Unit 14 / Sulphur Springs H_2S Abatement Process Screening and Stretford Improvements Study — Part 1

Brian Benn[1], Kenneth E. McIntush[2], Carrie Ann M. Beitler[2], Darryl L. Mamrosh[2], and Dr. O. E. Hileman[3]

[1]Calpine Operating Services Company, Inc., The Geysers Power Plant, Middletown CA
[2]Trimeric Corporation, Buda, TX
[3]Trimeric Senior Associate, Hamilton, Ontario, Canada
brianb@calpine.com • ken.mcintush@trimeric.com • carrie.beitler@trimeric.com
darryl.mamrosh@trimeric.com

Keywords

H_2S Abatement, Stretford, noncondensable gas, NCG, hydrogen sulfide removal, sulfur recovery

ABSTRACT

This report gives the results of Part 1 of a three part study performed in 2007 to improve the primary H_2S abatement system at Sulphur Springs Unit 14 Power Plant owned by Calpine Corporation and located at The Geysers. The existing Stretford system is approximately 30 years old and under-loaded due to reduced NCG as a result of Geysers Recharge water injection. The 2007 study investigated three lines of inquiry:

Part 1): Is replacement of the existing Stretford system economically advantageous, given the availability of modern, environmentally-friendly gas treatment technology that could handle the current low sulfur load with a much smaller footprint and less parasitic power load?

Part 2): In lieu of replacing the Stretford system, what operational improvements can be made to the existing system to reduce the total cost of treatment?

Part 3): What physical modifications can be made to the system to reduce process shutdowns caused by sulfur plugging?

Two primary conclusions that were identified follow. i) Every alternative technology considered proved to have a higher total treatment cost than continuing with the existing Stretford unit, even if no improvements are made, and even though it is operating at ~10% of original design loading. ii) Significant reductions in total treatment cost should be possible by implementing several recommended improvements described in Part 2 and Part 3 of the report.

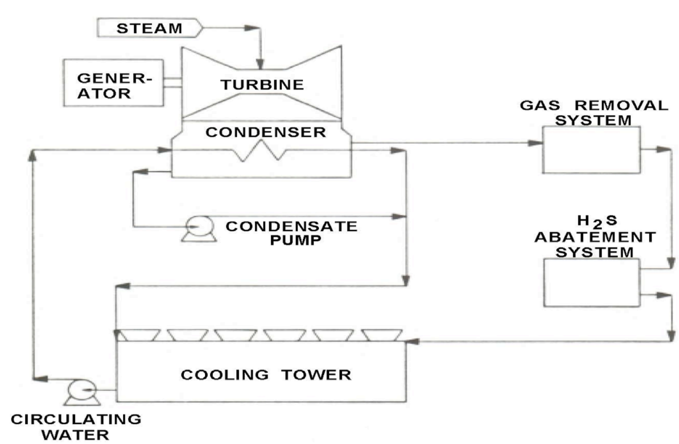
1.0 Scope

Part 1): The geothermal power production site at The Geysers known as Unit 14 / Sulphur Springs currently has a Stretford unit for the removal of H_2S from the noncondensable tail gas. The Stretford unit has operated since approximately September 1980, and the noncondensable gas volumes have dropped over time. Based on compositions and flows from source testing over the last few years, and based on stated original design capacities, the Stretford is currently operating at roughly 10-12% of original gas flows and original design sulfur loads. As a result of the low load on the unit, Calpine desired to determine if a more appropriately sized unit, possibly based on alternate technology, might be more cost effective than running the existing Stretford at a small fraction of original design capacity. The study considered technologies that would allow Calpine to replace their existing Stretford unit.

Calpine contracted Trimeric Corporation, a technical services company with expertise in H_2S removal in general as well as specific Stretford expertise, to study the situation at U14. This paper presents a high-level overview of the results discussed in detail in the ~100 page report that resulted from the work.

2.0 Background, Design and Operation of the U14 Stretford

As general background, Figure 1 shows a block flow diagram of a geothermal power station like U14. Higher pressure geo-



Source: "The Geysers Unit 1, Pacific Gas and Electric Company," National Historic Mechanical Engineering Landmark, The American Society of Mechanical Engineers, October 1985, p. 7.

