Properties of Dilbit and Conventional Crude Oils

Prepared by:

Haralampos Tsaprailis, Ph.D., P.Chem
Alberta Innovates - Technology Futures

Prepared for:

John Zhou, Ph.D., P.Geol.
Alberta Innovates Energy and Environmental Solutions

Copyright © 2014
Alberta Innovates – Technology Futures

Original May 2013
Revised February 2014
2480002

Notice

1. This Report was prepared as an account of work conducted at the Alberta Innovates Technology Futures ("AITF") on behalf of Alberta Innovates Energy and Environment Solutions ("AIEES"). All reasonable efforts were made to ensure that the work conforms to accepted scientific, engineering and environmental practices, but AITF makes no other representation and gives no other warranty with respect to the reliability, accuracy, validity or fitness of the information, analysis and conclusions contained in this Report. Any and all implied or statutory warranties of merchantability or fitness for any purpose are expressly excluded. AIEES acknowledges that any use or interpretation of the information, analysis or conclusions contained in this Report is at its own risk. Reference herein to any specified commercial product, process or service by trade-name, trademark, manufacturer or otherwise does not constitute or imply an endorsement or recommendation by AITF.

2. Any authorized copy of this Report distributed to a third party shall include an acknowledgement that the Report was prepared by AITF and shall give appropriate credit to AITF and the authors of the Report.

3. Copyright AITF 2014. All rights reserved.

Revisions

The following corrections and additions were made to the original report released in May of 2013:

1. The legend of Figure I (Executive Summary, pg. v) and Figure 3 (Appendix 1, pg. 3) incorrectly labelled the 'Heavy' and 'Medium Heavy' crudes.

2. References [Enbridge, 2011a] and [Enbridge, 2011b] were missing from the original document and added to the current version.

EXECUTIVE SUMMARY

INTRODUCTION

Alberta Oil Sands

The Alberta Oil Sands are calculated to be the third largest oil reserves in the world with an estimated 168.6 billion barrels of recoverable oil [Energy Resources Conservation Board, 2012]. Oils extracted from the oil sands are referred to as *bitumen*. In 2011, 1.7 million barrels per day (Mbbl/d) of bitumen were produced in Alberta and production is estimated to more than double in the next decade (3.7 Mbbl/d by 2021). The Canadian Association of Petroleum Producers (CAPP) estimates that the total oil sands production will reach over 5 Mbbl/d by 2030 [CAPP, 2012].

Due to its high viscosity, the bitumen is diluted with lighter petroleum products (e.g., natural gas condensate) to produce *diluted bitumen* (dilbit) that will satisfy the pipeline specifications for transportation (e.g., viscosity ≤ 350 centistoke, cSt). Currently, the majority of the dilbit from the oil sands is sent to upgrading and refining facilities in Canada and the United States of America (U.S.A.). TransCanada Pipeline Limited (TCPL), Kinder Morgan, Incorporated (Kinder Morgan) and Enbridge, Incorporated (Enbridge) have proposed developments that will facilitate the increased transportation and distribution of dilbit from Canada to refineries in the U.S.A. (e.g., TCPL – Keystone XL and Enbridge – Mainline Expansion) and to the pacific markets (e.g., Kinder Morgan – Trans Mountain Expansion and Enbridge – Northern Gateway).

SCOPE OF STUDY

The safe handling, transportation and spill remediation of dilbit have been topics of considerable discussion. Several reports published by environmental organizations in the last two years have raised safety-related questions about the transportation and spill remediation of dilbit ([Swift, 2011a] and [Swift, 2011b]).

Alberta Innovates - Technology Futures (AITF) was contracted by Alberta Innovates - Energy and Environment Solutions (AI-EES) in 2011 to address safety concerns related to the transportation of dilbit in transmission pipelines. In September 2011, AITF issued a report that summarized a detailed literature review of the corrosivity of dilbit in pipelines relative to conventional (i.e., non-oil sands derived) crude oil [Been, 2011]. The report addressed unsubstantiated claims of increased internal corrosion for dilbit transported in pipelines due to higher acid, sulfur and chloride concentrations, higher content of more abrasive solids, and higher operating temperatures. Within the report, the properties of Alberta conventional light, medium and heavy crude oils were compared with three dilbit

and one diluted synthetic bitumen (dilsynbit) crudes. The report concluded that the characteristics of dilbit are not unique and are comparable to conventional crude oils during pipeline flow based on chemical and physical characteristics of dilbit and other crude oils. In relation to pipeline transportation, the similarity between dilbit and conventional crudes were later echoed by NACE International at the National Academy of Science committee meeting on the "Study of Pipeline Transportation of Diluted Bitumen" [National Academy of Science, 2012] and by other researchers ([McIntyre, 2012], [Friesen, 2012], [Hindin and Leis, 2012] and [Penspen, 2013]).

AITF was contracted by AI-EES to continue these investigations and to provide additional information related to the viscosity (APPENDIX 1), dispersion (APPENDIX 2) and flammability (APPENDIX 3) of dilbit and conventional crude oils. Additionally, a literature review was requested to address topics related to leak detection (APPENDIX 4) and spill cleanup (APPENDIX 5) and the probability for internal corrosion of cargo oil tanks of double hull tankers during the marine transportation of dilbit (APPENDIX 6).

AITF assembled subject matter experts to provide a review of safety standards, regulations and best practices, and technologies for the various topics (leak detection, spill cleanup and cargo oil tanker corrosion). The following abbreviated conclusions have been drawn based on the information presented within the appendices of this report:

Viscosity

- **The viscosity of dilbit is comparable to conventional heavy crude oil and is managed relative to the lowest pipeline operating temperature to not exceed 350 cSt.**
- **The viscosity of dilbit will decrease rapidly from 350 cSt as the pipeline operating temperature increases during transportation.**

In the U.S.A., pipeline transmission of crude oils is regulated by Federal Energy Regulatory Commission (FERC). These specifications are equivalent to those found in the tariffs for the Canadian National Energy Board (NEB) and state that the kinematic viscosity shall not exceed 350 cSt at the pipeline reference line temperature. Accordingly, crude stocks that exceed 350 cSt, such as undiluted oil sands bitumen, are mixed with lower viscosity petroleum products (diluents) to satisfy regulatory requirements.

In APPENDIX 1, representative conventional light, medium-heavy and heavy crude oils and one representative dilbit were selected for comparative experiments related to their viscosities. The reference temperature is inversely proportional to the American Petroleum Institute (API) gravity and the behaviour of the dilbit is analogous to the

conventional heavy crude (API gravity values between 19 – 22 API) during the various months of the year. The viscosity property of representative conventional crude oils and dilbit were evaluated using a simple flow apparatus. The times to fill to 150 mL were grouped according to the date the crudes were collected and the conventional light crude oil had the quickest time followed by the conventional medium heavy. The fill times for the conventional heavy crude and dilbit were similar but longer than conventional light and medium heavy crudes.

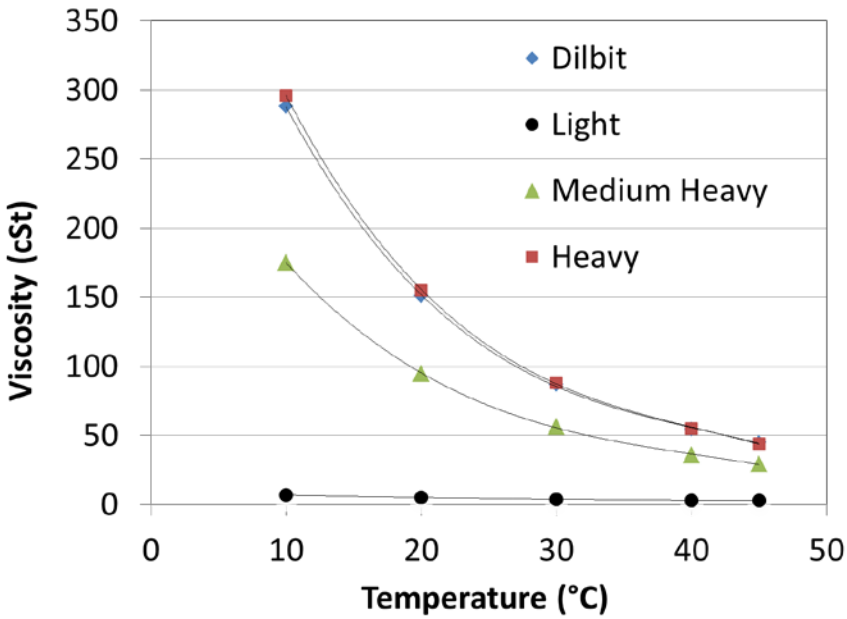

Figure I. Relationship between the temperature and viscosity of the conventional light, medium-heavy and heavy crude oils and dilbit.

Figure I shows the temperature-viscosity relationships are similar for the conventional heavy crude and dilbit and show a rapid decrease in the viscosity as the temperature is increased. Although, the dilbit will have viscosity values near 350 cSt at the lowest operating pipeline temperature, these values will rapidly decrease as the commodities are transported. For example, the pipeline operating temperature for the Keystone XL has been calculated to be approximately 8 and 18 °C for the winter and summer, respectively, at Hardesty, Alberta, while at the Canada-U.S.A. border, the temperature increases to 25 °C (winter) and 37 °C (summer) [US DOS, 2011]. The increase in operating temperature suggests that the viscosity of the crudes at the Canada-U.S.A. border will be significantly lower than at Hardesty and well below the regulated 350 cSt.

Dispersion

- **In terms of crude oil release, the dispersion of dilbit in sand is slower than conventional crude oils.**

Spilled crude oil dispersion has been studied in a number of different soils in the literature. These studies indicated little difference between the dispersion characteristics in sandy soil, top soil or loamy soil. Consequently, the current work in APPENDIX 2 used light colored sand to enhance the ability to observe the oil as it spreads. The literature also indicated that the oil spreads very slowly in the horizontal direction within these soils and that the process is controlled by molecular diffusion. The vertical penetration is controlled by molecular diffusion plus the added effects of gravity and capillary forces. The effect of gravity is more pronounced on crudes with low viscosity as these are more poorly adsorbed and, therefore, flow more easily. Furthermore, the capillary forces should be small relative to gravity because coarse sands are used, while the situation may be different in actual soil.

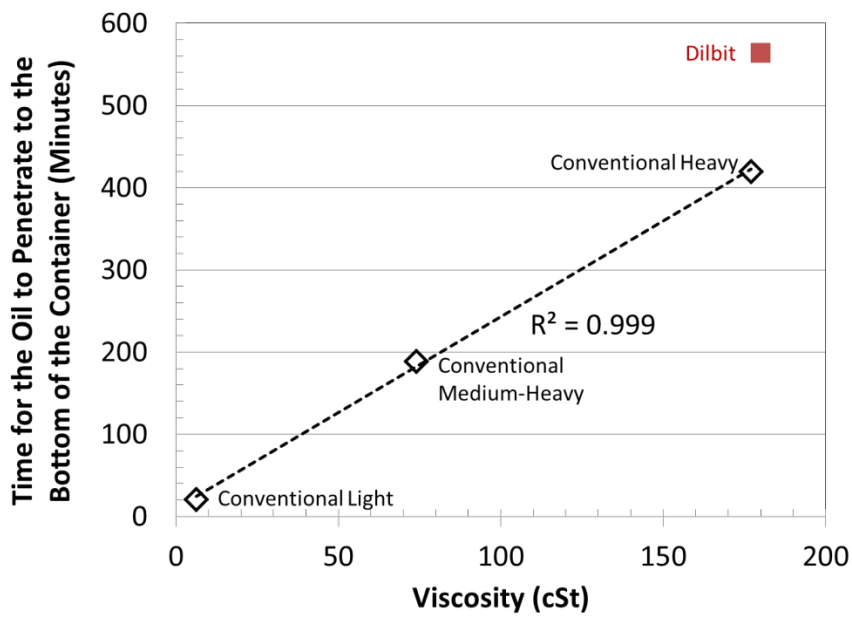

Figure II. Relationship between the viscosity of the crude oil and the time for the oil to penetrate to the bottom of the container. The difference between the Conventional Heavy and Dilbit is likely due to the loss of the diluent fraction within the dilbit during the experiment.

Similar to the viscosity work, representative conventional light, medium-heavy and heavy crude oils and one representative dilbit were selected for comparative experiments related to their dispersion. As shown in Figure II, the findings of this report (see APPENDIX 2) show that the conventional light and medium-heavy crudes rapidly penetrated the sand

column. Moreover, the conventional heavy crude (177 cSt) penetrated the sand column more quickly than the diluted bitumen (180 cSt) despite having similar viscosities. From the experiment, the dilbit behaves differently during the dispersion of these oils through a sand matrix. It has been theorized that the lighter ends from the diluent component contained within the dilbit could evaporate during the experiment (undergo weathering) and/or segregation of the light and heavy fractions leading to an increase in the viscosity of the crude oil; consequently, the dispersion through the sand will be impeded due to the increasing viscosity as the light ends evaporate and/or segregate. More importantly, the dispersion experiment could suggest that land-based dilbit releases would not penetrate vertically into the ground as quickly as conventional crudes.

Flammability

- **For all crudes, caution must be exercised for the initial 24 - 72 hours after a release, after which time all crudes become non-flammable.**
- **All conventional crudes, diluent and dilbit were found to be flammable under open conditions when initially released; after weathering, testing has shown that all conventional crudes, diluent and dilbit were found to be non-flammable.**
- **All conventional crudes and dilbit were found to be flammable under closed conditions when sufficient oxygen is available.**

The flash point is defined as the temperature that the fuel must be heated to in order to produce an adequate fuel/air concentration to be ignited when exposed to an open flame. The flash point of the crude oil is used as an index of fire hazard in North America. As discussed in APPENDIX 3, crude oils are initially flammable when released. As the crude oil undergoes weathering, the degree of flammability is reduced to the point where the conventional crude oil, diluent and dilbit would be non-flammable. The weathering and rapid evaporation of the volatile components in conventional light, medium and heavy crude oils and dilbit decrease the flammability of the crude spills with time. The extent of the reduction is dependent on several factors including the type of oil. In an open environment (e.g., above ground spill), recent tests at AITF show that weathered (48 hours) dilbit has a flash point of 88 °C (or 190 °F) suggesting that weathered dilbit would be non-flammable according to the federal definition. Supplementary to our findings, Environment Canada's Environmental Technology Centre (ETC) has also tested the flash point of Albian Heavy Synthetic both in the fresh and weathered conditions and found them to be -23 °C and 168 °C, respectively.

For closed environments (e.g., under ice coverage), experiments have shown that the representative conventional crudes and dilbit used for this study are comparable and all are flammable below - 30 °C. Generally, the heavier asphaltenic crudes becomes non-flammable in less than 9 hours compared to 18 - 72 hours for the light and waxy crudes, although, the diluent component added to the crudes could possibly extend the flammability window of dilbit to be more comparable with the conventional light crudes.

As mentioned above, oil exposed to the atmosphere undergoes a natural weathering process that is determined by the local environment (i.e., on-land or aquatic areas). For land-based spills, the primary method of weathering is evaporation. There have been several models developed to predict the evaporation rate of multi-component oils in both aquatic and land-based environments established over the last 30 years. The majority of these models have oil evaporating at a logarithmic rate with respect to time. The composition of the oil changes due to the loss of the lighter end components as the oil undergoes the weathering process. The constantly changing composition of the spilled oil adds a degree of complexity to the prediction of flammability behaviour. Conventional heavy crude oils may have as little as 10 % mass loss due to evaporation; considering a logarithmic rate, this leaves a short window for the potential for ignition. This is in contrast to conventional light and medium crudes that can lose as much as 75 % and 40 % mass, respectively. Dilbit crudes will contain 20 – 30 % volume diluent (lights) and weathering of these crudes will likely be greater than conventional heavy crude oils (but less than conventional light crude oils).

Spills in aquatic environments are more complex and will undergo weathering via several processes that include spreading of the oil, evaporation, dispersion, dissolution, emulsification, oxidation, sedimentation and biodegradation. By the time the oil is emulsified, the flammability of the oil is typically reduced to a non-flammable state, while evaporation alone can also accomplish this in many cases.

In summary, caution must be exercised for the initial 24 - 72 hours after a release, after which time all crudes become non-flammable.

Leak Detection

- **TCPL, Enbridge and Kinder Morgan utilize sophisticated Supervisory Control and Data Acquisition (SCADA) systems to detect pipeline leaks.**
- **Crude oils (including dilbit) are susceptible to column separation.**
- **Externally-based leak detection systems can operate under column separation conditions.**

In Canada and the U.S.A., there are sophisticated regulatory frameworks that govern leak detection technology. Within Canada, leak detection systems (LDSs) are mandatory for liquid hydrocarbon pipelines in Alberta according to the Alberta Pipeline Act/Regulation and Onshore Pipeline Regulations in combination with Canadian Standards Association Z662. According to the U.S.A. Code of Federal Regulations in combination with API recommended practises, LDSs installed on a hazardous liquid pipeline transporting liquid have to comply with API RP 1130. Unlike Alberta, LDSs were not mandatory within the U.S.A; however, the US Department of Transportation Pipeline and Hazardous Materials Safety Administration (PHMSA) can issue special conditions making LDS a mandatory requirement (e.g., Condition 27 for the Keystone XL [US DOT, 2013]).

In conjunction with Canada and U.S.A regulations, TCPL, Enbridge and Kinder Morgan utilize sophisticated Supervisory Control and Data Acquisition (SCADA) systems to detect pipeline leaks. These systems require calibrated field instrumentation that include pressure, temperature and flow meters that are installed along the pipeline at specific locations (e.g., pump stations). The SCADA system receives all the field data and shows the operational conditions of the pipeline. A number of complementary leak detection methods and systems would be available to the operator, such as balancing methods based on the principle of conservation of mass. In the steady state, summed over a sufficiently long time period, the mass entering a leak-free pipeline at inlet will balance the mass leaving it at outlet. Balance systems can detect leaks down to approximately 5 percent of pipeline flow rate. More complex, model-based leak detection (e.g., real time transient models, RTTM) approaches are required to further analysis the SCADA data and lower the overall leak detection limit to 1.5 to 2 percent of the pipeline flow rate. The detection thresholds could be lowered below the 1.5 to 2 percent by volume detection thresholds using non-real-time, accumulated gain/loss volume trending; although, this approach would require a larger data sample (i.e., more time). An alternative technique to lower the leak detection threshold is to employ external leak detection systems. External LDSs provide very good performance but initial investment and operational costs are usually very high because they need dedicated measurement equipment such as sensor cables that must be laid along the pipeline route. If any of the software-based leak

detection methods indicate that a predetermined loss threshold has been exceeded, an alarm is sent through SCADA and the operator can take corrective action.

Transient pressure changes within the pipeline can cause vaporization of liquid components (changing a fraction of the liquid to gas) resulting in column separation: pockets of vapour between columns of liquid. Column separation is particularly applicable to light petroleum products. Column separation usually has consequences for the operation of internal LDS. Compensation of transient effects using RTTM reduces the detection time significantly and depends on accuracy of model parameters (e.g., length of the pipeline, diameter, height profile, fluid parameters, etc.). Extended (E-) RTTM-based leak detection techniques are much less sensitive to deviations in model parameters, so the accuracy of model parameters is less significant for sensitivity and reliability. Modelling of column separation is still the subject of research. Adverse effects on the sensitivity and reliability of internally-based systems exist for operational conditions like column separation, although installation of pressure reducing stations downstream and operating these sections with positive pressure would minimize or eliminate column separation at problematic segments of the pipeline (e.g., significant elevation changes). Moreover, it should be noted column separation has no negative impact on most externally-based LDSs, with possible exception of acoustic emissions detectors. These sensors installed along the pipeline route are used to acquire local acoustic signals created by escaping fluid. Column separation could, in a few cases, create an acoustic sound pattern similar to the sound patterns of a leak resulting in a false alarm.

Spill Cleanup

- **On-land oil spills**
  - **Dilbit containment and remediation is effectively completed using the same approaches and technologies as conventional crude oils.**
  - **At least three remedial strategies have received detailed evaluation and proven to be effective based on remedial technology reviews completed for past dilbit and crude oil releases**
  - **Groundwater has been effectively treated on past pipeline releases using natural attenuation or oil-water separators to remove the bitumen and then followed by activated carbon treatment to remove the dissolved phase components**

Containment and remediation technologies have been designed to be robust, in that they should be able to work with a series of different crude oil compositions (i.e., light, medium and heavy crude oils). There are numerous environmental remediation companies (e.g., Hemmera, Stantec, AECOM, NewAlta, etc.) that can complete efficient and effective cleanup for most land based petroleum hydrocarbon releases regardless of crude oil type. On-site cleanup can be completed using low temperature thermal desorption. This approach requires heating the petroleum hydrocarbon contaminated soils to the temperature required to cause the oil to desorb (physically separate) from the soil and volatilize (turn to a gaseous state). The oil is then captured through a condenser or oxidized in a secondary oxidizing chamber. Conveniently, the soil can then be reused on-site. Alternatively, the contaminated soils can also be removed from the spill site and transported (off-site) to incineration facilities or bioremediation/landfilling sites. Incineration is very similar to low temperature thermal desorption, except instead of separating the petroleum hydrocarbons, the soil/oil mixture is heated to the point that the petroleum hydrocarbons undergo combustion within the unit. Bioremediation/landfilling of the contaminated soil requires actively mixing the soil with various nutrients and air to facilitate the breakdown of the oil by either naturally occurring or introduced bacteria. In summary, three remedial strategies have received detailed evaluation and proven to be effective based on remedial technology reviews completed for past dilbit and crude oil releases.

Groundwater has been effectively treated on past pipeline releases using natural attenuation or oil-water separators to remove the bitumen and then followed by activated carbon treatment to remove the dissolved phase components (i.e., activated carbon will absorb the dissolved phase portions). Natural attenuation limits the amount of additional disturbance to the site and would be associated with minor concentrations remaining at the end of spill cleanup projects.

- **Aquatic oil spills**
    - **Similar to conventional crudes, dilbit will collect debris and sink in an aquatic environment.**

In the case of aquatic spills, the impacts to the freshwater and marine environments are not as well understood and remedial technologies are continually being developed. A major clean-up issue associated with neutrally buoyant oils and other conventional crude oils is that once the weathering process removes the light ends (reduces the flammability), the heavy ends collect debris and can sink in aquatic (marine and fresh water) environments. Based on observations made during previous releases, when dilbit is introduced to the aquatic environment, similar to neutrally buoyant oils and other conventional crude oils, it begins a weathering process that will change the properties of the oil. Ultimately, bitumen globules will pick up sediment increasing the overall specific gravity above one and the bitumen will sink to the bottom of the aquatic environment (commonly referred to as "tar balls"). The speed at which the oil breaks apart and forms globules depends on the amount of weathering that occurs to the oil, the kinetic energy the oil is exposed to from wave action and tides, and the amount of small debris and sediment exposed to the bitumen balls.

Oil Tanker Corrosion

- **Characteristics of dilbit are not unique and are comparable to conventional crude oils during transport within an oil tanker.**
- **Corrosion mitigation methods have been developed for cargo oil tanks that include using coatings, corrosion resistant steels and removal of the sludge formations from the cargo oil tanker (after delivery at the receiving port using a technique referred to as crude oil washing).**

Oil tankers play an important role in the global transportation of approximately 2 billion metric tons of petroleum and petrochemical products. Although very rare, the potential consequences that can result from oil tanker accidents are particularly high. Oil spills are especially dangerous to ecological environments due to the toxicity of the crude products that contain poly aromatic hydrocarbons. Most oil spills related to oil tankers are caused by improper operations or human errors (e.g., loading/discharging oil, bunkering, etc.). Another contributing factor to these accidents is related to material degradation caused or influenced by undetected corrosion. The third most likely cause of large spills (> 5000 barrels) between 1970 – 2009 was related to hull failures (12%), including corrosion-

induced failures. The exact percentage of oil spills directly or indirectly related to corrosion is not known.

The structural components of the cargo oil tank could experience corrosion in vapor phase (headspace) or within the aqueous phase that can form within the cargo oil tank. Components of crude oil are complicated and there has been minimal relevant research conducted on corrosion of oil tankers in the presence of conventional heavy crude, dilbit and diluents. In general, hydrocarbons have an inhibiting effect on corrosion within the aqueous phase that can accumulate at the bottom of the cargo oil tank, while oxygen, sulphur compounds (e.g., hydrogen sulphide, H_2S) and chloride salts may cause or accelerate corrosion in the aqueous phase. Moreover, the cargo oil tanks have geometries that produce areas that may experience corrosion with various levels and under different mechanisms. Of particular note, sludge deposits at the tank bottoms could accelerate corrosion for cargo tankers if not coated or made from corrosion resistant steels. Sludge settling would be problematic of all conventional crude types and dilbit placed within the cargo oil tanker. Subsequently, sludge formations are removed from the cargo oil tanker after delivery at the receiving port using a technique referred to as crude oil washing. In addition to crude oil washing, the International Maritime Organization (IMO) has developed requirements for mitigating corrosion in cargo oil tanks following incidents resulting from structural failure in oil tankers. The requirements provide three acceptable options for corrosion protection of cargo oil tanks for new ship construction: coatings, alternative means of protection (e.g., corrosion-resistant steel) and exempt cargos (non-corrosive cargoes) [SOLAS II-1/3-11, 2012]. In summary, oil spill releases due to internal corrosion of the cargo oil tankers are highly unlikely due to regular inspections of the tankers and adherence to requirements set forth by the IMO and other authorities.

