CanmetMATERIALS

Internal Corrosion of Rail Tank Cars

A Primer

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1   Prologue

This primer has been written on behalf of the staff of Transport Canada, to assist them in identifying and understanding internal corrosion issues, specifically with regard to rail tank cars. As such, this document describes the basics of corrosion, presented in as simple manner as practicable, and highlights several areas of potential concern, that may or may not play an increasingly significant role in the future. Also considered are several areas for future improvement in terms of best practices and areas for further research.

A further objective, and indeed much of the work underpinning this primer, was to understand the significance of corrosion in the tank car industry. With this in mind, many industry players were contacted regarding observed trends in corrosion. Anecdotal evidence suggested that corrosion was increasing in prevalence, although actual data was lacking, as was an understanding of the likelihood and potential consequences of a corrosion-induced spill.

It is hoped that this primer will not only raise overall awareness of corrosion issues, but also enable a conversation to develop within Transport Canada such that identified issues be addressed early on, rather than later when the consequences can be more severe. Another intention behind this primer is to make Transport Canada staff aware that assistance and advice, if required, is readily available in other Federal laboratories such as our own.

2   Tank Car Industry Observations

Historically, tank cars have always been used to transport oil produced by conventional means (see section 3.2.1). Whilst internal corrosion did occur, it was infrequent, es-

pecially when compared to other sources of tank car damage such as impact damage or wearing of break pads and mechanical components. A review of the literature did not yield any articles discussing internal corrosion phenomena.[1] Nine tank car manufacturers, service shops and lessors were contacted for advice. Discussions with their engineers, all under terms of confidentiality, supported the view that internal corrosion was not considered a significant issue until the early 2000's. All correspondents did describe a growing concern with internal corrosion within the industry starting around a decade ago with the advent of hydraulic fracking, that has only grown worse with time. One service shop engineer described internal corrosion as 'a big issue'. Industry workshops have been held, and the overall feeling supports the lining of tank cars internally. However, there is insufficient capacity available to retrofit the existing rolling stock and much of the stock will become obsolete as new standards take hold and older DOT-111 tank cars are phased out of service. The cost of applying internal coatings, estimated at $7–9k for new cars, and $10–12k for existing cars, requires a considerable outlay that the industry is not keen to make. This is exacerbated by the current low oil price has effectively put further tight oil developments in the United States. This source of oil is a major driving force behind the rise in tank car usage over the last decade.

Another engineer, who had conducted research into the suitability of internal coatings to avoid exactly this issue, stated that internal corrosion had become obvious in the bottom of crude oil tank cars that were only one to two years old. Corrosion significantly worsened in years three through four, and took the form of shallow pits. With

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[1] All major journal article databases, such as Scopus, Web of Science, Metadex, etc., were queried.

decades of experience in the industry, he claimed that he had never seen such widespread corrosion, although he was keen to stress that he had yet to see a pit deep enough to risk penetrating the steel shell.

However, whilst the number of tank cars requiring remedial repairs has increased dramatically over the course of the last decade, so too has the number of tank cars in service. Also, the turn-around time (the return journey from field to refinery and back) has reduced from approximately 6 weeks in the 1990's, to only one week in recent years. Is the number of internal corrosion incidents still proportional to the rolling stock population, or is something happening that is causing internal corrosion to grow in significance? This is a fundamental question that is not easy to answer. Tank cars were described as being analogous to rental cars: the lessor provides rolling stock to a lessee for a period of time for an agreed cost. During this time, the tank car owners do not necessarily know where the tank car is, nor what it is carrying. Indeed, if the tank car suffers damage, the lessee can fix the damage and eventually return the tank car to the lessor, or return the tank car in a damaged state and pay for repairs at that point. It was found during this study that service shops were unwilling to provide data on the types and quantity of repair jobs conducted, as that knowledge belonged to the lessee or lessor. The lessee and lessors often amalgamated repairs into an O&M cost and did not have readily available data on specific repairs. Understanding the extent of the internal corrosion in this complex picture has been difficult, and it has been necessary to rely upon anecdotal evidence from a small number of engineers and managers within the industry.

