Coso Case Study: 22 Years of Reliable Sulfur Removal

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ABSTRACT

Terra-Gen Power operates a 300-megawatt electric generation facility at the China Lake Naval Weapons Station. The geothermal steam wells at the Coso facility provide a renewable source of energy. The non-condensable vapors from the steam well cannot be vented to the atmosphere until small amounts of hydrogen sulfide (H_2S) are removed. The LO-CAT® process has been successfully removing H_2S at this site for the past twenty-two years. Using LO-CAT technology greatly reduced sulfur emission exceedances and operating costs relative to previously used technologies.

The facility has three LO-CAT units. This paper analyzes over 500 hundred data points obtained during a 22-year period and calculates the current cost of removing sulfur at this facility. It also discusses typical operational issues including routine operator duties, H_2S removal efficiency and long-term unit reliability (planned and unplanned shutdowns). The paper also explains how the solid sulfur product is used in agricultural applications.

Introduction

LO-CAT® technology is a liquid reduction-oxidation process that uses catalyst in an aqueous solution to convert hydrogen sulfide into elemental sulfur.

Plant History

Terra-Gen Power operates a 300-megawatt electric generation facility at the China Lake Naval Weapons Station approximately 170 miles northeast of Los Angeles, California at Coso Junction. After they are tapped and gathered, the steam wells produce electricity from the renewable geothermal energy source. The produced steam is passed through a set of turbines / generators. Non-condensable vapors are separated from the condensed steam (water) at low pressure. Finally, the brine is reinjected into the geothermal field.

The non-condensable vapors cannot be vented to the atmosphere until small amounts of hydrogen sulfide (H_2S) are removed. When the plant initially started up, the H_2S-laden vapors were reinjected into the geothermal field with the water. Over time, this H_2S abatement method became more costly, mostly due to compressor maintenance. In 1993, the first of three LO-CAT units was installed. After startup the non-condensable carbon dioxide and hydrogen sulfide are flashed, compressed and routed to the LO-CAT unit for sulfur removal before being emitted into the atmosphere.

The LO-CAT process has been removing H_2S at this site for the past 22 years. This technology greatly reduced sulfur emission exceedances and operating costs relative to technologies used prior to installing the LO-CAT unit.[1]

The site has a total of four power generation facilities, two of them containing LO-CAT units: the Navy 1 power plant and Navy 2 power plant. There are a total of three LO-CAT units, per Tables 1 and 2. Note that at the Navy 2 site, there are two LO-CAT units, the Navy 2 unit, and the Navy 210 unit. Only the Navy 210 unit will be discussed because the Navy 2 unit is only periodically operated.

Overall, the units have operated well throughout their history. This paper reviews the performance data from the of the Navy 1 and Navy 210 LO-CAT unit operations, including the performance, stability and reliability of unit operations. The current cost per ton of sulfur produced will also be reviewed.

Table 1. Year Built and Current Status.

Plant Name	Power Generated (MW)	Year LO-CAT Installed	Currently Operating
Navy 1	75	1993	24/7
Navy 2	90	1993	On Standby
Navy 210	90	1996	24/7

Table 2. Unit Design Parameters.

Plant Name	Raw Gas Flowrate SCFM	Inlet H_2S (vol%)	LTPD* Recovered Sulfur
Navy 1	3688	1.18	2.4
Navy 2	6774	1.55	5.8
Navy 210	6228	3.00	10.0

*Long Tons Per Day

LO-CAT Process Description and Process Flow

The LO-CAT process converts H_2S contained in the raw feed gas into elemental sulfur via the following equation (see Figure 1 for the process flow scheme):

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

Before entering the LO-CAT unit, raw feed gas passes through an activated carbon bed to absorb mercury and other heavy metals. The raw gas then enters the autocirculation vessel where the H_2S is absorbed into a proprietary LO-CAT catalyst solution. The catalyst is deactivated in the absorber section where H_2S is converted to elemental sulfur. Subsequently, the catalyst is regenerated in the oxidizer section of the same autocirculation vessel. Regeneration is achieved by contacting the LO-CAT solution with oxygen contained in air. The air and sweetened gas exit to the atmosphere as vent gas. The LO-CAT solution is circulated between the absorber and oxidizer sections via a system of baffles and weirs with density difference as the driving force.

