May 18, 2007

Top of the Line Corrosion Joint Industry Project
TLC JIP Extension – "Lab to field"
Project Proposal

1. Background

Top of Line Corrosion (TLC) occurs when, in multiphase flow, water vapor condenses at the top and the sides of the pipeline, leading to a severe corrosion attack that is difficult to mitigate. TLC occurs typically in wet gas pipelines and in a stratified flow regime. In annular and slug flow, TLC is not an issue; the water chemistry is rather uniform around the pipe circumference as is the availability of any corrosion inhibitor. Severe TLC is usually associated with high condensation rates typically associated with partially or completely failed thermal insulation of the pipeline.

The understanding of TLC lags significantly behind our general knowledge of CO_2 corrosion. This is particularly true when organic acids and/or hydrogen sulphide (H_2S) are present. Consequently, mitigation techniques such as pH control and volatile inhibitors remain uncertain. There are very few instances in the open literature where TLC has been investigated experimentally: Olsen and Dugstad (1991), Vitse et al. (2003), Singer et al. (2004) and Mendez et al. (2005), and only a handful of empirical and semi-empirical models have been derived: de Waard and Lotz (1993), Pots and Hendriksen (2000), Gunaltun and Larrey (2000). On the other hand, a number of failures of wet gas pipelines have been recently reported in the industry.

Finally, the paramount problem of TLC is the large uncertainty associated with the use of traditional corrosion mitigation techniques. Standard corrosion inhibitors may not always be efficient enough to control TLC, as there is no simple way to make them "reach" the top of the line. Volatile inhibitors seem a better choice here, but their effectiveness has only been proven under stagnant conditions for protection of large liquid storage tanks.

2. Previous work performed at the ICMT

A TLC-related research project was initiated at the Institute for Corrosion and Multiphase Technology in 2000 by Total. The TLC JIP 1 was then created in 2003 to incorporate three additional companies (namely BP, ConocoPhillips and ENI). This JIP is currently running and is scheduled to end in July 2007. The main goals of the project are to better understand the mechanism of TLC and to develop a mechanistic model.

Therefore, the test matrices were designed to conduct a parametric study. The parameters were tested separately first (compared to a baseline) and then combined to evaluate the interacting effects. The complete test matrices selected for the TLC JIP 1 are presented in Appendix 1. A brief outline of the parameters tested is shown below:

- **CO_2 partial pressure**. CO_2 partial pressure as high as 8 bar and as low as 0.13 bar.
- **Condensation rate**. Condensation rates from 0.03 ml/m^2s (typical for well insulated pipeline conditions) to 1 ml/m^2s.
- **Acetic acid concentration**. The effect of acetic acid (up to 1000 ppm of free acetic acid in the liquid phase in the tank/bottom of line).
- **H_2S partial pressure.** The effect of the presence of H_2S. The H_2S concentration varied from 500 ppm up to 65000 ppm in the gas phase (the partial pressure of H_2S being up to 0.13 bar).
- **Gas velocity.** The effect of superficial gas velocity was tested from 5 to 20 m/s.
- **Gas temperature.** Three temperatures were selected 40°C, 70°C and 90°C.
- **Time exposure.** Corrosion rates were measured after 2, 7, 14 and 21 days of exposure to the corrosive environment.

On a smaller scale the effect of the following parameters were also investigated:

- **pH stabilization**. The pH in the tank (at the bottom of the line) was varied from the natural pH in condensed water (approximately pH 4) up to pH 7 to evaluate its effect on the reduction of the corrosion rate at the top of the line.
- **Glycol**. The effect of glycol on the vapor pressure and on TLC was investigated.
- **Steel type**. Three different steel types were tested: C1020, API X65 and pure Fe.
- **Brine composition**. Most of the tests were performed using DI water. However, a brine (known composition) was used for a few of them in order to evaluate the effect of salt concentration.

Overall, more than 70 experiments were carried out in the 3 large scale loops especially designed for Top of the Line Corrosion investigation. It is important to mention that a constant focus on the occurrence of **localized corrosion** was applied to each test.

In addition, a comprehensive liquid/vapor equilibrium study of water/acetic acid mixtures was performed in small scale apparatus (Master's student thesis subject). An experimental study related to the condensation regime prediction was also performed using in-situ observation of the condensation process.

The main deliverable of the TLC JIP project is TOPCORP V2, a fully mechanistic model predicting the condensation rate and the general corrosion rate at the top of the line. Modules indicating critical information about the occurrence and the severity of the localized attack as well as information about the condensation regime are also included in the software. The model is built on the MULTICORP platform.

However, even if this software constitutes probably the most advanced breakthrough ever accomplished in TLC modeling, there is still a lot of room for further development. There are gaps identified in the sour corrosion area and in the localized corrosion prediction. Moreover, the influence of the volatile hydrocarbons on TLC is not taken into account. Finally and probably most importantly, the software predictions still needs to be verified to field experience.

3. Goals

The main goal of the project is to develop a **practical tool** that will enable design and operational decision on whether, depending on the field conditions, there is risk of **Top of the Line Corrosion** (e.g. wall thickness loss rate of more than 0.1 mm/year due to uniform or localized corrosion).

4. Scope

The center point of this project is the **analysis and review of the field data** which will enable the identification of the remaining gaps between our present understanding (based on experiments) and the "real life" situation encountered by the operators. The sponsors will provide existing field data they have collected so far in order to create the most complete TLC data base ever put together. A number of companies have already committed to this exercise.

Moreover, the current **understanding of the TLC mechanisms will be improved** by conducted experimental studies inn specific areas such as localized corrosion, hydrodynamics and sour corrosion.

The knowledge gathered through the field data analysis will be combined with our experimental understanding of the phenomena in order to **improve the existing mechanistic model TOPCORP**. The objective here is to incorporate the field experience into the "laboratory based" mechanistic models. The TLC software is built on the MULTICORP V4.0 platform and is made available in the form of an add-on available to the TLC JIP sponsors only.

Industry guidelines module will then be superimposed on the main output of the TOPCORP software in order to simplify the simulation outputs and make them more "operator friendly". These guidelines could for example have the form of practical corrosion and condensation thresholds that would enable operational decisions.

This course of action will yield the main deliverable of this project: a **practical tool for Top of the Line Corrosion prediction** that will be based on laboratory understanding of the mechanisms and indispensable field experience.

The outline of the process is summarized in Figure 1. A more detailed presentation of each part of this outline is discussed in Chapter 6 (Work description -Test Matrix).