TABLE OF CONTENTS

Notice ii
Executive Summary iii

APPENDIX OF SUBJECT MATTER EXPERT REPORTS

APPENDIX 1. VISCOSITY STUDY 1

1.1 Objective 4
1.2 Experimental Procedure 4
1.2.1 Viscosity Measurements 4
1.2.2 Viscosity Comparison of Conventional and Dilbit Crudes 4
1.3 Results and Discussion 6
1.4 Conclusions from Viscosity Study 7

APPENDIX 2. DISPERSION STUDY 8

2.1 Experimental 8
2.2 Results and Discussion 9
2.3 Conclusions from Dispersion Study 11

APPENDIX 3. CRUDE OIL FLAMMABILITY 12

3.1 Introduction to Crude Oil Flammability 12
3.2 The Effect of Weathering on Flammability 13
3.3 The Safety Risks and Effect of Flammability on Spill Cleanup Decisions 14
3.4 Flash Point Comparison of Diluent, Conventional Crude Oils and Dilbit 15
3.5 Conclusion from Flammability Literature 17

APPENDIX 4. PIPELINE LEAK DETECTION TECHNOLOGIES 18

4.1 Introduction to Leak Detection Systems 18
4.2 Requirements and Performance Criteria for Leak Detection Systems 19
4.2.1 Type of Fluid 19
4.2.2 Kind of Operation 19
4.2.3 Leak Characteristics 19
4.2.4 Operational Phase 20
4.2.5 Steady State and Transient Operations 20
4.2.6 Performance Criteria 20
4.3 Regulatory Framework for Leak Detection Systems 21
4.3.1 CSA Z661-11 (Canada) 21
4.3.2 API RP 1130 (United States of America) 22
4.3.3 TRFL (Germany) 23
4.3.4 Summary 23
4.4 External Leak Detection Systems 24

4.4.1 Fiber Optic Hydrocarbon Sensing Probes or Cables 24
4.4.2 Liquid Sensing Probes or Cables 25
4.4.3 Hydrocarbon Sensor Cables 25
4.4.4 Acoustic Emissions Detectors 25
4.4.5 Leak Detection Pipeline Inspection Gauges (PIG's) 26
4.5 An Overview of Internal Leak Detection Methods 26
4.6 Balancing Methods 27
4.6.1 Improving Performance Using Statistical Approaches 30
4.6.2 Requirements for Leak Detection System 30
4.7 Model-Based Leak Monitoring 31
4.7.1 RTTM – Real Time Transient Model 31
4.7.2 E-RTTM – Extended Real Time Transient Model 32
4.7.3 Requirements for Model-based Leak Monitoring 33
4.8 Non-Balancing Leak Detection 33
4.8.1 Pressure/Flow Monitoring 34
4.8.2 Rarefaction Wave Methods and Pressure Point Analysis (PPA) 34
4.8.3 Requirements for Non-Balancing Leak Detection 34
4.9 Leak Monitoring During Shut-In Conditions 35
4.10 Internal Leak Detection on Crude Oil Transmission Pipelines 36
4.11 Leak Detection In the Event of Column Separation 36
4.11.1 Internally-Based Leak Detection Systems 37
4.11.2 Research approaches 37
4.11.3 Externally-Based Leak Detection Systems 38
4.12 Emergency Shutdown Protocols 38
4.13 Summary and Outlook for Leak Detection 40

APPENDIX 5. SPILL CLEANUP 42

5.1 Introduction to Crude Oil Spills 42
5.2 Mitigation of Oil Spills 43
5.2.1 Releases at Pumping Stations and Tank Farms 43
5.2.2 Mitigation of Releases to the Environment 43
5.3 Remediation Methodologies 44
5.3.1 Crude Oil Contaminated Soils 44
5.3.2 Crude Oil Contaminated Groundwater 46
5.3.3 Crude Oil Contaminated Waters 46
5.3.4 Removing Oil from Wildlife 48
5.4 Oil Spill Remediation Outlook 49

APPENDIX 6. CARGO OIL TANKER CORROSION 50

6.1 Introduction to Cargo Oil Tankers 50
6.1.1 Diluted Bitumen Export to the Canadian West Coast 50
6.1.2 Double Hull Oil Tankers 50
6.1.3 Corrosion of Cargo Oil Tanks 51
6.2 Mechanisms of Corrosion of Cargo oil tanks 52

6.2.1 Corrosion in Crude Oil 52
6.2.2 Corrosion in the Presence of Conventional Light Crude Oils 58
6.2.3 Corrosion in the Presence of Conventional Heavy Crude Oils 59
6.2.4 Corrosion in the Presence of Diluted Bitumen 60
6.2.5 Corrosion in the Presence of Diluents 62
6.3 Prevention of corrosion of oil tankers 62
6.3.1 Development of Corrosion Resistant Steels 62
6.3.2 Coating Systems 63
6.3.3 Corrosion Inhibitors and Biocides 64
6.4 Standards and Regulations for Prevention of Double Hull Oil Tanker Corrosion 65
6.4.1 IMO MSC 288(87) Performance Requirements for Protective Coatings and Testing Methods 66
6.4.2 IMO MSC 289 (87) Performance Requirements for Corrosion Resistant Steels and Testing Methods 67
6.5 Cargo Oil Tanker Corrosion Summary 67

REFERENCES 68

APPENDIX 1. VISCOSITY STUDY

Haralampos Tsaprailis, Ph. D., P.Chem.
Alberta Innovates – Technology Futures
Edmonton, Alberta

In the U.S.A., pipeline transmission of crude oils is regulated by Federal Energy Regulatory Commission (FERC). These specifications are equivalent to those found in the tariffs for the Canadian National Energy Board (NEB) and state that the kinematic viscosity shall not exceed 350 cSt at the pipeline reference line temperature. Consequently, crude stocks that exceed 350 cSt, such as undiluted oil sands bitumen, are mixed with lower viscosity crudes (diluents) to satisfy the regulatory requirements.

The viscosity is a measure of the resistance to shear or flow of a liquid. A frictional drag effect is produced when liquids flow and the related fluid viscosity can be reported as absolute (dynamic) or kinematic viscosity. The kinematic viscosity (cSt) is related to absolute viscosity (cP) as a function of the fluid's specific gravity (SG), while the American Petroleum Institute (API) gravity is dependent on the SG of the crude:

$$cSt = cP/SG$$

$$\text{API gravity} = 141.5/SG - 131.5$$

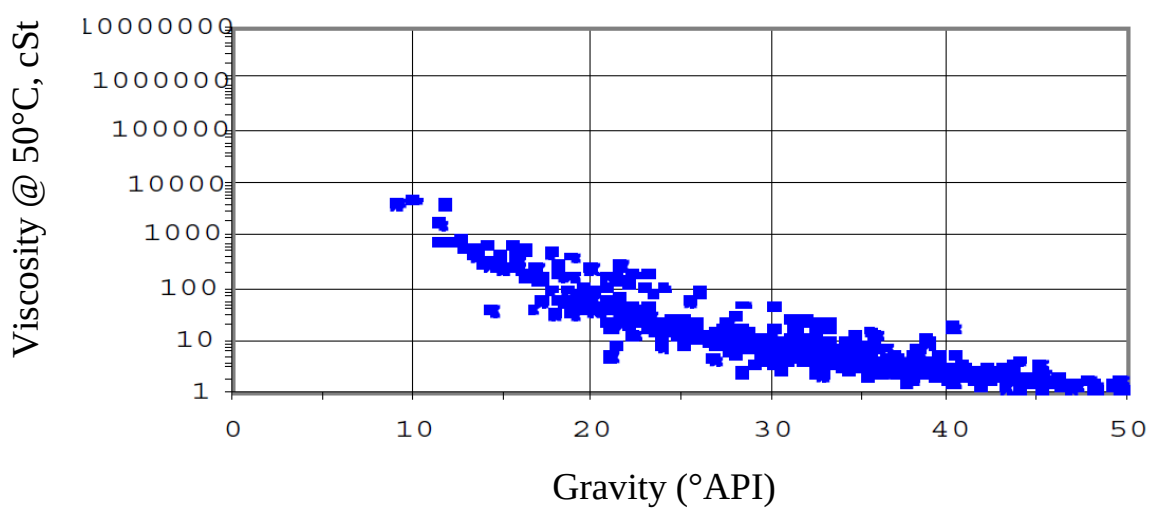

Figure 1.API Gravity and viscosity relationship for conventional crude oils [Boduszynski, 1998].

Figure 1 shows the relationship between the American Petroleum Institute (API) gravity of the conventional crude and the viscosity. According to the data reported by

[Crudemonitor.ca, 2012], the reported API gravities for conventional heavy conventional crude oils and dilbit crudes are similar (19 – 24 °API and 19 – 23 °API, respectively).

Representative conventional light, medium-heavy and heavy crude oils and one representative diluted oil sands bitumen were selected for comparative experiments related to their viscosities. Table 1 shows selective properties of these crudes reporting the 5 year averages along with the recent samplings (as of March 2012).

Table 1. Properties of the Representative Conventional Crude Oils and Diluted Oil Sand Bitumen [Crudemonitor.ca, 2012]

	Conventional Light Crude		**Conventional Medium-Heavy Crude**		**Conventional Heavy Crude**		**Dilbit**	
	5 yr Average	**Recent**	**5 yr Average**	**Recent**	**5 yr Average**	**Recent**	**5 yr Average**	**Recent**
Density (kg/m^3)	826.4	822.6	913.9	911.5	929.6	925.8	928.1	920.5
Gravity (°API)	39.6	40.4	23.2	23.6	20.6	21.2	20.8	21.1
Sulfur (wt%)	0.44	0.35	2.83	2.66	3.26	2.94	3.79	3.76
TAN (mgKOH/g)	-	-	0.4	0.28	0.94	1.04	0.98	0.97
Light End Analaysis (vol%)								
C3-	0.46	0.54	0.17	0.17	0.05	0.05	0.04	0.05
Butanes	3.61	4.21	0.96	0.70	1.71	2.15	1.09	1.14
Pentanes	3.50	3.89	3.27	3.02	5.42	5.05	6.24	6.72
Hexanes	5.90	6.10	3.27	3.23	3.26	3.63	5.26	6.01
Heptanes	7.25	7.34	2.93	3.14	2.20	2.28	3.33	4.00
Octanes	7.30	7.27	3.22	3.69	1.58	1.51	2.24	2.75
Nonanes	5.63	5.50	2.78	3.22	1.20	1.16	1.36	1.65
Decanes	2.50	2.78	1.36	1.74	0.55	0.59	0.62	0.85
BTEX Analysis (vol%)								
Benzene	0.29	0.26	0.10	0.09	0.15	0.14	0.23	0.27
Toluene	0.86	0.79	0.26	0.26	0.24	0.20	0.39	0.49
Ethyl Benzene	0.25	0.24	0.15	0.17	0.04	0.05	0.06	0.08
Xylenes	1.11	1.04	0.41	0.45	0.22	0.18	0.33	0.41

Table 1 shows that the dilbit has the same chemical constituents as the other crude oils with somewhat higher light ends and very similar aromatic content (BTEX analysis %). The API gravity of the crude oils within the pipeline system will fluctuate during the course of the year. For example, the reference line temperature from Enbridge ranged from 7.5 °C (January, 2011) to 18.5 °C (September, 2011) [Enbridge, 2011a]. Figure 2 shows the effect of the reference line temperature [Enbridge, 2011a] on the API gravity of the conventional heavy crude and dilbit from Table 1. The API gravities were obtained from [crudemonitor.ca, 2012] for oil samples collected from the conventional heavy crude and dilbit sources in 2011. The reference temperature is inversely proportional to the API gravity and the behavior of the dilbit is analogous to the conventional heavy crude (API gravity values between 19 – 22 API).

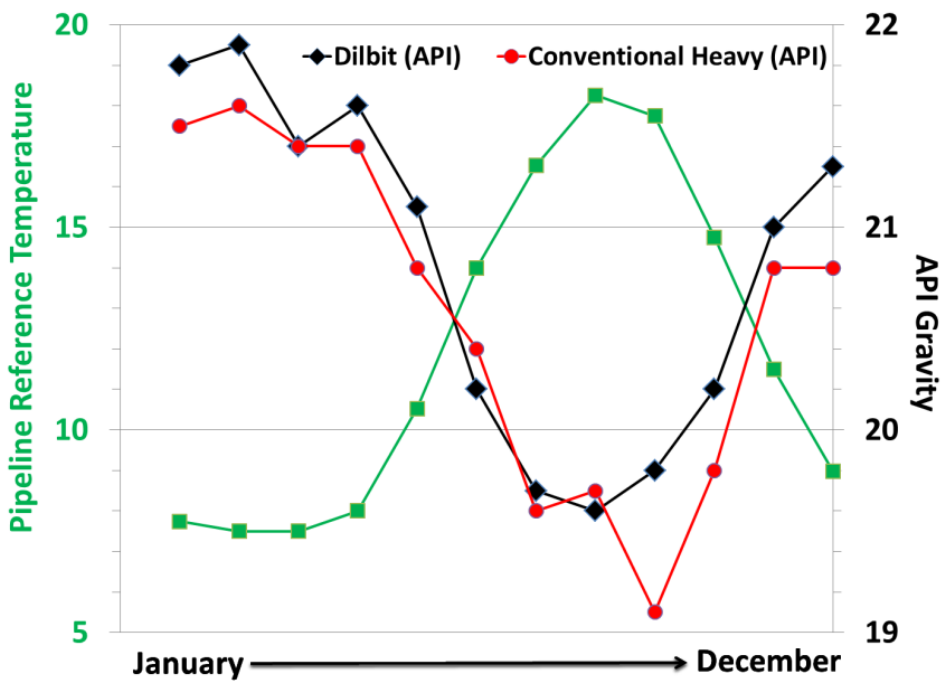

Figure 2. Relationship between the reference line temperature and API gravity of conventional heavy crude and dilbit.

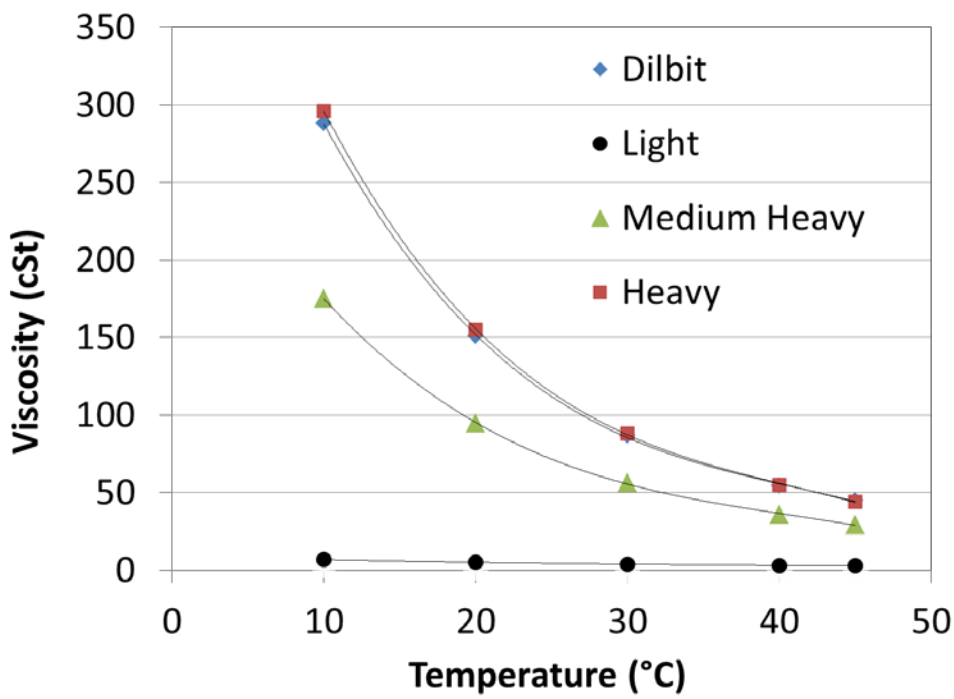

Figure 3. Relationship between the temperature and viscosity of the conventional light, medium-heavy and heavy crude oils and dilbit.

Figure 1 shows that a small change in the API gravity can lead to a significant shift in the viscosity of the crude; consequently, the variation in the reference line temperature will have a dramatic effect on the viscosity of the crude oils as shown in Figure 3. The viscosity of the

conventional light, medium-heavy and heavy crude oils and the dilbit were taken from crude characterization completed by Enbridge [Enbridge, 2011b]. At the lowest reference line temperature for the year (7.5 °C, Figure 2), the viscosity of the dilbit and conventional heavy crude oil will be below 350 cSt and have similar temperature trends (Figure 3). The conventional medium-heavy crude oil is consistently less viscous than the other two crudes at any referenced temperature.

Dilbit will typically contain diluent fractions between 20 – 30 % by volume. The range of the required diluent quantity is dependent on the reference line temperature as less diluent is required when transporting the dilbit at 18.5 °C to satisfy the 350 cSt acceptance criteria. For example, the dilbit shown in Figure 3 has a viscosity of ~ 350 cSt at 7.5 °C, while at 18.5 °C, the viscosity would lower to ~ 175 cSt. Therefore, the diluent fraction is adjusted to ensure the 350 cSt criteria is reached at the reference line temperature.

1.1 Objective

The objective of this task was to compare the viscosity properties of representative conventional light, medium-heavy and heavy crude oils and one dilbit.

1.2 Experimental Procedure

1.2.1 Viscosity Measurements

Representative conventional light, medium-heavy and heavy crude oils and one representative diluted oil sands bitumen were obtained for comparative experiments related to their viscosities. These crude oils were collected during the months with low (March) and high (August) reference pipeline temperatures. Unfortunately, the exact reference temperatures were not provided for these crude oils. Consequently, the viscosity experiments in the following sections were completed at room temperature to compare the crude oils; actual reference temperatures are expected to be lower than room temperature.

500 mL aliquots of the representative, as-received crudes were sent to Alberta Innovates - Technology Futures' Fuels and Lubricants Group. Viscosity measurements were collected according to the American Society for Testing and Materials (ASTM) D445, Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity). The viscosities of the crude oils were measured at the room temperatures used for the viscosity experiments (20 °C and 22.5 °C for the March and August supplies, respectively).

1.2.2 Viscosity Comparison of Conventional and Dilbit Crudes

This section outlines the approach developed to compare the conventional crude oils and dilbit. As previously mentioned, viscosity is the measure of the resistance to shear or flow of a liquid. By definition, a crude oil with a low viscosity should flow faster than one with a

higher viscosity. 250 mL of the oil was loaded into a standard separation flask (Figure 4a). A simplistic flow apparatus was assembled to equate the time to fill a receiving cylinder with 150 mL of oil. At point zero, the stopcock of the separation funnel is closed. The stopcock was then opened and the flow of oil was recorded using digital video to accurately obtain the time to fill the graduated cylinder to the 150 mL mark (final time, Figure 4c). The temperature of the conventional crude oils and diluted oil sands bitumen were 20 °C and 22.5 °C for the March 2012 and August 2012 samples, respectively, during the experiment.

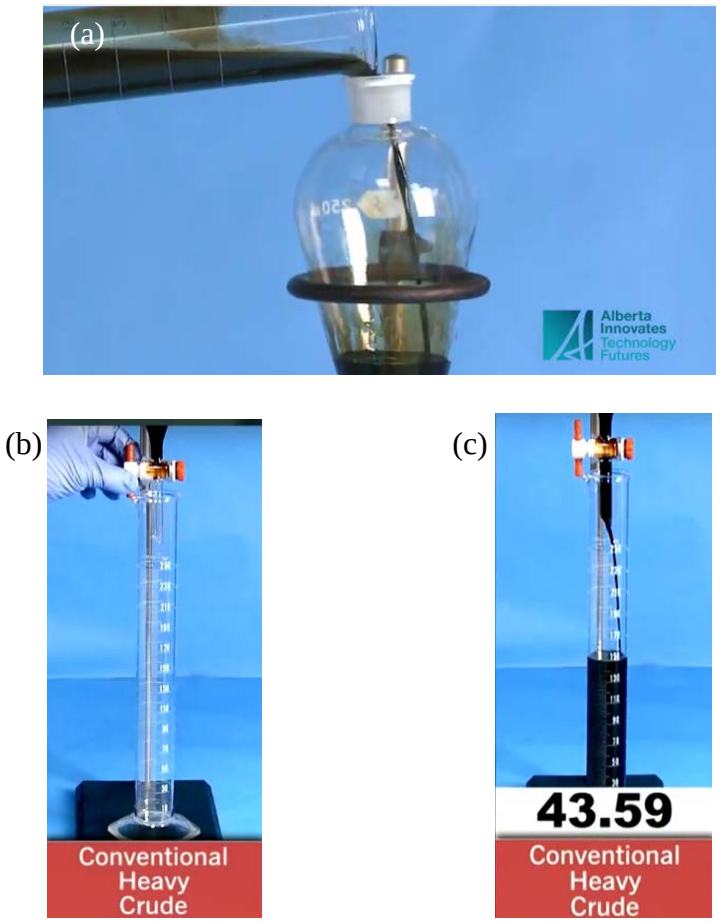

Figure 4. Digital images showing the apparatus used to compare the viscosities between conventional crudes and a diluted oil sands bitumen.

It should be noted that the experimental setups between the March 2012 and August 2012 trails were not identical. New separation flasks (FisherSci) were purchased for the August 2012 trail. *Post factum*, the separation funnels were found to have different geometries from those used for the March 2012 runs.

1.3 Results and Discussion

Table 2 shows the kinematic viscosity measurements and time required to fill to 150 mL for the representative crudes used within this study and collected during the months with low (March) and high (August) reference line temperatures. Figure 5 shows the relationship between the fill time and the viscosity of the crudes. The viscosity of the conventional light crude and conventional heavy crude are similar between samples from March and August. Significant increases in the viscosity for the samples collected in August of 2012 were seen for the conventional medium heavy crude (74 → 115 cSt) and the dilbit (177 → 273 cSt). As reported above, diluent fractions will be lowered in the summer as the reference line temperature will be higher (> 18 °C) and closer to the experimental temperatures within this report (i.e., 20 and 22.5 °C). Consequently, the viscosity of the dilbit is expected to be higher at ~ 20 °C for samples collected in summer and lower for the ones collected in the winter season. The significant viscosity change of the conventional medium heavy crude was also investigated and attributed to the variability in the crude stream.

Table 2. ASTM D445 Kinematic Viscosity Values for Representative Crudes

	Crudes Collected March 2012			Crudes Collected August 2012		
	Viscosity (cSt) at 20 °C	Time (sec) to Fill to 150 mL	Normalized to March 2012 Dilbit Time	Viscosity (cSt) at 22.5 °C	Time (sec) to Fill to 150 mL	Normalized to August 2012 Dilbit Time
Conventional Light Crude	6	9	0.25	5	14	0.12
Conventional Medium Heavy Crude	74	23	0.62	115	54	0.47
Conventional Heavy Crude	180	44	1.16	187	96	0.84
Diluted Bitumen	177	38	1.00	273	114	1.00

The times to fill to 150 mL were grouped according to the date the crudes were collected and the linear relationship to the viscosity is shown in Figure 5. Please note that the individual crude oil times have been normalized to the time it took the dilbit to fill the receiving cylinder to 150 mL; this was done to account for the variation in the experimental setup (different separation funnels) and allow for comparison between the two collected samples (March and August). The conventional light crude oil had the quickest time followed by the conventional medium-heavy regardless of the setup variation or crude oil collection date. The fill times from March 2012 show that the conventional heavy crude oil took 16 % longer to fill the cylinder to 150 mL when compared to the dilbit. Conversely, the conventional heavy crude oil was 16 % faster than the more viscous (at the experimental temperature), less diluted dilbit sample collected in August 2012. The viscosity of the dilbit crude at ~ 20 °C will vary dependent on the time of year that the dilbit is collected; this variability will affect the relative times to fill the cylinder.

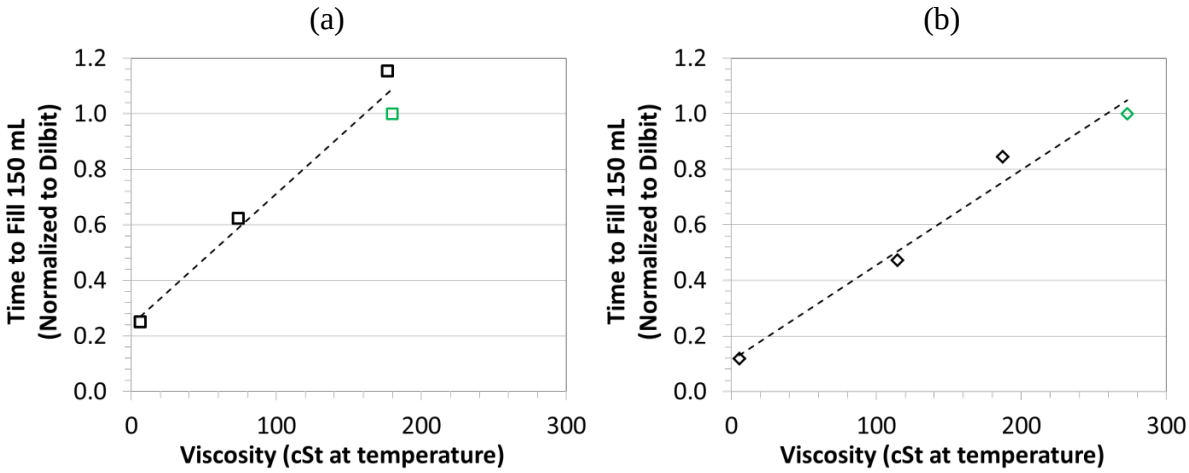

Figure 5. Relationship between time to fill to 150 mL and the viscosity of the crude for the experimental setup shown in Figure 4 for as-received crude oils collected (a) March 2012 and (b) August 2012. Green data points are associated with the dilbit.

1.4 Conclusions from Viscosity Study

The viscosity property of representative conventional crude oils and diluted oil sands bitumen were evaluated using a simple flow apparatus. A linear relationship between the time to fill 150 mL and the viscosity of the liquid was observed for the crudes evaluated within this study. The fill times for the conventional heavy crude and dilbit where dependant on the collection date and showed that dilbit collected in March 2012 was able to fill the receiving cylinder more quickly than the conventional heavy – the opposite effect was shown for the samples collected August 2012.

APPENDIX 2. DISPERSION STUDY

Haralampos Tsaprailis, Ph. D., P.Chem.
Alberta Innovates – Technology Futures
Edmonton, Alberta

Spilled crude dispersion has been studied in a number of different soils [Oghenejoboh, 2008]. This work indicated little difference between the dispersion characteristics in sandy soil, top soil, or loamy soil. Consequently, the current work used light colored sand to enhance the ability to observe the oil as it spreads. The same study also indicated that the oil spreads very slowly in the horizontal direction within these soils and that the process is controlled by molecular diffusion [Oghenejoboh, 2008]. The work also indicates that horizontal spread of the oil is not affected to a great extent by the volume of oil added to the experiment setup. Conversely, the distance migrated in the vertical direction increased with the volume of oil and the rate of spreading was greater than in the horizontal direction. The vertical spread is controlled by molecular diffusion plus the added effects of gravity and capillary forces [Oghenejoboh, 2011]. The effect of gravity is more pronounced on crudes with low viscosity as these are more poorly adsorbed and, therefore, flow more easily. Furthermore, the capillary forces should be small relative to gravity because coarse sands are used, while the situation may be different in actual soil.

The object of this section is to compare the dispersion of a representative light, medium-heavy and heavy conventional crude oil and dilbit in sand.

2.1 Experimental

The conventional light, medium-heavy and heavy crude oils and dilbit, which were selected for the viscosity work (APPENDIX 1), were also utilized for the dispersion study (see Table 1 for the selective properties of these crudes). A sand matrix (Mesh 16/18, SIL Industrial Materials) was selected for the dispersion media as the properties (composition, water content, distribution, etc.) were more controllable than soil mixtures. The sand was carefully added to the Plexiglas™ boxes to ensure that the packing was uniform (Figure 6a). The initial sand dimensions within the box were 15.24 cm (6”) x 15.24 cm (6”) x 20.32 cm (8”). 0.5 kg of crude oil was added to into a separation flask that was inserted 2.54 cm below the surface of the sand (grade). A representative photograph of the complete setup is shown in Figure 6b. A digital camera (RF-HDWEB, Rocketfish) connected to a personal computer (Windows 7) running capture software (Active Webcam, PY software) was used to record the footage (and time) for the oil to penetrate to the bottom of the container for the conventional light, medium-heavy and heavy crude oils and representative dilbit. All testing was completed in a temperature and relative humidity (RH) room at 23 °C and 50 %, respectively. The crude oils, sands and containers were equilibrated to the test environment (23 °C and 50 % RH) to

ensure that thermal or humidity gradients were minimized prior to the start of the dispersion experiments.

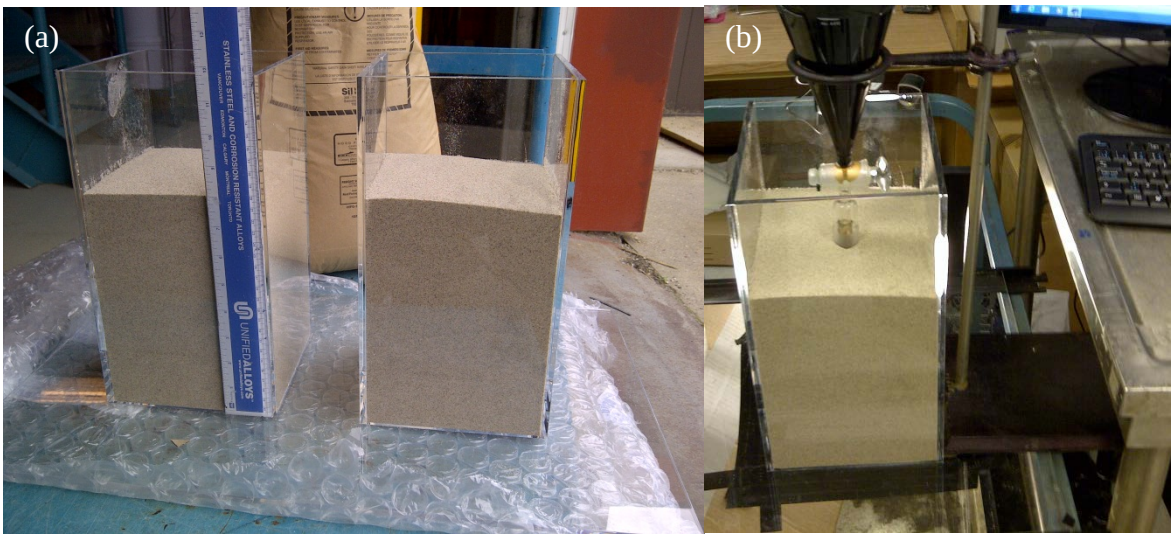

Figure 6. Photographs showing (a) the sand columns prepared for the dispersion work and (b) the representative experimental setup.