Elemental sulfur formed via the reaction becomes suspended in the catalyst solution. To remove the elemental sulfur from the process, a circulation pump sends a slip-stream of solution to a settler vessel which allows the sulfur to concentrate and form a slurry. The slurry is routed to a filter which separates the sulfur from the LO-CAT solution and washes the filter cake. The sulfur is discharged into a sulfur bin while the clarified solution, i.e., filtrate, is returned to the autocirculation vessel.

Even with water washing of the sulfur filter cake, some LO-CAT solution exits with the solid sulfur. Makeup catalyst is added to maintain the solution at optimum concentrations. A surfactant is added to help prevent foam and floating sulfur. Potassium hydroxide (KOH) is added for pH control.

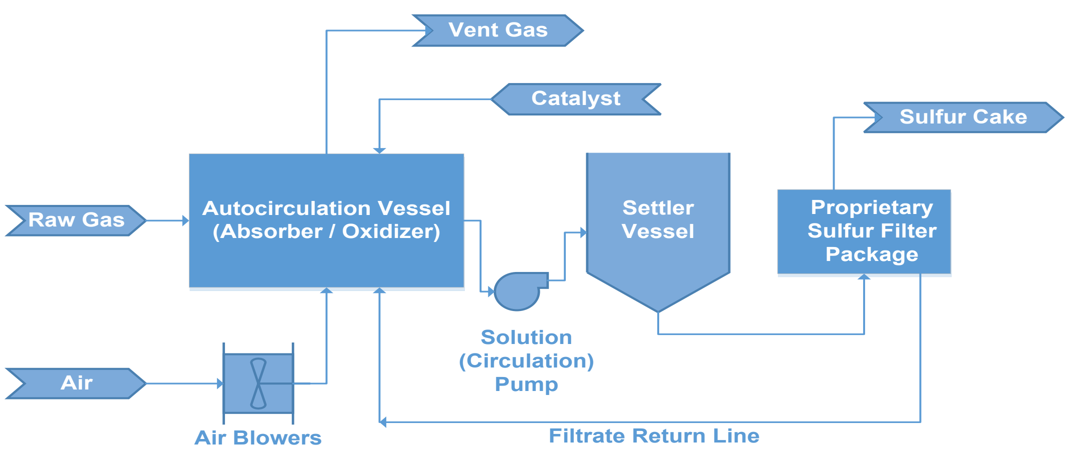

Figure 1. Simplified Flow Diagram of the LO-CAT Unit.

Operations Review

Two key parameters ensure consistent LO-CAT operations as follows: (1) Prevent sulfur from settling in incorrect places, and (2) Maintain proper solution chemistry. Catalyst makeup and chemical addition rates are discussed in the next section of this paper.

Operating practices keep sulfur from settling in the wrong places within the unit. The main method is to use “air blasts” that are placed strategically throughout the unit in regions of low flow. Nozzles send bursts of air into stagnant areas within of the autocirculation and settler vessels, preventing sulfur buildup. When feed gas flows through the unit at the process design rate, sulfur in solution is less likely to settle in the wrong places within the unit.

Coso and Merichem have developed special flushing and "sparger shuffling" methods to prevent sulfur settling when the unit is operating at low flow rates. The gas flow to each sparger head (internal vapor distributors) is blocked, allowing gas pressure buildup. Water is then periodically flushed through the spargers to keep them clean. This "shuffling" is done approximately every 4 – 8 hours to each sparger in rotation.