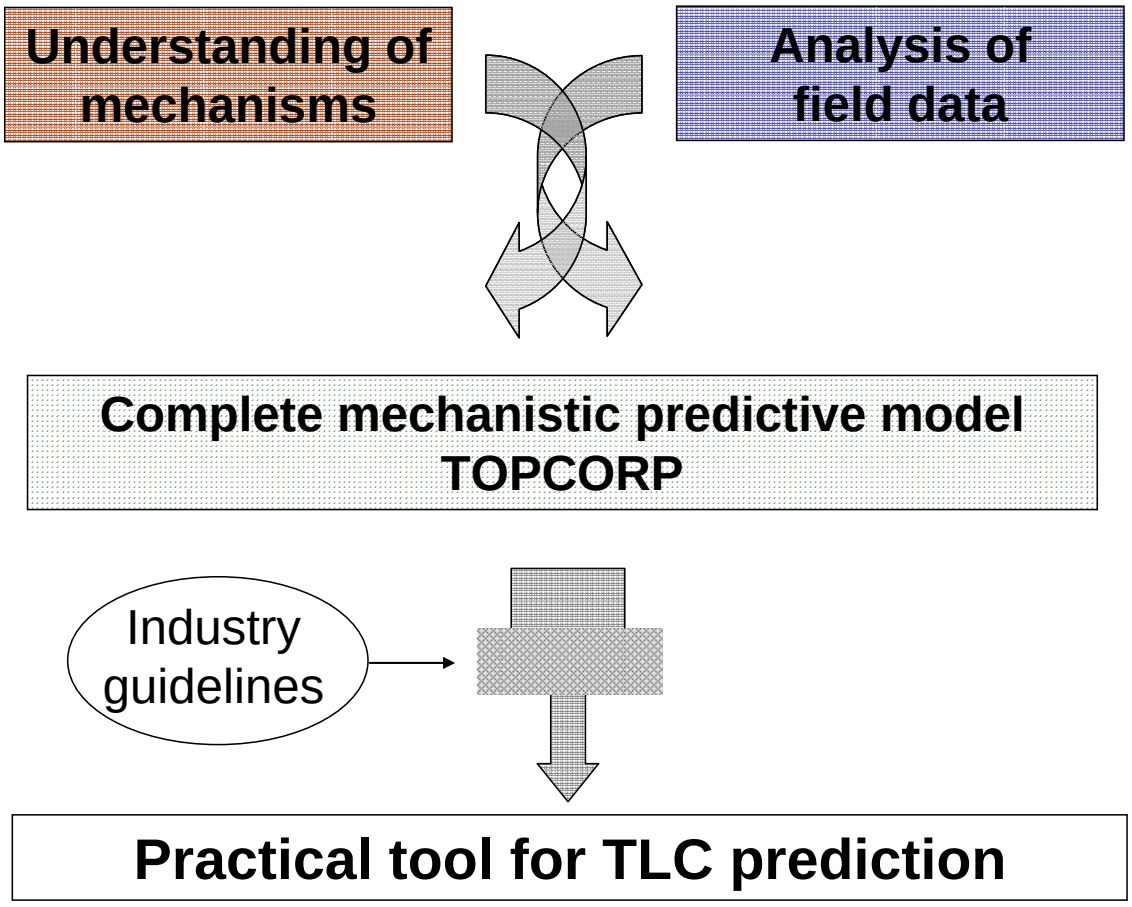

Figure 1: TLC JIP Extension "Lab to Field" – Representation of the course of action

5. Participants

The current TLC JIP sponsors (Total, BP, ConocoPhillips, ENI) have agreed to continue participating in this extension of the original TLC project and to allow the access to the existing data for newly joining companies. However, this agreement is pending on a minimum number of three new joining companies.

6. Work description -Test Matrix

Since at this stage it is too early to specify the details of the different test matrices, only an outline of each tasks involved in this project is presented in this chapter. It is understood that a complete description of each test matrix will be provided to the TLC JIP sponsors at a later stage. It is also understood that the test matrices could be partially or totally changed based on the discussion with the agreement of the majority of the sponsors and the Institute for Corrosion and Multiphase Technology.

The outline of the process is shown in Figure 1. This course of action is divided into four tasks which can be treated separately. Task 1 involves the review of the field data, Task 2 and 3 are related to corrosion and hydrodynamic laboratory tests and Task 4 covers the software development.

Analysis of field data

- ## Task 1: Collection and treatment of field data

In order to solve corrosion issues, participating companies (some of which have initiated some of the largest TLC control program ever performed) will contribute their filed data to the project. The data base will include a minimum of 20-25 sea lines, some of them inspected 3-4 times. The review of the data base should help identify the gaps between the current understanding / modeling and the "real" TLC. Further laboratory testing could be designed in order to tackle some of these issues. Moreover, the knowledge gathered in this phase of the study will be tested against the currently adopted corrosion mechanisms which could be modified accordingly. This should lead to the elaboration of a predictive model designed through controlled laboratory experiments and tested through field experience.

Understanding of mechanisms

A lot of work has already been performed during the past years of this JIP on the understanding of the mechanisms involved in TLC. Although the current understanding has lead to the design of a solid TLC predictive model, there are still some areas which deserve further attention. These remaining gaps can be divided into two main parts: Corrosion related issues (Task 2) and Hydrodynamic related issues (Task 3).

- ## Task 2: Corrosion study

a) The Top of the Line Corrosion study in H_2S environment.

This part consists of a series of experiments performed in the H_2S facilities. The objective is to simulate a wider range of H_2S partial pressures and provide information on general

and localized TLC rates. The main experimental parameters considered in this part are listed below:

- *CO_2 partial pressure:* From 1 to 8 bars.
- *H_2S partial pressure:* from 0.004 to 0.13 bar.
- *The ratio H_2S/CO_2:* 0.05% to 50%
- *Water condensation rate:* from 0.04 to 2 ml/m^2/s.
- *Gas temperature:* from 40 to 90°C.
- *Acetic acid or formic acid concentration.* Up to 650 ppm.

In order to optimize the number of experiments, these parameters are varied around one set of baseline conditions. All the other parameters (total pressure, pH, steel type …) are kept constant. Prior to any actual testing, the sour corrosion test matrix will be designed according to the TLC sponsors guidance and submitted to them for approval.

c) Localized corrosion occurrence, characterization, prediction

A constant focus will be on the study of localized corrosion since this phenomena has been identified as the main cause of pipeline failure (as opposed to uniform corrosion). A lot of information has already been gathered on this topic and the next phase involves the design of a mechanistic localized corrosion model.

b) The efficiency of inhibition techniques for TLC

This part consists of testing in large scale loops a selection of inhibitor and evaluate their ability to control the top of the line corrosion.

• Task 3: Hydrodynamic and thermodynamic study

a) The study of the thermodynamics of hydrocarbon/water mixtures.

This part will be conducted in specially designed autoclaves and will aim at studying the thermodynamic behavior (liquid/vapor equilibrium) of oil/water mixtures and its subsequent partition in the condensed liquid. The understanding of the phase separation at the top of the line is essential in the prediction of TLC occurrence. It would give very important information about which phase actually wets the internal pipe wall. In addition, the compatibility of already existing (and commercial) thermodynamics models will be investigated. This part of the study will cover:

1. **The prediction of hydrocarbon condensation rates**
2. **The modeling of condensed phase chemistry, makeup and wetting**
3. **The influence of all the above on TLC rates**

The main experimental parameters considered in this part are listed below:

- *Mixture of hydrocarbon/ water in the liquid phase*
- *System temperature:* from 40 to 90°C.
- *Total pressure:* up to 100 bars.
- *Condensation rates:* from 0.04 to 2 ml/m^2/s.

b) The study of the droplet transport to the top of the line.

This part consists of a series of experiments performed in our TLC facilities (excluding the H_2S loop). The objective of this part is to study the influence of flow parameters on the droplet transport from the bottom to the top of the line. The main parameters considered in this part are listed below:

- *Superficial liquid velocity:* from 0.01 to 0.1 m/s.
- *Superficial gas velocity:* from 1 to 10 m/s.
- *Gas density:* from 10 to 30 kg/m^3.
- *Pipe diameter:* 4" and 8".

Complete mechanistic predictive model TOPCORP

This part consists exclusively of software development.

- **Task 4: Modeling work**

a) Understanding and modeling of localized corrosion at the top of the line

The prediction of the localized corrosion occurrence (and rate) is probably one the most important issues of CO_2/H_2S corrosion research. It is particularly true for the Top of the Line Corrosion where pipe failures occur almost exclusively by localized corrosion (pitting or mesa attack). This part consists in validating localized corrosion mechanisms associated with the top of the line and developing accurate predictive model for localized corrosion occurrence, form and rate calculation (depending on the factors influencing TLC).

b) Constant update of the software to incorporate new or mature findings

The existing version of the Top of the Line Corrosion software TOPCORP will be used as a platform for future development. All the knowledge acquired during this JIP will be implemented, once mature, in TOPCORP. In addition, the MULTICORP updates obtained through the Corrosion Center JIP (in term for example of sour corrosion, scale formation and dissolution) will automatically appear in TOPCORP (since TOPCORP is a MULTICORP add-on).

7. Execution

The work is going to be completed at the Institute for Corrosion and Multiphase Technology at Ohio University. It is expected that different facilities will be used for the different parts of the project. Among the four tasks identified in this project, only two of them do involve actual experiments and consequently equipment.

Task 2: Facilities related to the Top of the Line Corrosion study

The ICMT is already equipped with three operational large scale TLC loops especially designed for TLC investigation under realistic temperature, water chemistry and flow conditions found in the field. They are all around 30 meters long, 4" ID, high-pressure high-temperature multiphase flow rigs. One of them has H_2S capabilities. These flow loops will be used for the corrosion study (Sour corrosion, localized corrosion and inhibitor evaluation). A schematic of one of the loop as well as information about the operating conditions are presented in the Appendix 2.