One of the most striking observations recounted during these discussions was that water, up to three feet in depth, has been found in tank cars. This is clearly not water

that has accumulated over the course of many journeys, and although such instances are likely to be very rare, the presence of water, and therefore corrosion, is common and may pose a risk in the future. To this end, this primer is intended to explain the phenomena as they pertain to tank cars.

3   An Overview of Corrosion

What is corrosion? Corrosion has been defined by the National Association of Corrosion Engineers (NACE) as 'a naturally occurring phenomenon [causing] the deterioration of a material (usually a metal) that results from a chemical or electrochemical reaction with its environment.'

More poetically, corrosion can be described as the perpetual battle between nature and Humankind; civilisation is built with metals, almost none of which exist in nature. Iron, copper, tin, nickel, chromium, aluminium, etc., are all found as minerals, which are the most stable forms of these elements. We take these ores, and put incredible amounts of energy into them to convert them to their metallic form. It is the release of this energy, and the conversion of the metal back to a more stable form, that is the driving force for corrosion. All nature requires is the opportunity, and time.

As this document is a primer, it is intended for an audience that includes staff not solely from engineering or science backgrounds. Therefore, it must contain the necessary information to enable Transport Canada staff to understand the corrosion processes that may be at work within rail tank cars. It is by no means an exhaustive document, and most topics discussed here are presented in a simplified manner. Indeed this document is oriented towards understanding when, where and how corrosion occurs, leaving

aside the more complex issue of 'how fast'. Corrosion is the phenomenon of concern, but it is entirely dependent upon the materials and the environment. In order to understand the environment, it is necessary to journey all the way back to the source of the oil being loaded into the tank cars. Before we get there, the fundamentals must be covered:

3.1 The Basics of Matter

Matter is composed of atoms, which can be subdivided further into protons and neutrons, which make the nucleus, or core, of the atoms; and electrons, which orbit around the nucleus, rather like satellites around the earth. Protons and neutrons are similarly heavy (relative mass of 1), and in comparison, electrons are incredibly light; only $1/1836^{th}$ of the weight of a proton. The number of protons in an atom, otherwise known as the atomic number, defines the element, as mapped by the periodic table (see reference material). For instance, hydrogen has one proton and no neutrons in its nucleus. The most common form of iron has 26 protons, and 30 neutrons – its atomic mass is 56, the sum of the protons and neutrons.[2] Protons have a positive charge of 1, neutrons have no charge, and electrons have a charge of -1. If an atom has an equal number of protons and electrons, then its overall charge is zero; this is the elemental state of the atom and the form in which all metallic elements are found when as metals.

The elemental state is, however, not necessarily the most stable form in which the atom can exist. Nature always seeks the lowest potential energy – the most stable

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[2]Every element has a range of possible atomic masses, caused by differing numbers of neutrons, and termed 'isotopes'. In the Periodic Table, the atomic mass provided refers to the average of naturally-occurring isotopes.

system. The way in which atoms increase their stability is through moving electrons.[3] If electrons are gained, termed 'reduction', the atom has a negative charge. If electrons are lost, termed 'oxidation', the atom gains a positive charge.[4] When an atom has a charge, it is known as an 'ion'; and described further as a 'cation' if it has a positive charge, and an 'anion' if it has a negative charge. The magnitude and charge on the atom is described as the 'oxidation state', i.e. iron in the form Fe^{3+} has an oxidation state of plus three.

In the periodic table, as a general rule, anything on the left and in the middle sections wants to lose electrons. These are the metals. The right-hand block consists of the non-metals, such as carbon, nitrogen, oxygen and chlorine. The further to the right of the table, the more keen the atoms are to accept electrons, with the exception of the final column, the noble gases, which are stable and do not readily gain or lose electrons. The atoms in this right-hand block are complex as atoms can both gain or lose electrons. For instance, sulfur can have an oxidation state of -2 when as hydrogen sulfide (the toxic gas), but can be oxidised all the way to +6 in sulfate (SO_4^{2-}). Between the metals and non-metals, heading downward diagonally to the right, there is a thin band of semi-metals, that behave both like metals and non-metals, but these do not concern us in this primer.

