Comparison of the Corrosivity of Dilbit and Conventional Crude

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EXECUTIVE SUMMARY

Pipeline expansions for the transportation of Canadian crude to refining markets in the United States are currently under regulatory review. The transported oil originates primarily from the Alberta oil sands and consists of diluted bitumen, also referred to as dilbit. Alberta Innovates – Technology Futures completed a project for Alberta Innovates – Energy and Environment Solutions reviewing the current status on the corrosivity of dilbit in pipelines as compared to conventional or 'non-oil sands derived' crude oil.

It has been suggested that dilbit has higher acid, sulfur, and chloride salts concentrations, as well as higher concentrations of more abrasive solids. It is furthermore suggested that dilbit transmission pipelines operate at higher operating temperatures compared with conventional crude, which would make the dilbit more corrosive, thus leading to a higher failure rate than observed for pipelines transporting conventional crude. This review examines these concerns in light of the properties of dilbit in comparison with conventional oils. In addition, statistical data are presented to show if the concerns are supported by operating experience.

Conventional crude and dilbit are subject to quality control measures and regulation. Pipeline operators employ further measures during transportation to manage and control the quality of delivered crude. Alberta crude quality information is available online and accessible to the public. The properties of heavy, medium, and light conventional Alberta crude oils were compared with three dilbit and one dilsynbit crude.

Whereas two of the four dilbit crudes displayed a slightly higher naphthenic acid and sulfur concentration than the conventional Alberta heavy crudes, there are conventional crudes on the market that have displayed higher values yet. The chloride salt concentrations were either comparable or lower than all grades of conventional crude. Naphthenic acid, sulfur, and chloride salt concentrations can result in corrosion at temperatures greater than 200 C at refineries, where mitigation is addressed through upgrading of materials and the use of inhibitors. At the much lower pipeline transportation temperatures, the compounds are too stable to be corrosive and some may even decrease the corrosion rate.

The sediment levels of the dilbit crudes were comparable to or lower than the conventional crudes, except for a dilsynbit crude, which showed more than double the quantity of solids than most other crudes, but was still well below the limit set by regulatory agencies and industry. The solids size distribution is unknown as is the role of larger size solids in the formation of pipeline deposits. Erosion corrosion was found to be improbable and erosion, if present, is expected to be gradual and observed by regular mitigation practices.

The dilbit viscosities are comparable to those of heavy conventional crudes, where the viscosity is controlled and adjusted for temperature through the addition of diluent. The

resulting dilbit viscosity supports acceptable operating temperatures, which will be monitored at and downstream of the pumping stations.

Adjustment of the Alberta and U.S. pipeline failure statistics to compare similar crude oil pipeline systems on an equivalent basis indicated that the Alberta systems (with a large percentage of dilbit lines) experienced comparable internal corrosion failure rates than the U.S. systems (predominantly conventional crude lines).

Pipeline steel wet by oil does not corrode. The basic sediment and water (BS&W) content of crude oil transmission pipelines is limited to 0.5 volume percent. This water is primarily present as a stable emulsion, maintaining an oil wet pipe, protected from corrosion. Pitting corrosion has been observed underneath sludge deposits. These deposits are a mix of sand and clay particles, water, and oil products. The corrosivity of these sludges varies but seems to be linked to water content, which can exceed 10%, and large bacterial populations. The sludge deposition mechanism and the contributions of each of its components to its corrosivity are not clear. Sludge deposition and similar underdeposit corrosion is not unique to dilbit lines and also has been observed in pipelines transporting conventional crudes.

This review has indicated that the characteristics of dilbit are not unique and are comparable to conventional crude oils. Additional work is recommended in areas of sludge formation, deposition, and underdeposit corrosion. It is further recommended to expand the current crude oil property database to include downstream qualities, as well as information on H_2S concentration, asphaltene and water content, and viscosity. Finally, it is recommended that better statistics be made publicly available with separate information on dilbit and conventional crude oil pipelines as well as for upstream gathering lines and transmission pipelines.

TABLE OF CONTENTS

1.0 INTRODUCTION

TransCanada Pipeline's (TCPL's) $13 billion Keystone pipeline system will provide a secure and growing supply of Canadian crude oil to the largest refining markets in the Unites States. The second Phase of this project has been completed in February 2011, enabling the transport of 591,000 barrels of oil per day from Hardesty, Alberta to Cushing, Oklahoma, and Patoka, Illinois. Phases III and IV will increase the pipeline's capacity to 1.3 million barrels of oil per day to major refineries in the Houston area. These latter two phases are under regulatory review. The transported oil primarily originates from the oil sands. Crude or bitumen obtained from the oil sands is too viscous to transport by pipeline and needs to be diluted with diluent, hence the name 'dilbit.' In the context of this report, conventional oil refers to 'non-oil sands derived' crude oil.

The same month that TCPL completed Phase II of the Keystone pipeline system, a report was issued by a group of environmental action groups on Tar Sands Pipeline Safety Risks [1]. The report contains many damaging statements to the use of dilbit, most notably that "diluted bitumen is more corrosive than conventional or crude products and is more likely to result in pipeline failures," and that "Alberta pipelines have had a higher failure rate than similar U.S. pipelines due to leaks caused by internal corrosion from transportation of diluted bitumen (dilbit)." The ERCB responded within hours of the release of the report and twice on the same day with news releases responding to 'falsehood' of the report's statements [2].

Environmental groups opposed to the pipelines continue to find material to fuel their concerns: the more than 800,000 gallons of oil spilled into the Kalamazoo River in Michigan last year came from the Cold Lake oil sands region, and the Exxon Mobil spill of 42,000 barrels of oil in the Yellowstone River may have contained dilbit. Protestors against the Keystone pipeline are gathering in demonstrations across North America leading to mass arrests and drawing widespread attention.

The arguments of these environmental groups don't go unheard with congressmen and other government officials, who have iterated reported statements and concerns [3]. The United States Department of States (DOS) has spent the last three years in review with the industry, scientific community, and other interest parties (including numerous public meetings), evaluating the purpose and need for the Project (pipeline), alternatives, and the associated potential environmental impacts. The result was issued on August 26, 2011 in a Final Environmental Impact Statement (FEIS), a comprehensive, detailed volume of work that is available to the public [4]. Public hearings were held and online comments were accepted.

The US Department of Transportation's (DOT) Pipeline and Hazardous Materials Safety Administration (PHMSA) administers the national regulatory program to ensure the safe transportation of hazardous materials by pipeline. In February 2011, PHMSA issued 57 Project-specific Special Conditions above and beyond the requirements of the pipeline code for the Keystone pipeline [Appendix U, 4]. In a news release on August 26, TCPL stated that they are pleased with the FEIS, which reaffirmed the environmental integrity of the project and concluded that oil sands derived crude oil does not have unique characteristics that would suggest the potential of higher corrosion rates during pipeline transportation. The company noted that incorporation of the 57 Special Conditions would result in a pipeline with a greater degree of safety than typical domestic pipelines.

Despite the review completed by the US DOS, there still exists confusion with regard to the corrosivity of dilbit versus that of conventional oil. The 57 Special Conditions are not sufficient according to the environmental groups opposed to the pipelines. Alberta Energy Minister Ron Liepert considers it a challenge of combating emotion with facts, and assures that the facts could be obtained without too much difficulty [5]. Concerns continue to surface in the media [6] and in the face of few factual studies and a strong confidence in the ERCB tracking statistics that dilbit is not more corrosive than conventional oil, corrosivity claims continue to be used as fuel by certain environmental groups. The current work will review the current status of information and concerns regarding the corrosivity of dilbit in pipeline transportation as compared to conventional crude oil. The focus of this work will be on transmission or transportation pipelines that transport oil over large distances to delivery points such as refineries and are subject to tariff quality specifications that include a limitation on the total amount of allowable sediment and water of 0.5 percent by volume. The Keystone pipeline is such a pipeline.