Typically, a mixture of CO_2, H_2S (if applicable) and water vapor would be circulated through the loop, which is rated for pressures up to 8 bara (Heavy gas like SF6 could be used to increase the gas density and simulate higher pressure). Heat is added to the system using immersed resistance-heaters in the separation tank. The H_2S loop is mainly made of hastelloy C276 (piping, tank …), but the wetted portions of the liquid and gas pump are made of stainless steel. The other two TLC loops are made completely of stainless steel. The loops are insulated from ambient conditions, and condensation is achieved by the use of heat exchangers mounted at the test section. The experimental conditions are simulated by controlling the cooling liquid flow rate through the heat exchanger. Since temperature is the critical parameter, it is monitored and controlled in the tank and at different locations in the system (heat exchanger, wall, and gas temperature at the test section). The pressure is also controlled and monitored. The test section is equipped with 4 to 8 measuring ports located at the top and the bottom of the line, suited for measurement of the corrosion rate by insertion of corrosion monitoring probes. A schematic representation of a typical test section is shown in Figure 2.

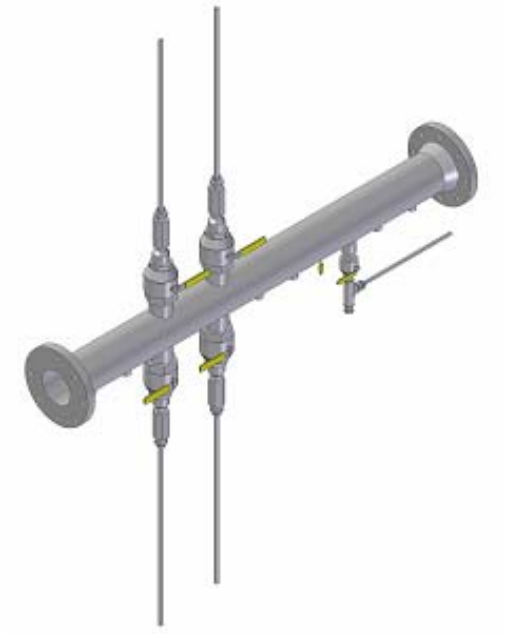

Figure 2: Schematic representation of a test section

Weight loss probes (see Figure 3) are the primary method for corrosion rate measurement because of their ability for surface and film analysis. Electrical resistance or electrochemical techniques do not show satisfactory results in sour environments due to

the formation of the semi-conductive FeS film. It is not planned to implement them in this part of the study but it could be considered if needed.

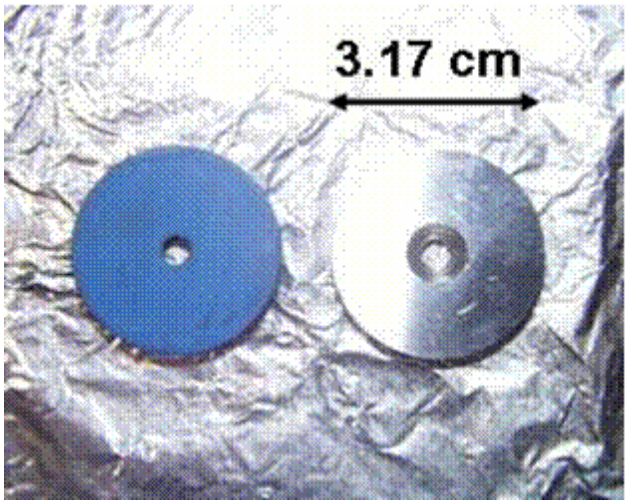

Figure 3: Corrosion monitoring techniques

An in-process optical system including high pressure, high temperature vision system will be implemented in line in order to observe the corrosion process at the top or the bottom of the line (Figure 4).


Figure 4: In-situ video camera for live observation of corrosion phenomena (org.: enviroptics.com)

Optical microscopy, SEM, EDS, and 3D surface profilometer (Figure 5) will be used in post processing to investigate the morphology of the attack, presence of localized corrosion, and composition of surface films.

Figure 5: SEM and 3D surface analysis capabilities

While all the loops are completely operational, it is proposed to upgrade the existing H_2S facilities in order to enable the collection of more corrosion measurements per test. As a summary, these modifications include the following items:

- Addition of a new test section in Hastelloy C276 to maximize the number of corrosion measurements taken for each test performed. Up to 3 corrosion ports at the top of the line and 3 corrosion ports at the bottom of the line are envisioned.

Task 3: Facilities related to the hydrodynamic and thermodynamic study

a) The study of the thermodynamics of hydrocarbon/water mixtures

The study of hydrocarbon/water co-condensation involves for the most part the use of (highly) flammable compounds. Part of the testing could be done in large scale loop since the H_2S facilities are already explosion proof. In addition, the hazardous components of the oil (most volatile species) could also be replaced by inert compounds with similar liquid/vapor properties enabling safer operational procedures. Nevertheless, the most part of the research work can be completed in glass cell, autoclave or small apparatus where the environment can be more easily controlled. A picture of one of our current autoclaves is shown below:

Figure 6: Autoclave

The autoclave would be specially designed for the study of the liquid/vapor equilibrium and top of the line corrosion study. Typically, a mixture of hydrocarbon and brine would be heated and pressurized to the required conditions. The created vapor would be condensed on a cooled section of the autoclave equipped with on line corrosion monitoring (Electrical Resistance probes) and conductivity probes. These two methods should be able to indicate whether the surface where the condensation occurs is water wet or oil wet. The condensation rate will be controlled by the difference of temperature between the system and the sensing element of the ER probe, thus simulating the difference of temperature between the vapor and the pipe wall. Figure 7 presents a schematic representation of the experimental setup.

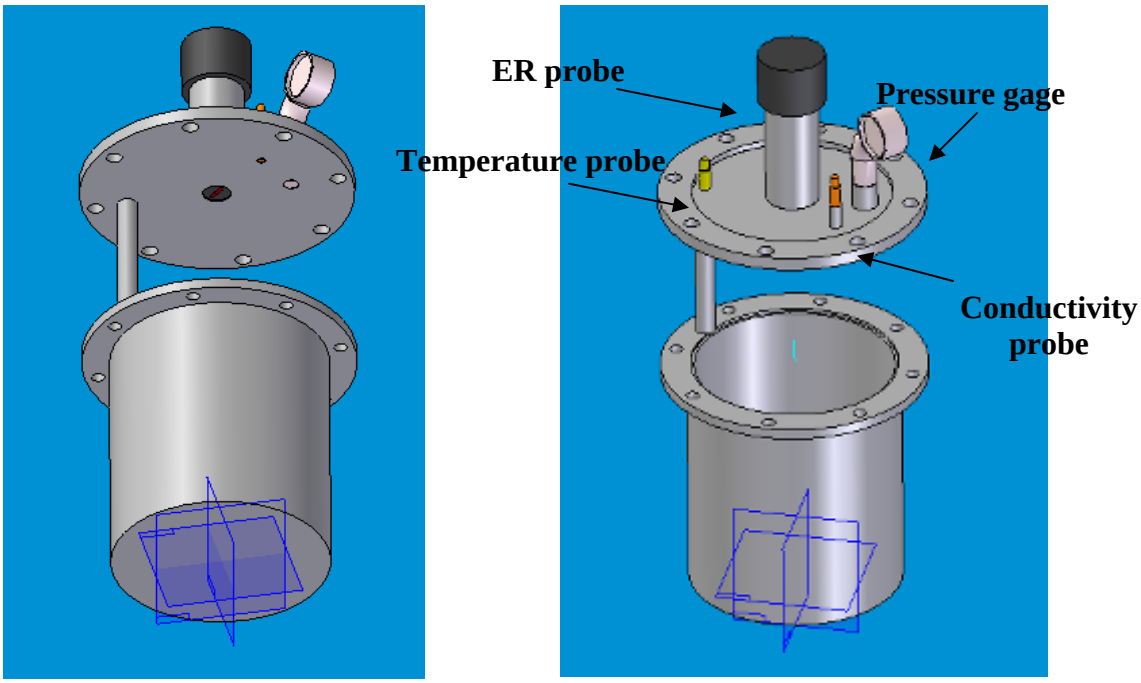

Figure 7: Schematic representation of the autoclave setup.

