

Unit 14 / Sulphur Springs H₂S Abatement Process Screening and Stretford Improvements Study—Part 2

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ABSTRACT

Presented in this report are the results of Part 2 of a three part study performed in 2007. The major goal of the study was to improve the primary H₂S abatement system at the 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 is now under-loaded due to reduced NCG, which was a result of Geysers Recharge water injection. The following three questions were investigated in the 2007 study:

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? [A report focused on Part 1 was presented at the 2010 GRC Annual Meeting in Sacramento, CA (Benn et al., 2010).]

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 2 is the basis of this article.]

Part 3): What physical modifications can be made to the Stretford system to reduce process shutdowns caused by sulfur plugging? [A future GRC paper will be published to summarize Part 3 of the study.]

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cost should be possible by implementing several recommended improvements described in Part 2 and Part 3 from the unpublished report presenting the work undertaken, the results obtained, and the conclusions drawn from the 2007 study.

1.0 Scope

The geothermal power production site at The Geysers known as Unit 14 / Sulphur Springs (U14) currently has a Stretford unit for the removal of H₂S from the noncondensable tail gas. The Stretford unit has operated since approximately September 1980. Based on compositions and flows from source testing over the last few years and based on the stated original design capacities, the Stretford is currently operating at roughly 10-12% of the original design sulfur loads and gas flows. As a result of the low load on the unit, Calpine desired to identify ways to reduce reduce operating costs at the H₂S abatement unit.

Calpine contracted Trimeric Corporation, a technical services company with expertise in H₂S removal in general as well as specific Stretford expertise, to study the situation at U14. Presented in this paper is a high-level overview of a portion of the results discussed in detail in the unpublished ~100 page report that resulted from the work.

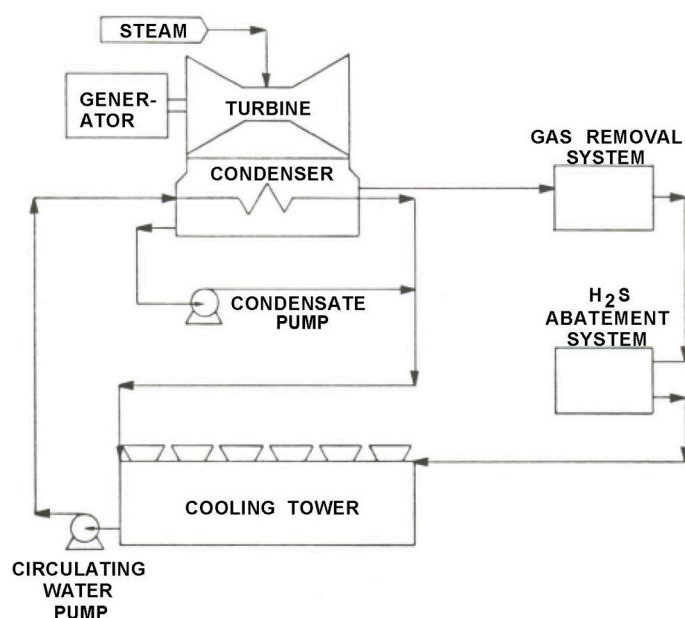


Figure 1. Block Diagram of Geothermal Power Plant.

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

LINE NO.	1	2	3						
	Approx. 2007 Actual	MOL/HR	MOL/HR	MOL/HR	4	5	6	7	8
CO ₂	29.54	233.50	233.50		2,911	1,456	7,842	564	2,256
O ₂	2.56	28.70	28.70	22.86	582,208	291,104	1,456,895	5,079	20,316
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 ₂ S	1.98	17.60							
H ₂ O	8.82	73.07	30.05	2.15					
TOTAL	66.04	547.34	486.77	112.06	585,119	292,560	1,464,737	5,643	22,572
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	95	95	98	98	98
PRESS. PSIA	14.2		13.2	21.2	53	53	65	65	65

LINE NO.	9	10	11	12	13
	LB/HR	LB/HR	Approx. 2007 Actual	LB/HR	LB/HR
SULFUR STRETTFORD			67.4	564	2,256
STEAM	1,034	5,079		25,395	519,829
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			

