Canadian Energy Pipelines Association



State of the Art Report

Dilbit Corrosivity

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1. EXECUTIVE SUMMARY

Background

The Canadian Energy Pipeline Association (CEPA) identified a need for a State of the Art Report on Dilbit corrosivity compared to conventional crude oils within oil transmission pipelines. This report has been prepared by Consultants from outside North America.

The production of bitumen extracted from oil sands and diluted with lighter crudes or synthetic crudes, otherwise known as 'Dilbit' and 'Synbit' is increasing. Dilbit and Synbit have been transported by pipelines for over 20 years. The volume of Dilbit and Synbit carried by transmission pipeline is increasing and will increase further over coming years. The oil and gas industry have viewed Dilbit and Synbit as much the same as any other heavy sour crude and there has been little published information on its potential corrosivity under transmission pipelines conditions. This void of information has led to speculation about the corrosive nature of these products. This absence of information has resulted in some literature that concludes these products are highly corrosive.

The corrosion mechanisms in pipelines are well understood and are the subject of continuous investigation both in the field and laboratory to fine tune that understanding. When pipeline failures due to corrosion do occur it is rarely through lack of knowledge in the industry, but a failure to apply that knowledge in a timely fashion.

A substantial amount of work has been carried out recently to demonstrate that Dilbit and Synbit are no more corrosive than conventional crudes.

This report confines itself to consideration of the corrosivity of Dilbit and Synbit compared with conventional crudes, and the implications this may have for pipeline integrity management. It:

- establishes the basic character of Dilbit and Synbit compared with other conventional crudes:
- describes the range of internal corrosion mechanisms that pipelines can suffer from;
- discusses these mechanisms in the context of crude oil transmission pipelines transporting both conventional crudes and Dilbit and Synbit;
- critically reviews the relevant published data; and,
- discusses the implications for pipeline integrity management of transmission pipelines conveying Dilbit and Synbit.

Conclusions

It is concluded that some of the literature is ill-informed and wrong: both Dilbit and Synbit in a crude oil transmission pipeline environment is no more corrosive than comparable heavy sour crudes and in many cases may be less corrosive.

Consequently, there are no significant additional implications for corrosion control in a pipeline carrying Dilbit and Synbit as part of pipeline integrity management over and above what is already standard practice.



2. INTRODUCTION

2.1 Oil Sands Production

Alberta contains some 95% of Canada's proven oil reserves in the form of oil sands. The oil sand deposits are contained in an area of some 55,000 square miles. This places it as the 3rd largest oil reserve in the world behind Saudi Arabia and Venezuela^[1]. The oil sands are recovered either by mining or in situ using a variety of techniques, the choice depending on the depth of the deposit. Surface mining is efficient if the deposits are within 80 m of the surface. After excavation and crushing the oil sands are transported to the main processing area by conveyor belt or slurry pipeline. The in-situ processes include cyclic steam stimulation (CSS), steam assisted gravity drainage (SAGD), Toe to Heel Air Injection (THAI or Fireflooding (in situ combustion), Cold Heavy Oil Production with Sand (CHOPS), Vapour Extraction Process (VAPEX).

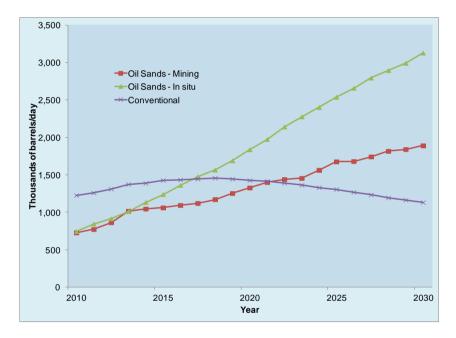


Figure 2-1: Production forecasts for Canadian Crude Oil^[2]

The bitumen is extracted from the oil sand at the extraction plants using a hot water process. Once extracted the bitumen is upgraded to make it suitable for transport by transmission pipeline and for refinery use.

2.2 Transmission of Oil Sands Production

Pipelines require a product with a density of 940 kg/m³ and or a viscosity of 350 cST at the pipeline reference temperature. Bitumen has a density of 960 - 1020 kg/m³ and a viscosity of 760,000 cSt at 15°C. Generally, the bitumen is diluted either with naphtha based diluents, NGL liquids, ultra light sweet crudes, condensates, etc with a density of 650 - 750 kg/m³ to produce Dilbit, typically with a 30:70 diluent to bitumen ratio; or the bitumen is diluted with synthetic crude which has a density 840 - 870 kg/m³ at a typical ratio of 50:50 synthetic crude to bitumen for Synbit. Dilbit has a typical viscosity of 350 cSt @15°C and Synbit has a viscosity of 128 cSt at 15°C. The actual diluents to bitumen ratio may change from winter to summer as the temperature changes [3].



Synthetic crude is produced by upgrading oil sand bitumen. It is a blend of naphtha, distillate and gas oil range materials produced by hydrotreating the naphtha, distillate and gas oil generated in a delayed coking unit.

2.3 Dilbit and Synbit Characteristics

Crude is usually classified according to its API gravity and sulphur content. Dilbit and Synbit are classified as heavy sour crudes and their API gravity compared with some other conventional Canadian crude is shown in Figure 2-2. Dilbit and Synbit have an API gravity around 20 which is similar to other conventional heavy crude.

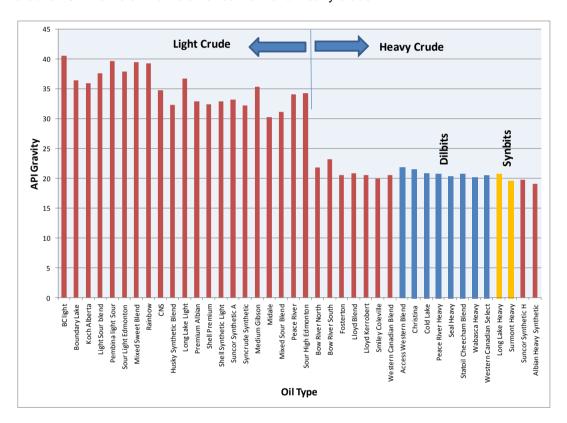


Figure 2-2: API Gravity of Dilbit and Synbit in Relation to Other Conventional Crudes from Canada^[4].

The sulphur content of Dilbit is higher than other conventional heavy Canadian crudes as shown in Figure 2-3. The Dilbit crudes have an average sulphur content of 4.1% compared with an average sulphur content in conventional heavy sour Canadian crudes of 3.1%.



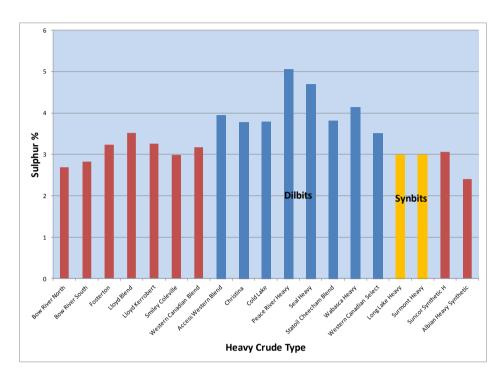


Figure 2-3: Sulphur Levels in Canadian Heavy Crudes^[4]

Canadian oil sand Dilbits and Synbits also appear to have a higher total acid number (TAN) than other Canadian conventional heavy crudes as shown in Figure 2-4.

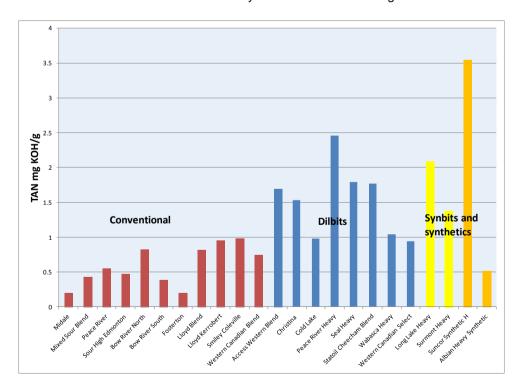


Figure 2-4: TAN content of some Canadian Oil Sand Dilbits and Synbits Compared to Other Conventional Canadian Medium and Heavy Sour Crudes^[4]

However in a global context, the high sulphur content and TAN values are surpassed by some Venezuelan crudes and a number of other conventional heavy crudes from around the



globe as shown in Figure 2-5. The relevance of these values is discussed in sections 4.5 and 4.6.

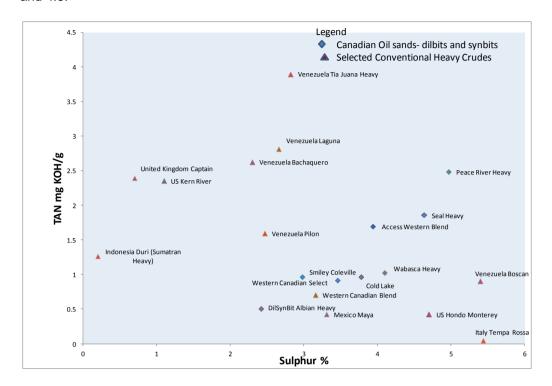


Figure 2-5: TAN and Sulphur Content of Canadian Oil Sand Dilbits and Synbits Compared with a Range of International Conventional Heavy Crudes^[38].

