

MODELING DIRECT INJECTION OF H₂S SCAVENGER IN PIPELINES: LABORATORY INVESTIGATIONS AND IMPROVED COMPUTER MODEL

Dennis Leppin, P.E.
Gas Technology Institute
Des Plaines, IL, U.S.A.

Kevin Fisher, P.E.
Trimeric Corp.
Buda, TX, U.S.A.

Diana Matonis, PhD
Hickory Hills, IL, U.S.A.

ABSTRACT

Gas Technology Institute (GTI) (USA) conducts a Joint Industry Project (JIP) on developing a computer model for H₂S removal from natural gas via the direct injection of triazine (1,3,5-tris(2-hydroxyethyl)-hexahydro-*s*-triazine) scavenger into pipelines. The model has been progressively improved to include two-phase behavior effects, detailed mass transfer calculations, the effect of upflow in the pipeline, and temperature effects. The model incorporates new experimental results of direct observation of two-phase flow regimes, higher temperature experiments, and addition of CO₂ to the gas as well as the effect of pipe diameter (between ¾ in. Sch 80 [0.74 in. ID]) and 1-¼ in. Sch 80 [1.28 in. ID].)

The new model continues to use mass transfer rates but replaces a kinetic approach with thermodynamic equilibrium which has been verified by laboratory data to model the system and incorporates improved properties models (diffusivities, viscosities, Henry's law constants) and measured interfacial surface tension.

Provided that the correct flow regime is calculated, for which we now have improved predictive methods, reasonable predictions of performance for applications of scavengers to H₂S removal are obtained, but additional work to validate and finalize the model remains. Data obtained in GTI's test loop are compared with model predictions in this paper.

INTRODUCTION

When H₂S is present in natural gas at low concentrations and relatively low total quantities, say less than around 50 kg per day, but in excess of what is allowable in the transmission line (usually not more than 1 - 4 ppmv), it is usually removed using “H₂S scavengers” which are frequently triazine (1,3,5 tris (2-hydroxyethyl)-hexahydro-1,3,5 triazine) chemicals.

The chemistry of reaction of the scavenger is understood to involve formation of products such as shown in Figure 1.

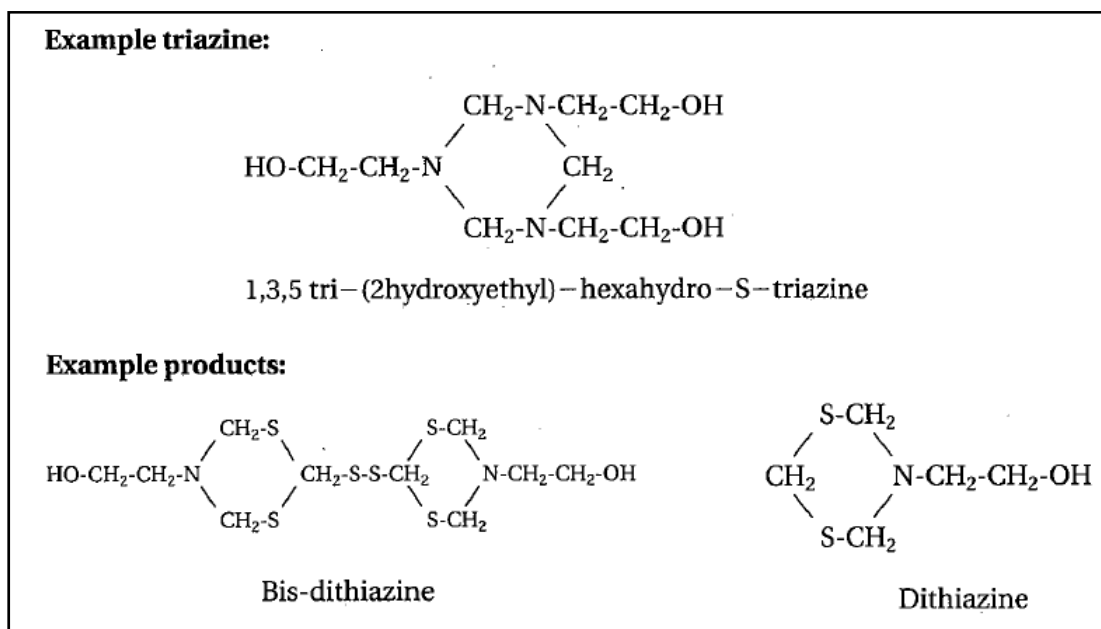


Figure 1 Triazine and Byproducts Chemical Formulae

Detailed discussion of the chemistry in conjunction with the model being developed here was presented recently in another forum (Ref. 1) and will not be repeated here.

In onshore applications, large towers in which the gas is bubbled up through a large inventory of triazine are sometimes used, but in offshore applications this equipment is generally too large and heavy for platform use, especially if its use has not been anticipated, as is frequently the case. In that event, direct injection of the scavenger into the available gas lines is the only feasible option. Several platforms are practicing this means of H₂S removal. For large production volumes of gas, the cost of the scavenger can be substantial, millions or even tens of millions of dollars (U.S.) per year as the quantities of H₂S removed are far in excess of what is normally considered the economic maximum for scavenger use.

Improving the efficiency of utilizing scavenger is therefore of great interest to those plagued with this problem, and should be of interest to operators who may potentially encounter reservoir souring in the future. Storage fields have also been victim of this and many also use direct

injection of scavengers as a remediation technique. Unfortunately, to date, there has been no reliable means of evaluating the operating conditions necessary to effectively and economically reduce the H₂S levels in the available piping. Too often, estimates provided by the chemical vendor have been the only available basis for system designs, where there was little incentive to minimize scavenger consumption. Safety has also been compromised as lack of knowledge has led to corrosive conditions and catastrophic pipe failures. Some typical questions which arise are:

- How much scavenger to inject?
- What type of nozzle or mixer is needed?
- What gas velocity is optimal?
- Are there differences between different vendor's scavenger products?
- What is the effect of downflow, upflow or bends in the pipe?
- How do pressure, gas temperature, gas velocity, gas CO₂ concentration, and pipe diameter affect the results?

Early work by GTI in the scavenger arena was focused on reviewing performance of solid and liquid-based tower systems. Figure 2 shows a typical multi-tower scavenger system at a site in Texas. GTI found that a representative range of scavenger utilization in the field was 0.47 to 0.85 lb_{sulfur}/gal_{scavenger} for Triazine (Ref. 2). Recent tests for a private client with several scavengers of interest have also been determined as within this range. Utilizations beyond this range can result in solid formation. It is quite straightforward to design these systems and achieve these utilizations, especially if a lead-lag reactor system is used. In the foreground of Figure 2, an experimental, GTI-owned direct injection test loop can be seen. There are actually 1 in., 2 in., and 6 in. direct injection test units at the site. These units have been used for numerous test campaigns including testing novel mixers as well as getting general parametric data on scavenger performance during injection in various size pipes. In 2002 GTI built a test loop at our Des Plaines facility to carry out more controlled experimentation. For example, at the south Texas site, it was not possible to reduce the pressure or vary the H₂S concentration as the gas was being cleaned up as sales gas. The large size and capacity of the equipment also made the cost of addition of special test equipment prohibitively high.