Because of this attention to detail, Coso is able to run both active LO-CAT units consistently for a full year until the entire plant takes the mandated geothermal field shutdown. The annual turnaround takes 2-3 days from gas-off to gas-in. The shutdown and turnaround are always completed, even if the unit may not need it. The need for a shutdown is determined by the back-pressure on the raw gas compressors. An increase in raw gas back-pressure indicates sulfur buildup on the floor or at the spargers of the autocirculation vessels. Unplanned outages due to high back-pressure are very rare. Outages are typically due to low or no-flow from the upstream power plants, which causes sparger plugging.

The H_2S removal performance of the Navy 1 and Navy 210 units is summarized in Figures 2 and 3.

The Navy 1 unit was designed for 1.2 vol% H_2S in the feed gas but experienced highs of 1.4-1.5 vol% during its first 5 years of operation. Those peaks came less often over the last 17 years. The inlet H_2S has been fairly consistent between 0.8 and 1.3 vol% (8,000 to 13,000 ppmv) with average concentrations close to 1.0 vol%.

Navy 1 initially produced sulfur at design rates of 2.4 LTPD with spikes up to 2.7 LTPD. Over time, average sulfur production actually increased before declining to current sulfur production of 1.25 – 1.75 LTPD. The reason for sulfur production decreasing over time is that water condensed from the steam wells (now free of sulfur) is injected into the geothermal reservoir. This dilutes the sulfur content of the produced steam. The LO-CAT unit was adapted to turndown conditions via the sparger shuffling procedure mentioned earlier.

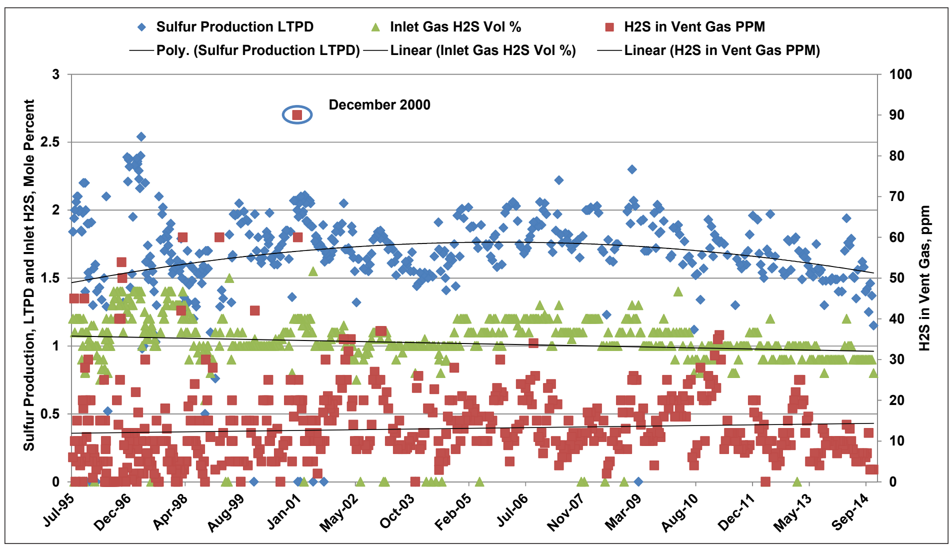

Figure 2. Sulfur Data for Navy 1 Unit.

During the early years of operation, the Navy 1 unit experienced periodic high H_2S in the vent gas. These few instances of exceedance were lower than for other technologies employed to meet environmental standards before the LO-CAT unit was installed. One incident occurred in December 2000 when the vent gas H_2S was reported at 90 ppmv. As shown in Figure 4, this happened because the solution chemistry was out of balance. All readings above 30 ppmv correlate to rapid changes in the feed gas conditions that required operator response. Since early in 2001, the vent gas H_2S has rarely exceeded 30 ppmv. Typical performance measures about 15 ppmv which maintains the unit within environmental permit requirements.