Figure 1. Block Diagram of Geothermal Power Plant.

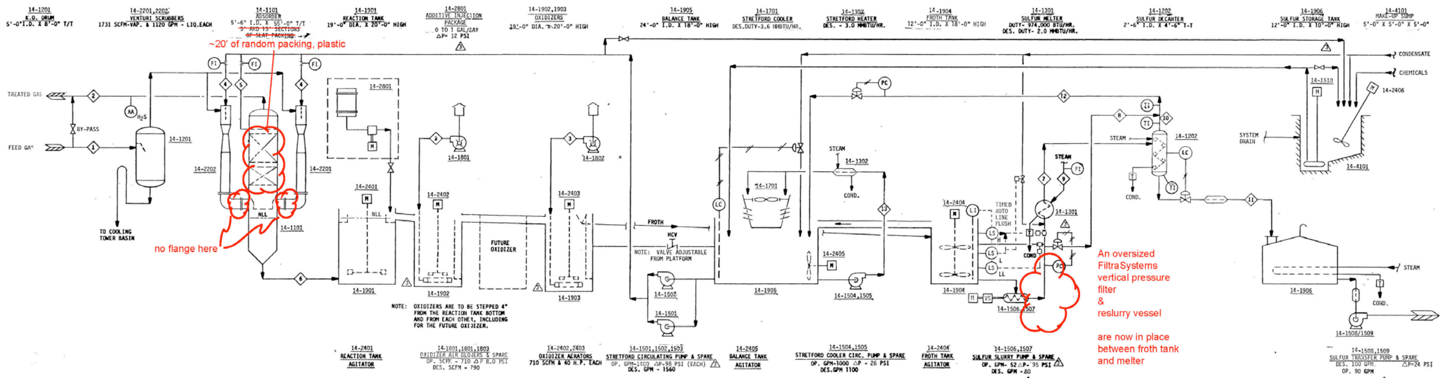


Figure 2. PFD of Calpine U14 Stretford Unit with Notations.

thermal steam passes through a Turbine, which drives the electric generator unit. The lower pressure steam exiting the turbine then passes into an indirect ("surface") condenser. Noncondensable gases exit the condenser and pass through one or more steam jet eductors and condensers in the Gas Removal System and into the Stretford H_2S abatement system. The noncondensables including H_2S (about 80% of the total H_2S contained in the incoming steam) pass to the Stretford unit. The sweet gas from the Stretford unit passes into the cooling towers.

Figure 2 shows an original PFD of the U14 Stretford with some current differences from original shown. Similarly, Table 1 shows the original material balance that was on the PFD with approximate current sour gas and elemental sulfur product flow rates.

Table 1. Material Balance for Calpine U14 Stretford with Notations.

LINE NO.	1 Approx. 2007 Actual	1 MOL/HR	2 MOL/HR	3 MOL/HR
CO_2	29.54	233.50	233.50	
O_2	2.56	28.70	28.70	22.86
CH_4	4.95	40.74	40.74	
H_2	6.35	77.36	77.36	
N_2	11.82	76.42	76.42	87.05
H_2S	1.98	17.60		
H_2O	8.82	73.07	30.05	2.15
TOTAL	66.04	547.34	486.77	112.06
MW	30.7	29.343	30.171	28.64
LB/HR	2027	16,061	14,686	3,209
SCFM	417	3,462	3,079	709
ACFS		67.14	60.99	9.93
TEMP.°F		124.5	95	170
PRESS. PSIA		14.2	13.2	21.2

Temp and Press assumed same as orig for water content in "Approx. Actual"

LINE NO.	4 LB/HR	5 LB/HR	6 LB/HR	7 LB/HR	8 LB/HR
SULFUR	2,911	1,456	7,842	564	2,256
STRETFORD	582,208	291,104	1,456,895	5,079	20,316
STEAM					
TOTAL	585,119	292,560	1,464,737	5,643	22,572
SP.GR.	1.04	1.04	1.04	1.09	1.09
GPM	1,120	560	2,818	10.33	41.32
TEMP.°F	95	95	98	98	98
PRESS. PSIA	53	53		65	65

