



the gas stream that is fed to the Stretford unit. Figure 1 shows a process flow diagram of the BRP Stretford unit.

About 99.9% of the H<sub>2</sub>S fed to the Stretford unit is scrubbed into the Stretford solution by contacting the gas with lean Stretford solution in a venturi scrubber followed by a 4-tray polishing tower. The gas that exits the polishing tower contains less than 10 ppmv H<sub>2</sub>S and is referred to as “sweet gas” by BRP staff. The Stretford solution exiting the venturi and polishing tower, which is now “rich” in captured H<sub>2</sub>S, collects in the delay tank below the polishing tower.

In the delay tank, dissolved alkali vanadates (V5+) in the Stretford solution react with the captured H<sub>2</sub>S to form solid elemental sulfur plus dissolved alkali vanadites (V4+). The slurry of Stretford solution and elemental sulfur particles is gravity fed to two oxidizer tanks that operate in parallel.

In the oxidizers, the vanadium in the solution is re-oxidized (from V4+ ions back to V5+ ions) with aerial oxygen introduced via a sparger located near the bottom of each oxidation tank. Anthraquinone disulfonic acid (ADA) present in the solution acts as an oxygen carrier / catalyst, assisting in the re-oxidation of the vanadium species. In addition to re-oxidizing vanadium species, the air bubbles that exit the sparger and rise through the solution also capture the micron-sized sulfur particles and carry them to the surface, thus generating the characteristic Stretford sulfur froth. This froth floatation is the primary means of separating the elemental sulfur from the (now) lean Stretford solution. An over/under weir in the oxidizers separates the sulfur froth from the lean solution. The lean solution is gravity fed to the balance tank, and the sulfur froth overflows to the stirred slurry tank.

Periodically, slurry is pumped from the slurry tank to a rotary drum vacuum filter, where the solid sulfur is exported as sulfur cake. Filtrate (Stretford solution) from the filter and water used to wash sulfur cake in the filtration process are currently being recycled back to the balance tank.

The Stretford unit also contains an evaporator to remove water from the system (the reactions produce water), if needed, and a chemical make-up tank. Required make-up chemicals are prepared in the make-up tank and then fed to the balance tank. Lean Stretford solution is pumped from the balance tank back to the venturi and polishing tower via the main circulation pump.

Prior to the work discussed in this paper, the unit had undergone several modifications over a period of years. The modifications included the installation of: a mercury removal bed between inlet knockout drum and venturi; an outlet discharge pressure control (bypass) valve on the sweet gas line after the polishing tower; a level control valve for the delay tank; and an air sparger device in each of the oxidizers (to replace the original venturi mixers that introduced air into the solution).

A well-designed and well-run Stretford unit is generally capable of producing a sweet gas with very low H<sub>2</sub>S, frequently less than 1 ppmv. Most units were constructed before 1990, and there are no licensors known to be actively licensing the technology, but appropriately knowledgeable parties can design Stretford units using open art. Stretford units also tend to have a few operating problems (Trofe, *et al.*, 1993; Benn, *et al.*, 2010; Benn *et al.*, 2011; and McIntush, *et al.*, 2008); sulfur plugging and sulfur byproduct salt buildup are two examples. And, the units require significant operator attention to function reliably. Specific

problems noted at the BRP Stretford unit include sulfur deposit buildup on the polishing tower trays, sporadic and sub-optimal froth production in the oxidizers, plugging of the original air/solution venturi mixers at the oxidizers, occasional higher-than-desired vanadium content in sulfur cake, and occasional plugging of in-line strainers to pumps.

## Historic and Future H<sub>2</sub>S Removal

Data on historic unit performance and operating practices were collected from several resources. Former operators of the plant were contacted, operator logs and public records (CEC, 2006) were reviewed, and analytical data measured on site were summarized. Key results regarding H<sub>2</sub>S removal that were gleaned from the data collection effort can be summarized as follows:

