

DESIGN OF DIRECT INJECTION H₂S SCAVENGING SYSTEMS

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ABSTRACT

Removal of small quantities of H₂S from natural gas is generally done with scavengers, chemicals which react more or less irreversibly with H₂S and which can then be disposed of safely. One of the approaches to using scavengers has been to inject them directly into a pipe line. This approach is favored at sites with existing pipelines, and at sites where large towers are not feasible or cost effective such as on offshore platforms. Another application is when sour gas has cropped up after the installation has been built. This direct injection (DI) approach has been a “black art” for the most part and as such has been improperly applied with concomitantly poor results in many cases. Not only has this led to waste and excessive consumption of expensive scavenger chemicals, but also corrosive and hazardous conditions which have led to failures on offshore platforms. GTI has developed a deep understanding of these systems through experimental testing at a commercial scale test loop, conducting a joint industry project (JIP) to develop a detailed model of direct injection scavenging, and has now designed four commercial installations, two of which are operational and working according to design. Previous application of DI scavengers at some of these sites was unable to achieve H₂S pipeline specifications of 4 ppmv irrespective of the quantity of scavenger employed. With the GTI design, achievement of H₂S pipeline specifications was possible at nominal injection rates on the order of 2 gallons of ethanol triazine scavenger per lb of H₂S removed. Some of the issues in design which arise are the effect of nozzles and mixers; pipe orientation and size; gas velocity; liquid rates and other variables. Recently GTI has constructed a ¾ in. diameter, 260 ft. long test loop to conduct controlled experiments with various scavengers at conditions representative of natural gas production operations. The new facility supplements the existing 2 in. and 6 in. diameter, 250 ft. long lines at ChevronTexaco’s McAllen Ranch site where most of the earlier work has been carried out. This lab scale unit enables us to test various schemes such as the effect of multiple scavenger feed points, new mixing approaches and devices and the effect of recycling spent scavenger chemical. This paper describes the two commercial installations that we have designed for gas storage fields in the Midwest and discusses their performance. The new laboratory test loop is also described and baseline test results are presented.

INTRODUCTION

Natural gas with low H₂S content (e.g., < 200 ppmv) is often treated with triazine-based liquid scavengers to reduce its H₂S level to below pipeline specifications of 4 ppmv. Two different gas-liquid contacting approaches are employed in the industry which can be classified as “tower type” and “direct-injection type”. In the first approach, the sour gas is brought into contact with a batch of liquid or solid scavenger in large carbon steel towers while in the second approach the liquid scavenger is directly injected into the pipeline via a quill or a dispersion nozzle. The gas operators frequently select the direct-injection approach because of its lower capital cost and reduced hardware requirement. The latter is particularly useful for offshore applications where space and weight are severely restricted. Despite many stated advantages of direct-injection over the batch contacting approach, the ability to predict the performance of the direct-injection systems or achieve treatment specifications without excessive chemical usage is usually a challenge. For these reasons, GTI and others in the industry have directed research over the past decade to develop an improved understanding of the fundamental mechanisms controlling the direct-injection scavenging process. The potential benefit of such an effort is substantial because the cost of removing small amounts of H₂S can be extremely expensive, easily topping \$25,000 per ton removed. In the U.S. alone about \$50 million is spent on H₂S scavenging chemicals every year [1].

H₂S scavenging research has been conducted primarily by independent research organizations such as GTI, product development groups within H₂S scavenging agent manufacturing companies, or companies that use the products to treat their gas. For example, a group of several companies involved in North Sea gas production sponsored a project to develop a better understanding of how scavenging applications might be made more efficient. As follow-on to this proprietary work, GTI, on behalf of three gas producer companies began a joint-industry project (JIP) in 2001 to gather specific engineering test data and to use those data to develop a software package to improve techniques for designing, troubleshooting, and optimizing H₂S scavenging systems. This package expands on the capabilities of an existing GTI software product, Scavenger CalcBase™, developed to allow rapid screening of H₂S scavengers in fixed tower applications. The first phase of this JIP was completed at the end of 2003 and the Phase II work was started in June 2004.

As stated earlier, GTI has been active in the field of H₂S Scavenging research since the mid-1990s. Research has been focused mainly on direct-injection of scavengers into the natural gas gathering or transmission line. Additional work is still continuing for better understanding and designing these systems. Recently, GTI has constructed a test loop to conduct controlled experiments with various scavengers at conditions representative of natural gas production operations. The new facility supplements the existing 2 in. and 6 in. diameter, 250 ft. long lines at ChevronTexaco’s McAllen Ranch site where most of the earlier work has been carried out [2, 3]. Although the diameter of the piping in the new test loop is only ¾ in., comparison of the data with earlier, larger-scale data indicates good agreement according to scaling rules already developed. The unit will enable data to be acquired at a range of conditions that cannot be achieved in the field, especially high temperature and with variable moisture, CO₂ and H₂S concentrations in the gas. The new lab unit will also be helpful in studying the effect of multiple scavenger feed points, new mixing approaches and devices and the effect of recycling spent scavenger chemical.

The recent research efforts at GTI have also focused on the application of direct-injection scavenging for natural gas storage field applications where the operators have increasingly started using the direct-injection technique to reduce H₂S levels in the contaminated gas. Unfortunately, there are no

established design rules for this technique and several installations have failed to perform adequately. GTI has developed a database of such operations, empirical and fundamental design techniques, and several patented contactor devices to ensure that such operations can be operated effectively. In the last three years, GTI has designed four multi-tube direct-injection facilities for commercial storage field operators out of which two are already in operation and they are performing according to the design. Two more installations are expected to be built and be operational by the end of 2005.

This paper describes GTI's latest test facility for studying direct-injection scavenging and the computer model that has been developed under the JIP program. The data obtained from the commercial installations designed by GTI are discussed and the results of a recent techno-economic analysis conducted for a storage field application are presented.

DIRECT-INJECTION H₂S SCAVENGING

Mechanism of H₂S Scavenging

Continuous direct-injection of scavenging agents into a natural gas pipeline is usually applied near the wellhead (after separation from produced water and hydrocarbons) or at centralized treating facilities prior to dehydration. The basic direct-injection scavenging installation consists of a chemical injection pump, a means of introducing the scavenging agent into the natural gas pipeline, a length of pipe to allow for gas-liquid contact, and a downstream device for separating spent or excess scavenging agent from the gas (See Fig. 1).

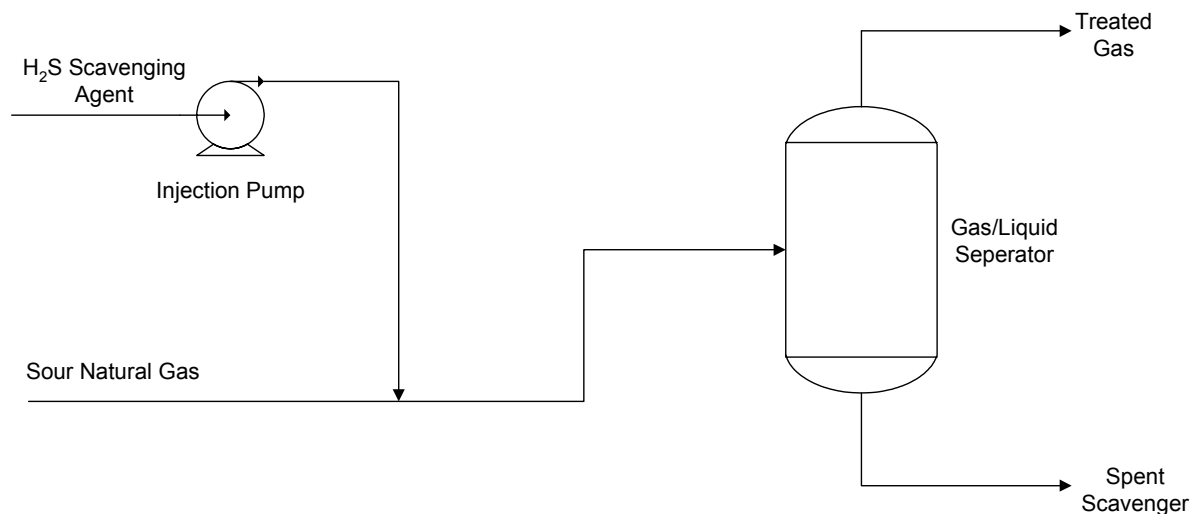


Figure 1. Continuous Direct-Injection using Liquid H₂S Scavenging Agent

Piping tees, quills, or atomization nozzles are used to introduce the scavenging agent into the pipeline. Atomization nozzles enhance mixing and promote wetting of the pipe walls when gas velocities are low. While static mixers have been used to enhance gas-liquid contact, test data from GTI's test loop in south Texas have raised questions about the benefit of using static mixers for this

application [3]. Scavenging liquids may be partially removed downstream using gravity separators and/or coalescing filter/separators. For facilities with existing sparged-tower contactors, some operators may prefer to fill the towers with water and use them to remove spent scavenging agent from the treated gas, effectively polishing the gas and increasing the efficiency of the system.