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

The non-condensable gas exported from the gas removal unit first passes into 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 H₂S appears to be removed across the Venturi scrubbers; gas enters the Venturi scrubbers with ~3 vol% H₂S and exits the

baffle/channel device into the main part of the absorber with only roughly 20-120 ppmv of H₂S remaining. The gas then passes upward through a single bed absorber in order to remove the remainder of the H₂S. The absorber contains Flexiring packing, which is a large diameter, open-type, plastic, random packing. H₂S is removed to less than 1 ppmv typically, a value well below 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 and suspended sulfur particles flow sequentially through two equally sized, round, stirred oxidizers. Individual blowers supply air to each oxidizer. The oxidizers serve two primary functions: 1) they separate the sulfur particles from the liquor via froth flotation, and 2) they re-oxidize the vanadium catalyst contained in the Stretford liquor. Diesel or other flotation / frothing aids are not currently used, although equipment is believed to be available to do so.

Lean Stretford solution underflows a weir mounted in the second oxidizer and is directed to the balance tank. Dedicated pumps circulate a stream of lean solution from the balance tank to 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), the Stretford circulating pumps, send lean Stretford solution from the balance tank back around to the Venturi scrubbers and to the top of the absorber.

2.0 Background, Design and Operation of the U14 Stretford

Note: Section 2 contains general background information about the Unit 14 Stretford system that is applicable to all three parts of the study. Thus, much of the material was presented previously in Part 1 (Benn et al., 2010) of the study that was given at the GRC Annual Meeting in 2010 in Sacramento, CA.

Figure 1 shows a block flow diagram of a geothermal power station like U14. Higher pressure geothermal 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. Non-condensable gases exit the condenser and pass through one or more steam jet ejectors and condensers in the gas removal system and into the Stretford H₂S abatement system. The non-condensable gases, including H₂S (about 80% of the total H₂S contained in the incoming steam) pass to the Stretford unit. The sweet gas from the Stretford unit passes into the cooling towers.

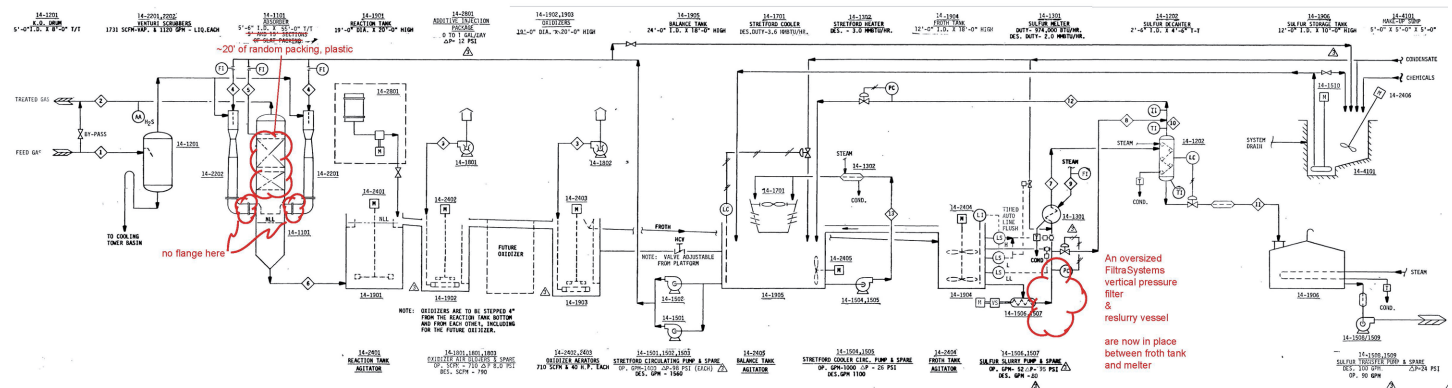


Figure 2. PFD of Calpine U14 Stretford Unit with Notations

Sulfur-laden froth created in the oxidizers overflows the weir mounted in the second oxidizer and is directed 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 to a transport bin and is sold for agricultural soil amendments.

2.1 Problems Noted at the U14 Stretford Unit

The following are known or suspected primary problems at the U14 Stretford unit. (The first two items listed were the drivers for conducting this project.)

