March 18, 2009

Water Wetting Joint Industry Project – WW JIP – Extension

1. Background

For crude oil and water two phase pipeline flow it is important to know whether the water comes into contact with the pipe walls and corrodes them or is entrained in the oil phase. Generally speaking the water can be considered to be entrained by the oil if the oil flow rate is high, particularly for heavier crudes, and it can be assumed that it will separate and flow along the bottom if the oil flow rate is low, particularly for lighter crudes. Another factor of water wetting is the amount of water. At a critical point, the phase inversion point at 40-60 % water cut, the continuous phase can change from oil to water. Below the phase inversion point the oil is the continuous phase and entrains the water and above the phase inversion point the water will entrain the oil.

It is easy to predict what happens at extreme conditions, such as very high or low flow rates or very high or low water cuts, but it is important to also know what happens in between these extreme points and when the transition occurs from oil wetting the pipe wall to water wetting the pipe wall. Furthermore, field cases have shown that corrosion problems can occur even for very low water cuts, when it would have been assumed that the water was easily entrained by the oil.

There are different factors that determine the wetting of the pipe wall. They can be both flow related and related to the steel surface. The diameter of the pipe, the flow rates and the properties of the crude are among the factors that determine whether the flow pattern is stratified or dispersed. Water wetting is more likely to occur in stratified flow and oil wetting is more likely to occur in dispersed flow. The flow pattern only tells a part of the story. It is also important to know what happens at the steel surface. Certain chemicals, either added chemicals (such as corrosion inhibitors) or compounds which are naturally occurring in the crude oil can affect the wettability of the steel surface.

The current knowledge about the water wetting phenomena is growing, but there are still many questions unanswered, for instance about what happens in three phase flow, in bends or elbows, at elevated temperature and how chemistry affects wettability and corrosion. In order to answer these questions and to improve the current water wetting model, a three year joint industry project is proposed as an extension of the work that has already been done on water wetting at the Institute for Corrosion and Multiphase Technology (ICMT) at Ohio University (OU).

2. Previous work on water wetting at ICMT

The first work on water wetting at ICMT was started in 2004 in a project sponsored by Saudi Aramco, which include experimental work done in 4" flow loop where phase wetting maps where constructed for one model oil and five different crude oils. In order to assess the wetting on the pipe surface a conductivity probe was designed, which consisted of stainless steel pins, which were flush mounted on the surface of a test section (see Figure 1). When oil is wetting the surface no conductance is detected but when water is wetting the surface the pins will sense conductance on the surface. Figure 2 is an example of a phase wetting map constructed for a model oil. Three wetting regimes are identified; pure water wetting, pure oil wetting and intermittent wetting, where the pipe wall is wetted periodically by both oil and water.

The results from the conductance probes where confirmed with visual observation of the flow pattern, water sampling from the bottom of the pipe and corrosion monitoring. A mechanistic model was developed based on the work of Brauner(1) and Barnea(2) for bubble flow in water. The modified water wetting model calculates the maximum droplets size depending on the flow parameters and if the droplet is small enough it will be entrained by the oil flow (dispersed flow) but if it is too large it will not be sustained by the flow and will drop out and flow at the bottom of the pipe (stratified flow). The modeling as well as the flow loop results have been reported elsewhere(3-11). The water wetting model has been incorporated in to MULTICORP, the mechanistic CO_2 corrosion and multiphase flow prediction software developed by the ICMT and made available to its sponsors. An example of a prediction of the transition between oil wetting and intermittent wetting can be seen in Figure 2.

Following the promising results of the initial water wetting project a 3-year joint industry project (WW JIP) was started in 2006 and was sponsored by eight companies, Saudi Aramco, BP, Petrobras, Total, ConocoPhillips, Shell, ExxonMobil and ENI. Five graduate students worked on the WW JIP, each focusing on different aspects of water wetting.

- Xuanping Tang (Ph.D.) looked at the effect of the surface state (effect of roughness and films) on wettability and developed a small scale apparatus, a goniometer, which can be used to measure the wettability of a steel surface.
- Francois Ayello (Ph.D.) looked at compounds that are naturally occurring in the crude oil, which can affect the wettability or inhibit corrosion.
- Chong Li (Ph.D.) looked at how inhibitors affect the wettability and CO_2 corrosion and developed a small scale apparatus, doughnut cell, which can be used to construct a phase wetting.
- Pankaj Ajmera (M.S.) looked at how asphaltenes affect wettability and CO_2 corrosion.
- Shanshan Yang (Ph.D.) is currently looking at how paraffins effect wettability and CO_2 corrosion and the mechanism by which the paraffins deposit on the pipe wall.