Key Parameters Affecting H₂S Scavenging

Most H₂S scavenging agents are designed to treat gas over a wide range of pressure, temperature, composition, and flow conditions. However, several gas stream characteristics should be evaluated carefully during the process design phase.

Gas Stream Characteristics

Water Saturation: Water addition is sometimes required if the gas is not saturated with water at the temperature and pressure where scavenging treatment is applied. This situation occurs sometimes when gas is heated before treatment or when previously dehydrated gas is present in the feed sour gas. In the case of triazine-based liquid scavengers, the reaction products are intended to stay dissolved in the spent scavenger, where they are ultimately separated from the gas stream for disposal. However, if the gas is sub-saturated with water, enough water may evaporate from the scavenger solution to cause unwanted precipitation of solid reaction products in the pipeline. Some operators operate a small water injection pump upstream to add the required amount of water to saturate the gas.

Oxygen Content: Oxygen is usually not present in natural gas unless gas is collected from wells under a partial vacuum. In these systems, oxygen sometimes leaks into the gas and may cause the formation of elemental sulfur in beds of iron oxide-based scavenging agents, resulting in a higher than normal pressure drop across the bed. Oxygen may also cause the formation of corrosive nitrogen dioxide when a nitrite-based scavenger is used.

Temperature: Low temperature gas can cause scavenger reaction kinetics to slow down and affect system performance. Normal gas well temperatures of 100-120°F, after air coolers if needed, are acceptable for direct injection scavenging. Midwestern storage field systems with withdrawal gas temperatures of 60°F have operated with negligible differences to the gas patch conditions at comparable pressures, however. Some offshore operators have injected scavengers into relatively hot gas after compression. Corrosive scavenger breakdown products may result with attendant hazards [5].

Pressure: H₂S scavenging is more difficult at low pressures because the partial pressure of H₂S is lower for a given concentration and because pipes and contactor vessels are generally larger in size. The effective absorption factor or mass transfer rates, sometimes expressed as NTUs, are strongly affected by pressure. Thus a given length of pipe will result in much less H₂S removal at low pressures. This particularly affects storage field systems where the withdrawal pressure declines as the withdrawal season progresses. End of season pressures of 300 – 600 psi are not uncommon.

Variations in Flow Rate: Direct-injection systems are vulnerable to changes in gas flow rate. The H₂S removal performance drops off severely as flow rate (and thus gas velocity) is reduced. The detailed hydrodynamics of the system and the multi-phase flow regime will vary in a fixed diameter pipe as pressure, flowrate and possibly temperature vary and the mass transfer will change accordingly.

Process Design Considerations

Many factors, including some that are site specific, require careful consideration during the process design for a particular direct-injection H₂S scavenging system. The following discussion provides a checklist of several items that need to be addressed during the process design.

Inlet and Outlet Knockout Separators: Vendors of H₂S scavenging agents frequently recommend the use of an inlet knockout separator to remove water and/or free hydrocarbon liquids from the gas before treatment. The presence of excess free liquids has the potential to increase scavenger usage and treatment costs because of the additional scavenger required to react with the H₂S present in these liquids. The liquids may also dilute the scavenger concentration in the system and reduce the mass transfer. Outlet knockouts are usually recommended to prevent entrained liquid droplets from reaching downstream glycol dehydrators or other process equipment that could be adversely affected.

Length and Inclination Angle of Pipe for Contact: Both the length of pipe available for gas-liquid contacting and the angle of inclination are important design parameters in direct-injection applications. In general, longer pipe lengths result in improved H₂S removal and reduced chemical consumption. Beyond a relatively long distance the additional removal obtained may not be justified by any associated costs. If the pipe is required for transport in any event then allowing the scavenger to remain in the system as long as possible may result in some further H₂S removal. The angle of inclination also strongly affects the amount of liquid holdup and consequent area of gas-liquid interfacial area available for mass transfer. Mass transfer may potentially be improved in situations where the flow is inclined upward allowing for increased holdup and gas-liquid mixing.

Atomization: The importance of atomizing the scavenging agent as it is injected varies by application. When gas velocities are low, pipe lengths are short, or when large pipe diameters are used, atomization can significantly improve performance. In other situations where long pipe lengths are available and gas velocities are high, atomization has little or no effect.

Scale Inhibition: The formation of scale is a consideration when hard water may contact highly alkaline scavenging agent formulations. This may occur if the scavenging agent is diluted with water before use or if hard water is injected to maintain water saturation and if the gas is produced along with water that has a propensity for scale formation. In other cases, the spent scavenger may be commingled with other sources of hard water in downstream separators and produced water facilities. Several formulations of scavengers which address scale formation issues are available. Shell NAM has reported the results of field testing some of these [4].

CO₂ Interference: Carbon dioxide does not normally present a major problem because the most commonly used H₂S scavengers react selectively with H₂S. In fact, triazine scavengers can be used to scavenge H₂S from pure CO₂ at high pressure. However, CO₂ is known to react at least partially with triazine-based scavengers and does compete for the scavenging chemical. In these cases, chemical consumption may be increased as a result of high levels of CO₂. In instances where H₂S scavenging is conducted at relatively high temperatures where triazines may break down into MEA, the CO₂ will react with the MEA and adversely affect the scavenger consumption required [5].

Environmental and Safety Considerations

Numerous federal, state, and local regulations in the United States, and similar governing authorities in many other countries, regulate the disposal of spent scavenger material. In addition to varying by jurisdiction, the regulatory requirements depend on the scavenging agent selected and the levels of other potentially hazardous components that are present in the natural gas stream.

All sour natural gas treating processes share the common hazards (fire, explosion, and worker exposure to H₂S) associated with handling high-pressure combustible gases containing toxic levels of H₂S. In addition to these obvious areas of concern, other potential hazards associated with the use of H₂S scavenging agents include: eye and respiratory irritation; benzene, formaldehyde and toxic metals exposure, and height and confined space entry hazards. Formaldehyde and caustic are not used much anymore because of the health and safety problems associated with their use. Similarly, the use of iron-sponge has declined over the years, in part because of the pyrophoric nature of the spent scavenging agent, but newer non- pyrophoric iron-based materials are increasingly being used.

For direct-injection scavenging systems, the potential for exposure to toxic materials is highest during maintenance operations or when handling spent scavenger material. Pump repairs, change-out of atomization nozzles, or repair and maintenance of spent-scavenger handling equipment are operations that have the potential for exposure. During these times, high levels of volatile organic compounds may be present and operators have more potential of coming into direct contact with scavenging agent or the spent scavenger material.

Economics

The economics of treating natural gas with non-regenerable scavengers strongly depends on the concentration of H₂S in the gas stream. For relatively low concentrations, capital cost becomes the dominant factor, favoring continuous direct-injection applications over the more expensive tower-based method of application. As H₂S concentration increases, the scavenging agent cost becomes dominant, favoring solid-based agents that, in many cases, have lower costs per pound of sulfur removed.

For preliminary analyses, scavenger treating costs in towers can be estimated using published data. GTI's Scavenger CalcBase™ program (version 1.01) provides a method for quickly estimating capital and operating costs for several H₂S scavenging processes [6, 7]. The program is intended primarily for initial screening of processes using algorithms based on design equations provided by scavenger vendors.

