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**OPERATING EXPERIENCES OF CONVERTING A STRETFORD TO A LO-CAT(R) H₂S ABATEMENT SYSTEM
AT PACIFIC GAS AND ELECTRIC COMPANY'S GEYSERS UNIT 15**

J. M. Henderson
Gary P. Dorighi

Pacific Gas and Electric Company

ABSTRACT

In January 1988, Pacific Gas and Electric Company (PG&E) converted the Stretford H₂S abatement system at Unit 15 to use LO-CAT(R) H₂S liquid redox process chemistry. The Stretford process is a vanadium-based aqueous phase H₂S scrubbing system, while the LO-CAT(R) technology uses a solution of chelated iron for H₂S treatment.

This paper describes the plant modifications required for the conversion. It characterizes the operating experience and H₂S abatement performance over the past year of evaluating the process.

Overall plant operability and H₂S removal efficiency of the LO-CAT(R) solution is at least as good as, or better than, Stretford. However, a plant considering the Stretford to LO-CAT(R) conversion needs to evaluate for its own situation the apparent redistribution of operating costs outlined in this report. One must also pay attention to the subtle changes in operating procedures required to use the LO-CAT(R) solution with existing Stretford process equipment.

INTRODUCTION

Pacific Gas and Electric Company owns and operates nineteen geothermal power plants located at The Geysers in Northern California. The geothermal steam produced at The Geysers contains several noncondensable gases, including hydrogen sulfide (H₂S). The H₂S concentration has ranged from 32 up to nearly 1,000 ppm (parts per million of steam by weight). H₂S has a pronounced characteristic odor and PG&E has been committed to reducing emissions of H₂S from the power generating units. Unit 15 was the first of seven surface condenser units to employ the Stretford process to remove H₂S from the noncondensable gas prior to release to the atmosphere. In January 1988, after nine years of operation, PG&E converted the existing Stretford H₂S Abatement Process at Unit 15 to a LO-CAT(R) H₂S Abatement Process. The plant changes required for the conversion and the operating experience are described in the following report.

PROCESS DESCRIPTION

The electric generators at The Geysers Power Plant are powered by turbines driven by slightly superheated geothermal steam. After passing through the turbine, the steam is condensed at a pressure of 3-5 inches of mercury absolute. The condensate is pumped from the condenser to the cooling tower where it provides make-up for the plant cooling water. The noncondensable gases are removed from the condenser by a two-stage gas ejector system. This condenser vent gas is ultimately released to the atmosphere through the cooling tower. Most of the incoming H₂S concentrates in the condenser vent gas from which it must be removed prior to release.

A liquid redox process such as the Stretford or LO-CAT(R) process is used to remove H₂S from the condenser vent gas at Unit 15. Conversion of the Stretford process, as shown in Figure 1, to the LO-CAT(R) process involved changing the entire solution inventory, but no functional changes were made in the process equipment. The

LO-CAT(R) process is an aqueous phase H₂S scrubbing system which utilizes a dilute solution of iron made soluble by organic chelates. The LO-CAT(R) process first removes the H₂S from the condenser vent gas in a two-step gas absorption process. The condenser vent gas is first contacted with LO-CAT(R) solution in the venturi scrubber where a large portion of the H₂S is absorbed into the solution. The gas leaving the venturi is then passed up through the absorber column where it contacts additional LO-CAT(R) solution in countercurrent fashion in order to remove the remaining H₂S. The treated gas is then discharged to the atmosphere.