- Removal of H<sub>2</sub>S from the vent gas to less than 10 ppmv was observed after startup in 1985 and 1986 when operating with incoming H<sub>2</sub>S concentrations of 180-250 ppmw and 0.42 wt% NCG in the feed steam to the turbines. (At this time, the power plant was operating near nameplate capacity, roughly 55 MW gross, according to operators);
- Removal to less than 10 ppmv H<sub>2</sub>S was observed in 1987 when operating at 30-35 MW and with ~150 ppmw H<sub>2</sub>S and 0.43 wt% NCG in the feed steam to the turbines; and,
- Removal to 10 ppmv was observed when the Stretford unit was fed vent gas with roughly 12 vol% H<sub>2</sub>S (611 ppmw in steam and 0.42 wt% NCG in the feed steam to the turbines) in the early 1990s. This H<sub>2</sub>S vent gas content is about 2 times higher in concentration than recent operations and almost twice that expected under the proposed 30 MW conditions.

The data show that the BRP Stretford unit has historically been able to produce sweet gas with 10 ppmv or less H<sub>2</sub>S under a variety of conditions. However, the proposed operational conditions (30 MW power production, 1 wt% NCG at 500 ppmw H<sub>2</sub>S in the steam feed to the turbines) are not within historical practice.

Two approaches were used to predict performance under the proposed operating conditions. First, it was assumed that the approximate total H<sub>2</sub>S removal efficiency of the abatement unit stayed constant. Some types of scrubbing equipment exhibit roughly constant removal efficiencies (e.g., trayed towers sometimes have roughly constant removal efficiency as gas rates increase due to increased tray froth and surface area and better mass transfer). Thus, the assumption of constant removal efficiency seems a reasonable first approximation. Historically, the total H<sub>2</sub>S removal efficiency of the BRP Stretford unit ranged from 99.986% to 99.997%. Using a H<sub>2</sub>S removal efficiency of 99.990%, the H<sub>2</sub>S content of the sweet gas would be expected to be less than 4 ppmv at the projected 30 MW conditions.

A second, less-optimistic estimate of the H<sub>2</sub>S removal performance for the Stretford unit was based on estimating the removal efficiency of the Venturi and polishing tower separately. The Venturi performance was estimated using a relationship in the published literature (Vancini & Lari, 1985) that relates the Venturi performance to total gas rate and H<sub>2</sub>S concentration. Using this relationship and historical Venturi efficiency data from the plant

(99.84 to 99.98%), the Venturi removal efficiency was predicted to be 98.75% at future maximum conditions. This agrees well with Venturi efficiencies at other Stretford units known to Trimeric. The polishing tower H<sub>2</sub>S removal efficiency was estimated by assuming a tray efficiency of 60-65%, which is close to observed historical efficiency. Literature data show that this tray efficiency range is on the low end of the typical range for gas absorption using trayed columns when the resistance in the liquid film dominates, as it does in well-buffered Stretford solutions. If the 4 trays in the BRP polishing tower averaged 62-63% efficiency, then the removal efficiency across the entire polishing tower would be 98%. This is also in the range of efficiencies observed at other Stretford polishing towers known to the authors. Using the 98.75% efficiency for the Venturi and 98% efficiency for the polishing tower gives an estimated 10 ppmv of H<sub>2</sub>S in the treated gas from the BRP Stretford unit at projected future 30 MW operating conditions (550,000 lb/hr of steam fed to the turbines with 1 wt% NCG and 500 ppmw H<sub>2</sub>S).

Based on the two approaches noted above, it was concluded that the BRP Stretford unit should be able to produce a sweet gas with 10 ppmv or less H<sub>2</sub>S while operating under the proposed conditions. Thus, modifications to the Stretford unit absorber equipment solely for the purpose of enhancing H<sub>2</sub>S removal were not recommended. It was suggested that BRP monitor the Stretford performance as the power plant load increases to 30 MW over a period of several months. If, during that time the H<sub>2</sub>S removal performance of the Stretford unit is less than anticipated, mitigation steps (i.e., running at higher than normal alkalinity) should be taken to improve H<sub>2</sub>S removal until physical changes to the unit (if needed) are made.

The remainder of this paper discusses the methods that were proposed to minimize plugging of the Stretford plant equipment, and lengthen the run time of the unit between shutdowns. These changes are not necessarily required to achieve the desired H<sub>2</sub>S removal efficiency, but they could improve reliability. Although the headings and text that follow below indicate “potential” changes, BRP has made some of these changes already. Where changes have already been implemented, observations from subsequent unit operation are given.