2.0 OBJECTIVES

To provide a confidential report including:

- Summary of the current concerns
- Status review on the corrosivity of dilbit in pipeline transportation as compared to conventional oil and
- Description and analysis of the current scientific information, assessing the validity of the concerns, identifying significant gaps, and recommending follow-up studies.

3.0 CURRENT CONCERNS

The Natural Resources Defense Council [1] has done an excellent job in summarizing the concerns presented by interest groups regarding the corrosivity of dilbit as compared to conventional crude oil and many of the same concerns have been expressed in other conversations and publications. The following is a summary of claims with regard to dilbit corrosivity [1] and include a few corrosion concerns from comments to the FEIS [4].

It has been suggested that dilbit may be more corrosive to pipeline systems than conventional crude and the following claims have been made:

Claim #1: Dilbit contains fifteen to twenty times higher corrosive acid concentrations than conventional crude oil [1].

Claim #2: Dilbit contains five to ten times as much sulfur as conventional crudes; the additional sulfur can lead to the weakening or embrittlement of pipelines [1].

Claim #3: Dilbit has a high concentration of chloride salts, which can lead to chloride stress corrosion cracking in high temperature pipelines [1].

Claim #4: Oil sands crude contains higher quantities of abrasive quartz sand particles than conventional crude, which can erode the pipelines [1].

Claim #5: It has been suggested that dilbit could be up to seventy times more viscous than conventional crude oil. It has been claimed that the increase in viscosity creates higher temperatures as a result of friction [1].

Claim #6: The Alberta pipeline system has had approximately sixteen times as many spills due to internal corrosion than the U.S. system, indicating that the dilbit is much more corrosive than the conventional oil that is primarily flowing through U.S. lines [1].

Claim #7: An increased risk of internal corrosion may be related to the sediment composition of dilbits and specific sediment characteristics, including particle hardness and size distribution [4].

Claim #8: A combination of chemical corrosion and physical abrasion can dramatically increase the rate of pipeline deterioration [1].

Claim #9: As a result of the high viscosity of dilbit, pipelines operate at temperatures up to 158 F, whereas conventional crude pipelines generally run at ambient temperatures. The high temperature would significantly increase the corrosion rate which doubles with every 20 degree Fahrenheit increase in temperature [1].

Claim #10: Dilbit pipelines may be subject to a higher incidence of external stress corrosion cracking [4].

These claims will be examined in light of the properties of dilbit in comparison with conventional oils. In addition, statistical data are presented to show if the concerns are supported by operating experience.

4.0 QUALITY CONTROL OF DILBIT PROPERTIES

Any discussion on the different risks and hazards of the transportation of dilbit versus that of conventional crude should start with a consideration of the differences in properties of the oils that enter the transmission pipeline system and how these properties are controlled and managed by the industry using regulatory and industrial quality assurance guidelines.

The Canadian Association of Petroleum Producers (CAPP) has established a crude oil committee to work with regulated segments of the industry such as transportation, storage, and market access. Crude oil quality subcommittees address specific crude quality issues and issues inherent in refining and shipping these crudes. Priorities that are addressed on an ongoing basis include [14]:

- management of oil quality issues to ensure maximum value amid growing crude oil types and blends, specifically,
  - condensate quality specifications and quality recommendations
  - new crude approvals process
  - quality test method improvements

One significant effort pertains to the definition of quality specifications of the condensate stream managed by Enbridge, also referred to as CRW [7]. This condensate stream consists of field condensates, ultra-light sweet crudes, and refinery and upgrader naptha streams from several supply sources. Historically, this condensate commodity was sold to downstream refiners. Currently, its main use is as diluent for Canadian heavy crude. Dilbit uses typically ~25% of condensate, where companies use their own supply sources of light hydrocarbons or purchase CRW. Establishment of a CRW criteria document provides a guideline for new streams that are proposed to be blended with the CRW stream and ensures that the CRW pool characteristics remain acceptable for the use as diluent. Quality specifications include minimum and/or maximum levels, a referee test method and test frequency, as well as comments on enforcement measures to be taken [8].

Crude Quality Inc. (CQI) is a private company in Edmonton with a mandate "to produce, provide, and manage crude quality information that increases the productivity of our customers and the petroleum industry" [9]. CQI's crude quality measurement and management system is supported by Canadian producer associations, Alberta/Canadian and US government departments, including the Energy Resources Conservation Board (ERCB), and Canadian and US technical organizations. CQI maintains a website with available data for most western Canadian crude oils, including conventional crudes as well as dilbit and other nonconventional grades and blends [10]. The site was established to enhance communication of data on the quality and quality issues of western Canadian crudes. Figure 1 summarizes some of the data in a series of graphs (see also Table 1). These are the properties of the crude oils entering the transmission pipeline system to be delivered to the refineries, after the addition of diluent in case of the dilbits. Enbridge has additional crude oil characteristics on their website [11]. Petroleum quality specifications of crude permitted in the pipeline system is further defined in National Energy Board (NEB) and Federal Energy Regulatory Commission (FERC) regulatory documents outlined in pipeline Tariffs (e.g. [12], [13], and [14]).

The above illustrates that conventional crude or dilbit is not transported indiscriminately without quality control measures and regulation. Work is ongoing continuously to improve overall quality control and product quality, primarily considering the effects on refining of the product.

The majority of pipelines are used for batches of different categories of crude. The pipeline operators are responsible for managing and controlling the quality of delivered crude and a number of measures are applied, including [15, 16]:

1. The use of turbulent flow, which minimizes the mixing area between batches. In laminar flow, the flow velocity near the pipe wall is much smaller than the velocity in the center of the pipe, which results in a relatively large mixing zone when one crude is followed by a different crude. The flow velocity is more even throughout the pipe cross-section in the case of turbulent flow, decreasing the subsequent mixing zone between different crudes.
2. The establishment of a crude ranking order, which serves as a guideline when changing crudes (e.g. a Medium Crude may be followed by a Medium Sour Crude, but not by a Heavy Crude).
3. The use of buffers at the front and the back of the batch to prevent mixing with the preceding batch or the following batch when the crude contains components that are undesirable by the refineries. In some instances, interface pigs can be used, but some contamination can occur at the pump and pig trap locations.
4. Maximization of batch size will minimize contamination from the mixing zones.
5. Minimization of start/stop operations.
6. Minimization of contamination in tanks from receipt to delivery

Although the operator will make an effort to deliver the same type of crude as received, the operator is not obligated to deliver the identical crude [12, 13, 14]. Changes in density, specification, quality and characteristics as a result of the transportation in the pipeline system are acknowledged. Unfortunately, crude quality information of the received oil product is not currently readily available. CQI is currently working with industry partners on the development of a downstream quality database for direct comparison with the upstream qualities with the goal to provide financial incentives for consistency and rateability [9]. The transparency offered by the information of crude oil quality databases on both the shipped and delivered product will be of tremendous assistance in communications between industry and the public.