When electrons are lost or gained, the atom has a formal *ionic* charge. As with many things in life, opposites attract; for solids, the chemical formula must be composed

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[3]Changing the composition of the nucleus is also a possibility, but requires energies typically only found in nuclear power stations, or within stars.

[4]One easy way to remember this is the acronym 'oilrig'; oxidation is loss, reduction is gain.

of equal positive and negative charges to remain neutral (no positive or negative charge) overall. A classic example is Na^+Cl^-, sodium chloride, also known as table salt. It comprises a metal (sodium), which is keen to lose an electron, and a non-metal (chlorine), which is keen to gain the electron. Thus the electron is transferred from one atom to the other. This transfer of electrons, from one atom to another, is typical of a salt – a group of metallic and non-metallic elements. In solution, the sum of the positive charges must equal the sum of the negative charges – a solution cannot carry an overall charge.

However, this is not the only type of charge that is found in nature. Depending on the type of the nucleus and the orbits in which the electrons lie, atoms have varying abilities to draw electrons to themselves. This is termed 'electronegativity'. Sometimes atoms are not enough to pull electrons off other atoms, and instead electrons are partially shared between atoms. This is typical where the atoms involved are all non-metals (the electronegativities are similar), and is termed a *covelant* bond. Clusters of atoms thus held together are called 'molecules'.

Both water and oils are covalently-bonded molecules, although they behave very differently from one-another. Despite its abundance, water is one of the strangest molecules that exists; the electrons that belong to the hydrogen atoms spend a sizable fraction of their time orbiting the oxygen atom. The end result is that the hydrogen atom has a slight positive charge ($\partial+$, significantly less than $+1$), and the oxygen has a slightly negative charge ($\partial-$). Where this charge separation occurs, the covalent bond is described as being a 'dipole', i.e. there are two poles, like the poles on a magnet or a battery. Water is odd in that this charge separation is relatively strong, but also that the oxygen atom has four un-bonded elec-
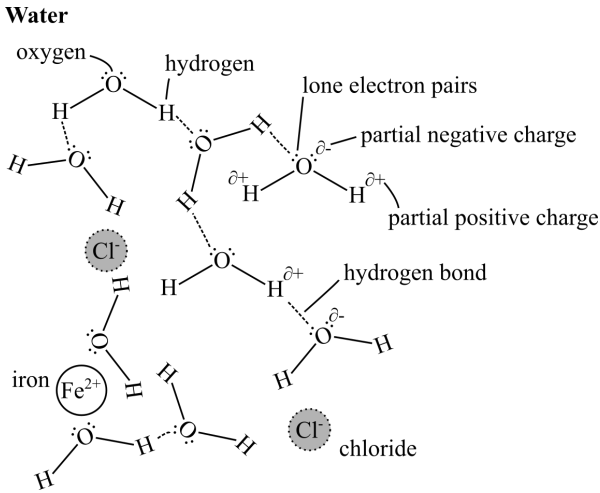
Figure 1: Schematic of water molecules, with temporary hydrogen bonding between oxygen and hydrogen atoms of neighbouring molecules, and stabilisation of ions through opposite charge attraction.

trons arranged as two pairs, that are strongly attracted to positively-charged species. Adjacent water molecules can form temporary bonds, called 'hydrogen bonds' between oxygen and hydrogen atoms. These bonds stabilise the water considerably, and this is the reason water exists as a liquid when other molecules of similar sizes are all gaseous under the same conditions. The water molecule is not linear either, as demonstrated in Figure 1, and is described as being 'polar'.

This is an important point – the partial positive charges on the hydrogen atoms and the partial negative charges and spare electrons on the oxygen are attracted to oppositely charged species in other molecules (in particular, other water molecules) and ions. So, a metal cation such as iron,

Fe^{2+}, can be surrounded and stabilised by the partially negatively-charged oxygen atoms in water (Figure 1). Similarly, a negatively charged anions such as chloride, Cl^-, are stabilised by the positively-charged hydrogen atoms in water. Oppositely-charged species can approach one another to stabilise their charges, but they can't approach too closely. This is because, with the exception of hydrogen, all atoms have other electrons orbiting their nuclei, and when atoms get too close, these electrons start to repel. A key outcome of this ability to stabilise opposite charges is that water, which is polar, can dissolve other polar molecules and ions. As we will see later, this is crucial for corrosion to occur.