2.2 Results and Discussion

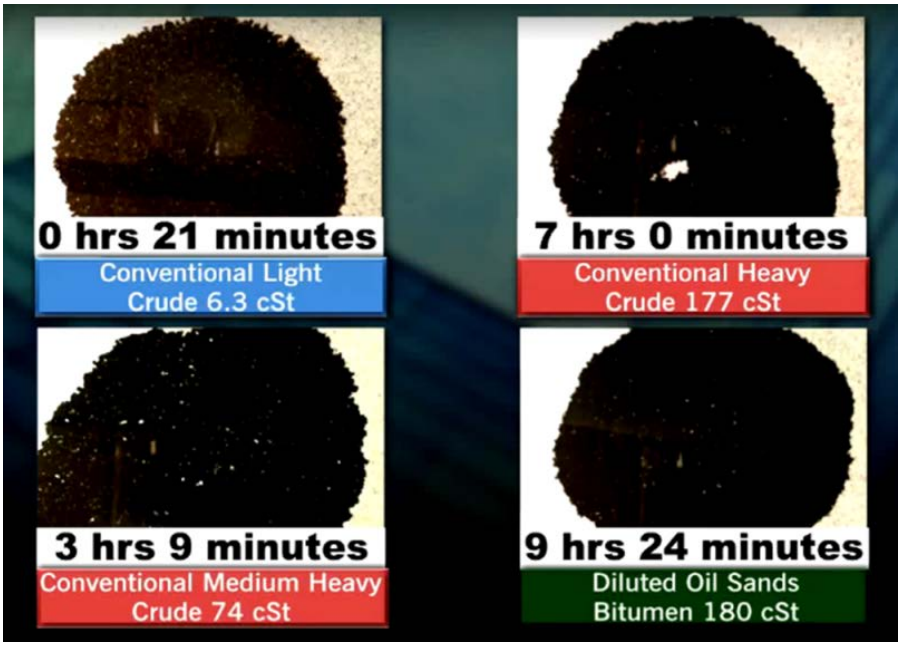

Figure 7. Digital image showing the times that were required for the first drop of oil to reach the bottom of the container for the light, medium-heavy and heavy conventional crude oils and diluted oil sands bitumen.

Figure 7 shows the final results and associated times that were required for the first drop of oil to reach the bottom of the container for the various crude oils. The conventional light crude penetrated quickly into the sand matrix requiring only 21 minutes to transverse a vertical column length of approximately 18 cm (7”). The conventional medium-heavy and heavy required 189 and 420 minutes, respectively. The relationship between the viscosity and the time to penetrate to the bottom of the container shows a linear trend (R^2 of 0.999) for the conventional crude oils as seen in Figure 8 and suggests that the heavier, and more viscous the conventional crude oil is, the more resistive to flowing through the sand matrix. In comparison, the dilbit required 564 minutes to reach the bottom of the container despite having a similar viscosity to the conventional heavy crude oil (180 vs. 177 cSt, respectively). The results obtained using the experimental setup suggests that the dilbit behaves differently during the dispersion of these oils through a sand matrix. It has been theorized that the lighter ends from the diluent component contained within the dilbit could evaporate during the experiment (see *weathering* in Section 3.2) and/or segregation of the light and heavy ends that leads to an increase in the viscosity of the crude oil; consequently, the dispersion through the sand will be impeded due to the increasing viscosity as the light ends evaporate. More research is required to confirm this hypothesis and would require a measurement of the crude oil viscosities after the experiment to observe any changes.

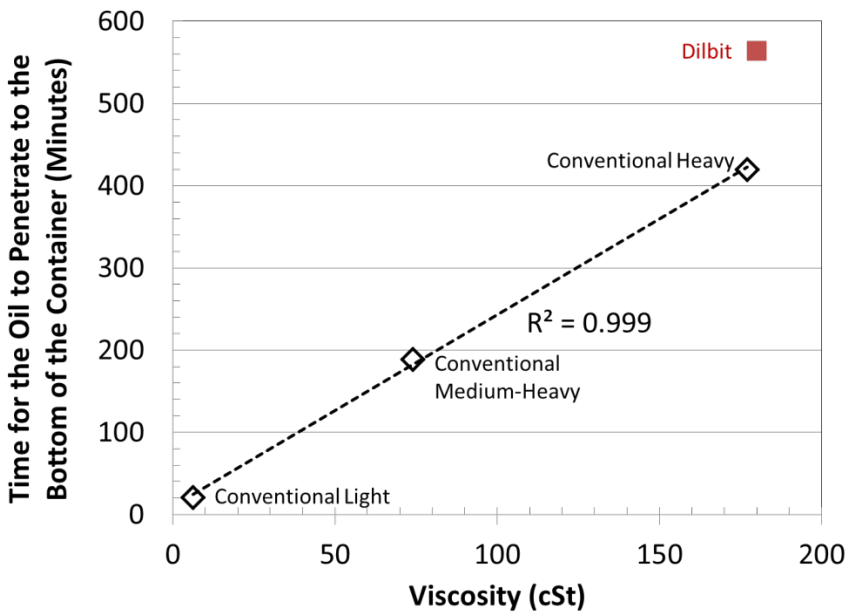

Figure 8. Relationship between the viscosity of the crude oil and the time for the oil to penetrate to the bottom of the container. The difference between the Conventional Heavy and Dilbit is likely due to the loss of the diluent fraction within the dilbit during the experiment.

2.3 Conclusions from Dispersion Study

The object of this section was to compare the dispersion of a representative light, medium-heavy and heavy conventional crude oil and dilbit in sand. Based on the information presented within this section, the following conclusions have been drawn:

- The conventional light crude penetrated quickly into the sand matrix
- The conventional heavy crude (177 cSt) penetrated the sand column more quickly than the diluted bitumen (180 cSt), suggesting that the dilbit is more resistive to dispersion. The implication is that the dilbit will spread and penetrate less into sand than the other crudes in the event of a spill.

APPENDIX 3. CRUDE OIL FLAMMABILITY

Michael Mosher, MASc., P.Eng.
Advanced Materials, Alberta Innovates – Technology Futures
Edmonton, Alberta. Canada

3.1 Introduction to Crude Oil Flammability

This section considers the variation and impact of the flammability of various types of crude oil. The literature was reviewed and supplemental experimental testing was performed by AITF. Flammability is an important property of crude oil, primarily with regards to safety. The principal concern in the case of an oil release is the safety of the public. Oil with increased flammability has a higher propensity for combustion and, consequently, can create serious safety concerns to the neighbouring population and to cleanup personnel. Furthermore, understanding the flammability of crude oil can allow for *in-situ* burning as a method of spill clean-up, which will be discussed later in this section. The combustion of crude oil is a complex event because the crude oil is comprised of a mixture of several hydrocarbons and as it burns and/or evaporates its properties are continuously changing (e.g., viscosity, density and composition). It is understood that the combustion properties vary with different types of oil [Iwata, 2001]. The combustion properties and vapour pressures of numerous oils have been researched in the past with the intention of better predicting the fire hazard and adapting fire and safety responses accordingly ([Pichler, 2012] and [Jokuty, 2005]).

Vapor pressure is one of the most important crude oil properties in relation to flammability. The evaporation rate of a liquid depends on the vapor pressure [Roberts, 2011]. The vapor pressure of crude oil is of importance to the industry because bubbles of gas will begin to evolve from the oil when the oil is depressurized into a state lower than the vapor pressure. Moreover, there is a potential for the gas emissions to become an explosion hazard if strict control is not maintained of the vapor pressure.

The following sections consider the flammability of crude oils and are subdivided under the following headings:

1) The Effect of Weathering on Flammability

2) Safety Risks and Effect of Flammability on Spill Cleanup Decisions

3) Flash Point Comparison of Conventional Light, Medium and Heavy Crude Oils and Dilbit

3.2 The Effect of Weathering on Flammability

Oil exposed to the atmosphere undergoes a natural weathering process that is determined by the local environment (i.e., on-land or aquatic areas). For land-based spills, the primary method of weathering is evaporation. Spills in aquatic environments are more complex and will undergo weathering via several processes that include spreading of the oil, evaporation, dispersion, dissolution, emulsification, oxidation, sedimentation and biodegradation [Gunter, 2009]. By the time the oil is emulsified, the flammability of the oil is typically reduced to a non-flammable state, while evaporation alone can also accomplish this for many cases. Evaporation involves the phase change of the volatile components of the oil from a liquid to a gas state. During evaporation, the volatile component will mix with the surrounding air and the resulting gas mixture can be combustible in specific concentrations. There have been several models developed to predict the evaporation rate of multi-component oils in both aquatic and land-based environments established over the last 30 years ([Stiver, 1984], [Okamoto, 2010] and [Fingas, 2012]). The evaporation rate or degree of weathering is typically believed to be complicated by the effect of the elements (e.g., temperature, wind and waves) [Stiver, 1984]; however, some believe the elements such as wind and waves have little effect [Fingas, 2005]. The majority of these models have oil evaporating at a logarithmic rate with respect to time. The composition of the oil changes due to the loss of the lighter end components as the oil undergoes the weathering process. The constantly changing composition of the spilled oil adds a degree of complexity to the prediction of flammability behaviour. Conventional heavy oils may have as little as 10 % mass loss due to evaporation, considering a logarithmic rate this leaves a short window for the potential for ignition. This is in contrast to conventional light and medium crudes that can lose as much as 75 % and 40 % mass, respectively [Fingas, 1994]. Dilbit crudes will contain 20 – 30 % volume diluent (lights) and weathering of these crudes will likely be greater than conventional heavy crude oils (but less than conventional light crude oils).

The most recent studies on the effect of weathering on flammability have focused on the practicality of *in-situ* burning in the event of off-shore oil spills ([Wu, 2000] and [Torero, 2003]). The intentional burning of an oil slick as a means to minimize environmental damage is not a new concept [Carrier, 1992]. In the case of the more recent BP Horizon spill, *in-situ* burning was utilized in an attempt to prevent a large oil pool from reaching the coast and it is reported that up to 5 % of the released oil was burned from this spill [Ramseur, 2010]. The weathering and rapid evaporation of the volatile components in conventional light, medium and heavy crude oils and dilbit generally mean that the flammability of the crude spills will decrease with time [Fritt-Rasmussen, 2012]. [Fritt-Rasmussen, 2012] studied the effect of weathering on three types of crude oils that included an ashpaltenic, waxy and a light. Specifically, they studied the propensity of the oils to ignite at cold temperatures and under ice coverage (i.e., arctic conditions). In the arctic, *in situ* burning is considered to be the principal method of spill cleanup due to the logistical difficulty of operating the standard mechanical and chemical cleanup methods (see Section 5.3 for other spill cleanup

approaches). [Fritt-Rasmussen, 2012] demonstrated that oil spill spreading is constricted due to the ice and the window of ignitability is extended under arctic conditions, while crude oil spills rapidly become "not ignitable" in open waters due to weathering. In open waters or aquatic environments evaporation is accelerated due to spreading of the oil that will increase the surface area of the oil for the evaporation process. Moreover, another weathering factor effecting ignitability is the tendency for oils to form stable water/oil emulsions as this phenomenon decreases the flammability of a spill in aquatic specific cases [Wu, 2000]. In marine spills, wave action may effectively coat the oil with water (froth) that would also decrease the flammability potential of the spill. In the case of land or ice based spills, the heavier asphaltenic oil has the shortest window for *in situ* burning and becomes non-flammable in less than 9 hours compared to 18 - 72 hours for the light and waxy crudes. Consequently, in-situ burning could be more difficult for asphaltenic oils such as bitumen from oil sands sources, although, the diluent component added to the crudes could possibly extend the flammability window. As a result of these limited flammability windows, there have been a limited number of crude spills that have produced fire related incidents. Nonetheless, all crude oil spills have the potential to produce a hazardous environment with the possibility of ignition, which is discussed in the subsequent section.

3.3 The Safety Risks and Effect of Flammability on Spill Cleanup Decisions

The safety risks involved in the cleanup of crude oil are considerable, from the toxicity of the chemicals in the vapours surrounding the spill to the potential explosion and fire hazards associated with the flammable gas emissions from the oil. The majority of pipeline releases that result in an unexpected explosion or fire hazard are sourced from natural gas pipelines [NTSB, 2010] with a few references in the news to refined gasoline fires [Holt, 2004]. Crude oil releases have limited mention of fire incidents with the exception of a Horizon clean-up barge that caught fire due to ignition of the oil spill from a lightning strike [BBC, 2010a].

As mentioned in the previous section, the flammability of a crude oil released by a pipeline decreases rapidly with time especially in aquatic environments. Caution must be exercised for the initial 24 - 72 hours after a release, after which time the majority of the flammable components will have been lost. In the case of *in-situ* burning, where the crude oil is intentionally set ablaze, water cooled fire booms are typically used to contain the fire to a designated area, maintaining a safe and controlled burn.

Another key safety concern regarding flammability of crude oil is a phenomenon referred to as 'boilover' and is observed when a thin layer of oil catches fire on top of water. When the oil layer is thin enough for the heat to initiate boiling of the superheated water underneath the oil, the result can be catastrophic. It has been described as a "violent explosive character of the combustion with intense splashing and generation of a flame-ball-type burning of the fuel" [Garo, 2004]. Boilover is a phenomenon that has been observed both in aquatic

environments and in oil storage tanks [Gaspard, 2012]. The risk of boilover in oil storage tanks can be averted with proper firefighting strategies. There are no characteristics of dilbit that would increase the probability of boilover when compared to other conventional crude oils.

3.4 Flash Point Comparison of Diluent, Conventional Crude Oils and Dilbit

The flash point is the defined as the temperature that the fuel must be heated to in order to produce an adequate fuel/air concentration to be ignited when exposed to an open flame. The flash point of the crude oil is used as an index of fire hazard in North America [Jokuty, 2005]. Oil is considered to be flammable when it has a flash point lower than 37.8 °C (100 °F) [16CFR1500.3, 2011]. Flash point measurements can be obtained using an open or closed cup testing methodology. With an open cup tester, the volatile components can easily escape and more accurately mimic an above ground oil spill scenario. Conversely, closed cup testers prevent the loss of the volatile components and are more representative of an oil spill below ground or the environment that could be produced within a storage tank.

Table 3: Open Cup Flash Point Values for Various Crude Types [Jokuty, 2005]

Oil Type	Flash Point (°C)
Dilbit	-35
Conventional Light/Medium	7
Conventional Heavy Crude	<12
Light Sweet Crude	-9.1
In Situ Heavy Crude	151
Diluent	< -35

Environment Canada, Emergencies Science and Technology Division, created and manages a large database of crude oil properties to assist responders during a spill. This database includes parameters regarding flammability (e.g., open cup flash point [Jokuty, 2005]). With data on over 450 crude oils and oil products, a small relative sample of flash point data from a dilbit, conventional light/medium, conventional heavy, light sweet, in-situ heavy and a diluent are included in Table 3. According to Table 3, most fresh oils are initially considered flammable by the provided flash point definition. However, medium, heavy and dilbit oils move into the non-flammable classification after a short weathering period as described in the previous sections. The results also show that the flash point of fresh dilbit is initially lower than that found in other oils types and comparable to a diluent. As mentioned previously, the flash point is determined by the lowest boil point components (volatiles). Consequently, the flash point of the dilbit is governed by the 20 – 30 % volume diluent component and will increase as the diluent is evaporated due to weathering. For example, Canada's Environmental Technology Centre (ETC) has tested the flash point of Albian Heavy

Synthetic both in the fresh and weathered conditions and found them to be -23 °C and 168 °C, respectively [Jokuty, 2005]. Furthermore, the increase in the flash point was attributed to the considerable mass loss (22.6 %) during the weathering process.

Table 4: Comparison of Flash Points (ASTM D92) of Diluent, Conventional Crude Oils and Dilbit Before and After Weathering

Oil Type	Flash Point (°C)		Mass Loss (%)
	Fresh	Weathered	
Dilbit	< -35	88	16
Conventional Heavy	< -35	96	15
Conventional Medium-Heavy	< -35	142	19
Conventional Light	< -35	146	37
Diluent	< -35	128	81

As shown in Table 4, flammability experiments were conducted by AITF using the American Society for Testing and Materials (ASTM) D 92 methodology to further supplement the currently available technical data for diluent, conventional crudes and dilbit. AITF utilized the representative conventional crudes and dilbit used in APPENDIX 1 and APPENDIX 2 and a similar weathering protocol as the Canada's ETC (a rotary evaporator was utilized at 80 °C for a period of 48 hours while the oil was exposed to ambient air). The initial flash points of fresh diluent, light, medium heavy and heavy conventional crude oils and diluted oil sands bitumen were obtained and all values were found to be flammable (< 37.8 °C, Table 4). However, oil exposed to the atmosphere after an initial release will undergo a natural weathering process that is determined by the local environment (i.e., on-land or marine zones). As such, the flash point values were collected for the crude oils after weathering the samples for 48 hours. Table 4 shows that the flash point temperatures increase significantly after weathering due to the evaporation of lighter ends within the diluent, conventional crude oils and dilbit and all weathered flash point values are above 37.8 °C. The dilbit was found to behave similarly to the conventional heavy crude oil after weathering with similar flash points and weight losses. More importantly, the data shows weathered dilbit has a flash point of 88 °C (or 190 °F) suggesting that the flammability and explosion potential would be reduced as dilbit undergoes weathering after release.

Table 5: Closed Cup Flash Point Values of As-Received and Weathered Representative Conventional Crude Oils and Dilbit Measured by AITF

Oil Type	Flash Point (°C)		Mass Loss (%)
	Fresh	Weathered	
Dilbit	< -30	-27.9	4.52
Conventional Heavy	< -30	-23.8	3.76
Conventional Medium-Heavy	< -30	< -30	1.20
Conventional Light	< -30	< -30	3.64

Flash point tests were also conducted at an AITF laboratory using closed-cup determination [ASTM D3828, 2009] method B to more accurately represent the cold weather conditions and under ice coverage that could occur for pipeline systems traversing the Rocky and Coastal mountain ranges. The representative conventional crude oils and diluted oil sands bitumen tested in APPENDIX 1 and APPENDIX 2 were analyzed using the close cup approach and, as shown in Table 5, all four crude sources were ignitable below -30 °C (Table 5). In agreement with ETC's database, the closed cup flash points indicate that the crudes will be flammable at the source of an oil spill. The testing conducted at AITF for the purpose of this report included testing the effect of weathering on the flash point. Subsamples of the fresh oil were weathered using a less aggressive approach via a rotary evaporator at 60 °C for a period of 72 hours without exposure to flowing ambient air. As seen in Table 5, the closed cup flash points remained below 37.8 °C suggests that the rotary evaporator approach did not significantly weather the crude oils – this was confirmed by mass loss measurements that were only 1.2 – 4.5 % for these crudes. Future closed-cup flash point testing should incorporate weathering approaches similar to those employed by Environment Canada's ETC.

3.5 Conclusion from Flammability Literature

Crude oils are initially flammable when released; as the crude oil undergoes weathering, the degree of flammability is reduced. The extent of the reduction is dependent on several factors including the type of oil. With the exception of dilbits, the literature indicates the heavier the oil, the less flammable it is (Table 3). Dilbit has been found to behave similar to a diluent with respect to flammability until weathering removes the majority of the light ends at which point the dilbit behaves similar to conventional heavy crudes oil.

APPENDIX 4. PIPELINE LEAK DETECTION TECHNOLOGIES

Professor Dr.-Ing. Gerhard Geiger
Westphalian University Gelsenkirchen
Department of Electrical Engineering and Applied Sciences, Germany

4.1 Introduction to Leak Detection Systems

Pipelines are the least expensive and most efficient way to move liquids and gases over land, but there is a potential safety or environmental risk in the event of a release. This section of the report describes pipeline leak detection technologies and emergency shutdown protocols ensuring reliable and safe pipeline operations. The materials in this section of the report is well known in the literature and is divided in different parts:

The first part (Sections 4.2 and 4.3) introduces the subject by listing requirements and performance criteria and highlighting regulation issues concerning leak detection. Relevant regulations related to leak detection from North America (Canada and the United States of America) and Europe (i.e., Germany) are listed and compared in these sections.

The second part (Section 4.4) is an abbreviated summary of external-based leak detection systems according to the definition found in recommended practises [API RP 1130, 2007]. These systems provide good performance but investment and operational costs are usually high, and in many cases it is impossible to retrofit existing pipelines with this type of leak detection system (LDS). Therefore, external systems will only be used in critical applications (e.g., pipelines crossing nature reserves or high consequence areas).

Consequently, the main focus will be on internal leak detection systems that are subject of the third part consisting of Section 4.5 (overview) and Sections 4.6 to 4.8 (methods). Internal systems usually run continuously. Sensitivity is somewhat lower than for external systems, but so are investment and operational costs. For this reason, internal systems are very common and are required by law for some countries. Internal methods that detect leaks during paused flow or shut-in condition will also be discussed in Section 4.9.

Section 4.11 addresses leak detection of diluted bitumen. Transient pressure changes within the pipeline can cause vaporization of liquid components changing from liquid to gas resulting in column separation; this is particularly applicable to lighter petroleum products (e.g., gasoline, naptha and components within the diluent) . Column separation usually has consequences for the operation of leak detection systems (LDSs), and Section 4.11 will discuss the behavior and suitability of the presented leak detection methods.

After a LDS leak alarm declaration, appropriate actions are required to limit the consequences of a leak, to protect people and the environment, to take appropriate emergency actions etc. Section 4.12 is devoted to emergency shutdown protocols initiated manually and/or automatically after a leak alarm.

4.2 Requirements and Performance Criteria for Leak Detection Systems

Leak detection systems (LDSs) have to fulfill different requirements.

4.2.1 Type of Fluid

LDSs should be able to monitor pipelines transporting specific type of fluids like liquids, gases and fluid compositions. In Canada, examples for transported liquids are [Canadian Standards Association, 2011]:

- Liquid hydrocarbons including crude oil, multiphase fluids, condensate, liquid petroleum products, natural gas liquids, and liquefied petroleum gas
- Oilfield water and steam
- Carbon dioxide used in oilfield enhanced recovery schemes
- Water and waste water

Most of the applications for LDSs are for liquids, so this report has a strict focus on LDS principles and methods that are useful for the detection of diluted bitumen. It is worth noting that sophisticated model-based technologies like Real Time Transient Model (RTTM) based (Section 4.7.1) and Extended Real Time Transient Model (E-RTTM) based LDS's (Section 4.7.2) permit leak detection (and localization) also for gas applications (carbon monoxide and dioxide, ethylene, oxygen etc.).

4.2.2 Kind of Operation

Some pipelines may be operated nearly 365 (366) days per year and 24 hours per day without interruption in single-batch operation. Other product pipelines used for transporting refined liquid petroleum products will be operated on a scheduled base in multi-batch operation. Sometimes the operational procedures result in slack-line flow where the liquid pipeline locally is not entirely filled; at times, a result of vaporization of the transported product that could also lead to column separation. LDSs have to cope with the operational characteristics of a specific application.

4.2.3 Leak Characteristics

Depending on the causes and circumstances, leaks may have a sudden or gradual characteristic. For example, external damage to a pipeline may lead to the development of a sudden leak, while gradual leaks may occur due to pipeline corrosion. Sudden leaks usually show significant effects on physical variables (i.e., flow, pressure, temperature, etc.) and

therefore may successfully be detected by internally-based LDSs. Gradual leaks usually are very low in magnitude, and their effects on these physical variables are often very small and can continue below the alarm threshold (sensitivity) of internally-based leak detection systems (e.g., Enbridge's Norman Wells KP 380 incident [Canadian Broadcast Company, 2011]). Therefore, dedicated externally-based LDSs, visual inspection or aerial patrols may be required to detect these kinds of leaks.

4.2.4 Operational Phase

There are two main pipeline conditions: *pumping* conditions, where the product will be transported by means of fluid flow, and *paused flow* conditions, where fluid flow is (near) zero. In some applications, valves will be used to block the fluid flow in the monitored segment. This special paused flow condition will be called *shut-in* or *blocked-line* conditions.

The main focus of this segment of the report is on leak detection during pumping conditions, but, for completeness, Section 4.9 shortly deals with leak detection during shut-in conditions.

4.2.5 Steady State and Transient Operations

Steady state conditions exist when all relevant physical variables such as flow, pressure, temperature and density are sufficiently constant along the pipeline to ensure that no wave effects can be observed. *Transient conditions* exist when the physical variables change significantly with time, so wave effects propagating with speed of sound (c) are present. Reasons for these transient effects are product compressibility and pipe elasticity, together with special operational conditions such as:

- Starting and stopping pumps or compressors during start-up and shutdown
- Valve operation anywhere before, along or beyond the monitored pipeline segment
- Flow or pressure control actions
- Changes of target throughput
- Special cases such as column separation, see Section 4.11

Liquid pipelines are often operated in a steady state, but on close examination transient effects can also frequently be observed. In comparison, experience has shown that gas pipelines are usually in a (moderately) transient state as a result of the high gas compressibility.

4.2.6 Performance Criteria

[API RP 1130, 2007] defines the following important performance criteria for an LDS:

- *Sensitivity:* The sensitivity is a composite measure of the size of a leak that a system is capable of detecting and the time required for the system to issue an alarm in the event that a leak of that size should occur. Volume or mass lost

between the occurrence of a leak and its detection is a more objective measure of performance than the smallest detectable leak flow.

- *Reliability:* Reliability is a measure of the ability of a leak detection system to render accurate decisions about the possible existence of a leak on the pipeline, while operating within an envelope established by the leak detection system design. It follows that reliability is directly related to the probability of detecting a leak, given that a leak does in fact exist, and the probability of incorrectly declaring a leak, given that no leak has occurred.

- *Accuracy:* Accuracy covers estimation of leak parameters such as leak flow rate, total volume lost, type of fluid lost, and leak location within the pipeline network. These leak parameter estimates should be as accurate as possible.

- *Robustness:* Robustness is a measure of the leak detection system's ability to continue to function and provide useful information even under changing conditions of pipeline operation, or in conditions where data is lost or suspect. A system is considered to be robust if it continues to function under such non-ideal conditions.

An ideal LDS should be able to detect arbitrary small leaks immediately (sensitivity) without any missing or false alarms (reliability) and under all circumstances (robustness). If leak flow and/or leak location are calculated, these values should be exact (accuracy). A real LDS has to come as close as possible to this ideal case.

4.3 Regulatory Framework for Leak Detection Systems

Safe pipeline transport of liquids is important due to the high consequences that could be associated with a leak. Industrialized countries like Canada, U.S.A. and Germany regulate design, construction, operation, and maintenance of pipelines. Parts of these regulations address leak detection systems (LDSs) and the guidelines are summarized in the following section.

4.3.1 CSA Z661-11 (Canada)

The sixth edition of CSA (Canadian Standards Association) Standard Z661-11 "Oil and gas pipeline systems" was published in 2011 [Canadian Standards Association, 2011]. It covers the design, construction, operation, and maintenance of oil and gas industry pipeline systems that convey liquid hydrocarbons, oilfield water and steam, carbon dioxide used in oilfield enhanced recovery schemes, and gas. The Canadian standard is intended to establish

recommendations, essential requirements and minimum standards. Following this standard, "operating companies shall make periodic line balance measurements for system integrity" for liquid hydrocarbon pipeline systems. [Canadian Standards Association, 2011] defines material balance as "a mathematical procedure, based upon the laws of conservation of matter and fluid mechanics that is used to determine whether a leak has developed in a pipeline segment." The standard also includes model-based leak detection methods.