Table 1 Crude Designation Used in Figure 1

Crude	**Type of Crude and Designation Used in Figure 1**
Bow River North	Heavy Sour A
Bow River South	Heavy Sour B
Lloyd Blend	Heavy Sour C
Fosterton	Heavy Sour D
Lloyd Kerrobert	Heavy Sour E
Midale	Medium Sour A
Mixed Sour Blend	Medium Sour B
Sour High Edmonton	Medium Sour C
Sour Light Edmonton	Light Sour A
Light Sour Blend	Light Sour B
Mixed Sweet Blend Crude	Light Sweet A
Access Western Blend	Dilbit A
Cold Lake	Dilbit B
Seal Heavy	Dilbit C
Albian Heavy Synthetic Crude	Dilsynbit A

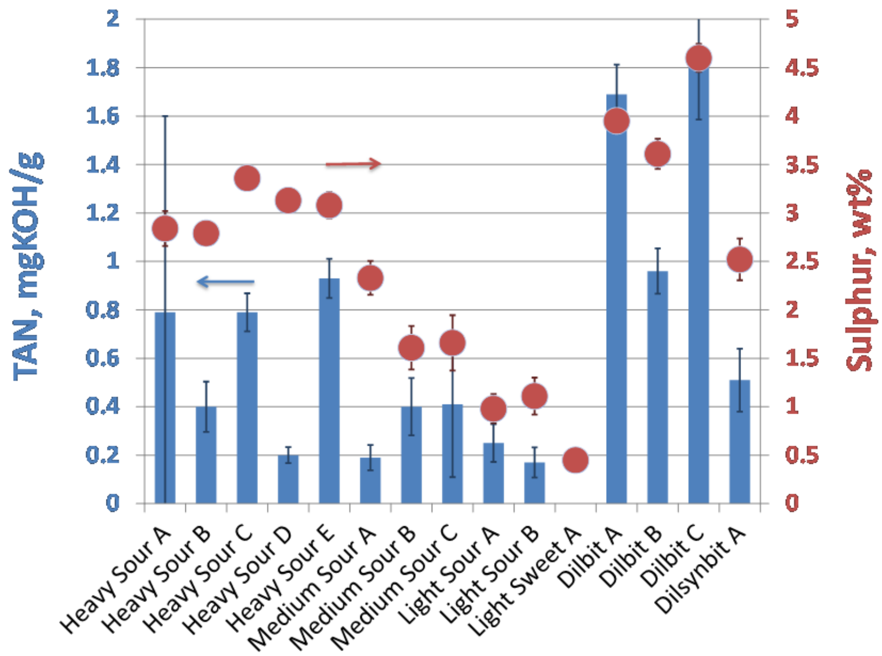


Figure 1a Properties of various conventional crudes and dilbits in Western Alberta illustrating acidity and sulphur contents. The data were obtained from Crude Quality Inc.'s website crudemonitor.ca [10]. Error bars represent the standard deviation over five years of data.

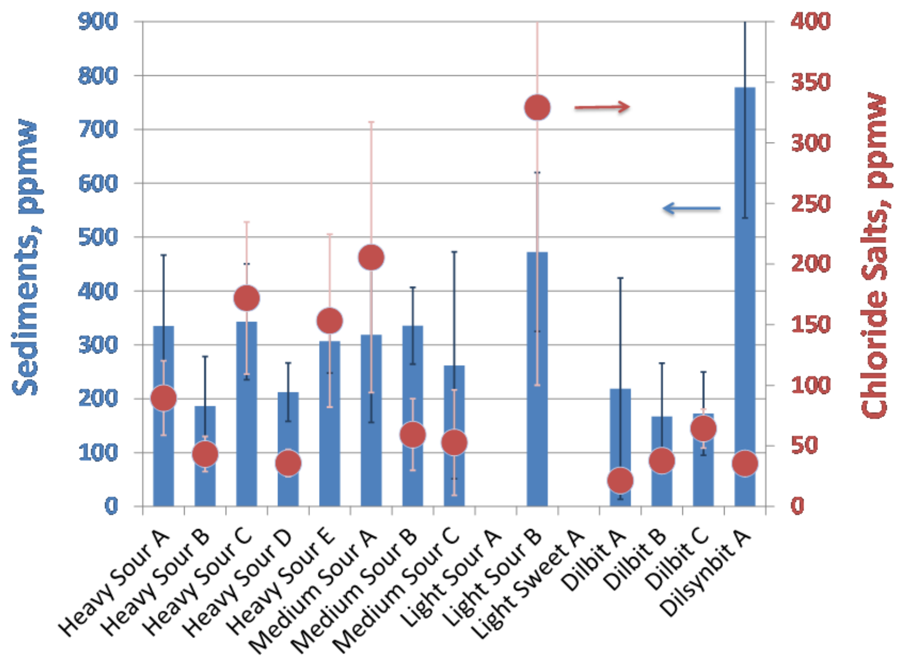


Figure 1b Properties of various conventional crudes and dilbits in Western Alberta illustrating the content of sediments and chloride salts. The data were obtained from Crude Quality Inc.'s website crudemonitor.ca [10]. Error bars represent the standard deviation over five years of data.

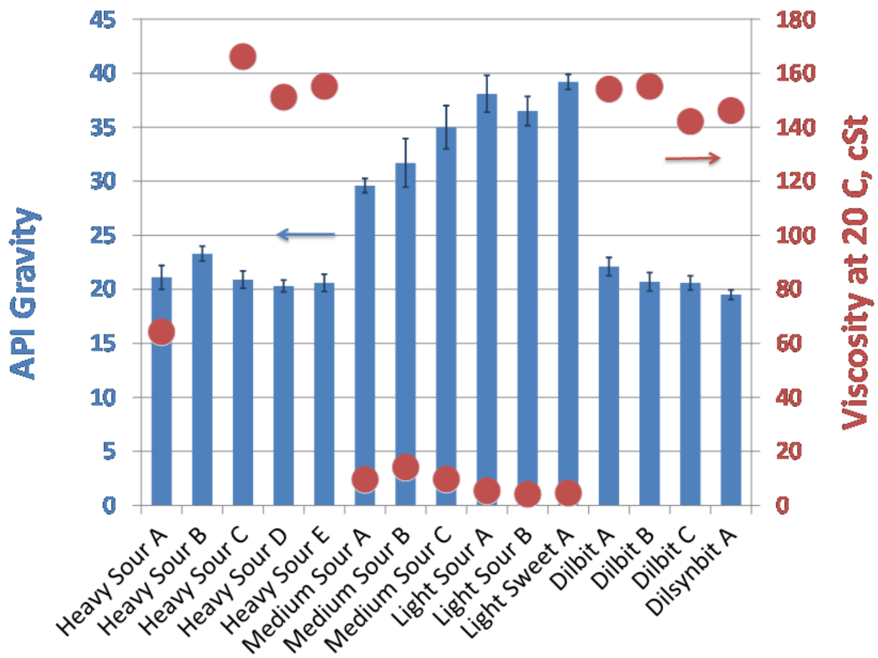


Figure 1c Properties of various conventional crudes and dilbits in Western Alberta illustrating the degree of API gravity and viscosity (after ref [11]). The API gravity data were obtained from Crude Quality Inc.'s website crudemonitor.ca [10]. Error bars represent the standard deviation over five years of data. One representative set of viscosity data is plotted.