## Potential Improvements to the Oxidizer System

One of the ways to reduce plugging in the polishing tower is to reduce the total suspended solids (TSS) in the lean liquor going to the absorption section. BRP analytical data show that the TSS ranges from 0.1% to 0.7% (from mid-2009 to mid-2010), while the design target for a Stretford unit is typically 0.1% TSS maximum. The TSS can be lowered by establishing good froth flotation in the oxidizers. Some changes that could be made to improve the froth flotation in the oxidizers are discussed below.

### New Air Sparger Design

BRP noted that they were not observing steady froth production in the oxidizer vessels in 2010. Properly designed air spargers are an important factor in achieving good, consistent froth flotation. Air spargers typically used in Stretford oxidizers without mechanical stirrers often consist of a number of diffuser plates mounted on top of short, open-bottomed cylinders. These

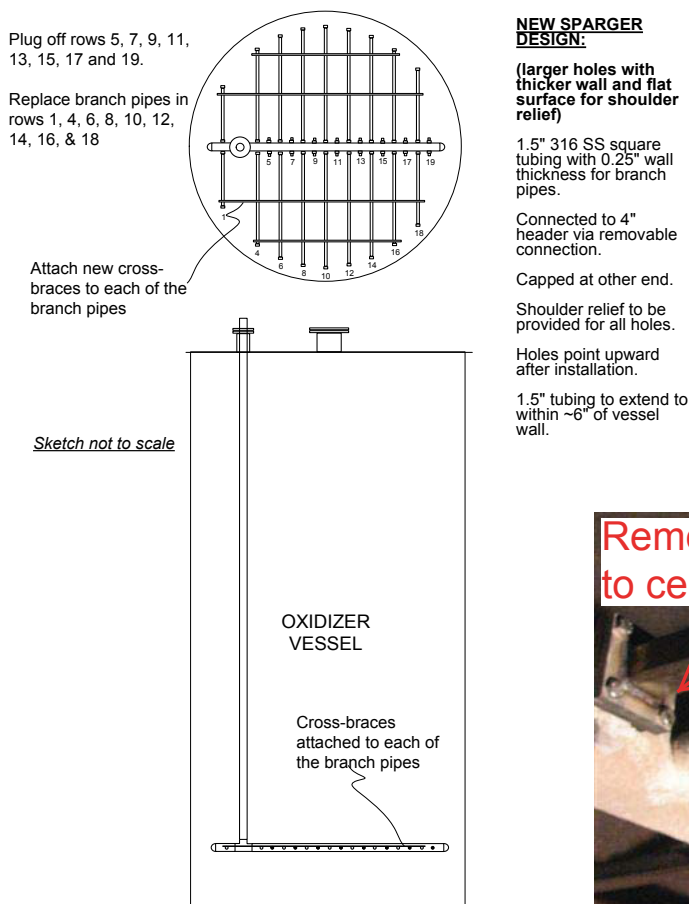
assemblies are commonly called “diffusers”. The diffusers are elevated off of and attached to the bottom of the oxidizer via short legs. A small pipe conducts compressed air into each of the diffusers. The diffuser plates are drilled to provide holes of an appropriate size and number to give good air distribution and proper up-flow rates. In contrast to this “typical” air diffuser design, the air spargers that were previously added to the BRP Stretford unit (called the “old air spargers” here) consisted of a central distribution pipe to which are connected smaller branch pipes drilled with air sparger holes. Although not typical, this type of system could function well if designed properly. However, the available data at the plant indicate that the old air spargers were not likely to provide even distribution of air.

The one-inch-diameter branch pipes in the old air spargers had two 1/8 inch, horizontally oriented holes every inch. Calculations indicate that the old air sparger had too many holes (3,496) for the desired air flow rates. As a result, the air flow was very likely not evenly distributed across the cross-section of the oxidizer vessel with the old air sparger. The holes were also only 1/8 inch (0.125 inch) in diameter, which is smaller than the usual size range of roughly 4.5 millimeters (~0.177 inch) to 6 millimeters (~0.236 inch). Holes that are too small may plug more easily than larger holes. In addition, the use of small-diameter, thin-walled, round pipe for the branch pipes in the old air sparger made it more difficult to provide consistent shoulder relief around the circumference of the holes. (Shoulder relief / rounding off the sharp corners at the exit of the holes is thought to reduce plugging of the holes.) These branch pipes also had a history of breaking loose from the central distributor, indicating that the old sparger design did not contain adequate bracing.