For this reason, GTI invested in the test loop which was also partially funded by the JIP programs. GTI has managed a JIP for developing a computer model of direct injection scavenging funded by major oil companies (Maersk Oil and Gas, Chevron, Shell UK and others) since 2001 and, more recently, a scavenger producer (Clariant). GTI has also designed (Ref. 3) and licensed several patented (Ref. 4) scavenger injection facilities at North American storage fields. Figure 3 illustrates a GTI-designed 6 in. diameter, multi-pipe injection system being installed by a major pipeline company in the Midwest at a storage field. There are several others including a 10-pipe system. Some results have been published earlier (Ref. 5). At this point, a model has been developed which matches real world data in most situations quite reasonably. The model is based on fundamental mass transfer and fluid hydrodynamic principles. Careful experiments in a purpose-built flow unit at GTI have confirmed key model assumptions and an extensive database of industry data has been compiled and evaluated. Unlike the tower systems, direct injection systems, if not properly designed or otherwise constrained in their operating parameters, for example by having to use existing large diameter pipe, will neither operate with

efficient scavenger utilization nor will necessarily achieve the desired reduction in H₂S concentration.



Figure 2 Tower-Based Scavenger Installation in South Texas

The details and assumptions used in developing the model and experimental methods used in the GTI flow loop will be described. Comparison of model predictions with results obtained in GTI's test loop will be used to illustrate the use of the model. Comparisons with actual offshore direct injection operations have also been made.

EXPERIMENTAL BACKGROUND

GTI has collected several hundred data points of scavenger injection field operations over the years. As typical of field data, some of the data in this dataset are questionable. This is due to various methods of sampling and measuring H₂S at varying accuracies, often not knowing certain key parameters pertaining to the datasets, limited range of certain parameters, random errors and so on. It would be impossible to validate a computer model on such a dataset. GTI therefore built a dedicated "scavenger test loop" at our facility in Des Plaines, IL. Initially, this system consisted of a recycle compressor, 240 ft. long test section of ¾ in. insulated pipe, gas line heater, sample ports (roughly at 20 ft. intervals), scavenger feed tank and flow metering system, and various cleanup and knockout vessels. The system is designed in such a way as to enable all the H₂S to be fed into the loop and all residual H₂S removed at the loop exit so that the compressor handles clean gas. The pressure range is up to 1000 psi and circulation rates on the order of 400 scfm. Most of the testing has been done at 95 °F, but some experiments were carried out at up to 260 °F. Hydrogen sulfide concentrations have been measured with an on-line

“TAC” analyzer as well as Drager tubes and most recently with a Varian micro GC.



Figure 3 Direct Injection Scavenger System under Construction

Figure 4 is a highly simplified schematic of the unit. Not shown in this figure in order to keep it simple is the second diameter piping loop which is interleaved on the original system and the risers and viewing windows which were recently added. The apparatus is situated in a Plexiglas[®] enclosure and is kept at negative pressure to the laboratory work area outside due to the presence of H₂S in the system. Personnel monitors are worn and an area H₂S monitor is also used. All of GTI's Gas Processing personnel working with H₂S are certified by “H₂S Alive” training.

BASIS OF THE MODEL

The schematic diagram in Figure 6 illustrates the structure of the model. After collecting inputs which would generally be known in a design case, and having defaults in place for more obscure inputs such as scavenger interfacial tension, various intermediate quantities are calculated which are necessary further on in the calculations.

GTI and Trimeric continued to make improvements to the steady-state mechanistic model, based on more rigorous modeling of the two-phase flow, mass transfer, and reactive absorption kinetics. This section presents a general description and flow chart for the overall computational algorithm. The detailed description of the model is confidential.

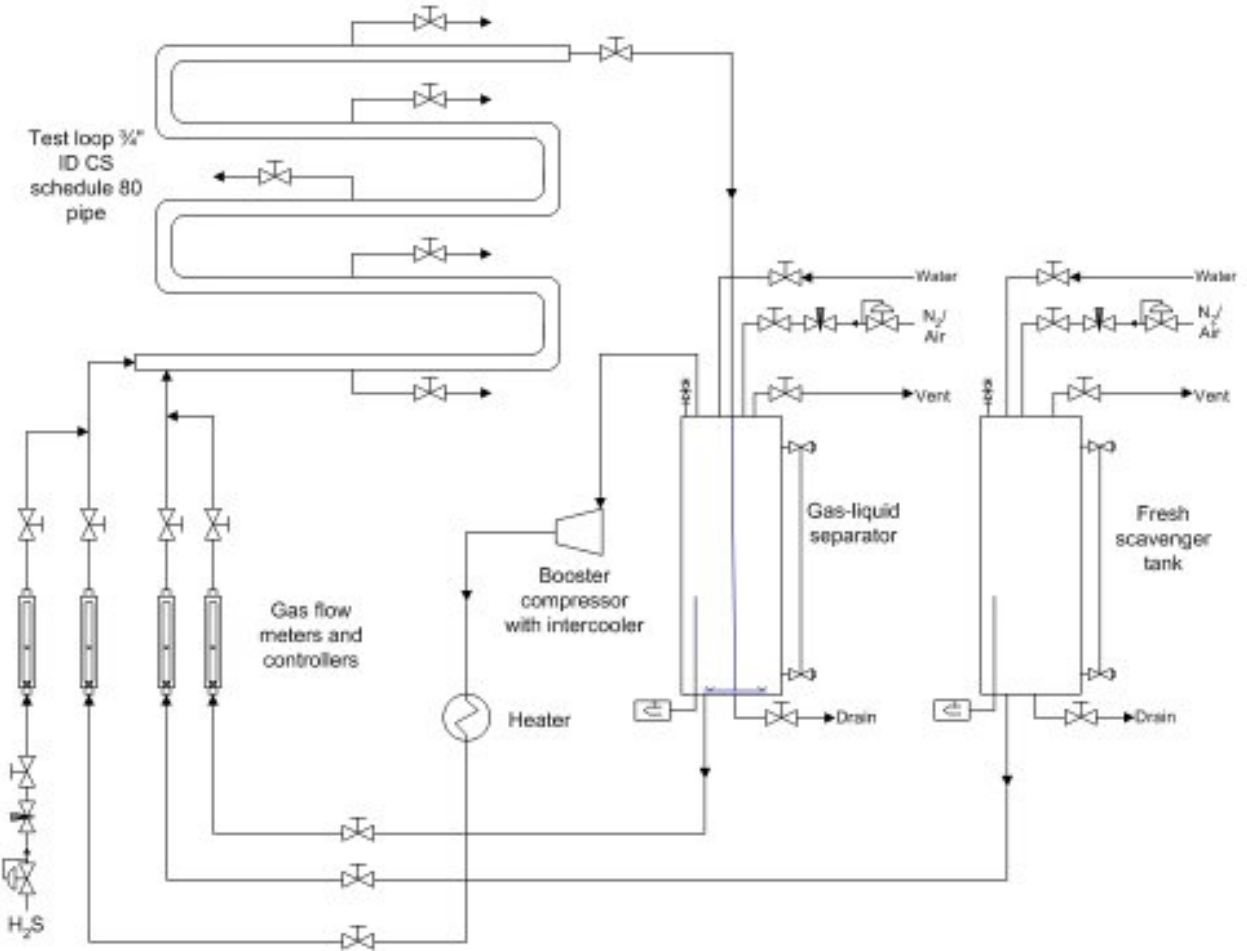


Figure 4 Simplified Schematic of Direct Injection Scavenger Test Loop

The model is based on calculating the mass transfer rate of H_2S from the gas to the liquid at each point along the flow path inside the length of pipe or heat exchanger being modeled. The rate of H_2S absorption is therefore described by a differential equation whereby the rate of absorption per unit length is expressed as a function of the local conditions at that point. The equation is then solved using a standard Runge-Kutta method.