Annex E of this standard is a recommended practice for liquid hydrocarbon pipeline system leak detection; it focuses on material balance methods that provide leak detection capability in keeping with industry practice and commonly used technology. Annex E also includes subchapters concerning maintenance, internal auditing, testing and employee training. This annex is informative (non-mandatory) and expresses recommendations, not requirements, for the Canadian provinces and territories - with the exception of Alberta. The Alberta Pipeline Act/Regulation [Province of Alberta, 2011] regulates important aspects concerning pipelines operated in the province of Alberta (Canada). This act/regulation determines that "leak detection requirements contained in Annex E of CSA Z662 are mandatory for liquid hydrocarbon pipelines".

The Onshore Pipeline Regulations [NEB, 2008] for Canada also regulates important aspects concerning pipelines operated in Canada. This regulation determines that "a company shall develop and implement a pipeline control system that … includes a leak detection system that, for oil pipelines, meets the requirements of CSA Z662 and reflects the level of complexity of the pipeline, the pipeline operation and the products transported".

4.3.2 API RP 1130 (United States of America)

The first edition of API (American Petroleum Institute) Recommended Practice (RP) 1130 “Computational Pipeline Monitoring for Liquid Pipelines” was published 2007 [API RP 1130, 2007] and does not directly impose legal requirements but:

- Gives a technical overview of leak detection technology
- Describes infrastructure support for LDS
- Discusses LDS operation, maintenance and testing

It provides the necessary technical information for conscientious operators and pipeline controllers to manage their pipelines safely. [API RP 1130, 2007] covers liquid pipelines only. LDSs are divided into two groups:

- *External systems* using dedicated measurement equipment such as a sensor cables. Such systems are listed in Section 4.4.
- *Internal systems* using existing measurement sensors for flow, pressure etc. Corresponding systems are listed in Section 4.5 (overview) and Sections 4.6 to 4.8 (methods).

[API RP 1130, 2007] also defines criteria (or metrics) for comparing LDSs from different manufacturers. For further details please refer to Section 4.2.6.

[API RP 1130, 2007] is well known worldwide. Within the United States of America (U.S.A.), the Code of Federal Regulations Title 49 … Part 195 [49CFR195, 2011] references to [API RP 1130, 2007] by stating that "each computational pipeline monitoring (CPM) leak detection system installed on a hazardous liquid pipeline transporting liquid in a single phase (without gas in the liquid) must comply with API 1130 in operating, maintaining, testing, record keeping, and dispatcher training of the system".

4.3.3 TRFL (Germany)

Technische Regeln für Rohrfernleitungsanlagen (TRFL) provides technical rules for pipeline systems that apply to most pipelines transporting liquids or gases in Germany.

[TRFL, 2010] requires two autonomous, continuously operating LDSs that can detect leaks in the steady state. Either of these systems, or both, or a third one, must be able to detect leaks in transient conditions. Special attention should be paid to the difference between the steady state and the transient state; for details refer back to Section 4.2.5.

The [TRFL, 2010] also requires that each pipeline has one system to detect leaks in paused flow conditions (Section 4.9). In this context, paused flow just means "flow equal or close to zero"; nothing is said about how this will be achieved. If the flow is blocked by valves locking pressure with the pipeline segment, it is said to be in the shut-in condition.

In addition, gradual leaks (for example caused by corrosion) have two important characteristics: leak flow usually is (very) small, and it develops slowly. Installations according to TRFL are not well-suited to detecting this type of leak, so [TRFL, 2010] requires a dedicated LDS for this purpose. An external LDS can be used (Section 4.4), but usually this is expensive considering the length covered by transmission pipelines in North America. Some sophisticated internal LDS techniques and leak detection procedures intended for pipelines during shut-in operation (e.g. pressure test) may also be used to detect gradual leaks.

Lastly, the TRFL additionally requires a system (or other procedure) to locate leaks rapidly, enabling targeted actions for repair and re-establishing safety. This function may be part of an externally or internally-based LDS.

4.3.4 Summary

In summary, there is a sophisticated regulatory framework in all three countries, but it is interesting to note the differences.

Within Canada, LDSs are mandatory for liquid hydrocarbon pipelines only according to Alberta Pipeline Act/Regulation [Province of Alberta, 2011, 2011] and Onshore Pipeline Regulations [NEB, 2008] in combination with CSA Z662 [Canadian Standards Association, 2011]. There are no special recommendations, requirements or regulations concerning steady state or transient pipeline operation. Issues like redundancy, paused flow monitoring, detection of gradual leaks or leak localization are not covered. Please note that other relevant Canadian regulations might exist.

According to the U.S.A. Code of Federal Regulations Title 49 … Part 195 [49CFR195, 2011] in combination with [API RP 1130, 2007], LDSs installed on a hazardous liquid pipeline transporting liquid have to comply with [API RP 1130, 2007]. That means that LDSs are not mandatory within the U.S.A. There are no special recommendations, requirements or regulations concerning steady state or transient pipeline operation. Similar to Canada, issues like redundancy, paused flow monitoring, detection of gradual leaks or leak localization are not covered. Please note that other relevant U.S.A. regulations might exist.

In Germany, LDSs that are able to detect leaks during steady state and transient state are mandatory for liquid and gas pipelines (with some exceptions) according to [TRFL, 2010]. Redundancy of LDSs, leak detection in paused flow conditions, for gradual leaks and for leak localization are also required.

4.4 External Leak Detection Systems

Externally-based systems according to [API RP 1130, 2007] use dedicated measurement equipment, such as probes and sensor cables; this equipment is often called a leak detector. These systems provide very good performance but investment and operational costs are usually very high because they need dedicated measurement equipment such as sensor cables that must be laid along the pipeline route. Furthermore, in many cases it is impossible to retrofit existing pipelines with this type of LDS. Therefore, external systems will only be used in critical applications (e.g., pipelines crossing high consequence areas) or considered for new builds.

The main focus of this segment of the report will be on internal leak detection systems due to the high cost and limited application of external-based systems. A short overview of externally-based systems is presented below [Alaska Department of Environmental Conservation, 1999]. Manual inspection methods (e.g. using trained dogs) are omitted as well as air-based and satellite-based methods.

4.4.1 Fiber Optic Hydrocarbon Sensing Probes or Cables

Fiber optic sensing probes are driven close to the pipeline, or cables are laid throughout the pipeline system with this technology. When fluid escapes, the local changes in temperature, pressure or soil environment (concentration of hydrocarbons) causes a change in the

transmission character of the optical fiber. This change in the transmission characteristics is monitored using lasers and optical detectors. Sensing probes are used for point-type monitoring areas, while sensing cables are used for longer line-shaped monitoring areas like pipelines. Fiber optic hydrocarbon sensing cables based on local temperature change can also provide leak localization for liquid and gas pipelines; although, the temperature change due to fluid escape must be sufficiently large to trigger an alarm condition. These sensing cables operate continuously and the required time for leak detection is usually short. Cable replacement may be necessary after a leak occurrence.

4.4.2 Liquid Sensing Probes or Cables

Similar to fiber optic systems, liquid sensing probes or cables are driven close (probes) or are laid throughout (cables) the pipeline. Again, probes are particularly suitable for point-type monitoring areas, while cables are preferable for longer line-shaped monitoring areas like pipelines. When a leak occurs, the cable is saturated with liquid changing the electrical properties (electrical resistance, and impedance, dielectric constant etc.) of the cable locally. These changes can be detected using a dedicated evaluation unit connected to the cable. Liquid sensing cables additionally permit leak localization but can only be used for liquid pipelines. They operate continuously, and the required time for leak detection is usually short. Cable replacement may be necessary after a leak occurrence.

4.4.3 Hydrocarbon Sensor Cables

With this technology, a secondary conduit is installed along the entire route of the pipeline. The conduit may be a small-diameter perforated tube attached to the pipeline, or it may completely encompass the pipeline allowing the annular headspace to be tested. When a leak occurs, the escaping fluid will diffuse into the conduit and will be transported to the evaluation unit using an appropriate (vacuum) pump. At the evaluation unit, the fluid will be analyzed by hydrocarbon sensors to determine the presence of a leak. Usually more than one monitoring segment is required for longer pipelines. Additionally, Hydrocarbon sensing cables permit leak localization and can be used for liquid and gas pipelines. They operate continuously and the time required for leak detection may increase for longer pipeline segments. Cable replacement may be necessary after a leak occurrence.

4.4.4 Acoustic Emissions Detectors

Escaping fluid in pipelines creates a local acoustic signal when it passes through a perforation in the pipe and acoustic sensors can be installed along the pipeline route to acquire these signals. Evaluation units connected to these sensors perform signal assessment and determination for leak alarm decision. Distinguishing acoustic patterns created by the leak rather than normal acoustic components like flow noise and other phenomena is required for the successful implementation of this technology (i.e., reduction of false alarms). In addition, a large number of acoustic sensors are required to monitor longer pipelines. Acoustic emissions detectors additionally permit leak localization and can be used for liquid and gas

pipelines, but the technology is unable to detect small leaks that do not produce acoustic emissions at levels substantially higher than the background noise. These sensors operate continuously and the required time for leak detection usually is short. Unlike the previous technologies, there is no need for component replacement after a leak occurrence.

4.4.5 Leak Detection Pipeline Inspection Gauges (PIG's)

As mentioned above, escaping fluid in pipelines creates a local acoustic signal when it passes through a perforation in the pipe. This local acoustic signal will be acquired by acoustic sensors installed within a leak detection pig. This device is inserted into the pipeline using a pig launcher (or launching station). The launcher is then closed and the pressure driven flow of the fluid in the pipeline is used to push it down the pipe until it reaches the pig catcher (or receiving station). As for acoustic emissions detectors, the main problem here is to distinguish acoustic patterns created by the leak from normal acoustic components like flow noise and other phenomena. Leak detection pigs additionally permit leak localization but can only be used for liquid pipelines. The technology is unable to detect very small leaks that do not produce acoustic emissions at levels substantially higher than the background noise. Leak detection pigs are operated non-continuously either in regular time intervals (e.g. once a month) or on-demand in case of suspicious pipeline behaviour.

4.5 An Overview of Internal Leak Detection Methods

Internal systems usually run continuously. Sensitivity is slightly lower than external-based detection systems, but so are investment and operational costs. For this reason, internal systems are very common and are required by law for some countries. The focus of this report is on internal systems being classified into two categories shown in Figure 9.

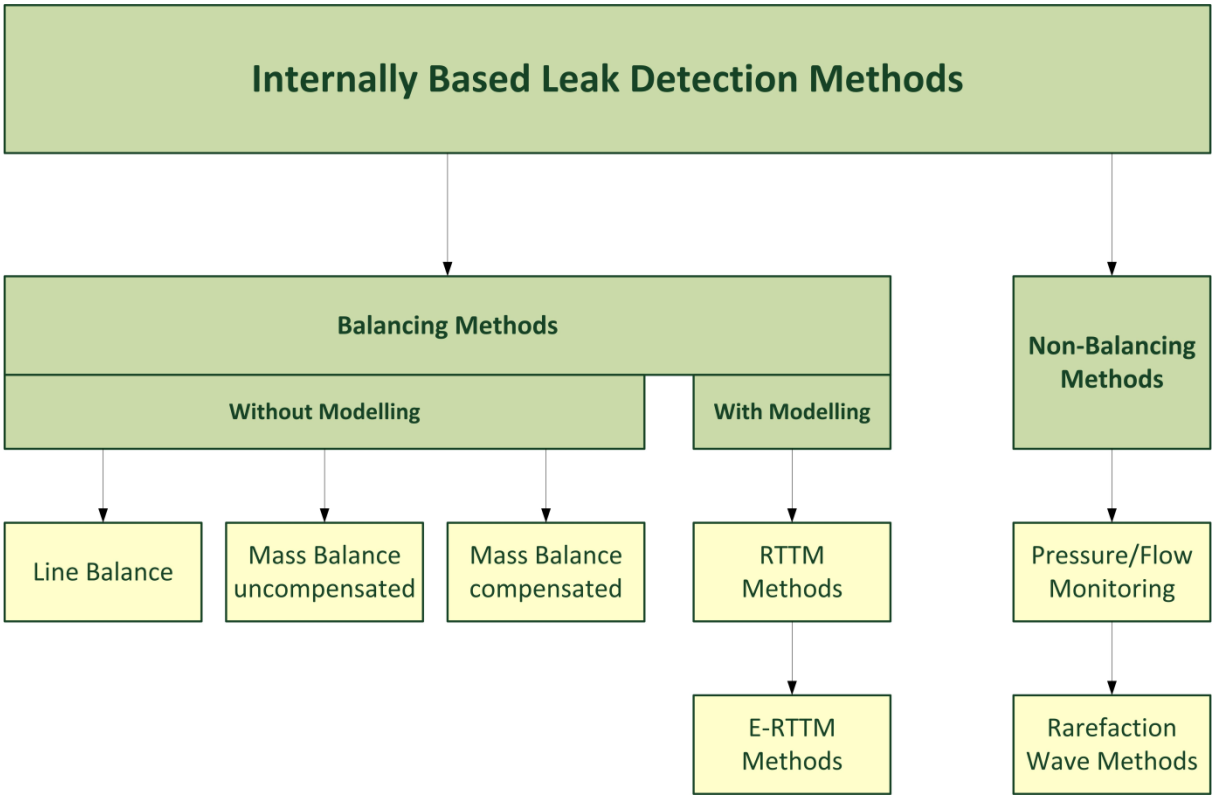

Figure 9. An overview of internally-based leak detection methods.

- *Balancing methods* use the principle of *mass conservation*: In absence of a leak, all mass (or material) entering a pipeline must leave it after some time. Without real-time modelling, these methods are limited to basic approaches like mass balancing where the difference between mass ΔM_I entering the pipeline within some time interval Δt to corresponding mass ΔM_O leaving the pipeline within Δt is analyzed (Section 4.6). Applying *model-based techniques* permit compensation for change of mass inventory hence resulting in a significantly shorter detection time. See Section 4.6 for *non-model-based* methods and Section 4.7 for *model-based methods.*

- *Non-balancing* methods do not use the mass conservation principle. Instead, signals for pressure and/or flow are monitored and evaluated according to assumptions about signal behaviour (Section 4.8).

4.6 Balancing Methods

Balancing methods are based on the principle of *conservation of mass*. In the steady state, summed over a sufficiently long time period (Δt), the mass entering a leak-free pipeline at inlet (ΔM_I) will balance the mass leaving it at outlet (ΔM_O).

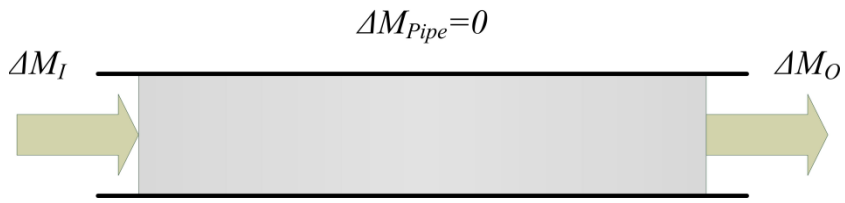

Figure 10: Mass balancing for a pipeline in steady state conditions.

Steady state operation ensures that the change of mass inventory (ΔM_{Pipe}) is sufficiently small, so $\Delta M_{Pipe} = 0$ for sufficiently long Δt and, if there is no leak, hence we can say:

$$\Delta M_I = \Delta M_O \quad \Leftrightarrow \quad \Delta M_I - \Delta M_O = 0 \tag{0}$$

Any additional mass imbalance indicates a leak. This can be quantified by adding a term for leak mass yielding:

$$\Delta M_{Leak} = \Delta M_I - \Delta M_O \tag{0}$$

where ΔM_{Leak} denotes the mass lost by the leak during Δt. These equations are valid for liquid and gas pipelines in single- or multi-phase flow in any consistent mass units.

Many balancing methods require steady state operation because the system is based on the assumption that $\Delta M_{Pipe} = 0$. Given this pre-condition, the smallest detectable leak rate under steady-state conditions is only limited by the accuracy of the flow measurement system, [API 1149, 1993].

In practical applications the use of such methods is limited because there are significant time periods and events where non-steady state or *transient* pipeline operations are present (Section 4.2.5). For gas pipelines, the larger fluid compressibility compared with liquid pipelines is a further problem leading to the conclusion that gas pipelines are rarely in steady state. As a result, balancing systems without compensation for change of inventory need longer times to detect a leak during these states and events, or must be switched off to avoid false alarms. This can only be avoided by considering the change of mass inventory yielding

$$\Delta M_{Leak} = \Delta M_I - \Delta M_O - \Delta M_{Pipe}\,. \tag{0}$$

The principal differences among the various balance methods are outlined below.

- Basic *line balance* uses fluid volume ΔV_I and ΔV_O instead of ΔM_I and ΔM_O, and hence can be used with volumetric flow meters (e.g., turbine and ultrasonic meters). As such, line balance does not compensate for changes of mass inventory ΔM_{Pipe}, and application is limited to cases where densities at inlet (ρ_I) and outlet (ρ_O) are sufficiently close. Therefore, line balancing is only suitable for liquid pipelines at steady state where inlet and outlet fluid temperature varies only slightly.

- *Uncompensated mass balance* uses Eq. (0) and requires mass flow meters (e.g., Coriolis type) or alternatively volumetric flow meters together with flow computers and additional temperature and pressure measurements. Uncompensated mass balance does not compensate for changes of mass inventory (ΔM_{Pipe}), but, temperature at inlet and outlet may differ in contrast to line balancing methods. This approach can be used for liquids as well as for gases. Application is limited to steady state or a longer detection threshold time has to be accepted.

- *Compensated mass balance methods* use additional pressure sensors at each end of a pipeline segment in order to calculate ΔM_{Pipe} (Eq. (0)) by means of a *fluid bulk modulus*. This type of calculation for ΔM_{Pipe} yields only an approximation of the real value. *Real-time transient models* have to be used in order to calculate the change of pipeline inventory correctly. These methods are presented in detail in Sections 4.7.1 and 4.7.2.

Balancing methods are very common and several references address the topic in literature ([Alaska Department of Environmental Conservation, 1999], [API RP 1130, 2007], [Geiger, 2003] and [Parry, 1992]). Examples of definitions found in the literature include:

- Mass balance
- Material balance
- Line balance
- Volume balance
- Modified or compensated volume balance

Unfortunately, some of the listed definitions are misleading. Volume balance, for example, might sometimes be confused with mass balance. *But there is no principle that allows for the conservation of volume for leak-free pipelines, even under ideal steady state conditions, so*

$$\Delta V_I - \Delta V_O \neq 0 \tag{0}$$

Definitions used with this report consider strictly the physical facts and thereby insure consistency.

4.6.1 Improving Performance Using Statistical Approaches

Statistical approaches can improve the performance of balancing methods introduced previously. An example is *hypothesis testing* using methods from *decision theory* [Barkat, 1991]. The hypothesis test for leak detection based on the uncompensated mass balance uses:

$$\Delta \dot{M}[i] \equiv \dot{M}_I[i] - \dot{M}_O[i] \tag{0}$$

where $\Delta \dot{M}[i]$ denotes sample i of the instantaneous imbalance between inlet ($M_I[i]$) and outlet mass ($M_O[i]$) flow [Zhang, 1993]. These samples can be used to decide between two hypotheses, H_0 (no leak) and H_1 (leak). *Likelihood ratio tests* may be used as decision principles to determine the existence of a leak. An example of common l*ikelihood ratio tests* include variations like the *generalized likelihood ratio test [Kay, 1998]* and *sequential probability ratio test* (SPRT, [Wald, 1947])

4.6.2 Requirements for Leak Detection System

All balancing methods require at least two flow meters, one at the inlet and the other at the outlet. All mass balance methods require mass flow, either directly measured (using mass flow meters) or indirectly measured (using volumetric flow meters together with flow computers using pressure and temperature sensors), while volume balancing only requires volumetric flow meters.

Line balancing is basically limited to steady state pipeline conditions because the change of pipeline mass inventory is not considered. Density at inlet must be sufficiently close to the density at outlet. Density at inlet and outlet may differ for uncompensated mass balancing, but still the change of pipeline mass inventory is not considered.

Compensated mass balance methods need additional pressure sensors at each end of a pipeline to estimate the change of pipeline mass inventory. The calculated values are only approximations; RTTM are required to calculate the correct values.

4.7 Model-Based Leak Monitoring

During the operation of a pipeline, physical variables like pressure, flow, temperature and density vary with time (Section 4.2.5). These effects change the mass inventory (M_{Pipe}) of a pipeline; therefore, liquid and gas pipeline often are in a *transient state* meaning that sudden changes in these variables may occur and propagate with the speed of sound (c) through the pipeline. Gas pipelines are almost always in a transient state, because gases are very compressible. Even in liquid pipelines transient effects cannot be disregarded most of the time. In these transient states, balancing methods presented so far (line balance, uncompensated and compensated mass balance according to Section 4.6) must be switched off or need a longer detection time in order to minimize false alarms. Use of statistical procedures may alleviate the effect of transient events but not solve the problem.

4.7.1 RTTM – Real Time Transient Model

Using mathematical models, it is possible to compensate for the transient change of mass inventory M_{Pipe} , but two requirements have to be met [API RP 1130, 2007]:

- The corresponding solution algorithms have to be calculated *in real time*
- The mathematical model must be able to *describe the transient flow behaviour* within the pipeline sufficiently accurately

RTTMs may be used in different ways ([Colombo, 2009] and [Whaley, 1992]). The method presented within this report is the *residual approach* ([Billmann, 1985]).

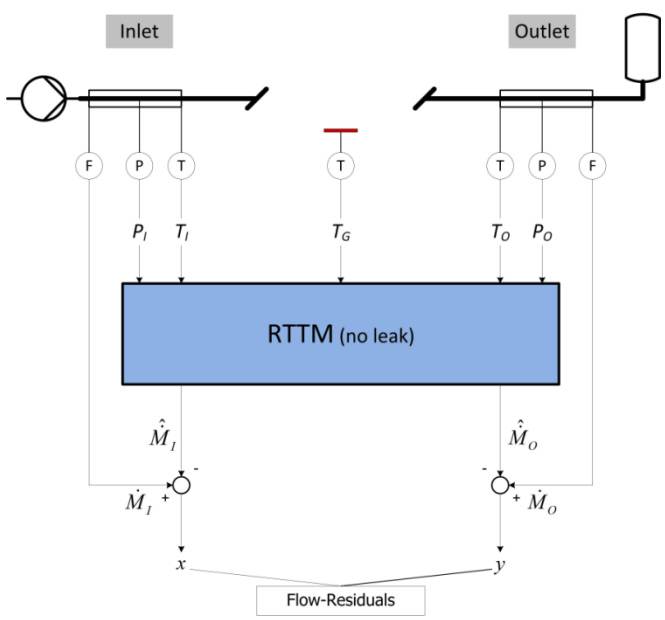

Figure 11. RTTM-based residual approach for leak detection.

The RTTM calculates mass flow estimates $\hat{\dot{M}}_I$ and $\hat{\dot{M}}_O$ at inlet and outlet, respectively, using appropriate pressure (P_I, P_O) and temperature (T_I, T_O) readings at inlet an outlet as well as ground temperature (T_G). For these calculations it is assumed that no leak exists. It is possible to check for the difference between measured and calculated flow. A difference between the two indicates a leak. Both of the *flow-residuals can be used:*

$$x \equiv \dot{M}_I - \hat{\dot{M}}_I$$
$$y \equiv \dot{M}_O - \hat{\dot{M}}_O$$

where $x \approx 0, y \approx 0$ if there is no leak, and $x > 0, y < 0$ in case of a leak. As such, the residuals can be used as leak indicators.

4.7.2 E-RTTM – Extended Real Time Transient Model

RTTM-based LDSs quickly detect small leaks during steady states as well as transient states, but these methodologies are prone to false alarms. An extension of RTTM-based leak detection had been proposed to minimize false alarms [Geiger, 2003].

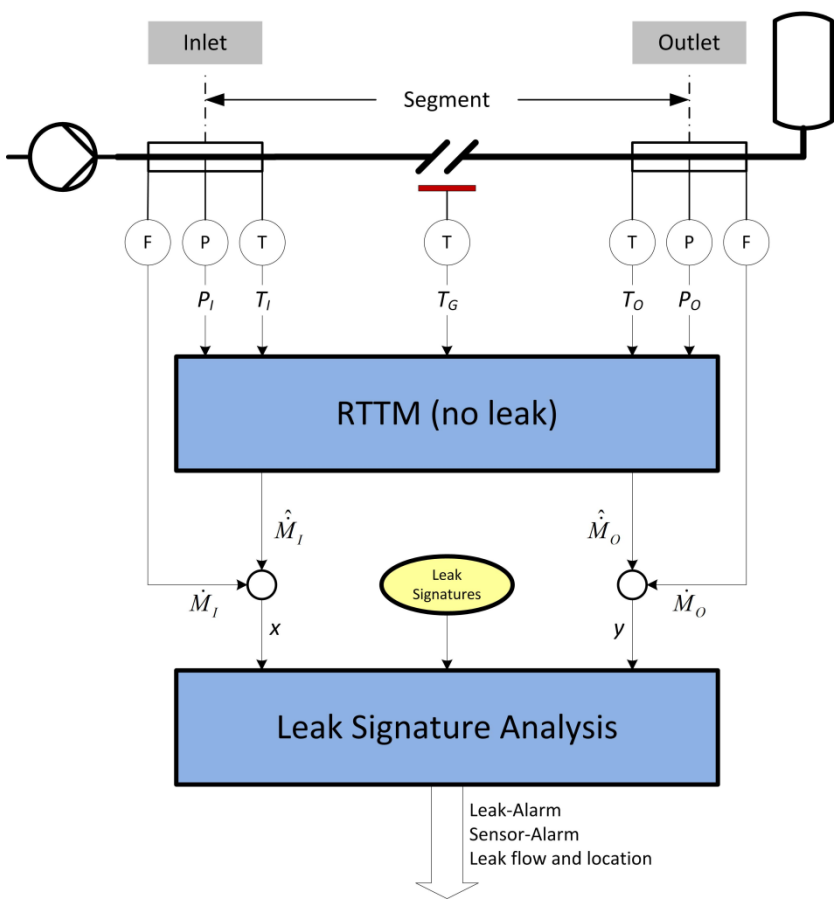

Figure 12. E-RTTM-based leak detection.

The task of the first RTTM component is to calculate the flow residuals before the second component analyzes the residuals for leak signatures (Figure 12):

- *Sudden leak.* This "classical leak" develops quickly (e.g., external damage to the pipeline). It causes a dynamic signature in residuals. When such a leak is recognized, a *leak alarm* is declared.

- *Sensor drift or gradual leak.* These may occur by contamination of the flow meters or by small leaks caused by corrosion. They result in indistinguishable, slow signatures. When drift is recognized, a *sensor alarm* is declared.

This approach boosts the reliability and the robustness of the system without compromising sensitivity and accuracy. False alarms are prevented, even with low alarm thresholds.

4.7.3 Requirements for Model-based Leak Monitoring

Model-based leak detection methods usually require flow meters and pressure and temperature sensors at inlet and outlet, respectively. Moreover, the accuracy and minimum detection threshold for an RTTM improves with installation of metering, pressure and leak detection instrumentation along the route. For sophisticated approaches, a temperature model considering heat transfer into the ground is also required.

RTTM-based leak detection is useful for steady states and transient states as long as the operational transient effects are modelled accurately. System configuration is more complex than for other methods presented because model parameters (e.g., length of the pipeline, diameter, height profile, fluid parameters, etc.) are required and the accuracy of these input parameters is significant for the sensitivity and reliability of the model.

Extended (E)-RTTM-based leak detection is also useful for steady states and transient states as long as the operational transient effects are modelled accurately. System configuration again is more complex than for other methods presented within this report because additional inputs are required for the model (i.e., parameters like length of the pipeline, diameter, height profile, fluid parameters, etc.). E-RTTM-based leak detection is less sensitive to deviations in model parameters, so the accuracy of the model parameters is less significant for the overall sensitivity and reliability.

4.8 Non-Balancing Leak Detection

A leak changes the hydraulics of the pipeline, which changes the pressure and flow readings after some time [Krass, 1979]. Therefore, local monitoring of pressure and/or flow at only one point can provide leak detection.