Turning back to oil, the main constituents of oil are carbon (C) and hydrogen (H). The electronegativity difference between them is small, and they both supply one electron to the shared bond; oils are non-polar. There is no charge separation and there can thus be no stabilisation of ions.[5]

The outcome is a common observation: water and oil will not dissolve in one-another. The bonds between the water molecules are much stronger than the water-oil bonds and will squeeze the oil out from between them. But of course, there are many carbon-based (organic) molecules that do dissolve in water, such as vinegar (acetic acid), soap and chemicals such as ethanol, acetone, etc. These molecules have several things in common; they are small, they have an organic component but they also all have a polar component too that can interact with water. One

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[5]In Canadian bitumen, there can be significant vanadium and nickel in the oil itself. These metal ions are stabilised by complex organic species that, due to their structure, can include polar regions. These species overall do not affect corrosion that can occur in tank cars and are thus not considered in greater detail here.

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example is an alcohol group that comprises an oxygen and hydrogen (two thirds of a water molecule) attached to the organic part of the molecule, that can interact with water sufficiently to allow it to dissolve.

If we turn to metals and alloys (combinations of different elemental metals) we deal with another case again. Metallic materials are composed of atoms in their elemental states (oxidation state of zero). Unlike molecules or salts, where the electrons are held onto tightly by the atoms, metallic atoms can share electrons, which move freely from atom to atom, i.e. the metal can conduct electrical current (electrons). By pushing an electron into the metal, an electron is pushed out of the other side to maintain electroneutrality. The strength with which the electron is pushed is measured by the voltage, and the number of electrons moving into and out of the material is described by the current. Metal atoms cannot exist as individual atoms in a solution, such as water or oil, as they would be unstable – they are at their most stable when surrounded by other metal atoms. However, if the metal atoms lose electrons and become cations, then they are only stable in the solution, where the charge can be supported by water and other dissolved salts. This, very simplistically, is the first half of the corrosion process: metals are oxidised to cations, going into solution. This process removes metal from the tank car shell causing wall thinning. It also brings us to two important points:

Key Point 1: For tank cars, corrosion can only occur if water is present and touching the steel surface.

Key Point 2: Crude oils alone are not corrosive under conditions that oil tank cars experience.

Whilst non-polar oils cannot dissolve metals ions, and therefore prevent corrosion, they can contain chemical species that are corrosive when these species move from the oil phase into the water. Examples of corrosive species include carbon dioxide, hydrogen sulfide and oxygen (all dissolved gases), and volatile organic acids such as acetic acid. With the exception of oxygen, which comes exclusively from the air, these other species originate in the reservoir. If water is present in the tank car (sources of water are described in Section 3.2), they may make the water more corrosive than it would otherwise be in their absence.

A key concept of chemistry is that of 'concentration' – the amount of substance A that is mixed or dissolved in substance B. For corrosion, this is typically a gas, such as oxygen or hydrogen sulfide, or dissolved species, such as hydrogen and salt ions, dissolved in water. Due to the small size of atoms, it is necessary to use a term that defines an amount of substance, making chemical calculations more practical.[6] The 'mole' is defined as 12 grams of carbon 12 (i.e. exclusively with six protons and six neutrons per atom).[7] This corresponds to 6.022×10^{23} atoms, or 0.6 trillion trillion atoms. The unit of the mole is written as 'mol'. If one mole of substance A is dissolved in 1 litre of water, this gives a concentration of 1 mol/L.

Another important concept is that of acidity and alkalinity. The water molecule can split in two as follows: $H_2O \rightleftharpoons H^+ + OH^-$, forming hydrogen cations (protons) and hydroxide, respectively.[8] The concentrations of the

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[6]The smallest atom, hydrogen, is ~0.0000000001 meters in diameter (1×10^{-10} m), and the largest, caesium, is ~0.0000000006 meters in diameter (6×10^{-10} m).

[7]Originally an 1897 translation from the German word 'Molecül' (molecule in English), although it is no longer used strictly in this manner.