In a similar way, some test could be done in low pressure glass cells as it is described in Figure 8 and Figure 9. These tests would be also easier to set up and conduct. The corrosion rate would be measured using weight loss probes and Electrical Resistance (ER) probes and conductivity probes could be used as well

Both probes are flushed mounted to the bottom face of the lid. Two identical sets of cooling coils, in contact the top face of the lid, are installed around each probe in order to create artificial cooling conditions. The temperature of the corroding metal can only be measured with the ER probe and enables the calculation of a local condensation rate. The only way to ensure that the condensation rates are the same of the surface of the ER probe and the surface of the weight loss coupon is to ensure that the cooling conditions (controlled by the cooling liquid flow rate) are identical in each case. Moreover, since the glass cell is transparent, the condensation process happening on the lid could be observed

directly. The presence of water in condensed water could be investigated by using volatile hydrophilic dyeing agents.

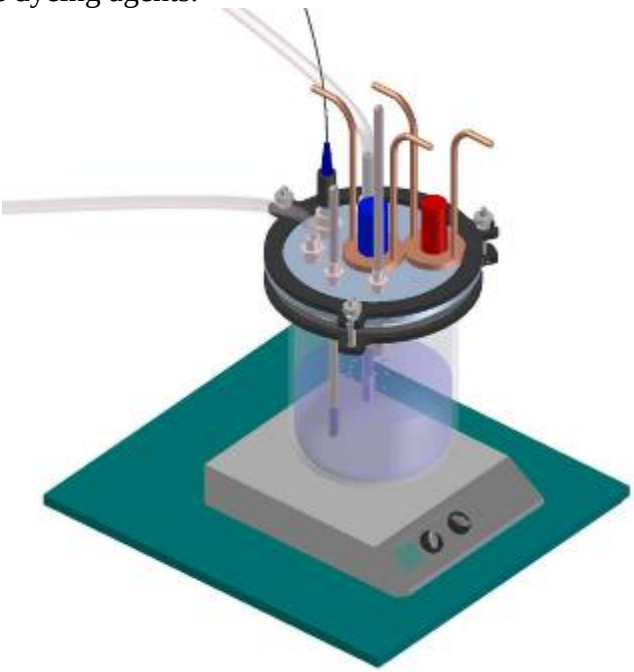

Figure 8: Experimental set-up of the small scale corrosion study
(from J.Addis, Institute for Corrosion and Multiphase flow Technology, Athens OH)

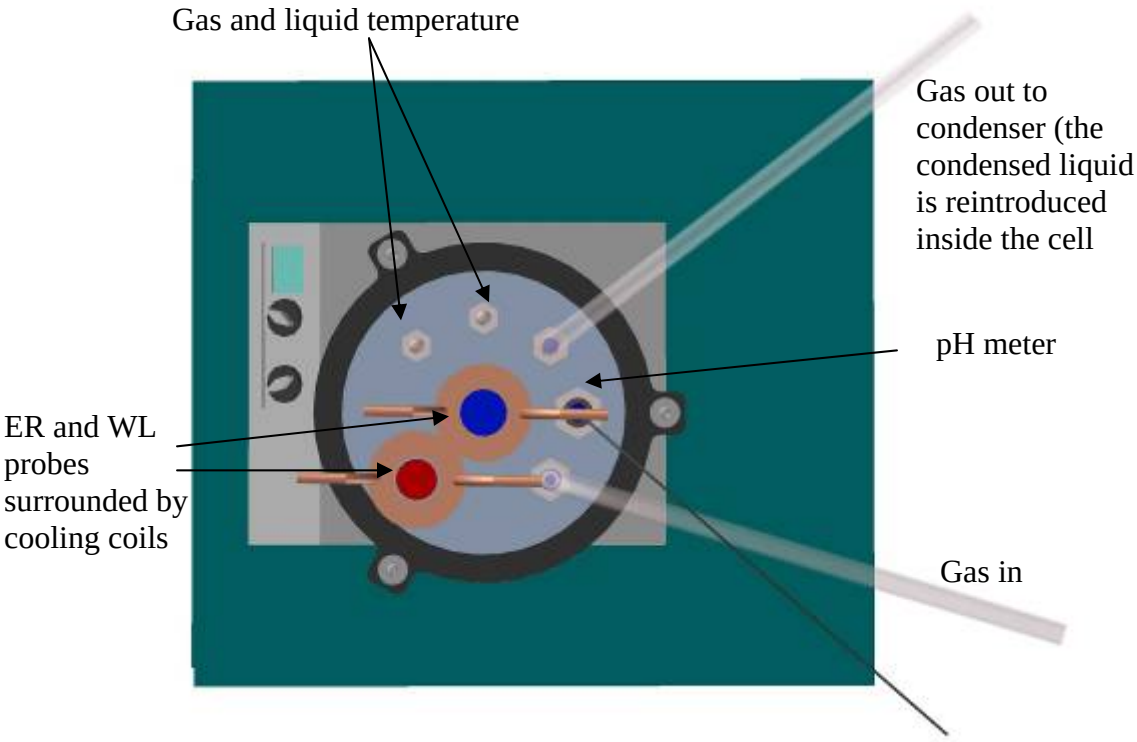

Figure 9: Experimental set-up of the small scale corrosion study (Top view)
(from J.Addis, Institute for Corrosion and Multiphase flow Technology, Athens OH)

b) The study of the droplet transport to the top of the line

The droplet transport study will be performed in the high pressure and high temperature TLC loop#2 and in the low pressure low temperature Hilly Terrain loop (the H_2S facilities will not be used in this part). A description of the TLC Loop#2 and the Hilly Terrain Loop is available in Appendix 2.

The TLC loop #2 is a 30 meters long, 4" ID, high-pressure high-temperature multiphase flow rig. This loop is currently equipped with a gas blower enabling a maximum gas velocity of 12 m/s. The loop will require a few modifications in order to enable the study of the droplet transport (including a liquid pump). There is a need to have a method to differentiate between the liquid coming from the condensation process at the top of the line and the liquid coming from the droplets transported from the bottom. This will be done by using a set of conductivity probes around the pipeline. If there is only condensed water at the top of the line, the conductivity will be very low. If droplets of liquid are transported from the bottom of the line (using a 5% NaCl solution at the bottom of the line) to the top, the conductivity of the liquid at the top of the line will be increased. The value of the conductivity measured will indicate if droplets of liquid actually reach the top and in what quantity. This technology has been developed and validated at the Institute. In addition, a high pressure 4" ID transparent pipe section will be installed in order to visually observe the flow regime and to verify whether droplet transport can be observed. A schematic of the droplet transport test section is presented in Figure 10.

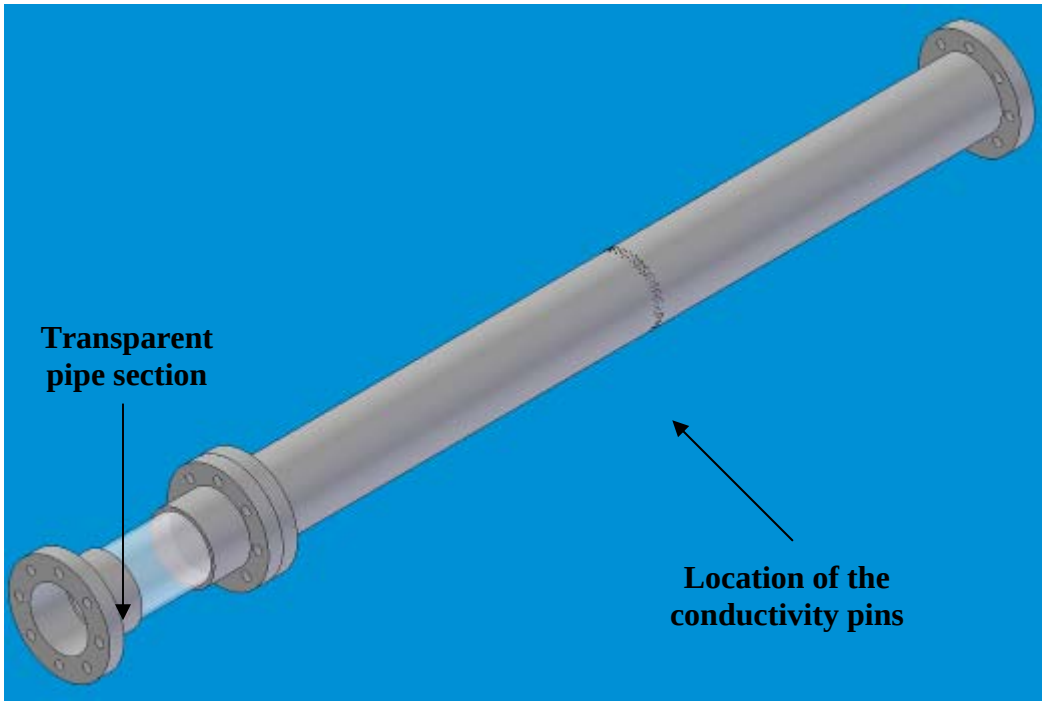

Figure 10: Schematic representation of the entire test section

Moreover, a low pressure, low temperature, clear PVC loop (the hilly terrain loop) could be used as well to perform experiments in lager-diameter pipes (8 inches ID). The costs associated with the loop modification would be consequently minimized and simple

visual inspection with colored fluid should enable proper droplet transport observation. A picture of the existing loop is displayed in Figure 11. This system is a 30 meters long, 4”ID, once through gas system equipped with a liquid pump. Pipe sections could easily be replaced with larger diameter pipe in different configurations.