The sediment content of most Dilbit and Synbit is less than many other types of Canadian conventional heavy crudes, as shown in Figure 2-6. The implications this may have for internal corrosion mechanisms in pipelines is discussed later.

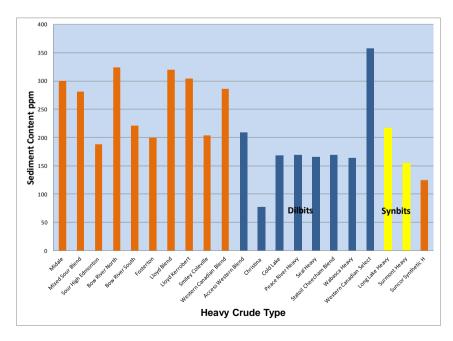


Figure 2-6: Sediment Levels in Dilbit and Synbit Compared with Other Conventional Canadian Heavy Crudes^[4].



The salt content of Dilbit and Synbit is lower that most Canadian conventional heavy crudes as shown in Figure 2-7.

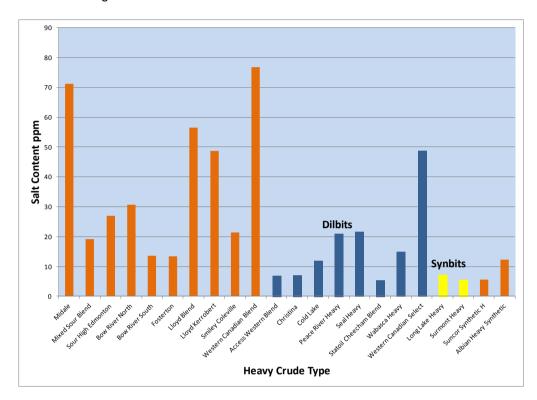


Figure 2-7: Salt Content of Canadian Heavy Crudes^[4].

In summary, Canadian oil sand Dilbit and Synbits are classified as heavy sour crudes and have low sediment and chloride contents compared with other conventional Canadian heavy crudes. Whilst they have higher TAN numbers and sulphur contents than most other conventional Canadian heavy crudes they are not exceptional globally.

The gravity, TAN number, and sulphur content are important parameters for refineries. Refineries are configured to process particular types of crude and these parameters give some idea of the possible corrosion processes at the high temperatures found in refineries.

2.4 Typical Operating Envelope for a Dilbit pipeline

The operating envelope for a transmission pipeline carrying Dilbit or Synbit will vary between pipelines, but would typically be:

TAN Value	1.6	Mg KOH/g ^[5]
Sulphur	3.9	Wt% ^[5]
Density	915 to 940	kg/m³
Viscosity	340 to 350	cSt
Temperature	17 to 40	°C

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Velocity $1 - 2.5 \text{ m/s}^{[6]}$

Operating pressures 60%-80% of SMYS

Typical BS&W* 0.25 to 0.5 %

Some pipelines carrying dilbit are operated under a batch regime; e.g., Keystone, and Enbridge^[7] Some are dedicated to Dilbit service, e.g., Inter Pipeline Corridor, and Cold Lake pipeline systems^[8].

Refineries are usually configured to deal with particular types of crude; therefore, it is important to preserve the crude oil specification when the crude is being transported. Off specification crude can cause damage to refinery equipment. Thus similar product types are batched in sequence to minimize cross contamination. Typical categories would be Heavy – TAN, heavy, medium, sour, sweet, synthetic and condensate. Batch sizes may vary but are typically in the range 60 - 100,000 bbls.

^{*}Basic sediment and water.



3. WATER IN OIL TRANSMISSION PIPELINES

3.1 How Water Behaves in an Oil Pipeline

The density and viscosity of Dilbit and Synbit are adjusted so that these hydrocarbons can be transported in existing pipelines or, if new pipelines are built, they will be constructed using standard pipelining design and construction techniques that will allow conventional oil as well as Dilbit and Synbit to be transported. This section discusses pipelines in general including those used for Dilbit and Synbit.

A long oil-service pipeline acts as a separator and even small quantities of water can form a separate water phase at the bottom of the pipeline. Separators do not remove all the water from the oil and some micro-droplets remain in suspension. During their transit along the pipeline the droplets may coalesce and eventually achieve a size at which they settle to the bottom of the pipeline to form a water phase. Many corrosion inhibitors contain compounds that enhance emulsion breaking, and therefore the presence of inhibitor (including residuals from upstream treatment) may enhance water separation.

Another possible mechanism for water or moisture drop out is where water becomes associated with the sediment entrained in the crude and, if the sediment settles, then a deposit is formed containing moisture. Settlement of sediments may be associated with flow distortions that occur at certain changes in pipeline geometry^[11].

3.2 Entrainment of Water

The presence of an electrolyte, essentially water, is necessary for corrosion to occur in crude oil pipelines. Potable quality water is not a good electrolyte but the water in oil pipelines contains dissolved salts that will make the water an effective electrolyte. Water may enter a pipeline during an operational upset or be dissolved in the oil. Crude oil, Dilbit and Synbit transmission lines are, however, limited to 0.5% BS&W (solids and water) and the water will be present as an emulsion of water in oil. In this dissolved form water is less corrosive than it would be as free water because the water droplets are encased in an oil shroud. It is normally necessary for the emulsion to be an oil-in-water emulsion for corrosion to occur. The inversion point when the emulsion changes from water-in-oil to oil-in-water emulsion requires a high water cut, well above the 0.5% target value. Figure 3-1 illustrates the effect of water cut on emulsion stability.



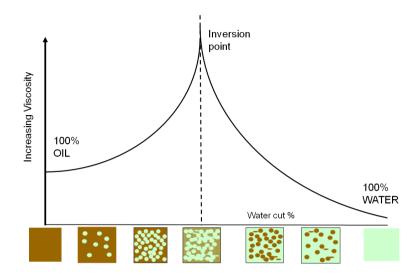


Figure 3-1: Inversion of Water-in-Oil to Oil-in-Water Emulsions.

In normal operation at a low BS&W free water is unlikely to be present. Upsets may introduce sufficient water into a pipeline to allow free water to be present. If the oil flow velocity is sufficiently high the free water will be entrained with the oil and the pipeline surface will remain oil wetted. Under such conditions corrosion is most unlikely to occur. Below a critical oil velocity the oil-water shear forces are too low to sweep the water and a semi-permanent water phase may persist for long enough at the bottom of the pipeline for corrosion to occur. This 'entrainment velocity' can be calculated if the physical properties of the water and oil are known.

Below the entrainment velocity the effect of the rate of flow on the corrosion rate is not well quantified. At very low velocities a change in flow velocity will have little effect on corrosion; corrosion product films form sufficiently fast to stifle excessive corrosion. Over the intermediate range of flow velocities up to the entrainment velocity, flow increases the corrosion rate slightly. Norwegian research indicated that corrosion rates increased in proportion to Re^{0.2}, where Re is the Reynolds Number. At flow rates well above the entrainment velocity there is a potential risk of flow enhanced corrosion. At a critical flow velocity the shear forces, imposed on the pipe wall by the crude oil, are sufficiently high to remove the corrosion product films. This may result in an increase in the corrosion rate: essentially this marks the initiation of 'erosion corrosion', though this term leads to confusion, and is now generally replaced by the term 'flow enhanced corrosion'. At these high flow rates and a low BS&W there would be no free persistent water and corrosion would not occur.

3.3 Flow Enhanced Corrosion

The shear stress, τ , imposed on the pipeline wall by the flow is calculated as:

$$\tau = 0.0395 \text{ Re}^{-0.25} \rho \text{ v}^2$$



where ρ is the density of the fluid, v is the velocity (m/s), and Re is the Reynolds Number. The shear forces to remove iron carbonate films at moderate temperature are low; removal of iron sulphide occurs at higher shear force.

The velocity at which shear forces are excessive appears to depend on the corrosiveness of the environment including: temperature, acidity, ferrous iron concentration and salinity. Norwegian research indicated that corrosion rate increased in proportion to Re^{0.8} for flow above the flow enhanced corrosion velocity. The enhanced corrosion velocity, sometimes termed the critical velocity, is often calculated from API RP-14E^{9:}

$$V_{critical} = \frac{Constant}{\sqrt{\rho}}$$

where $V_{critical}$ is the critical flow velocity (fps).

constant is a value dependant on the material; API RP-14E value is 100.

 ρ is the fluid density (lb/ft³).

Field experience indicates that the constant in the API RP-14E equation can be increased to 130 for steel. The critical velocity for heavy crude oil pipelines is shown in Table 3-1 and is around 4 m/s. Crude oil transmission pipelines operate typically at 1-2.5 m/s and will rarely operate at a flow velocity above the enhanced corrosion velocity. Dilbit and Synbit pipelines will be operated in a similar manner to conventional oil pipelines and consequently there would be no higher risk than with conventional oil systems.



