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SAMPLING AND ANALYTICAL METHODS DEVELOPMENT AT THE HGP-A GENERATOR FACILITY

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ABSTRACT

During shakedown operations for the HGP-A generator plant sampling and analytical problems were encountered during the process chemistry monitoring effort. Acid-preservation of brine for cation analysis required the use of nitrous oxide-acetylene flame for accurate A-A analysis of calcium. Analysis of gases for carbonate and sulfide was by specific ion electrode and alkalinity titration, respectively. Sulfide caused substantial interferences with the alkalinity method and corrections for sulfide were required. Sulfide also interfered with chloride analyses in the steam phase requiring removal of the sulfide by boiling. Analysis of dissolved silica in the brine was complicated by the presence of colloidal silica which produced erratic analytical results. An accurate evaluation of the hydrogen sulfide abatement system was possible only when the hydrogen sulfide concentrations in the treated and untreated steam were compared with a second component in the steam phase that was unaffected by caustic injection.

INTRODUCTION

Construction of the HGP-A turbine generator facility on the island of Hawaii was completed in June of 1981 and operations for start up of the plant were initiated on June 12, 1981. Beginning then, and continuing to the present, the chemical compositions of a number of process streams throughout the plant have been monitored.

PLANT PROCESS

The HGP-A generator facility (Figs. 1 and 2) is fed by a single geothermal well with an output capacity of approximately 23,000 kg/hr (50,000 lb/hr) of steam and 23,000 kg/hr (50,000 lb/hr) of water. Mixed fluid from the well is piped to a centrifugal separator/demistor vessel where the brine fraction is removed from the steam phase at 1,200 kPaa (175 psia). The brine stream is passed through a pressure reduction valve to atmospheric pressure and, after passing through a muffler box and silica settling pond, it is allowed to percolate into the ground.

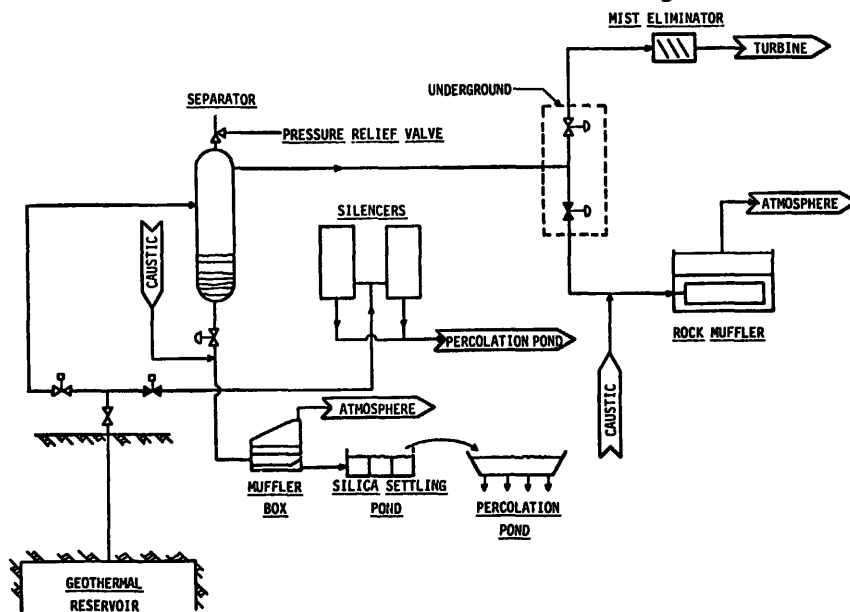


Fig. 1 HGP-A Geothermal Generator Project steam supply process.

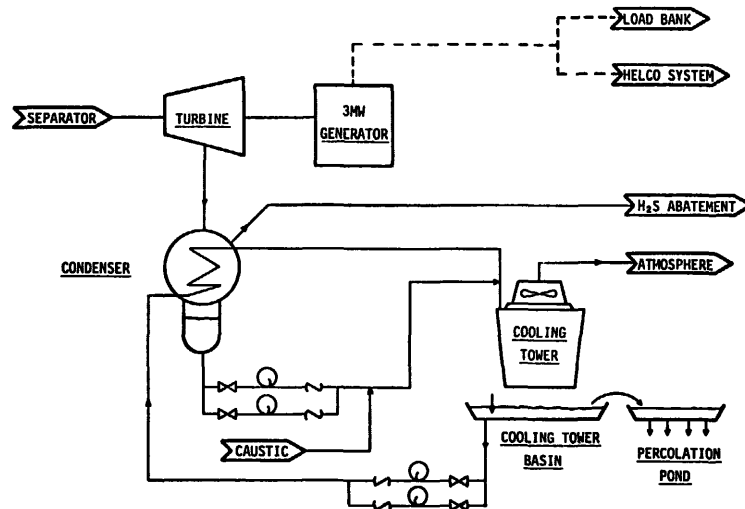


Fig. 2 HGP-A Geothermal Generator Project output and heat rejection.