4.8.1 Pressure/Flow Monitoring

If a leak occurs, the pressure (p) in the pipeline will fall by an amount Δp. As pressure sensors are almost always installed, it is natural to use them for leak detection. The pressure in the pipeline is simply compared against a lower limit after reaching the steady state condition. When the pressure falls below this lower limit, a leak alarm is raised. This approach basically requires no data communication (e.g., having to compare flow rate at inlet and outlet) as local monitoring of pressure or flow rate is sufficient. The same methodology can also be used with regards to the flow of the liquid where flow readings are tested against limit values, but it is more convenient to use flow for balancing leak detection methods.

4.8.2 Rarefaction Wave Methods and Pressure Point Analysis (PPA)

A sudden leak will lead to a *negative pressure wave* propagating at the speed of sound (c) up- and downstream through the pipeline. Such a wave, called a *rarefaction wave*, can be recognized using installed pressure transmitters that can process and assign a leak alarm. In contrast to pressure/flow monitoring, these methods analyzes the *signature* of the acquired pressure signals. A positive pressure wave (e.g., as result of a closing valve) would not lead to an alarm.

[Farmer, 1989] proposed and patented a statistical procedure called *pressure point analysis* (PPA) evaluating the manner in which each individual pressure reading changes. Pattern recognition algorithms determine whether these specific changes show a significant movement away from the recent, normal operations of the system. The algorithms are designed to filter out background hydraulic noise, thereby increasing the resolution of the expansion wave associated with a leak visible.

4.8.3 Requirements for Non-Balancing Leak Detection

Pressure/flow monitoring is very simple and easily implemented but only useful in steady state conditions. Positioning of the sensors has to consider operational conditions. For example, pressure sensors cannot be placed at positions where pressure controls are in operation. Sensitivity and/or reliability of the model would be lowered due to the transients created during normal operation and would lead to an increased frequency of false alarms.

Rarefaction wave methods (e.g., PPA) analyze the pressure signal *signature*, thereby theoretically enhancing the sensitivity. Appropriate LDSs only require pressure sensors with local signal evaluation. Note that there is only one opportunity for the sensors to detect the leak; therefore, if the rarefaction wave passes the sensor and does not trigger an alarm condition, the ability of that sensor to detect the leak event is no longer possible. Consequently, positioning of the sensors has to consider operational conditions. Moreover, a longer pipeline segment has to be divided in shorter segments as the rarefaction wave will be attenuated while propagating through the pipeline, which would cause a loss in the leak signature. Practical applications prove that operational transients within a pipeline system

will often show signatures similar to those associated with a leak and would lead to a significant number of false alarms. During highly transient states like start-up and shut-down, corresponding LDSs have to be switched off and would not detect leaks associated with these events.

4.9 Leak Monitoring During Shut-In Conditions

As stated previously, there are two main pipeline conditions: pumping and paused flow. The focus of the methods presented up to now were on pumping conditions, but leak monitoring in paused flow conditions is also important if pause times cannot be neglected. In particular, this applies to multi-product pipelines where pause times between two batches may be significant. In some applications, valves will be used to block the fluid flow in the monitored segment. This special paused flow condition is referred to as *shut-in* or *blocked-line* condition.

In shut-in conditions, valves will lock a pressure into one or more segments of the pipeline. It is possible for considerable pressure changes to occur in this case as a result of thermal effects, but any rapid or unexpected fall in pressure indicates that a leak has occurred. After closing the valves, during temperature equalization, transient effects decay and fluid pressure (p) and fluid temperature (ϑ) will approach their equilibrium values. If there is no leak, the resulting pressure trend only depends on fluid temperature. Leak testing is performed by balancing changes in the measured pressure within the test segment against theoretical pressure changes calculated from the measured temperature. Leak detection modelling using systemic errors and bias [Christie, 2012] instead of random errors [API 1149, 1993] have been proposed to more accurately simulate shut-in conditions.

This method can also be used for *hydrostatic testing* where the pipeline segment is filled with water. Pressure testing requires pressure sensors and temperature sensors (for temperature compensation). The pipeline must be in *shut-in condition*, and the blocking valves have to be sufficiently tight; double block and bleed valves are a good choice. Hydrostatic testing is regulated in many countries, for example, new pipeline installation, a pipeline relocation, replacement of existing pipeline segments, or when there are other changes to a pipeline system that may affect integrity, For details refer to:

- *Alberta Pipeline Act/Regulation [*Province of Alberta, *2011]* in combination with CSA Z662 [Canadian Standards Association, 2011] for Canada.

- *Code of Federal Regulations Title 49 … Part 195* [49CFR195, 2011] in combination with [API RP 1110, 2007] for the U.S.A.

- *Technische Regeln für Rohrfernleitungsanlagen [TRFL, 2010]* in combination with [VdTÜV 1051] for Germany.

4.10 Internal Leak Detection on Crude Oil Transmission Pipelines

4.11 Leak Detection In the Event of Column Separation

In Canada, U.S.A. and Germany, (Section 4.3), transportation of diluted bitumen in pipelines is not specifically addressed by the guidelines and regulations. It should be noted that crude oil sources such as conventional light, medium and heavy crudes are also not individually addressed by these references.

This section strictly focusses on *leak detection in the event of column separation.* Transient pressure changes within the pipeline can cause vaporization of liquid components (changing a fraction of the liquid to gas) resulting in *column separation*: pockets of vapour between columns of liquid. Column separation is particularly applicable to the diluent component of the dilbit that is usually a light petroleum product. Column separation occurs when the operating pressure of the pipeline falls below the vapor pressure of homogeneous fluids or fluid components. Within this context, it is important to note that pressure during transient states may be significantly lower than steady-state pressure. Other conventional crude oils are a mixture of various different hydrocarbons and it is possible that (volatile) components exist with relatively high vapor pressure. In that case, column separation has been reported with conventional crude oils (e.g. crudes transported in the Trans Alaska pipeline [Norton, 1998a]) and numerous pipelines operate at least part of the time under transient conditions [Burnett, 1995]. Column separation usually has consequences for the operation of LDSs. It should be noted that column separation can be minimized by installing pressure reducing stations downstream and operating these sections of the pipeline system with positive pressure [Norton, 1998b].

4.11.1 Internally-Based Leak Detection Systems

Column separation generally causes transient hydraulic effects leading to transient changes of mass inventory. The impact on LDS operation depends on the method used.

- *Non-balancing methods* like pressure/flow monitoring including *rarefaction wave methods* and *pressure point analysis* evaluate pressure and/or flow readings at one point searching for a specific leak signature, e.g. negative pressure drop. Transient hydraulic effects caused by column separation can produce signal signatures close to those caused by leak events. Consequently, these methods tend to raise false alarms. This significantly limits *sensitivity* and *reliability*.

- *Balancing* methods like line balance, uncompensated and compensated mass balance as well as model-based methods apply the *mass conservation principle* that is also valid for multi-phase flow including column separation. Without compensation of transient change of mass inventory, column separation could have adverse effects on *sensitivity* and *reliability* too.

- *Model-based methods* like RTTM and E-RTTM compensate for the transient change of mass inventory and are basically able to account for column separation. However, proper mechanistic modelling of column separation is still a subject of active research [Bergant, 2006] and is not practically useful within the context of leak detection at this time. So, again, adverse effects on *sensitivity* and *reliability* exist.

In all three cases, statistical methods are able to alleviate these negative effects but the basic problem of uncompensated change of mass inventory still exists leading to an increased probability of false alarms.

4.11.2 Research approaches

Model-based methods seem to have the best potential to solve the problem of column separation. Two concepts are available:

- Some effort is made to develop *theoretical models* of column separation [Bergant, 2006]; although, this work is not yet completed in a manner that is useful within the context of model-based LDSs.

- It is also possible to develop *empirical* or *pragmatic* models of column separation. For example, n*eural nets* are able to describe empirically the transient behaviour of pipelines after training with field data [Geiger, 2001]. Similar to the above approach, this work is also under development and not ready for commercialization.

4.11.3 Externally-Based Leak Detection Systems

Externally-based systems according to [API RP 1130, 2007] use dedicated measurement equipment, such as probes and sensor cables. For that reason, column separation has no negative impact on most of the externally-based LDSs presented in Section 4.4. One exception is acoustic emissions detectors. These sensors installed along the pipeline route are used to acquire local acoustic signals created by escaping fluid. It cannot be excluded that column separation could create an acoustic sound pattern similar to the sound patterns of a leak resulting in a false alarm.

Within the context of pipeline transport of diluted bitumen, it is important to note that externally-based LDS are in most cases only useful for new pipeline systems and are limited to shorter pipeline segments (e.g., high consequence areas).

4.12 Emergency Shutdown Protocols

Pipelines are usually equipped with Emergency Flow Restriction Devices (EFRDs) such as an automated block valve or check valves in order to reduce consequences in case of a leak. Dedicated emergency equipment as well as an emergency response plan may be required by law:

- *Alberta Pipeline Act/Regulation [*Province of Alberta, 2011*]* in combination with *Emergency Preparedness and Response Requirements for the Petroleum Industry Directive* [Energy Resources Conservation Board, 2009] for Alberta.

- *Rohrfernleitungsverordnung Technische Regeln für Rohrfernleitungsanlagen [TRFL, 2010]* for Germany).

Leak alarm declaration of a leak detection system (LDS) poses the question of leak alarm handling. The strict and most obvious answer is to *automatically* shut down pumps, activate EFRDs and activating responsible organizations like the fire department. However, even the most sophisticated system like E-RTTM-based LDS may raise false alarms (e.g., critical sensor fails). Consequently, most operators will utilize a leak handling strategy (Figure 13).

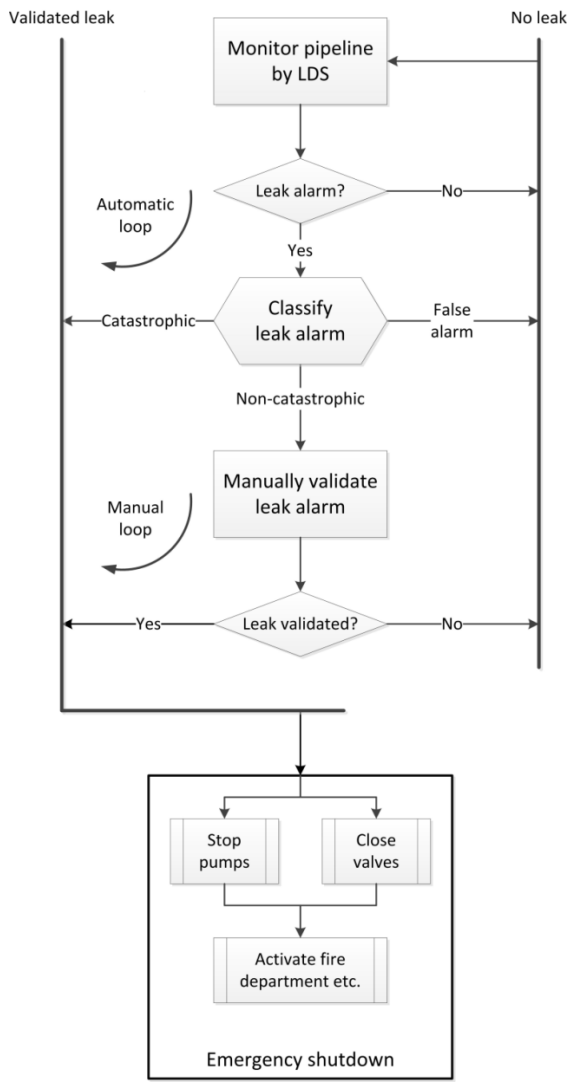

Figure 13. Flow diagram of leak alarm handling.

Any leak alarm declaration will be assigned to one of following classes:

- In the event of a leak resulting from a pipeline rupture, no further validation is required, and immediate reactions (shut down of pumps, activating check valves, activating fire department etc.) are absolutely necessary. These actions should be initiated automatically without participation of pipeline controllers resulting in an *automatic leak evaluation loop*, see Figure 13.

- *Smaller* leaks should be validated manually. To this end, pipeline controllers interactively use the pipeline control system to check LDS connected devices like sensors, evaluate pipeline operation and check the leak declaration state of redundant LDSs, if they exist.

The emergency shutdown procedure will be initiated manually if the leak will be validated resulting in a *manual leak evaluation loop*, see Figure 13.

- Leak declarations that are not validated are handled as *false alarms* and therefore do not initiate emergency shutdown actions.

It should be noted that emergency shutdown protocols are usually part of emergency response plans, and hence more actions are required in case of a leak incident than those listed in Figure 13. More importantly, leak detection systems and emergency shutdown protocols reduce the risk of a large oil spill when the leak is detected and when following the emergency shutdown protocols. For example, several low pressure alarms and a severe leak alarm were dismissed by control room operators as related to column separation during the 2010 Enbridge Line 6B pipeline rupture [National Transport Safety Board, 2010]. The control room ignored operator procedures and two start-ups were attempted that also triggered severe leak detection alarms. In total, 20,000 barrels of oil were release; 81 % attributed to the two attempted start-ups initiated by the control center after dismissal of the leak detection alarms.

4.13 Summary and Outlook for Leak Detection

This section presented pipeline leak detection technologies and emergency shutdown protocols. Relevant regulations for Canada, U.S.A and Germany were analyzed and reviews of current internal and external LDSs were discussed.

Non-balancing methods like *pressure/flow monitoring* and *rarefaction wave methods* might be easily installed, but usage is strictly limited to steady state pipeline operation. Therefore, a significant number of false alarms must be accepted in practical applications. Usage for diluted bitumen and lighter petroleum products is doubtful considering the transient effects caused by column separation.

Classical balancing methods like *line balancing* as well as *uncompensated* and *compensated mass balancing* have been successfully employed for pipeline systems for decades. A major disadvantage for these classical balancing approaches is the longer detection time in practical applications where transient effects are unavoidable. This may lead to very large fluid mass loss in case of a leak applying in particular to problematic operational conditions like column separation.

Compensation of transient effects using *real time transient models* (RTTM) reduces the detection time significantly, but LDS configuration is more complex, and LDS behavior depends on accuracy of model parameters (e.g., length of the pipeline, diameter, height profile, fluid parameters, etc). *E-RTTM-based leak detection* techniques are much less

sensitive to deviations in model parameters, so the accuracy of model parameters is less significant for sensitivity and reliability. Unfortunately, modelling of column separation is still subject of research. So, again, adverse effects on *sensitivity* and *reliability* exist for problematic operational conditions like column separation although installation of pressure reducing stations would minimize or eliminate column separation at problematic segments of the pipeline (e.g., significant elevation changes).

This segment of the report is concluded listing some improvements that can be expected within the next years.

- Improved *statistical procedures for signal analysis* from the field of pattern recognition could help to reduce the number of false alarms for rarefaction wave methods. Within the context of E-RTTM-based leak detection, sensitivity and reliability could be improved using *more sophisticated statistical classification* methods (e.g., [Duda, 2001]).

- Some effort has been made to develop *theoretical real time models for complex flow conditions* like multi-phase flow, slack-line flow and column separation [Bergant, 2006]. Increasing computing power could help to integrate sophisticated model algorithms into model based leak detection schemes; this again could improve sensitivity and reliability. The problem here is that LDS configuration will become more complex and the effort to describe the physics theoretically may be enormous.

- It is also possible to develop *empirical* or *pragmatic models* or *model extensions* instead of theoretical real time models. *For example, neural nets* are able to describe empirically the transient behaviour of pipelines after training with field data [Geiger, 2001]. The general approach here is *knowledge-based leak monitoring* using methods from the field of knowledge-based neurocomputing [Cloete, 2000].

APPENDIX 5. SPILL CLEANUP

Peter T. Reid, M.Eng., P.Eng., CSAP
HEMMERA
Vancouver, British Columbia. Canada

5.1 Introduction to Crude Oil Spills

Releases of crude oil from a pipeline differ from releases of petroleum hydrocarbons from a leaking underground tank in an urban environment. As the crude oil within a pipeline is shipped under pressure, releases usually consist of larger volumes of oil over a shorter time period. These oil spills result in higher concentrations of oil over smaller areas if the release is identified early and the initial migration of the oil is limited.

Small releases over time move vertically through the soil grains and possibly into the groundwater, large releases of oil have a propensity for horizontal flow and the oil spreads preferentially in the lateral direction (analogous to rain water) and can contaminate nearby waterways (e.g., rivers, streams, lakes, etc.). Restricting the movement of large oil spills becomes more challenging as the spill progresses and more oil is released into the environment. As such, the key to minimizing the effects of a large oil release is a quick and an efficient response to mitigate the movement of the oil so it can be recovered prior to moving through the environment. Once the oil spill is contained, the oil spill cleanup process (remediation) begins to remove the contaminated oil from the environment.

Within Canada, each province has different environmental remedial objectives and the federal government has the Canadian Council of Ministers of Environment Canadian Environmental Quality Guidelines [CCME, 2012]. Pipelines can either be federally or provincially regulated, with the remedial objectives (either standards or risk based) depending on the pipeline and location of the leak. Regardless of the remedial standards, the Remedial Process Guide, published by the National Energy Board [NEB, 2011] provides an excellent approach to the remediation of the release with appropriate public engagement and regulatory oversight.

The following section provides information on the techniques that have been successfully used to minimize the impacts of crude oil releases including mitigation approaches and remedial technologies. In addition, the developments of new innovations for spill cleanups are also noted within this section. It should be noted that these findings were based on the mitigation and remediation approaches for crude oil pipeline releases from engineering and science firms conducting spill response consulting (such as Hemmera and others) and information from literature sources.

5.2 Mitigation of Oil Spills

5.2.1 Releases at Pumping Stations and Tank Farms

New pumping stations are designed to have secondary containment throughout the stations that are integrated with the storm water run-off systems. The secondary containment system can take many forms including oil resistant geomembranes (e.g. Layfield geotextiles) that can operate during extreme changes in temperature. The storm water run-off ponds are sized for a design storm and are equipped with automatic valves at the pump station that will shut the flow of drainage water when oil is detected in the line and mitigate the spread of a release from the site. Once contained, the released oil can be removed with minimal consequences to the local environment. For high consequence areas, the secondary containment system within the pumping stations can be drained to a lined tertiary structure to contain any oil released during the incident.

Tank farms are usually designed with additional protection that includes an oil/water separator and a tertiary containment system that can remove released water collected by the drainage system. Similar to the pumping stations, automatic valves (e.g. agarcorp) are equipped with monitoring probes that measure the amount of petroleum hydrocarbons in the runoff water. These valves can be set for the type of oil being stored within the tanks (or transported by the pumping stations) and facilitate the closing of the valves and further discharge of the oil should the threshold concentration be exceeded. These automated valves are integrated into the leak detection system of the pumping house/tank farm and will trigger spill alarms to the control center.

Commissioning and maintenance of the systems is advantageous to restricting the movement of oil from the release site. Prior to installation of the pumping station equipment or tanks, the retention ponds need to be flooded to determine leaks within the containment system and proper operation of the automatic valves is verified through the introduction of oil to ensure they trigger an alarm condition (i.e., close). Additionally, the retention basins and oil-water separators can gather sediment over time requiring regular maintenance to ensure adequate retention abilities and functionality. When effectively designed, installed, operated and maintained, these technologies have advanced to the point whereby a release at a pumping station and a tank farm can be easily contained at the facilities without release to the surrounding environment. Recently, oil releases have been successfully contained within facilities in British Columbia [Wintonyk, 2009] and Alberta [Enbridge, 2012].

5.2.2 Mitigation of Releases to the Environment

When a release does occur there needs to be a system put in place to remove the oil from the environment as soon as possible. Unfortunately, there is no *one size fits all* solution for oil releases and the mitigation and spill response, although, confining the crude oil to the leak site is essential in minimizing the environmental impact that could be caused by an oil

release. The response time to an incident is critical and requires the availability of cleanup equipment and the ability to quickly deploy this equipment after a release has occurred.

As mentioned earlier, above ground crude oil releases will flow along the top of the land surface analogous to water. Oil will also penetrate down through the ground until it encounters a less permeable layer (e.g., clay bed or rock formation) or the groundwater table. Below ground crude oil releases will behave similarly and (dependent on the release rate) crude oil will surface above ground, while significantly more of the crude oil will be held within the local soil environment. It should be noted that crude oils will be absorbed by local vegetation and soils with high organic carbon content (e.g. topsoil and peat), which would impede the flow of oil through the soil. Depending on the release area, the impacted soil and groundwater may be managed on-site until remediation occurs or may need to be secured with pumping wells or a temporary storage cell prior to ultimate remediation.

If oil encounters waterways (e.g., streams, rivers, etc.), the oil will flow along the surface of the water until it encounters an encumbrance to that flow. Underflow weirs are used on smaller streams and rivers downstream of the release site, while booms are used on larger rivers to capture oil floating on the surface. For smaller waterways, temporary dams can also be placed upriver from the spill site to capture water and then pumps used to direct the water around the impacted stream area. This mitigation approach removes the driving force that would normally transport the released oil downstream. Releases to larger rivers and to marine environments require a different response mechanism as the oil release is not confined to small finite systems. Moreover, tidal activities, marine environment variability and local weather create a situation that is much more difficult to deal with than land based spills. Releases from the land migrating to the marine environment should be contained as quickly as possible with shore seal booms and several layers of booms designed for the particular situation. Mitigating the spread of the oil release into marine environments as much as possible will create a defined work area and limit the overall environmental impact.

5.3 Remediation Methodologies

5.3.1 Crude Oil Contaminated Soils

Although there are many different remedial strategies that can be employed for petroleum hydrocarbons in soil and groundwater, most of those remedial systems are designed for shorter chained refined gasoline or diesel spills, which are more common than crude oil releases. In the case of crude oil, the longer chain petroleum hydrocarbons do not easily volatilize or dissolve. Three remedial strategies have received detailed evaluation and proven to be effective based on remedial technology reviews completed for past dilbit and crude oil releases.

5.3.1.1 Low Temperature Thermal Desorption

Low temperature thermal desorption is the heating of petroleum hydrocarbon contaminated soils to the temperature required to cause the oil to desorb (physically separate) from the soil and volatilize (turn to a gaseous state). After the soil is dug up and desorbed, the oil is then captured through a condenser or oxidized in a secondary oxidizing chamber. Conveniently, the soil can then be reused on-site. Recovered oil can be placed back in the refining stream or used to aid in heating the soil (alternative fuel source). Various air emission control devices are employed on the unit to keep air emissions within the applicable discharge limits in its *Certificate of Authorization*. The main concern with low temperature thermal desorption for a pipeline release is the access of a fuel source at the release site. However, MI Swaco has a compact thermal phase separation system that could be mobilized to remote locations for the treatment of drilling muds that would be effective for use with crude oil [MI SWACO, 2012]. The first generation of this technology has been used for crude oil remediation in Canada and other low temperature thermal desorption units have been effectively used on pipeline releases in Alberta.

Currently, low temperature thermal desorption is being actively researched in China. The main research efforts are associated with developing a more effective heating mechanism to allow desorption and volatilization of oil within the contaminated soil. Interestingly, microwaves have been effectively proven for low temperature thermal desorption in laboratory scale studies [Dawei, 2009]; although, the technology has not been verified in field trials and is commercially limited due to the cost of creating the temperatures for desorption and volatilization (i.e., limiting factor for this technology).

5.3.1.2 Incineration

Incineration is very similar to low temperature thermal desorption, except instead of separating the petroleum hydrocarbons from the contaminated soil, the soil/oil mixture is heated to the point that the petroleum hydrocarbons undergo combustion within the unit. The main limitation with incineration methods for remediation of contaminated soil from a pipeline release is that units require a continuous supply of a fuel for incineration, which is more difficult to secure for releases that occur at remote locations. Also, permits are required for the emissions that are subject to local, provincial and/or federal regulations.

5.3.1.3 Off-Site Bioremediation/ Landfilling

The final technology that has been effectively utilized for the remediation of dilbit spills is off-site bioremediation and landfilling of the contaminated soils. Effectively, the contaminated soils are removed from the spill site and transported to a treatment pad. At these pads, the soil is actively mixed with various nutrients and air to facilitate the breakdown of the oil by either naturally occurring or introduced bacteria. The controlled environment of a treatment centre allows for optimal conditions to be created and maximum removal of the oil. The treated soil from the bioremediation process is then used as intermediate or final

cover at an adjacent or nearby landfill in accordance with the bioremediation facility and landfill permits. Off-site bioremediation/ landfilling approaches require access to the release site.

5.3.2 Crude Oil Contaminated Groundwater

In addition to soil being impacted at a land based release, the oil can affect the underlying groundwater as well. These methodologies have been effectively utilized in the remediation of groundwater contamination in recent crude oil spills and are discussed in the following section of the report.

5.3.2.1 Water Treatment Systems

Within dilbit, the diluent will dissolve into the groundwater and this mechanism is similar to gasoline contamination of groundwater in an urban environment. [USGS, 2011] Subsequently, the technology used in the treatment of groundwater impacted with gasoline can also be used at a dilbit release site and this treatment technology is well advanced and understood. [American Petroleum Institute, 2003] Groundwater has been effectively treated on past pipeline releases through oil-water separators to remove the bitumen and then followed by activated carbon treatment to remove the dissolved phase components (i.e., activated carbon will absorb the dissolved phase portions). The removal of oil from the water using separators and filtration can be completed on-site at the source of the contamination or at a water treatment facility (off-site) should it be more effective to collect and truck the water off-site.

5.3.2.2 Source Removal – Natural Attenuation

Groundwater contamination originates from the free oil that has penetrated through the soil layer. The source of the dissolved diluent in the groundwater is removed when the free oil and contaminated soil is treated using the remediation approaches mentioned previously (*Section 5.3.1*). The remaining groundwater can then be removed for treatment (on-site/off-site) or left within the groundwater formation to be broken down by naturally occurring bacteria (i.e., natural attenuation). Natural attenuation limits the amount of additional disturbance to the site and requires monitoring to verify the remediation is complete. Typically, natural attenuation would be associated with minor concentrations remaining at the end of spill cleanup projects.

5.3.3 Crude Oil Contaminated Waters

5.3.3.1 Interaction of Crude Oil in the Aquatic Environments

The remediation of crude oil releases contained to land is well understood with established methods to contain and remediate spills. In the case of aquatic spills, the impacts to the freshwater and marine environments are not as well understood, and remedial technologies are continually being developed.

The interaction of crude oil in the marine environment depends on three main parameters; the type of oil released, the type of marine environment, and the amount of localized weathering that has occurred. In June 2010, the National Oceanic and Atmospheric Administration (NOAA) published Characteristic Coastal Habitats – Choosing Spill Response Alternatives [NOAA, 2010]. The document summarizes the environmental impacts for the selection of oil spill response technologies based on five types of petroleum hydrocarbons, twenty-five aquatic ecosystems, and twenty-six remedial technologies. The report emphasises the wide range of properties observed by various petroleum products and the differing behaviors observed in each spill scenario and highlights that highly refined products have very specific properties, whereas the properties of crude oil depends on the reservoir it was extracted from.

Dilbit is a partially manufactured product and should behave consistently when exposed to a marine environment. Based on observations made during previous releases, when dilbit is introduced to the aquatic environment, it begins a weathering process that will change the properties of the oil. The degree of weathering that occurs can be related to the environment (i.e., waves, wind, temperature, etc). Dilbit, when released to the aquatic environment has a specific gravity less than one and will initially float on the surface of the water. As weathering occurs, the diluent will volatilize leaving the heavier portions of the oil behind. The released oil will form smaller bitumen globules with strings of oil extending from the spheres as the oil breaks away from the main plume. These bitumen globules will pick up sediment and debris increasing the overall specific gravity above one and the bitumen will sink to the bottom of the aquatic environment (commonly referred to as “tar balls”). The speed upon which the oil breaks apart and forms globules depends on the amount of weathering that occurs to the oil, the kinetic energy the oil is exposed to from wave action and tides, and the amount of small debris or sediment that the bitumen balls are exposed to. It is important to note that this phenomenon also occurs with neutrally buoyant oils and other conventional crude oils with specific gravity close to one. For example, conventional oil spilled into the Gulf of Mexico from the BP Deepwater Horizon incident produced tar balls that were washed ashore after the release in 2010 [BBC, 2010b] and after Hurricane Issac in 2012 [Reeves, 2012]. The persistence of these tar balls and the changes of oil properties over time are one of the major challenges in designing effective oil spill remediation technologies [Curwin, 2012].