Figure 11: Picture of the inclined section of the transparent hilly terrain flow loop

8. Budget

Our current understanding of TLC phenomena is based on the findings of the current TLC JIP 1, which is a proprietary project. It would be impossible to separate the TLC JIP 1 and the present extension of this project.

The most effective method of going forward and including new companies into the TLC extension project is to equitably share both the funding burden and accumulated information. Thus we propose that newly-joining companies would sponsor the forthcoming TLC extension project phase almost entirely, while gaining access to all the data from the project's previous phases lasting 4+ years (this including the software TOPCORP). Likewise, the companies who are currently sponsoring the TLC JIP (TOTAL, ConocoPhillips, ENI and BP) would have only small financial obligations in the new TLC extension project while continuing to have full access to new research results, i.e. their contribution will be “in-kind”. In this way, both new and existing sponsoring companies would end up paying approximately the same fees over a 7-8 year period of the whole TLC project, and all would have equal access to the same data and software.

The research team will consist of a project leader (Marc Singer), a post-doctoral researcher, a PhD student and a Master’s student. Srdjan Nesic will oversee the research

work and John Goettge, Danny Cain and Albert Schubert will provide their technical expertise and dedicate part of their time to this project.

Standard annual operating cost

The target project cost for each year of the TLC JIP extension "Lab to field" is set at $280,000. This cost will be divided between the "old" and "new" sponsors. The newly joining companies will contribute to the project with **$80,000 per company and per year**. The "old" sponsors (**Total, BP, ConocoPhillips and ENI**) will have a **yearly contribution of $10,000 per company**. Each company will have to commit to support the JIP for a fixed period of three years. The prospective budget of the TLC JIP Extension is summarized in the table below:

Table 1: Operating cost per year and per company

	Year 1 2007-08	**Year 2 2008-09**	**Year 3 2009-10**	**Total for 3 years**
"New" sponsor	$80,000 per company	$80,000 per company	$80,000 per company	$240,000 per company
"Current" sponsor (TOTAL, COP, ENI, BP)	$10,000 per company	$10,000 per company	$10,000 per company	$30,000 per company

It is expected that the available funds for the each of the projects will be distributed in the following way:

- 50% - Time: Project leader, Principal Investigator, Engineer and Technician
- 30% - Support for graduate students
- 20% - Consumables

It is worth noting that a 47% overhead rate has been included in the projected budget, payable to Ohio University, on all the expenditure categories listed above in accordance with current Ohio University policies. This overhead cost is already included in the proposed budget (i.e., there are no additional hidden costs).

It is also important to mention that any new company joining the TLC JIP Extension project must be or become a sponsor of the Corrosion Center JIP.

9. Timing

The TLC JIP Extension will last a minimum of 3 years. The target start date is July 1, 2007. Reports on the findings and results will be delivered at the end of each month after the beginning of the project. The timing of various activities within the project is graphically outlined in the table below:

Table 2: TLC JIP Extension - Time line

	Year 2007			**Year 2008**				**Year 2009**				**Year 2010**	
	April to Jun	**Jul to Sept**	**Oct to Dec**	**Jan to Mar**	**April to Jun**	**Jul to Sept**	**Oct to Dec**	**Jan to Mar**	**April to Jun**	**Jul to Sept**	**Oct to Dec**	**Jan to Mar**	**Apr to Jun**
Proposal													
Contracting stage													
H_2S facilities upgrade													
Other systems modifications													
Task 1: Field data analysis													
Task 2: Corrosion study													
Task 3: Hydrocarbon/water and Droplet transport study													
Task 4: Modeling work													
Reporting													

10. Deliverables

- Reports documenting the experimental work and the analysis.
- TLC Database of experimental results.
- Top of the Line Corrosion predictive Software TOPCORP which:
    - Will include fully mechanistic models of the following phenomena
        - *The hydrocarbon/water mixture condensation regime and rate,*
        - *The droplet transport rate from the bottom to the top of the line,*
        - *The general and the localized corrosion rates in sweet and sour conditions in the presence of organic acids and hydrocarbon*
    - Will be tested against the largest TLC field database ever created and modified accordingly
- Practical and "operator friendly" tool for TLC prediction (simplified version of TOPCORP and its outputs) designed by industry guidelines.

11. Contact

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APPENDIX

Appendix 1

TLC JIP 1 SCOPE AND TEST MATRICES

SCOPE

During the first years (Phase I) of the Top-of-the-Line Corrosion Joint Industrial Project (TLC-JIP 1) several experimental matrices were evaluated, each one including specific field concerns from the sponsoring companies. The experiments performed were mostly short term (2 to 5 days long) and constituted the Phase I of the TLC JIP 1. The results of the Phase I helped understand the overall mechanism of TLC and allowed the evaluation of mitigation procedures under a wide range of operational conditions. The Phase I of the project will have covered investigation of the following influential parameters in TLC:

- **CO_2 partial pressure**. CO_2 partial pressure as high as 8 bar and as low as 0.13 bar.
- **Condensation rate**. Condensation rates from 0.05 ml/m^2s (typical for well insulated pipeline conditions) to 1 ml/m^2s.
- **Glycol**. The effect of glycol and methanol.
- **HAc**. The effect of acetic acid (up to 1000 ppm concentration in the liquid phase in the tank).
- **pH stabilization**. A feasibility study for the pH stabilization technique. The pH was varied from the natural pH in condensed water (approximately pH 4) up to pH 7 to evaluate the effect it has on reduction of the corrosion rate.
- **H_2S.** The effect of the presence of H_2S will be investigated. The H_2S concentrations will be varied from 500 ppm up to 65000 ppm in the gas phase.
- **High flow rates.** The effect of superficial gas velocity in the presence and absence of HAc will be investigated. Gas velocities in excess of 20 m/s will be used if required.

The main objective of the TLC JIP 1 project is the creation of a mechanistic model to predict TLC occurrence (general corrosion rate and localized corrosion). Long terms experiments are therefore needed due to the fact that the corrosion rates obtained in short term tests are very different and that any signs of localized corrosion require at least two weeks exposure to be visible.

Therefore, the Phase II of the TLC JIP 1 focuses on long term experiments (3 weeks long) and on the construction of a TLC prediction model. During the last board meeting held on April 2005, analysis of the results indicated a need for conducting more experiments by changing just one variable at a time in order to properly evaluate trends and find possible threshold values. This method is primordial in order to understand the specific effect of each parameter. Six main influencing parameters have been identified and are studied separately. The focus is also on localized corrosion. SEM and other analytical techniques will used to identify the risk of localized attack in TLC.

Based on this reasoning, a new test matrix for the Phase II was created that will complement the results obtained in the Phase I, and will allow the design of a reliable mechanistic model. The complementing series include isolated effects of **gas velocity** (Series I), concentration of **H_2S** (series II), concentration of **acetic acid** (series III), **condensation rate** (series IV), **CO_2 partial pressure** (series V) and **gas temperature** (series VI). In addition, two other series of experiments (for a total of six experiments) will be dedicated on the study of interacting effects. It is proposed to study the **acetic acid/pH_2S** (series VII) and the acetic **acid/pCO_2**(series VIII) effects. However, it is understand that the parameters studied could be changed upon the results of the previous series.
The support for this project is in the form of a TLC-JIP. Currently four companies have expressed the readiness to participate in the project and have helped define the experimental matrix for the first year of the project. These are TOTAL, ConocoPhilips, ENI and BP.