LINE NO.	9 LB/HR	10 LB/HR.	11 Approx. 2007 Actual	11 LB/HR.	12 LB/HR.	13 LB/HR
SULFUR			67.4	564	2,256	2,599
STRETFORD		5,079			25,395	519,829
STEAM	1,034					
TOTAL	1,034	5,079		564	27,651	522,428
SP.GR.	1.0	1.04		1.80	1.08	1.04
GPM		9.77		0.63	5,109	1,000
TEMP.°F	337	280		280	131	95
PRESS. PSIA	113	63				

The noncondensable gas from the gas removal unit first passes into the two Venturi scrubbers in parallel. Most of the lean Stretford solution passes through the Venturi scrubber(s) as the motive fluid. In the case of U14 with its very low current gas flows, an unusually large fraction of the H_2S appears to be removed across the Venturi scrubbers; gas enters the Venturi scrubbers with ~3 vol% H_2S and exits the baffle/channel device into the main part of the Absorber with only roughly 20-120 ppmv of H_2S remaining. The gas then passes upward through a single bed Absorber in order to remove the remainder of the H_2S. The absorber contains Flexiring packing, which is a large diameter, open-type, plastic, random packing. H_2S is removed to less than 1 ppmv typically, well under the 10 ppmv permit limit.

From the sump at the bottom of the absorber, the solution then flows via gravity through a line that enters near the bottom of an open topped, stirred reaction tank. The purpose of the reaction tank is to allow the sulfide that was dissolved into the liquor in the Venturis and absorber to react to form elemental sulfur particles. From the reaction tank, the solution flows sequentially through two equally sized, round, stirred oxidizers. Two blowers supply air to the oxidizers. The oxidizers serve two primary functions, 1) they separate the sulfur particles from the liquor via froth floatation, and 2) they reoxidize the vanadium catalyst contained in the Stretford liquor. Diesel or other floatation / frothing aids are not currently used, although equipment is believed to be available to do so.

Lean Stretford solution underflows a weir in the second oxidizer to the balance tank. Dedicated pumps circulate a stream of lean solution from the balance tank up and into a cooling tower / evaporator located above the balance tank. The purpose of the cooling tower / evaporator is to maintain the water balance of the system. Another set of 3 pumps (two operating and one spare), Stretford Circulating Pumps, send lean Stretford solution from the balance tank back around to the Venturi scrubbers and to the top of the absorber.

Froth created in the oxidizers overflows the second oxidizer via a weir into the stirred froth tank. From the froth tank the sulfur froth is pumped via a progressive cavity pump through a FiltraSystems vertical pressure filter. The washed cake discharges through a cake chopper (to aid in reslurrying) and, as of 2007, is reslurried, melted, and sold.

3.0 Technology Screening Study

Numerous technologies or technology combinations were considered in the technology screening study portion of this project in order to determine if there were any technologies that could reduce costs by replacing the under loaded Stretford unit with something more appropriately sized.

A spreadsheet tool was generated in Excel to evaluate the capital and operating costs for the various H_2S removal technologies.

The spreadsheet tool was set up so that important input variables (e.g., gas flow, sulfur content, and operating costs) can be varied, within a narrow range, to determine the effect on the overall treatment cost for the different H_2S removal processes. The remainder of this report discusses the design basis for the study and the results of the screening study. Further information on the different H_2S removal processes evaluated is available from the authors.

3.1 Design Basis

Table 2 shows the design basis for the sulfur technology study for U14. The design basis gas flow, composition, and outlet H_2S specification were set to be the same as Calpine provided to Trimeric for use in the screening study, however the current actual gas flows are slightly smaller at the U14 Stretford. This is not particularly important, because as long as all technologies use the same basis, it is still possible to accomplish the purpose of determining which technologies provide the least expensive total treatment cost.

The spreadsheet tool was organized so that important variables in the design basis could be changed, within narrow limits, to evaluate the effect on treatment costs of the different H_2S removal technologies considered in the study. These variables are highlighted in green on the design basis page of the spreadsheet and include: the inlet gas flow rate, outlet H_2S content of treated gas, and the CO_2 and H_2S content of the inlet gas. User changes to the outlet H_2S gas specification as well as the H_2S content in the inlet gas will result in different quantities of sulfur removal and will affect treatment costs. The spreadsheet will normalize the gas composition based on H_2S and CO_2 changes in the feed gas so the total mole percent sums to 100.