3. Goals

The main goals of the proposed project are:

- to investigate water wetting in three-phase (gas-oil-water) flows theoretically and in a multiphase flow loop, using a model oil as well as a specific crude oils as provided by the sponsoring companies;
- to investigate the effect of flow disturbances, such as in bends, weld beads, etc., in the multiphase flow loop;
- to continue developing the methodology for water wetting testing investigation, including the benchtop scale apparatus (doughnut cell);
- to continue uncovering the effect of the crude oil chemistry on corrosion inhibition and wettability,
- to investigate the effect of elevated temperatures and pressures on water wetting,
- to use the knowledge that has been gained to improve the water wetting model already developed in the previous stages of this project.

4. Scope

It is proposed that the current water wetting joint industry project being conducted at the ICMT is extended for another three years.

The main topic to be covered in the extended JIP is the investigation of wettability in three phase flow. In previous work on water wetting it has been discovered that the wettability depends on both the flow pattern and the surface wettability. There are more flow patterns which exist under three phase flow (oil-water-gas) than there are for two phase oil-water flow. The biggest difference is the addition of plug and slug flow as well as annular flows. Water wetting has not before been investigated under these flow regimes.

While three phase flow will be the main focus of this investigation, there are more unanswered questions to be investigated, such as how wetting is affected by pressure and temperature or disturbance of the flow. Water wetting depends on the flow pattern, and the transition from one flow pattern to another depends, among other things, on the physical parameters of the fluids, such as viscosity and interfacial tension. These parameters are dependent on temperature as well as pressure. On top of that, the whole nature of the oil flow can change from being newtonian to being non-newtonian at lower temperatures.

Disturbances in the flow can be in the form of slugs as well as a change in the flow direction (such as through bends). The slugs could help to cover the pipeline walls with helpful surface active chemicals from the oil phase and provide oil wetting or alternatively they could break a protective layer already formed on the steel surface so water wetting could occur. The heavier liquid phase (water) has a tendency to be accumulated at bends, but at the same time disturbances in the flow could help to coat the steel's surface in the bend with surface active chemicals which would promote oil wetting and corrosion inhibition.

In the previous WW JIP it was discovered that a water wetting condition did not only depend on the flow pattern (water wet during stratified flow and oil wet during dispersed flow), but there was also a chemical factor, which could change the surface wettability and make the steel surface hydrophobic so that oil wetting would prevail even for stratified flow. It is important to be able to test the tendency of different crude oils to make the surface hydrophobic.

In order to make this information accessible and useful for the participating companies, biannual progress meetings will be held throughout the duration of the JIP and progress reports will be made available biannually as well. Once the new results of the JIP have been scientifically proven, they will be implemented into the existing software package: WWCORP and made available to the participating companies. This module will be made compatible with ICMT flagship multiphase flow and corrosion prediction software MULTICORP, but also with other flow simulators.

5. Work description

In order to achieve the project goals, experiments will be conducted both in large scale (flow loop) and small scale (doughnut cell, glass cell, etc.). The flow loop experiments will be tested in different test series, one for each parameter to be varied. All of the flow loop tests will be initiated using the LVT200 as the model oil, 1 wt% NaCl water and CO_2 gas unless otherwise noted. The main test parameters can be reviewed in Table 1.

It is anticipated that each of the test series will take 6 months to be executed and prior to test series 2-3, the varying parameter will be tested with small scale equipments in order to assess trends that will optimize the testing in the large scale flow loop tests.

The description of the equipment will be given in Section 6.

Task 1: Three phase flow

Flow loop: Test series 1

This test series will be conducted at **ambient temperature, ambient pressure and at zero inclination** (horizontal flow at 0°). The water cut will start at 1% and the fluid mixture velocity will be varied in 0.5 m/s increments from 0.5 m/s to 2 m/s and the gas flow rate will be started at 0.5 m/s and stepwise increased until annular flow is reached for each of the . This procedure will then be repeated for 2%, 5%, 10%, 15% and 20% water cut. This series includes at least 120 experimental points which will be used to construct a 3D flow maps.

Flow loop: Test series 2

This test series will repeat the first test series except that the fluids will be heated to maintain around 60°C in the test section to achieve **higher temperatures**.

Flow loop: Test series 3

This test series will repeat the first test series except by using SF_6 as the gas phase instead of or in combination with CO_2 in order to simulate three phase flow at **higher pressure**. In order to simulate high pressures (500 ~900 psi) for three-phase flow tests, a combination of heavy inert gas SF_6 (sulfur hexafluoride) and CO_2 (carbon dioxide, which causes the corrosion process) will be used. The density of SF_6 at standard conditions is around 9.3 times higher than that of a typical hydrocarbon gas such as methane at the same conditions. Density wise, the working pressure 100 psi for this heavy gas is equivalent to a 930 psi working pressure for methane.

Flow loop: Test series 4

This test series will repeat the first test series except at the most extreme **inclination**, 90° or vertical.

Flow loop: Test series 5

This test series will repeat the first test series except a medium to heavy **crude oil**, which as been identified as having good water entrainment properties, will be used as the oil phase.