A new air sparger design was recommended, approved, constructed, and installed in 2011. Figure 2 shows some details of the new air sparger. The new spargers provide good air distribution over an appropriate range of air flows and temperatures from 100°F to 250°F while also providing the proper air up-flow rate to give proper froth flotation. It has fewer, larger sparger holes, and approximately half (nine) of the sparger pipe connections were used (in comparison to the old air sparger design, which had 17 connections). Square tubing of 1.5 inch size with 6 millimeter holes was used as the branch piping. The square tubing provides for a flat surface with an increased wall thickness, which allowed the holes to be manufactured with the proper shoulder relief. The holes are directed upward in the new design, instead of horizontal as in the old air sparger design.

A guideline for good air distribution in this type of device is that the pressure drop across the hole should be at least 10 times higher than the pressure drop down the sparger pipe (or branch pipe) (Perry & Green, 1984). As can be seen in Table 1, the ratio of the hole pressure drop to the pressure drop down a branch pipe was much less than 10 for the center sparger pipe (branch) of the old air sparger that had been previously added to the unit, which means that the old air sparger had poor air distribution. In comparison, the new design has a ratio of greater than 50.

Figure 3 shows a photo of the new device including the plugged ports that had been previously part of the old air sparger design (but were no longer needed), the removable connection of the sparger branch connections to the 4-inch header, and the bracing support and welding to the tank walls.



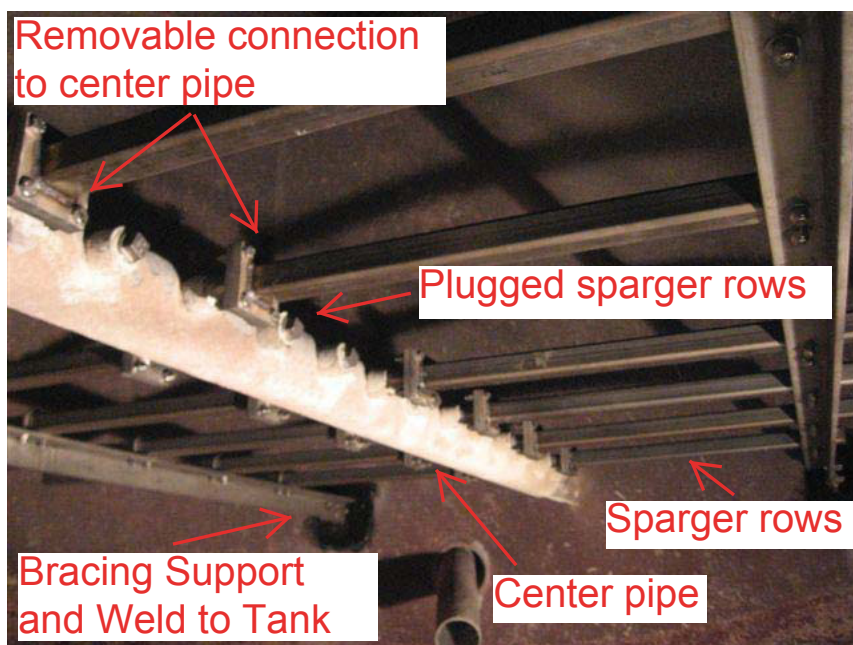
**Figure 2.** Some Features of New Air Sparger for Oxidizer Tanks.

With the new air spargers in operation, BRP has noticed continuous good froth in both oxidizer tanks. The new sparger design has lowered the TSS from the 0.7% measured in past years to 0.15%, approaching the target level of 0.1% mentioned previously. The lower TSS should result in less plugging in the polishing tower.

**NEW SPARGER DESIGN:**  
 (larger holes with thicker wall and flat surface for shoulder relief)  
 1.5" 316 SS square tubing with 0.25" wall thickness for branch pipes.  
 Connected to 4" header via removable connection.  
 Capped at other end.  
 Shoulder relief to be provided for all holes.  
 Holes point upward after installation.  
 1.5" tubing to extend to within ~6" of vessel wall.