TEST MATRICES

The test matrices related to the two phases of the project are detailed in the following chapters.

PHASE I
Short term experiments

There are four series in this Phase I name after the name of each sponsoring companies:

- TOTAL Series
- ConocoPhillips Series
- ENI Series
- BP Series

CONOCO-PHILLIPS Series

Test conditions

The COP test matrix objective was to investigate the influence of these parameters on TLC:

- Condensation rate
- Glycol
- Acetic acid concentration
- pH stabilization at the bottom of the line

The test matrix is presented in Table 4. One of the principal characteristics of these tests is that the liquid phase in the tank was not de-ionized water but was brine. The composition of the brine is shown in Table 3.

Table 3: Phase I COP - Brodgar Brine Composition

Ion	Concentration (mg/L)
Na^+	1,360.00
K^+	1.60
Mg^{2+}	0.80
Ca^{2+}	148.00
Fe^{2+}	5.00
Cl^-	3,300.00
SO_4^{2-}	5.10
HCO_3^-	5.00

Table 4: Phase I COP - Test matrix

Common parameters:
T = 80°C
Absolute pressure = 3 bar
pCO_2 = 1.5 bar
pN_2 = 1 bar
Vgas = 5 m/s
Steel type= API X65

Experiment #	0	1	2	3	4	5	6	7	LT1	LT2
Investigating:	*Baseline*	*Cond Rate*	*Glycol*	*HAc*	*pH*	*HAc*	*pH*	*HAc*	*Long term of test 4*	*Long term*
Condensation rate (mL/m2/s)	0.25	1	1	1	1	1	1	1	1	1
Total HAc concentration (ppm)	0	0	0	100	100	500	500	1000	100	1000
Glycol (MEG) in Brodgar Brine)	0	0	50%	50%	50%	50%	50%	50%	50%	50%
pH control (base solution pH between 4-4.5)	Measured	Measured	Measured	Measured	pH 5.5	pH 5.5	pH 6.5	pH 6.5	pH 5.5	pH 5.5
Duration (days)	2	2	2	2	2	2	2	2	29	14

ENI EXPERIMENTS

Test Conditions

The ENI test matrix objective was to investigate the influence of these parameters on TLC:

- Gas velocity
- Acetic acid concentration

The test matrix is presented in Table 5. Seven short term tests and one long term test were performed for the ENI test matrix.

Table 5: Phase I ENI - Test matrix

Common parameters:

Temperature:	70 ^{o}C	Glycol / methanol:	none
Absolute pressure:	8 bar	pH control:	none
CO_2 partial pressure:	2 bar	Steel type:	API X65
H_2S:	none	Condensation rate:	0.25 $\frac{ml}{m^2 s}$

Experiment #	0	1	2	4	5	6	8
Investigating:	*Velocity*			*Velocity/ HAc*			*Long term*
Gas Velocity	10 m/s	15 m/s	20 m/s	10 m/s	15 m/s	20 m/s	10 m/s
Free HAc concentration	0	0	0	180 ppm	180 ppm	180 ppm	180 ppm

- The goal of this series is to determine the maximum/critical gas velocities that can be reached in a wet gas pipeline or in a stratified multiphase flow without having erosion-corrosion problems. Critical velocity will be investigated first without HAC (experiments #0 – #2) and then in the presence of HAc (experiments #4 - #6).
- Experiment 8 is a long term test. It lasted 3 weeks.
- A C1020 carbon steel spool(s) will be installed in the loop to obtain additional information on the erosion-corrosion attack. This carbon steel spool piece will be installed only during the long term test (experiment 8)
- Experiments 3 and 7 have been dropped from the original test matrix.

TOTAL EXPERIMENTS

Test Conditions

The TOTAL test matrix objective was to investigate the influence of these parameters on TLC:

- Undissociated acetic acid concentration
- Glycol
- pH stabilization
- H_2S partial pressure

The test matrix is presented in Table 6. Nine short term tests and one long term test were performed for the TOTAL test matrix..

It is important to mention that the loop got contaminated with copper during the long term test (Test 8). The bottom of the line coupons were plated with a thin copper layer invalidating any corrosion rate measurements. As copper does not evaporate, it is believed that the results obtained at the top of the line are completely valid.

Table 6: Phase I TOTAL - Test Matrix

Common parameters:

Condensation rate = 0.25 ml/m^2/s.
Test is not repeated except tests #0 to #3 which were repeated one time
Material: AISI 1020
T = 70 °C
Absolute pressure = 8.3 bar
pCO_2 = 8 bar
Vgas = 5 m/s

Experiment #	0	0*	1	2	3	4	5	6	7	8
Investigating	Baseline	HAc	Glycol	HAc		H_2S				Test duration
Free [HAc] (ppm)	0	180	0	180	30	0	500	1000	1000	180
H_2S partial pressure (bar)	0	0	0	0	0	0.005	0.005	0.005	0.04	0
Glycol percentage in liquid phase	0 %	0%	50 %	50 %	50 %	0 %	0 %	0 %	0 %	50%
pH control	No	No	No	No	pH = 6.8	No	No	No	No	No
Test duration (days)	2	2	2	2	2	4	4	4	4	21

BP EXPERIMENTS

Test Conditions

The BP test matrix objective was to investigate the influence of these parameters on TLC:

- Gas temperature
- CO_2/H_2S partial pressure

The test matrix is presented in Table 7. Eight short term tests were performed for the BP test matrix.

Table 7: Phase I BP - Test Matrix and test conditions

Common parameters:

Test duration: 2 days. Test is repeated once.
Absolute pressure: 3 bar
HAc: 0 ppm
pH control: No
Gas velocity: 5 m/s
Condensation rate: 0.25 $mL/m^2/s$
Steel type: API X65

Experiment #	0	1	2	3	4	5	6	7
Investigating:	*Baseline*	*Temperature*	*H_2S*				*CO_2*	*H_2S*
Temperature, °C	70	40	70	70	70	70	70	70
H_2S partial pressure	0	0	0.004 bar	0.013 bar	0.07 bar	0.13 bar	0.07 bar	0.13 bar
CO_2 partial pressure	0.13 bar	0.13 bar	0.13 bar	0.13 bar	0.13 bar	0.13 bar	1.3 bar	1.3 bar
pH measured - **Tank**	4.9	4.82	5.23	5.16	5.1	4.5	4.5	4.46

PHASE II
Long term experiments

Based on the results obtained in the phase I, the following matrices are recommended for the phase II. Duration of the tests will be around 24 days and there will be no repeat.

In addition, a complementary glass cell study is suggested, to evaluate the effects of glycol and Acetic Acid on pH in order to complete the condensed water chemistry module.

Table 8: Phase II - Baseline conditions

Parameters	Baseline conditions
Absolute pressure (bar)	*3*
pCO_2 (bar)	*2*
Gas temperature (°C)	*70*
Condensation rate (mL/m^2/s)	*0.25*
Gas velocity (m/s)	*5*
pH_2S (bar)	*0*
Free HAc concentration in the tank (ppm)	*0*
Steel type	API X65
Liquid phase composition	DI water
pH (tank)	4.5
Glycol, methanol, inhibitor content (ppm)	0
Test duration (weeks)	3

Only the value of the parameters in italic will be varied on this study

Table 9: Phase II - Range of variables

Parameters	Range	
	Min	Max
Absolute pressure (bar)	3	8
pCO_2 (bar)	0.13	8
Gas temperature (°C)	40	90
Condensation rate (mL/m^2/s)	0.05	1
Gas velocity (m/s)	5	15
pH_2S (bar)	0.004	0.13
Free HAc concentration in the tank (ppm)	0	1000

NB: The absolute pressure and the partial pressure of CO_2 represent only one parameter

Series I
Experimental matrix for the **Gas velocity** effect evaluation

Common parameters:
Steel type: API X65
Liquid phase composition: DI water
pH (tank): 4.5
Glycol, methanol, inhibitor content: 0 ppm
Test duration: 3 weeks

Absolute pressure: 3 bars
pCO_2: 2 bars
Gas temperature: 70 °C
Condensation rate: 0.25 mL/m^2/s
pH_2S: 0 bar
Free acetic acid concentration in the tank: 0 ppm

Experiment #	Baseline	1	2
Investigating	Gas velocity		
Gas velocity (m/s)	5	10	15