Other important factors include: project life, seasonal operations; installation location (offshore versus onshore); and spent scavenger disposal costs. A short economic project life or seasonal operations tends to penalize technologies with higher capital costs because there are fewer standard cubic feet (scf) of natural gas to amortize the capital, and therefore costs per scf are higher. As a result, direct-injection scavenging becomes more favorable for these operations because of the lower capital costs. For example, direct-injection scavenging has been used to successfully treat slightly sour gas (10 – 20 ppmv H₂S) from underground natural gas storage systems that operate for only four months during the year.

When gas must be treated offshore, equipment size and weight greatly affect treatment costs. The large size and weight of tower contactors largely makes them prohibitive for offshore operations, leaving only the direct-injection option. In addition to the size and weight limitations, the handling of

spent scavenger becomes more difficult offshore. All of these factors tend to favor the use of liquid scavenging agents in a direct-injection configuration for offshore application. In some cases, spent liquid scavenger can be blended with produced water and disposed of via injection wells or discharged to the sea after treatment. In the North Sea this is not possible and is a major concern [8].

The cost for disposal of spent scavenging agent varies widely, depending on how these wastes are regulated by the governing authorities. In some cases, the spent scavenging agents must be handled and disposed of as a hazardous waste, greatly increasing disposal costs. A careful study of applicable regulations for a particular site location is an important part of the scavenger-selection process. It should also be noted that while scavenging agents themselves may not be hazardous, the spent scavenging agent could become hazardous because of the concentration of contaminants such as benzene or mercury removed from the gas.

Attributes of Multi-Pipe Design

It has been found that treating in large diameter pipe is difficult and usually requires a large multiple of the minimum amount of scavenger. As a solution to this dilemma, GTI developed a multi-pipe approach as described in detail in U.S. Patent 6,136,282 [9]. The approach calls for the division of the gas stream to be treated into parallel flow channels, typically in separate pipes. For example, instead of treating 120 MMscfd of gas in a 12-inch diameter pipe, an operator might install four separate 6-inch lines, each treating 30 MMscfd. Gas would be treated in parallel by injecting scavenging agent into each of the four 6-inch lines. The multi-pipe approach provides several advantages over conventional single-pipe systems: (i) higher surface area for mass transfer resulting in higher H₂S removal efficiencies; (ii) better turndown capability; and (iii) reduced chemical usage. The improvement in surface area results directly from the smaller pipe diameters. The wetted surface area available from the walls of the pipe is inversely proportional to the diameter of the pipe:

$$a = 4/d$$

where a is the interfacial area per unit volume of pipe, and d is the inside diameter of the pipe. In contrast to many other systems, the surface area provided from the droplets is usually small in comparison to the area provided by the pipe walls. This unusual phenomenon results from the very low liquid/gas ratios typical of H₂S scavenging applications. For example, it is not uncommon to inject as little as 1 gallon of H₂S scavenging liquid to treat 1 MMscf of natural gas. In this case, even fine atomization of the liquid into 25 micron diameter droplets would not provide as much surface area as the pipe walls themselves.

The improved turndown capability of the multi-pipe design arises from the ability to shut-off one or more of the parallel pipe flow paths. By directing the flow into fewer pipes, the same gas flow velocities can be maintained over a range of gas throughputs. With a conventional single-pipe system, the gas flow velocity decreases as the gas flow decreases. At lower gas velocities, the two-phase flow regime can change from an annular-dispersed regime to a stratified flow regime. When this happens, the upper walls of the pipe are no longer wetted, resulting in a large reduction in mass transfer, leading to excessive chemical usage or poor H₂S removal. The ability to handle large turndowns is especially important in gas storage field applications where gas flow varies seasonally.

The improved mass transfer and turndown capability of the multi-pipe design generally leads to a reduction in chemical usage compared to the conventional pipe design. Operators in many cases have to

increase their chemical usage by two or three times the expected rate in order to achieve acceptable H₂S removal efficiencies with the conventional single-pipe design. In some cases this can affect their ability to deliver gas from storage if there is not sufficient sweet gas for blending.

GTI COMPUTER MODEL

Modeling Approach

GTI and JIP participants are developing a new software modeling package to make process calculations for direct-injection H₂S scavenging systems. In 1998, GTI published a set of equations, largely based on empirical correlation of field data that could be used for direct-injection systems [3]. The new model currently being developed is more mechanistic in nature and is based on rigorous modeling of the two-phase flow hydraulics, mass transfer, and chemical kinetics. Further, the new model has been incorporated into a user-friendly program with a graphical user interface. The program is not available to the general public, but will be available to the JIP participants and potentially to other parties expressing interest in the program.

Theoretical models of the direct-injection process require knowledge of the following:

- Reaction stoichiometry and kinetics between H₂S, CO₂, and the scavenging agent;
- Physical solubility of H₂S in the scavenger solution;
- Liquid- and gas- film mass transfer coefficients; and
- Interfacial surface area available for mass transfer.

Once these above quantities are known, the H₂S absorption can be calculated based on the following mass balance equation, which is at the core of the model:

$$\frac{dy_{H_2S}}{dz} = \frac{-K_G a P y_{H_2S}}{G} = f(z)$$

where

y_{H_2S}	=	Mole fraction H ₂ S in the gas phase
G	=	Molar gas velocity, lbmol/hr/ft ²
z	=	Pipe length, ft
K_G	=	Overall mass transfer coefficient, lbmol/hr/ft ² /atm
a	=	Interfacial area for mass transfer, ft ² /ft ³
P	=	Pressure, atm

This equation is a first-order linear ordinary differential equation and can be solved using standard numerical techniques (e.g., a fourth-order Runge-Kutta method) as long as the function can be evaluated at each point in the pipe. Evaluation of the function requires an estimation of the interfacial area, gas and liquid mass transfer coefficients, and enhancement factors used to describe the enhancement of mass transfer in the liquid phase due to rapid chemical reactions taking place in the diffusion film near the gas-liquid interface.

Description of GTI Model Software Program

GTI's direct injection H₂S Scavenging Simulator program uses the previously described model to make process calculations of direct-injection systems. The program is complete with a graphical user interface and several features to provide more flexibility to users:

- Metric or English engineering units;
- Default or user-defined reaction kinetics/stoichiometry;
- Default or user-defined physical properties;
- Various equipment configurations are supported – atomization nozzles, injection quills, vertical or horizontal pipe segments, shell-and-tube heat exchangers; and
- Ability to store and retrieve previously run cases.

The results are reported both in data tables and with graphical displays. Graphical results include the H₂S and/or scavenging agent concentration profile along the pipe after the point of injection as shown in Fig. 2. The model also generates a full spreadsheet report of all intermediate quantities such as mean droplet size, interfacial areas, gas and liquid film coefficients, and kinetic rate coefficients (see Fig. 3).

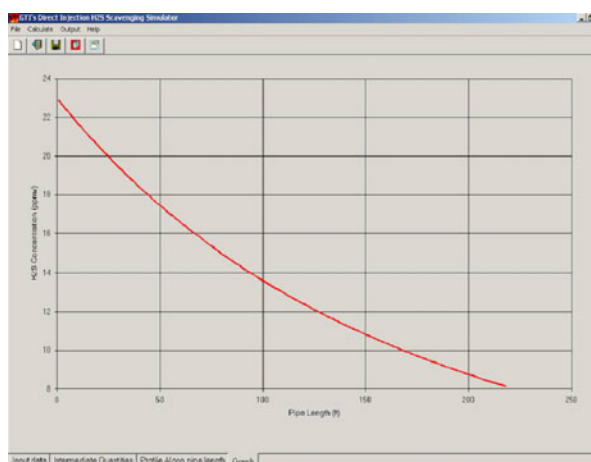


Figure 2. GTI Direct-Injection Simulator Output – Conc. Profile

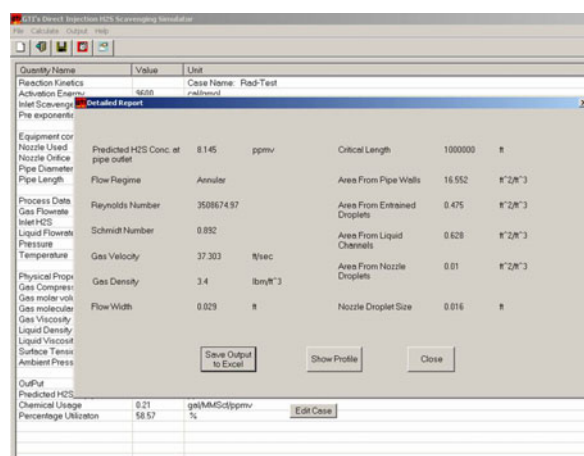


Figure 3. GTI Direct-Injection Simulator Output – Excel Report

Planned Improvements

Under Phase II of the JIP program, GTI is continuing to work on upgrading the simulation model to improve the accuracy of the results and to allow more flexibility to simulate more complicated systems. Several new features are planned for future versions of the simulator:

- Economic analysis modules with emphasis on calculating chemical usage requirements;
- Ability to model recycling of scavenging agent;
- Multiple injection points;
- Higher temperature operations; and
- Rigorous multiphase flow analysis for offshore systems.