Crude API	Density (kg/m³)	Flow Enhanced Corrosion Velocity (m/s)
17.5	951	4.00
25.5	901	4.11
35	851	4.22
45	801	4.35

Table 3-1: Flow Enhanced Corrosion Velocities Defined by API RP-14E
Dilbit and Synbit Densities are Marked in Bold

If there is an upset then free water layers may form and persist along the pipeline, usually at low spots, but the water will eventually be removed as it is absorbed into the oil or, if the oil superficial velocity is sufficiently high, then the water layers will not persist for any length of time because the water will be entrained into the oil and be carried through the pipeline. In this case the surface of the pipeline is oil wetted and corrosion will not occur. Dilbit and Synbit will behave in a similar manner.

As the viscosity of the oil increases, the velocity at which the oil will entrain separated water decreases slightly; the oil acts more like a piston. Until recently, the most widely-accepted method of calculating the entrainment velocity relied on research by Wickes & Fraser^[10]. Recent advances in calculation of entrainment velocity suggest that the early method was not conservative: even so, it provides useful estimates. Entrainment velocities for heavy oils with typical densities and viscosities are given in Table 3-2. Most oil transmission pipelines operate at superficial oil velocities above 1 m/s. Published data for two transmission pipelines that carry Dilbit indicate velocities of 1.5 - 2.5 m/s above the velocity required for entrainment, and well below the critical velocity for flow enhanced corrosion.



Dina Diameter	Entrainment Velocity		
Pipe Diameter (inch)	(m/s)		
	API 18°	API 26°	
18	0.49	0.65	
24	0.51	0.74	
30	0.54	0.75	
36	0.55	0.78	
48	0.65	0.82	

Table 3-2 Water Entrainment Velocities for Heavy Crude Oils Including Dilbit and Synbit

Heavy oils including Dilbit and Synbit may not, in all cases, remove the precipitated water from all geometries of a pipeline. In some cases sediment containing water may be trapped at over bends and some corrosion can then occur^[11]. This has been attributed to the particular flow conditions downstream of the overbend. Under deposit corrosion is the subject of continuing research to see if the particle size and mass also plays a role and whether inhibitors and biocides can be developed to penetrate the deposits^[12,13,14,15,16,17]. It is worth noting that most of the research into this phenomenon was prompted by the discovery of corrosion on operating pipelines using routine integrity management tools. The same tools will be used for evaluation of Dilbit and Synbit pipelines.



4. CORROSION MECHANISMS

4.1 Introduction

Internal corrosion can occur in crude oil transmission pipelines when there is water present. The corrodants and the associated corrosion mechanisms are detailed below. The corrodants are:

- 1. Carbon dioxide
- 2. Hydrogen sulphide
- 3. Oxygen
- 4. Organic acids
- 5. Sulphur
- 6. Bacteria

4.2 Carbonic Acid Corrosion

When there is only, or predominantly, carbon dioxide present in the transported fluids the corrosion that occurs is termed sweet corrosion. Carbon dioxide is a highly soluble gas that produces acidity in solution. For example carbonated drinks have a pH around 3 - 4. The ions that are formed can react with the metal surface in several ways and for this reason carbon dioxide is more corrosive than mineral acids of the same molarity over the range of partial pressures found in production pipelines. Corrosion increases as:

- · concentration of carbon dioxide increases
- · system pressure increases
- temperature increases.

The corrosion process occurs in steps. Carbon dioxide dissolves in the water to form carbonic acid that dissociates to hydrogen ions and the bicarbonate anion. The hydrogen ions remove electrons from the metal surface, and the carbonic anion may also discharge an electron to form carbonate.

$$CO_2 + H_2O = H_2CO_3 \rightarrow H_2CO_3 = H^+ + HCO_3^-$$

$$H^+ + electron = H$$

$$HCO_3^- + electron = H + CO_3^{2-}$$

$$H + H = H_2$$

On the bare metal surface corrosion commences at a high rate but the rate falls rapidly, within 24 - 48 hours, as a film of corrosion product is formed on the metal surface. This film



will then persist unless removed by a mechanical or frictional force. The surface film is formed by the reaction of the corroding steel with bicarbonate ions to form iron carbonate, termed 'siderite', though some oxides and hydroxides may also be present. The films are visible and appear as a pale brown tarnish on the metal. This is enough however to reduce the corrosion rate by a factor of five to ten depending on the local conditions. It is this stable corrosion rate which is used to evaluate the corrosion risk to a pipeline. Any process that aids formation and stability of the iron carbonate film will reduce corrosion. Any process or action that removes the film or prevents its formation will increase corrosion. Crude oil transmission pipelines, including those carrying Dilbit and Synbit, are operated over the flow range where the corrosion product films are stable and the low BS&W reduces risk of damage to these protective films.

A very simple rule of thumb used in low pressure, low temperature fields and relevant to crude oil, Dilbit and Synbit, pipelines was:

Partial pressure of carbon dioxide below 1 bara low corrosion

Partial pressure of carbon dioxide 1 to 2 bara: modest corrosion

Partial pressure of carbon dioxide above 2 bara: high corrosion

The partial pressure (psia/bara) is calculated from the molar or volume percentage multiplied by the total system pressure (bara).

Partial Pressure
$$CO_2$$
 = system pressure $x \frac{mol \% CO_2}{100}$

In oil pipelines the partial pressure of the carbon dioxide is calculated from the conditions in the final separator. Here the oil is in equilibrium with the associated gas at the separator conditions. Most of the carbon dioxide (and hydrogen sulphide) will be stripped from the oil phase into the gas phase at the low separator pressure. After the separator, the partial pressure of the carbon dioxide is not increased by an increase in the oil pressure at the pumps, for transmission through the pipeline. The worst-case corrosion in an oil line would be expected somewhere downstream of the pumps where the temperature is high and where water might settle out.

The rule of thumb approach has been replaced by predictive models of corrosion rates. A commonly used formula is:

$$log_{10}CR = 5.8 - \frac{1710}{(t + 273)} + 0.67 log_{10}(f_{CO_2})$$

where CR is the corrosion rate (mm/year)

t is the temperature (°C)

f CO_2 (bara) is the partial pressure of carbon dioxide adjusted for the non-ideal behaviour of carbon dioxide by use of a fugacity coefficient and is calculated as $fCO_2 = ppCO_2 \times f_a$.



The fugacity coefficient, f_a , is used to moderate the effect of dissolved carbon dioxide because some of the dissolved carbon dioxide is combined as undissociated carbonic acid in which form it does not cause corrosion.

There are limitations to the reliability of these corrosion rate predictions, and several allowances must be made. Firstly the constants were derived from experimentation in weak brine (around 0.5% chloride), and in systems with low agitation. A BP-Amoco modification makes an allowance for the brine strength by reducing gas solubility in high concentration brines in proportion to the change in Henry's constant, though the effect only becomes significant at brine concentrations \geq 10% TDS. The basic algorithm is considered to be valid up to about 60 °C and this is within the operating temperature of crude oil pipelines.

Because the concentration of carbon dioxide in stabilised oil will be low, and the operating temperature of the pipeline is around the soil ambient temperature, the corrosion rate will also be low. For most crude oil pipelines, atmospheric separators are used, and for a carbon dioxide concentration of 3 mol% (fairly typical for North American production) the partial pressure of carbon dioxide would be 0.06 bara. Representative corrosion rates based on the equation above are given in Table 4-1. Pipelines where corrosion was anticipated would be treated with corrosion inhibitor, and the corrosion rates would be below 0.05 mm/year. Dilbit and Synbit pipelines will show similar corrosion rates because the carbon dioxide concentration will be low.

Partial pressure of	Temperature °C		
carbon dioxide (bara)	5	10	15
0.02	0.03	0.04	0.05
0.04	0.05	0.07	0.08
0.06	0.07	0.09	0.11
0.08	0.08	0.11	0.13
0.1	0.10	0.12	0.16

Table 4-1: Potential Corrosion Rates (mm/year) from Carbon Dioxide in Pipelines
Transporting Stabilized Crude Oil.

Empirical formulae have been developed based on the assumption that the formation water will form protective scales on the metal surface. These formulas use the pH of the water and the salinity for calculation of a corrosion rate. Calculated rates are generally low and similar to those given in Table 4-1.



Relevance to Dilbit and Synbit

Given the production route for Dilbit and Synbit, they are unlikely to contain any significant amounts of carbon dioxide, and even if they did the corrosion rates would be low because the partial pressure would be low.