This approach requires knowledge of the interfacial area, gas-film and liquid-film mass transfer coefficients and enhancement factors, the H_2S concentration in the liquid and gas phases, and the active scavenger concentration at each point of calculation. The methods used to estimate each of these quantities are described separately in the following paragraphs.



Figure 5 GTI Direct Injection Scavenger Test Loop

Interfacial Area: The interfacial area depends on the flow hydraulics and injection atomization characteristics. The flow regime must be identified correctly in order to estimate the interfacial areas (see further discussion of the flow regime which appears later in this paper). At low gas velocities, the liquid scavenging agent tends to flow along the bottom of the pipe in a stratified layer. This stratified flow regime is generally to be avoided if possible since it results in the smallest surface area for mass transfer. At intermediate gas velocities, a partial wetting of the pipe walls begins to occur as the onset of liquid entrainment begins. At still higher gas velocities, the liquid becomes entrained and flows in both a mist of droplets and as an annular film which wets the pipe walls. This annular flow regime has higher surface area for mass transfer and a marked improvement in H_2S scavenging performance can be observed when transcending from the stratified into the annular-mist flow regime. The model computes the interfacial area for the entrained droplets, the wetted walls of the pipe, and the free-liquid interface for the liquid flowing along the bottom of the pipe, if applicable. Atomization nozzles introduce another element of complexity in that a different droplet size distribution is produced, and in cases where the flow regime is stratified and a nozzle is used, it is necessary to estimate the trajectory of the droplets to determine how long they are entrained in the gas stream before settling to the bottom of the pipe. The amount of liquid holdup and associated surface area for mass transfer also changes if the gas is flowing in pipes at angles other than horizontal.

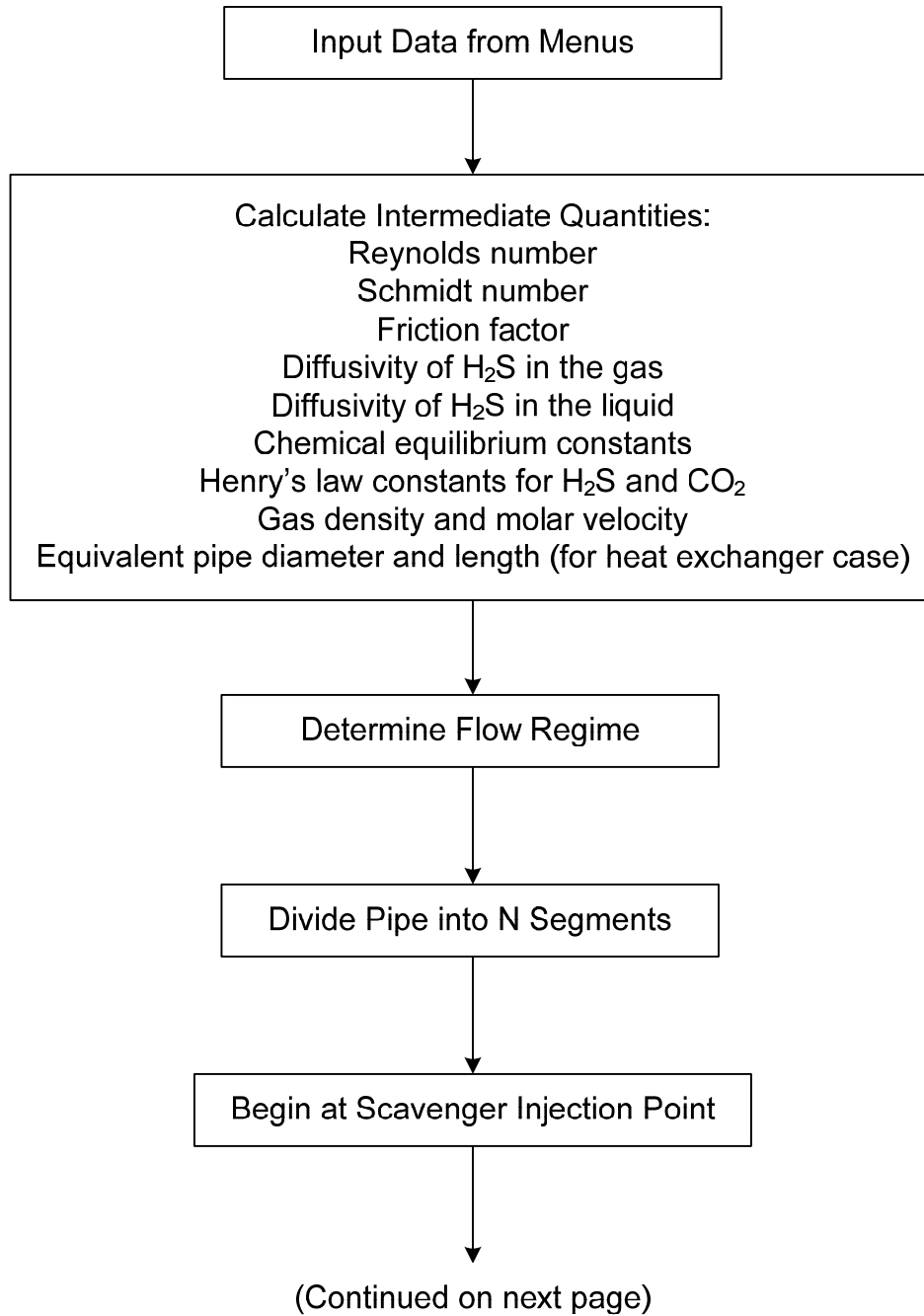
Gas- and Liquid-Film Mass Transfer Coefficients: The gas-film mass transfer coefficient is

readily calculated from standard engineering correlations for turbulent flow in circular ducts or inside heat exchangers. The liquid-film coefficient is similarly calculated for the various modes of transport and then adjusted using an enhancement factor approach. For example, different coefficients are used for estimating the mass transfer to the wetted walls of the pipe, the open-channel or free liquid interface in the stratified case, and the transfer to entrained droplets.