In addition to expanding the features of the program, the underlying model will be improved on several fronts to increase the accuracy and robustness of the model to handle a wider range of operating conditions:

Development of a rigorous kinetic model: GTI has recently developed a new laboratory test apparatus to conduct accurate kinetic studies. These kinetic data will be used to develop a more rigorous enhancement factor model to include the effects of CO₂ and pH on the absorption rate of H₂S. The details of the kinetics apparatus are given in the next section.

Improvements to the physical property methods: GTI will continue to improve the physical properties methods in the model to account for temperature and composition dependence over a wider range of conditions.

Development of an improved two-phase flow model: GTI has conducted extensive literature reviews of available two-phase flow models in the public domain as well as those offered commercially under licensing arrangements. Plans for improving the current model using more robust flow regime mapping and droplet size distributions are underway. Recently, GTI has signed a license agreement with a commercial software company and may choose to incorporate its two-phase flow model into the current GTI direct-injection scavenging software. The improved two-phase flow model will enhance the ability of current GTI model to handle inclined pipes and to accurately calculate pressure drops and local phase volume fractions at any location in the pipeline.

DIRECT-INJECTION SCAVENGING TEST FACILITIES AT GTI

New Laboratory Test-Loop

GTI has recently completed the construction of the direct injection test loop to study H₂S scavenging from gaseous streams under controlled conditions. Fig. 4 shows a simplified schematic diagram of the unit. The main contact loop is made of ¾-in. schedule 80 carbon steel pipe with total contact length of 260 ft. The loop along, with other associated equipment including a gas-liquid separator, scavenger feed tank, heater, impregnated carbon bed for vent gas treatment, control panel, H₂S analyzer and gas and liquid injection system are housed inside a 20 ft. x 12 ft. x 8 ft. walk-in fume hood (see Fig. 5). The booster compressor that continuously circulates the carrier gas in the loop is housed in a separate room located in the basement of the same building about 200 ft. away from the main contact loop (see Fig. 6). The unit is designed for gas flow up to 0.6 MMScfd (or 420 scfm) with maximum operating temperature and pressure of 400°F and 1000 psig respectively. The concentration of H₂S in the carrier gas can be varied from 0 to 50 ppmv.

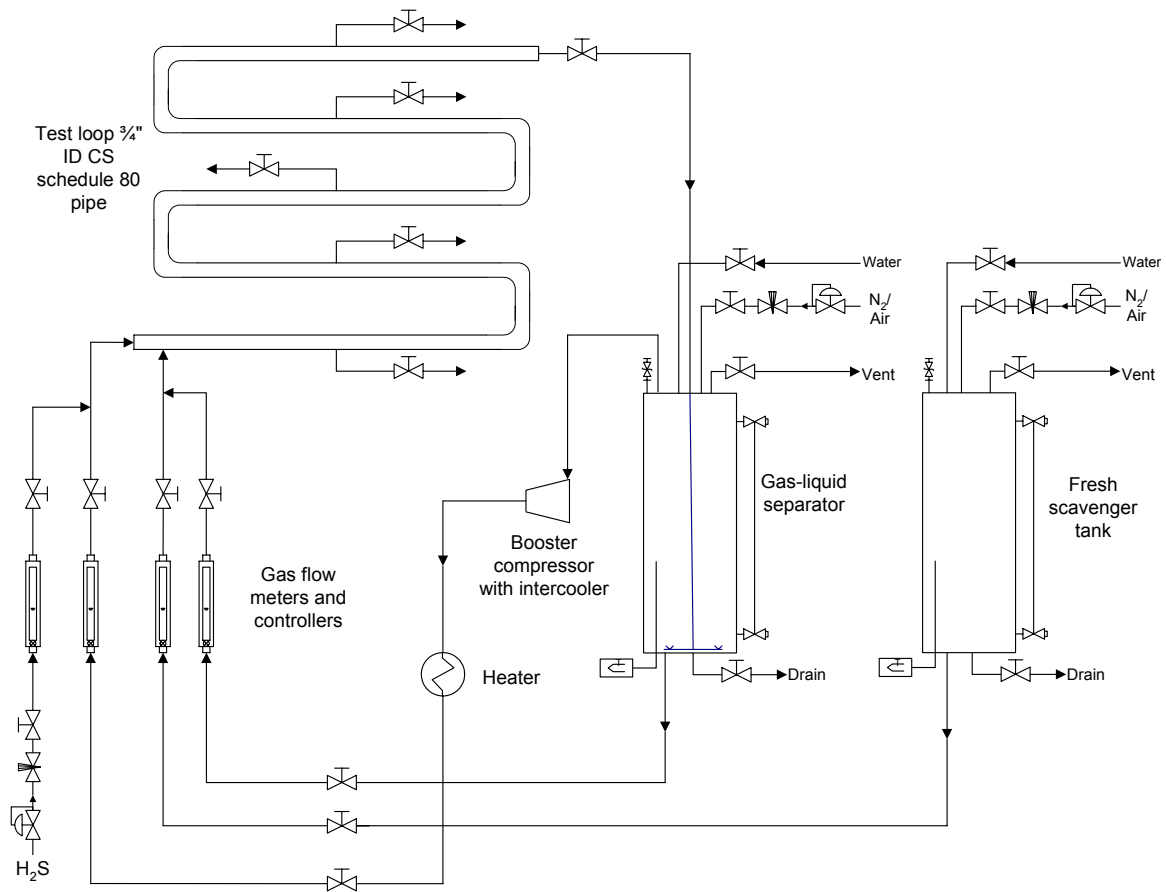


Figure 4. Schematic of the Direct Injection H₂S Scavenging Test Loop

During a typical test, the loop is pressurized with the carrier gas, which could be either pure nitrogen or methane, to a desired pressure. Then the compressor is turned on and the gas starts circulating in the pipe loop. Once the desired gas flow rate is set using an automatic bypass control loop installed at the compressor discharge, the carrier gas is mixed with an appropriate amount of H₂S gas from a cylinder containing 10% H₂S in nitrogen via a Brooks mass flow controller. The H₂S injection point is located inside the fume hood about 200 ft. from the compressor discharge point. The H₂S contaminated carrier gas then flows to the 3/4-in. main pipe loop via an electric heater, which heats up the gas to the desired temperature (max. of 400°F). Note that if required there is a provision to bypass the heater. The main loop is located about 40 ft. downstream of the H₂S injection point providing sufficient time for H₂S to mix with the carrier gas. At about 10 ft. downstream of the heater exit and right before the scavenger injection point a gas sampling port is installed to measure H₂S composition in the feed gas.

At the point where the H₂S contaminated carrier gas enters the main loop, a liquid scavenger is injected using a 1/4-in. quill. The liquid scavenger is stored in a 12.75 in. OD by 5.8 ft. long carbon steel storage tank equipped with a magnetic level indicator (see Fig. 7). The tank is pressurized to about 200 psi above the system pressure by connecting it to a pressurized nitrogen cylinder. The scavenger flow to the loop is controlled using a precision liquid mass flow controller supplied by Brooks Instrument. The main loop has 10 gas sampling ports at approximately every 20 ft. along the length of the pipe. After about 226 ft. of pipe an additional scavenger injection is provided to knock out any leftover H₂S in the carrier gas before it flows back to the compressor.