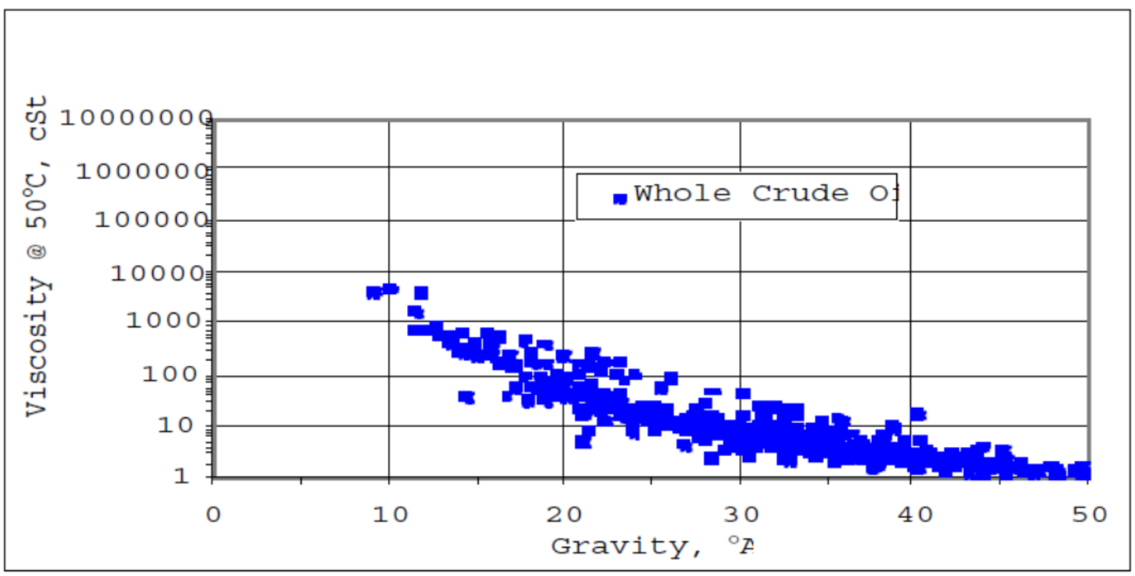


Figure 1d The gravity-viscosity relationship of conventional crude oils (after ref [17]).

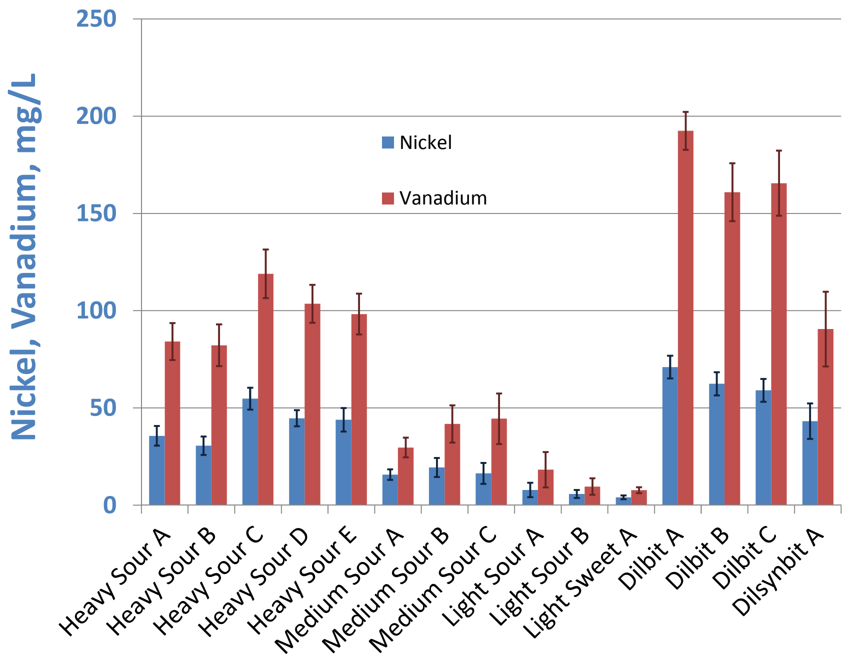


Figure 1e Properties of various conventional crudes and dilbits in Western Alberta illustrating heavy metal concentrations. The data for were obtained from Crude Quality Inc.'s website crudemonitor.ca [10]. Error bars represent the standard deviation over five years of data.

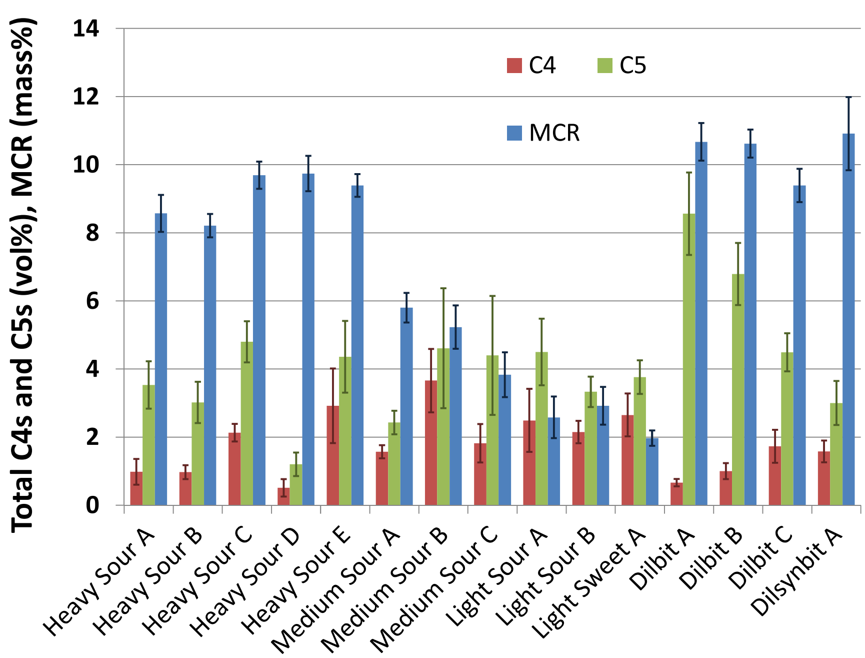


Figure 1f Properties of various conventional crudes and dilbits in Western Alberta illustrating fractions of light carbons and Micro Carbon Residue (MCR). The data were obtained from Crude Quality Inc.'s website crudemonitor.ca [10]. Error bars represent the standard deviation over five years of data.

5.0 DILBIT AND CONVENTIONAL CRUDE OIL PROPERTIES

With quality control measures in place, the properties of crudes entering the pipeline will be within defined boundaries. Yet, differences can be observed across the different crudes as well as within each crude category. Figure 1 displays data obtained from the Crude Monitor [10], where the plotted data are averages over periods of approximately five years. Error bars indicate the standard deviation. Data is presented for five different conventional heavy sour crudes, three conventional medium sour crudes, two conventional light sour crudes, one conventional light sweet crude, three dilbit crudes and one dilsynbit crude. Whereas dilbit can also refer to heavy conventional crudes that have been diluted with diluent or diluted crudes obtained by other means e.g. enhanced oil recovery, the dilbits in Figure 1 refer to oil sands crudes, where dilbit A is obtained from steam assisted gravity drainage (SAGD) processes and dilbits B and C from cyclic steam stimulation (CSS). Oil sands crude obtained from mining operations were either upgraded or blended with other crudes. For this reason, dilsynbit A has been added, which originates from mining operations, but is partially upgraded.

5.1 Naphthenic acids

Claim #1: Dilbit contains fifteen to twenty times higher corrosive acid concentrations than conventional crude oil [1].

Under refinery conditions and temperatures, naphthenic acids compounds can be corrosive. Naphthenic acids are a group of organic acids measured in terms of a total acid number (TAN), which is obtained by titration of the oil with KOH. TAN numbers have, therefore the units of mg KOH/g. Crude oils with TAN values greater than 0.5 are generally considered corrosive. However, recent work has indicated that not all naphthenic acids are equally corrosive and the acid groups attached to large hydrocarbon molecules found in heavy crudes and dilbits are more stable and less corrosive [19, 20, 21, 22]. Consequently, the TAN number is not necessarily reflective of the corrosivity of crude at elevated temperatures.

Figure 1a indicates a higher TAN for dilbits A and C, whereas dilbit B and dilsynbit A are comparable to the conventional heavy sour crudes. Research is continuing into the effects of these parameters at refineries, where upgrading of materials and the use of inhibitors can be used to mitigate any increase in corrosivity [19]. However, the acids are too stable to be corrosive under transmission pipeline temperatures. On the contrary, long chain organic acids have been found to decrease the corrosion rate at room temperature [23]. Furthermore, a number of Californian crudes have TAN numbers up to 3.2, and these crudes have been produced and transported by pipeline throughout California for many years [24].