[8]The use of the $\rightleftharpoons$ term implies that the reaction can go from

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protons and hydroxide ions are low in neutral water, being equal at 1×10^{-7} mol/L. If the proton concentration is greater than this, the solution is acidic (the hydroxide concentration is depleted through reaction with protons to form the water molecule). If, instead, hydroxide is the dominant species, then the solution is alkaline. As these concentrations can cover many orders of magnitude, a simplifying term was developed, that of 'pH', which is numerically defined as $-\log_{10}[H^+]$. For instance, if the pH is 1, the proton concentration is 0.1 mol/L. If the pH is 7, the proton concentration is 1×10^{-7} mol/L (0.0000001 mol/L) – neutral water. Above pH 7, the solution is alkaline. An important point to note is the use of the logarithm in determining pH. For a pH change of one unit (i.e. from 3 to 2), the proton concentration increases by a factor of ten.

3.2   Sources of Water

So if water is a necessary prerequisite for corrosion, where does it come from? There are several sources. The first is accidental: rain water that accumulates in the tank car from open hatches during services and inspection, accumulated water in fittings, etc. A second source, minor in comparison, is condensation from the air – although this can have an effect on corrosion at the top of the tank car at fittings via galvanic coupling. Thirdly, there may be residual water in the tank car from cleaning processes, but the most likely source of water is actually the oil itself.

Industry representatives raised the opinion, on numerous occasions, that oil produced through hydraulic fracturing was more 'corrosive'. Whilst this demonstrates a misunderstanding of the corrosion processes at play, a few

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left to right, and right to left, and will stabilise until reactions in both directions are equal, at equilibrium.

engineers that had inspected tank cars at servicing facilities did describe significantly greater quantities of water accumulated in the tank cars that were believed to have serviced the Bakken Formation. One single engineer collected water samples which ranged from perfectly clear water, to an oil-in-water emulsion. These samples were not analysed for water chemistry.

Crude oils can be produced from the reservoir by a variety of means, chosen primarily by the type of oil. It is important to understand not only the types of oil but also the processes involved as there are numerous potential consequences for internal tank car corrosion. Different oils have very different compositions; may or may not support microbial activity; can carry various amounts of water; and may or may not contain oil-soluble corrosive species described earlier.

3.2.1   Conventional Oil Production

Fossil fuels are derived from ancient organisms, such as zooplankton and algae, that existed in water bodies millions of years ago. Having settled on the lake or sea-bed under anoxic (oxygen-free) conditions, which prevented rapid decay, they were gradually buried under layers of sediment hundreds of meters thick. The sands and clays that incorporated this biomass (the 'source rock') underwent a process called 'diagenesis': Heat and pressure caused the organic mass to convert to kerogens and bitumens (also known as asphalt), both very large classes of organic molecules. If buried at sufficient depth, the temperature degraded some kerogens further into crude oil (50 – 150 ℃) and natural gas (150 – 200 ℃). Bitumens subsequently dissolved in the crude oil.

Crude oil and natural gas are mobile and less dense

than water so they rise, where possible, through porous rock strata or cracks in the rock, toward the surface. Oil and gas reservoirs are formed where the petroleum accumulates, primarily due to having reached an impermeable barrier such as limestone (a 'cap-rock'), although there are many naturally occurring petroleum seeps, where the surface is reached. Depending on the history and composition of the source rock, conventional oil reservoirs can range from light sweet crude (i.e. low viscosity, smaller oil molecules, no hydrogen sulfide) to less degraded heavier crudes. The reservoir is tapped by drilling vertical wells permitting the oil to continue its journey to the surface.

The term 'conventional' refers primarily to the economic returns of producing oil and gas from a given field. This is not a fixed benchmark, and where many new technologies enter service as 'unconventional', as they are developed, adopted, and economic margins improve, they become conventional. One of the defining characteristics of conventional oil production, over the last few decades, is the high permeability of the reservoir rock. Permeability is defined as the ability of a porous rock to allow fluid to pass through it. For highly permeable rock, such as partially-consolidated sandstone, relatively small over pressures are required to push oil toward the producing wells. For low permeability rocks, the over pressures required to move oil may result in the fracturing of the rock, or only an uneconomically slow rate of oil production.