The Navy 210 unit was designed for 3.0 vol% H_2S in the feed gas but H_2S levels have never exceeded 2.8 vol%. Today, inlet H_2S has declined from an average of 2.0 vol% to about 1.0 vol%.

At startup, the Navy 210 LO-CAT unit initially produced sulfur at rates of 4-6 LTPD with spikes up to 7.2 LTPD. Over time, average sulfur production declined to 3-4 LTPD.

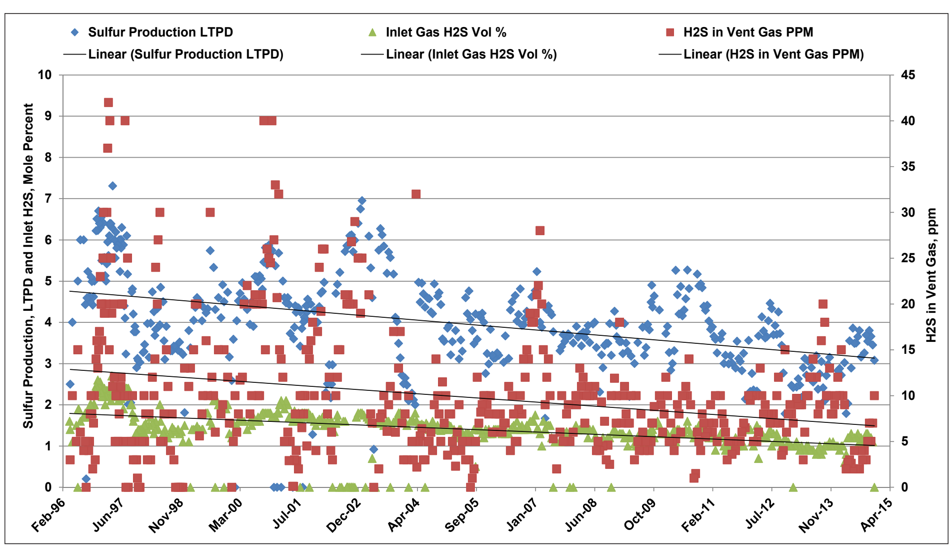

Figure 3. Sulfur Data for Navy 210 Unit.

The startup and operations experience from Navy 1 helped the startup and operation of Navy 210 unit. Initially, the H_2S in the vent gas averaged 15 ppm with occasional spikes ranging from 30-40 ppmv. Since 2007, the vent gas H_2S has averaged less than 10 ppm with occasional spikes up to 20 ppm. Despite these spikes, the treated gas has consistently complied with environmental permit requirements.

LO-CAT Solution Maintenance

In general, LO-CAT units offer robust, consistent performance that meet unit design criteria over a wide range of operating conditions, including varying inlet gas flow rates and composition. This performance is possible by maintaining the working catalyst solution within a defined range of alkalinity, catalyst concentration, and sufficient regeneration. Trending daily solution analysis results helps operations keep the solution within an optimum range. However, rapid changes in the inlet gas rate and composition can cause excursions that could result in off-specification treating. Additional solution testing immediately after measurable inlet gas changes helps operations maintain solution chemistry during the "upset" and mitigate any adverse treating effects.

Merichem recommends monthly detailed analysis but Coso decided to send a sample to Merichem every two weeks. This generated a large amount of operating data for analysis. Merichem's detailed analyses show that the proprietary chemicals solution concentrations have stayed relatively stable throughout the 22 years of operating both of these LO-CAT units.

Coso measures the alkalinity and oxidation-reduction potential (ORP) of the regenerated LOCAT solution daily. This ensures the unit operates reliably because these measurements determine the chemical addition rates needed to keep the solution chemistry within the required guidelines. Coso also performs a shake test that measures how quickly the sulfur particles sink to adjust the rate of surfactant addition.