- Plugging of the tailpipes of the Venturi scrubber causing forced outages of 3 days duration approximately once per year for cleaning; both Venturi scrubber tailpipes and absorber packing are cleaned when the unit is brought down. If the Stretford unit were not a source of downtime, the U14 power plant is capable of running continuously for several years between turnarounds.
- High operating costs, dominated by electricity usage (~0.4 to 0.5 MW of the ~50 MW [net] generated at U14 is consumed by the Stretford unit).
- Plugging of absorber packing, which occurs from the bottom up. The depth to which plugging rises in the packing depends on length of time between cleanouts.
- High thiosulfate concentrations, averaging 300-400 g/l.
- Occurrence of “floc” on the reaction tank; this material is stiff in consistency, and, when it occurs in quantity (floc is sometimes up to 2’ tall in elevation above the liquor level), requires the use of a hose and sprayer to herd the floc out of the reaction tank. Floc is said to cause problems with vacuum filters in that it is hard to get the material to come off of the belts, even with a cake knife mounted on the filter.
- Inaccurate or nonexistent Stretford solution flow, air flow, sour gas flow, and sweet gas flow measurements.
- Additionally, a general problem for troubleshooting is that process data (e.g., temperatures, flow rates, pressure drops) around the unit are few in number and generally must be collected manually.

3.0 Potential Operational Improvements to the U14 Stretford Unit

This section of the paper discusses operational changes that were considered to help address the first four bulleted problems listed above. (Physical changes were also recommended as part of the un-published report mentioned previously. Physical changes will be summarized in a future paper covering Part 3 of the study.)

3.1 Reducing Consequences of Venturi Scrubber Plugging

The most costly issue at the U14 Stretford unit is reported to be plugging of the Venturi tailpipes with solid material. Solids build up over time on the surface of the metal and harden. Plugging is thickest at the bottom of the tailpipe and thinnest at the top. The Venturi nozzle itself and the converging and diverging



Figure 3. Picture of Scale from U14 Stretford Unit.

sections that make up the body of the Venturi do not plug up. The plugging only occurs in the tailpipe. As shown in Figure 3, the material has the classic tree-ring layered appearance of scale removed from many other Stretford units in all types of service. The Venturi scrubber tailpipe plugging eventually restricts gas flow and causes back-pressure to build up on the upstream generation equipment to the point where the entire U14 facility must be shut down so that the Venturis and tailpipes can be removed for cleaning or to be cleaned in place. The frequency of downtime caused by Venturi scrubber plugging is said to be once per year with 3 days of downtime required for cleaning. Lost power generation and third party cleaning and disposal costs are estimated to be in the range of \$180,000 per shutdown occurrence.

There are at least two approaches for minimizing the consequences of Venturi scrubber plugging: 1) avoid scale in the first place by addressing the root cause of plugging via the chemistry and the design of the Venturi scrubber for appropriate velocities and residence times, and 2) deal effectively with the scale by creating an arrangement where a spare Venturi scrubber is always available and where dirty Venturi scrubbers can be cleaned without a shutdown. The remainder of this section discusses the operational changes that help accomplish the first of these two items. (Physical modifications are presented in the un-published report noted above and will be covered in Part 3 of this publication, to be issued later.)

3.1.1 Operation with a Single Venturi to Increase Velocity and Reduce Venturi Residence Time

In the original design of U14, two Venturi scrubbers were installed with the sour NCG flow split equally between the two units. Due to the decrease in NCG flow rate that occurred over time at U14, the velocity in the Venturi scrubbers was now much lower than the design velocity. Based on the original U14 design information, it was believed that all of the sour NCG could be processed by one of the two Venturi scrubbers and still be within the Venturi design limits. The routing of all of the sour NCG through one Venturi would result in the capability to switch to the other unit when the on-line unit becomes plugged, thus avoiding

a shutdown due to plugging of the first unit. Additionally, it was thought that having two Venturis on-line with the low gas flow rate could contribute to the plugging problems in the tail pipes due to excessive residence time in the tail pipes.