For conventional oil fields, there are typically a number of injection wells – used to inject water to maintain reservoir pressure and push the oil out – and production wells. Early in the field's life, the production wells will yield only gas and oil, but eventually injection water, or water that was already present in the reservoir, will 'break through'. The total crude oil production for a conventional field de-

clines between 2 and 5% per year, and operation of fields for in excess of 20 years is not uncommon. Towards the end of an oil field's life, the water fraction (the 'water cut') can often be very high. As conventional fields are large assets, they include, or have access to considerable infrastructure, such as facilities to knock out water and remove gases from the produced oil, storage tanks for large quantities of oil, and often direct connections to pipelines.

In addition to the water and oil that is produced, wells produce natural gas, which has no effect on corrosion, and carbon dioxide, which originates from the formation of the oil in the source rock. Many fields also produce hydrogen sulfide (H_2S), which can be released from reservoir rocks (geological souring) or produced in the reservoir through microbial activity (microbial souring). Hydrogen sulfide is a gas that causes considerable concern. It is both highly toxic (see section A), but can be a major contributor to corrosion when present. In the case of geological souring, where H_2S is released from minerals in the rock, it is detected with water break through, and may increase slightly over the course of the reservoir's working life. Microbial souring, on the other hand, is caused by the injection of microbes (bacteria, archaea and fungi) with the injection fluids. The microbes consume organic molecules and reduce sulfate (SO_4^{2-}), which may be initially present but often is introduced into the reservoir with the injection fluids, to H_2S. Often taking many years to establish, microbial souring increases significantly with time and can cause problems for the producing facilities which may not have been designed to handle H_2S. Hydrogen sulfide is co-produced with carbon dioxide. The preferred carbon source of the microbes is volatile fatty acids (VFA's), small organic acids such as acetic acid (vinegar), which dissolve in both the oil and water phases, and are always present

in light crudes. These can be readily metabolised in the following manner: $\mathrm{CH_3COOH + SO_4^{2-} \longrightarrow 2\,CO_2 + H_2S + 2\,OH^-}$. Oils, on the other hand, are hard to break down, and microbial populations that specialise in degradation of light oils grow much more slowly than when VFA's are available.

Thus conventional reservoirs produce natural gas, oil and water, which contain volatile fatty acids, carbon dioxide and may include hydrogen sulfide. The gases and water are stripped from the oil, but depending on the facility, production rate and initial hydrogen sulfide content, oil can be loaded into tank cars that contains small quantities of water, volatile fatty acids and hydrogen sulfide.

3.2.2   Production of Heavy Oil

In Alberta, approximately half of the proven oil reserves are heavy oils, otherwise described as bitumen crudes, or oil sands. These are found where the oil has reached close enough to the surface that it is infected by microbes that consume the lighter (smaller) oil fractions. What is left over are oils that are larger than the pentanes (five carbon atoms); a highly viscous mixture that will not ordinarily flow. The reservoirs can also include the gases carbon dioxide and hydrogen sulfide; both products of the microbial degradation (although significant carbon dioxide is also generated when the oil is formed). The density and viscosity of these oils can be very high compared with light crudes, and they cannot be pumped from the reservoir like conventional crudes. Instead, other methods have been developed for in situ recovery such as Steam-Assisted Gravity Drainage (SAGD) and Cyclic Steam Stimulation (CSS). In the case of SAGD, two horizontal wells are drilled, the injection well several meters above the production well.

Steam is injected into the reservoir, heating the oil and reducing its viscosity (increasing oil mobility), pushing it into the production well. CSS is a similar process, where steam is injected into the reservoir and then the flow direction reversed to produce oil from the same pipe. If the oil is sufficiently close to the surface, the overburden (forest, soil and rock) can be removed, exposing the oil sands to surface mining.