Once the H₂S is absorbed in the solution it is immediately oxidized to elemental sulfur by the iron chelate. As the iron chelate reacts with H₂S it is reduced from iron (III) chelate to iron (II) chelate. The solution leaves the absorption stage and enters the reaction tank. The LO-CAT(R) solution reacts so quickly with the H₂S that the reaction tank delay is not necessary. The solution next enters the two oxidizer vessels. Air is bubbled into these vessels to reoxidize the iron (II) chelate back to iron (III) chelate. The sulfur is drawn to the surface as a thick froth in the second oxidizer vessel where it is skimmed off and sent to the froth tank for further processing. The reoxidized solution passes into the balance tank which serves as an inventory control volume, as a location for make-up chemical addition, and as the evaporative cooler sump. The sulfur slurry from the froth tank, containing about 20% solids, is pumped to a vacuum belt filter where most of the solution is reclaimed through a wash process, the filtrate being returned to the balance tank. The solid sulfur leaves the belt about 80% in solids content, and is sent to waste disposal.

BACKGROUND ON GEYSERS UNIT 15

The representative data acquired during the testing of the LO-CAT(R) process show Unit 15 generating 30,000 kW of electricity. The typical condenser vent gas process rate was 1,500 scfm or the equivalent 2.1 mmcf/d. The typical molar composition of the gas on a dry basis is 4% hydrogen sulfide, 56% carbon dioxide, 16% hydrogen, 14% methane, 8% nitrogen and 2% oxygen. The sulfur loading was found to be 3.2 tpd. The LO-CAT(R) process has a solution inventory of 130,000 gallons. One venturi scrubber is used with a solution flow rate of 2,250 gpm. One absorber column, packed with redwood slats, has a solution flow rate of 700 gpm.

REASONS FOR THE CONVERSION

The overlying reason the Unit 15 Stretford was converted to LO-CAT(R) technology was the increasing cost of treating Stretford process wastes. The Stretford process chemistry is based on the metal vanadium, of which the disposal is regulated in California. Liquid purge streams from the Stretford containing over 24 ppm vanadium must be disposed of as a hazardous waste. Escalating costs in hazardous waste disposal prompted the evaluation of other process technologies that were non-hazardous and that could be retrofitted in the existing Stretford equipment with minimum modifications. The LO-CAT(R) process solution is non-hazardous and any purge of the solution could be easily recycled at Unit 15. Pilot testing of the LO-CAT(R) process indicated that it could be used in the existing Stretford unit operations. The risk of increased corrosion

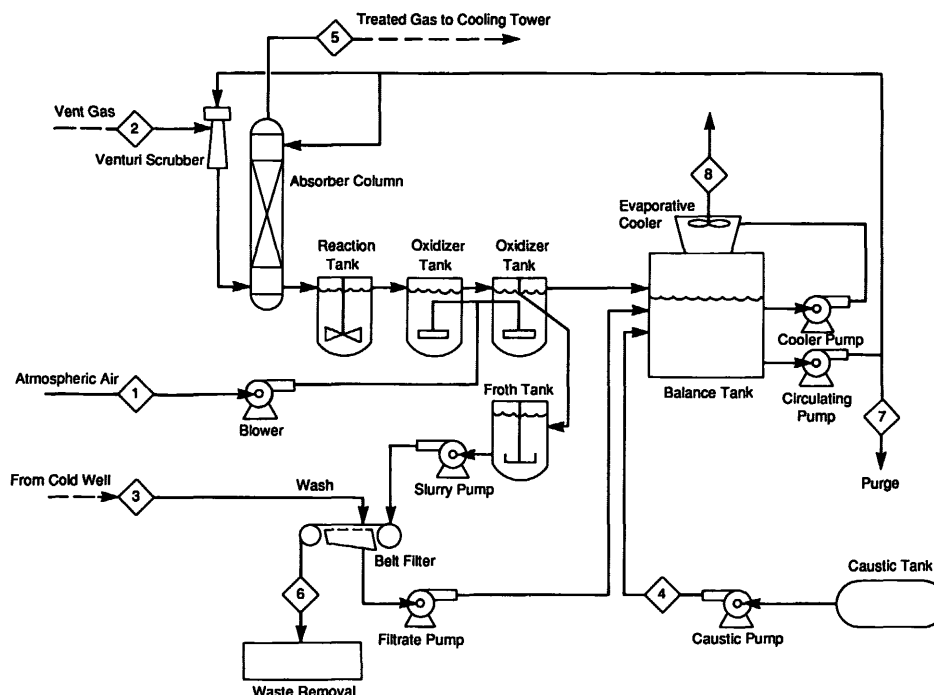


Figure 1.

of carbon steel was considered at the outset but protective measures were deemed adequate to minimize the corrosion risk.