Testing by Calpine showed that a single Venturi scrubber could handle the entire current gas flow without excessive backpressure on the sour gas inlet line. Although the H₂S content after the Venturi scrubber rose from ~20 ppmv to ~120 ppmv, the H₂S content of the sweet gas after the packed absorber section remained at around 1 ppmv or less. Thus, it appears that the unit could operate successfully with a single Venturi scrubber in operation. These single Venturi scrubber test results seem reasonable because each of the two Venturi scrubbers was originally designed to handle a gas flow ~5 times as large as current gas flows.

Running the U14 Stretford unit with a single Venturi scrubber may also help reduce plugging of the Venturi scrubber that is in operation. In explanation, a potential cause of Venturi scrubber and tailpipe plugging is low velocity in this equipment, which may allow a portion of the absorbed H₂S enough time to react to form elemental sulfur before exiting the Venturi. Elemental sulfur formed in the Venturi scrubber and tailpipe could add to Venturi scrubber plugging. By running with a single Venturi scrubber, twice as much gas flow will pass through the Venturi scrubber and tailpipe, causing the velocity to roughly double and the residence time to decrease by a factor of approximately two.

Small sulfur particles are known to initiate and to stabilize foam. The presence of elemental sulfur particles exiting the Venturi scrubber tailpipe into the absorber may also promote foaming in the absorber and subsequent packing plugging. Thus, running at conditions with higher velocity with less time for elemental sulfur formation should also tend to reduce foaming in the absorber and reduce packing plugging. (Further discussion of this topic can be found in the section on reducing packing plugging.)

Once the problem of Venturi scrubber and tailpipe plugging is eliminated through sparing, the Venturi scrubber and tailpipe should no longer be a cause of U14 downtime.

3.2 Reducing Electricity Usage

Careful analysis of the use of electric power by each of the sub-units of the Stretford unit clearly led to the conclusion that most savings could be achieved by operating with a single main circulation pump, rather than the two units operated in parallel that was specified in the original design. Running on a single pump could only occur after the unit is converted to operating on a single Venturi and only after the control system is changed so that a second, spare pump starts up if the first pump fails. Provided that these two conditions are met, then it appears from the pump curve for the main solution pumps that a single main solution pump should be capable of supplying a flow of 1680 gpm, which is enough to allow the full design flow of liquid to the absorber (560 gpm) and the full design flow of liquid to one Venturi (1120 gpm). From the pump curve, the pump outlet pressure at this condition would be expected to be about ~90 psig and, the 150 hp motor would be near capacity at about 145 hp, assuming that the solution specific gravity stays at the typical value of ~1.25. By running with a single pump instead of two, it is expected that the total power required by the main solution pumps would drop from 200 hp (149 kW)

(840 gpm and 100 hp/ 75 kW each) to 145 hp (108 kW), saving about 55 hp (41 kW).

Another potential power saving idea was to reduce air flow to the oxidizers. However, Trimeric recommended that air flow should not be turned off to one oxidizer in order to reduce electrical load. The benefit of running with air to just one oxidizer (reduced electrical load) does not outweigh the significant potential downside. Older Stretford papers and the original Parsons manual for the U14 Stretford may state or imply that extra liquid residence time and extra air feed to the oxidizers leads to increased chemical consumption. While this may be a sound theory (based on the assumption that some elemental sulfur may re-dissolve and form thiosulfate if oxidizer residence time is too long), negative effects of too much oxidizer liquid residence time are not known to be actually encountered in practice. As Calpine has observed in their own experiments, turning air off to an oxidizer makes no noticeable difference in chemical consumption or thiosulfate production. Thus, the only clear potential cost-savings benefit is from reduced electricity usage.

In contrast, however, the operational dangers of not fully re-oxidizing the solution and of not creating a good sulfur froth are well known. In particular, if reduced vanadium species are pumped back around to the absorber, they can precipitate, causing higher chemical costs and increased plugging. And, poor froth formation may lead to higher TSS and even more plugging. Thus, since there is little cost benefit and significant potential operating downside, it was recommended that air flow be maintained to both oxidizers.

3.3 Reducing Absorber Packing Plugging

3.3.1 Description of Packing Plugging

The single bed absorber is packed with plastic Flexiring packing. The plastic packing tends to plug with a mud-like material that is relatively easy to remove, in comparison with the layered scale material that is found in the Venturi tailpipes. The mud-like material is found at the bottom of the bed only and decreases in amount with increasing elevation through the bed. Plugging has not been reported to start at the top of the packing.