Table 1: Test parameters for three phase investigation in the flow loop

Oil phase	Model oil and/or a crude oil provided by sponsoring company
Water phase	1 wt% NaCl solution
Gas phase	CO2 and/or SF_6
Phase fractions	Will be selected depended on field experience and values required to reach different flow regimes.
Superficial oil-water mixture velocity	0.1 to 3 m/s
Superficial gas velocity	0.5 to 25 m/s
Pipe inclination	Horizontal and $\pm 90^o$
Pipe diameter	4”
System temperature	25 ^{o}C, 60°C
System pressure	Ambient with higher pressure simulated with the use of SF_6.

Small scale testing

Small scale experiments will be conduced mainly in the doughnut cell but also by conducting property tests (density, viscosity and interfacial and surface tension). For instance prior to test series 2 it will be investigated how the properties of LVT change with increasing temperature and a doughnut cell test will be conducted at 60°C.

Prior to test series 3, it will be tempted to achieve three phase flow in the doughnut cell by using SF_6 as a gas phase and by researching how pressure affects oil properties such as density.

Prior to test series 5, the properties of the crude oil (density, viscosity and surface/interfacial tension) will be investigated and the surface wettability will be assessed with the goniometer and the doughnut cell.

Task 2: The effect of disturbances in the flow on the wettability

Task 2 is divided into two parts. *Wetting in bends* and *Wetting after weld beads*, and will be conducted for oil and water two phase flow initially.

These tests will be conduced in the hilly terrain flow loop by inserting conductance probes in the bends of the flow loop in place of corrosion probes.

Another piece of equipment – a flow loop equipped with a standing slug set-up with a conductance probe strategically placed will be used to better assess wetting under slug flow conditions.

Task 3: The effects of crude oil chemicals on steel wettability.

In Task 3 a methodology will be developed based on the previous work done at the ICMT to evaluate the inhibition potential of a crude oil. The methodology would identify both qualitatively and quantitatively which components in the crude oil, such as surface active compounds, aphaltenes or paraffins contribute to both the corrosion inhibition and to the steel surface wettability as well as its extent.

Crude oil assays are designed to give information about the characteristics of the crude oil to the refineries as well as to buyers and traders of the crude oil. It is very desirable for the assays to also give information about the corrosion inhibition characteristics of the crude oil, where specific classes of compounds known to have a favorable or unfavorable effect on corrosion would be quantified.

In the previous water wetting JIP, the emphasis was to test model compounds in a model oil in order to identify which components in the crude oil have an effect and how. The next step would be to look more closely to the crude oils themselves, for instance by comparing crude oils from different origin. Asphaltenes and certain N-compounds where shown to have a significant effect on corrosion inhibition and surface wettability. To better understand this effect, real crude oils need to be put through the same or similar tests as was done with extracted asphaltene.

6. Execution

The work for the extended water wetting JIP will be completed at the Institute for Corrosion and Multiphase Technology at Ohio University. Professor Srdjan Nesic will be the Principal Investigator with 10% of his time devoted to this project. Other staff will include a project leader, students and laboratory staff.

During previous Water Wetting projects specialized equipment, techniques and methods have been developed in order to study the water wetting phenomenon. The extended water wetting project would make full use of the existing equipment as well as adding on to it if needed.

The three phase flow loop tests will be carried out in a 200’ long, 4” ID multiphase flow loop mounted on a fully inclinable rig (Figure 3). The multiphase flow rig at the ICMT are specially designed to investigate corrosion under realistic flow conditions found in the field. The wettability of the steel surface is measured with a conductance probe (Figure 1) and the flow patterns are recorded visually with a video camera. The hilly terrain flow loop (Figure 4) is already in place but has until now only been used for single phase or gas-water two phase flow. In order to use it for oil-water two phase flow it needes to be rehauled and reconfigured with an oil tank, an extra positive replacement pump and a oil/water separator. Same is true for the stanging slug system.

An improved version of the doughnut cell has been developed to study wetting at higher temperatures and pressure. The prototype of the doughnut cell (Figure 5) has already been used with good success at ambient temperature and pressure. The prototype was made with acrylic components for increased visibility but in the high temperature version the doughnut cell is build out of stainless steel (Figure 6).

A goniometer (Figure 7) has been successfully designed and used at the ICMT in order to capture contact angles of both oil droplets in a water phase (oil-in-water) and water droplets in an oil phase (water-in-oil). The prototype of the goniometer was built out of acrylic for increased visibility but a stainless steel goniometer was later built in order to allow for contact angles to be recorded at higher temperatures. Glass windows are mounted on either side of the goniometer in order for a light source to be able to penetrade through the goniometer and for a video of the droplet to be recorded. An original dynamic wettability testing apparatus involving a horizontal rotating cylinder will also be utilized to assess the wettability of steel under intermittent flow conditions (Figure 8).