Other variables can be changed on the Design Basis worksheet to impact utility and operating costs of the H_2S removal processes.

Table 2. Design Basis for Screening Study.

Calpine Sulfur Technology Review -- Design Basis			
Denotes input values that can be changed			
Stream Properties	**Units**	**Value**	
Inlet gas flow	MMscfd	0.5	
Inlet gas pressure	psig	0.5	
Inlet gas temperature	F	120	
Target maximum H2S in treated gas	ppmv	7	
Inlet gas concentration:		Input	Normalized
Oxygen	mol%	4.50	4.5
Nitrogen	mol%	20.6	20.6
CO2 (maximum from analytical)	mol%	51.6	51.6
H2S (maximum from analytical)	mol%	3.5	3.5
Methane	mol%	8.7	8.7
Hydrogen	mol%	11.10	11.1
Water	mol%	saturated	saturated
Total	mol%	100.00	100.0
Saturated inlet gas density at above conditions	lb/ft3	0.08	
Saturated inlet gas molecular weight	lb/lbmole	31.07	
Utility and Other Information	**Units**	**Value**	
Continuous operation	day/yr	350	
Caustic cost, FOB site	$/ton, dry	400	
Cost of DEA	$/lb	1.1	
Cost of ammonia	$/ton, dry	320	
Cost of unloaded operator	$/hr	29	
Cost of loaded operator	$/hr	58	
Loaded cost of adding 1 operator	$/yr	120640	
Assumed cost of electrical power	$/kW-hr	0.06	
Assumed cost of water	$/1000 gallons	0.8	
Assumed cost of heat (steam or fuel gas) consumed	$/MMBtu	10	
Fraction of capital that is added to operating cost to get to total treating cost (capital recovery)	d-less	0.2	
July 1982 ChE Plant Cost Index	d-less	314.2	
1990 ChE Plant Cost Index	d-less	358	
1992 ChE Plant Cost Index	d-less	358.2	
1999 ChE Plant Cost Index	d-less	390.6	
Current ChE Plant Cost Index	d-less	509.8	
Version 071907			

These include the operating days per year, chemical costs, operator salary, and utility costs for electricity, water, steam, and fuel. Any variables that are not shown in green have been locked and are not intended to be changed. The Chemical Engineering Plant Cost Index is used to bring past capital costs to present value.

3.2 Results of the Screening Study

Table 3 summarizes the capital and operating costs for the technologies evaluated in the study. Given the design basis conditions and assumptions of the study, it appears clear that continuing to operate the Stretford unit, even without any improvements or operating cost reductions, results in lower total treatment costs than would result from installing and operating any new plant based on different technology. Normally, this result would not be surprising. A new plant has cost of capital associated with it. As a rough rule of thumb, if an existing H_2S removal plant is adequately doing the job, then the cost of capital disadvantages any new plant. However, given that the U14 Stretford is operating at roughly 10% of original design capacity, it was not known at the outset that this rule of thumb would prove accurate for U14.

Although the costs for new technologies in Table 3 are believed roughly accurate, the data should not be used to compare one new technology with another except in a gross sense. The work is accurate enough to demonstrate clearly that no new technology would be able to compete with running the existing underloaded Stretford unit. However, the work was not intended to indicate which of the new technologies was the most cost effective; a more thorough study would be needed to make that determination.

It also appears clear from the results table that modifications to the U14 Stretford could reduce total treatment cost further.

Note, however, that the Stretford operating costs assumed 1 power station shutdown per year. However, the Stretford has recently run longer than 1 yr between plugging-forced cleanings. For example, there was a ~514 day run that ended in February 2006 and a run of ~13 months that ended in March 2007. In March 2007, although Venturi tailpipes and packing were cleaned, the shutdown during which they were cleaned occurred for other reasons and was not a result of Stretford plugging. If the assumption of 1 plugging-caused shutdown per year were changed to 1 event per 2 yrs, then the existing Stretford as-is would be even more favored over new plants. And, there would also be slightly less economic driver to make modifications. (Although not covered in this paper, the project also resulted in suggestions for troubleshooting and improvement of the existing Stretford.)