Enhancement Factors: The enhancement factor is customarily defined as the ratio of the liquid-film mass transfer coefficient with chemical reaction occurring to the liquid-film mass transfer coefficient that would occur in the absence of chemical reaction. The program estimates the enhancement factor using a simplified reactive absorption model that accounts for the reactions of H₂S and CO₂ with scavenger and other species in the liquid. The estimation of the enhancement factor for mass transfer requires computation of the concentration gradients of the participating chemical species as they diffuse across the mass transfer film while being produced or consumed by various chemical reactions. The inclusion of CO₂ in the model is important since it changes the local pH and effectively slows down the absorption of H₂S.

Concentration of H₂S and Active Scavenger: The initial conditions define the beginning concentrations of H₂S in the gas and the scavenging agent in the liquid. As the H₂S absorption occurs in each incremental segment of pipe, the reaction stoichiometry and mass balance determine the remaining H₂S in the gas phase and the remaining scavenging agent in the liquid phase.

Predicting the correct flow regime is very important in the model. The flow regime determines the gas-liquid interfacial area. Obviously it is very different in entrained flow compared to stratified flow. Many correlations are known for predicting the two phase flow regime, but unfortunately, none of these were based on the very low levels of scavenger liquid that are generally used in direct injection. Low levels are used because the scavenger concentration is generally less than 10¹ ppmv and scavenger injection for economical removal is on the order of 10⁻¹ gal/ppmv/MMscfd. This positions the values of liquid superficial velocity V_{SL} well below the region for which data are available on the transition values between flow regimes. Although the Figure 7 below extends to low values, the data (circles) do not. Several data sets obtained from a JIP participant from direct injection operations on an offshore platform indicated agreement only if the flow regime was changed from that predicted by the correlation used in the model.



(Continued from prev. page)