Figure 5. GTI Test-Loop



Figure 6. Booster Compressor and Ancillary Equipment



Figure 7. Fresh Scavenger Storage Tank



Figure 8. Gas-Liquid Separator

The gas along with the spent scavenger coming out of the main contact loop enters into a vertical gas-liquid separator equipped with a pneumatic level control valve. The spent scavenger is collected at the bottom of the separator and whenever the liquid level in the separator rises above a certain set point, the pneumatic control valves opens up and dumps the spent liquid into a scavenger discharge tank. The dimensions and the pressure ratings of the gas-liquid separator are identical to that of fresh scavenger storage tank described above (see Fig. 8). The clean carrier gas coming out of the gas-liquid separator flows back to the suction side of the booster compressor via a stainless steel online filter mounted immediately before the suction vessel. The booster compressor as shown in Fig. 6 is a metal diaphragm compressor supplied by Fluitron Inc. ideal for a unit where gases must be contained within a sealed system, such as the present system. The compressor is attached to a double-pipe pre-cooler and an after-cooler and an internal recycle system to control the discharge gas flow to the system within 70 to 100% of maximum discharge flow.

Gas Sampling Arrangement

As mentioned above, the test loop has 11 sampling ports (1 before scavenger injection and 10 after scavenger injection). A schematic of the sampling arrangement is shown in Fig. 9. The first seven sampling ports are manifolded and routed to channel B of the H₂S analyzer, which measures H₂S concentrations higher than 10 ppmv, and the last 4 ports are manifolded to direct the flow to channel A which gives more accurate readings for H₂S concentrations less than 10 ppmv. If needed, the flow from the first seven ports or the last four ports could be switched to either channel A or Channel B by using the 3-way valve A or B. There is also a provision to take a gas sample in a Teflon-coated 500 mL stainless steel cylinder for analysis using a GC for routine confirmation of analyzer readings. For higher temperature runs, the sampling gas is cooled down to about 70°F by contacting the sampling lines with continuously flowing tap water in small double-pipe heat exchanger (see Fig. 10). As shown in Figs. 9 and 10, each sampling port is connected to the main loop via a ball valve and a needle valve. While sampling, the ball valve is fully open and the needle valve is only slightly open, enough to send sufficient flow to the analyzer which is about 0.5 liter/min. Under normal conditions both channels A and B could be operated simultaneously.

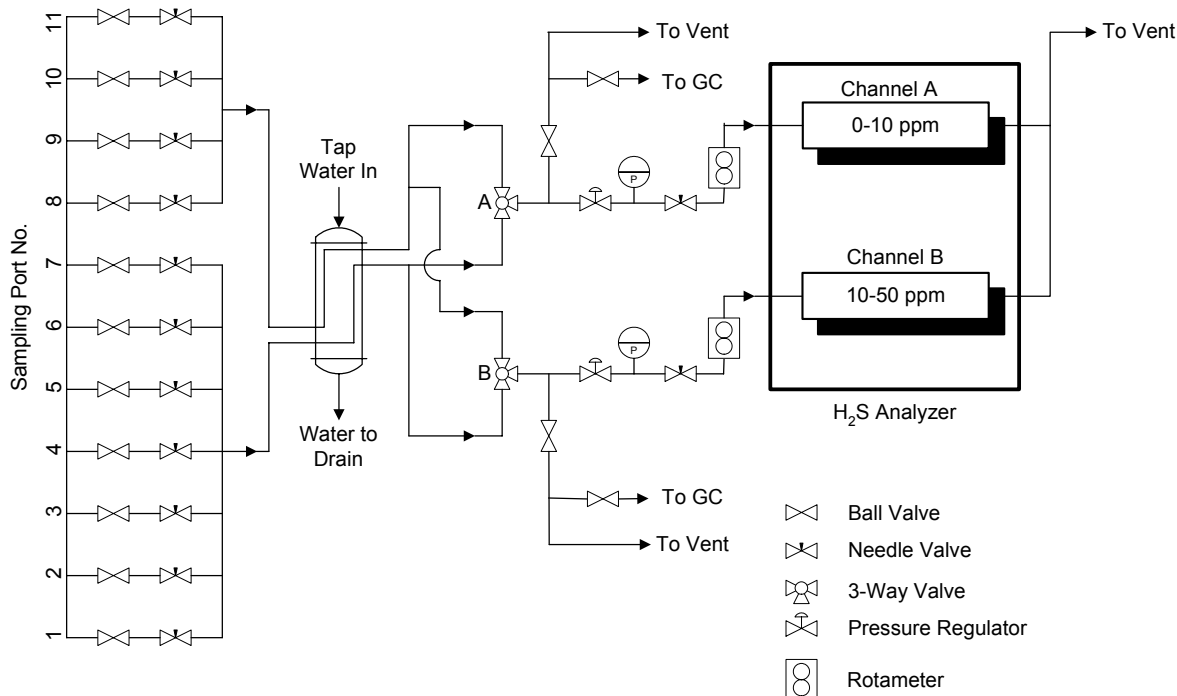


Figure 9. Schematic of Gas Sampling Arrangement



Figure 10. Sampling Port Connection



Figure 11. Sampling Lines to H₂S Analyzer

Online Gas Analysis

Fig. 12 shows the picture of the online H₂S analyzer supplied by Texas Analytical Control Inc. As mentioned earlier, this analyzer has two separate channels – channel A is for 0-10 ppmv H₂S and channel B is for 0-50 ppmv H₂S in the carrier gas. The carrier gas could be either nitrogen or methane or mixture of the two. The presence of CO₂ does not have any adverse effect on the measurements. This analyzer is already in use for similar industrial applications. According to the vendor's literature, if properly calibrated, the analyzer measurement error is generally less than 1%.



Figure 12. Online H₂S Analyzer

The above test loop was designed and commissioned by GTI engineers and is operational since Nov. 2004. Base line test results obtained from this unit are presented later in this paper.

Apparatus for Scavenger Kinetics Study

In order study the kinetics of H₂S absorption in various liquid scavengers, GTI has recently acquired a new vapor-liquid equilibrium (VLE) unit (see Figs. 13 to 16). Under the current JIP program, this unit is routinely used for measuring kinetics and VLE data under different operating conditions. This high pressure VLE cell is made of stainless steel and has an internal working volume of 1 liter. The cell is fitted with a magnetic-drive stirrer at the top and is placed inside an environmental chamber. Also connected to the side wall of the VLE cell are the two precision computer-controlled ROLSI sampling valves for gas and liquid phase sampling. The volume of the samples taken is generally less than a micro-liter. The samples are analyzed using a GC dedicated for this apparatus. The cell can be operated in the temperature range of -90°F to 350°F (-68 to 177°C) and pressure up to 5000 psig (340 bar).



Figure 13. High Pressure VLE Apparatus



Figure 14. Gas Feeding System



Figure 15. VLE Cell and the Environmental Chamber

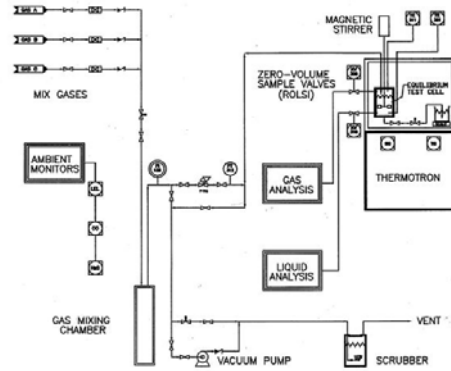


Figure 16. Schematic Diagram of the VLE Apparatus

Other Field Facilities

In addition to the above $\frac{3}{4}$ in. in-house test loop, GTI also has field testing facilities at McAllen Ranch, South Texas, which consist of 1 in. 2 in. and 6 in. schedule 80 carbon steel pipe loops, each with about 220 ft. of total pipe length (see Fig. 17). These loops have been extensively used to collect data during the mid 1990s for the development and verification of GTI's multi-pipe design for direct-injection scavenging and the empirical model. Some of those results have been published previously [2, 3]. The field test loops have also been used to collect data under the current JIP program. The major limitations of these field units are the cost of running the units and the inability to vary test conditions at will to perform controlled experiments because in all these loops a slip stream from an operating commercial gas treating plant is used, and it is not possible to vary the inlet H_2S concentration, pressure or inlet temperature significantly.



