Coso Geothermal Field

15 Years of Successful H_2S Emission Abatement

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Introduction

Geothermal power plants are environmentally attractive since they employ a renewable energy source, which unlike wind and solar is continuous. However, geothermal steam contains varying amounts of non-condensable gases (NCG) such as carbon dioxide (CO_2, hydrogen sulfide (H_2S), mercury vapor (Hg) and in some cases benzene (C_6H_6), which if not disposed of properly may cause environmental, health and safety problems. This article describes the operating history of three geothermal power facilities, which have been operating for over 15 years while meeting strict California emission regulations.

Facility History

Terra-Gen Power LLC operates a geothermal power facilities located on the China Lake Naval Weapons Center in southeastern California. As illustrated in Figure 1 (*see* page 23), hot brine is extracted from high pressure, underground wells. The brine is flashed and the produced steam is passed through condensing turbine/generator sets, which produce approximately 250 MW of electrical power, which is sent into the local power grid. This is enough power to service approximately 250,000 homes. The unflashed brine and condensate from the turbine/generator sets are reinjected into the geothermal reservoir and the non-condensable gas (NCG), consisting mostly of carbon dioxide (CO_2), is sent to treatment facilities. Initially, the NCG was reinjected back into the reservoir; however, over time this practice began to affect the performance of the reservoir and the practice was stopped. It

Navy II Geothermal Power Facility, China Lake Naval Weapons Center, California. PHOTOS AND GRAPHICS COURTESY OF MERICHEM.

was then decided to remove the hydrogen sulfide, H_2S, and mercury, Hg, from the NCG and exhaust the remaining gas, CO_2 and water vapor, to the atmosphere. In 1993, a former owner of the facility began an investigation into various H_2S and mercury removal systems. This investigation resulted in the selection of the LO-CAT® process for H_2S removal, with a sulfided, activated carbon media upstream of the process for mercury removal. These systems were initially installed at the Navy I and Navy II facilities. A third system was later added at Navy II due to larger gas loading than previously anticipated. The LO-CAT process is licensed by the Merichem Chemicals & Refinery Services LLC.

The LO-CAT® Process

The LO-CAT process is an isothermal, low operating cost method for carrying out the direct oxidation of H_2S to elemental sulfur as depicted in equation 1.

$$H_2S + 1/2\ O_2 \rightarrow H_2O + S^o \quad (1)$$

This reaction is accomplished in an aqueous (water based) scrubbing system by using a water soluble metal ion which is capable of being oxidized by oxygen in ambient air or in the process gas stream, and has a suitable electropotential for oxidizing the sulfide ion to elemental sulfur. In other words, the reaction is carried out in a water solution which contains a metal ion which is capable of removing electrons (negative charges) from a hydrosulfide ion (HS^-) to form sulfur and, in turn, can transfer the electrons to oxygen (O_2) in the regeneration process. Although there are many metals that can perform these functions, iron (Fe) was chosen for the LO-CAT process because it is inexpensive, non-toxic and is a good oxidation catalyst.

The basic reactions of the LO-CAT process can be divided into the **ABSORPTION** and **REGENERATION** portions as follows:

H_2S ABSORPTION:

$$H_2S\ (gas) + H_2O \leftrightarrow H_2S\ (aq) + H_2O \quad (2)$$

First Ionization

$$H_2S\ (aq) \leftrightarrow H^+ + HS^- \quad (3)$$

Oxidation by Ferric ions (Fe^{+++})

$$HS^- + 2Fe^{+++} \rightarrow S^o\ (solid) + 2Fe^{+++} \quad (4)$$

OVERALL ABSORPTION REACTION

$$H_2S\ (gas) + 2Fe^{+++} \rightarrow 2H^+ + S^o + 2Fe^{++} \quad (5)$$

REGENERATION:

Absorption

$$1/2\ O_2\ (gas) + H_2O \leftrightarrow 1/2\ O_2\ (aq) + H_2O \quad (6)$$

Regeneration of Ferrous Ions (Fe^{++})

$$1/2\ O_2\ (aq) + H_2O + 2Fe^{++} \rightarrow 2OH^- + 2Fe^{+++} \quad (7)$$

OVERALL REGENERATION REACTION

$$1/2\ O_2\ (gas) + H_2O + 2Fe^{++} \rightarrow 2OH^- + 2Fe^{+++} \quad (8)$$

aq = aqueous

Adding Equations 5 and 8 yields Equation 1.