5.3.3.2 Advances in Containment and Response Technologies for Aquatic Oil Spills

The National Commission on the BP Deepwater Horizon Spill and Offshore Drilling commented that although there have been incremental improvements in oil spill containment and clean-up since 1990 (e.g., new skimmers and less toxic dispersants), the advances in spill response and containment have not matched other areas of oil exploration. However, promising technologies were developed during the BP Deepwater Horizon spill response. These include subsea application of dispersants and beach cleaning machines that reclaimed 24% of the oil released from the wellhead. Since the release, the Coast Guard received

hundreds of reclamation concepts that are being actively researched and development at their facility in Connecticut. [National Commission on the Deepwater Horizon Oil Spill and Offshore Drilling, 2011]

The Wendy Schmidt Oil Cleanup X Challenge also produced two promising technologies that were able to process 2500 gallons per minute of oil-contaminated water with at least 70% efficiency of oil collected over water. The winning design, a grooved disc skimmer from Elastec/American Marine incorporated, was able to process 4670 gallons per minute with a combined efficiency of 88.9 %. The second place design from NOFI was a v-shaped surface boom that corrals oil and directs it to a separator and was able to process 2712 gallons per minute with a combined efficiency of 83.0 %. Another eight designs showed promise, but did not meet the volume or efficiency requirements [XPrize Foundation, 2011].

There have also been academic advances in on-water oil spill containment and remediation. The following paragraphs provide information on advances in enhanced natural biodegradation and booms. Many more advances are expected as the information learned during the BP spill is further examined.

Natural degradation takes place when naturally occurring bacteria breakdown the petroleum hydrocarbons to carbon dioxide and water. Laboratory experiments have shown that the addition of biosurfactant alone or a biosurfacant/fertilizer blend have the ability to enhance the degradation of crude oil; however, this has not been field tested to determine if unintended adverse effects would occur with the addition of biosurfactants [Thavasi, 2011]. Another experiment was conducted where bioremediation was simulated in the lab with the addition of nitrogen and phosphorous to seawater, soil, and crude oil. Over 28 days, natural degradation resulted in 22.6 % removal of the oil from the closed system. The amount removed increased to 53.3 % with addition of a bio nutrient and was further increased to 58.6 % with nutrient optimization [Zahed, 2010]. Although both of these experiments were lab scale, they both show promise for being able to enhance natural degradation of crude oil in the event of a spill to the marine environment using bioremediation.

Air bubble booms have previously been used for dissolved air floatation and separation of oil globules and this process has now been extended for use as an effective boom. [SINTEF, 2012] have been able to show the effectiveness of the technology at currents ranging from 0.3 m/sec to 0.5 m/sec depending on the amount of air. [Wang, 2010] was able to show that dissolved air flotation can also be used to remove crude oil from beach sands and this process decreases the amount of weathering and the viscosity of the oil, but increases the amount of surfactants or solvents present.

5.3.4 Removing Oil from Wildlife

One of the major concerns with an oil spill is the effect on aquatic mammals, reptiles, and birds. From 2008 to 2010 Focus Wildlife has attended several releases of bitumen and

bitumen-based crude oil. Over that time, they have been able to develop successful care protocols so that the vast majority of the wildlife can be rehabilitated and released. Proper medical stabilization within 48 hours of being contaminated is key to successful rehabilitation and can be achieved through proper planning prior to the release occurring. During the most recent release in Marshall Michigan 2,836 amphibians, reptiles, birds and mammals were taken into care with 2,224 released and 473 pending release at the time the paper was written [Schlieps, 2012].

5.4 Oil Spill Remediation Outlook

Remediation technologies have been designed to be robust, in that they should be able to work with a series of different crude oil compositions (i.e., light, medium and heavy crude oils). Dilbit is a partially refined product with high concentrations on both the heavy and light end of the spectrum. The largest clean-up issue associated with dilbit is that once the weathering process removes the light ends, the heavy ends collect debris and can sink in aquatic (marine and fresh water) environments. It should be noted that this is not a unique property associated with dilbit as this phenomenon also occurs with neutrally buoyant oils and other conventional crude oils.

With each successive oil release, more information is collected on the interaction of oil with the environment. Based on these field experiences, advanced treatment systems are being designed that can increase the efficiency and success in recovering and remediating larger portions of the oil. Currently, remediation can be completed efficiently and effectively for most land based petroleum hydrocarbon releases, while these field experiences are limited and not fully developed for oil spills in aquatic environments.

APPENDIX 6. CARGO OIL TANKER CORROSION

Professor Frank Cheng, Ph.D., P.Eng.,
Mechanical and Manufacturing Engineering (University of Calgary)
Calgary, Alberta. Canada

6.1 Introduction to Cargo Oil Tankers

6.1.1 Diluted Bitumen Export to the Canadian West Coast

Potential expansion and new construction pipeline projects will facilitate the transportation of dilbit to the west coast of Canada (up to 1.375 Mbbld/day). Crude oil exports arriving from the Kinder Morgan Trans Mountain pipeline to the west coast can be redistributed to local refineries in Vancouver (Westridge Marine Terminal) and Washington state (Puget Sound) where the current capacities allow for processing of 0.68 Mbbl/d [CAPP, 2012]. Alternatively, crude oil delivered by Kinder Morgan and Enbridge to Kitmat would require further transport by sea to access potential markets (U.S.A. and Asia). Consequently, the Kinder Morgan expansion and the Enbridge Northern Gateway system will rely heavily on the use of oil tankers for transportation of the crude oils to processing facilities.

6.1.2 Double Hull Oil Tankers

Oil tankers play an important role in the global transportation of approximately 2 billion metric tons of petroleum and petrochemical products [Huber, 2001]. As highlighted in Section 5.3.3, the potential consequences that can result from oil tanker accidents are particularly high. Oil spills are especially dangerous to ecological environments due to the toxicity of the crude products that contain poly aromatic hydrocarbons [Royal Society of Canada, 2004]. In the past decades, there have been a number of oil tanker accidents that have resulted in disastrous consequences whereby millions of gallons of oil per year have leaked into the ocean ([Guedes Soares, 2008] and [Peet, 2008]). In particular, the oil spill of Exxon Valdez on March 24, 1989 lead to spillage of 0.26 million barrels of oil into Gulf of Alaska. This accident caused significant energy loss and environmental damage. The Exxon Valdez oil spill also directly influenced the U.S.A. government into legislating (Oil Pollution Act, 1990) upgrades to the tanker design, i.e. the double hull tanker design ([Peet, 2008] and [Skinner, 1989]). In 1992, the [International Convention for the Prevention of Pollution by Ships, 1992] (MARPOL 73/78) was passed by the International Maritime Organization (IMO) that aligned international regulations with those in the OPA 90 [Oil Pollution Act, 1990] and called for gradual replacement/upgrading of single hull tankers to double hull configurations. Within Canadian jurisdictions, international oil tanker transports are regulated according to MARPOL 73/78, while domestic voyages and travels into the U.S.A. are governed by the OPA 90.

6.1.3 Corrosion of Cargo Oil Tanks

According to The International Tanker Owners Pollution Federation (ITOPF) limited, over 65 % of large scale global oil spills (> 5000 barrels) were attributed to collisions or grounding between 1970 – 2009 [ITOPF, 2010]. Within the U.S.A., groundings alone account for 65 % of the total volume of oil spilled [Dickins, 1995]. It should be noted that natural seepage of crude oil from the seafloor in North America has been estimated at over 1 million barrels of oil each year [National Research Council, 2003]. Unlike oil tanker spills, the natural seepage rate is sufficiently low enough that the surrounding ecosystem can adapt to the introduction of the crude oil.

The highest likelihood of a collision or grounding occurs near ports where the oil tankers are travelling at lower speeds in congested and constricted water ways. Double hull oil tankers can reduce the consequence of collisions or groundings at lower speeds, minimizing the potential spillage of crude oil into the environment [Dickins, 1995]; Subsequently, all oil tankers operating in U.S. waters will be double-hulled vessels by 2015 ([Australian Maritime Safety Authority] and [American Petroleum Institute, 2009]) and all large crude oil tankers operating in Canadian waters must now be double hulled, while smaller vessels must be double-hulled by the end of 2014 [National Resource Canada, 2012].

While oil spills can be caused by improper operations or human errors (e.g., loading/discharging oil, bunkering, etc.), another contributing factor to these accidents is related to material degradation caused or influenced by undetected corrosion ([Guedes Soares, 2008] and [Tscheliesnig, 2004]). Unfortunately, the ITOPF does not specify corrosion-related incidents of oil spills. Instead, the organization reports that the third likely cause of large spills (> 5000 barrels) between 1970 – 2009 was related to hull failures (12%), under which corrosion-induced failures would reside [ITOPF, 2010].

It is well known that corrosion is the interaction between a material and its surrounding environment, resulting in the degradation of that material. Within the cargo oil tanks of these vessels, corrosion is caused by the chemicals contained in aqueous phase that can include dissolved O_2, H_2S and/or CO_2, chloride salts, water and some organic acids ([Guedes Soares, 2008], [Shiomi, 2007] and [Guedes Soares, 2009]). Generally, uniform corrosion occurs on the upper deck plates of the vessel, while localized corrosion (e.g., pitting) is more likely to occur on the bottom of the tanker. A direct consequence of corrosion is the reduction of thickness of the ship hull, and sometimes this reduction is severe, especially when pitting corrosion happens. For example, some very large crude carriers (VLCC) have pit densities up to 150 per square meter with the pit diameters up to 150 mm and pit depths up to 6 mm after only one to three years of service [Hartley, 1984]. Moreover, the sinking of the double hull oil tanker *Nakhodka* was attributed to corrosion of up to 40% of the deck steel [Watanbe, 1998]. The reduced deck steel lowered the structural strength of the tanker and resulted in the hull failure of the vessel due to the cyclic stresses (fatigue) placed on the hull during a storm at sea.

Protective techniques such as the use of corrosion resistant steels, coatings and chemical inhibitors have been developed to control corrosion in the cargo tanks of double hull vessels. Meanwhile, regulatory organizations like IMO, International Association of Classification Societies (IACS) and some relevant societies have made regulations and guidelines for the protection of oil tankers ([Maritime Safety Committee, 2010a], [Maritime Safety Committee, 2010b] and [International Association of Classification Societies, 2005]).

In this section of the report, the corrosion mechanisms of the cargo oil tanks for double hull oil tankers loaded with conventional and non-conventional (dilbit) crude oils are reviewed and discussed. The protective techniques and methods for corrosion prevention are also summarized for double hull oil tankers along with relevant regulations and standards.

6.2 Mechanisms of Corrosion of Cargo oil tanks

6.2.1 Corrosion in Crude Oil

6.2.1.1 Effect of Crude Oil Chemistry on Corrosion of Oil Tankers

Crude oils are mainly composed of paraffinic, naphthenic (cyclo-paraffinic) and aromatic compounds, and also contain varying amount of non-hydrocarbon sulphur, nitrogen, oxygen and trace metals [Guedes Soares, 2008]. Most of these compounds are surface active and are able to adsorb on the surface of metals via weak interactions such as Van Der Waals forces (characteristic of physisorption) or strong covalent bonding (characteristic of chemisorption). Adsorption processes can create a very thin organic film on the metal surface. Furthermore, the accumulation of the surface hydrophobic active compounds can change the wettability of metals, which is usually hydrophilic by nature.

Generally, the dominant classes of surface active compounds in crude oil contain aromatics, oxygen-containing compounds, sulphur-containing compounds and nitrogen-containing compounds([Castillo, 2000] and [Ayello, 2011].

Aromatic compounds adsorb onto the steel surface by sharing π-electron density from the aromatic ring with the metal surface. This binding can possibly decrease corrosion rate or change the steel-oil interfacial tension, as shown in Figure 14 [Ayello, 2011]. The adsorption of oil on the metal can change the affinity of the steel from hydrophilic to hydrophobic. This alteration of phase wetting at the metal surface is caused by a change of steel-oil and steel-water interfacial tensions.

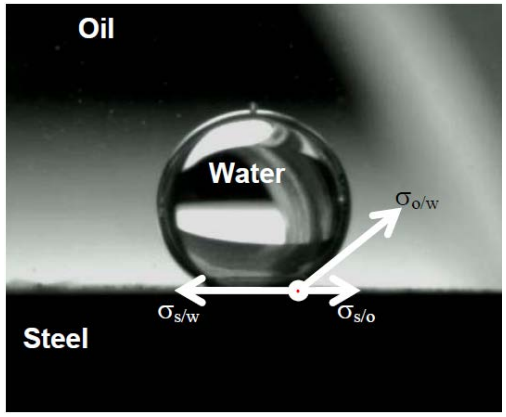

Figure 14. Interfacial tension forces applied to a water droplet in oil resting on a steel surface. The shape of the water droplet is determined by the interaction of the interfacial forces of oil-water ($\sigma_{o/w}$), steel-oil ($\sigma_{s/o}$) and steel-water ($\sigma_{s/w}$) [Ayello, 2011].

An oil-wetting of steel is beneficial for corrosion prevention due to the low conductivity of the oil. In this condition, a water droplet approaching the steel surface does not wet the steel, and, therefore, will not be corrosive [Ayello et al., 2011].

Oxygen containing compounds adsorb onto the steel surface by sharing electron pairs on oxygen with the metal. The resulting physical interaction blocks the surface active sites of the steel and will decrease the corrosion rate in the presence of water. The class of oxygen-containing compounds with the highest potential for adsorption contained in crude oil is organic acids. While small chain organic acids increase corrosion rate of steels, long chain organic acids are able to inhibit corrosion, and thus used as corrosion inhibitors in industry [Ayello et al., 2011].

Similarly, sulphur containing compounds also adsorb on the metal surface using unshared electrons, but they have a greater tendency to chemisorb via formation of sulphur-metal bonds [Ayello et al., 2011]. Sulphur is present either as H_2S or as thiols, mercaptans, sulphides, benzothiophenes, polysulphides, or as elemental sulphur. H_2S is very soluble in water and forms weak acids that can enhance corrosion or even pitting of steels because of the acid created and the porous sulphide film that is formed from sulphide ions (HS^- and S^{2-}) [GuedesSoares, 2008]. For sulphide films that are sufficiently compact in structure, the film could protect the underneath metal from further corrosion.

Nitrogen containing compounds can adsorb on metals similar to both oxygen- and sulphur-containing compounds. Nitrogen-containing compounds are subdivided in two categories: pyridinic forms known as basic nitrogen and pyrrolic forms known as neutral nitrogen. These compounds can inhibit the steel corrosion as their molecules are similar to the ones present in typical corrosion inhibitors used in oil fields [Store, 2011].

In most crude oils, chloride salts are either dissolved in water that is emulsified in crude oil or as suspended solids. Salts originate from brines injected for secondary recovery or from seawater ballast in marine tankers [Guedes Soares, 2008]. The existence of chloride salts will accelerate corrosion of oil tankers especially when promoting localized corrosion mechanisms such as pitting.

There have been attempts to establish the relationship between the inhibitive properties of oils and their composition. The mechanism of corrosion inhibition is dependent on the nature of oils, i.e., paraffinic or asphaltenic oils. Moreover, the corrosion inhibition also depends on water-cut of the oil-water mixture. For paraffinic oils, when the water-cut is low, the total nitrogen content, resins and asphaltenes are the contributing factors of the inhibition. At a high water-cut, only the nitrogen content is important. However, for asphaltenic oils, the contents of resins, asphaltenes and sulphur compounds govern the inhibition process at high water-cut, whereas at low water-cut the sulphur content is not important [Store, 2011]. It is worth pointing out that, despite the numerous studies conducted up to now, there has been no direct relationship established between the characteristics of oils and their inhibitive behaviour [Store, 2011].

6.2.1.2 Mechanisms and Models for Corrosion of Oil Tanks in Double Hull Vessels

Figure 15 shows the schematic diagram of mechanistic illustration of cargo oil tanker corrosion proposed by Panel SR242 committee of the Shipbuilding Research Association of Japan ([Kashima, 2007] and [NK, 2011]). The vapour space of the tank contains the inert gas for prevention of explosion and SO_2, CO_2 and H_2S originating from the crude oil, which results in generation of a complex corrosion environment in cargo oil tanks. The inert gas systems on all new tankers are regulated under the 1978 Protocol to the International Convention for the Safety of Life at Sea (SOLAS) and oxygen is controlled to levels that would prevent risk of explosion within the cargo oil tanks (i.e., below 8% O_2) [Aalborg, 2009]. Furthermore, cargo tank temperatures in double hull tankers (up to 50 °C) have been reported to be 20 °C higher than comparable single hull tankers due to the insulating effect of the double hull configuration [Rauta, 2004].

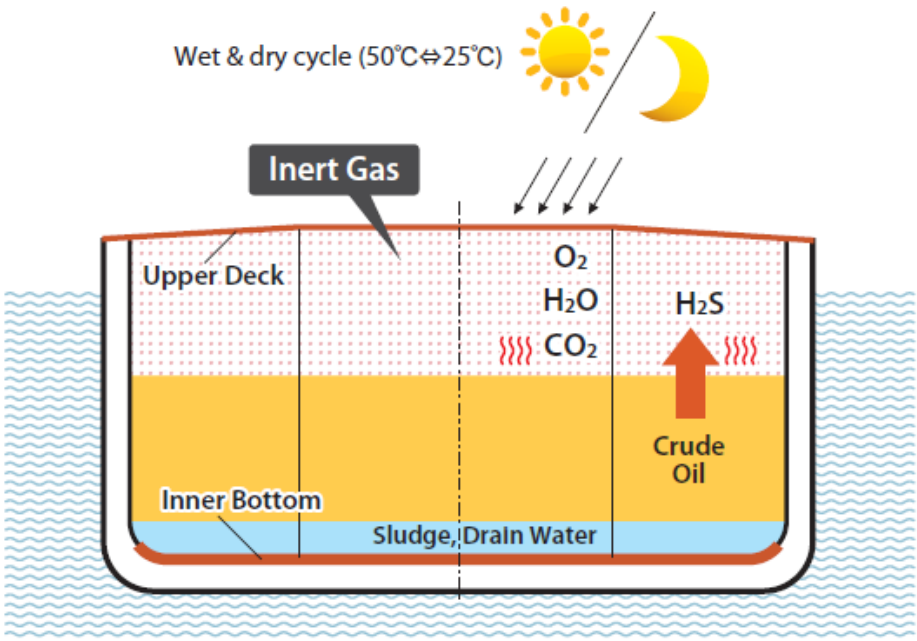

Figure 15. Schematic diagram for mechanism of corrosion of cargo oil tankers [Kashima, 2007].

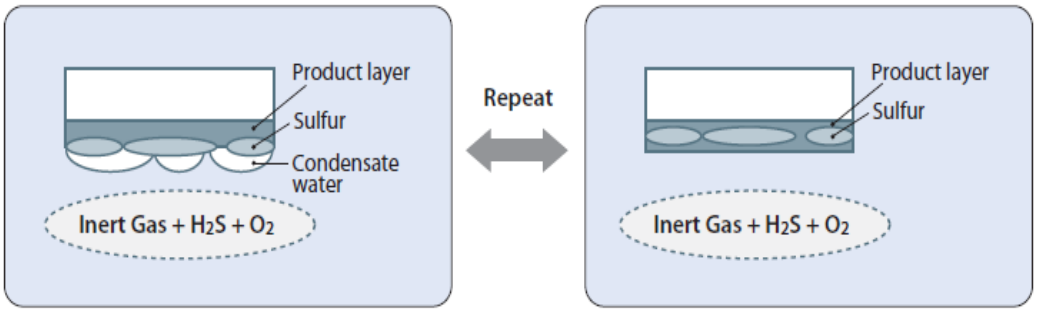

Figure 16. Mechanistic description of corrosion occurring at upper deck plate [NK, 2011].

Figure 16 illustrates the corrosion mechanism of upper deck plate of oil tankers [NK, 2011]. It is seen that the backside of the upper deck is exposed to the wet and dry conditions periodically due to temperature changes in the daytime and evening. Condensation of water thus occurs on the upper deck. Dissolution of H_2S, CO_2 and SO_2in the water causes the pH to drop, resulting in general corrosion of the upper deck plate [NK, 2011]. The corrosion product consists primarily of iron oxide (a-FeOOH) and elemental sulphur that is generated by oxidation of H_2S and has a layered structure [Kashima, 2007]. According to the field examination results, the deposit consists of a maximum 60 weight percent (wt. %) of elemental sulphur and the amount of corrosion product generated does not correspond to the corrosion induced weight loss of the upper deck plate ([Kashima, 2007] and [NK, 2011]). Generally, the corrosion rate of upper deck plate is not high, with an average below 0.1

mm/year, although cases have been reported with up to 40% loss in the upper deck plate [Watanbe, 1998].

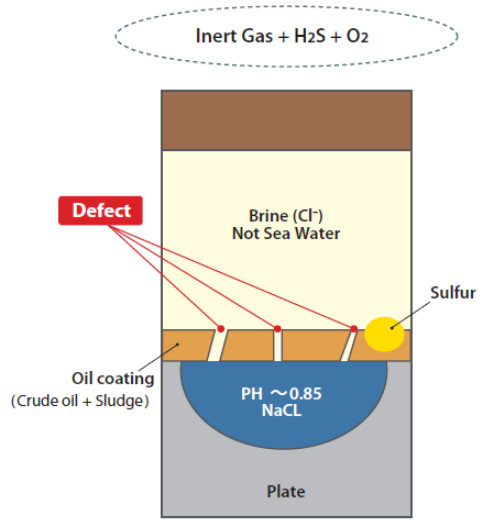

Figure 17. Corrosion mechanism at inner bottom plate of oil tankers [NK, 2011].

Drain water contains a high concentration of chloride and dissolved gases (H_2S and/or CO_2) and can be present at the inner bottom of the tank. As shown in Figure 17, the bottom plate is covered with an oil layer containing sludge. In general, the oil layer inhibits corrosion; however, defects present in the oil layer can be generated by crude oil washing and water can penetrate to the underlying metal through the defects. Consequently, the plate at the defective position is exposed to a more corrosive environment that contains concentrated chloride ions and corrosive gases (H_2S and CO_2) and this environment could promote the formation of corrosion pits. Pits grow due to the galvanic coupling effect that is formed between the steel at the defect (anode) and the adjacent steel under the oil layer (cathode) in the environment. The growth of pits can be stopped by cleaning the inside of cargo oil tanker prior to dock inspection. Pits are then re-coated by new crude oil after inspection ([Shiomi, 2007], [Kashima, 2007] and [NK, 2011]).

Models have been developed to predict the service life of oil tankers based on the thickness measurements ([Guedes Soares, 2008], [Parunov, 2008] and [Wang, 2003]). For example, a time dependent corrosion rate r(t) model has been proposed and expressed as follows [Guedes Soares, 2009]:

$$r(t) = r_s(1 - e^{\frac{t-\tau_i}{\tau_t}}) \tag{7}$$

where r_s is the steady-state corrosion rate, t is time, and τ_i is the organic liner coating lifetime.

The transition time, τ_t, is determined as:

$$\tau_t = \frac{r_s}{\tan \alpha} \tag{8}$$

where α is the angle defined in Fig. 5. By integrating Eq. (2), the corrosion depth at time *t*, *d*(*t*), can be obtained by:

$$d(t) = r_s \left[t - (\tau_i + \tau_t) + \tau_t e^{-\frac{t-\tau_i}{\tau_t}} \right] \tag{9}$$

The predicted corrosion rate based on the model is shown in Figure 18. Such models are all non-linear, and must be corrected when used for cargo oil tankers loaded with different crude oils because of the complexity of chemical composition ([Parunov, 2008] and [Wang, 2003].

Unfortunately, these models do not account for microbial induced corrosion (MIC) that could accelerate the corrosion of the cargo oil tank bottoms. MIC has also been reported for several newly constructed double hull crude oil tankers that have noted corrosion pits on uncoated cargo oil tanks that were 2 – 3 mm/year [Huang, 1997]. The microbial communities mainly consisted of sulfate-reducing bacteria (SRB) and acid producing bacteria (APB) within the systems studied by the authors. SRB have been associated with MIC-related concerns for pipelines, storage tanks and power generation systems [Lane, 2005]. These bacteria thrive in anaerobic (oxygen-free) environments such as the bottoms in cargo oil tanks and some strains can thrive in temperatures as high as 60 °C. The MIC mechanism will be discussed in further detail in *Section 6.3.3*.

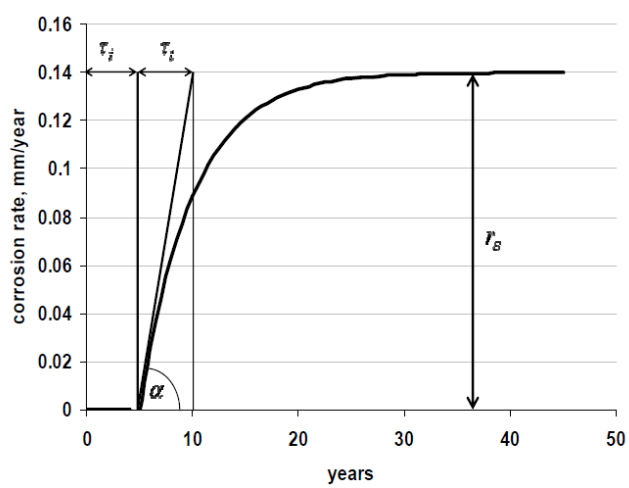

Figure 18. Model of corrosion rate variation with time of the main deck plating in cargo tanks [Parunov, 2008].

6.2.2 Corrosion in the Presence of Conventional Light Crude Oils

Table 6.Solubility of Oxygen in Petroleum and Petroleum Fractions [Foroulis, 1981]

Partial Pressure of O_2 (mmHg)	Oxygen Solubility (ppm)			
	Pentane (24.5 °C)	Kerosene (18.3 °C)	Gas Oil (24.5 °C)	Paraffin Oil (24.5 °C)
100	76	20.9	20	15
400	304	83.7	81	60
760	576	159	154	114

Crude oils are generally classified, according to API gravity (inversely proportional to the crude oil density, see Section APPENDIX 1), as sweet or sour, and asphaltenic or paraffinic (hydrocarbon characteristics).In cargo tanks used for storage of light petroleum products like gasoline, significant corrosion at the shell side is frequently encountered [Foroulis, 1982]. In light oils, the oxygen solubility is quite high as shown in Table 6. Recall from *Section 6.2.1.2*, the inert gas can contain up to 8 % oxygen, which at atmospheric pressures (760 mm Hg) equates to a partial pressure of ~ 61 mm Hg in the cargo oil tanks .

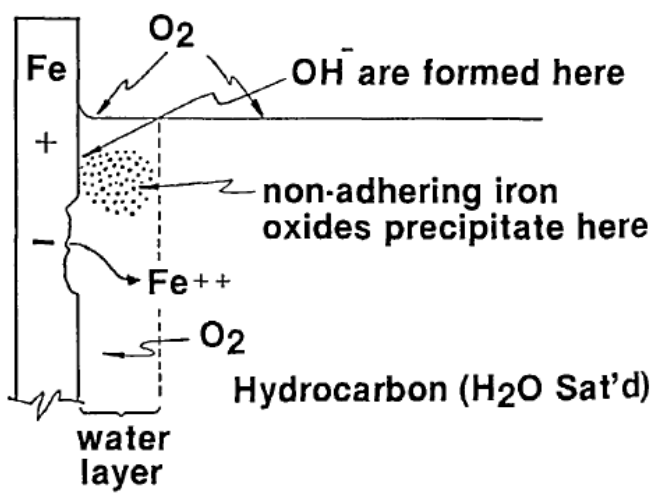

Figure 19. Mechanism of shell-side corrosion in light oil storage tanks [Foroulis, 1981].

