution. An o-ring was replaced and the problem was corrected.

Attached are test procedures, graphs and recorded DO readings in reference to this project.

7.0 CONCLUSION

AMERZINE™ 35 has proven to be a cost effective and efficient means to reduce dissolved oxygen levels in a geothermal power plant reinjection fluid system. Dissolved oxygen levels are continuously controlled at 4 to 6 ppb, using only 1.5 kg per day of chemical. This low cost alternative has enabled the power plant to meet established reinjection fluid control limits. This has resulted in the power plant avoiding huge capital expenditures to solve potential corrosion problems.

ACKNOWLEDGMENTS

The attempt to reduce dissolved oxygen to a level of less than 10 ppb was a service provided to Cal-Energy whose Cebu Geothermal Power Plant in Malitbog is being treated by Global/Drew. The team who worked on this project was S. Corros (Cal-En), G.Taplac, R. Palad, D. Cordova (from Global), and Dr. P.S. **Hb** (Drew).

All probable causes (e.g. retention time, elements affecting AMERZINE™ 35 performance, air intrusion during sampling, creation of vacuum during low loads, etc.) that had an impact on DO measurements were

finally eliminated. This could not have been possible without the contribution of the Malitbog laboratory personnel. Their efforts played a major role in developing a viable solution to these problems.

ATTACHMENTS

I. SAMPLING

A one-liter gas sampling flask with one end attached to hose connected to condenser sampling port. Both valves at both ends of flask are opened to let sample overflow at the other end. Water sample is allowed to flow for five minutes, making sure that gases are trapped inside the flask. Both valves are closed and sample is analyzed immediately.

Flow rate of cooling water of the condenser is adjusted so that final sample is within 23° to 25°C.

II. DO ANALYSIS

1. Glasswares/Equipment

- One-liter gas flask
- UV-Vis Spectrophotometer
- 100 mL VF
- 5 mL syringe
- 200 mL Griffin beaker

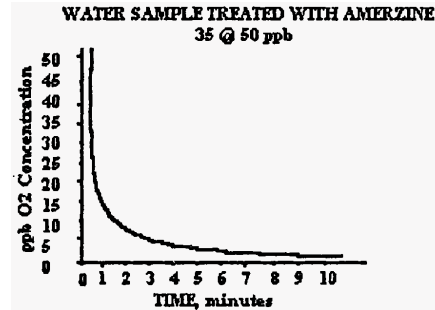
2. Reagents

- a. Azide reagents - dissolve 750 g KOH and 150 g KI in 500 mL distilled water, add solutions of 10 g NaN₃ dissolved in 40 mL water. Dilute to one liter.
- b. Manganous sulfate solutions - dissolve 364 g MnSO₄ · H₂O in 500 mL water and dilute to one liter.
- c. Sulfuric acid, concentrated
- d. Potassium permanganate solution (1%)
- e. DPD Powder Pillows

3. Analysis

Dissolved Oxygen is analyzed using modified Azide method, Iodometric test. It is based on the

addition of divalent Manganese solution, followed by alkali iodide azide reagent. Dissolved Oxygen rapidly oxidizes an equivalent amount of the disperse divalent Manganous Hydroxide precipitate to hydroxide of higher valency state. In the presence of iodide ions in an acidic solution, the oxidized Manganese reverts to its original divalent state. With the liberation of iodine equivalent to the original DO contents of the sample. The liberated iodine is then determined using DPD colorimetric method.

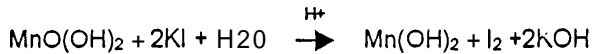


Note all reagents were added using 5 mL syringe.

4. Chemical Reactions



Mn(OH)₂ floc act as gathering agent for oxygen



III. GRAPHS

1. The curve formed during lab test was at same trend on curves from DREW Principles of Industrial Water Treatment Book
2. The following graphs from DREW Principles Of Industrial Water Treatment were used as reference to arrive at the usage of AMERZINE™ 35. See figures 12-2 and 12-4. A graph using water sample from reinjection well with DO at approximately 50 ppb was treated with 50 ppb A-35.