NECESSARY CHANGES IN THE PLANT

The modifications made to the plant were performed entirely to repair existing corrosion damage or minimize potential corrosion risk. Nine years of Stretford operation yielded severe corrosion of the carbon steel piping and vessels. Replacement of the carbon steel piping with stainless steel was already planned even prior to the initiation of the LO-CAT(R) conversion proposal. The evaporative cooler was also scheduled to be replaced with a stainless steel cooler. A new type of coating, tougher than coal tar epoxy, was also planned to be used for the carbon steel vessels. After all the vessels were drained and cleaned, inspection showed extensive corrosion from Stretford solution had already occurred to the tank bottoms and a portion of the absorber column. Cleaning and repair was performed and the new tank liner, Cellcote Flakeline 180, was applied to all carbon steel surfaces. The air spargers in the oxidizer vessels, which were corroded beyond repair, were replaced with PVC material. An additional PVC sparger was added to the reaction tank to provide agitation to prevent sulfur from settling out in that vessel. The 1988 cost of the new stainless steel equipment was \$270,000. The cost to repair the corrosion damage, prepare all vessels for liner application and install the new air spargers was \$55,000. The application of the liner was \$175,000. The initial charge of LO-CAT(R) solution was \$80,000. The total installed cost was \$580,000.

TESTING OBJECTIVES

The LO-CAT(R) process was evaluated in four categories.

The most critical test objective to be determined was the H_2S abatement efficiency. The Northern Sonoma County Air Pollution Control District requires that the concentration of H_2S in the treated gas not exceed 40 ppm.

Make-up chemical addition rates needed to be evaluated and compared to the cost of Stretford make-up chemicals.

Potential changes in operating procedures needed to be identified. An example is that LO-CAT(R) usually removes sulfur from the process by sinking, whereas the Stretford process floats the sulfur then skims off the froth. The conversion required the flotation of LO-CAT(R) sulfur. Other operational concerns were the filtration characteristics of the LO-CAT(R) sulfur and the solution purge requirements due to salt production.

Because LO-CAT(R) solution is known to dissolve carbon steel, a long term performance evaluation of the coating and other components in the system was performed.

PROCESS START-UP AND PERFORMANCE EVALUATION

The initial start-up of the LO-CAT(R) process was a relatively smooth operation. The problems encountered were insufficient alkalinity to provide adequate H_2S removal, difficulty in making sulfur froth, and sulfur accumulation in the balance tank. No sodium bicarbonate had been added to the solution prior to start-up. When the condenser vent gas was introduced to the process H_2S removal was not as effective as desired. The pH of the solution dropped rapidly due to a lack of buffering from alkalinity. Caustic was quickly added to the process to remedy the problem and the H_2S concentration in the treated gas dropped well below the compliance level. Caustic had to be added continuously to the make-up sump for four days until sufficient alkalinity was achieved to maintain a proper pH in the process. Once the alkalinity reached steady state conditions the addition of caustic was the same as required for the Stretford process.

The production of sulfur began as soon as condenser vent gas was introduced to the process. Sulfur froth for the first week to ten days was light and not much sulfur was produced from the system. Diesel and turbine lube oil were added to the oxidizer vessels as a means of aiding sulfur flotation. However, these agents did not adequately improve the sulfur removal and concern about sulfur build-up in the system increased. It was discovered that the anti-foaming agent, supplied for foaming during start-up, greatly enhanced the flotation of sulfur. Anti-foam was then added to remove sulfur from

the system as fast as it could be processed.