5.2 Sulphur content

Claim #2: Dilbit contains five to ten times as much sulfur as conventional crudes; the additional sulfur can lead to the weakening or embrittlement of pipelines [1].

Under refinery conditions and temperatures, organic sulphur compounds can be corrosive. A wide variety of sulphur compounds are present in crude oil, which, when heated, will be released as corrosive hydrogen sulphide. The release of hydrogen sulphide again depends on the stability of the organic sulphur compound, and high temperatures between 220 and 400 C are required. With a wide variety of sulphur compounds and stabilities, the sulphur content of crude is also not a good measure of the corrosivity of crude at refinery conditions [22].

Similar to the TAN numbers, Figure 1a indicates a higher sulphur concentration for dilbits A and C, whereas dilbit B and dilsynbit A are comparable to the conventional heavy sour crudes. Under transmission pipeline temperatures, organic sulphur compounds are too stable to be corrosive. At room temperature, sulphur containing compounds were found to have no effect or resulted in a decrease in the corrosion rate [23].

The sulphur content does not correlate to the hydrogen sulfide content, which is not typically reported. As an example, two Mexican crudes with sulfur contents of 3.4% and 0.9% contained 100 ppm and 116 ppm of H_2S, respectively [4]. Small concentrations of H_2S may be present in sour as well as sweet crudes. Concentrations could vary from a few ppm to over a hundred ppm. The CRW diluent is limited to 20 ppm of H_2S [8]. Although the H_2S concentrations in dilbits are not available, there is no indication that these levels would be higher than in conventional crudes [4]. If available hydrogen sulfide could separate from the oil into an aqueous phase in the pipeline, the corrosivity of the water could increase. This would be valid for all oil systems and not specific to dilbit lines.

5.3 Chlorides

Claim #3: Dilbit has a high concentration of chloride salts, which can lead to chloride stress corrosion cracking in high temperature pipelines [1].

Figure 1b illustrates the levels of chloride salts for the crudes; light sour crude A and light sweet crude A did not have any data. The highest chloride salt concentration was observed for the conventional light sour B crude, with the dilbits displaying some of the lowest salt concentrations. Chloride salts can lead to the formation of strong hydrochloric acid in the presence of steam at upgrading and processing temperatures greater than 150 C, which can result in serious corrosion problems [26]. These conditions are not encountered in transmission pipelines. In fact, it has been shown that high salinity brines in contact with oils did not affect the corrosion rate [25]. Chloride stress corrosion cracking can be an issue in stainless steel equipment, but is not a mechanism encountered in carbon steel transmission pipelines [53].

5.4 Sediments

Claim #4: Oil sands crude contains higher quantities of abrasive quartz sand particles than conventional crude, which can erode the pipelines [1].

Figure 1b illustrates the levels of sediments for the crudes; light sour crude A and light sweet crude A did not have any data. The sediment content in Figure 1b is far below the limit of 0.5 volume percent (water + sediment) specified in the pipeline tariffs [12, 13, 14]. The sediment levels of the dilbit crudes were comparable to or lower than the conventional crudes, except for the dilsynbit crude with an oil sands mining origin, which showed more than double the quantity of solids than most other crudes. However, at ~800 ppmw (~0.027 volume percent), it is still well below the limit set by regulatory agencies and industry.

5.5 API gravity and viscosity

Claim #5: It has been suggested that dilbit could be up to seventy times more viscous than conventional crude oil. It has been claimed that the increase in viscosity creates higher temperatures as a result of friction [1].

The API gravity is a measure of how ‘heavy’ the crude is; heavy crudes have low degrees of API gravity (10-25) and light crudes have high degrees of API gravity (30-40). The formula for API gravity is defined by:

$$\text{API gravity (in degrees)} = (141.5/SG) - 131.5 \qquad \text{Equation 1}$$

where SG = specific gravity at 15.6 C

Based on the density of water, any oil with an API value greater than 10 degrees at ~15.6 C is lighter than water. Figure 1c illustrates that the dilbit crudes have similar degrees of API and viscosities to the conventional heavy sour crudes. All of the crudes are well above the minimum of 19 degrees API gravity; only dilsynbit A has an average value below 20 at 19.5 degrees API gravity. Also, the viscosities are well below the limited receipt viscosity of 350 cSt specified by the crude petroleum tariffs [12, 13, 14]. The lower the viscosity, the easier the oil flows, where water has a viscosity of one cSt at 20 C. The viscosity is very sensitive to temperature and will increase at colder temperatures. To compensate for fluctuations in viscosity as a result of varying seasonal temperatures, the amount of diluent added to the crude will be adjusted to control the viscosity to the desired level. Figure 1d [17], shows how the API gravity is related to the viscosity at 50 C, representing gravities and viscosities of conventional heavy crudes. Based on the data from Figures 1c and 1d, the dilbit viscosities are not different from the conventional oil viscosities as a function of degrees API gravity.

Figure 1c shows that viscosities of the dilbit are comparable to those of conventional heavy crudes, but are significantly lower for the conventional medium and low sour crudes, which means that these crudes are easier to pump. Consequently, they require less pumping energy and/or the pumping capacity can be increased. The requirement for higher pumping energy to maintain a certain throughput of more viscous oil can translate into an increase in temperature at the pump station. Downstream of the pump station, the pipeline temperature decreases as a result of heat loss to the environment [18]. The maximum allowable temperature on the proposed Keystone line has been set at 70 C with a normal operating temperature of 49 C. Temperatures must be measured at the pump and at a downstream location to ensure compliance ([48], Appendix U). The dilbit crude quality and viscosity that are accepted for transportation support operating temperatures within an acceptable range.

5.6 Other properties for consideration

The following properties are important for downstream processing of the crude and further illustrate where differences can be expected between dilbit and conventional crude. These properties have not been linked to pipeline transmission corrosion.

5.6.1 Heavy metals: nickel and vanadium

Crude oil analyses often include the nickel and vanadium content, since these metals have detrimental effects on catalysts used in refinery cracking and desulphurization processes. Figure 1e shows that the vanadium levels are markedly higher for the dilbit crudes as compared to the conventional crudes. The nickel levels are more comparable with the conventional heavy sour crude levels. These metals have not been linked to corrosive processes in oil transmission pipelines [25].

5.6.2 Total C4s and C5s

The C4s and C5s in Figure 1f represent the lighter fractions of the crude. The higher fractions of C5s in Dilbits A and B are likely largely originating from the added diluent.

5.6.3 Total MCR

The Micro Carbon Residue (MCR) content in Figure 1f is a measure of the crude oil tendency to form coke, where crudes with a high MCR are more expensive to refine. The MCR content increases with the content of large high carbon molecules and can, therefore, be considered a measure of the heavy fraction of the crude [17, 27]. The MCR content of the dilbits are only slightly higher than that of the conventional heavy sour crudes. The asphaltenes content was not reported in the Crude Monitor database [10].

The above illustrates that the dilbit properties as displayed in Figure 1 are not significantly different from the conventional heavy crude oils for pipeline transportation. However, internal pipeline corrosion has occurred in some dilbit lines whereas others have enjoyed a long trouble free existence [28]. Our understanding of some of the parameters and their interactions are discussed in the following sections.