4.3 Hydrogen Sulphide

The effect of hydrogen sulphide is to reduce the general corrosion rate that would occur in the presence of carbon dioxide alone. Hydrogen sulphide is more soluble than carbon dioxide and the two gases compete. The presence of hydrogen sulphide also modifies the corrosion product film; the films become predominantly iron sulphide at about 100 ppm hydrogen sulphide in the water phase. Below a hydrogen sulphide concentration of 10 ppm any beneficial effect on corrosion rate is generally ignored though the predictive models caution that low concentrations of hydrogen sulphide may initiate pitting corrosion. The corrosion rate at low hydrogen sulphide concentrations is very sensitive to the pH^[19,20]. The reduction factor is uncertain and varies with other parameters; for example, the ratio of carbon dioxide to hydrogen sulphide, chloride content, total dissolved solids, temperature, and pH, but the reduction of the carbon dioxide corrosion rate is in the range 10 to 50%.

Relevance to Dilbit and Synbit

When hydrogen sulphide is present in the crude oil at a sufficiently high concentration there is a risk of cracking of the pipeline steel by a hydrogen embrittlement process. In crude oil pipelines that transport stabilized crude oil, the associated gas will have been removed and there will be little or no hydrogen sulphide present. This applies to Dilbit and Synbit as well as conventional crudes. As a consequence there will be no risk of pipeline steel cracking.

4.4 Oxygen

Oxygen can cause corrosion. Oxygen can enter into a pipeline through seals on the suction side of pumps and through storage tanks if the oil is exposed to the air (for example, floating roof tanks). Generally the concentration of oxygen in the crude oil will be low because there is sufficient dissolved gas in the oil at equilibrium to prevent a high concentration of oxygen dissolving in the crude oil: this is because carbon dioxide and hydrogen sulphide are more soluble in crude oil and water than oxygen. If there is any trace of hydrogen sulphide present this would react with the oxygen. The corrosion by oxygen will occur at the inlet of the pipeline, and reduce further downstream as the oxygen concentration is depleted. The ingress of oxygen will be low and the oxygen will be dispersed into the oil stream. Oxygen is more soluble in oil than in water and as a consequence a small ingress of oxygen will not necessarily result in a high corrosion rate because the oxygen in the water will be low. If the water that entered the pipeline was saturated with oxygen at 8 ppm (the saturation concentration of oxygen in water at ambient temperature) the concentration in the 0.5% water phase in a crude oil pipeline would be below 40 parts per billion.

Typical corrosion rates for concentrations of oxygen of the order of 10 - 50 ppb in a water layer within an oil pipeline can be calculated using the following equation:

$$CR_{oxygen} = \frac{0.00226.C.U}{\text{Re}^{0.14}.\text{Pr}^{0.706}}$$



Where CR is corrosion rate (mm/year), C is the concentration of oxygen (ppb), U is the flow velocity (cm/s), Re is the Reynolds number and Pr is the Prandtl number which is a dimensionless number that accounts for the rate of diffusion of oxygen through the water film.

For a crude oil pipeline, C will be 40 ppb at most, U will be near 0 as the water layer would be stagnant, but for this calculation a value of 10 cm/s is used. Re will be below the transition (from laminar to turbulent flow) value (Re = 2100), and Pr will depend on the temperature but will be in the range 500 - 1000 for a saline water. The calculated corrosion rates for a range of oxygen concentrations and operating temperatures are given in Table 4-2.

Temperature	Pr	5	10	15
°C				
5	933	0.0004	0.0007	0.0011
10	803	0.0004	0.0008	0.0012
15	690	0.0005	0.0009	0.0014
20	594	0.0005	0.0010	0.0015

Table 4-2: Corrosion Rates Due to Oxygen (mm/year)

Relevance to Dilbit and Synbit

The values in this Table would apply to both conventional crudes and both Dilbit and Synbit, and the corrosion rates are negligible.

Very high oxygen contaminations would however result in severe pitting corrosion, but this is not a normal scenario for a high pressure transmission pipeline and, in any case, would affect all types of oil pipelines. Heavy crudes do however show lower gas absorption and oxygen corrosion would be less in heavy crude than a light crude.

4.5 Organic acids

Organic acids may be present in the water associated with crude oil and some undissociated acid may be dissolved in the oil. The concentration of the acids is identified by the total acid number (TAN), which is a chemical measure of the total soluble acid in the oil. In general the higher the molecular weight of the acid the higher its boiling point. Organic acid species in bitumen are relatively large molecules with 70 weight% boiling above 524 °C (975.2 °F)^[5]. The principle acids of concern are naphthenic acids, which are cyclopentyl or cyclohexyl carboxylic acids. Naphthenic acid corrosion has been studied extensively because it is a serious concern in refineries. It occurs primarily in high velocity areas of crude distillation units in the 220 to 400 °C temperature range. It does not occur in crude oil transmission pipelines carrying either conventional crude or dilbit and synbit.

The most abundant of the lower molecular weight organic acids are aliphatic acids often referred to as fatty acids, such as formic and acetic acid. At low concentrations and typical



pipeline temperatures these organic acids do not cause significant corrosion in themselves but can be associated with bacterial processes that cause corrosion. The concentration of these organic acids in Dilbit and Synbit will be low because of the method of extraction of the oil from the oil sands.

4.6 Sulphur and Sulphides

Sulphur in crude oil can be involved in corrosion processes under certain well-defined conditions. When present as sulphates it can provide a necessary source of sulphate for sulphate-reducing bacteria to become active. When present as hydrogen sulphide it can react with the iron to form iron sulphide. Low levels of hydrogen sulphide can create a protective film on the metal that reduces the corrosion rate. Most of the sulphur in crude oil is bound in the hydrocarbon structure and plays no part in corrosion processes until the hydrocarbon structure is broken down in the refinery at temperatures in the range 230-455 $^{\circ}$ C^[5,21].

Sulphur compounds found in crude oil include^[22]:

- Elemental sulphur, S
- Hydrogen sulphide, H₂S
- Mercaptans (organic compounds that contain sulphur)
- Aliphatic and cyclic sulphides
- Aliphatic disulphides (similar to mercaptans but higher sulphur and lower volatility),
- Thiophene and homologues, C₄H₄S

Elemental sulphur, if present, is corrosive if it contacts the pipeline surface at an area where there are persistent water layers.



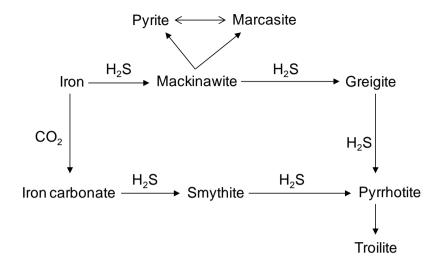


Figure 4-1: Inter-relationships of the Iron Sulphides^[23].

Solid sulphides may settle in a pipeline: these sulphides may be chemically generated by reaction of hydrogen sulphide with metal ions or biogenic. Each of the solid iron sulphides, as shown in Figure 4-1, has a characteristic corrosiveness in that a given weight of a particular sulphide causes a given amount of steel corrosion. After the iron sulphide has completed its "quota" of corrosion it remains relatively inactive. The relative corrosiveness of the different sulphides is given in Table 4-3. The different sulphides are formed either as reactions over time, or by changes in environmental conditions. For example, iron sulphide exposed to acidic micro-aerobic environments that may occur in storage tanks may transform into a form of FeS₂ (marcasite and pyrite); these materials are particularly corrosive. The high viscosity of heavy crude and Dilbit and Synbit would reduce the risk of formation of marcasite and pyrite because diffusion of oxygen would be lower than in a light or medium crude oil.

Sulphide Species	Corrosion (gm) per mole of sulphide	Corrosion (gm) per mole of sulphur in sulphide	Formula	%S
Pyrite	61.53	123.06	FeS ₂	52.5
Greigite	12.53	50.12	Fe ₃ S ₄	42.4
Smythite	19.51	78.04	Fe ₃ S ₄	42.4
Mackinawite	10.08	10.08	FeS _(1-x)	35
Pyrrhotite	6.39	6.39	Fe _(1-x) S	36

Table 4-3: Corrosion by Iron Sulphides



4.7 Bacteria and Microbiological Induced Corrosion (MIC)

Crude oils may become contaminated with bacteria. Studies on debris removed from pipelines shows DNA present in almost all cases, but this does not have any direct relationship to potential corrosion. Much of the trace DNA may have arisen from contamination of the pipe surfaces during transport and storage, installation and hydrotesting, pigging, etc., and in most cases the bacteria are innocuous.

There are some bacteria that can cause corrosion. The most widely-dispersed and recognised corrosive organisms are the sulphate-reducing bacteria (SRB). These bacteria are strict anaerobes and are inactive in the presence of oxygen. They gain energy for activity and growth by oxidising fatty acids to carbon dioxide and water using the oxygen in the sulphate radical; they produce copious quantities of sulphide in the process. The bacteria require a stable water environment, and the presence of sufficient organic acid and sulphate for their metabolism.