****

Series II
Experimental matrix for the **H_2S** effect evaluation

Common parameters:
Steel type: API X65
Liquid phase composition: DI water
pH (tank): 4.5
Glycol, methanol, inhibitor content: 0 ppm
Test duration: 3 weeks

Absolute pressure: 3 bars
pCO_2: 2 bars
Gas temperature: 70 °C
Condensation rate: 0.25 mL/m^2/s
Gas velocity: 5 m/s
Free acetic acid concentration in the tank: 0 ppm

Experiment #	Baseline	3	4	5
Investigating	H_2S			
pH_2S (bar)	0	0.004	0.07	0.13

****

Series III
Experimental matrix for the **Acetic acid** effect evaluation

Common parameters:
Steel type: API X65
Liquid phase composition: DI water
pH (tank): 4.5
Glycol, methanol, inhibitor content: 0 ppm
Test duration: 3 weeks

Absolute pressure: 3 bars
pCO_2: 2 bars
Gas temperature: 70 °C
Condensation rate: 0.25 mL/m^2/s
Gas velocity: 5 m/s
pH_2S: 0 bar

Experiment #	Baseline	6	7
Investigating	Acetic acid concentration		
Free HAC tank (ppm)	0	100	1000

****

Series IV
Experimental matrix for the **Condensation rate** effect evaluation

Common parameters:
Steel type: API X65
Liquid phase composition: DI water
pH (tank): 4.5
Glycol, methanol, inhibitor content: 0 ppm
Test duration: 3 weeks

Absolute pressure: 3 bars
pCO_2: 2 bars
Gas temperature: 70 °C
Gas velocity: 5 m/s
pH_2S: 0 bar
Free acetic acid concentration in the tank: 0 ppm

Experiment #	8	Baseline	9
Investigating	Condensation rate		
Condensation rate (mL/m^2/s)	0.05	0.25	1

****

Series V
Experimental matrix for the **pCO_2** effect evaluation

Common parameters:
Steel type: API X65
Liquid phase composition: DI water
pH (tank): 4.5
Glycol, methanol, inhibitor content: 0 ppm
Test duration: 3 weeks

Gas temperature: 70 °C
Condensation rate: 0.25 mL/m^2/s
Gas velocity: 5 m/s
pH_2S: 0 bar
Free acetic acid concentration in the tank: 0 ppm

Experiment #	10	Baseline	11
Investigating	pCO_2		
Absolute pressure (bar)	3	3	8.3
pCO_2 (bar)	0.13	2	8

****

Series VI
Experimental matrix for the **Gas temperature** effect evaluation

Common parameters:
Steel type: API X65
Liquid phase composition: DI water
pH (tank): 4.5
Glycol, methanol, inhibitor content: 0 ppm
Test duration: 3 weeks

Absolute pressure: 3 bars
pCO_2: 2 bars
Condensation rate: 0.25 mL/m^2/s
Gas velocity: 5 m/s
pH_2S: 0 bar
Free acetic acid concentration in the tank: 0 ppm

Experiment #	12	Baseline	13
Investigating	Gas temperature		
Gas temperature (°C)	40	70	90

****

Series VII
Experimental matrix for the **acetic acid/pH_2S** effect evaluation

Common parameters:
Steel type: API X65
Liquid phase composition: DI water
pH (tank): 4.5
Glycol, methanol, inhibitor content: 0 ppm
Test duration: 3 weeks

Absolute pressure: 3 bars
pCO_2: 2 bars
Gas temperature: 70 °C
Condensation rate: 0.25 $mL/m^2/s$
Gas velocity: 5 m/s

Experiment #	Baseline	3	6	14	7	15	5	16
Investigating	Acetic acid / pH_2S							
Free HAc tank (ppm)	0	0	100	100	1000	1000	0	1000
pH_2S (bar)	0	0.004	0	0.004	0	0.004	0.13	0.13

The grey columns represent tests related to the pH_2S/ Acetic acid interaction but which have been already performed in previous series

****

Series VIII
Experimental matrix for the **Condensation rate/Gas velocity** effect evaluation

Common parameters:
Steel type: API X65
Liquid phase composition: DI water
pH (tank): 4.5
Glycol, methanol, inhibitor content: 0 ppm
Test duration: 3 weeks

Gas temperature: 70 °C
pCO_2: 2 bars
Absolute pressure: 3 bars
pH_2S: 0 bar
Free acetic acid concentration in the tank: 0 ppm

Experiment #	8	17	18	2	1	Baseline	9	19
Investigating	Condensation rate / Gas velocity							
Condensation rate ($ml/m^2/s$)	0.03	0.03	0.03	0.25	0.25	0.25	1	1
Gas velocity (m/s)	5	10	15	15	10	5	5	10

The grey columns represent tests related to the condensation rate/ gas velocity interaction but which have been already performed in previous series

****

SERIES OF REPEATS

REPEAT ON SOME NON CONCLUSIVE EXPERIMENTS

Series IX

Common parameters:
Steel type: API X65
Liquid phase composition: DI water
pH (tank): 4.5
Glycol, methanol, inhibitor content: 0 ppm

Experiment #	6*	5*	8*	11*	14*
Investigating	Acetic acid	pH_2S	Condensation rate	pCO_2	HAc/pH_2S
Absolute pressure (bar)	3	3	3	8	3
pCO_2 (bar)	2	2	2	7.7	2
pH_2S (bar)	0	0.13	0	0	0.004
Free HAc in the tank (ppm)	100	0	0	0	100
Condensation rate ($ml/m^2/s$)	0.25	0.25	0.03	0.25	0.25
Gas temperature (°C)	70	70	70	70	70
Gas velocity (m/s)	5	5	5	5	5
Test duration	3 weeks	6 weeks	3 weeks	3 weeks	3 weeks
Reason for repeating	Unexpected O_2 contamination	Corrosion rate not stable after 21 days	Unexpected localized corrosion	Corrosion rate not stable after 21 days	Too much scatter and possible localized corrosion

****

SERIES OF SPECIAL EXPERIMENTS

STUDY OF ADDITIONNAL FACTORS INFLUENCING THE TLC

Series X
Experimental matrix for **pure iron testing**

Common parameters:
Liquid phase composition: DI water
pH (tank): 4.5
Glycol, methanol, inhibitor content: 0 ppm
Test duration: 3 weeks

Conditions of Series I Test 0 (Baseline):
Absolute pressure: 3 bars
pCO_2: 2 bars
pH_2S: 0 bar
Free acetic acid concentration in the tank: 0 ppm
Gas temperature: 70 °C
Gas velocity: 5 m/s

Experiment #	20	0 and 9
Investigating	Steel type	
Steel type	Pure Fe	API X65
Condensation rate ($ml/m^2/s$)	0.25 and 1	0.25 and 1

The grey columns represent tests related to the glycol effect study but which have been already performed in previous series

The tests investigating the effect of the inclination will be performed using standard coupons and by rotating the test section.

The pure iron samples will be tested to clarify the effect of iron carbide on localized corrosion. The presence of Fe_3C has been associated, in the surface analysis, with the occurrence of pitting. A pure iron coupon would not have any carbon structure and could lead to different results.