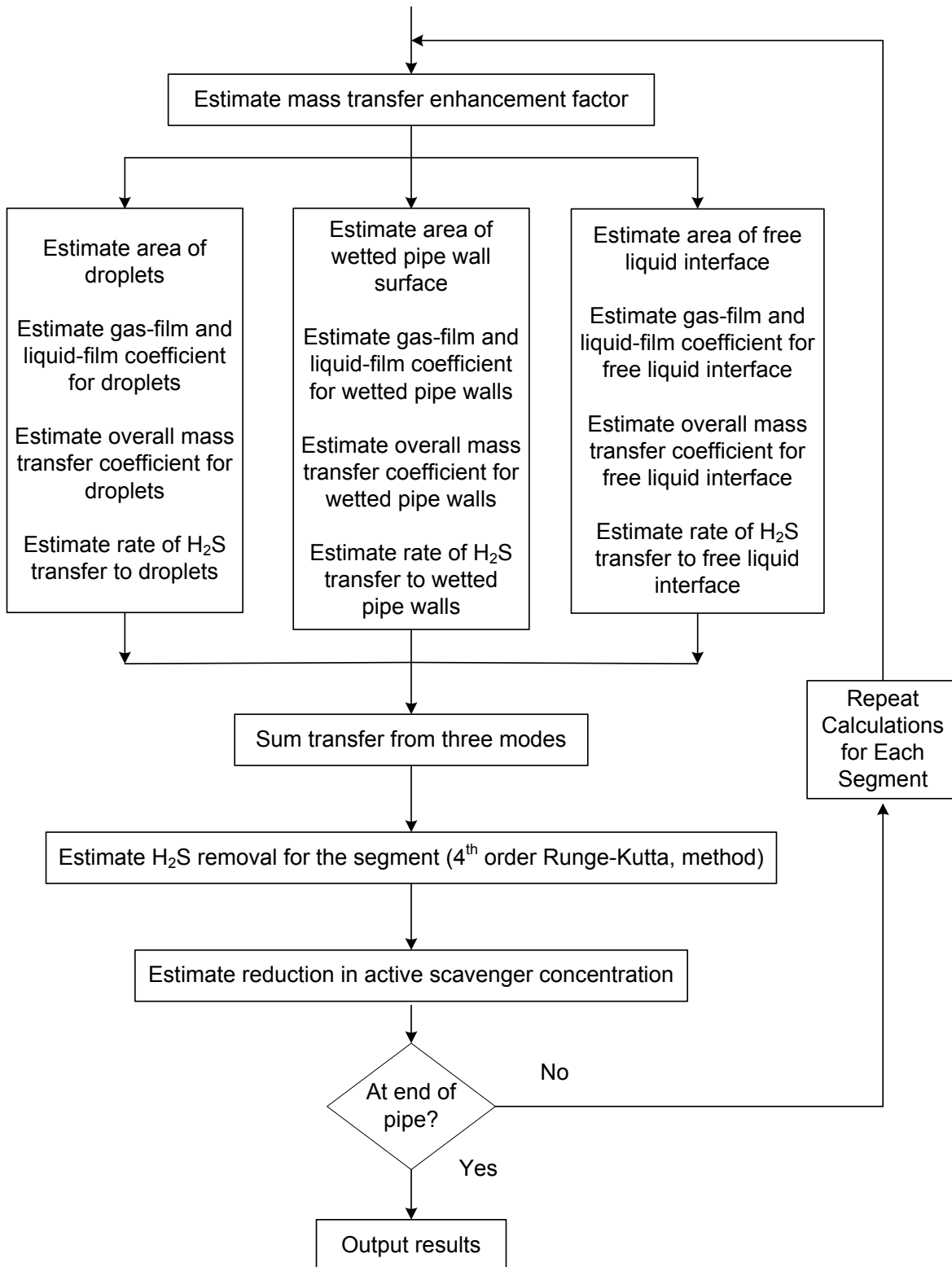


Figure 6 Schematic of Computer Model

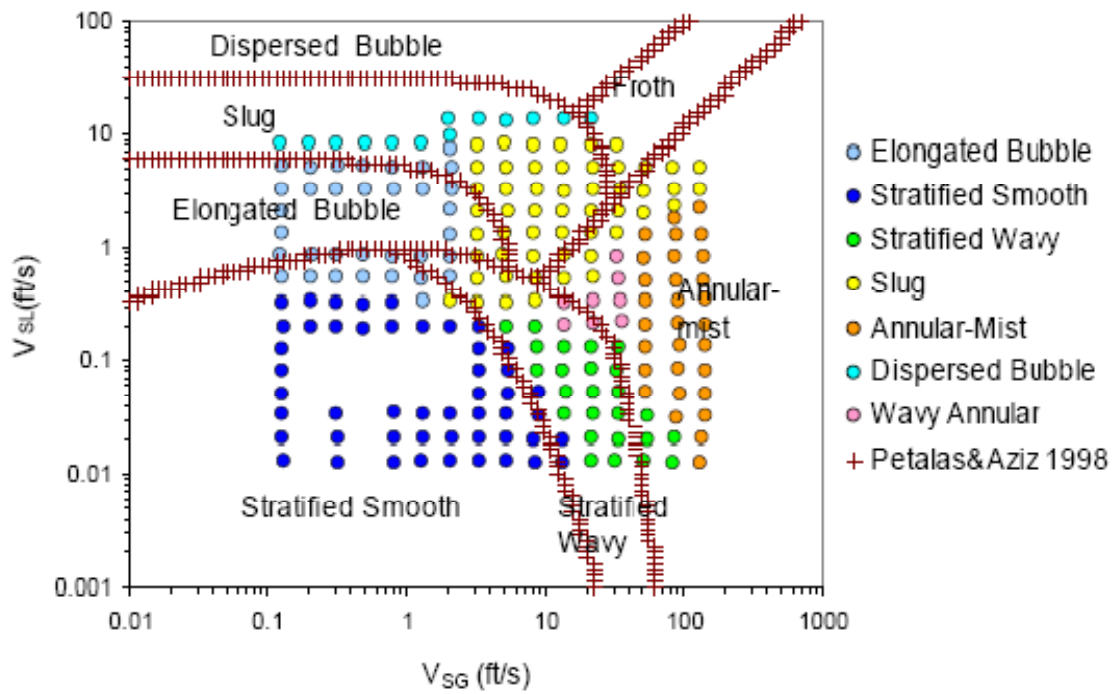


Figure 7 Two Phase Flow Regime Map

For this reason GTI and JIP partners installed a set of sapphire viewing windows in both an upflow and horizontal pipe segment (Figure 8).



Figure 8 Horizontal Observation Window

During a recent test the flow regimes were observed and some computer movies and photographs

were recorded. Figure 9 illustrates what can be observed in such an experiment.



Figure 9 View through Horizontal Observation Window

At this point we have not had the opportunity to systematically observe a range of operational points and verify whether the existing correlations for phase transition are adequate nor develop an appropriate modification or new correlation if necessary.

In summary, as currently embodied in the model, temperature and CO₂ affect the system as follows:

- > Temperature
 - Physical solubility of H₂S and CO₂
 - Diffusivity
 - Viscosity
 - Density
 - Acid-base and carbamate equilibrium constants change with temperature
- > CO₂
 - Partial pressure of CO₂ lowers pH
 - CO₂ competes with H₂S for triazine and MEA

For most of the species, acid-base equilibrium constants were available from the public literature. For triazine, equilibrium coefficients were determined experimentally using acid-base titrations.

EXPERIMENTAL RESULTS

A series of tests was conducted for the current JIP program in order to investigate a number of factors of interest. This included the effect of larger diameter piping (1-¼ in.), pressure, CO₂ concentration, temperature as well as investigation of the prevailing flow regime as already

discussed. The data that are obtained consists of measurements of H₂S concentration at a particular sample point and the recorded values of scavenger flow, gas flowrate, pressure, temperature, etc. These have not yet been rigorously analyzed but a few conclusions can be made by direct examination of the results.

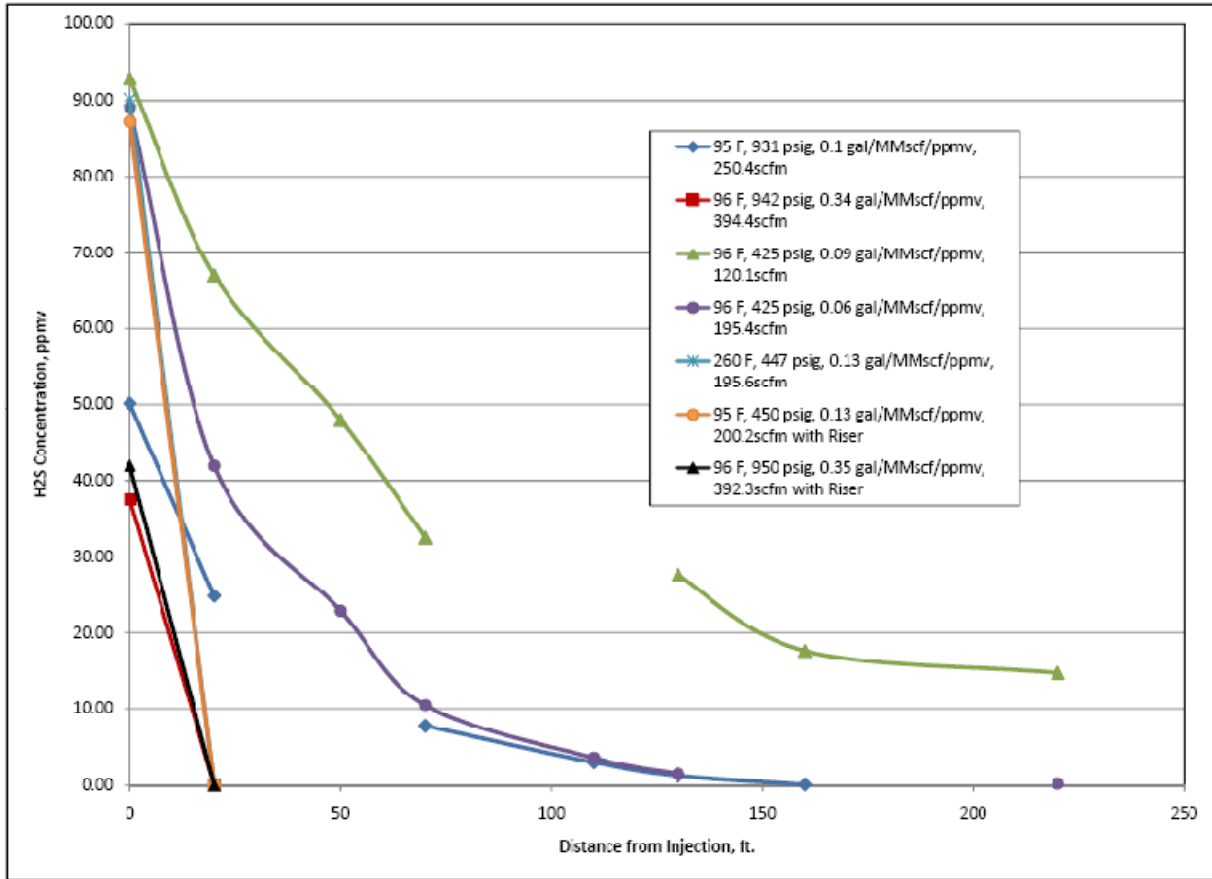


Figure 10 Test Results in 1-1/4 in. Pipe Loop

For example, the fourth and fifth tests (in the order listed in the legend of Figure 10 above, differ in the temperature and the scavenger loading but also have similar starting H₂S concentrations around 90 ppmv. The loading is higher in the fifth test, but the loading itself, provided it is in excess of that needed for complete conversion, should not affect the results too strongly unless it forces a transition to a different two phase flow regime. It does affect the local concentration of scavenger. Very high loadings would result in a pseudo-constant concentration of scavenger in the liquid phase. The H₂S removal in the higher temperature case is noticeably higher. The graph is potentially misleading since when the first H₂S concentration measurement point at 20 ft. is effectively zero, it is not possible to know whether the H₂S was also zero at a closer point to the scavenger injection (“zero” location). The third and fourth data points indicate the effect of gas flow (or velocity) significantly increase overall rate of H₂S removal.