### Oxidizer Capacity

The volume and the height-to-cross-section ratio of the oxidizers relative to the process requirement are also important for good froth production. The BRP Stretford unit currently has two oxidizers with a total liquid residence time of 36 minutes, which is less than the usual range of residence times of 45-60 minutes. The original design air up-flow rate is 5.7 ft<sup>3</sup>/min per square foot of oxidizer cross-sectional area, which is well above typical up-flow rates of Stretford systems. Because the oxidizers have a residence time lower than typical and an air up-flow rate higher than most rules of thumb for good froth flotation, it was recommended that BRP carefully track the TSS levels as the power load to the plant increases to ensure that the TSS can be maintained around 0.1%. Additionally, it was recommended that BRP closely monitor any increased tendency for plugging of equipment.



**Figure 3.** Photo of New Air Sparger Installed in Oxidizers.

**Table 1.** Features of Old Air Sparger and New Air Sparger Design.

Sparger Option	Temp, °F	Air Density, lb/ft <sup>3</sup>	# of Sparger Rows	Hole Size, Inches	Hole Size, mm	Branch Pipe Diameter, Inch	# of Rows of Holes	Hole Orientation	Hole Pressure Drop, psia	Ratio of Hole Pressure Drop to Pipe Pressure Drop
Old Air Sparger Design	100	0.120	17	0.125	3.2	1	2	Horizontal	0.0037	-2.4
New Design	100	0.120	9	0.236	6	1.5	1	Vertical	0.2434	-55.9
	250	0.094	9	0.236	6	1.5	1	Vertical	0.3085	-57.9
	100	0.120	9	0.236	6	1.5	1	Vertical	0.0604	-69.7
	250	0.094	9	0.236	6	1.5	1	Vertical	0.0766	-74.6
	100	0.120	9	0.236	6	1.5	1	Vertical	0.9734	-49.5
	250	0.094	9	0.236	6	1.5	1	Vertical	1.2341	-50.5

### Potential Improvements to Absorber System and Delay Tank

The absorber system and delay tank equipment discussed here consists of the venturi scrubber, polishing tower, delay tank, and associated piping and instrumentation. The historic plant data and calculations discussed earlier suggest that the current absorber system may be able to achieve 10 ppmv or less H<sub>2</sub>S at all planned future conditions. While the existing absorber design may not be ideal, it appears likely to provide sufficient gas/liquid contact to remove the H<sub>2</sub>S to the necessary concentration under the anticipated future

feed gas load. For this reason, the absorber system recommendations listed below are mainly directed at improvements that could potentially be made to existing equipment to achieve longer run time and allow better operation and easier troubleshooting.

### ***Caustic Addition Point***

Makeup caustic was previously added at the main circulation pumps. However, as a result of this study, the caustic supply tubing was modified so that the caustic is fed only into the solution that is going onto the top tray of the polishing tower. The pH of the solution on the top tray should increase slightly as a result of this change. Higher pH at the top of the polishing tower should result in some improvement in H<sub>2</sub>S removal from the gas. Also, at other Stretford plants, higher pH in the operating solution is often associated with softer sulfur deposits and less plugging. BRP has noticed lower sweet gas H<sub>2</sub>S concentrations since the feed point has been modified. Enough operating time has not accrued since this change was made to determine if it will also reduce plugging.

### ***Consider Replacing Trays With Plugging-Resistant Packing***

The replacement of the trays in the polishing tower with plugging-resistant style packing may allow the polishing tower to operate over extended run times before plugging causes excessive pressure drop and/or loss of H<sub>2</sub>S removal. However, retrofitting the polishing tower to allow for the installation of packing may be complicated and require significant down time. Given that some of the other recommendations included in this paper (e.g., caustic addition to top tray, and tray flushing) may decrease plugging occurrences and increase run time, installation of packing should only be considered further if the other measures do not significantly improve operations.