The fact that plugging is the worst at the bottom of the bed and has never occurred at the top of the packing at U14 is important, because it indicates that the cause of packing plugging probably originates from below the bed rather than from above; therefore the lean solution TSS may be a factor, but is probably not the key factor in packing plugging.

The longer the Stretford unit runs between packing cleanings, the more of the packing that is plugged. For example, when the packing was cleaned in February 2006, after a longer than usual run (reported by operations to be ~514 days), the plugging was said to extend more than halfway up the ~20' bed of packing. In contrast, when the site went down in late March 2007 (for reasons unrelated to the Stretford unit) and the absorber was cleaned again, the plugging only extended about 1' to 1.5' up into the packing.

3.3.2 Likely Causes of Packing Plugging from Below

Conventional wisdom says that a key cause of plugging of packing from below is foaming or frothing at the surface of the liquor in the collection basin of the absorber and inside the disengaging section of the tower. The inlet gas picks up this froth and

carries it into the bottom of the packing. Once in the packing, the sulfur particles find quiet places to settle and plug.

Abundant floating material on the surface of the liquid in the downstream Stretford reaction tank is believed to be closely associated with foaming in the collection basin of the Stretford absorbers. As described previously, the U14 Stretford and some of the other Stretford units at The Geysers are known to have “floc” on the reaction tank from time to time. Taken together, the observation of floc on the reaction tank and the observed pattern of packing plugging from below likely indicate that there is foaming in the U14 absorber, at least part of the time.

3.3.3 Mitigating Packing Plugging

Potential concepts for mitigating packing plugging include addressing the cause of the foaming in the absorber and maintaining plenty of packing irrigation. Some concepts for alleviating packing plugging are discussed below.

Reducing foaming in the absorber and/or the effects of foaming in the absorber – The issue of foaming in the absorber, between the bottom of the packing and the liquid surface in the collection basin, can be addressed in at least two ways, 1) address the cause of foaming, and 2) implement means of minimizing the effects of foaming. In this case, it was recommended that both items be addressed. The text below discusses operational changes to address the cause of foaming. Part 3 of the study, to be published in the future, will address the implementation of physical means to minimize the effects of foaming (e.g., use of sprays to “knock down” the foam resident on the liquor surface in the collection basin).

The best way to limit foaming in the absorber is to limit the causes of foaming. Foaming is believed to typically be caused by surface active agents and/or small particles. Hydrocarbons, which can be surface active agents, can contaminate the Stretford solution from a variety of sources, including the feed sour gas, pump and mixer lubricants, or other intentional or accidental additions. Sources of potential hydrocarbon contamination of the Stretford solution in U14 were sought. Mixer gear boxes were observed to not be leaking. Frothing aids (e.g., diesel) were not being used. And, no other ingress of surface active agents was found. Although ‘floc’ on the reaction tank is a periodic problem, foaming of the oxidizers is much less common at U14. U14 does not return any liquids from the melter to the system, thus, foaming induced by dead bacteria cell contents is unlikely.

Counter-intuitively, in the absence of evidence of a source of unwanted surface active agent, one could try addition of tiny amounts of carefully selected surface active agent. Addition of raw diesel is practiced at some Stretford units. (The organic sulfur compounds in the raw diesel are believed to be the active ingredients.) The addition of raw diesel can sometimes promote better frothing in the oxidizers, which could lower TSS in the lean solution, thus reducing one source of the small particles that can stabilize foaming. This may help alleviate absorber foaming, plugging, and floc on the reaction tank. Addition of raw diesel was recommended by the original process licensor. The likelihood of serious negative side effects is low. Pending results of other changes mentioned below, experimentation with raw diesel as a frothing aid was recommended for U14.