The nature of the water is important. Bacteria only flourish over a range of water activity(a measure of the energy status of a water), a_W , and water potential, Ψ , which are calculated from:

$$aw = \frac{55.51}{v.\,m.\,o + 55.51}$$

$$\Psi = \frac{RT.\ln aw}{V_w}$$

where

v = ions generated/mole solute,

m = molality of solute

o = molal osmotic coefficient and

 $V_w = partial molal volume of water (18 cm³/mol at 4 °C);$

55.51 = moles/kg of water, R is the universal gas constant, and T, °K

Pure water has a_W = 1, and the water potential, Ψ , is 0. Generally a_W is < 1.0 and Ψ is negative. In saturated salt solution a_W = 0.75. For bacterial growth a_W must be in the range 0.83 – 0.94 and for fungal growth a_W must be in the range 0.78 – 0.84. For most systems the water activity becomes too high when the total dissolved solids exceed 15%. However, the water activity must be calculated for each pipeline system.

There are no hard and fast rules about the sulphate needed to support bacterial corrosion, but it is generally recognised that a concentration of 50 ppm or higher is required to support sufficiently high bacterial activity for corrosion processes to be significant.

Bacterial corrosion cells take time to establish, usually about 6 months. Initial growth, often in conjunction with other bacteria, results in the formation of a biofilm on the pipeline surface. Biogenic sulphide reacts to form a protective layer of an iron sulphide (mackinawite) on the steel surface. Over time, the mackinawite (tetragonal) converts to greigite (cubic) and the change in crystalline structure results in cracking and failure of the initial sulphide film. The



relationships between the sulphide species is shown in Figure 4-1. The exposed steel will be anodic to the iron sulphide film, typically there is a voltage difference of ~50 mV. If the area of exposed steel is small then the anodic current may be too high for a new, protective mackinawite film to form. Instead, the biogenic sulphide reacts to form a colloidal precipitate of mackinawite.

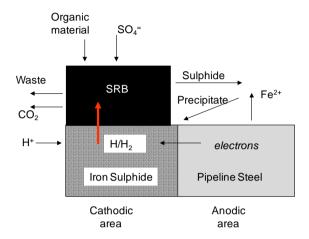


Figure 4-2: Microbial Corrosion Cell^[24].

The hydrogen evolution reactions occur on the cathodic mackinawite and, because the mackinawite is not stoichiometric, hydrogen bonding occurs, which results in a slow decline in the corrosive activity of the mackinawite. The SRB that cause corrosion contain hydrogenase, an enzyme that allows them to utilise hydrogen for sulphate reduction and, when there is a shortage of organic material, the SRB switch to a hydrogen metabolism. The removal of hydrogen from the mackinawite maintains the activity of the corrosion cell. The corrosion mechanism is shown schematically in Figure 4-2. The precipitated biogenic iron sulphide is colloidal, and the surface area has been calculated to be 13.3 m²/gm[25]. As additional iron sulphide is precipitated the ratio of cathodic to anodic area increases rapidly, and the corrosion of the steel beneath the iron sulphide packed biofilm also increases. The corrosion rate is limited by diffusion processes but becomes approximately linear. Typical corrosion rates are in the range $1.6-2.0 \, \text{mm/year}^{[26]}$.

The high corrosion rate makes MIC one of the main potential corrosion hazards for oil transmission pipelines. If the water meets the criteria for SRB activity then the fatty acids in the oil will provide the nutrient for the proliferation of bacteria. The bacteria also need free water and a surface to colonise before they can multiply, and this is the key to controlling the threat of MIC. As the colonies usually take 6 months to become established regular cleaning pig runs along the pipeline is one of the most effective methods of reducing the threat. Biocide batch treatment can also be used if it is thought colonies have become established.

Bacteria are temperature sensitive and the most widespread strains of SRB are only active at temperatures below ~45°C. Although there are thermophilic strains that can tolerate temperatures up to 80 °C these are rarely encountered in oil fields. Pipelines operating in excess of 45 °C have a very low risk of MIC.

Relevance to Dilbit and Synbit

Water is necessary to support bacterial growth and activity. The low BS&W combined with the ability of heavy crudes, including Dilbit and Synbit, to sweep water from pipelines at low



flow velocities would prevent persistent water layers and the likelihood of bacterial growth becoming established.

4.8 Under Deposit Corrosion

Adherent wax and scales and loose debris may form in pipelines partly on the walls but mainly at the bottom of the pipeline. Wax and scale do not prevent corrosion unless they are continuous over the pipeline surface and are sufficiently robust to prevent free water from contacting and wetting the pipeline surface.

Wax in particular may form over a water pocket and corrosion can continue beneath the wax at a rate determined by the rate of diffusion of the carbon dioxide or hydrogen sulphide through the wax layer.

Scale is rarely continuous and will be porous or fractured and water may fill the pores and cracks in the scale.

Other debris, for example sand and loose scale, can accumulate in pipelines and may trap water that would otherwise be removed by the flowing oil. In such a case, corrosion may occur under the deposits. The rate of corrosion will be largely fixed by the concentration of corrodants such as carbon dioxide, hydrogen sulphide, and fatty acids.

Bacteria may also be sheltered under deposits, and the corrosion rate will be determined by the rate of diffusion of an organic food source and sulphate to the sulphate-reducing bacteria.

Deposits interfere with corrosion inhibition programmes because some of the inhibitor will adsorb onto the debris rather than the pipeline surface where it is needed. Underdeposit corrosion sometimes associated with bacteria is recognised as one of the main internal corrosion threats to oil transmission pipelines and is the subject of continued research.

Relevance to Dilbit and Synbit

Dilbit and Synbit typically carry ~25% less sediment than conventional heavy or medium crudes and so a pipeline carrying Dilbit or Synbit would be at no greater risk that one carrying conventional heavy crude (see Table 4-4).

Average Sediment Level			
Conventional Medium and Heavy Crude	Dilbit and Synbit	Lighter Products	
277 ppm	205 ppm	169 ppm	

Table 4-4: Sediment levels in different types of transmission pipeline specification crudes^[27].



Strategic crude oil pipelines are regularly pigged to remove wax and debris and to control scale. Under deposit corrosion will be limited to the short periods between deposition and pigging. This applies to all crude oil pipelines including those transporting dilbit and synbit.

4.9 Erosion

The presence of solids, in particular sand, can alter the corrosion behaviour by damaging the protective corrosion product films. For a given flow, the damage is clearly more pronounced at bends and other areas of high turbulence or flow, such as manifolds. Usually, small amounts of solids are tolerable, typically 3 - 5 lb/1000 bbls oil would not be considered significant for a horizontal pipeline.

Erosion rates may be calculated from:

$$CR_{erosion} = \frac{K(0.65W)V^2L\beta}{gP(\frac{\pi}{4}D^2)}$$

where:

CR_{erosion} is the erosion corrosion rate (mm/year).

K is the Rabinowicz constant related to wear rate, and for pipelines is taken as 0.071.

W is the sand production rate (bbl/month).

V is the average flow velocity (f/s)

ß is a coefficient relating to the impingement angle: 1 for angles 10° to 60° and 0.5 otherwise. It is usually taken as 0.75 for pipelines.

g is the gravitational constant (32.2 f/s²).

P is the penetration hardness of the material, for steel a typical value is 1.55×10^5 psi.

D is the internal diameter of the pipe (in).

This equation may be simplified to give a critical velocity below which a defined erosion rate of 0.2 mm/yr will not occur:

$$V_{critical} = \frac{4D}{\sqrt{W}}$$

Note the importance of pipeline diameter: the larger the diameter, the higher the critical velocity. Crude oil transmission pipelines are large diameter.



As would be expected, bends represent a special case. The present approach to predicting the erosion effect at a bend is to calculate a "stagnation length" for the particular geometry of bend or elbow. A stagnation zone occurs in areas where the fluid flow is at right angles to a surface. At a bend the flow must turn, but at the heel of the bend the fluid forms a low flow zone locked at the surface by the force of the flow at right angles to the bend. The dimensions of the stagnation zone depend on: pipeline geometry, flow, and the fluid properties. An erosive particle must cross the stagnation zone to impact the pipe wall, and the distance it must cross is the stagnation length.

If the stagnation length is long, then the erosion corrosion rate will be reduced, because the momentum of the particle will be reduced in its passage across the stagnation length. The impact velocity of the particle, V_{impact}, is related to fluid properties and pipeline dimensions. The nature of the damage ensuing depends on the impact velocity and fluid velocity. At low impact velocities the protective scale remains intact, at high velocities the scale is completely removed and general uniform corrosion occurs. The highest risk is at the intermediate velocities where localised pitting damage occurs.

Relevance to Dilbit and Synbit

Experimental testing^[28] indicated that a sand production rate of 0.1 m³/day (200 bbl sand/month) in water would not cause excessive corrosion at 1.5 D bends if the flow velocity was <5 m/s. This was in a 150 mm diameter pipe. In crude oil the threshold values were very high, over 30 m/s; as this would be above the API RP-14E critical velocity the risk of erosion at bends can be discounted in all crude oil transmission pipelines including those transporting Dilbit or Synbit.