Figure 9 shows a typical three electrode glass cell setup where electrochemical measurements take place. The glass cell has been used to assess corrosion inhibition properties of inhibitors and model compounds in a model oil as well as for crude oil by itself. A procedure has been developed in which the glass cell testing is divided into three parts, *partitioning*, *direct inhibition* and *persistancy*.

Other small scale equipment include a *tensiometer* and *viscometer*, which is used to measure the physical properties of the oil. The tensiometer employs a ring pull method, where a platinum ring is placed into the water and then pulled up through the interphase between water and oil. The force it takes to break the interface is directly related to the interfacial tension, which can be read of a dial on the tensiometer. In order to measure the viscosity of a liquid it is placed in a tube and the time for a sphere to fall through the liquid can be related to its viscosity if the density is know.

7. Timeline

The timeline for the extension of the WW-JIP is shown in Table 2.

8. Deliverables

- Improved understanding of water wetting and the key factors affecting it.
- Full reports (every six months) documenting the results, analysis and outlining future work.
- An updated model of water wetting in oil/water two- and gas/oil/water three-phase flows WWCORP, which will be fully compatible with MULTICORP and other major multiphase flow simulators.

9. Budget

The scope of work described above and the budget in this WWII-JIP is based on an annual fee of $50,000 per company with an anticipated minimum of 6 companies participating. In case a different number of companies commits to the project, the budget and the scope of work will be adjusted accordingly. Also, it should be pointed out that the cost for procuring and shipping crude oils will be carried by projected sponsoring companies. It is estimated that the available funds on the project will be distributed in the following way:

- 60% - Manpower: Project leader, post-doc, engineers, technicians, students.
- 40% - Flow loop modifications, consumables, instrumentation, handling/disposal of fluids, safety.

It is worth noting that a 47% overhead rate has been included in the projected budget, which is payable to Ohio University on all the expenditure except for equipment in accordance with current Ohio University policies.

10. Contact information

Dr. Srdjan Nesic / Principal Investigator nesic@ohio.edu tel.: 1-740-593-9945

11. References

1. "The prediction of dispersed flows boundaries in liquid-liquid and gas liquid systems". Brauner N., Int. J. Multiphase Flow, May 2001, 27(5), 885-910.
2. "A unified model for predicting flow pattern transitions for the whole range of pipe inclintations", Barnea D., Int. J. Multiphase Flow, 1097, 11, 1-12.
3. "Effect of Corrosion Inhibitor on Water Wetting & CO_2 Corrosion in an Oil-Water Two Phase System" Chong Li, Sonja Richter and Srdjan Nesic, ICC2008 Paper No. 2662, Las Vegas, October 2008.
4. "Crude Oil Chemistry Effects on Inhibition of Corrosion and Phase Wetting" Francois Ayello, Winston Robbins, Sonja Richter and Srdjan Nesic, ICC2008 Paper No. 3149, Las Vegas, October 2008.
5. "Study of Wettability of Different Steel Surfaces" Xuanping Tang, Sonja Richter and Srdjan Nesic, Paper No. 3109, ICC2008, Las Vegas, October 2008.
6. "Experimental Studies of Wetting in Large-Diameter Horizontal Oil/Water Pipe Flows," J. Cai, S. Nesic, C. Li, X. Tang, F. Ayello, C.I.T Cruz and J.N. Al-Khamis. SPE Paper No. 95512
7. "Determination of Phase Wetting in Oil-Water Pipe Flows," Francois Ayello, Chong Li, Xuanping Tang, Jiyong Cai, Srdjan Nesic, C.Ivan T. Cruz, Jamal N Al-Khamis. NACE Paper No. 08566, 2008
8. "Effect of oil type on phase wetting transition in oil-water flows," Xuanping Tang, Francois Ayello, Chong Li, Srdjan Nesic, Jiyong Cai, C.Ivan T. Cruz, Jamal N Al-Khamis. NACE Paper No. 07170, 2007
9. "Experimental Study on Water Wetting and CO2 Corrosion in Oil-Water Two-Phase Flow," Cai,J.; Li,C.; Ayello,F.; Tang,X.; Nesic,S.; Cruz,I.; Al-Khamis,J. NACE paper No. 06595, 2006
10. "A multiphase flow and internal corrosion prediction model for mild steel pipelines," Nesic,S.; Cai,J.Y.; Lee,K.-L.J. NACE paper No. 05556, 2005
11. "Modeling of Water Wetting in Oil-Water Pipe Flow," Cai, J.; Nesic, S.; NACE International Conference and Exhibition, Paper No. 04663, New Orleans, Louisiana, April 2004