6.0 INTERNAL PIPELINE CORROSION IN WATER-WET CONDITIONS

Steel wet by oil does not corrode. Consequently, for corrosion to occur, separation of a water phase from the oil is required. Unlike transmission pipelines, gathering oil pipelines can contain significant quantities of water when transporting oil from wells to nearby treatment facilities and internal corrosion is observed when the pipe is water-wet. The corrosion generally consists of localized pitting. The corrosivity of the water phase depends on the water chemistry, which is also dependent on the oil chemistry. Water soluble inhibitive or corrosive components may separate from the oil into the water phase, either inhibiting corrosion or increasing the water corrosivity [23, 25]. Work by Papavinasam et al. has considered pipeline characteristics, and operating conditions in the development of an internal pitting corrosion model using laboratory and field measurements [29, 30]. The model addresses water-wet conditions with no corrosion occurring in oil-wet conditions. Parameters that increased the pitting corrosion rate included flow turbulence, temperature, and chlorides. The pitting corrosion was decreased by protective scale formation (sulfide or carbonate scales) [31]. The model was validated using data obtained from seven operating pipelines [29]. A comprehensive review of other predictive models of internal pipeline corrosion is provided from a corrosion science perspective [32], electrochemical perspective [33], and using a corrosion engineering approach [34].

7.0 INTERNAL CORROSION OF DILBIT TRANSMISSION PIPELINES

Claim #6: The Alberta pipeline system has had approximately sixteen times as many spills due to internal corrosion than the U.S. system, indicating that the dilbit is much more corrosive than the conventional oil that is primarily flowing through U.S. lines [1].

The ERCB responded to the above statement that the comparison is not valid since the ERCB statistics includes a much broader array of pipelines [2]. For example, the US Code of Federal Regulations does not include all gathering lines in their hazardous liquids classification [35], whereas a large percentage of all Alberta lines are upstream gathering lines. Gathering lines are generally more prone to failure since they contain more water and can contain corrosive carbon dioxide and hydrogen sulfide gases. Furthermore, the ERCB requires operators to report any pipeline incident that results in a loss of pipeline product, whereas the US data is based on incidents with a release of 5 gallons or more. In response to the above concern, PHMSA and the ERCB adjusted the statistics to comparable crude oil systems, where the oil sands derived crude oil consisted of a much larger percentage in Alberta than in the entire U.S. [4]. The criteria used to produce the Alberta statistics are quite open and based on pipe diameter, where, as a rule, larger diameter pipelines (12” dia. and up) transport oil over longer distances and are oil-wet [54]. Table 2 is reproduced from the FEIS, page 3.13-38 [4]. The data shows that the internal corrosion rates in Alberta and in the U.S. are comparable, which indicates that there is no evidence that dilbit would be more corrosive than conventional crudes.

The publicly available ERCB data do not separate the statistics for dilbit and conventional crude pipelines or for upstream gathering lines and long distance transmission pipelines. Whereas the ERCB licenses pipelines for the use of crude oil, they may not be aware of what type of crude is shipped through the lines, which is further complicated by the fact that lines can transport dilbit and conventional crude at different points in time. It is recommended that better statistics be provided as an improved presentation of the integrity of the Alberta pipeline system and to facilitate continuous monitoring of the performance of dilbit pipelines. The required information for these statistics may need to come from the operators and could be managed by the ERCB or other company organizations such as CAPP or the Canadian Energy Pipeline Association (CEPA). CEPA represents Canada’s transmission pipeline companies; its members transport 97% of Canada’s daily production of crude oil and natural gas.

The remainder of this chapter considers how a corrosive situation can occur in crude oil pipelines and considers the role of dilbit and conventional crude oil properties.

Table 2 Crude Oil Pipeline Failures U.S. and Alberta (2002-2010) [4]

Incident/Failure Case	Failures/Year	Failures per 1,000 Pipeline Miles per Year
U.S. Crude Oil Pipeline Incident History[a]		
Corrosion - External	9.8	0.19
Corrosion - Internal	22.1	0.42
All Failures	89.3	1.70
Alberta Crude Oil Pipeline Incident History[b]		
Corrosion - External	2.3	0.21
Corrosion - Internal	3.6	0.32
All Failures	22.0	1.97

[a]PHMSA includes spill incidents greater than 5 gallons. U.S. has 52,475 miles of crude oil pipelines in 2008.
[b]Alberta Energy and Utility Board Report. Alberta has 11,187 miles of crude oil pipelines in 2006.

7.1 Presence of Water

The internal corrosion models referred to in the previous chapter have been developed for a wide range of operating pipelines varying from upstream to transmission, for both oil and gas lines, as well as multi-phase pipelines with high cuts of water. The current review is aimed primarily at transmission pipelines, which will have a limitation on the basic sediment and water (BS&W) content entering the pipe of 0.5 volume percent [12,13,14]. The presence of a small quantity of water is inevitable, since complete removal of emulsified water is not possible with the current techniques such as desalting and naphtha-froth treatment. A survey performed in 1997 of Western Canadian oil producers indicated an average BS&W of 0.35%, with solids up to 60% of the BS&W [36]. At that time, some American pipeline companies shipped crude containing as much as 3% water, but did not experience a great increase in the corrosion rate. A typical BS&W of the CRW diluent is as low as 0.003 vol% [8]. The critical water content that will lead to water-wet conditions during transportation can vary widely depending on chemistry and operating conditions, but is generally much greater than 10 percent [30]. Consequently, less than 0.5% of water is usually not a corrosion concern unless conditions exist that enable the precipitation and accumulation of this water on the pipe wall. The following paragraphs discuss some of the crude oil components that could promote the accumulation of water and the formation of a corrosive environment. The discussion does not consider entry of water through batch upsets or water remaining in the system after hydrostatic testing. These are operational issues and not unique to the transported crude.

7.2 Asphaltenes

Asphaltenes are found in heavy crude oil and consist of positively charged complex large multi-ring hydrocarbon systems. They are in effect a solubility class, i.e. a fraction of the crude oil that is not soluble in paraffinic solvents, which are chained non-polar hydrocarbons [37, 38]. They are known to aggregate in solutions in a micro-emulsion, where an asphaltene core is surrounded by resins (with fewer hydro-carbon rings), which are surrounded by smaller hydro-carbon ring molecules, which in turn are dissolved in the non-polar solvent. This micro-emulsion structure allows the asphaltenes to dissolve in the crude oil [39]. When this micro-emulsion structure is disrupted through, for example, the addition of a paraffinic solvent that removes the protective resin layer, the asphaltenes will become insoluble and precipitate out.

Depending on the characteristics of the diluent, its addition to bitumen could result in the formation of unstable asphaltene micro-emulsions that could deposit during pipeline transportation [37, 40]. The asphaltene content of typical oil sand bitumens is 15-17 wt% and is partly responsible for the high viscosity. Complete removal of the asphaltenes does not reduce the viscosity to the required 350 cSt, but partial removal of the asphaltenes reduces the diluent requirement significantly. The additional benefit is that asphaltene precipitation is much less likely to occur [37].

The quality specifications of the CRW pool are primarily directed towards the downstream properties of the crude for refinery purposes, which affects the economic value of the crude. The Crude Monitor database contains 5-year averages of the CRW hydrocarbon composition, which indicates that ~80% consists of paraffinic solvents of eight carbons or less [10]. The remaining 20%, however, may contain the required properties to provide suitable compatibility with the mixed heavy crude oil. The Canadian Crude Quality Technical Association (CCQTA) is considering the compatibility of blending crude oils and diluent [52] in an effort to ensure that the product can be processed and refined. Calculator tools are provided on the Crude Monitor website [10]. Whereas asphaltene deposition can occur in response to incompatible blends in pipelines, the role of asphaltenes in pipeline sludge formation is unclear.

7.3 Emulsified water droplets

The solubility of water in oil is very small and of the order of 50 – 100 ppm [41]. The remainder of the water is primarily present as an emulsion, where the pipeline surface remains protected from corrosion by the continuous oil phase. These water droplets are very small and typically less than 10 microns in diameter [42, 43]. They carry chlorides and solids and can result in corrosion when the emulsion breaks up on the pipe wall, wetting the carbon steel surface. The stability of water-in-oil emulsions is a function of the oil chemistry, the water chemistry, and operating conditions.