Figure 19 shows the corrosion environment and mechanism of tankers in light oil whereby corrosion occurs at the liquid/gas interface. In the liquid layer immediately below the hydrocarbon liquid line, dissolved oxygen is locally concentrated and water condenses in the shell (relative humidity within the cargo tank could be as high as 95% [Rauta, 2004]). This produces a differential aeration cell, where the tank shell area adjacent to the vapour-liquid interface becomes a cathode and oxygen is reduced lowering the local alkalinity and leading to the precipitation of non-protective rust. The shell area immediately below is an area

deficient in oxygen and becomes anodic, where preferential iron dissolution in the form of general corrosion and pitting corrosion occurs [Foroulis, 1981 and 1982]. The probable reactions contributing to shell side corrosion include [Foroulis, 1981]:

Anodic reactions: $Fe \rightarrow Fe^{2+} + 2e$

$Fe^{2+} \rightarrow Fe^{3+} + e$

Cathodic reactions: $O_2 + 2H_2O \rightarrow 4OH^- + 4e$

Precipitation reactions: $Fe^{2+} + 2H_2O \rightarrow Fe(OH)_2 + 2H^+$

$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$

The presence of chloride and sulphate salts in the condensed water layer tends to accelerate corrosion due to hydrolysis at the anodic areas that produces a drop in pH. This process not only accelerates the rate of iron dissolution, but also prevents the formation of protective oxide films in the anodic sites [Foroulis, 1981].

It should be noted that research relating to the severity of corrosion for cargo oil tanks based on the crude oil source (e.g., conventional heavy crude oils, dilbit and diluent) have not been found during the literature review presented within this report. As such, the susceptibility of the cargo oil tanks to corrosion must be deduced based on the known corrosion mechanisms of the tanks, and the known properties of the crude oil sources.

6.2.3 Corrosion in the Presence of Conventional Heavy Crude Oils

Conventional heavy crudes oils have different physical and chemical properties from conventional light crude oils, e.g., greater viscosity, and greater amount of asphaltenes, heavy metals, sulphur and nitrogen ([Saniere, 2004] and [Hannisdal, 2007]). Conventional heavy crudes have complex and diverse chemistries based on the source of the oil. To date, limited research has been found correlating the source of the crude oil to its corrosivity in cargo oil tanks.

In general, the proportion, stability and complexity of sulphur compounds are greater in heavier crude oils and the API gravity decreases as the sulphur content increases [Guedes Soares, 2008].For example, conventional light U.S.A. crude oil that has an API gravity of 42.8 contains 0.28 wt% total sulphur, while a heavy crude from Venezuela having an API gravity of 9.5 has 5.25 wt% total sulphur [Guedes Soares, 2008].

The H_2S concentration in the crude will contribute to the total sulfur value; although, higher total sulfur content does not necessarily relate to a higher H_2S concentration. For example, two Mexican crudes that were reported to contain total sulfur contents of 3.4 % and 0.9 % were found to have similar H_2S concentration, 100 ppm and 116 ppm, respectively [US DOS,

2011]. H_2S is a primary contributor to corrosion in storage units.H_2S is very soluble in water and forms weak acids that can lead to corrosion and pitting corrosion of steels and other alloys. The relationship between the corrosion rate of oil tankers and H_2S concentration in crude oil was developed [Guedes Soares, 2008]:

$$\frac{\partial d(t)}{\partial t} = 0.5363[H_2S]^{0.3973} - 1.439, \quad R^2 = 0.987 \tag{10}$$

where $\partial d(t)/\partial t$ is the corrosion rate (mil/year), $[H_2S]$ represents the H_2S concentration (ppm), and R^2 measures how successful the fit is in explaining the variation of the data.

The content of CO_2 in heavy crude is also higher than that in conventional light crude oil [Guedes Soares, 2008]. Dependent on the origin of the crude oil, enhanced oil recovery techniques using CO_2 injection can also increase the relative CO_2 content [Palacios, 2000]. CO_2 is also present in the inert flue gas used to blanket the cargo tank. Like H_2S, when CO_2 is dissolved in water, it generates an acid (carbonic acid) and becomes potentially corrosive. There are various prediction models for CO_2 corrosion and the model shown below correlates the relation between the corrosion rate, temperature and CO_2 partial pressure [Guedes Soares, 2008]:

$$\log \frac{\partial d_B(t)}{\partial t} = 7.96 - \frac{2320}{T + 273} - 0.00555T + 0.67 \log(P_{CO_2}) \tag{11}$$

Where $\partial d_B(t)/\partial t$ is the corrosion rate (mm/year), T is temperature (^oC), and P_{CO2} is the partial pressure of CO_2(bar). The model above has also been modified to adapt to different conditions like high temperature, the effect of Fe^{2+} and pH.

Asphaltenes, part of the “bottom of the barrel” [Simanzhenkov, 2003], have a large content in conventional heavy crude oils, and they are the heaviest, most aromatic and polar fraction of a crude oil [Saniere, 2004]. Asphaltenes that have greater viscosity can co-precipitate with water, sand, bacteria and salts on the steel surface forming “sludge” on the bottom of the cargo tank. The localized environment created between the sludge and steel surface could lead to water-wetted conditions that, dependent on the water chemistry, promote pitting corrosion. This phenomenon is often referred to as “sludge corrosion” or “underdeposit corrosion”. Moreover, strong bonds can also be formed between the asphaltene’s polar components and the steel surface and this interaction could result in the formation of a protective film [Morales, 2000]. For example, field and laboratory tests have shown that an asphaltene film could reduce the corrosion rate by as much as 70 % [Morales, 2000].

6.2.4 Corrosion in the Presence of Diluted Bitumen

Bitumen is the raw material that is extracted from oil sands mined or in-situ recovered in Alberta, Canada. As mentioned earlier, bitumen is too viscous to transport by pipelines and

needs to be diluted with diluents, hence named dilbit [NEB, 2000]. Diluents are natural gas condensate, pentanes plus gasoline, or naphtha and will typically comprise 25 – 30 % of the volume of the dilbit [Casey-Lefkowitz, 2011]. Currently, dilbit has been transported mainly by pipelines to refineries in Canada and the United States and the relevant research on corrosion of steels and metals exposed to dilbit mainly relate to pipeline systems that operate under dynamic conditions (i.e., flow). Similar to conventional light and heavy crude oils, there has been no investigation to date performed on corrosion of cargo tankers containing dilbit.

[Swift, 2010] has reported that dilbit is more acidic, thick, and sulphuric than conventional crude oils. Moreover, [Swift, 2010] stated that dilbit contains five to ten times as much sulphur as conventional crudes, and that oil sands crude contains higher quantities of abrasive quartz sand particles than conventional crude, which can erode the pipelines. It has a sediment composition that can lead to the occurrence of sludge corrosion. However, a comprehensive literature review [Been, 2011] on dilbit properties and the pipeline transporting records suggests that the characteristics of dilbit are not unique and are comparable to conventional crude oils. As mentioned earlier in this report, these findings were also echoed by various researchers at the NACE Northern Area Eastern Conference on crude corrosivity ([McIntyre, 2012] and [Friesen, 2012]).

As stated, dilbit contains acids, sulphur and chloride salts, which would induce corrosion by the mechanism similar to that in conventional crudes listed above for conventional light and heavy crude oils. Enbridge and Kinder Morgan will transport the dilbit to the western Canadian coast via existing and proposed pipeline systems. These pipelines will transport the dilbit under turbulent flow conditions to minimize batch mixing and prevent the deposition of sludge within the lines [Been, 2011].

In dilbit and other conventional crude oils, larger sand particles are uniformly coated with very fine clays surrounded by a film of water in oil. Under low flow or stagnant conditions within a cargo oil tank, these particles are heavy enough to precipitate out with the water, oil products and, possibly, asphaltenes, forming a sludge layer at the bottom of the tank. Sludge deposits are mixtures of hydrocarbons, sand, clays, corrosion by-products, biomass, salts, and water. The water layer on deposited sand particles in pipeline sludge can coalesce to form a water layer on the steel. The water would contain chloride salts as well as bacteria that form a corrosive environment that can promote localized corrosion and MIC. The sludge chemistry varies widely, where some sludges have a large percentage of waxy oil and exhibit low or no corrosion, and others can contain more than 10% water and large bacterial populations and can contribute to underdeposit pitting corrosion [Been, 2011]. Sludge formations are removed from the cargo oil tanker after delivery at the receiving port using a technique referred to as crude oil washing. Cargo oil washings are required under the MARPOL 73/78 [International Convention for the Prevention of Pollution from Ships, 1992] and significantly reduce the crude oil that would remain on board the vessel.

6.2.5 Corrosion in the Presence of Diluents

Enbridge has proposed the import of approximately 0.2 Mbbl/d of diluents from Kitmat to Edmonton. Similar to the export of the dilbit, the diluent will be imported to Kitmat utilizing double hull oil tankers. The diluents used to dilute bitumen are mainly composed of natural gas condensate, pentanes plus gasoline and naphtha [Brown, 2011]. In particular, pentanes and naphtha are light oils, and the presence of a layer of oil film has an inhibitive effect on corrosion of tankers. Natural gas condensate condenses out of the raw gas if the temperature is reduced to below the hydrocarbon dew point temperature of the raw gas. It is a low-density mixture of liquid hydrocarbons that are present as gaseous components in the natural gas [Verma, 2012], containing minor amounts of H_2S and CO_2. It, thus, may cause corrosion of oil tankers similar to the conventional light in *Section 6.2.2*. However, there has been no literature to report on the study of corrosion of cargo tanks caused by diluents.

6.3 Prevention of corrosion of oil tankers

There have been a number of techniques developed to prevent and mitigate corrosion within the cargo tank of double hull vessels, including the use of corrosion resistant alloys, coatings and inhibition/biocides.

6.3.1 Development of Corrosion Resistant Steels

Development of corrosion resistant steels is an alternative means for prevention of corrosion of oil tankers suggested by International Maritime Organization [Maritime Safety Committee, 2010b]. Japan is currently in a leading position in developing corrosion resistant steels and, since 1999, the Panel SR242 committee of The Shipbuilding Research Association of Japan was established to study cargo oil tank corrosion of oil tankers([Shiomi, 2007], [Kashima, 2007] and [NK, 2011]). The panel was formed by many organizations, including research institutes, ship owners, shipbuilders and steel makers [Shiomi, 2007]. Valuable information for corrosion environment and mechanism of cargo oil tanks was obtained after three years. Based on the information, steel makers like JFE Steel Corporation started the development of anti-corrosion steels that recently resulted in the development of high corrosion resistance steels for cargo oil tankers [JFE Steel Corporation, 2008]. When used as upper deck plates, the losses due to corrosion were40% less than conventional steel [Yoshida, 2007]. Additionally, the corrosion observed for the conventional steel was found to bemuch more severe than the corrosion resistant steel when used as bottom plates. Corrosion resistant steels also exhibited an increased resistance to pitting corrosion due to the effect of the micro-alloying elements present. It was found that no corrosion pits could be observed for the corrosion resistant steels after 4 years of service as bottom plates in a cargo oil tank. Conversely, the numbers of pits on conventional steels was as high as 1300 after only 2.5years of service [Yoshida, 2007]. Recently, Maritime Safety Committee (MSC) of IMO has passed the resolution that allows using corrosion resistant steels as an alternative means for corrosion protection of oil tankers [NK, 2010].

6.3.2 Coating Systems

In corrosion prevention of cargo tanks using coatings, there are primarily three principles that are employed, either alone or in various combinations [American Bureau of Shipping, 2007].

(1) Create a barrier layer that blocks chemical ions, water and oxygen from reaching the steel.

(2) Ensure metallic contact between the tanker steel and a less noble metal, such as zinc in the paint, providing protection to the steel through the galvanic effect.

(3) Ensure that water on its passage though the paint coating works with compounds inhibiting the corrosive action.

In cargo oil tankers, coatings play an essential role of blocking the diffusion or transport of H_2S, CO_2, water and salts [Hartley, 1984]. The pitting corrosion of the inner bottom of the tank and corrosion of upper deck plates can be inhibited by applying coatings. However, conditions in cargo oil tankers are complicated and coatings may be damaged or contain defects at various positions. In addition, the coatings chemical resistance to the crude oil is essential in maintaining the service life of the protection system. For example, epoxy based coatings are susceptible to the benzene and toluene contained in crude oil. Over time, these compounds could penetrate into the epoxy and cause swelling and eventual disbondment of the coatings from the steel plate. Benzene and toluene exist in all conventional crudes and dilbit in comparable concentrations (depending on the source of the crude) that are typically below 1 % in volume [Crudemonitor.ca, 2012].

Figure 20 shows the schematic diagram of several modes of coating failure [Eliasson, 2005]. Osmosis blistering (Figure 20a) is usually caused by permeation of water through the coating from the environment at areas of low ionic concentration to the areas of high ionic concentration, resulting in the coating disbondment as a result of the pressure difference. Moreover, ions, particularly, anions, can be driven to enter the blister by the difference in potential between the anodic and the local cathodic sites, called electro-osmotic blistering, resulting in the further growth of the blister (Figure 20b). Rust jacking or rust leverage is the predominant mechanism resulting in coating failure at the late stage of the service life of coatings, where a change in volume occurs due to the presence of corrosion product beneath the coating and mechanically disbands the coating from the steel surface (Figure 20c).

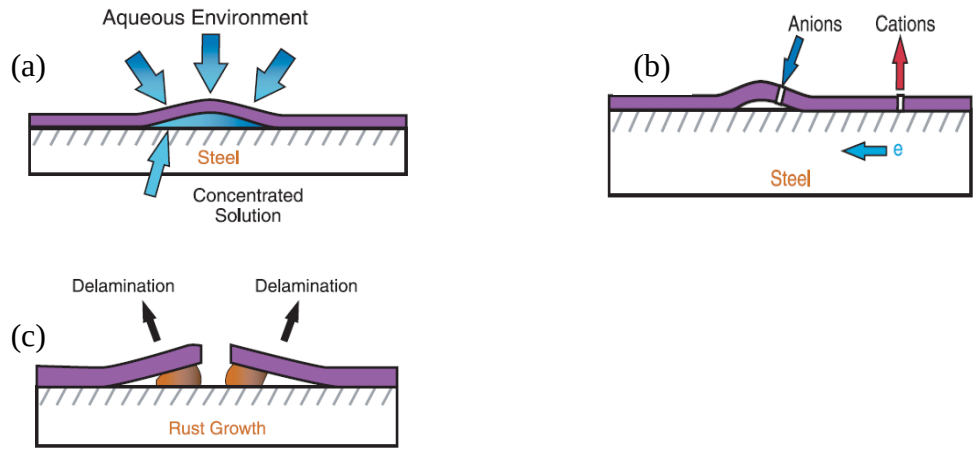

Figure 20. Schematic diagram of the coating failure mechanisms (a) osmotic blister, (b) electro-osmotic blister and (c) rust jacking [Eliasson, 2005].

Conventional coatings need solvents to dissolve the binder and reduce the viscosity of the paint to a level that is suitable for the various methods of application (e.g., brush, roller, conventional spray, airless spray, etc.). After application of the coating, the solvent evaporates and plays no further role in the final paint film. Frequently solvents cannot evaporate completely and can be subsequently trapped within the coating. During service the solvents will slowly migrate to the surface and evaporate. Such delayed solvent removal causes a build-up of internal strain (stress) as the coating attempts to shrink to account for the lost volume. Eventually this can, and often does, lead to pre-mature coating failure by cracking, especially at corners, and eventually to detachment [Devanney, 2006; International Association of Classification Society, 2007].

6.3.3 Corrosion Inhibitors and Biocides

Chemical compounds that will decrease the corrosion rate for a given system are collectively referred to as *corrosion inhibitors*. The corrosion inhibitors can react directly with the tank surface or with the environment to lower the susceptibility of the system to corrosion. Typically, organic inhibitors work through an adsorption mechanism with the metallic surface resulting in the formation of a thin film. The resulting inhibited surface will lower the overall corrosion rates by reducing the anodic and/or cathodic reactions. Petroleum corrosion inhibitors are water-soluble and oil dispersible and are thus more suited for protection of the cargo oil tank bottoms and the liquid/air interface [Nestle, 1973]. Corrosion of the upper deck requires inhibition using volatile chemicals called vapour phase corrosion inhibitors. These corrosion inhibitors volatilize into the gas phase and deposit on the upper deck surface complexing with the metal via a chemical or physical process. These types of inhibitors have been found to mitigate corrosion in the headspace of stationary oil storage tanks [Byars, 1999]. Additionally, environmental scavengers for O_2 and H_2S can also be added to remove these aggressive species from the water contained within the crude oils.

As mentioned earlier, bacteria colonies can also form residue within the crude oils and the sludge deposits at the tank bottoms. The bacteria within the sludge deposits can contribute to corrosion via a mechanism known as MIC [Kremer, 2000]. The bacteria are resilient and require treatment with biocides to sufficiently lower the colony numbers to negate the possibility of MIC. Moreover, biocide treatments will vary dependant on the crude oil source and therefore, require customization [Huang, 1997]. As such, an effective mitigation strategy for cargo oil tanks would incorporate a combined package of corrosion inhibitors (mentioned above) and biocides. Chemical additives such as alkaline could also be used to raise the pH and minimize the growth of the sulfate reducing bacteria (SRB) colonies or provide an alternative food for the SRB [Hill, 1998]. An inhibitor/biocide package could be added to the cargo oil tank at the export location and effectively inhibit the crude oil on route to the final destination (i.e., the processing facility). It should be noted that the potential toxicity and relatively slow biogradability of the corrosion inhibitors and biocides are a concern when transporting the crude in a confined space such as a cargo oil tank. A spillage of inhibited crude would introduce additional biocides and chemicals to the spill site that could be detrimental to the immediate ecosystem and spill responders. Additionally, some biocides may act to prevent naturally occurring beneficial bacteria in the sea from digesting the spilled crude oil.

6.4 Standards and Regulations for Prevention of Double Hull Oil Tanker Corrosion

Most recently, the IMO has developed requirements (SOLAS: regulation II-1/3-11, Corrosion Protection of Cargo Oil Tanks of Crude Oil Tankers) for mitigating corrosion in cargo oil tanks following incidents resulting from structural failure in oil tankers (e.g., Nakbodka). The requirements provide three acceptable options for corrosion protection of cargo oil tanks for new ship construction: coatings, alternative means of protection (e.g., corrosion-resistant steel) and exempt cargos (non-corrosive cargoes) [SOLAS II-1/3-11, 2012].

The MSC has adopted the SOLAS requirements under resolution MSC.291(87) and have provided additional standards and regulations for coatings and prevention of oil tanker corrosion: MSC 288 (87) "**Performance standard for protective coatings for cargo oil tanks of crude oil tankers**" and MSC 289 (87) "**Performance standard for alternative means of corrosion protection for cargo oil tanks of crude oil tankers**" [Maritime Safety Committee, 2010a; Maritime Safety Committee, 2010b]. These two resolutions were passed by the 87th session of MSC of IMO, and recently took effect on January 1st, 2012. In these resolutions, the performance requirements for protective coatings and corrosion resistant steels as well as testing methods are specified. Another important directive for double hull oil tankers is IACS Rec. 87 "**Guidelines for coating maintenance & repairs for ballast tanks and combined cargo/ballast tanks on oil tankers**". This recommendation focuses on survey, maintenance and repair procedures of coatings. It provides methods to assess coating breakdown.

It is worth acknowledging that corrosion inhibitors and biocides (*Section 6.3.3*) are not regulated by these standards as a primary prevention method for corrosion of cargo tankers. Instead, they can be used for corrosion prevention of more aggressive crudes or cargo oil tankers that are currently in-service and not mandated by the new requirements.

6.4.1 IMO MSC 288(87) Performance Requirements for Protective Coatings and Testing Methods

Protective coating systems are required for the cargo oil tanks for all new ship construction. These requirements include (but are not limited to) selection of the coating system, coating type, coating tests, job specifications, surface treatments and coating inspections. Resolution [Maritime Safety Committee, 2010a] requires a useful coating life of 15 years from initial application, over which the coating system is intended to remain in "GOOD" condition. Coatings are required to pass the testing protocol as outlined by Annex 1 of the resolution [Maritime Safety Committee, 2010a].

A crude cargo oil tank of a tanker vessel is exposed to varying environmental conditions and the standard addresses two testing methods applied to these conditions. When the cargo tank is loaded, there are three distinct zones, i.e., the *lowest part* and horizontal parts on stringer decks exposed to water that can be acidic and can contain sludge/anaerobic bacteria; *mid part* where the oil cargo is in contact with all immersed steel; and *vapour space* where the air is saturated with various vapours from the loaded cargo tank such as H_2S, CO_2, SO_2, water vapour and other gases and compounds from the inert gas system (O_2).

Coating systems can be quantified for fitness for service using field experiences or laboratory testing methodologies. The experimental approaches for laboratory qualification of coating systems in the MSC document are designed to simulate the environmental conditions that the crude cargo oil tank coating will be exposed to. The two methods are *gas-tight chamber* simulating the vapour phase of the loaded tank, and the *immersion test* simulating the loaded condition of the crude cargo oil tank.

After a system is qualified for service, guidelines have been established for inspection and assessment of these. The International Association of Classification Society (IACS) REC 87 “Guidelines for coating maintenance & repairs for ballast tanks and combined cargo/ballast tanks on oil tankers” aims at assisting the surveyors, owners, yards, flag administrations and other relevant parties involved in the survey, assessment, and repair of coatings in ballast tanks and combined cargo/ballast tanks [International Association of Classification Society, 2006]. The work of repair is dependent on coating conditions, e.g., GOOD, FAIR or POOR. Coating conditions are graded by assessment scales, which include scales for scattered, localized, and linear coating failures. A combination of these diagrams helps to assess the coating condition of the area under consideration in accordance with the grading definitions [Eliasson, 2005].

6.4.2 IMO MSC 289 (87) Performance Requirements for Corrosion Resistant Steels and Testing Methods

The resolution [Maritime Safety Committee, 2010b] requires a useful life for corrosion resistant steel of 25 years, which is considered to be the time period from initial application, over which the thickness reduction of the steel is less than the reduction allowance, and the integrity is maintained in cargo oil tanks. The estimated corrosion loss of the upper deck after 25 years should be less than 2 mm (less than 0.08 mm/yr), and the corrosion rate of inner bottom should be less than 1.0 mm/yr. Assessment of the corrosion resistant steels are required and testing of the simulated upper deck and inner bottom conditions should be done, respectively.

In addition to these two standards, other organizations have issued supplementary standards for the prevention of corrosion in cargo oil tanks. These include DNV1992, IACS 2002, SOLAS 2004, TSCF 2002, and ABS 2007 [Guedes Soares, 2008].

6.5 Cargo Oil Tanker Corrosion Summary

Oil tankers provide an important means to transport crude oil. However, the internal structural components could be subject to corrosion. This section reviewed the mechanism of corrosion of steels in crude oil, the effect of chemical composition of oil on the steel corrosion, and the corrosion prevention techniques as well as the regulations and standards for controlling and mitigation of corrosion of double hull oil tankers.

Components of crude oil are complicated and there has been no relevant research conducted on corrosion of oil tankers in the presence of conventional heavy crude, dilbit and diluents. In general, hydrocarbons have an inhibiting effect on corrosion while oxygen, sulphur compounds and chloride salts may cause or accelerate corrosion of tankers under certain conditions. Moreover, the cargo oil tanks have geometries that produce areas that may experience corrosion at various rates, and governed by different corrosion mechanisms.

The IMO has developed requirements for mitigating internal corrosion in cargo oil tanks following incidents resulting from structural failure in oil tankers. The requirements provide three acceptable options for corrosion protection of cargo oil tanks for new ship construction: coatings, alternative means of protection (e.g., corrosion-resistant steel) and exempt cargos (non-corrosive cargoes).

REFERENCES

Aalborg Industries, Inert Gas Systems (2009). http://www.aalborg-industries.com/business_areas/documents/InertGasSystems-10AUG09.pdf [Aug. 10, 2012]

Alaska Department of Environmental Conservation, "Technical Review of Leak Detection Technologies" Vol. 1, State of Alaska, Juneau, Alaska (1999).

American Bureau of Shipping, "Guidance notes on the Inspection, Maintenance and Application of Marine Coating Systems", 3rd Edition, American Bureau of Shipping (2007).

American Petroleum Institute, "Groundwater Remediation Strategies Tool", Regulatory Analysis & Scientific Affairs Department, API, Washington, D.C. (2003). http://www.api.org/ehs/groundwater/upload/4730_final.pdf [Sept. 05, 2012]

American Petroleum Institute, "Tankers Have a Great Safety Record!", February 25 (2009). http://www.api.org/oil-and-natural-gas-overview/transporting-oil-and-natural-gas/oil-tankers/tankers-have-a-great-safety-record.aspx

American Petroleum Institute (API) 1149, "Pipeline Variable Uncertainties and Their Effect on Leak Detectability". API, Washington, D.C. (1993).

American Petroleum Institute Recommend Practice (API RP) 1130, "Computational Pipeline Monitoring for Liquid Pipelines", Recommended Practice from the API, Washington, D.C. (2007).

American Petroleum Institute Recommend Practice (API RP) 1110, "Pressure Testing of Steel Pipelines for the Transportation of Gas, Petroleum Gas, Hazardous Liquids, Highly Volatile Liquids or Carbon Dioxide", Recommended Practice from the API, Washington, D.C. (2007).

American Society for Testing and Materials (ASTM) D445 – 06, "Standard Test Methods for Flash Point by Small Scale Closed Cup Tester" (2009).

American Society for Testing and Materials (ASTM) D3828 – 12, "Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)" (2012).

Anderson, I., "Kinder Morgan Canada", Kinder Morgan 2011 Analyst Conference, March 24 (2011). http://www.kindermorgan.com/investor/presentations/2011_Analysts_Conf_05_KM_Canada.pdf [Aug. 24, 2012]

Australian Maritime Safety Authority, " Comparison of Single and Double Hull Tankers", Australian Maritime Safety Authority, Australian Government, http://www.amsa.gov.au/Publications/Comparison_of_single_and_double_hull_tankers.pdf [Sept. 10, 2012]

Ayello, F., Robbins, W., Richter, S. and Nešić, S., "Crude oil chemistry effects on inhibition of corrosion and phase wetting", CORROSION 2011, paper 11060, NACE International, Houston, TX (2011).

Barkat, M., Signal Detection and Estimation, Artech House (1991).

British Broadcasting Corporation (BBC), "US Oil Firms 'Unprepared' for Major Offshore Disaster", BBC News, June 15 (2010a). http://www.bbc.co.uk/news/10317817 [Sept. 5, 2012]

British Broadcasting Corporation (BBC), "Gulf oil spill reaches Texas as tar balls wash ashore", BBC News, July 6 (2010b). http://www.bbc.co.uk/news/10520458 [Oct. 22, 2012].

Been, J., "Comparison of Corrosivity of Dilbit and Conventional Crude", Alberta Innovates – Energy and Environmental Solutions, Edmonton, Canada, September (2011). http://www.ai-ees.ca/media/6860/1919_corrosivity_of_dilbit_vs_conventional_crude-nov28-11_rev1.pdf [Sept. 10, 2012]

Bergant, A., Simpson, A.R. and Tusseling, A.S., "Water hammer with column separation: A historical review", *Journal of Fluids and Structures*, 22(2), 135–171 (2006).

Billmann, L., "Methoden zur Lecküberwachung und Regelung von Gasfernleitungen", Fortschrittsberichte VDI Reihe 8, VDI-Verlag, 1985.

Boduszynski, M.M., Rechsteiner, C.E., Shafizadeh, A.S.G., and Carlson, R.M.K., "Composition and Properties of Heavy Crudes," 7th United Nations Institute for Training and Research (UNITAR) International Conference on Heavy Crude and Tar Sands, Beijing, China, paper 1998.202 (1998).

Burnett, R.R., "Predicting Unbalanced Forces In Liquid Lines Can Avert Damage", *Oil and Gas Journal*, 93(13), March 27 (1995).