The screening study results have implications for other under-loaded Stretford units at The Geysers. It is likely that repairing and/or improving the existing units will be less expensive than bringing in new technology. Further, it is the authors' opinion that for Stretford units at The Geysers that are slightly over loaded, it is also likely that improving/expanding those units will be less expensive than adding any new H_2S abatement unit.

Another factor in favor of continuing with Stretford is Calpine's depth of experience with the technology. Few companies with Stretford units have as many as Calpine, and even fewer have as many staff with long term knowledge of Stretford units. As a result, Calpine has developed

Table 3. Results of Sulfur Technology Screening.

Preliminary Results

Process Summary	Units	Value
Inlet gas rate	MMscfd	0.5
Inlet gas H_2S content	mol%	3.50
Inlet gas sulfur content	LTPD	0.65
Target maximum H_2S in treated gas	ppmv	7
Inlet gas CO_2 content	mol%	51.6

Technology	Capital Cost of Process ($)	Capital Contribution to Total Treating Cost ($/yr)	Average Major Operating Cost ($/yr)	Average Total Treating Cost ($/yr)	Average Total Treating Cost ($/LT sulfur)	Process Description	Commercial Status	Operator Competency	Ability to Operate Unmanned?	Pros	Cons
Unit 14 Stretford, as-is	na	na	$384,990	$384,990	$1,703	Rough approximations of Unit 14 costs associated with Stretford system as it currently operates. Includes chemicals, electrical, and losses associated w/ 3-day downtime. For reference only	na	na	na	na	na
Unit 14 Stretford, with improvements	$500,000	$100,000	$224,035	$324,035	$1,434	Assumes Stretford unit is modified to eliminate downtime and minimize utility costs (i.e., 1 pump running at higher rate instead of 2 and absorber configuration changed to possibly replace packing, add small spray section, etc.). Other costs may include purchasing isolation valves for both venturis so that one can be isolated for cleaning while the other is running, installing retractable spray cleaning lances and designing a method to allow the lance wash water and any solids removed to run to an appropriate container, etc. Exact modifications and cost not currently known, but estimates are thought to be reasonable.	na	na	na	Lower overall costs; operators familiar with current technology	Downtime while making modifications; may require some testing of different equipment alternatives
Replacement Sulfur Treatment Options:											
Paques / Thiopaq	$2,859,000	$571,800	$217,000	$788,800	$3,490	Technology uses dilute caustic to scrub H_2S from gas. The sulfidic caustic from the absorber is regenerated via microbes in a biological oxidizer.	Limited commercial units	Medium	No		Unfamiliarity with microbe based process and associated equipment
LO-CAT	$2,346,000	$469,200	$356,000	$825,200	$3,651	Basic liquid treating option that absorbs H_2S into solution where it reacts with iron to form elemental sulfur. The spent iron is regenerated with air in an oxidizer and a portion of the sulfur is settled from the slurry. The thick slurry goes to a filtration system and the thin slurry is recycled back to the absorber. Typical H_2S removal is 99%.	Proven	High	No		Chemical costs; some operational issues (foaming/plugging)
Burn / Caustic Scrub (new equipment)	$2,119,158	$423,832	$309,000	$732,832	$3,242	This alternative receives the sour gas and combusts it in an incinerator, followed by caustic scrubbing to selectively remove the SO_2 to form Na_2SO_3 or sulfate. This process is used routinely with casinghead gas in the California steam flooded oil fields. Little wasted caustic since SO_2 is a much stronger acid than CO_2 and can be scrubbed selectively. The estimated percent reduction is 99%.	Proven	Medium	No	Reliable	Caustic costs; other permitting issues?
Burn / Caustic Scrub (used equipment)	$1,589,369	$317,874	$309,000	$626,874	$2,774	Same as above but assumes that the unit can be built from used equipment. The capital cost of the used equipment was assumed to be ~20-25% less than with new equipment	same as above	same as above	same as above	same as above	same as above