ORP measurements indicate whether the catalyst solution is properly regenerated in the oxidizer, a key parameter for determining catalyst activity. As shown in Figures 4 and 5, ORP typically stayed within the optimum operating range. If the catalyst is over regenerated (e.g. data points above the optimum range), chemical usage is higher. Under regenerating the catalyst (e.g. data points below the optimum range) reduces the active catalyst available for sulfur reaction and may cause off-specification treating in the absorber section. It appears this was the case early in the operation of the Navy 1 unit which may have caused some of the high H_2S in the vent gas that was noted in Figure 2.

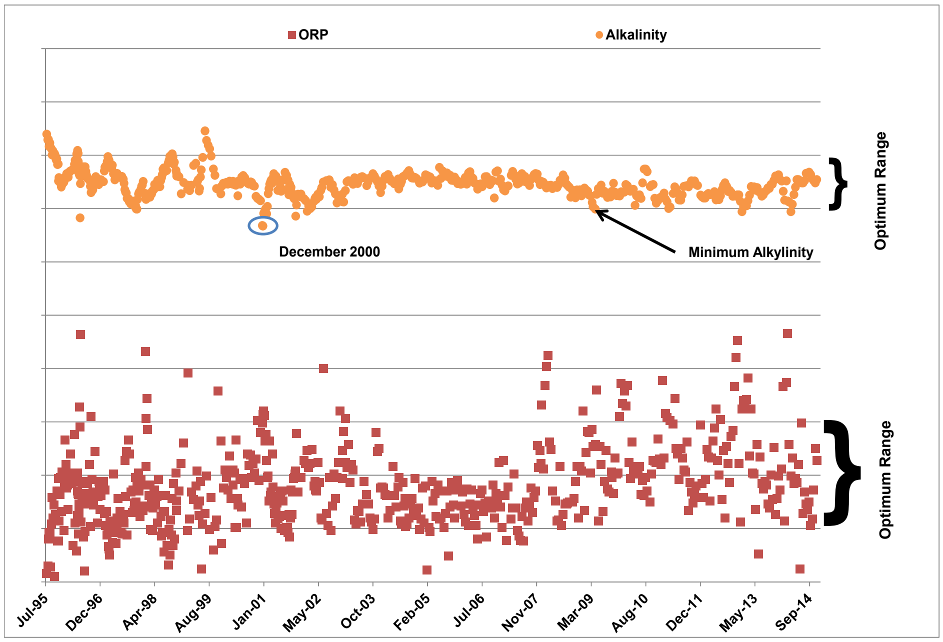

Figure 4. Solution Analyses for Navy 1 Unit.

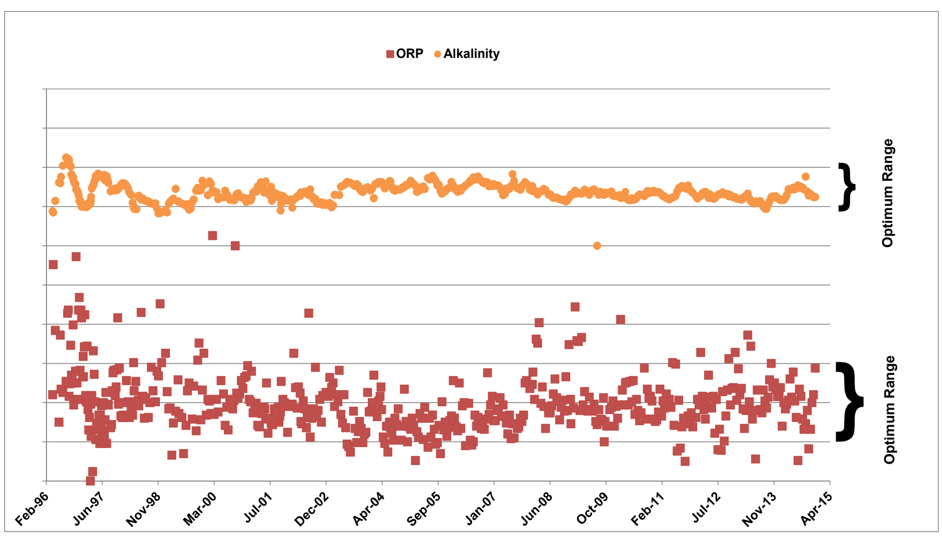

Figure 5. Solution Analyses for Navy 210 Unit.