The steam phase from the separator, under normal operating conditions, passes through a second mist eliminator and the power plant trip and control valve manifolds to the turbine. The turbine exhaust is piped to a stainless steel surface condenser and the steam condensate, after pH adjustment, is pumped into the cooling water return line as make-up water for the forced draft cooling tower. The non-condensable gases are ejected from the condensate into a thermal oxidizer where the hydrogen sulfide fraction is incinerated to form sulfur dioxide that is subsequently scrubbed with caustic soda in a packed column. The tail gas from the scrubber column is piped to the air intake of the cooling tower where, as a final treatment, the cooling water cascade removes sulfur particulates from the gas stream.

When the power plant turbine is not operating at full capacity, part or all of the steam from the plant separator is diverted to a pressure reduction valve where it is passed to the atmosphere through a caustic abatement system and rock muffler.

PROCESS MONITORING

The locations at which the process chemistry was monitored, and the species for which analyses were made, are as follows.

(1) The high pressure brine discharge line immediately downstream of the plant separator was monitored for major element compositions including SiO_2 , Cl^- , H_2S , Na , K , Ca , Mg , SO_4 . Silica was monitored to indicate the changes in reservoir temperatures; chloride, to determine the stability of the production aquifers; and H_2S to determine sulfide emission rates from the brine discharge

point. The other species were analyzed as a check on scale formation within the production zone of the well.

(2) The high-pressure steam line immediately downstream of the plant separator was monitored for non-condensable gases, chloride, and silica. The N-C gases were used to evaluate the gas load and air requirements of the incineration system, and chloride was used to determine the fraction of brine particulate that was being passed by the plant separator/demister vessel.

(3) The condensate discharge line from the plant condenser was monitored for pH and N-C gas content and for chloride concentrations. The former data were used to evaluate partitioning of the N-C gases between the condensate and gas phase, and the latter to check on the chloride measurements upstream of the turbine.

(4) The incinerator column gas discharge line was monitored for hydrogen sulfide and sulfur dioxide to evaluate the abatement efficiency and compliance with emission requirements for the plant.

(5) The silica precipitation tank was monitored for silica concentration to check the effectiveness of the pond in removing dissolved silica.

(6) The rock muffler discharge was monitored for hydrogen sulfide to check the effectiveness of the abatement system and compliance with emission regulations, and for pH to ensure that the steam discharge was not emitting significant quantities of the caustic soda injected into the steam line for hydrogen sulfide abatement.

SAMPLING AND ANALYTICAL PROCEDURES

The sampling procedure for the pressurized brine was essentially that described by Kindle and Woodruff (1981). Although their recommended

on-site analytical procedures for chloride, silica and dissolved gases were satisfactory, later analysis of the major element chemistry did encounter one significant problem. The sample preservation and analytical method recommended for cation samples was acidification of raw and filtered samples and later analysis by atomic absorption spectroscopy. Using this method, we found that the calcium concentrations in the acidified samples were indicated to be approximately 30% of those in the non-acidified samples for both filtered and unfiltered splits. Subsequent analysis indicated that a nitrous oxide/acetylene flame was required to obtain accurate concentration values for calcium ion. This situation suggests that silica polymerization or complexing is in some way binding the dissolved calcium ions. It is not presently known whether a similar effect is occurring for the trace elements in the brine; however, this possibility is being investigated.

Initially, steam samples were obtained from a $\frac{1}{2}$ -inch insulated line attached to a port on the side of the main steam line. This sampling procedure was found to be unacceptable because of condensation in the sampling line. Subsequent experimentation found that, lacking sample probe access directly into the steam line, an acceptable alternative was a steam jacketed $\frac{1}{8}$ -inch probe (Fig. 3). The steam samples obtained were condensed into a cooling water-jacketed evacuated bottle containing 4 N sodium hydroxide.

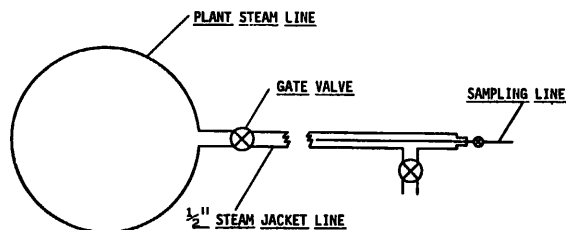


Fig. 3 Steam Jacket Sample Line.