5. FORMS OF CORROSION

5.1 Introduction

There are several morphologies of corrosion, and these are discussed briefly below. The forms of corrosion, shown in Figure 5-1, are:

- General
- Localised
- Pitting
- Crevice
- Intergranular attack
- Sulphide Stress corrosion cracking (SSC)
- Hydrogen blistering (HIC)
- Corrosion fatigue

5.2 General Corrosion

General corrosion is rarely observed in crude oil pipelines, because continuous water layers are not present for sufficiently long period of time for this form of corrosion to be established. If persistent water layers are present then a high concentration of low molecular weight organic acids can result in general corrosion over the wetted area. This is sometimes found in crude oil tanks, but not in flowing crude oil transmission pipelines. The key control measures are BS&W and flow velocity, and would apply to Dilbit and Synbit as well as conventional crude oil pipelines.

5.3 Localised Corrosion

Localised corrosion is probably the most common form of corrosion attack in pipelines. It is really a localised form of general corrosion and results from small variations in the environmental/metallurgical conditions that become amplified by a corrosion process. Carbon dioxide is the most common mechanism causing localised corrosion in upstream oilfield pipelines. These are pipelines upstream of separators where the partial pressure of carbon dioxide may be significant. Prevention of this form of corrosion is relatively straightforward, by the addition of corrosion inhibitors. It is not a significant risk in crude oil transmission pipelines that are downstream of separators where the partial pressure of any carbon dioxide, if present, is low.



5.4 Pitting

The distinction between localised corrosion and pitting is often confused. True pitting is isolated attack where the main area of the metal is relatively unaffected. Pits in carbon steel tend to be hemispherical, and often several pits overlap to produce a scalloped area of damage. Carbonic acid corrosion can form isolated pits, but usually the pits initiate at areas where there is a defect in the steel surface; for example, a surface emergent sulphide inclusion. Hydrogen sulphide causes notable pitting corrosion. The iron sulphide films that are formed by the reaction of the sulphide with the steel surface are protective but when the sulphide film breaks down over a small area the protective sulphide film may not reform. In this case there will be continued corrosion as the film defect resulting in a pit.

Microbiological activity results in pitting of the steel beneath established colonies of bacteria. As the colonies die off and are replaced by an adjacent colony, an additional overlapping pit is formed. Pitting corrosion rates may be high and in the range 2 – 10 times typical localised corrosion rates.

If pitting does occur in crude oil transmission pipelines it is usually triggered by under deposit corrosion. It is controlled by batch inhibition and periodic pigging.

5.5 Crevice Corrosion

Crevice corrosion can occur where there are occluded areas; for example, under partially detached coatings, at gaskets, and flange gaps. Crevice corrosion in a transmission pipeline is generally limited to the flange connections at valves and pipeline offtakes. In heavy crude systems the crevices become filled with oil as a result of pigging that forces the oil into the crevice and this oil persists. Crevice corrosion rates are similar to pitting corrosion rates.

Transmission pipelines are usually fully welded, so crevices are limited to flanged valves in stations, which are regularly inspected. This applies to all crude oil transmission pipelines including those transporting Dilbit and Synbit.

5.6 Intergranular Corrosion

Intergranular corrosion is rare in carbon steel pipelines, unless there has been an inappropriate weld procedure. Hydrogen sulphide can cause this form of damage, and the intergranular corrosion will, over time, convert to pitting corrosion.

The risk of this occurring is controlled by weld procedure qualification, inspection and very low content of any hydrogen sulphide. This applies to all crude oil transmission pipelines including those transporting Dilbit and Synbit.

5.7 Sulphide Stress Cracking

Sulphide stress cracking (SSC) results from the conjoint action of stress and a specific set of environmental conditions. Susceptible pipeline steels can crack in sour service if the concentration of hydrogen sulphide is high enough. Sulphide stress cracking is prevented by correct materials selection and fabrication and the avoidance of mechanical damage to the pipeline (this type of damage can cause a severe increase in plastic strain) during service. The concentration of hydrogen sulphide in the crude oil in a transmission pipeline (conventional, Dilbit or Synbit) will be below the critical concentration for SSC to occur and can be prevented anyway by material selection.



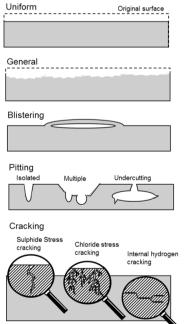
5.8 Hydrogen Induced Cracking

Hydrogen induced cracking results from the formation of blisters filled with hydrogen that can occur in the wall of a pipeline in sour service because of migration of atomic hydrogen, generated by corrosion, becoming trapped at laminations and other unfavourable metallographic features in the steel. The hydrogen cannot escape and collects to produce high pressures that distort the steel to form blisters. HIC only occurs when there is a high concentration of hydrogen sulphide present and the water pH is acidic. In crude oil transmission pipelines transporting convention crudes, Dilbit or Synbit, the concentration of hydrogen sulphide is below the critical concentration for HIC to occur.

5.9 Corrosion Fatigue

Corrosion fatigue is rarely observed in crude oil pipelines and when it is it is an external phenomena. Fatigue loading of a pipeline is possible downstream of a pumping station, or when a pipeline is pressure or thermally cycled, or if a pipeline is subject to repeated external loading. Strategic crude oil pipelines are usually operated so that they are not extensively pressure or thermal cycled, and the design and route of the pipeline is carefully selected to avoid risk of external loading.

When fatigue occurs it does so at a weak point. The failure of the crude oil pipeline carrying Dilbit at the Kalamazoo River was attributed to external fatigue cracking that initiated at stress corrosion cracks under a detached and shielding coating^[29]. The fact that it was carrying Dilbit at the time was incidental to the failure mechanism. Corrosion fatigue is not an issue for internal corrosion of operating oil transmission pipelines.



Uniform corrosion is relatively rare. It occurs in acid medium (e.g. during acid pickling to clean the steel) and in inhibited solutions. It is not usually uniform at the micro-scale.

General corrosion is uneven highly distributed corrosion and is common in in pipelines though it may be restricted to parts of the pipeline, usually the 6 o'clock position.

Blistering is caused by hydrogen generation within the steel and occurs in acidic conditions (e.g. pickling) and sour service. The blisters form at inclusions within the steel.

Pitting corrosion is common in pipelines. Pits may be individual and deep or in clusters and sometimes overlapping. Undercutting pits occur in sour service where the sulphide films act as a cathodic surface.

Cracking is associated with high stress and may be intergranular or transgranular. Hydrogen cracking is usually single unbranched cracking which may be associated with blistering. Corrosion resistant alloys show multiple branching cracking.



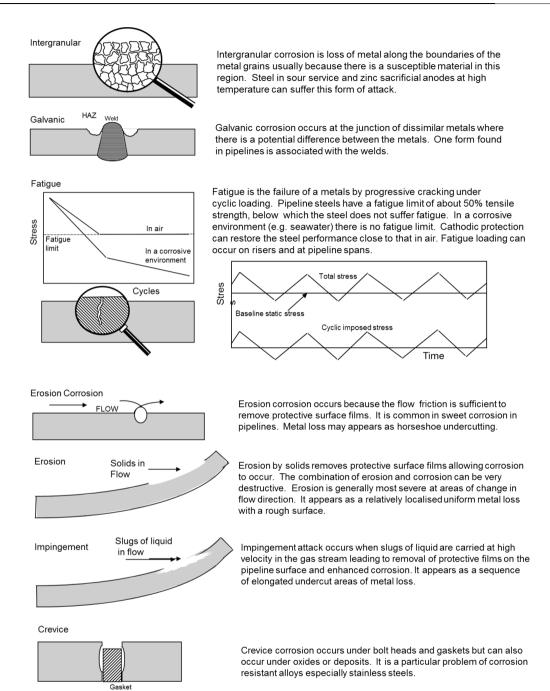


Figure 5-1: Summary of Corrosion Morphologies.



6. DILBIT AND SYNBIT CORROSIVITY AND EXISTING PIPELINES

6.1 Dilbit and Synbit Corrosivity Compared to Conventional Crude Oils

Laboratory tests have shown that there is no straight forward correlation between crude oils basic properties, such as gravity, sulphur content and TAN and its corrosivity.

The recently introduced ASTM G 205^[30] provides a standard test method for assessing the corrosivity of a crude oil under pipeline conditions. It recognises that all corrosion mechanisms, both corrosion to the outside surface of the pipe and the internal surface of the pipe, have to have an electrolyte. For internal corrosion in a pipeline to occur, the electrolyte must wet the internal surface of the pipe. Crude oil is not an electrolyte; the water in crude oil is the electrolyte. If the water wets the surface of the pipe there is the potential for corrosion. The rate of corrosion will be determined by the corrosive species in the water, and many of these species may come from the crude oil.

Many crude oils also contain species that inhibit corrosion and testing in accordance with ASTM G 205 allows crude to be classified as inhibiting, non-inhibiting or corrosive.