### ***Delay Tank Residence Time***

The Stretford system has a delay tank liquor residence time of roughly 5 minutes, while the usual design minimum is 7-10 minutes. Although considered to be a minor area of improvement, a longer delay tank residence time could allow more of the dissolved hydrogen sulfide to react to form elemental sulfur prior to the oxidizers, which could reduce the rate at which sulfur salt byproducts are made.

### ***Instrumentation and Spare Equipment***

Flow meters are currently not installed to measure the flow rates of the scrubbing liquor to the top of the polishing tower, to the venturi scrubber, and to the delay tank vapor space sprays; it was recommended to consider the addition of flow meters to these lines in order to allow for easier troubleshooting. It was also noted that the inlet H<sub>2</sub>S analyzer was not functioning properly, and the vent gas flow measuring device that is installed did not appear to be accurate. Repair or replacement of these devices was recommended so that the sulfur load to the plant could be calculated more accurately. In addition, BRP could consider keeping a spare venturi scrubber and dip tube assembly on hand to allow for quicker replacement should it develop a crack or become plugged with sulfur.

## **Considerations for Improvements to Operations Practice**

In addition to modifications to equipment, suggestions were also made for improvements related to operations practice and training. These are items that may enhance operational reliability but are not critical to the H<sub>2</sub>S removal performance of the unit.

### ***Exercise the Plant***

It was recommended that BRP operations staff practice regular exercising of the plant, as was known to have been done in the 1980s. Here “exercise” means using the available controls to occasionally increase liquid flow rates (or introduce a liquid flow where there is normally no flow) in certain areas of the plant so that solids that may have collected are flushed through the system to the oxidizers for removal as froth. It was recommended that BRP utilize all of the connections around the polishing tower to wash the trays or flush the lines on a regular basis (e.g., once per shift). BRP’s staff has since begun putting this recommendation into practice.

A written protocol for regularly exercising the Stretford unit and preventing solids buildup has been established and should help to reduce plugging in the equipment. The bottom tray wash spray valves are operational currently and cycle 6 times per day for 120 seconds per tray. The top tray liquor feed valves and piping have been plumbed for future utilization. The mist eliminator in the top of the polishing tower also has a spray which BRP has recently plumbed and it is exercised 6 times per day for 30 seconds. Exercising the plant could also include flushing the delay tank froth control spray bar and evaporator by surging flow to these devices. Delay tank drain valves and lines are currently being flushed by cycling levels and level control valves, and the practice should also be used for all liquid lines, if possible.

### ***Optimize ADA Concentration to Promote Re-Oxidation***

The ADA concentration could be optimized to make sure that it is in the appropriate range for good operation. ADA is a re-oxidation catalyst for the vanadium (V<sup>4+</sup>). Stretford plants typically run with ADA concentrations from 0.5 grams per liter to as high as 5 gpl. The recent concentration target at BRP is around 1.5 gpl. If the concentration levels in the fresh solution of V<sup>5+</sup> and total V are monitored regularly on site, then the ADA concentration could be adjusted to optimize the re-oxidation of V<sup>4+</sup> to V<sup>5+</sup> in the oxidizers. Higher ADA results in better re-oxidation of V to a point. The target of greater than 90% of total V as V<sup>5+</sup> in the lean Stretford solution results in the ability to operate the solution with a lower sodium vanadyl vanadate concentration. Sodium vanadyl vanadate is the cause of the black color in sulfur deposits that is sometimes seen in the absorbers of many Stretford systems, and it is believed to cause very hard deposits. Thus, keeping the V fully re-oxidized to prevent sodium vanadyl vanadate formation leads to reduced plugging.

### ***Run at Higher Alkalinity and at pH ~9***

Operating the Stretford unit at higher alkalinity and at pH of about 9 promotes H<sub>2</sub>S removal, enhances re-oxidation of vanadi-

um, and reduces plugging tendencies. Higher pH also favors better H<sub>2</sub>S capture from the vent gas in the absorption section. Higher alkalinity improves the re-oxidation rate, which allows for lower sodium vanadyl vanadate concentrations and reduces plugging. As mentioned earlier, conventional wisdom with Stretford units is that higher pH also results in somewhat softer sulfur deposits, which can also help reduce plugging or allow plugs to be flushed free more easily. A pH of 9 is about as high as is usually recommended for most Stretford systems. pH values higher than 9 can rapidly increase sulfur byproduct salt production rates. BRP was operating the liquor pH at a target of 8.7 but has recently increased their target to 9.0, and the sulfur deposits have been notably softer with less plugging.