Analysis of the samples for non-condensable gases was by gas chromatography for the non-absorbable gases (N_2 , H_2 , CO) and by specific ion electrode and alkalinity titration for H_2S and CO_2 , respectively. Sulfide concentrations in the samples were high enough to result in substantial interferences from HS^- ion in the carbonate determinations. Precipitation and oxidation of the sulfide were attempted, but the results were inconsistent; the only reliable method found for overcoming the sulfide interferences was to perform the alkalinity titration over a pH range of 11.5 to 3.5 and then correct the acid volume used by that required for a similar titration (over the same pH range) of a carbonate blank having a sulfide concentration identical to that of the sample.

Chloride analyses of the steam condensate also encountered interferences from dissolved sulfide ion even for raw condensate taken without caustic. Precipitation of the sulfide by nickel

nitrate or lead nitrate did not reduce the sulfide concentration sufficiently to eliminate the interference. The only method effective for eliminating the interference was to acidify and boil the sample down to one-tenth its original volume to drive off the sulfide and concentrate the chloride in the remaining liquid. Another method presently being investigated is pre-concentration of the chloride and removal of sulfide through the application of ion exchange resins.

The condensate discharge sampling procedures for non-condensable gases were straightforward provided that the liquid was introduced directly into a caustic medium (Kindle and Woodruff, 1981). Without this precaution, dissolved H_2S and CO_2 were rapidly lost to the atmosphere. The analytical procedures were identical to those described above for carbonate, sulfide and chloride ions.

The incinerator packed-column gas discharge was monitored with a lead acetate tape continuous monitoring system. Under normal operating conditions this method was successful; however, under flame-out of the incinerator, the sulfide levels in the column gases were sufficiently high to affect the entire tape spool in the instrument and render it useless. Sulfur oxides from the column effluent were initially sampled intermittently by disposal gas detection tubes; however, absorption of a measured volume of effluent into a caustic impinger is presently believed to yield more reliable results for total sulfur emission rates.

Analysis of silica concentration in the silica precipitation pond proved to be an intractable problem. Whereas the silica present in the high-pressure brines seemed stable enough to allow dilution before polymerization occurred, the change in pH of the liquid phase from 7.5 to 8.5, brought about by the atmospheric flashing of the hot pressurized brine, induced the rapid formation of colloidal silica in the brine phase. Filtered and diluted (10:1) brine samples yielded inconsistent results with the molybdate blue method even after several days of reequilibration. Later analysis of these samples by nitrous oxide/acetylene atomic absorption provided better results, although the variations in the data suggest that there still may be analytical problems to be resolved.

A precise evaluation of the sulfide concentration present in the steam emissions from the rock muffler was a relatively straightforward procedure. Steam condensate and non-condensable gases were drawn into a caustic solution through an evacuated flask. The major requirement with this procedure is the exclusion of air from the sample solution; the introduction of atmospheric oxygen into the sample allows oxidation of sulfide to sulfate to occur in the basic medium.

Although the above procedure yields an accurate representation of the sulfide present in the atmospheric steam emissions, an evaluation of the efficiency of the abatement system, in terms of

percent removal of the original sulfide present, required a further step. As the hydrogen sulfide-to-water vapor ratio in the steam phase is altered by the addition of de-superheat water to the steam line downstream of the pressure reduction valve, it is necessary to ratio the H₂S concentration in the emitted steam to another component in the steam phase that is unaffected by caustic treatment. In the present case, the hydrogen concentration in the steam emissions was used as the second component. Comparison of the H₂S:H₂O ratios in the steam before and after caustic treatment yielded the required abatement efficiency values.

SUMMARY OF CURRENT DATA

A summary and discussion of the plant process chemistry data acquired during this monitoring program is presented elsewhere in this volume (Thomas, 1982). However, in general terms the following observations have been made during the first nine months of operations of HGP-A:

1. The HGP-A well fluid chemistry is following a slow but predictable trend of increasing chloride concentration.
2. The non-condensable gases make up about 0.2% of the steam phase.
3. Brine carryover through the separator/demistor system is about 0.03%.
4. Less than 1% of the non-condensable gases are partitioned into the exhaust steam condensate from the exhaust steam condenser.
5. The turbine off-gas hydrogen sulfide abatement system is operating at better than 99% efficiency.
6. The abatement efficiency of hydrogen sulfide in the turbine standby (rock-muffler) system is about 90% at a mole ratio of 3 NaOH to 1 H₂S.
7. Silica precipitation in the silica settling pond is occurring at a very slow rate.

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