One thing discovered during the early years of Navy 1 unit operations was the importance of alkalinity as an operating variable rather than pH. Most LO-CAT units monitor pH only, however, that is not the case when treating streams with high concentrations of carbon dioxide (CO_2). Large amounts of acidic CO_2 in solution reach equilibrium with the basic LO-CAT solution and serve as a buffer, stabilizing the pH. This makes pH measurement a less responsive indicator of the solution's H_2S solubility. In addition, raising the alkalinity is known to reduce the solubility of CO_2 in the LO-CAT solution.

In December 2000, the Navy 1 unit data (Figure 4) indicated the solution alkalinity was at an all-time low. This corresponded to the highest treated gas H_2S content of 90 ppmv shown in Figure 2. The low alkalinity caused the solubility of the H_2S in the LO-CAT solution to become so low that significant amounts of H_2S were measured in the vent gas.

The alkalinity and ORP in the Navy 210 unit has been more tightly controlled versus the Navy 1 unit due to the lessons learned during early operation of the Navy 1 unit.

LO-CAT Sulfur Product

The two outputs from the LO-CAT unit are the vent gas (discussed previously) and the sulfur cake. The sulfur cake is approximately 65% sulfur and 35% moisture. Washing the slurry during the drying process minimizes the loss of chemicals (and operating cost). The elemental sulfur produced by the LO-CAT unit is sold to Hondo Incorporated in lieu of going to landfill. Hondo blends the sulfur with gypsum and sells it as a soil "amendment". The Coso LO-CAT sulfur has recently been certified as meeting the guidelines for use in fertilizing organically grown crops.

Cost of Operation

LO-CAT units' two largest operating cost components are chemicals consumption and electrical usage. Tables 3 and 4 show the current operating costs of the two units at Coso facility.

The electrical demand is fairly constant, even with changing sulfur load. The Navy 210 unit has a larger inventory of solution and therefore it requires more air to regenerate the catalyst.

The basis for the values above is a total of 5.6 LTPD: 1.6 produced by Navy 1 and 3.9 from Navy 210. Minor costs include 2-3 hours per day of operator time to conduct solution testing and other operator tasks. Operator responsibilities include activities for other process units within the power plant in addition to the LO-CAT unit.

Table 3. Electrical Demand.

Major Electricity User	Navy 1	Navy 210
Air Blowers (kW)	50	300
Circulation Pump (kW)	20	30
Belt Filter (kW)	15	20
Total Electricity (kW)	**85**	**350**

Table 4. Operating Cost per amount of sulfur removed.

Operating Cost	$US / Long Ton	$US / pound
Merichem Catalyst / Chemicals	420	0.19
Potassium Hydroxide (KOH)	93	0.04
Electrical ($0.07/kW-hr)	130	0.06
Major Operating Cost	**643**	**0.29**

Conclusion

The three LO-CAT units at the Terra-Gen Coso facility continue to be an economical and environmentally beneficial solution over 22 years of continuous operation. The data shows the units consistently meet H_2S specifications with operating costs in the range of just 29 cents per pound of sulfur removed. Additionally, the Navy 210 LO-CAT unit achieved significant throughput turndowns of 25-35% without adverse process effects with only minor operational adjustments.

References

1. Geothermal Resources Council Bulletin, June 1996, Mason, Thomas R., *CalEnergy's Coso Operation: A Substantial Commitment to the Environment Pays Off*