Selective Amine Claus-type	$4,171,500	$834,000	$322,500	$1,156,500	$5,117	Selective amine used to limit CO_2 pickup and acid gas enrichment to get H_2S to levels needed in Claus unit (20-30%). Claus unit processes acid gas from the amine unit, producing molten elemental sulfur as product. The amine acid gas is burned in a reaction furnace with enough air to combust any hydrocarbons and 1/3 of the H_2S. The SO_2 produced then reacts with the remaining H_2S to produce elemental sulfur vapor. This 'Claus' reaction occurs in the reaction furnace and in the downstream catalyst beds. The sulfur vapor is condensed and removed after the reaction furnace and then again after each catalyst bed. Total H_2S removal for this type of system is typically in excess of 95% . Capital costs for a used Claus plant may be 85% of that of a new unit.	Proven	Medium	No		Difficult to operate consistently on small applications; typically used on higher tonnage streams (10 tpd). High capital.
Produce NaHS in Selective Scrubber (treat spent caustic stream or dispose downhole)	$989,315	$197,863	$738,188	$738,188	$3,266	Use selective scrubber to produce caustic sulfide stream to 10 ppmv (two-stages likely required). Assumes disposal of low-quality NaHS product/treatment of spent caustic. Caustic costs based on CO_2 pickup of 15% per operation of another selective scrubber unit. Even so, caustic cost makes up majority of operating costs and these are very high compared to other technologies.	Limited past commercial units	High	Yes	Somewhat less reliable than burn/caustic scrub and may require more operator attention initially.	Dispose of product or treat downhole
Ammonium Thiosulfate (ATS)	$1,627,000	$325,400	$109,000	$434,400	$1,922	This gas scrubbing technology uses ammonia to scrub H_2S from sour gas. The ammonia and H_2S are then stripped in a sour water stripper and are then fed to another process to convert them to ammonium thiosulfate. Ammonia must be purchased but cost is relatively low for this small tonnage stream.	Unproven	High	No		Costs considered "best case" since technology is unproven and unforeseen issues/expenses may occur.
Liquid Scavenger	$60,000	$12,000	$10,556,000	$10,568,000	$46,758	This process is fairly simple since the basic direct injection scavenging installation consists of only a chemical injection pump, a means of introducing the scavenger into the sour gas pipeline, a length of pipe to allow for gas/liquid contact, and a downstream device for separating spent or excessive scavenging agent form the treated gas. Can remove 99+% of H_2S.	Proven	Low	Yes	Simple and reliable.	Very high operating costs for scavenger agent
Solid Scavenger	$828,000	$165,600	$4,282,000	$4,447,600	$19,678	Sour gas passes through a packed bed where H_2S is removed using an iron-based solid material. Usually two vessels are used in lead-lag arrangement so that when the scavenger media is spent in one vessel, sour gas flow can be redirected to the fresh scavenger vessel while the spent material in the first vessel is changed. Can remove 99+% of H_2S.	Proven	Low	Yes	Simple and reliable.	Very high operating costs for scavenger agent

Notes:
1) Acid gas injection not considered since there is no access to an injection well and no suitable reservoir to put the acid gas into at this facility.
2) Non-selective caustic scrubbing was eliminated since all of the CO_2 would be absorbed to form Na_2CO_3 with the caustic solution and the cost of the caustic alone would be prohibitive (approximately $20,000/LT). The spent caustic would need to be further treated or sent downhole,.
3) Selectox and other gas-phase, catalytic, direct oxidation type processes were eliminated since typical removal efficiencies are in the range of 90-97% and this is not high enough for the Calpine application (99.97% removal required), without additional downstream treatment.
4) CrystaSulf considered and eliminated, because the technology is best suited for higher pressure applications of this sort. At this pressure, total treating costs for CrystaSulf are expected to be as high or higher than LO-CAT.

efficiencies (e.g., efficient methods of removing, cleaning, and replacing absorber packing) associated with operating Stretford units that would not exist with most new technologies (burn / scrub approaches are an exception, since Calpine also has a few of those).

Due to length restrictions, it was not possible to provide all the details contained in the screening study, including descriptions of the technologies considered, flow diagrams, and the data used.

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