### Other

Operations staff could be regularly trained on the basic operations of Stretford systems and solution chemistry so that they can understand the optimal conditions for running the unit. On-site chemical analysis and tracking is very important to help evaluate the performance of the Stretford unit. BRP analyzes for pH, total alkalinity, thiosulfate, total vanadium, ADA, TSS, specific gravity, and boron; but V<sup>5+</sup>, TDS, and sulfate could also be included to aid in troubleshooting the unit.

### Summary

The results of this study show that the absorber unit in the current Stretford system should be able to remove H<sub>2</sub>S down to 10 ppmv or less at the expected future conditions (30 MW, estimated 550,000 pounds of steam per hour, 1 wt% NCG, and 500 pppw H<sub>2</sub>S). This conclusion was based on rough calculations of the absorber performance using historic removal data and relationships found in the literature. If it turns out that 10 ppmv is not achievable, then mitigation steps (e.g., running at extra high alkalinity) could be used until physical modifications could be made to the absorber equipment.

The oxidizer system should be monitored for proper froth flotation and TSS reduction as the power load to the plant increases. Recommended modifications to the air spargers in the existing oxidizers have been implemented and are successfully making good froth in the oxidizers. Good froth production helps reduce the total suspended solids in the liquor to the absorber and helps reduce plugging in the polishing tower and other locations in the Stretford unit.

Because the absorber equipment appears to be capable of meeting the 10 ppmv H<sub>2</sub>S specification at future conditions, only suggestions for improvements to minimize plugging were made. These included potentially moving the caustic addition point, considering the replacement of the polishing tower trays with plugging resistant packing, maintaining a spare venturi scrubber and dip tube assembly, adding liquid flow measurement (to the venturi scrubber, to the delay tank vapor space sprays, and around the top of the polishing tower), and maintaining inlet gas analyzers and flow meters for troubleshooting purposes.

BRP's staff has begun to exercise the plant by regularly flushing equipment, which promises the potential of significant improvement to the run time of the Stretford. Other more minor suggestions for better operation were to optimize the ADA concentration for vanadium regeneration and, as put into practice in 2011, to operate at higher alkalinity and pH for better H<sub>2</sub>S removal and plugging reduction.

### References

- Benn, B., K. McIntush, C.M. Beitler, D.L. Mamrosh, and O.E. Hileman, "Unit 14 / Sulphur Springs H<sub>2</sub>S Abatement Process Screening and Stretford Improvements Study – Part 1", Geothermal Resources Council Transactions, v. 34, pp 1209 – 1212, 2010 Annual Meeting, 24-27 October 2010.
- Benn, B., K. McIntush, C.M. Beitler, D.L. Mamrosh, and O.E. Hileman, "Unit 14 / Sulphur Springs H<sub>2</sub>S Abatement Process Screening and Stretford Improvements Study – Part 2", Geothermal Resources Council Transactions, 2011 Annual Meeting, 23-26 October 2011.
- CEC, "Existing Geothermal Facility Improvements", Hetch Hetchy / SFPUC Programmatic Renewable Energy Project Deliverable D2.1.4.c, Final Report, California Energy Commission, Public Interest Energy Research Program, 15 February 2006.
- McIntush, K.E., N.A. Hatcher, J.A. Stavros, T.A. Andreatta, B. Christlieb, "Revised from 2007: Sharing Best Practices for Optimization of Beavon Stretford TGUs", Proceedings of the 58th Laurance Reid Gas Conditioning Conference, 24 February to 27 February 2008, Norman, Oklahoma, USA, pp. 429-460.
- Perry, R.H. and D.W. Green, Perry's Chemical Engineers' Handbook 6th Edition, McGraw Hill Book Company, 1984, p. 5-48 and p. 5-49.
- 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.
- Vancini, C. A. and R. Lari, "The Peabody-Stretford Process on Geothermal Incondensable Gas", Paper No. 82d, AIChE Spring National Meeting, Houston, TX, 27 March, 1985.