This standard test method has limitations and will no doubt be further developed^[31]. It would not fully assess the risk from bacteria, as the colonies take months to become established, but if the water does not wet the surface of the pipe then this would certainly limit the scope for any corrosion mechanism including bacterial processes. It also has limitations with regard to gases, depending on sample conditioning, but it would detect issues with other species such as sulphur.

Tests on 11 crude oils, which included 4 bitumen derived crudes, showed all of them to be inhibitive according to the ASTM G 205 standard. The maximum corrosion rate measured in the crude oils, including the Dilbits, was 2.1 mpy \pm 1.9 (0.05 mm/yr \pm 0.047)^[32]. This is a very low value.

6.2 Upstream Pipelines Compared With Transmission Pipelines

The upsteam pipelines in the oil sands production chain include hydrotransport, waste water, tailings, and diluent pipelines, as well as oil transmission pipelines.

The hydrotransport pipelines carry the sand/bitumen/hot water slurry containing more than 50% water at temperatures up to 90 °C. These, or conveyor belts, are used to transport the oil sand to the processing plant. The slurry can contain a number of corrosive species depending on the oil sand extraction method. Open mining will introduce oxygen and in-situ production can enable carbon dioxide, oxygen and/or hydrogen sulphide to enter the pipeline depending on the extraction process. The hydrotransport pipelines operate at velocities of 3-6m/s and in common with most slurry pipelines can suffer erosion and flow assisted corrosion^[33].

Waste water pipelines carry wastewater separated from the crude oil. Extraneous matter and acid gases are usually taken out of the water, and oxygen is excluded where possible. A variety of materials are used for waste water pipelines, but where carbon steel is used it is reported to sometimes corrode.

Tailings pipelines contain water and sediments (25-30%) left over from the processing. They operate at up to 70 °C and may also have internal corrosion, particularly from oxygen



ingress, exacerbated by erosion depending on the fluid velocity. The critical velocity for erosion occurring is >5 m/s.

Diluent pipelines contain crude oil or crude oil fractions and have very low water contents, so only have internal corrosion if water is present and it wets the internal surface.

Some upstream oil transmission pipelines carry very waxy crudes which are heated before they enter the pipeline to reduce the probability of wax deposition within the pipeline, the idea being to heat the oil sufficiently so that during transit through the pipeline the temperature does not reach the pour point at which wax deposition occurs. This type of pipeline operates at higher temperatures, and is often thermally insulated.

Apart from the diluents pipelines, upstream pipelines operate under completely different conditions to downstream oil transmission pipelines which carry products with very strict control on BS&W. Upstream pipelines often have significant corrosion issues, downstream crude oil transmission pipelines, including those transporting Dilbit and Synbit do not.

6.3 Incident Records

Crude derived from oil sands has been transported by pipeline since 1968. Diluted bitumen has been transported for more than 25 years.

PHMSA incident data from 2002 to mid-2012 show there were no releases of oil caused by internal corrosion from pipelines carrying Dilbit. There were no known examples prior to 2002^[34]

The data from Canada is more difficult to interpret because of the different reporting levels and the fact that Dilbit pipelines are not reported separately. Failure rates for similar crude pipelines in Alberta are comparable to those in the USA despite the fact that Alberta has far more pipelines carrying Dilbit^[38].



7. INTEGRITY MANAGEMENT OF CRUDE OIL TRANSMISSION PIPELINES

7.1 General

Pipelines in the USA and Canada are managed using an integrity management system. Part of that system includes assessment and control of internal corrosion. The requirements to control internal corrosion of pipelines carrying Dilbit or Synbit are exactly the same as for conventional crude oil pipelines.

Any significant internal wall thickness loss caused by internal corrosion should be detected by inline inspection using inspection tools based on Magnetic Flux Leakage (MFL) or Ultrasonic Thickness (UT) technologies. Aside from control of product specification, in particular BS&W, there are two principle methods for controlling internal corrosion should it occur: cleaning the pipeline; and, chemical treatment. Regular cleaning of pipelines is a standard good practice and can help to prevent corrosion initiation; for example, from under deposit corrosion. Inhibition is usually only used if corrosion is detected.

7.2 The Need for Pipeline Cleaning

Pipelines carry many contaminants during their normal operation. These contaminants and associated deposits can pose a corrosion risk, have an adverse effect on product flow, and lead to problems with downstream process. A list of typical pipeline contaminants and associated deposits is shown Figure 7-1.

Source	Contaminant
Product	Sand, Silt and Sludge
Hydrocarbons	Wax and Paraffin
Corrosion By-Product	Scale and Rust
Chemicals	Biocides and Corrosion Inhibitors
Water	Carbonic Acid, Salts and Scale
Pipeline Construction and Maintenance	Welding rods, Spacer, Mud, Gloves and General Debris

Figure 7-1: Typical Pipeline Contaminants and Deposits.



Regular cleaning of pipelines can be used to prevent build-up of pipeline contaminants. This includes conventional crude oil pipelines and those transporting Dilbit and Synbit. A pipeline may need to be cleaned for:

- general operational cleanliness; and/or,
- · cleanliness for internal pipeline inspection.

There is a distinction between both levels of cleanliness.

7.2.1 Operational Cleaning

Operational cleaning pigging is conducted on pipelines to ensure that an accumulation of pipeline deposits are not affecting product flow, or potentially causing downstream process flow upsets. This activity is often referred to as either production pigging or maintenance pigging.

Operational pipeline cleaning can be conducted to:

- prevent under deposit corrosion, such as SRB colonies;
- increase the efficiency of injected chemical inhibitors; and/or,
- reduce the levels of deposits (e.g., wax or scale) on a pipeline wall. High wax levels for example, can reduce product flow or potentially block the pipeline.

7.2.2 Pre-inspection Cleaning

Cleaning a pipeline in preparation for an ILI usually requires the pipeline to be cleaned to a much greater level than for operational cleaning. A pipeline containing gross debris deposits may result in incomplete or degraded inspection data being gathered, and the completeness or accuracy of the inspection being adversely affected. For example:

- MFL Tool may experience sensor lift-off if the pipeline wall is heavily coated with debris, potentially causing data quality issues.
- UT Ultrasonic tools may give spurious readings if there is a large accumulation of wax on the pipe wall.

In addition to debris adhering to the internal pipe wall, debris deposits can also accumulate on an ILI tool as it transits through the pipeline. In this case it is possible for relatively low levels of deposits to build up, giving rise to similar problems.

The cleaning of a pipeline can be conducted by:

- Mechanical cleaning (i.e., pigging);
- Chemical cleaning;
- A combination of both.



It should be noted that chemical cleaning of pipelines is usually done in conjunction with some mechanical pigging.

7.3 Mechanical Cleaning Pigging

Mechanical cleaning is achieved by physically removing pipeline debris using pigs. There are a variety of pigs available for different levels of cleanliness and removing different types of debris; however, they all clean pipelines by using attachments including brushes, scrapers and magnets to loosen and push debris along the pipeline to an egress point.

Debris removed from the pipe wall is pushed ahead of the pig. If a significant amount of debris accumulates it may result in a blockage being created in the pipeline. This is a known issue and pigs are often fitted with bypass portals to keep the debris mobilised in front of the pig.

7.4 Corrosion Inhibition

If corrosion is identified as an operational risk it can be markedly reduced by the addition of corrosion inhibitors. For new designs where corrosion is anticipated the corrosion allowance can be much reduced with a consequent saving in capital expenditure. However, the addition of inhibitors is not a cheap option and, when logistics and manpower are taken into account, the cost of inhibition may be over \$100,000 per annum. The cost of the inhibitor itself is generally less than 25% of the total cost to the pipeline operator. The additional cost is the delivery of the inhibitor, servicing the injection pumps and corrosion monitoring to check the efficiency of inhibition. An alternative approach used for treating pipelines where the corrosion rate is low, such as transmission pipelines, is to batch dose the pipeline periodically.

The efficiency of an inhibitor is markedly affected by the "cleanliness" of the pipe. Pipes containing a high level of debris (rust, mill scale and solids from production) are more difficult to protect with inhibitor because the chemical is adsorbed onto the surfaces of the debris. Inhibitors are also sensitive to flow rates. Inhibitor efficiency is reduced in low and stagnant flow conditions. For cases where stratified water layers will be persistent the inhibitors recommended are generally oil-dispersible water soluble so that the inhibitor partitions preferentially into the water phase. For cases where water layers are not persistent, the more efficient oil soluble-water dispersible or oil soluble inhibitors can be used provided there is confidence that the oil phase will repeatedly wet the pipeline walls to ensure fresh inhibition of the metal surface.

It is necessary to implement a corrosion monitoring programme to ensure that the inhibition programme is functioning adequately. Such a programme should include regular analysis of the transported crude and associated water, corrosion monitoring (e.g. weight loss coupons, electrical resistance) and periodic inspection using ultrasonic surveys or intelligent pigging. The frequency of the analyses and inspections would be decided by the perceived risk and the measured corrosion rates, which would feed back into the corrosion risk assessment. The techniques used for conventional oil would be equally applicable to Dilbit and Synbit pipelines and would be expected to produce similar information.