After about two weeks of operation, the sulfur which had accumulated in the system was discovered floating in the balance tank. The sulfur had to be removed by vacuum trucks and was processed as capacity allowed. Insufficient agitation in the balance tank had caused a stagnant layer of sulfur to build-up. This problem was solved by providing additional mixing in the balance tank. A four-inch line was added to the system to take solution from the cooler pumps and deliver it into the balance tank. A flow of about 400 gpm, aimed tangential to the tank wall, was added just below the solution level. This produced a swirling motion of the solution in the tank. By keeping the tank level between 40%-60%, solution returning to the balance tank provided sufficient mixing to prevent a stagnant sulfur layer from forming. After this modification was performed, sulfur flotation in the oxidizer vessels occurred without the addition of anti-foam or hydrocarbons.

The H₂S abatement efficiency has been very good. The concentration of H₂S in the treated gas was less than 5 ppm, normally about 1 ppm. This removal is as good as or better than Stretford. Prior to the conversion the rate at which the unit could receive steam often was a function of the capability of the Stretford to process the gas and remain in emission compliance. The LO-CAT(R) process at no time limited the rate at which steam could be added to the generating unit.

Make-up chemical consumption is about twice what was expected at the onset of the project. The make-up chelate, 310M, was added at a rate of 18 lb./100 lb. sulfur. The iron catalyst, 310C, was added at a rate of 3.6 lb./100 lb. sulfur. Caustic addition, about the same as Stretford, was added at a rate of .7 lb./100 lb. sulfur.

Operating Procedures

There was no major change in the operating procedures for the LO-CAT(R) with respect to Stretford. LO-CAT(R) sulfur was able to be removed in the second oxidizer by flotation. Proper maintenance of the solution level in the balance tank was critical to establish the needed agitation and thus minimize sulfur accumulation in the balance tank. This also helped to promote sulfur flotation in the second oxidizer vessel. The two oxidizer vessels were satisfactory at regenerating the LO-CAT(R) solution. It was determined that one oxidizer was not sufficient and the solution would ultimately become over-reduced. The reaction tank was determined to be a redundant vessel and is not needed in this process. Leaving the reaction tank in service is the most cost-effective mode and poses no problem to the system.

The production rate of salts in the system was acceptable and no purge has been performed to date. Thiosulfate concentrations averaged between 50-70 g/L and sulfate was about 20 g/L. It appears that enough salt leaves with the sulfur cake to balance their production rate.

Sulfur slurry from the LO-CAT(R) process produced a much drier cake leaving the vacuum belt filter. The solids content was between 80%-90% as compared to 50%-60% for Stretford sulfur. The production of very dry sulfur translated into large savings in waste removal costs. The cost savings in waste removal were the major factor in reducing operating costs at Unit 15.

No incidents of uncontrolled frothing have occurred to date. In the previous Stretford operation uncontrolled frothing happened occasionally requiring cleanup of the plant area.

The tank liner has performed satisfactorily to date. Some corrosion has occurred at locations where the coating has been damaged. Physical damage happened to the coating on the mixer blade in the second oxidizer when an elbow failed from the PVC air sparger and chipped the coating on the mixer blade. The exposed carbon steel was severely pitted but repair of the blade was possible. The 24-inch valve between the second oxidizer and the balance tank was replaced due to severe corrosion of the carbon steel valve body.

CONCLUSIONS

The Stretford process at Geysers Unit 15 has been successfully converted to the LO-CAT(R) process technology. The LO-CAT(R) process was able to meet or exceed all test objectives on a technical basis.

Several areas must be evaluated to determine if the conversion of a Stretford to a LO-CAT(R) process is economically sound. Comparisons must be made between the cost of the changes required for the LO-CAT(R) process to the cost of necessary maintenance and upgrades of the plant. Make-up chemical addition rates for both Stretford and LO-CAT(R) need to be evaluated to obtain accurate operating costs. The disposal of hazardous waste must be factored into the operating costs.

The conversion of the Stretford process to the LO-CAT(R) process at Geysers Unit 15 was a good decision both technically and economically.