Figure 17. 1 in., 2 in. and 6 in. Direct Injection Test Facility at McAllen Ranch

INDUSTRIAL DIRECT INJECTION UNITS DESIGNED BY GTI

Since 2001 GTI has designed four commercial direct-injection facilities based on its patented multi-pipe design. Out of these four, two units are already in operation and remaining two are expected to be operational by the end of 2005. Table 1 summarizes the design conditions for each of these units. The challenge on these designs is steadily the length and number of pipes to employ while still meeting pressure drop constraints (usually 10-20 psi) while achieving acceptable H₂S removal at near the minimum stoichiometric amount of H₂S scavengers over the full range of flow and pressure over a withdrawal season.

Table 1. Commercial Plant Design Conditions

Design Parameter	Plant-1	Plant-2	Plant-3	Plant-4
Gas Flow Rate (MMscfd)	10 – 40	50 – 150	75 – 500	35 – 250
Gas Pressure (psig)	350 – 900	450 – 900	400 – 900	250 – 650
Nominal Pipe Diameter (inch)	3	6	6	6
No. of Pipe Runs	2	4	12	6
Initial H ₂ S Conc. (ppmv)	20-50	15-70	10-50	10-25
Treated Gas H ₂ S Conc. (ppmv)	< 4	< 4	< 4	1-6
Max. Pressure Drop (psi)	< 20	< 20	< 20	< 10
Operational Since	Mid 2001	Nov. 2003	To be built	To be built

Plant-1

Plant-1 was the first commercial multi-pipe DI scavenging facility designed by GTI for a storage field application located in southern Illinois. This is a relatively small unit, which processes about 10 to 40 MMscfd sour natural gas containing between 20 to 40 ppmv H₂S. The unit consists of 2 runs of 3 in. nominal diameter carbon steel pipes each about 500 ft. in length. The sour gas from the storage field is brought in via a 6 in. pipe to the multi-pipe DI unit where, depending on the gas flow rate, it is diverted to one or two, 3 in. lines as shown in Fig. 18. The scavenger is injected through a ¼ in. stainless steel tube right before the junction where the 6 in. line splits. Each 3 in. line has a gas sampling port approximately every 60 ft. along the pipe length. The unit has been operational since April 2002 and has performed according to the design.

Plant-2

Plant-2 is the latest operational multi-pipe DI facility designed by GTI. Initially this facility was using direct-injection scavenging to treat sour natural gas from a storage field in Iowa using 20 inch diameter carbon steel pipe with available length of 3000 ft. In this facility, the gas flow ranges from 50 to 150 MMscfd and the H₂S concentration varies from 15 to 70 ppmv. During the start of the withdrawal season the gas pressure is about 900 psig and towards the end it goes down to about 400 psig. Using the existing facility, the operator was never able to achieve H₂S specifications of 4 ppmv in the treated gas even when higher scavenger dosage was employed.



Figure 18. 3 in. Double Pipe DI Unit in southern Illinois

In 2003, GTI designed a new direct injection facility for this application based on its patented multi-pipe design. The new facility consists of 4 runs of 500 ft. long 6 in. schedule 80 carbon steel pipes as shown in Fig 19. The gas from the storage field enters the main gathering line (an underground 20-inch diameter carbon steel schedule 80 pipe of about 3000 ft. length) and after about 25 ft., the main gathering line is bypassed and the gas is equally distributed into as many as 4, 500 ft. long 6-inch runs depending on the desired flow rate (see Fig. 20). After 500 ft., the gas from all 6-inch runs is returned to the main gathering line that carries it to the gas-liquid separator located about 2500 ft. away from this point. The scavenging liquid is pumped through a PULSA Series 8480 diaphragm metering pump housed inside a separate enclosure. The scavenger is brought to the injection station by a 1-inch carbon steel schedule 80 pipe which then distributes the scavenger in equal proportions into each open 6-inch run via a $\frac{1}{4}$ -inch diameter stainless steel manifold connected at the start point on each run. One of the 6-inch runs has 5 sampling points located at 100 ft. intervals. Samples are also taken at the start and end of the 20-inch main gathering line and at the point where all 6-inch runs are combined together just before the gas returns back to the main gathering line. This unit has been operating since Nov. 2003 without any major problem. Initially, the plant operators were having problems with frequent plugging of the scavenger injection nozzles attached to each of the four scavenger injection points. These nozzles were later removed because in our experience, for most situations, the nozzles seem to have negligible effect on the scavenger efficiency. As discussed elsewhere in this paper, the nozzles and other contacting devices may be beneficial in certain circumstances.

ANALYSIS OF RECENT DATA FROM GTI DESIGNED COMMERCIAL PLANTS AND NEW LAB TEST-LOOP

Commercial Plant Data

GTI has been monitoring the performance of the aforementioned commercial units by regularly analyzing field data collected during the withdrawal seasons. Table 2 lists the latest data sets collected from these facilities. So far both units have been performing according to the design and the average scavenger consumption rate has been about 1.8 gal per lb of H₂S removed. Also, if required, both units are able to treat the sour gas down to 4 ppmv of H₂S, which was previously not possible even when higher scavenger flows were injected into the existing lines. Both facilities have been using conventional ethanol triazine based scavengers.

It has also been found in a prospective design of a new unit that for low pressures and low flows, at the end of the withdrawal season, the efficiency of the system may still be too low even if only one pipe is being utilized. Fortunately, for such low flows, it may be possible to blend treated gas into the mainline without exceeding the H₂S specifications. Alternatively, a fixed tower using solid or liquid scavenger but sized for only the low pressure and low flow situation might be a suitable but somewhat expensive solution. Occasionally, not all the wells from a storage field are equally sour, so by producing selectively from the low H₂S wells, the H₂S requirement can be met during the low flows and low pressure situations, despite the marginally effective DI system under those conditions.

Table 2. Field Data from Plant-1 and Plant-2

Plant	Pres. (psig)	Liquid Rate (gph)	No. of Open Runs	Gas Flow (MMscfd)	H ₂ S-in (ppmv)	H ₂ S-out (ppmv)	Scavenger Consumption Rate (gal/lb of H ₂ S removed)
1	870	1.3	1	10	23	3	1.84
1	606	1.2	1	6	41	4	1.48
2	695	38.9	3	88	51	2	1.84
2	634	33.0	4	93	62	13	1.94
2	552	36.0	4	109	56	5	1.73
2	493	30.0	4	110	53	9	1.66

Fig. 20 shows the plots of measured and predicted H₂S concentrations as a function of pipe length for both commercial units. The solid line represents the predictions from the empirical model based on which these units were designed; open square symbols represents measured data from Plant-1; the solid square symbols represents the measured data from Plant-2; and the dotted line represents the predictions from the empirical model when only 1 run of 20 in. diameter pipe is used instead of 6 in. multiple pipes as was initially the case for Plant-2. Clearly, our empirical model predicts the H₂S profiles quite accurately in both the 6 in. and 3 in. pipes. It can also be seen from this figure that if, for example, the same gas in Plant-2 was treated in the existing 20-inch diameter pipe, the H₂S concentration in the treated gas after 500 ft. of pipe would be about 22 ppmv as opposed to 2 ppmv obtained in 3 runs of 6-inch diameter pipe of the same length. For the same facility, it can further be shown using our model that even if the entire 3000 ft. of existing 20 in. line is utilized, it would still not

be possible to achieve the H₂S concentration of less than 4 ppmv in the treated gas even though the scavenger injection rate is tripled.