One of the major players in stabilizing water in oil emulsions is asphaltene, forming an interfacial layer together with smaller surface active molecules and submicron mineral solids that is several tens of nanometers thick [44]. Ultrafine submicron clay particles are thought to be just as important in the stabilization of the water droplets, behaving similar to the asphaltenes [45, 46]. The formed skin is strong enough to resist coalescence of the droplets when they touch each other. These small micro-emulsions are too light to settle out in turbulent flow of crude oil and are expected to travel harmlessly through the pipeline. However, if bitumen is mixed with paraffinic solvents resulting in the precipitation of asphaltenes, these polar asphaltene flocs could bind to water droplets and clay particles forming much larger 100 to 1000 micron clusters that could settle out during transportation [43].

7.4 Pipeline sediment and sludge formation

Claim #7: An increased risk of internal corrosion may be related to the sediment composition of dilbits and specific sediment characteristics, including particle hardness and size distribution [4].

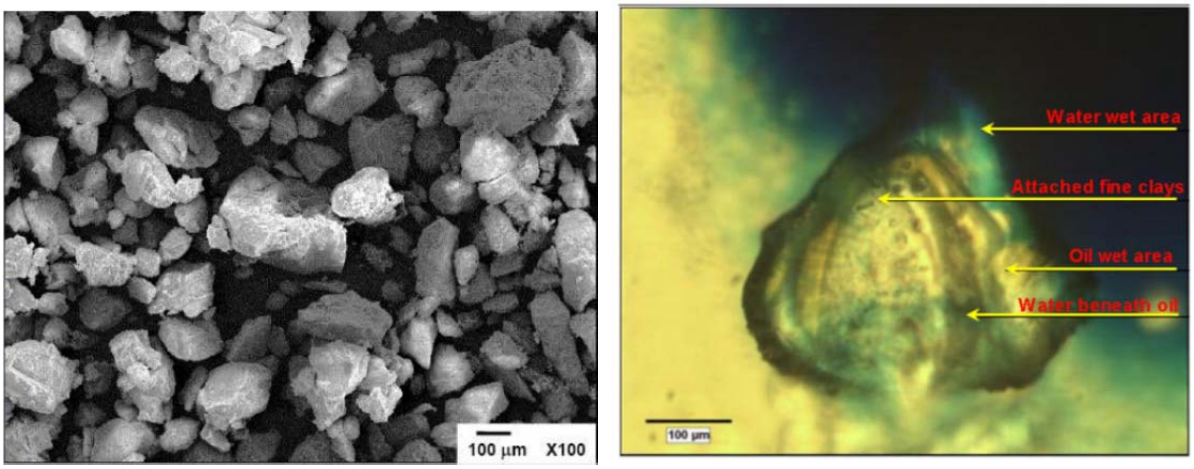
Figure 1b did not indicate a much higher content of sediments for the dilbit crudes compared to the conventional crudes, except for dilsynbit A. The data, however, only indicates the total amount of sediments and does not provide information on the size distribution. It is unknown how the solids in the conventional crudes compare to those in dilbits.

Analyses of pipeline deposits obtained from pigging operations have indicated the presence of larger solids to over 400 microns [47]. Most of the solids, however, were fine particles less than 44 microns in diameter (see Figure 2a), where the larger and fine particles consist primarily of silica sand and iron compounds. The larger sand particles were uniformly coated with very fine clays surrounded by a film of water in oil (see Figure 2b) [47]. Under low flow conditions, these particles are heavy enough to precipitate out with the water, oil products, and possibly asphaltenes, forming a sludge deposit. Sludge deposits are mixtures of hydrocarbons, sand, clays, corrosion by-products, biomass, salts, and water.

One might expect deposition of sludge to occur at the lowest spots. However, Enbridge observed underdeposit corrosion in their dilbit lines near over-bends, which are locations of low fluid shear stress (low fluid flow pressure) [47]. Little is known about the sludge deposition mechanism and it is not known if sludge formation would occur in the presence of only fines.

7.5 Underdeposit corrosion

The water layer on deposited sand particles in a pipeline sludge can subsequently join to form a water layer on the pipeline steel [47]. The water will contain chloride salts as well as bacteria, which now form a corrosive mix. The sludge chemistry can vary widely, where some sludges have a large percentage of waxy oil and exhibit low or no corrosion. Other sludges can contain more than 10% water and large bacterial populations, which can contribute to underdeposit pitting corrosion [48]. Figure 3 shows extensive pitting of a sludge covered test coupon, whereas a bare coupon showed no corrosion after both were exposed to dilbit for a month. No significant corrosion has been measured in a wide variety of different dilbit crudes in the absence of sludge, where the measured corrosion rate generally was within the standard deviation of the measurement technique.



(a) (b)

Figure 2 Micrograph of (a) washed sludge solids and (b) a large solid (from [47])

(a) (b) (c)

Figure 3 Corrosion coupons exposed to dilbit for 4 weeks, where (a) was left bare and (b) was covered with (c) sludge

The pipeline sludges used for analysis and testing are obtained from pigging runs and are considered averages over the length of the pipe and the time between pigging runs. The actual sludge chemistry may vary within a stratified sludge deposit or between different locations or with time as a function of transported crude. Questions remain regarding the controlling corrosion parameters and little is known with regard to the sludge deposition mechanism and the role of the dilbit chemistry. Whereas underdeposit corrosion has been observed on transmission pipelines transporting dilbit, there are also dilbit pipelines that have operated trouble-free for 25 years [28].

Underdeposit corrosion, however, is not unique to dilbit lines. Earlier this year, BP shut down their Trans-Alaska pipeline, which transports oil from their Prudhoe field. Previous leaks in 2006 resulted in the shutdown of 57 oil wells in Alaska [49]. Corrosion was attributed to the deposition of sludge, the presence of carbon dioxide, and, what was considered to be the biggest threat, the presence of bacterial populations resulting in microbiologically influenced corrosion (MIC) [50]. It is not known what the solid content or solid size distribution was in this line, but the conditions obviously favoured sludge deposition.

7.6 Erosion and Erosion Corrosion

Claim #8: A combination of chemical corrosion and physical abrasion can dramatically increase the rate of pipeline deterioration [1].

Erosion by sediment particles would occur by impact. Since corrosion can only occur in the presence of a water phase, which most likely requires sludge formation in dilbit pipelines, a combination of erosion and corrosion is improbable. No information could be found on dilbit pipeline erosion in the scientific literature or from field experience. Erosion in a uniform smooth pipeline generally displays itself as even wear as opposed to the localized pitting corrosion observed underneath sludge deposits. If present, effects are generally more gradual and should not be a concern due to the fact that regular mitigation strategies such as intelligent pigging and monitoring technologies will catch this wall loss.

8.0 TEMPERATURE EFFECTS

8.1 The effect of temperature on the internal corrosion rate

Claim #9: As a result of the high viscosity of dilbit, pipelines operate at temperatures up to 158 F, whereas conventional crude pipelines generally run at ambient temperatures. The high temperature would significantly increase the corrosion rate which doubles with every 20 degree Fahrenheit increase in temperature [1].

An increase in the temperature can increase the rate of corrosion if the corrosion mechanism is controlled by kinetics or diffusion. There are, however, many other factors that affect the rate of corrosion such as scale formation, limiting concentration of reactants, or chemical reactions. Especially in a complex aqueous environment, possibly with dissolved organics, acid gases, oxygen, sub-micron clay particles, etc., the corrosion rate can either increase or decrease as a function of temperature. The concentration of oxygen or carbon dioxide is generally not known and, if present, may change along the length of the pipeline. The most likely internal corrosion mechanism in dilbit pipelines consists of underdeposit corrosion as a result of sludge formation. As discussed in the preceding section, microbiologically induced corrosion could play a dominant role in the corrosion process. Complex populations containing multiple types of bacteria are known to be present and support each other's viability such as sulfate reducing bacteria (SRB), heterotrophic aerobic bacteria (HAB), and acid producing bacteria (APB) [48]. These bacteria are most active between 10 C and 40 C. Consequently, higher temperatures up to 70 C may reduce the corrosion rate underneath sludge deposits, if the mechanism is controlled by microbial action.