Maintaining plenty of packing irrigation – As a general rule of thumb for Stretford, LO-CAT, SulFerox, and all other similar processes, the higher the circulation rate through the absorber (relative to the sulfur load) the less problems with plugging of the absorber. Calpine U14 was running about 400 gpm of Stretford solution to the top of the absorber in 2007. The original design flow rate is 560 gpm. It is unknown why the flow rate to the top of the absorber was lowered. In any case, raising the flowrate to the top of the absorber back to design levels, preferably even higher, should tend to reduce packing plugging, regardless of the cause. With more liquid flow, there is more chance of flushing solids off of the packing.

Turning up the liquid flow rate to the top of the absorber should benefit operations as long as reasonable rates are used so that the pressure drop of the gas through the packing does not increase to too high a level (e.g., below flood limits). The extent of H₂S removal may improve somewhat. Packing plugging should lessen somewhat. Given that the U14 Stretford is currently operating at lower-than-design total liquid flow rates to the Venturi scrubbers and absorber, and given that Trimeric recommended operating on one Venturi with an even lower total liquid flow-rate (although with higher flow rates to each of the absorber and the one Venturi in operation, individually), there should not be any negative impacts on the reaction tank, oxidizer and other downstream equipment.

3.4 Reducing Thiosulfate Concentrations

Thiosulfate at U14 is generally between 300 g/l and 400 g/l, well above the ~250 g/l normally used as a target maximum for most Stretford units. The likely primary reason for high levels of thiosulfate is that U14 uses a vertical pressure filter and returns the wash water to the Stretford unit. The vertical pressure filter, which uses air pressure in elastomeric bladders to squeeze solution out of the sulfur cake, does not leave much Stretford solution in the cake. Then, the water wash removes the remainder of the Stretford solution and the wash water with the thiosulfate goes back into the Stretford system.

There are a number of reasons why high thiosulfate concentrations are harmful to Stretford operation, including:

- Thiosulfate production rates increase with increasing thiosulfate concentration in the liquor.
- Plugging in general is worse when salts levels are high.
- Salt precipitation, subsequent possible foaming problems, filtration problems, and/or other precipitation-related problems are possible with high salts levels.
- Vanadium solubility is lessened, and precipitation may occur at high salts levels.
- Pump horsepower requirements are higher with higher salts concentration levels with concomitant increasing specific gravity levels.
- Corrosion is worse at high salts levels.

Of these, the first issue will be discussed further below, along with some steps that could be taken to lower thiosulfate levels.

The conventional wisdom is that high salts levels worsen plugging in Stretford units. Scale formed under conditions of high salts is harder and may build up more quickly than it does under

conditions of low salts concentrations. High salts concentrations lower oxygen solubility in the Stretford solution which reduces re-oxidation in the oxidizers. If the vanadium is not re-oxidized fully in the oxidizers, then there is more chance of sodium vanadyl vanadate (a reduced form of vanadium) precipitation, especially in the Venturi scrubbers and in the absorber. (Sodium vanadyl vanadate is the black material that occurs in the layers of sulfur scale.)

The thiosulfate production rate is higher if the concentration of thiosulfate is high; this has been described as “auto-catalytic” by some. Thus, if lower thiosulfate levels are maintained, less thiosulfate in total will also be produced. Since production of thiosulfate consumes caustic, reducing thiosulfate production rates should reduce chemical caustic consumption.

If thiosulfate production is auto-catalytic, then it is theoretically possible to reduce its production rate and to reduce the required solution purge rate by operating at a lower thiosulfate concentration. It has been said that optimum thiosulfate concentrations for most plants fall between 100 g/l to 150 g/l (Keene, 1989).

Two operational improvements to reduce thiosulfate levels that were suggested for Unit 14 follow:

Inject filter wash water back into geothermal reservoir with recharge water - One way to reduce thiosulfate concentration would be to stop sending the filter wash water back into the Stretford unit. Instead, the wash liquid could be sent, along with other sources of geothermal recharge water, to injection, as is done at other Stretford units at The Geysers. Sending filter wash water to injection removes some thiosulfate from the system and will result in lower total thiosulfate concentrations.

Increase ADA concentration - Although the function of ADA is to increase the oxidation rate of vanadium, it may have the opposite effect on the oxidation of sulfur to thiosulfate. Laboratory testing indicates that the oxidation of polysulfide to thiosulfate may be inhibited by the presence of ADA (Trofe & DeBerry, 1993). Calpine currently maintains ADA concentrations in the 0.7 g/l to 1.2 g/l range. It is possible that Calpine could reduce thiosulfate production by increasing ADA concentrations.