Table 2 Timeline for WW-JIP

<table>
<tr><td rowspan="2"></td><td colspan="6">2009</td><td colspan="12">2010</td><td colspan="12">2011</td><td colspan="6">2012</td></tr>
<tr><td>7</td><td>8</td><td>9</td><td>10</td><td>11</td><td>12</td><td>1</td><td>2</td><td>3</td><td>4</td><td>5</td><td>6</td><td>7</td><td>8</td><td>9</td><td>10</td><td>11</td><td>12</td><td>1</td><td>2</td><td>3</td><td>4</td><td>5</td><td>6</td><td>7</td><td>8</td><td>9</td><td>10</td><td>11</td><td>12</td><td>1</td><td>2</td><td>3</td><td>4</td><td>5</td><td>6</td></tr>
<tr><td>Water wetting in three-phase flows</td><td colspan="6">Test series 1</td><td colspan="6">Test series 2</td><td colspan="6">Test series 3</td><td colspan="6">Test series 4</td><td colspan="6">Test series 5</td><td colspan="6"></td></tr>
<tr><td>Small scale testing</td><td colspan="30"></td><td colspan="6"></td></tr>
<tr><td>Analysis and modeling</td><td colspan="6"></td><td colspan="27"></td><td colspan="3"></td></tr>
<tr><td>Software development</td><td colspan="18"></td><td colspan="18"></td></tr>
<tr><td>Reporting</td><td colspan="5"></td><td></td><td colspan="5"></td><td></td><td colspan="5"></td><td></td><td colspan="5"></td><td></td><td colspan="5"></td><td></td><td colspan="5"></td><td></td></tr>
</table>

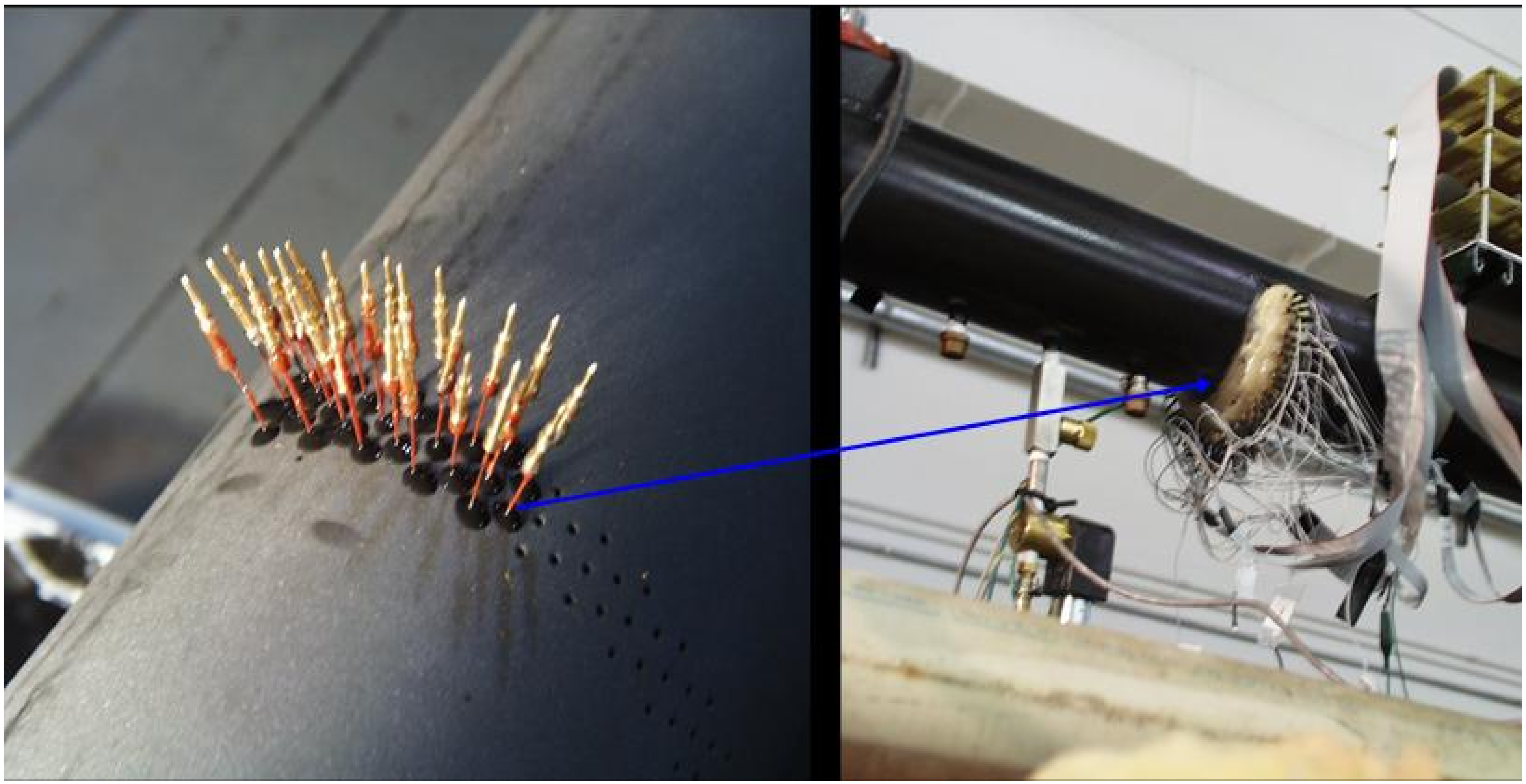

Figure 1. Flush-mounted wall conductance probe for phase wetting determination on the pipe surface