Results from the recent tests in the original, 3/4 in. Sch 80 pipe loop are presented in Figure 11, below.

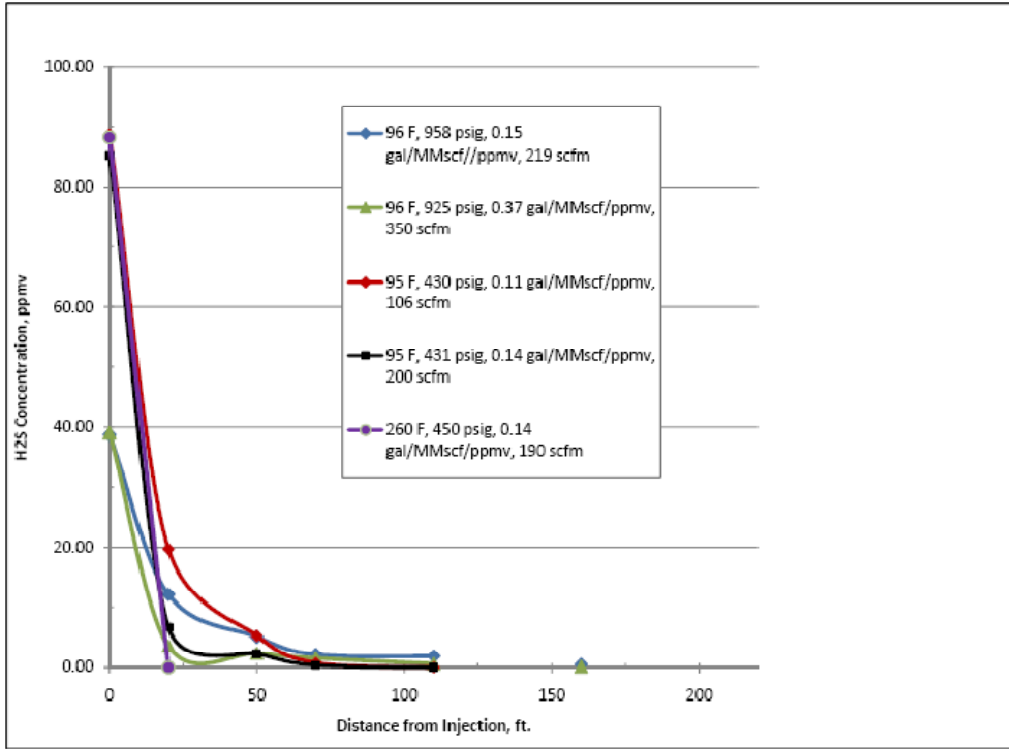


Figure 11 Test Results from 3/4 in. Pipe

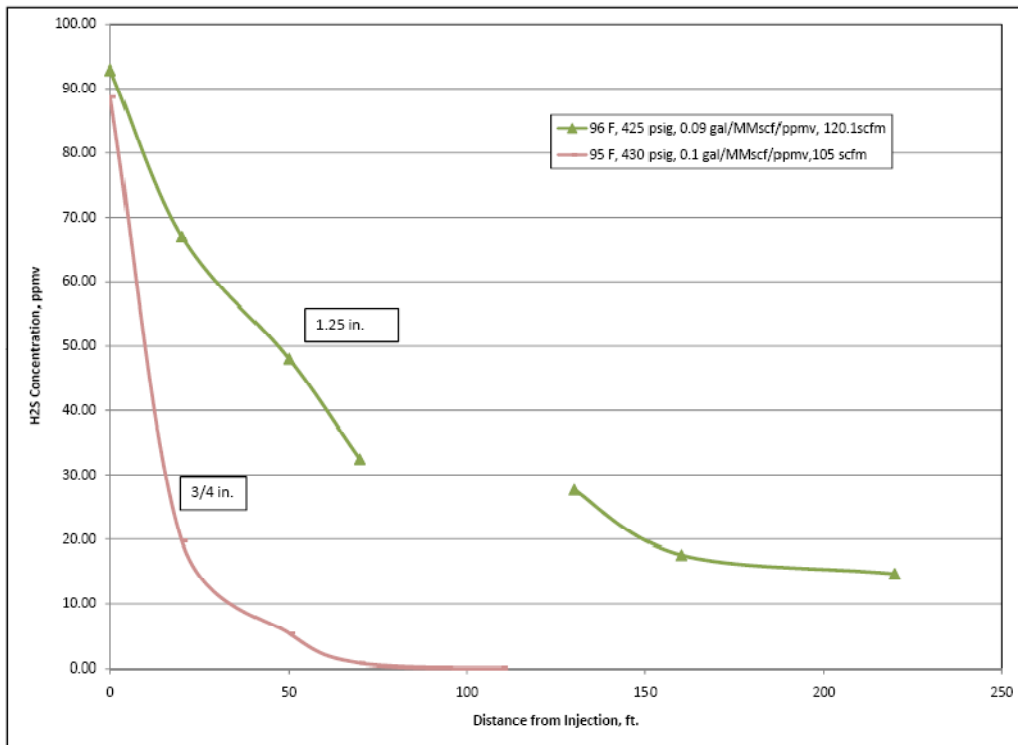


Figure 12 Effect of Pipe Diameter at Lower Pressure

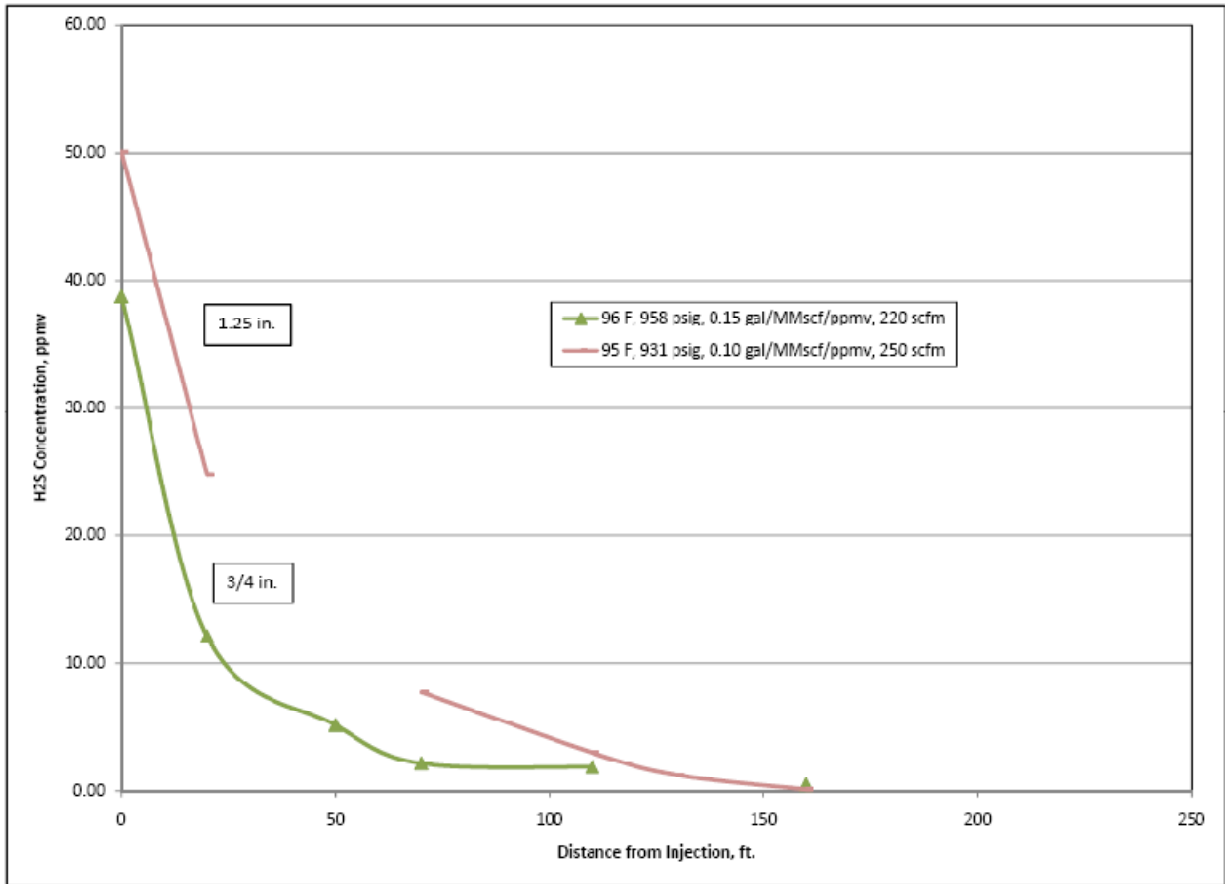


Figure 13 Effect of Pipe Diameter at Higher Pressure

Figure 12 shows two runs with substantially identical parameters except the pipe diameters. This indicates that lower diameter pipe removes H₂S more rapidly. This principle is used in GTI's patented commercial designs for multi-pipe injection wherein multiple smaller pipes are employed than would otherwise be used. The effect is not as pronounced in the high-pressure comparison, Figure 13. Various CO₂ concentrations were also used in the tests in order to more realistically simulate what occurs in real world situations where CO₂ is present usually at least at a few percent. In the lower pressure tests, the CO₂ concentration was increased from about 5% to somewhat above 9% in order to keep the partial pressure approximately the same as the high pressure tests. Ultimately, it is very difficult to hold parameters at exact values during the tests. The model could be used for data analysis to account for the multiple factors changing between the runs and to infer the degree to which the various factors are important. Statistical tools were also used previously since multiple values