7.5 Summary

Regular cleaning of pipelines is good practice where the product carried may leave deposits on the inner wall. The running of cleaning pigs helps to remove deposits and any free water from the pipeline greatly reducing the risk of corrosion, particularly microbially influenced corrosion and/or under deposit corrosion, the two greatest internal corrosion threats to crude oil transmission pipelines

If internal corrosion is detected, then the use of inhibition is standard practice. The use and limitations of inhibitors is well-understood. Treatment of Dilbit and Synbit would not be different to conventional oils or heavy oils.



8. PUBLISHED LITERATURE ON DILBIT CORROSIVITY FROM ENVIRONMENTAL GROUPS

Until recently, there has been little published work on the corrosivity of Dilbit and Synbit. This apparent void has allowed speculation about how corrosive the products are in transmission pipelines^[35,36]. Much of the speculation is ill informed, misleading and wrong^[37,38]. This speculation includes:

Dilbit is more corrosive than conventional crude because they have total acid concentrations 15-20 times higher than benchmark conventional crudes [35,36].

The benchmark reference crudes used in this assessment are not given, so the figure of 15-20 times is misleading. The average TAN number for the Canadian oil sand Dilbits shown in Figure 2-4 is 1.5 compared with the average for the conventional Canadian heavy crudes of 0.59, approximately 3 times the value but when compared with heavy crudes internationally as shown in Figure 2-5, the average value of the International heavy crudes is 1.6 compared with 1.3 for the Dilbits shown in the figure, and is therefore comparable. Total acid concentrations are a parameter that is important under refinery conditions where the product is exposed to temperatures in excess of 240C. It cannot be used to assess the likelihood of corrosion occurring in a transmission pipeline.

Dilbit contains 5 to 10 times more sulphur than conventional crudes [35,36].

Again this is misleading. The average sulphur content for the Canadian oil sand Dilbits in Figure 2-3 is 4.1% compared with 3.1% for Canadian conventional heavy sour crudes, a difference of 1.32. When compared with other international heavy sour crudes in Figure 2-5 the Canadian oil sand Dilbits have an average sulphur content of 3.78% compared with 3.09% for the international heavy sour crudes, a difference of 1.22. So, although the Canadian oils sand Dilbits may well contain more than the average sulphur content of other heavy sour crudes, the difference is not large. Moreover, the sulphur content cannot be used to assess the likelihood of corrosion in a transmission pipeline.

Dilbit contains high concentrations of chloride salts which can lead to chloride stress corrosion in high temperature pipelines^[35,36].

The soluble salt content of Canadian oil sand Dilbits is actually less than other conventional Canadian heavy crudes, as shown in Figure 2-7. The average value for Dilbits is 17 ptb (pounds per thousand barrels) compared with 37 ptb for the Canadian conventional heavy crudes. The Synbits have even lower salt contents than the Dilbits.

In any case, chloride stress corrosion cracking is not a corrosion mechanism that carbon steel transmission pipelines suffer from. Chloride stress corrosion is of particular concern for corrosion resistant alloys such as austenitic grade stainless steels. The impact chloride has on any internal corrosion in a carbon steel transmission pipeline varies with the corrosion mechanism but is usually quite small, and is not one of the main considerations. It is however a significant concern for refineries where there is a more widespread use of corrosion resistant alloys, and the chloride content will have a significant impact at refinery temperatures.

Dilbit contains contain significant quantities of quartz, silicates and pyrite which will increase the erosion of the pipeline^[35,36].



The inference given here is that because the particles are hard, they are more likely to cause erosion. This is not correct. Physical erosion is determined predominantly by both mass and velocity, not just type of particle. Transmission pipelines operate at velocities well below the erosional velocity, and even below that where flow assisted corrosion may occur. The biggest concern with sediments in transmission pipelines is the settlement of particles increasing the risk of under deposit corrosion and microbiologically influenced corrosion. This is why there is strict control of BS&W, and why crude oil including Dilbit and Synbit transmission pipelines operate at velocities in the range 1 - 2.5 m/s, above the velocity where water and sediment drop out tend to occur, but well below the velocities where erosion may be a concern.

Dilbit pipelines operate at high temperatures which will significantly increase the corrosion rate, an accepted rule of thumb being that corrosion rate doubles for every 10°C increase in temperature. Diluted bitumen pipelines operate at 60 C [35,36].

Crude oil can increase in temperature as it moves through the pipeline system due to friction. This is true for Dilbit where a heavy crude is diluted with a lighter crude [39]. TransCanada asserts that the Keystone XL pipeline will operate between $80-120~{}^{\circ}\mathrm{F}$ (26 - 48 °C). Most crude oil pipelines, including transmission pipelines carrying Dilbit, operate in the region of 17 - 40 °C. On batch transmission pipelines the temperature will vary somewhat with the viscosity and blend of the product being shipped and the season, hence the temperature will vary.

The impact temperature has on corrosion depends on the corrosion mechanism:

- It would certainly be the case that the corrosion rate doubles for every 10 °C rise in temperature for carbon steel exposed to a strong acid like hydrochloric acid.
- In oxygenated systems where the rate is diffusion controlled, the rate doubles with every 30 °C rise in temperature up to about 80 °C where it falls thereafter in an open system, but continues to rise in a closed system^[40]. In other systems the effect temperature has on scale formation has the biggest impact.
- In a system where carbon dioxide is the main threat the corrosion rate increases to about 80°C then may fall thereafter due to the formation of scale. As with oxygen this is not considered a significant threat in crude oil transmission pipelines.
- The greatest threat to crude oil transmission pipelines is usually considered to be bacterial corrosion and in particular corrosion caused by sulphate-reducing bacteria often associated with sediment deposits. As discussed earlier MIC can cause high corrosion rates. However whilst there are thermophilic strains of SRB, these are rarely encountered in oilfield systems. The usual strains of SRB are active at temperatures below 45 °C so any increase in temperature above this would actually reduce the risk of corrosion from MIC.

It has been suggested that increasing the temperature increases the risk of external stress corrosion cracking. There are two forms of external stress corrosion cracking that carbon steel pipelines are susceptible to, high pH stress corrosion cracking and near neutral pH stress corrosion cracking. High pH cracking occurs in a narrow potential range associated with some cathodic polarization but not enough to achieve cathodic protection – so poor levels of cathodic protection caused by, for example, disbonded shielding pipeline coatings or rocky ground conditions. It is most commonly found on gas pipelines with enamel or tape wrap coatings, within 20 miles of compressor stations.



Increasing temperature does increase the propagation rate of high pH stress cracking. Near neutral pH stress corrosion cracking occurs at the free corrosion potential, i.e., a complete lack of cathodic polarization. Temperature appears to play no role in increasing the risk of low pH stress cracking.

In either case, high pH or near neutral pH, pipelines coated with fusion bonded epoxy are not considered to be at risk from SCC. These two corrosion mechanisms are largely found on pipelines coated with coatings such as enamels, tape wraps and heat shrink sleeves.



9. CONCLUSIONS

- 1) Dilbit and Synbit have similar characteristics as conventional heavy sour crudes in terms of density, TAN and sulphur content.
- 2) The TAN number, sulphur and salt content are important parameters for refineries, but cannot be used to assess the corrosion threat to an oil transmission pipeline, and these parameters are not used by pipeline corrosion engineers.
- 3) The presence of an electrolyte, essentially water, is necessary and that water must wet the internal surface of the pipeline for corrosion to occur in crude oil pipelines.
- 4) The corrosion mechanisms that oil transmission pipelines suffer from are well understood and transmission pipelines carrying Dilbit and Synbit have similar corrosion threats as those carrying conventional heavy sour crudes. The highest risks are associated with under deposit corrosion and sulphate-reducing bacteria. The key parameter used to reduce the risk of internal corrosion is the basic sediment and water (BS&W) value which is 0.5% for conventional crude as well as Dilbit or Synbit. This reduces the risk of water wetting the surface of the steel and of settlement of sediment which may lead to under deposit corrosion.
- 5) Crude oil transmission pipelines including those that carry Dilbit and Synbit are operated at flow velocities above that at which water and sediment drop out tend to occur but below the velocities where erosion corrosion can occur.
- 6) ASTM G205 has been used to assess the corrosivity of a number of conventional crude oils and Dilbit and Synbit. The results show that the Dilbit and Synbit are no more corrosive than comparable conventional crude oils^[31].
- 7) Crude oil transmission pipelines have carried Dilbit and Synbit for over 20 years with no discernible increase in corrosion failure incidents.
- 8) All pipelines have a corrosion control strategy as part of an integrity management plan. For a crude oil transmission pipeline this will include the running of cleaning pigs as required to remove any deposits and stationary moisture. It may also include batch treatment of inhibitor and or biocide. It will also include inline inspection using an MFL or UT inspection tool.
- 9) The corrosion risks associated with Dilbit and Synbit are considered to be no greater than with conventional crude oils in transmission pipelines, and existing integrity management techniques are capable of mitigating these risks.



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