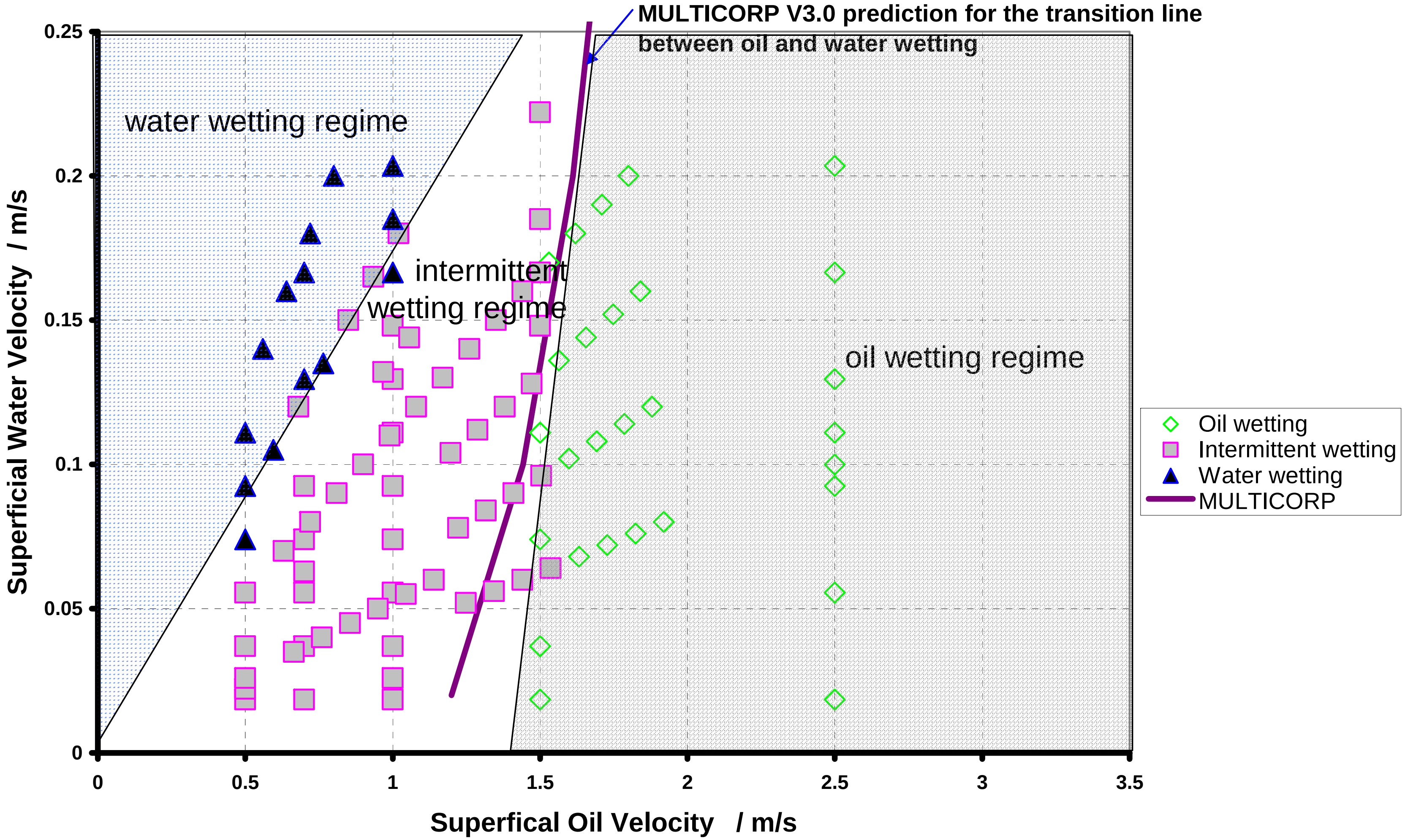

Figure 2. Phase wetting map for LVT200 oil and water two-phase horizontal pipe flow including a line predicted by MULTICORP for a transition between oil and water wetting.

Figure 3. Fully inclinable flow rig at Institute for Corrosion and Multiphase Technology at Ohio University.