of H₂S at each location exist enabling a test of a hypothesis that the mean value of H₂S at a particular location is equal to that from another test where a certain treatment was applied, e.g., higher flow of scavenger or higher pressure. Data taken in the original 3/4 in. loop setup in a previous program has yet to be analyzed to determine if they can be used to infer additional conclusions. Most of those did not have significant CO₂ concentrations so we expect that we will be able to determine the CO₂ effect when compared to the 1- 1/4 in. data.

The baseline low pressure test was compared to the model and the result is plotted in Figure 14.

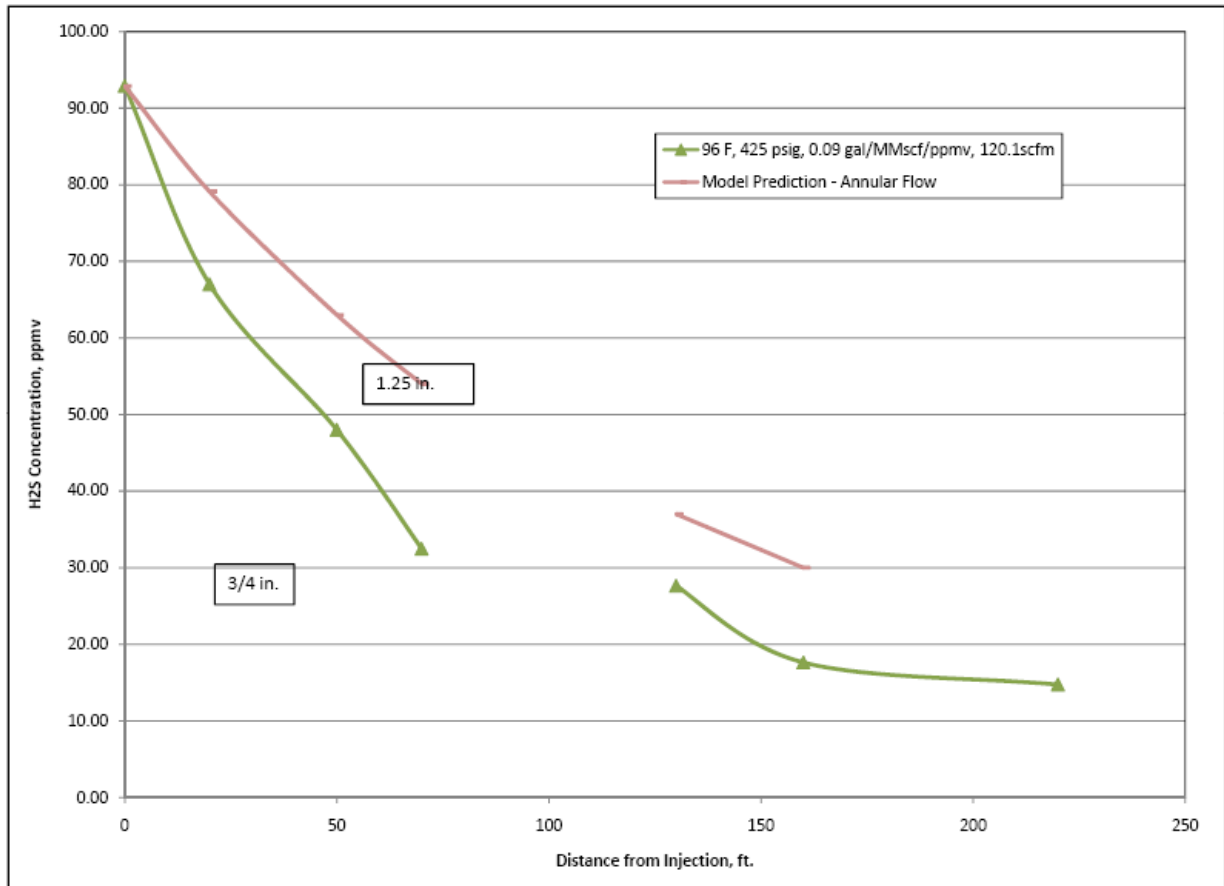


Figure 14 Model Prediction Compared to Baseline Low Pressure Results in 1-1/4 in. pipe

The model predicts the general trend of the data but the absolute value of the predicted H₂S concentration is higher than the observed value. Further, this used a forced “Annular Flow” regime which was, unfortunately, not verified by direct observation in that particular case.

FIELD DATA VALIDATION

Maersk Olie og Gas is a division of the well-known, for shipping and containerized cargo distribution activities, A. P. Moller-Maersk AS in Denmark. Their oil and gas group operates for the DUC consortium a number of fields and offshore facilities that produces a substantial portion of the gas for Denmark from the North Sea. One of these units, GORM C, is configured as shown in Figure 15.