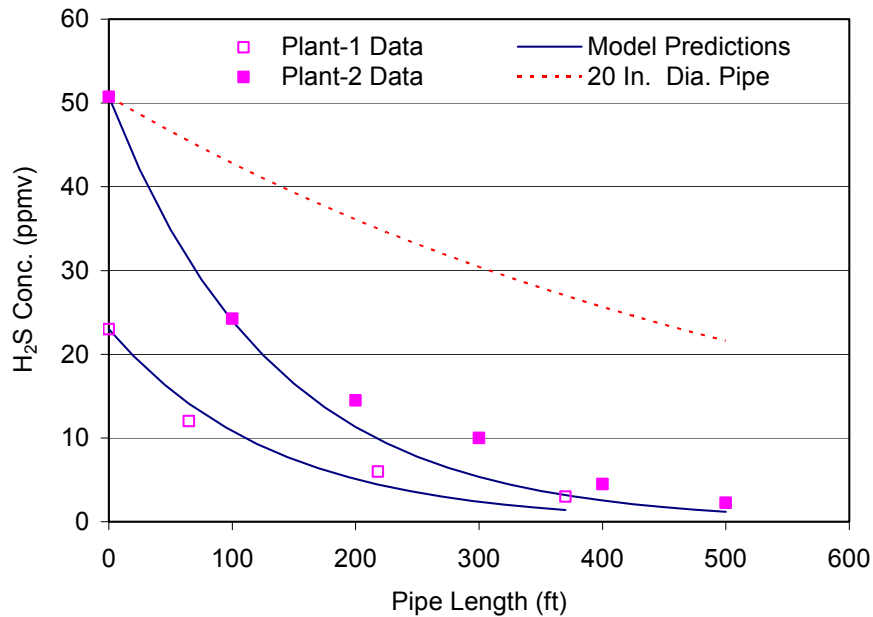


Figure 21. Predicted and Measured H₂S Conc. in 3, 6 and 20 inch Diameter Pipes

Status of Rigorous Kinetic Model under Development at GTI

GTI developed its first published model for direct-injection H₂S scavenging systems in 1998 [2, 3, 9-12]. The first generation model was empirical in nature and did a reasonable job of predicting the performance of the GRI test loop data from which it was regressed. This model was later further improved by including a larger set of data that GTI collected from various commercial DI scavenging units operating in the U.S. and Europe (see Table 3). Although the semi-empirical model has performed well and we have been able to successfully design commercial DI units using this model as discussed in the previous section, this model does not provide deeper insight into the DI scavenging process, thus limiting our ability to further optimize existing DI scavenging processes and develop more innovative gas-liquid contacting devices that could improve scavenger efficiencies.

Table 3. Range of Variables of Available Data

Variable	Range
Pipe Diameter (in)	1-24
Pipe Length (ft)	20-350
Gas Velocity (ft/s)	10-50
L/G (gal/MMscf)	0.5-6.0
Temperature (°F)	50-300
Pressure (psig)	300-1100
Inlet H ₂ S Conc. (ppmv)	10-70

Under the ongoing JIP program, GTI and JIP participants are developing a new software modeling package to make process calculations for DI scavenging systems. The new model is more mechanistic in nature and is based on rigorous modeling of the two-phase flow hydraulics, mass transfer, and chemical kinetics. Further, the new model has been incorporated into a user-friendly program with a graphical user interface. The first edition of the software has already been released to JIP members and has been used to analyze currently available DI scavenging data at GTI.

Fig. 22 shows a graph of the predicted H₂S concentrations versus the actual H₂S concentrations for the GTI's 2 in. and 6 in. test loop data set. This graph shows that the predicted and actual outlet H₂S concentrations are in reasonable agreement for this data set. For example, of the group of data points where the model predicted less than 4 ppmv, only 20% of the observed data were above 4 ppmv. For the group of data where the model predicted less than 2 ppmv, only 1 measurement (2.8%) of H₂S above 4 ppmv was observed.

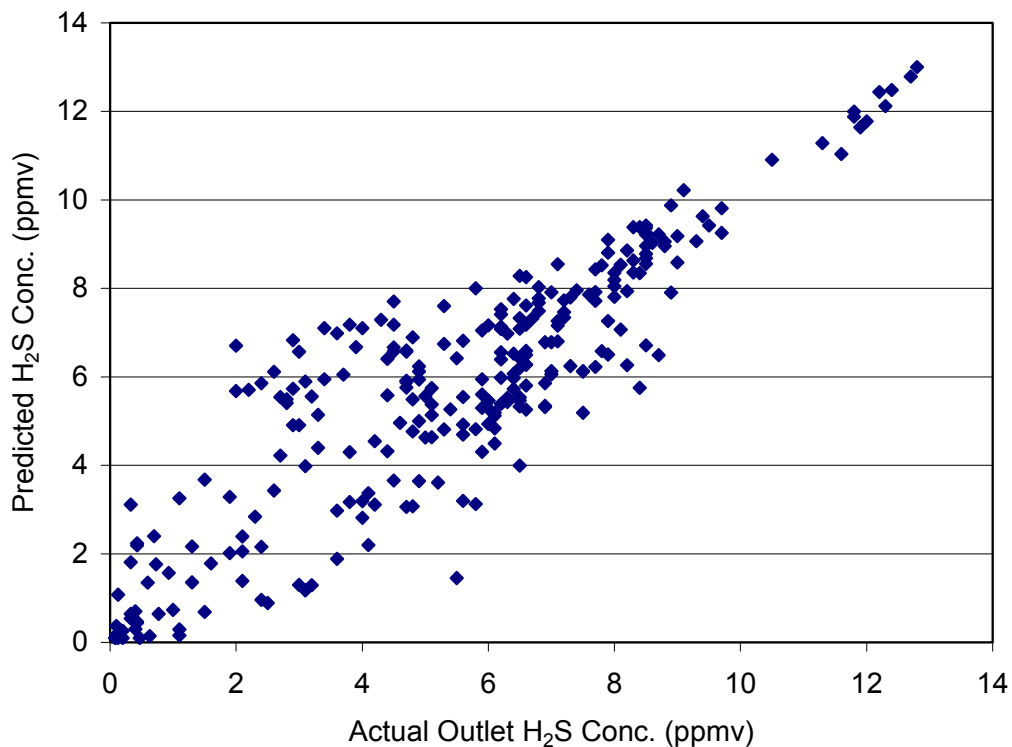


Figure 22. Model Performance – GTI's 2 in. and 6 in. Test Loop Data

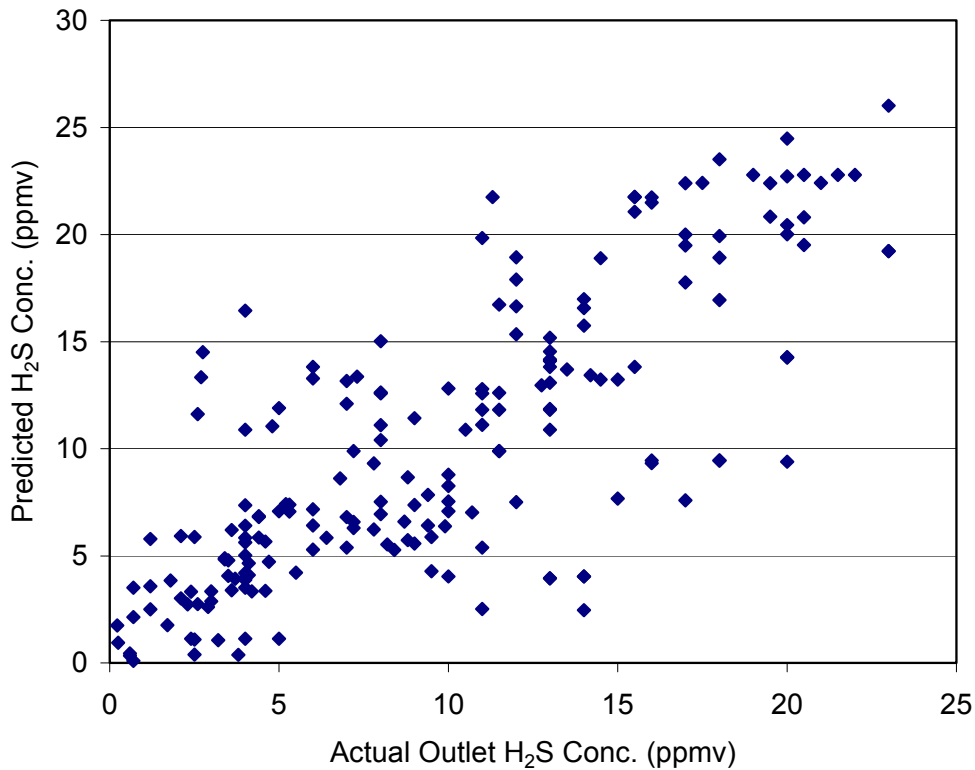


Figure 23. Model Performance – Commercial Data Set

The new model was evaluated further by comparing the predicted outlet H₂S concentrations from 192 datasets obtained from commercial installations. Fig. 23 shows a graph of the predicted H₂S concentrations versus the actual H₂S concentrations for the commercial data set. These data were taken from a number of commercial installations, but some data were also taken in 2002 at GTI's 2 in. and 6 in. test loops. This data set covers a wider range of conditions which are shown in Table 3. Note that these data were taken by commercial operators under less controlled conditions. Much of the error in predicting these data is believed to be associated with errors in the measurement data as opposed to errors in the model itself. This graph shows that the predicted and actual outlet H₂S concentrations are in reasonable agreement, but the larger error is visually apparent in the data scatter. For this data set, of the group of data points where the model predicted less than 4 ppmv, only 19% of the observed data were above 4 ppmv. For the group of data where the model predicted less than 2 ppmv, only 1 measurement (7.7%) of H₂S above 4 ppmv was observed.