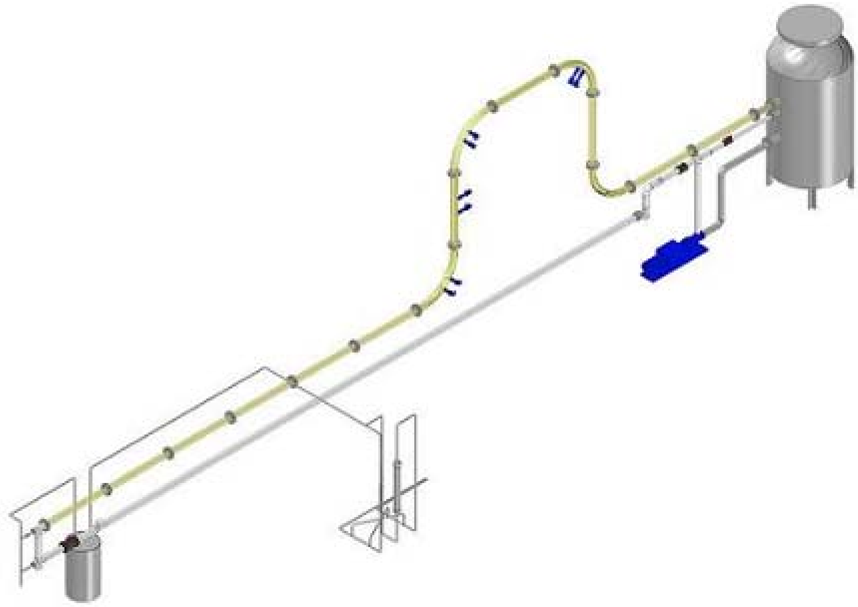

Figure 4: Hilly terrain flow loop is employed in order to investigate wetting in bends (Courtesy of Josh Addis).

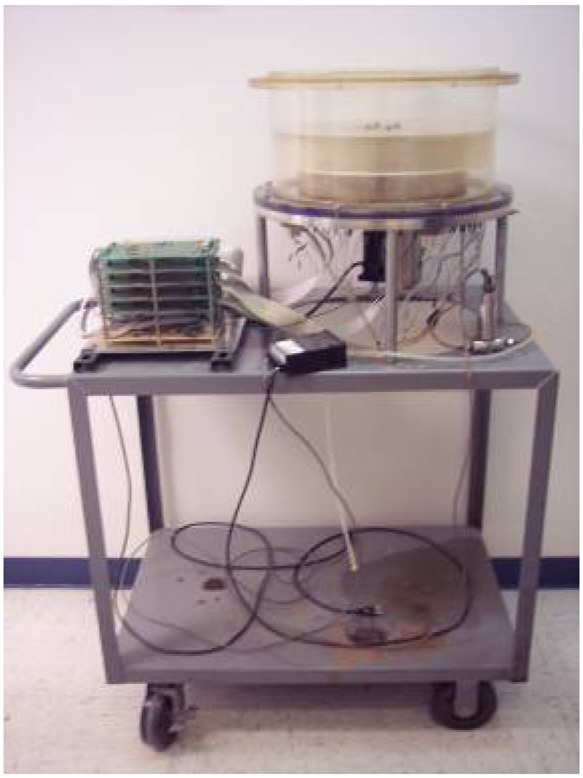

Figure 5. A prototype of a doughnut cell for phase wetting determination (courtesy of Chong Li).

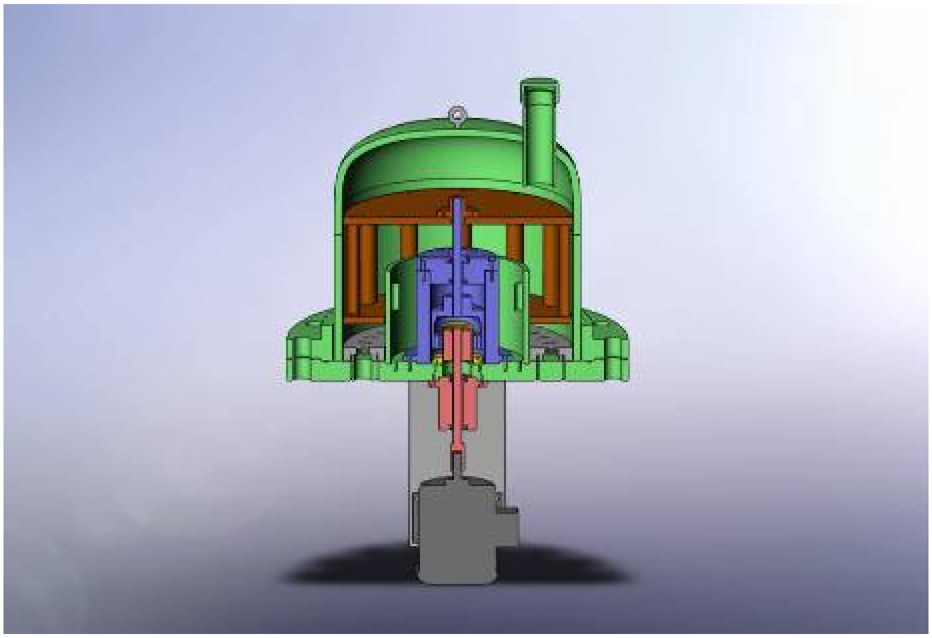

Figure 6: A cross section view of the stainless steel, high temperature, high pressure doughnut cell (Courtesy of Al Schubert).