Little is known about the controlling factors of corrosion underneath sludge deposits and it is recommended that research continue to improve our understanding of sludge formation, the resulting corrosion mechanism, the role of dilbit chemistry and solids, mitigation practices and frequencies, and preventive measures. Enbridge has been quite successful in mitigating underdeposit corrosion through a pigging and inhibition program. However, there are still many uncertainties regarding the effectiveness of each and the required frequency [47].

8.2 The effect of temperature on external stress corrosion cracking

Claim #10: Dilbit pipelines may be subject to a higher incidence of external stress corrosion cracking [4].

In the field, the pipeline is protected by coatings and cathodic protection. Increased temperatures may result in coating disbondment, which would expose the bare pipe to the soil environment, which can be corrosive containing water, dissolved oxygen and carbon dioxide. Together with fluctuating pipeline operating stresses, this has resulted in stress corrosion cracking (or fatigue cracking) of pipelines covered with tape or asphalt coatings. These coatings can behave as shielding coatings, preventing the secondary protection of applied cathodic current. The Keystone pipeline is coated with Fusion Bonded Epoxy (FBE), which is considered permeable to the cathodic protection current. Temperatures up to 60 C have indicated a higher rate and extent of coating disbondment, but it has also been shown that, in the presence of cathodic protection, the pipe will remain protected, and blistering and coating disbondment does not present an integrity threat to a pipeline [51]. No stress corrosion cracking failures have been reported for FBE coatings in over 40 years of experience.

9.0 SUMMARY

Pipeline expansions for the transportation of Canadian crude to refining markets in the United States are currently under regulatory review. The transported oil originates primarily from the Alberta oil sands and consists of diluted bitumen, also referred to as dilbit. Alberta Innovates – Technology Futures completed a project for Alberta Innovates – Energy and Environment Solutions reviewing the current status on the corrosivity of dilbit in pipelines as compared to conventional or 'non-oil sands derived' crude oil.

It has been suggested that dilbit has higher acid, sulfur, and chloride salts concentrations, as well as higher concentrations of more abrasive solids. It is furthermore suggested that dilbit transmission pipelines operate at higher operating temperatures compared with conventional crude, which would make the dilbit more corrosive, thus leading to a higher failure rate than observed for pipelines transporting conventional crude. This review examines these concerns in light of the properties of dilbit in comparison with conventional oils. In addition, statistical data are presented to show if the concerns are supported by operating experience.

Conventional crude and dilbit are subject to quality control measures and regulation. Pipeline operators employ further measures during transportation to manage and control the quality of delivered crude. Alberta crude quality information is available online and accessible to the public. The properties of heavy, medium, and light conventional Alberta crude oils were compared with three dilbit and one dilsynbit crude.

Whereas two of the four dilbit crudes displayed a slightly higher naphthenic acid and sulfur concentration than the conventional Alberta heavy crudes, there are conventional crudes on the market that have displayed higher values yet. The chloride salt concentrations were either comparable or lower than all grades of conventional crude. Naphthenic acid, sulfur, and chloride salt concentrations can result in corrosion at temperatures greater than 200 C at refineries, where mitigation is addressed through upgrading of materials and the use of inhibitors. At the much lower pipeline transportation temperatures, the compounds are too stable to be corrosive and some may even decrease the corrosion rate.

The sediment levels of the dilbit crudes were comparable to or lower than the conventional crudes, except for a dilsynbit crude, which showed more than double the quantity of solids than most other crudes, but was still well below the limit set by regulatory agencies and industry. The solids size distribution is unknown as is the role of larger size solids in the formation of pipeline deposits. Erosion corrosion was found to be improbable and erosion, if present, is expected to be gradual and observed by regular mitigation practices.

The dilbit viscosities are comparable to those of heavy conventional crudes, where the viscosity is controlled and adjusted for temperature through the addition of diluent. The resulting dilbit viscosity supports acceptable operating temperatures, which will be monitored at and downstream of the pumping stations.

Adjustment of the Alberta and U.S. pipeline failure statistics to compare similar crude oil pipeline systems on an equivalent basis indicated that the Alberta systems (with a large percentage of dilbit lines) experienced comparable internal corrosion failure rates than the U.S. systems (predominantly conventional crude lines).

Pipeline steel wet by oil does not corrode. The basic sediment and water (BS&W) content of crude oil transmission pipelines is limited to 0.5 volume percent. This water is primarily present as a stable emulsion, maintaining an oil wet pipe, protected from corrosion. Pitting corrosion has been observed underneath sludge deposits. These deposits are a mix of sand and clay particles, water, and oil products. The corrosivity of these sludges varies but seems to be linked to water content, which can exceed 10%, and large bacterial populations. The sludge deposition mechanism and the contributions of each of its components to its corrosivity are not clear. Sludge deposition and similar underdeposit corrosion is not unique to dilbit lines and also has been observed in pipelines transporting conventional crudes.

This review has indicated that the characteristics of dilbit are not unique and are comparable to conventional crude oils.

10.0 RECOMMENDATIONS

The following recommendations are provided based on the completed review. It has to be understood that this was a high-level review and a focused, peer-reviewed study has not been conducted. The scope of the work did not include interviews with industry, regulators, or colleagues.

1. CQI is currently working with industry partners on the development of a downstream quality database for direct comparison with the upstream qualities with the goal to provide financial incentives for consistency and rateability. The data provided on upstream qualities has been instrumental in the evaluation of differences between dilbit oils and conventional crude oils. The transparency offered by the information of crude oil quality databases on both the shipped and delivered product will be of tremendous assistance in communications between industry and the public. It will

also be a valuable resource for the evaluation of sludge deposition and underdeposit corrosion during transportation. It is recommended that this effort be supported.

2. To further increase the value of the above database, it is recommended that the following information be added:
   a. H_2S concentration
   b. Asphaltene content
   c. Water content
   d. Viscosity (currently available from [11])
   e. Sediments' identity and size distribution, if possible

3. The compatibility between diluent and bitumen should be investigated further with regard to sludge formation and deposition, and the role of asphaltenes. It is recommended that current efforts by CCQTA on crude oil compatibility be supported and expanded to link the crude oil chemistry to pipeline sludge formation and sludge corrosivity, including the ability of the sludge to support microbial populations.

4. The underdeposit corrosion mechanism should be studied further with regard to the effect of dilbit chemistry, sludge deposition mechanism, microbial activity, temperature, and effectiveness of mitigation tools (chemicals and cleaning pigs). Current work by Enbridge as well as by the industry working group PiCoM (Pipeline Corrosion Management) is addressing these issues through long-term testing and correlating sludge corrosivity with a chemical and microbial geochemical characterization of the sludge. The work is further considering and optimizing monitoring technologies to enable measurement of the effectiveness of mitigation treatments. It is recommended that this effort will continue to be supported.

5. The publicly available ERCB data does not separate the statistics for dilbit and conventional crude pipelines or for upstream gathering lines and transmission pipelines. It is recommended that better statistics be provided as an improved presentation of the integrity of the Alberta pipeline system and to facilitate continuous monitoring of the performance of dilbit pipelines. The required information for these statistics may need to come from the operators and could be managed by the ERCB or other company organizations such as CAPP or the Canadian Energy Pipeline Association (CEPA).

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