Brown, P., "Tar sands bitumen 'hell on pipelines' says new report", Island Tides, 23(5), March 10 (2011). http://www.islandtides.com/html/oil.htm [Sept. 10, 2012]

Byars, H.G. Corrosion Control in Petroleum Production, TPC publication 5, NACE International, Houston, TX, p. 181 (1999).

Canadian Association of Petroleum Producers (CAPP), Crude Oil: Forecast, Markets and Pipelines, June (2012). http://www.capp.ca/getdoc.aspx?DocId=209546&DT=NTV [July 7, 2012]

Canadian Standards Association (CSA), Z662-11, "Oil and gas pipeline systems", CSA, Mississauga, ON (2011).

Casey-Lefkowitz, S., Hayes, D., Westbrook, C., Blackburn, P., Smillie, J. and Trechock, M., "Comments to the Office of Pipeline Safety in Response to the Advanced Notice of Proposed Rulemaking Titled "Safety of On-Shore Hazardous Liquid Pipelines"", Natural Resources Defense Council, Sierra Club, National Wildlife Federation, Plains Justice, Western Organization of Resource Councils, Dakota Resource Council, February 18 (2011). http://switchboard.nrdc.org/blogs/sclefkowitz/NRDC%20et%20al%20Comments%20Proposed%20Rulemaking%20On-Shore%20Hazardous%20Liquid%20Pipelines%20Feb%2018%202011%20rev.pdf [Sept. 10, 2012]

Castillo, M., Rincon, H., Duplat, S., Vera, J., and Baron, E., "Protective properties of crude oils in CO_2 and H_2S corrosion", CORROSION 2000, paper 00005, NACE International, Houston, TX (2000).

Canadian Council of Ministers of the Environment (CCME), Canadian Environmental Quality Guidelines. http://ceqg-rcqe.ccme.ca [Sept. 05, 2012]

Canadian Broadcast Company (CBC), "No coverup in N.W.T. pipeline leak: Enbridge", CBC News, June 7 (2011). http://www.cbc.ca/news/canada/north/story/2011/06/07/nwt-enbridge-pipeline-spill.html [Sept. 10, 2012]

Carrier, G., Fendell, F. Mitchell, J., "In-Situ Burning via Towed Boom of Oil Spilled at Sea", *Combustion and Flame* 90 295-306 (1992)

Christie, B., "Predicting Shut-in and In-Station Leak Detection Sensitivities", 43rd Annual Pipeline Simulation Interest Group (PSIG) Meeting , Santa Fe, NM, May (2012).

Cloete, I. and Zurada, J.M., Knowledge-Based Neurocomputing, MIT Press, Cambridge, MA, February (2000).

Code of Federal Regulations Title 49 Subtitle B Chapter 1 Subchapter D Part 195 (49CFR195), "Transportation of Hazardous Liquids by Pipeline", Government of the United States of America, Oct. 1 (2011).

Code of Federal Regulation Title 16 Chapter II Subchapter C Part 1500 (16CFR1500.3), "Hazardous Substances and Articles; Administration and Enforcement Regulations", Government of the United States of America, Jan. 1 (2011).

Colombo, A. F., Lee, P., and Kamey, B.W., " A selective literature review of transient-based leak detection methods", *Journal of Hydro-environment Research*, 2(4), 212 – 227 (2009).

Crude Monitor, http://www.crudemonitor.ca/ [Sept. 12, 2012].

Curwin, T., "Hope After an Oil Spill: Breakthrough Cleanup Technology", CNBC.COM, April 23 (2012) http://www.cnbc.com/id/46222428/ [09.05.2012]

Dawei, L., Zhang, Y., Quan, X. and Zhao, Y., "Microwave thermal remediation of crude oil contaminated soil enhanced by carbon fiber", *Journal of Environmental Sciences*, 21(9), 1290 – 1295 (2009).

Devanney, J., The Tankship Tromedy: The Impending Disasters in Tankers, 2nd Edition, The CTX Press (2006).

Dickins, D.F., "The Double Hull Issue and Oil Spill Risk On the Pacific West Coast", Enforcement and Environmental Emergencies Branch, Ministry of Environment, British Columbia, Canada (1995).

Eliasson, J., Rauta, D. and Gunner, T., "Ballast Water Tank Coatings for the Future" CORROSION 2005, paper 05001, NACE International, Houston, TX (2005).

Enbridge Mainline Expansion, Mainline Expansions, http://www.enbridgeus.com/Delivering-Energy/Growth-Projects/Mainline-Expansions/ [Sept. 12, 2012]

Enbridge Northern Gateway, Project at a Glace, http://www.northerngateway.ca/project-details/project-at-a-glance/ [Aug. 24, 2012]

Enbridge, Enbridge Reports Oil Release At Pump Station Facility (Elk Point), June 19 (2012). http://www.enbridge.com/MediaCentre/News/ElkPoint.aspx [09.04.2012]

Enbridge, Enbridge 2011 Reference Temperatures, Provided from Enbridge to Canadian Association of Petroleum Producers (CAPP) (2011a).

Enbridge, 2011 Crude Characteristics, No. 42 (2011b). http://www.enbridge.com/DeliveringEnergy/Shippers/~/media/www/Site%20Documents/Delivering%20Energy/2011%20Mainline%20Crude%20Characteristics.ashx [Sept 2, 2012]

Energy Resources Conservation Board (ERCB) Directive 071, "Emergency Preparedness and Response Requirements for the Petroleum Industry", Energy Resources Conservation Board, Government of Alberta, Canada (2009).

Energy Resources Conservation Board (ERCB), News Release, June 20 (2012). http://www.ercb.ca/RSS/yp-starter/2268.aspx [Sept. 10, 2012]

Duda, R. O., Hart, P.E. and Stork, D.G., Pattern Classification. 2nd Edition, John Wiley & Sons, Inc., New York, NY (2001).

Farmer, Ed., "System for Monitoring Pipelines", US Patent 4,796,466, June 10 (1989).

Fingas, M., Fieldhouse, B., Mullin, J., "Studies on the Evaporation of Oil Spills", 17th Artic and Marine Oil Spill Program Technical Conference 182-212 (1994)

Fingas, M, "Studies on the Evaporation Regulation Mechanisms of Crude Oil and Petroleum Products", *Advances in Chemical Engineering and Science* 2 (2) 246-256 (2012)

Fingas, M, "Evaporation of Oil Spills: Development and Implementation of New Prediction Methodology" International Oil Spill Conference (2005)

Friesen, W.I., Petrovic, S., Donini, J.C. and Revie, R. W., "Corrosivity Evaluation Methodologies: Experience from Testing 60 Crudes Under pipeline operating Conditions", NACE Northern Area Eastern Conference 2012, NACE International, Houston, TX (*submitted*).

Fritt-Rasmussen, J, Brandvik, P.J, Villumsen, A. and Stenby, E.H., "Comparing Ignitability for In-situ Burning of Oil Spills for an Asphaltenic, a Waxy and a Light Crude Oil as a Function of Weathering Conditions Under Artic Conditions", *Cold Regions Science and Technology* 72 (2012)

Foroulis, Z.A., "Causes, mechanisms and prevention of internal corrosion in storage tanks for crude oil and distillates", *Anti-Corrosion Methods and Materials*, 28 (9), 4–9 (1981).

Foroulis, Z.A., "Corrosion and corrosion inhibition in the petroleum industry", *Materials and Corrosion*. 33 (3), 121-131 (1982).

Garo, J.P., Vantelon, J.P., Souil, J.M., Breillat, C. "Burning of Weathering and Emulsified Oil Spills", *Experimental Thermal and Fluid Science* (28) 753-761 (2004)

Gaspard, B., "Boilover – The Sleeping Giant" CODE Red Resource http://www.williamsfire.com/Libraries/CODE_Red/Boilover_Sleeping_Giant.pdf [Sept 12, 2012]

Geiger, G., Werner, T. and Matko, D., "Knowledge-based Leak Monitoring For Pipelines", 4th International Federation of Automatic Control (IFAC) Workshop on On-Line Fault Identification and Supervision in the Chemical Process Industries, Jejudo Islands (Korea), June (2001).

Geiger, G., "Leak Detection and Locating – A Survey". 35th Annual Pipeline Simulation Interest Group (PSIG) Meeting, Bern, Switzerland, October (2003).

Guedes Soares, C., Garbatov, Y., Zayed, A. and Wang, G "Corrosion wastage model for ship crude oil tanks", *Corrosion Science*, 50 (11), 3095–3106 (2008).

Guedes Soares, C., Garbatov, Y., Zayed, A., and Wang, G., "Influence of environmental factors on corrosion of ship structures in marine atmosphere", *Corrosion Science*, 51(9), 2014–2026 (2009).

Gunter, P., "The particularities of heavy oil response" International Conference and exhibition for spill prevention, preparedness, response and restoration, Interspill limited, May 13 (2009). http://www.interspill.com/previous-events/2009/13-May/pdf/1530_gunter.pdf [Oct. 1, 2012]

Hamilton, G., and Morton, B., "Kinder Morgan to proceed with $5-billion Trans Mountain pipeline expansion to Burnaby", Vancouver Sun, April 13(2012). http://www.vancouversun.com/business/Kinder+Morgan+proceed+with+billion+pipeline+expansion+Burnaby/6449009/story.html [Aug. 24, 2012]

Hannisdal, A., Orr, R. and Sjoblom, J., "Viscoelastic properties of crude oil components at oil-water interfaces 1.The effect of dilution", *Journal of Dispersion Science and Technology*, 28(1), 81-93 (2007).

Hartley, R.A., "Aspects of corrosion control in ships' tanks", Naval Engineers Journal, 96 (1), 33 – 52 (1984).

Hill, G.C., "Mechanisms of Microbial Corrosion", Inter-Industry Seminar on Corrosion in Cargo Tanks (CRUCOR), INTERTANKO, London, UK, October 8 and 9 (1998).

Hindin, B. and Leis, B., "Diluted Bitumen-Derived Crude Oil: Relative Pipeline Impacts", Battelle, Columbus, Ohio, USA, July 20 (2012). http://oilsandsfactcheck.org/wp-content/uploads/2012/07/Battelle_Dilbit-Relative-Pipeline-Impacts_072012.pdf [May 31, 2013]

Holt G., Mcclure R., "Wear caused gas leak in Olympic Pipeline" Seattle Post-Intelligencer May 24th (2004). http://www.seattlepi.com/local/article/Wear-caused-gas-leak-in-Olympic-pipeline-1145599.php [Nov.26, 2012]

Huang R.T., McFarland B.L. and Hodgman R.Z., "Microbial influenced corrosion in cargo oil tanks of crude oil tankers", CORROSIN 1997, paper 97535, NACE International, Houston, TX (1997).

Huber, M., Tanker Operations: A Handbook for the Person-In-Charger (PIC), Cornell Maritime Press, Cambridge, MD (2001).

International Association of Classification Society, "Guidelines for Coating Maintenance & Repairs for Ballast Tanks and Combined Cargo/Ballast Tanks on Oil Tankers", Rev.1, London, UK, June (2006).

International Association of Classification Society, "Double Hull Oil Tankers - Guidelines for Surveys, Assessment and Repair of Hull Structures", No. 96, London, UK, April (2007).

International Convention for the Prevention of Pollution from Ships, Regulations 13F and 13G to Annex 1 of the MARPOL 73/78 convention, 32nd session of the marine environmental protection, International Maritime Organization, March (1992).

International Tanker Owners Pollution Federation (ITOPF), "Oil Tanker Spill Statistics: 2009", London, England (2010).

Iwata, Y., Koseki, H., Janssens, M.L. and Takahashi, T., "Combustion Characteristics of crude oils", Fire and Materials, 25(1), p. 1 – 7 (2001).

JFE Steel Corporation, Development of New Corrosion-Resistant Steel for Greater Safety of Crude Oil Tankers, January 29 (2008). ,http://www.jfe-steel.co.jp/en/release/2008/080129.html [Sept. 10, 2012]

Jokuty, P. "Properties of Crude Oil and Oil Products" Environment Canada – Emergencies Science and Technology. (2005)

Kashima, K., Tanino, Y., Kubo, S., Inami, A,. and Miyuki, H, "Development of anti-corrosion steel for cargo oil tanks", International Symposium on Shipbuilding Technology (ISST), Osaka University, Japan, September (2007).

Kay, S. M., Fundamentals of Statistical Signal Processing, Volume 2. Prentice Hall, January 27 (1998).

Kremer, L. N. and Nguyen J., "On Line Method For Reducing Sludge Volume In Crude Oil Storage Tanks", CORROSION 2000, paper 00445, NACE International, Houston, TX (2000).

Krass, W., Kittel, A. and Uhde, A., Pipelinetechnik. Verlag TÜV Rheinland (1979).

Lane, R.A, "Under the Microscope: Understanding, Detecting, and Preventing Microbiologically Influenced Corrosion", *Journal of Failure Analysis & Prevention*, 5(5), 10 – 38 (2005).

Maritime Safety Committee (MSC), Resolution MSC 288 (87), "Performance Standard for Protective Coatings for Cargo Oil Tanks of Crude Oil Tankers", Maritime Safety Committee 87th session, International Maritime Organization (IMO) (2010a).

Maritime Safety Committee (MSC), Resolution MSC 289(87), "Performance Standard for Alternative Means of Corrosion Protection for Cargo Oil Tanks of Crude Oil Tankers", Maritime Safety Committee 87th session, International Maritime Organization (IMO) (2010b).

McIntyre, D. R,, "Laboratory Tests Comparing the Corrosivity of Dilbit and Synbit With Conventional Crudes Under Pipeline Conditions", NACE Northern Area Eastern Conference 2012, NACE International, Houston, TX (*submitted*).

MI Swaco, TPS-1S: Compact Thermal Phase Separation System (2012). http://www.slb.com/services/miswaco/services/drilling_waste_management/cuttings_treatment/tps1_compact.aspx [Sept. 9, 2012]

Morales, J.L., Perdomo, J.J., Ramirez, M. and Viloria, A., "Effect of crude oil contaminants on the internal corrosion in gas pipelines", CORROSION 2000, paper 04366, NACE International, Houston, TX (2000).

National Academy of Science (NAS), Committee on the Study of Pipeline Transportation of Diluted Bitumen, Presentation by Oliver Moghissi, Washington, DC, July 23 (2012). http://onlinepubs.trb.org/onlinepubs/dilbit/Moghissi072312.pdf [Aug. 24, 2012]

National Commission on the Deepwater Horizon Oil Spill and Offshore Drilling, "Response/Clean-Up Technology Research & Development and the BP Deepwater Horizon Spill", Staff Working Paper No. 7, January 11 (2011). http://www.oilspillcommission.gov/sites/default/files/documents/Updated%20Response%20RD%20Working%20Paper.pdf [Sept. 11, 2012]

National Energy Board (NEB), "Onshore Pipeline Regulations", SOR/99-294. Minister of Justice, Government of Canada, 1999. Amended Sept. 5 (2008).

National Energy Board (NEB), "Canada's Oil Sands: A Supply and Market Outlook to 2015", National Energy Board, Calgary, Alberta, October (2000). http://www.neb-one.gc.ca/clf-nsi/rnrgynfmtn/nrgyrprt/lsnd/lsndsspplymrkt20152000-eng.pdf [Sept. 12, 2012]

National Energy Board (NEB), "Remediation Process Guide, Cat. No. NE23-156/2011E", National Energy Board (2011). http://www.neb-one.gc.ca/clf-nsi/rsftyndthnvrnmnt/nvrnmnt/rmdtnprcssgd/rmdtnprcssgd-eng.pdf [Sept 9, 2012]

National Resources Canada (NRCan), "Maritime Safety in Canada" (2012). http://www.nrcan.gc.ca/media-room/news-releases/2012/6487 [Dec. 7, 2012]

National Transport Safety Board (NTSB), Board Meeting Presentation on "Enbridge Hazardous Liquid Pipeline Rupture and Release" by Matthew Nicholson on July 25 (2010). http://www.ntsb.gov/news/events/2012/marshall_mi/presentations.html [Sept 13, 2012]

National Transport Safety Board (NTSB), Pipeline Accident Brief (2010) http://www.ntsb.gov/doclib/reports/2010/PAB1001.pdf [Sept 5, 2012]

National Oceanic and Atmospheric Administration (NOAA), "Characteristic Coastal Habitats, Choosing Spill Response Alternatives", U.S. Department of Commerce, Washington, D.C., June (2010). http://response.restoration.noaa.gov/sites/default/files/Characteristic_Coastal_Habitats.pdf [09.05.2012]

National Research Council, Oil in the Sea III: Inputs, Fates, and Effects, The National Academic Press, Washington, DC (2003).

Nestle, A., Corrosion Inhibitors in Petroleum Production Primary. Recovery, Corrosion Inhibitors, ed. C.C. Nathan, NACE International, Houston, TX, p. 61-65 (1973).

Nippon Kaiji Kyokai (ClassNK), "Guideline for Corrosion Resistant Steel for COT", ClassNK, December (2010). http://www.ingenierosnavales.com/uploaded/Corrosion%20Resistant%20Steel%20for%20COT%20Guidelines.pdf. [Sept. 10, 2012]

Nippon Kaiji Kyokai (ClassNK), "Development of guidelines on corrosion resistant steels for cargo oil tanks", ClassNK Magazine, 63, 4-6 (2011).

Norton, J. D., Tonkins, W. and Flanders, B., "Slackline Operation of the Trans-Alaska Pipeline System at Thompson Pass", Energy and Sources Technology Conference and Exhibition, ETCE98-4690, American Society of Mechanical Engineers (1998a).

Norton, J. D., Tonkins, W. and Flanders, B., "Alyeska Remedies TAPS' Pipeline Vibrations at Thompson Pass", *Oil and Gas Journal*, 96 (22), July 1 (1998b).

Oil Pollution Act, "101 H.R.1465, P.L. 101-380", 101st United States Congress, Government of the United States of America, Washington, D.C. (1990).

Oghenejoboh, K.M., Puyate, Y.T. and Abowei, M.F.N., "Concentration distribution of spilled crude petroleum in different soils 2: Effects of volume of oil on spatial spread", *Pollution Research*, 27(4), 605-610 (2008).

Oghenejoboh, K.M. and Puyate, Y.T., "Experimental investigation of the effects if crude oil physical properties on its diffusion rate in soil medium", *Journal of Industrial Pollution Control*, 26(2), 131-137 (2010)

Okamoto, K., Watanabe, N., Hagimoto, Y., Miwa, K. and Ohtani, H., "Evaporation characteristics of multi-component liquid", *Journal of Loss Prevention in the Process Industries*, 23(1), 89 – 97 (2010).

Palacios, C.A., Hernandez, Y., "Application of simulation techniques for internal corrosion prediction", CORROSION 1997, paper 97002, NACE International, Houston, TX (1997).

Parry, B., MacTaggart, R. and Toerper, C., "Compensated Volume Balance Leak Detection on a Batched LPG Pipeline", Proceedings Offshore Mechanics & Arctic Engineering Conference (OMAE), New York, NY (1992).

Parunov, J., Žiha, K. and Mage, P., "Corrosion wastage of oil tankers – a case study of an aged ship", International Congress of International Maritime Association of the Mediterranean (IMAM), Guedes Soares and Kolev Editors, Varna: Taylor & Francis Group, p. 271-276 (2008).

Peet, G., "Tanker design: recent developments from an environmental perspective", Environmental Technology in the Oil Industry, 2nd Edition, Springer Science Media B.V., Dordrecht, p. 215-218 (2008).

Penspen Integrity (Penspen), "State of the Art Report - Dilbit Corrosivity", Canadian Energy Pipelines Association, Richmond Upon Thames, United Kingdom (2013). http://www.cepa.com/wp-content/uploads/2013/02/FINAL-Penspen-Report-Dilbit_Corrosivity_Final.pdf [May 31, 2013]

Pichler, H. and Hense, H., "Crude oil vapour pressure testing is an important safety check in the transport, storage and blending of crude oil", Petroleum Technology Quarterly, 1362-363X, p. 17 (2012).

Province of Alberta, "Pipeline Act", Alberta Queen's Printer, Edmonton, Alberta (CANADA), Revised May 13 (2011).

Ramseur, J.L., "Deepwater Horizon Oil Spill: The Fate of the Oil", Congressional Research Service (2010) http://fpc.state.gov/documents/organization/154155.pdf [Sept 30, 2012]

Rauta, D., "Corrosion in Double Hull Tankers", Tanker Operator, p. 15, May (2004).

Reeves, J., "Gulf Oil Spill Remnants From Hurricane Isaac Wash Up Years After Disaster", Huffington Post, September 6 (2012). http://www.huffingtonpost.com/2012/09/06/gulf-oil-spill-hurricane- isaac_n_1861657.html#slide=865459 [Oct. 22, 2012].

Roberts, R. "Using Physical and Chemical Properties to Manage Flammable Liquid Hazards" Methanol Institute – Technical Bulletin (2011). http://www.methanol.org/Health-And-Safety/Technical-Bulletins/Technical-Bulletins/UsingPhysicalandChemicalPropertiestoManageFlam-%283%29.aspx [Nov.26, 2012]

Royal Society of Canada (RSC), "Report of the Expert Panel on Science Issues Related to Oil and Gas Activities, Offshore British Columbia", Natural Resources Canada, February (2004).

Saniere, A., Hénaut, I. and Argillier, J.F., "Pipeline transportation of heavy oils - a strategic, economic and technological challenge", *Oil Gas Science Technology Review*, 59(5), 455-466 (2004).

Schlieps, J. and Battaglia, C., "Rehabilitation of Bitumen Contaminated Wildlife", 11th International Effects of Oil on Wildlife Conference, Focus Wildlife Canada, New Orleans, LA, January 24 - 28 (2012)

Shiomi, H., Kaneko, M., Kashima, K., Imamura, H. and Komori, T., "Development of anti-corrosion steel for cargo oil tanks, Tanker Structure Co-Operative Forum (TSCF) 2007 Shipbuilders Meeting, Busan, Korea, October 24th and 25th (2007).

Simanzhenkov, V. and Idem, R., Crude Oil Chemistry, Marcel Dekker Inc., New York, NY August 8th (2003).

SINTEF, "Oil Spill Containment by use of Air Bubbles", SINTEF Materials and Chemistry, Trodheim, Norway (2012). http://www.sintef.no/project/OilandGas/pdf/bubble-booms.pdf [Sept. 9, 2012]

Skinner, S.K. and Reilly, W.K., "The EXXON VALDEZ Oil Spill: A Report to the President", The National Response Team, Government of the United States of America, May (1989).

SOLAS, "Corrosion Protection of Cargo Oil Tanks of Crude Oil Tankers", International Convention for the Safety of Life at Sea (SOLAS) Regulation II-1/3-11, Intermaritime Certification Services (2012).

Stiver, W., Mackay, D., "Evaporation Rate of Spills of Hydrocarbons and Petroleum Mixtures", *Environmental Science and Technology*, 18 834-840 (1984)

Store, M., Passade-Boupat, N., Bonis, M. and Adams, B., "Inhibitive properties of crude oils: can we count on them?", CORROSION 2011, paper 11061, NACE International, Houston, TX (2011).

Swift, A. and Shope, E., "Tar Sands Pipelines: Presenting Unaddressed Hazards to Public Safety, Natural Resources Defence Council, New York, NY. December (2010). http://dirtyoilsands.org/files/NRDC_TarSandsBitumen.pdf [Sept. 12, 2012]

Swift, A., Casey-Lefkowitz, S. and Shope, E., "Tar Sands Pipelines Safety Risks", National Resource Defense Council, New York, NY, February (2011a). http://www.nrdc.org/energy/files/tarsandssafetyrisks.pdf [Sept. 11, 2012]

Swift, A., Lemphers, N., Casey-Lefkowitz, S., Terhune, K. and Droitsch, D., "Pipeline and Tanker Trouible: The Impact to Britich Columbia's Communities, Rivers, and Pacific Coastline from Tar Sands Oil Transport", National Resource Defense Council, New York, NY., November (2011b). http://www.nrdc.org/international/ files/PipelineandTankerTrouble.pdf [Sept. 11, 2012]

Technische Regeln für Rohrfernleitungsanlagen (TRFL). Carl-Heymanns-Verlag, Germany, 2010.

Thavasi, R., Singaram, J., and Banat, I., "Effect of biosurfactant and fertilizer on biodegration of crude oil by marine isolates of Bacillus megaterium, Corynebacterium kutscheri and Pseudomonas aeruginosa", *Bioresource Technology*, 102(2), 772-778 (2011).

Torero, J., Olenick, S.M., Garo, J., and Vantelon, J.P., "Determination of the Burning Characteristics of a Slick of Oil on Water", Spill Science & Technology Bulletin, (8) 379-390 (2003)

TransCanada Pipeline Limited (TCPL), Keystone XL Pipeline Project. http://www.transcanada.com/keystone.html [Sept. 11, 2012]

Tscheliesnig, P., "Detection of corrosion attack on ships, especially oil tankers, with Acoustic Emission", Proceedings 16th World Conference on Nondestructive Testing (WCNDT), Montreal, QC, August 30 – September 3 (2004).

United States Geological Survey (USGS), "Toxic Substances Hydrology Program – Regular Gasoline – Galloway Township, New Jersey", USGS (2011). http://toxics.usgs.gov/sites/gall_page.html [09.05.2012]

United States Department of State (US DOS), "Final Environmental Impact Statement for the Keystone XL Project", August 26 (2011). http://www.keystonepipeline-xl.state.gov/ [Sept. 3, 2012].

United States Department of Transportation (US DOT), "Appendix B: PHMSA 57 Special Conditions for Keystone XL and Keystone Compared to 49 CFR 195", March (2013). http://keystonepipeline-xl.state.gov/documents/organization/205595.pdf [May11, 2013].

VdTÜV 1051, Wasserdruckprüfung von erdverlegten Rohrleitungen nach dem Druck-Temperatur-Messverfahren (D-T-Verfahren). VdTÜV-Merkblatt (Germany).

Verma, M.K., "Calculation of Hydrocarbon-in-Place in Gas and Gas-Condensate Reservoirs—Carbon Dioxide Sequestration", United States Geological Survey, U.S. Department of the Interior, Open-File Report, 2012–1033, Reston, VA (2012)

Wald, A., Sequential Analysis, John Wiley and Sons, New York, NY (1947).

Wang, G., Spencer, J. and Elsayed, T., "Estimation of corrosion rates of structural members in oil tankers", 22nd International Conference on Offshore Mechanics and Arctic Engineering (OMAE), Cancun, Mexico, June 8 –13 (2003).

Wang, J., Yin, J., Ge, L. and Zheng, J., "Using Floatation to Separate Oil Spill Contaminated Beach Sands" , *Journal of Environmental Engineering*, 136(1), 147-151 (2010).

Whaley, R. S., Nicholas, R.E. and Van Reet, J.D., "Tutorial on Software Based Leak Detection Techniques", 24th Annual Meeting, Pipeline Simulation Interest Group (PSIG), October 22 – 23 (1992).

Wintonyk, D., "Major oil spill at Kinder Morgan B.C. facility", CTV News, May 7 (2009). http://bc.ctvnews.ca/major-oil-spill-at-kinder-morgan-b-c-facility-1.396578 [Sept. 11, 2012]

Wu, N., Kolb, G. & Torero, J.L., "The effect of weathering on the flammability of a slick of crude oil on a water bed", *Combustion Science and Technology*,161, 269-308 (2000).

XPrize Foundation, Wendy Schmidt Oil Cleanup X Challenge (2011). http://www.iprizecleanoceans.org/ [Sept. 9, 2012]

Yoshida, M., "Corrosion Protection for COT of Crude Oil Tankers by Corrosion- Resistant Steel", Japan Ship Technology Research Association (JSTRA), Asian Shipbuilding Experts' Forum (2007).

Zahed, M.A., Aziz, H.A., Mohamed, H.I., Mohajeri, L. and Mohajeri, S., "Optimal conditions for bioremediation of oily seawater", *Bioresource Technology*, 101(24), 9455-9460 (2010).

Zhang, X. J., "Statistical Leak Detection in Gas and Liquid Pipelines", *Pipes and Pipelines International*, 38(4), 26 – 29 (1993).