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SERIES OF ADDITIONNAL EXPERIMENTS

FILLING THE GAPS IN THE UNDERSTANDING OF TLC INTERACTING EFFECTS SERIES

Series XI
Experimental matrix for the **Condensation rate/Acetic acid** effect evaluation

Common parameters:
Steel type: API X65
Liquid phase composition: DI water
pH (tank): 4.5
Glycol, methanol, inhibitor content: 0 ppm
Test duration: 3 weeks

Gas temperature: 70 °C
Gas velocity: 5 m/s
pCO_2: 2 bars
Absolute pressure: 3 bars
pH_2S: 0 bar

Experiment #	0, 8, 9	21	22	6	7
Investigating	Condensation rate / Free acetic acid				
Condensation rate ($ml/m^2/s$)	0.03, 0.25 and 1	0.03 and 1	0.03 and 1	0.25	0.25
Free acetic acid in the tank	0	100	1000	100	1000

The grey columns represent tests related to this series but which have been already performed in previously

****

SERIES OF CONDENSATION EXPERIMENTS

INVESTIGATING THE CONDENSATION PROCESS AND DEFINING THE CRICTICAL CONDITIONS FOR THE CHANGE IN CONDENSATION REGIME

Series XII (proposed)
Experimental matrix for the **Condensation regime** investigation

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For each test, the following data will be collected:

- Critical droplet size (maximum droplet size before detachment)
- Droplet growth rate
- Condensation regime (sliding or stagnant)

Common parameters:
Liquid phase composition: DI water
Test duration: A few hours for each test
All the tests will be performed in large scale high pressure, high temperature flow loop

	Range investigated
Condensation rate (ml/m^2/s)	0.03 to 3
Gas temperature (°C)	25 to 80
Gas velocity (m/s)	3 to 20
Total pressure (bar)	1 to 7

****

Appendix 2

The Hydrogen Sulfide Multiphase Testing Facility

H2S Flow Loop

Test Section

Combustion system

Breathing apparatus

H_2S SYSTEM SPECIFICATIONS

Gas Velocity	1 to 8 m/s
Total pressure	1 to 20 bar
Temperature	40°C to 90°C
Condensation rate	0.02 to 3 ml/m^2/s
Gas Mixtures	Various mixtures of nitrogen, carbon dioxide, and hydrogen sulfide

The hydrogen sulfide system is a large scale flow loop currently testing concentrations of hydrogen sulfide below 60000 ppm in the gas phase on corrosion rates in multiphase flow at 70°C, 3 bar.

The hydrogen sulfide system was commissioned to determine the influence of various concentrations of hydrogen sulfide gas on corrosion rate in a controlled multiphase environment. This system is comprised of 4" diameter, Sch 80, Hastelloy© C-276 for resistance to corrosion and stress corrosion cracking, two progressive cavity pumps for conveying liquid and gas, and three separate test sections for corrosion monitoring. The current value of the system, not including labor necessary for construction, is well over $500,000 USD.

The hydrogen sulfide system is located in an isolated "environmental chamber" of the Multiphase Technology Center for better control of temperature and hazardous gases. All operational controls for the hydrogen sulfide test loop are located just outside the environmental chamber providing a higher level of safety for the operator and more convenience for data collection. Flowing gas mixtures of nitrogen, and/or carbon dioxide are mixed with flowing liquid mixtures of water and/or oil producing flow regimes of stratified flow, slug flow, or annular flow in the multiphase environment.

Various types of corrosion-monitoring equipment can be installed in each of two test sections, such as: electrical resistance probes, linear polarization probes, or coupons for weight loss measurement. With system temperatures capabilities ranging from 40°C to 70°C and pressures from atmospheric to 400 psi, corrosion rate prediction and field simulation tests are easily accomplished in a controlled environment.

The hydrogen sulfide system has been updated recently and is now capable to study the effect of operating parameters on the corrosion of carbon steel under dewing condition during the transportation of wet gas.

The Wet Gas Corrosion Flow Loop #2
TLC Loop #2

Full View

Tank and blower

Test section

Gas flow meter

OPERATIONAL CONDITIONS

Gas Velocity	1 to 12 m/s
Total pressure	1 to 7 bar
Temperature	40°C to 80°C
Condensation rate	0.02 to 3 $ml/m^2/s$
Gas Mixtures	Various mixtures of nitrogen, carbon dioxide

The Wet Gas Corrosion Flow Loop #2 is designed to study the effect of operating parameters on the corrosion of carbon steel under dewing condition during the transportation of wet gas. Several corrosive gases such as CO_2 and HAc are under investigation. This loop also provides a mean to quantify the efficiency of volatile inhibitors.

This closed system is comprised of 4" diameter, Sch 40, Stainless steel 316 for resistance to corrosion. It is 25 meters long, horizontally leveled, and it is fully insulated from the ambiant. The tank used for liquid storage contains $1m^3$ of water. The concentration of acid present in the water is controlled by injection. Heat is added to the system using resistance-heaters, which are immersed in the tank. The power available is 11kW. A blower provides gas velocities up to 12 m/s. A system of cooling coils is used for the cooling of the gaseous phase, allowing condensation to occur. The test section provides 8 ports, 4 at the top of the line and 4 at the bottom of the line, which are available for the measurement of the corrosion rate by insertion of flush-mounted corrosion monitoring probes.

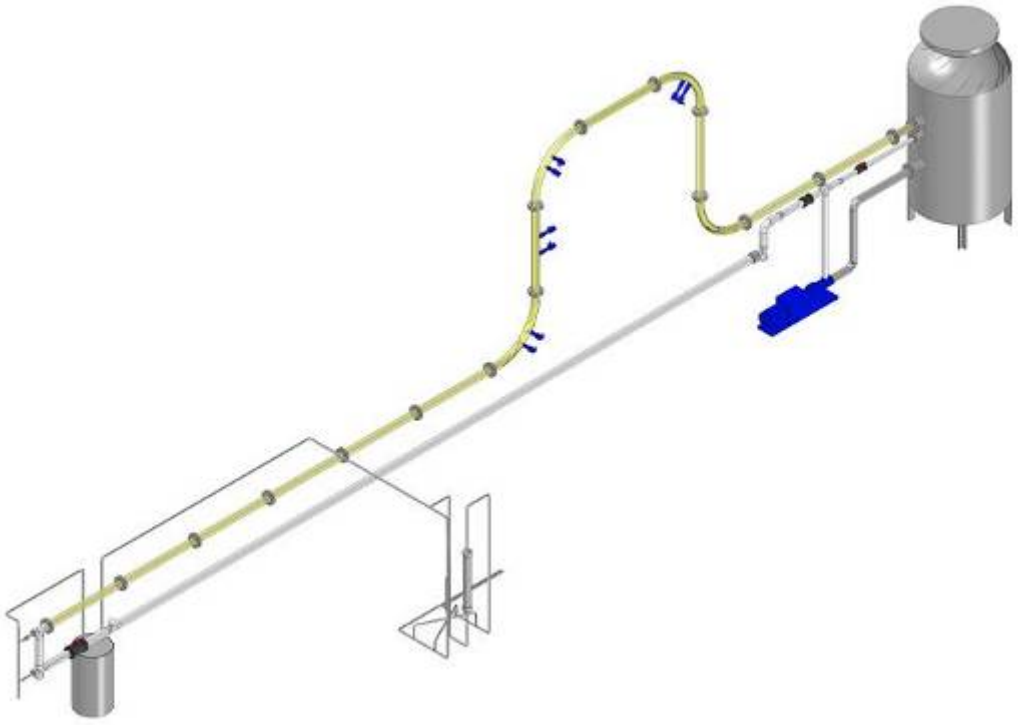
Instrumentation

The temperature is controlled by a Proportional Integrator Differential (P.I.D) regulator (+/- 1°C). Monitoring of the temperature occurs in the gas phase all around the 25-meter-long loop, between the inlet and the outlet of the heat exchangers (both in the gas phase and in the cooling liquid), and at the wall temperature (by a thermocouple installed in the head of a flush-mounted probe). Moreover, a system of thermistors is installed at the test section in order to monitor the temperature of the gas, the inner wall and the outer wall (+/- 0.1°C). The pressure in the tank is controlled (+/- 0.1 psi). A gas flow meter is installed in line and is used to monitor and control the gas velocity. The volume of condensed water is measured after being separated from the gas phase. Ceion Technology (E.R probes) is presently used to measure the corrosion rate in low conductivity-discontinuous condensed water

The Hilly Terrain flow loop

Full View

Inclined section



Schematic representation of the loop

OPERATIONAL CONDITIONS	
Gas Velocity	Up to 12 m/s (once through gas)
Total pressure	Up to 2 bars
Temperature	20 to 40°C
Liquid velocity	Up to 2 m/s

A unique, 10-cm diameter, 18-m long pipeline has been constructed to simulate localized multiphase oil/water/gas flow and corrosion in the vicinity of road and river crossings and in hilly terrain topography with short, abrupt inclination changes. The multiphase flow line involves flow over a horizontal distance of 6 m before reaching the crossing section. Four 9D (nine-diameter radius) bends with 2-m pipelines for the riser, crossing, and downcomer sections make up the crossing section. The multiphase mixture then flows through a 4-m horizontal discharge section into a separation tank. This highly complex system exhibits flow regimes from horizontal, inclined, and vertical flows. At any given gas and liquid flow rate, this system can experience 9 different flow regimes in different regions at the same time. The corresponding corrosion mechanisms and corrosion rates will vary dramatically. Research is just beginning in this important area.