Two additional views of the Navy II facility.

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System Design

As previously mentioned, three LO-CAT units were installed at the Coso facility to handle the gas streams from 6 geothermal power plants. The design parameters for each of these units were as follows:

	Inlet NCG Gas Flow	Outlet H_2S Concentration	Sulfur Removed
Unit I	3,688 SCFM	< 10 ppm	2.41 LTPD
Unit II	6,774 SCFM	< 10 ppm	5.77 LTPD
Unit III	9,822 SCFM	< 10 ppm	10.0 LTPD

SCFM = Standard Cubic feet per minute
LTPD = Long tons per day
ppm = Parts per million

Since the treated NCG from each unit could be exhausted to the atmosphere in accordance with air permit requirements, an "Autocirculation LO-CAT unit" was selected for these applications. In this process configuration (Figure 1), the Autocirculation vessel contains a series of baffle and weir combinations, which not only separates the Absorption sections from the Regeneration sections but also provides a series of hydraulic pumps produced by the aerated liquid on one side of the baffle and the non-aerated liquid on the other side of the baffle, which provide the motive force for circulating solution from one chamber to the next. The process flow diagram for each Unit is shown in Figure 2.

The discharge gas from the NCG compressors is initially processed through a bed of pre-sulfided, activated carbon in which the mercury vapor is removed from the gas stream by