As can be seen from Figs. 22 and 23, the new GTI model has performed reasonably well given the varied operating conditions and methods of collecting data from commercial installations. Further improvements are planned under the ongoing JIP program. Among the improvements planned is the inclusion of a more rigorous model for predicting flow regime transitions, pressure drops, and local phase volume fractions at any location in the pipeline for varying angles of inclination.

GTI has built a new laboratory test loop described earlier in the paper, which will enable us to conduct controlled experiments under different operating conditions to verify the new model. This test loop was recently commissioned and the baseline data were obtained.

Baseline Tests using New Lab Unit

Fig. 24 shows a set of baseline data obtained from the $\frac{3}{4}$ in. test loop. This test was conducted at 500 psig, 0.6 MMscfd of gas flow and 0.12 gph of scavenger flow rate. As shown in this figure, the measured data are in good agreement with the predictions from the empirical model described earlier. The predicted results from the latest kinetic model, however, are still not in good agreement with the measured values for this particular case and for some specific data-sets from commercial installations designed by GTI. Thus more work is needed to improve the predictive ability of the new rigorous model.

The measured scavenger consumption rate in this case was found to be 1.41 gal per lb of H₂S removed, which is still less than the minimum consumption rate measured in our lab for this scavenger (i.e., 1.65 gal/lb of H₂S removed). We will continue to explore the discrepancy in the data. Further baseline tests are continuing according to the plan and some of those results may be presented in future publications.

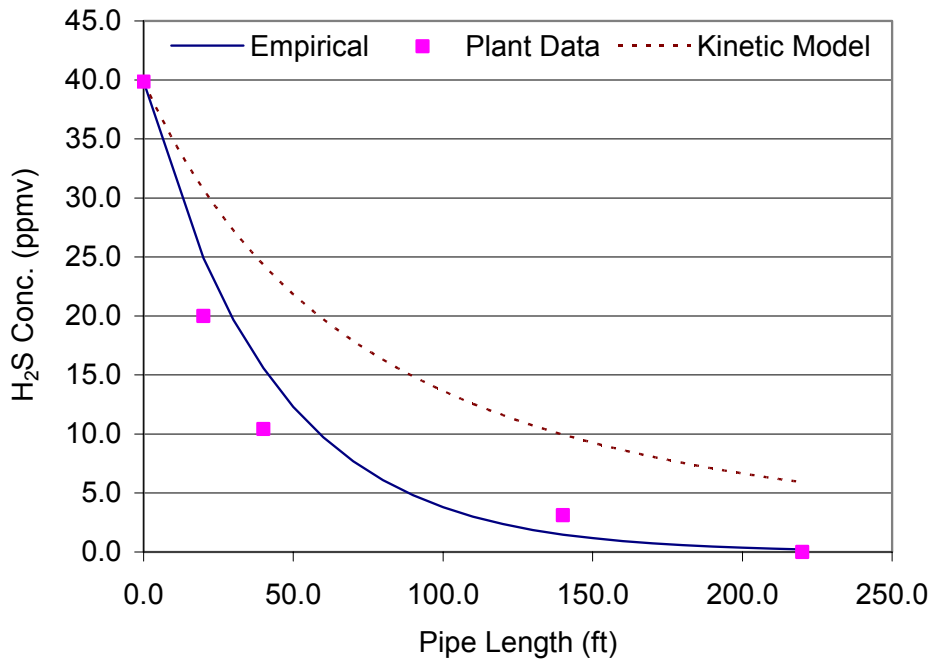


Figure 24. Baseline data set-2: H₂S Concentration Profile in the $\frac{3}{4}$ -in. Test Loop

CONCLUSIONS

GTI has successfully employed its patented multi-pipe direct injection H₂S scavenging design for treating sour gas at storage field applications. Two commercial installations are currently operational and performing according to design. The average scavenger consumption rate at these installations has been observed to be about 1.8 gal per lb of H₂S removed and in both cases the operators are able to treat the sour gas down to less than 4 ppmv of H₂S. GTI has been engaged in a joint industry project to develop a rigorous DI scavenging model that could be used to optimize existing facilities and design new more innovative ways to handle low-level H₂S in the gas stream through direct injection. The new lab facility at GTI will compliment this research.

REFERENCES

1. GRI Topical Report No. GRI-96/0241 (1996), "Hydrogen Sulfide Scavengers Market Assessment," Gas Technology Institute, Des Plaines, IL.
2. Fisher, K. S. Killion, S.J., and Lundeen, J.E. (1999), "GRI Field Testing of Novel Approaches for Reducing H₂S Scavenging Treatment Costs," *Paper presented at 49th Laurance Reid Gas Conditioning Conference*, Feb. 21-24, Norman, OK.
3. Fisher, K.S. (1998), "Direct-Injection Testing of H₂S Scavenging at GRI's Pipe Loop in South Texas," *Paper presented at the 48th Annual Laurence Reid Gas Conditioning Conference*, March 1-4, Norman, OK.
4. Eylander, J.G.R., Holtman, H.A., Salma, T., Yuan, M., and Johnstone, J.R. (2001), "The Development of Low-Sour Gas Reserves Utilizing Direct-Injection Liquid Hydrocarbon Sulphide Scavengers," *Proceedings - SPE Annual Technical Conference and Exhibition*, p 1817-1830.
5. Rasmussen, K., Wright, A., Schofield, M. and Lund, H. (2004), "Investigation of a corrosion failure in an offshore gas compression system: The role of H₂S Scavenger and organic acids," *NACE Corrosion Conference 2004*, Paper 04360.
6. GRI Software No. GRI-96/0482 (2000), "GRI Scavenger CalcBase™," version 1.01, Gas Technology Institute, Des Plaines, IL.
7. Guillory, G. and Leppin, D. (1995), "GRI Scavenger CalcBase™, Resource for Scavenger Comparison and Screening," *Paper presented at the 7th GRI Sulfur Recovery Conference*, September 24-27, Austin, TX.
8. Knudsen, B., Tjelle, S., and Linga, H. (2002), "A New Approach towards Environmentally Friendly Desulfurization," *SPE International Conference on Health, Safety, and Environment in Oil and Gas Exploration and Production*, March 20-22, Kuala Lumpur, Malaysia.
9. Fisher, K.S. (2000), "Method for Removal of Hydrogen Sulfide from Gaseous Streams," U.S. Patent 6,136,282.
10. Fisher, K.S., Lundeen, J.E. and Leppin D. (1999), "Fundamentals of H₂S Scavenging for Treatment of Natural Gas," *Paper presented at the 9th GRI Sulfur Recovery Conference*, October 24-27, San Antonio, TX.
11. Fisher, S.K., Killion, S.J., and Lundeen, E.J. (1999), "GRI Field Testing of Direct-Injection H₂S Scavenging," *Proceedings, Annual Convention - Gas Processors Association*, p 155-166.
12. Fisher, K.S., and Lundeen, J.E. (1995), "GRI Evaluation of Direct-Injection H₂S Scavenging at Ten Sites," *Paper presented at the 7th GRI Sulfur Recovery Conference*, September 24-27, Austin, TX.