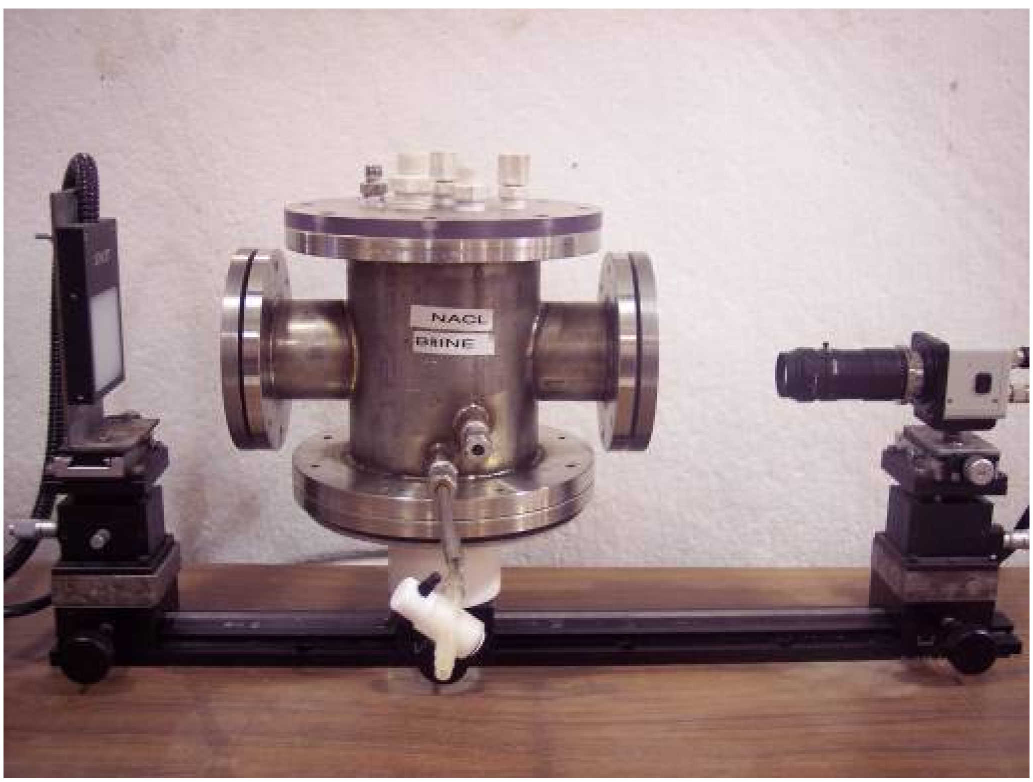

Figure 7: A goniometer with a camera and a light source, used to capture contact angles of oil droplets in a water phase or water droplets in an oil phase (Courtesy of Xuanping Tang).

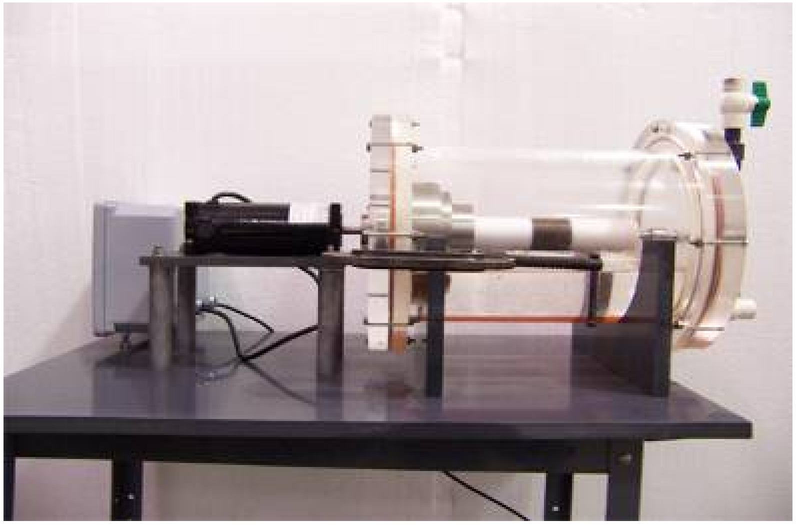

Figure 8: Horizontal rotating cylinder is a benchtop apparatus designed to assess wettability under flowing condition.

Figure 9: A three electrode glass cell set-up with a heater/stirrer, rotator, lugin capillary, condenser, reference probe, platinum counter electrode and a rotating cylinder working electrode (Courtesy of Haitao Fang).