3.5 Other Potential Changes to Unit Operations

Although it is not recommended to eliminate air flow to an oxidizer, to reduce reaction tank size, to eliminate an oxidizer, or to replace the existing pressure filter, there are other possible improvements that could be attempted as part of an evolutionary operating improvement program. Two examples are 1) turning off the mixer to the reaction tank, and 2) optimizing the oxidizers for optimal oxidation and froth production.

As mentioned previously, solids tend to build up on the surface of the liquid in the reaction tank in the U14 Stretford unit. The fact that this vessel is stirred may not help this floating solids situation. Further, there is a school of thought that says that a plug flow reaction tank functions better than a stirred reaction tank in that less thiosulfate is produced. (This has to do with residence time in the reaction tank. At least 7 minutes are required in the reaction tank to allow the reaction time for elemental sulfur formation, primary particle formation and agglomeration to 100 micron-sized particles that will be separated in the froth. Thus, there is a decreasing probability of salts formation with plug flow in the vessel.) It should be possible to turn off the reaction tank mixer for a few weeks to test if the floating solids situation is

improved. Or, if there are concerns about solids buildup in the bottom of the reaction tank, then it might be possible to run the mixer only intermittently, for example, an hour per shift or an hour per day. If this test begins to cause a problem with operations, the mixer could be turned back on. If the test causes improvement or no change at all, then the mixer could be left off or left on intermittent use. However, until the tests can be completed, removal of the floc on the reaction tank should be made part of the routine operations drill.

Similarly, it may be possible to optimize the oxidizer operation for optimal oxidation and optimal froth floatation. One such test might be to keep both air and the mixer going in the first oxidizer in order to achieve good re-oxidation of the vanadium, but to optimize the second oxidizer for froth formation by turning off the mixer and adjusting air flow to achieve the best froth possible. This potential test would require that the air sparger in the second oxidizer be evaluated for its ability to provide appropriate bubble sizes with the mixer turned off. Potential positive outcomes include lower TSS in the solution going back to the Venturis and to the absorber, and better feed for the filter (e.g., higher solids content). If the test proved to have a negative outcome, then the mixer could be turned back on and the air rate adjusted back to original levels.

4.0 Summary

Calpine intends to test some of these operational changes in the near future to help reduce total treating costs of the Stretford unit. At the forefront are switching the absorber functionality to a single Venturi unit to allow for an on-line spare and running on a single main pump. Adding raw diesel as a froth aid and reducing thiosulfate concentrations would be examined next. Part 3 of this study also identifies physical modifications to further reduce sulfur plugging and process shutdowns, including recommendations for some instrumentation and analytical data for process monitoring and control.

5.0 References & Bibliography

5.1 References

Benn, B.; K.E. McIntush, C.M. Beidler, D.L. Mamrosh, O.E. Hileman, “Unit 14 / Sulphur Springs H₂S Abatement Process Screening and Stretford Improvements Study – Part 1”, GRC *Transactions*, Vol. 34, 2010.

Keene, D.E., “British Gas Stretford Process, The Basis of Good Process Design and Operation,” Proceedings of the 1989 GRI Liquid Redox Sulfur Recovery Conference, Austin, Texas, 7-9 May 1989, report number GRI 89/0206, pp. 72-115.

Trofe, T.W., D.W. DeBerry, “Sulfur By-product Formation in the Stretford Process,” Topical Report, Report Number GRI-93/0107, September 1993, p. 4-17, p. 3-25

5.2 Bibliography

Nicklin, T., B.H. Holland, “Further Development in the Stretford Process,” *Gas World* 158, 7 September 1963, pp 273-278... as referenced in Trofe, T.W., D.A. Dalrymple, F.A. Scheffel, “Stretford Process Status and R&D Needs,” Topical Report, Report Number GRI-87/0021, p. 5-79.

Trofe, T.W., K.E. McIntush, M.C. Murff, “Stretford Process Operations and Chemistry Report,” Final Report, Gas Research Institute, Report Number GRI-93/0121, November 1993.