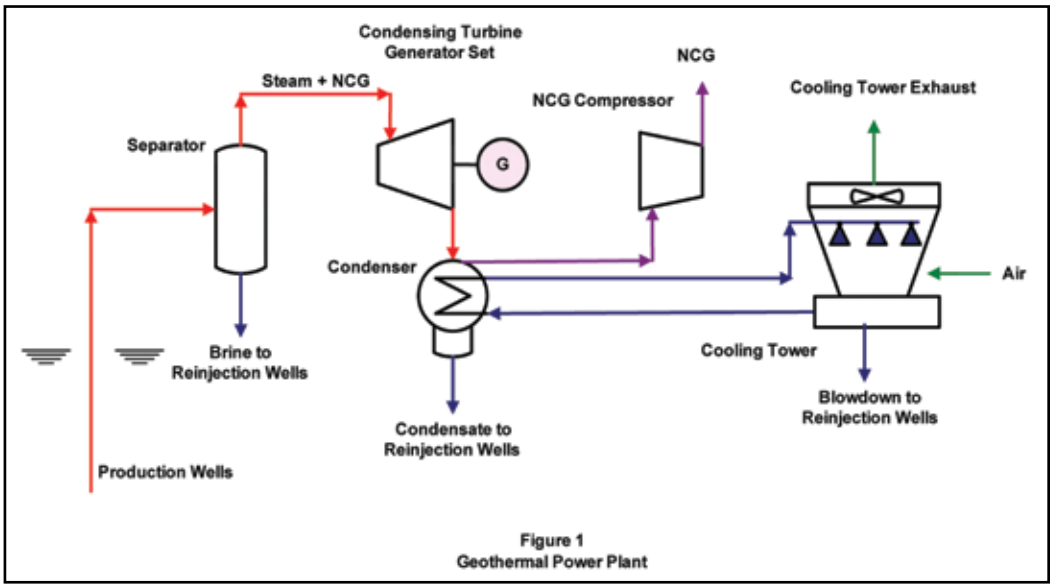

Figure 1
Geothermal Power Plant

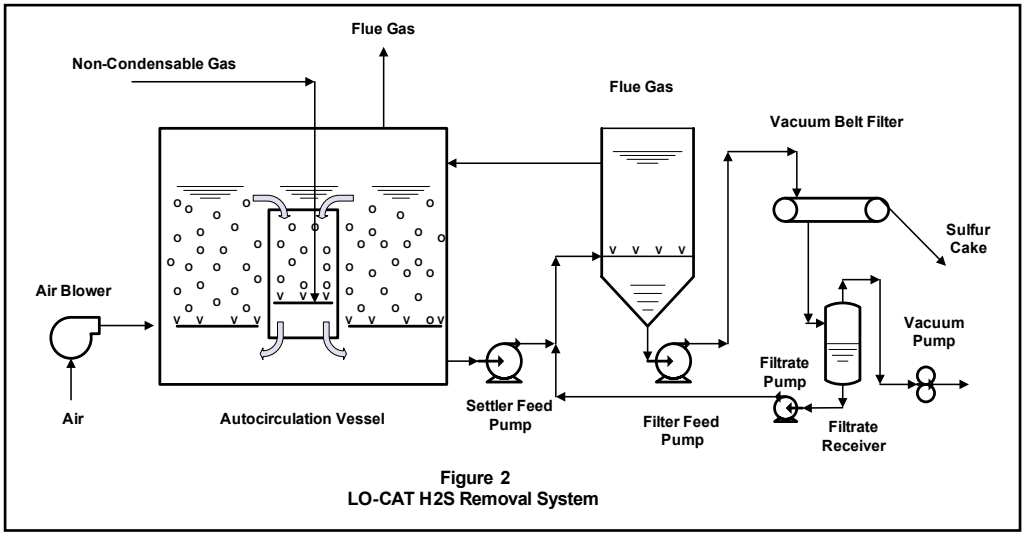

Figure 2
LO-CAT H2S Removal System

adsorption onto the activated carbon. The NCG is then directed into the Autocirculation LO-CAT vessel where the H_2S is absorbed into the LO-CAT solution and rapidly converted into solid, elemental sulfur, which remains suspended in the circulating solution. The LO-CAT solution is then contacted with air in a separate chamber(s) and the iron is reoxidized. The spent air and sweet NCG are combined and exhausted to atmosphere.

A small slip stream of solution is pumped from the Autocirculation vessel and directed to a Settler where the sulfur is allowed to settle into a concentrated slurry, which is directed to a vacuum belt filter. The sulfur cake is washed with water on the filter, the filtrate is returned to the unit and the sulfur cake is sold as fertilizer/fungicide at approximately 70 wt. % sulfur. LO-CAT sulfur has excellent soil absorption characteristics. In addition, residual surfactant, which is employed in the LO-CAT process, enhances the hydrophilicity of the sulfur and the chelated iron and thiosulfate contained in the process solution also add micronutrients to the product sulfur.

Operating History

As required in the operating permits, the effluent gas streams from each unit are continuously monitored via lead acetate type monitors provided by Delmar Inc. Over the 15 years of operation, the three LO-CAT units have consistently exceeded the H_2S removal efficiency required by the operating permits, which equates to greater than 99.9% removal efficiency. In 1996 Tom Mason, the President and Chief Operating Officer of CalEnergy Company, Inc – the owners of the facility at that time, stated(A) "The statistics clearly demonstrate the success of the company's efforts. CalEnergy believes that the LO-CAT H_2S abatement systems currently in place at Coso constitute the best available control technology (BACT)".

Normally LO-CAT units have fairly large solution inventories, and for units processing CO_2, as in these cases, the LO-CAT solution is well buffered with $KHCO_3$ and K_2CO_4; consequently, changes to the solution chemistry and the unit's performance are never immediate but occur over a fairly long time period. This operating characteristic results in minimum monitoring of the operations. Generally, the only duties of an operator is to measure the pH and redox potential of the solution on a daily basis and the iron concentration on a weekly basis and then make the corresponding adjustments to the chemical addition pumps. This takes no longer than 2 to 3 hours per day of an operator's time.

Maintenance

The original Autocirculation and Settler vessels for all three units have not experienced any corrosion or significant repair over the 15 years of operation. The original progressive cavity pumps, which were employed to transfer sulfur slurry from the Autocirculation vessel to the Settler did experience stator erosion and were replaced with a gravity feed system. The filter cloths on each vacuum belt filter are normally replaced every 3 to 6 months. The rubber belt drive is replaced every 2 to 3 years. The LO-CAT units are designed such that the filter cloth and belt can be replaced while the LO-CAT unit continues to run.

The entire power trains are shut down for maintenance once a year. During that shut down period, the LO-CAT units are also serviced. This service includes removal of the NCG and oxidizer air spargers for inspection, cleaning, and repair as necessary, as well as cleanout of the LO-CAT vessels, and pump and equipment maintenance as required. Through detailed planning by plant personnel, a complete turnaround of a LO-CAT unit can be conducted in 2 days.

Summary

After 15 years of operation, Terra-Gen Power LLC considers that the LO-CAT units at its geothermal power facilities located in the China Lake Naval Weapons Center in southeastern California continue to provide "Best Available Control Technology" (BACT) for its geothermal power plants. ■

(A) Mason, T. L., "CalEnergy Coso Operation: A Substantial Commitment to the Environment Pays Off", The GRC *Bulletin*, June 1996.