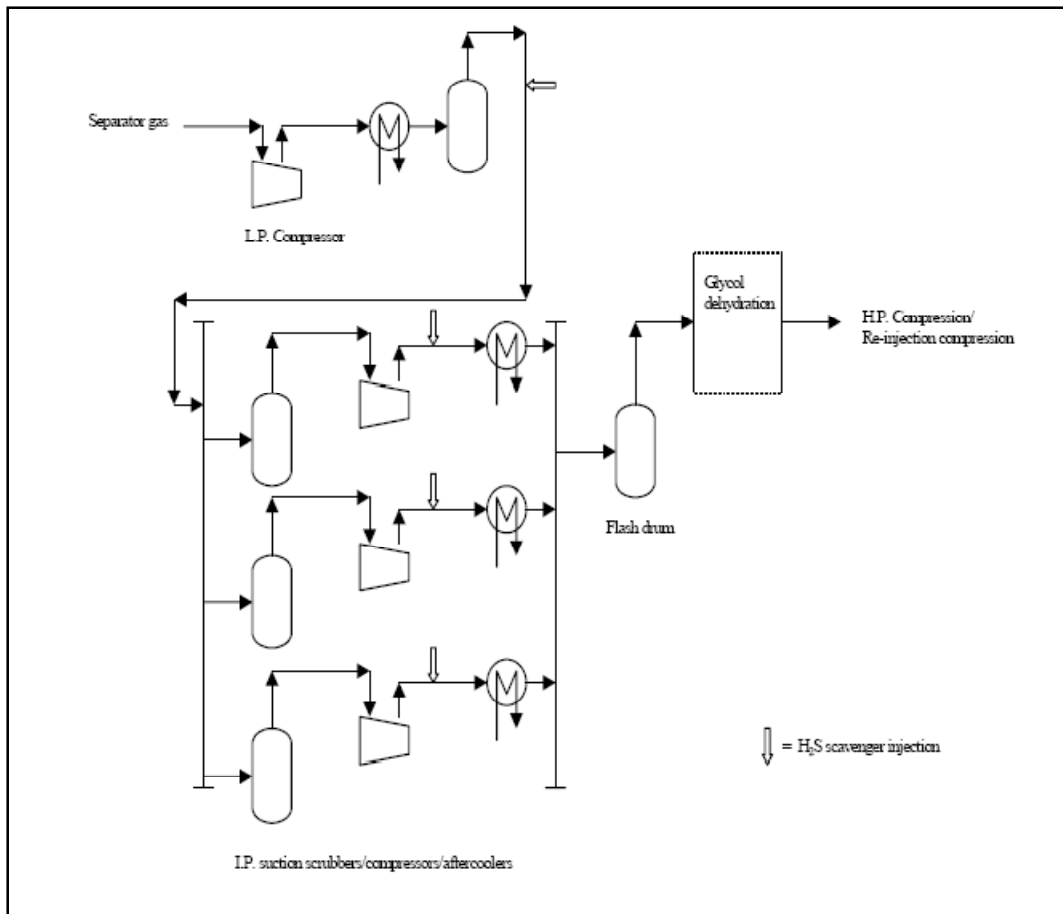


Figure 15 GORM C Layout

Maersk reports that they can use the GTI model to predict the H₂S concentrations of interest for this facility. Evaluations of the data from this facility have been made at various stages in the model development (Ref. 6) to guide it. A number of assumptions that have yet to be independently validated are required however, and it is hoped the current program can resolve these issues. As discussed above, assumptions of the flow regime were required for these predictions as well as assumption that the stoichiometry corresponds closer to that which occurs when two H₂S molecules react with scavenger. Potentially three molecules of H₂S could react but solid formation would likely result. Other sponsor data have also been evaluated with some success. These analyses will be reported elsewhere, most likely in 2009 when work has progressed further.

CONCLUSIONS

A mechanistic model of direct injection scavenging is being developed while systematic data for validation of the model is being obtained in an experimental setup. Field data are also being evaluated and are the ultimate test of the model's utility. It needs to be recognized that field data are difficult and expensive to obtain, especially for offshore facilities where this type of treating is employed, often for want of any other feasible approach. Through interactive model development and field and laboratory data gathering, steady improvements in the model are anticipated, and a version suitable for general use may be ready in the near future.

A unique facility was built in order to conduct controlled scavenger injection experiments. These were the first tests in the setup after the addition of the sightports, riser zone, and second, larger diameter loop. The preliminary tests were not as definitive as needed in that test parameters such as initial H₂S concentration, scavenger flow rate, gas flow rate, etc. varied, which confounds some of the conclusions. The very high rates of mass transfer/reaction for some conditions obscures the results since important concentration information is unavailable before the first measuring point. Additional work in a new experimental/modeling program to remedy some of these shortcomings will be proposed to continue this effort.

Also, since the data has just recently been made available it has not been thoroughly reviewed or evaluated and all the conclusions in this section should be regarded as tentative and merely illustrative of the sort of analysis which will follow in the near future. In fact, one of the remaining project tasks is to conduct a comprehensive evaluation of the model fit with the extensive GTI data base.

ACKNOWLEDGEMENT

Timothy Tamale of GTI was instrumental in operating the test loop and taking the data for the tests reported herein. The support and input of the JIP sponsors was of extreme value throughout all three phases of this program. Contributions of Jan Larsen, Kim Rasmussen and Steffen Fredberg Hansen of Maersk Olie og Gas, Ed Koldziej of Chevron Technology Corp., and Andrew McDonald and Catherine Smart of Clariant are particularly noted.

REFERENCES

1. Matonis, D. T., "Modeling of Direct Injection Scavenging", Energy Institute Reservoir Microbiology Forum, November, 2008, London
2. Fisher, K.S. and D.A. Dalrymple. "GRI Field Evaluation of Liquid-based H₂S Scavengers in Tower Applications at a Natural Gas Production Plant in South Texas." Topical Report to Gas Research Institute", GRI-94/0437, February 1995
3. Fisher, Kevin S., Dennis Leppin, Raj Palla and Dr. Aqil Jamal, "Process Engineering for Natural Gas Treatment using Direct-Injection H₂S Scavengers", GasTIPS, Spring 2003
4. US Patents 6,136,282, (2000) - Method for removal of hydrogen sulfide from gaseous streams, Fisher, K.S., and 7,326,392 (2008) – H₂S Scavenging Method, Fisher, K.S. and McIntush, K.E. , licensed to GTI.
5. Leppin, D., Jamal, A, and Fisher, K.S., "Application of Direct Injection Scavenging to Treatment of Sour Storage Field Withdrawal Gas", Presented at GTI Natural Gas Technologies III, Orlando Florida, February, 2005.
6. Rasmussen, K. et al., "Investigation of a Corrosion Failure in an Offshore Gas Compression System: The Role of H₂S Scavenger and Organic Acids", Corrosion 2004, New Orleans, Paper No. 04360