As the oil sands have already been degraded biologically, there are no volatile fatty acids present and the reservoir starts its production life with both CO_2 and H_2S. A significant difference between oil sands and conventional crudes is that bitumen crudes dissolve considerably more hydrogen sulfide. Following production and treatment of the heavy crudes, hydrogen sulfide can remain dissolved in the oil. This is not necessarily a risk if the hydrogen sulfide is more stable in the oil than the head space, but may become one when the oil is heated in excess of 100 ℃ for loading: the solubility of hydrogen sulfide decreases with temperature, and it may move into the gas head above the oil when the heated crude is pumped into an insulated tank car. *This may be both hazardous to personnel should the tank car be opened or should it vent, and can cause corrosion of components at the top of the tank car.* In particular, hydrogen sulfide can be absorbed by a number of elastomeric gaskets, o-rings, etc., rapidly degrading them. This could cause failure of components such as pressure release valves, especially if the elastomers were not chosen for hydrogen sulfide service. Additionally, should there be condensed water between fittings of different alloys (such as between a stainless steel vacuum preventer and the carbon steel shell), this can result in galvanic corrosion, described in section 3.7. Finally, these oils can carry emulsified water and can form water-rich sludges that result in corrosion un-

derneath the sludge (a type of 'under-deposit corrosion'), although the risk is low because the facilities are available for treating the produced fluids.

3.2.3 Hydraulic Fracture of Oil Wells

Where conventional oil fields contain oil in relatively permeable rock, 'tight oil' is trapped in rock that is insufficiently permeable for the oil to be produced in an economic manner. Similar to shale gas, the oil can be released through fracturing of the reservoir rock, which is then produced through the cracks.[9] As a technology used in oil and gas fields, this method dates back to the 1940's, but it was not until the late 1990's that advances in horizontal drilling and fracturing permitted fields such as the Barnett Shale (natural gas, Texas) and the Bakken Formation (tight oil, North Dakota and Montana) to become economically viable.[10] The US Department of Energy, in 2013, stated that at least 2 million hydraulically-fractured oil and gas wells had been drilled in the US, and that 95% of new wells were fractured.

From the Canadian perspective, the Bakken Formation is of particular interest. Comprising relatively light oil and natural gas, a boom in drilling from 2000 to 2010 saw production rates reach 458,000 barrels per day from the Formation, exceeding the pipeline capacity to transport oil from the region. The natural consequence was the dramatic rise in use of rail tank cars. By the end of 2013,

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[9]The term 'shale oil' is sometimes erroneously used to refer to 'tight oil', as it sounds synonymous with 'shale gas', natural gas located in low permeability rock. Shale oil is another type of oil entirely; it was not sufficiently heated and pressurised, and the original biomass has not been converted past kerogen.

[10]For thin formations, horizontal drilling permits much greater access to the field than vertical drilling.

965,000 barrels of oil were being transported in tank cars from the Bakken fields (pipeline capacity having been increased but limited to 515,000 barrels/day). [11]

A single tank car carries ∼800 barrels. Until mid-2015, it was Bakken crude that was found in many rail cars heading east towards the Canadian Quebec and East Coast refineries. Since then, however, the depressed oil price has resulted in the refineries switching to cheaper imported crudes from the Middle East and Africa.

Fracturing can be simplistically described as follows: A well is drilled and fracturing fluids injected until the pressure at the bottom of the well exceeds the mechanical strength of the rock, which fractures. The fracturing fluids are comprised of water with a number of chemicals, such as proppant (typically sand or ceramic, to stop the fractures closing back up), guar gum (a thickener, to help the water carry the proppant), acids (for cleaning the injection pipe perforations at the bottom of the well, and initiating fracture by dissolving rock), salts and assorted other chemicals. Once the fracturing process is complete, the flow direction is reversed, with the fracking slurry, gas and oil, being produced whilst the reservoir depressurises. Tight oil can only be produced in the presence of 15 to 20% natural gas within the reservoir, which drives oil to the borehole. However, during the fracking process, a considerable amount (up to 70%) of the injected slurry is retained by the well — at least in the short-term.

The mentality associated with fracking is different to conventional fields — many wells are drilled and the reservoir depressurises without interference. Unlike a conventional field that can produce continuously over decades, a well that is stimulated through horizontal fracturing has a short half-life; production trends typically follows an expo-

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[11]http://www.eia.gov/todayinenergy/detail.cfm?id=16631

nential decline. For the Bakken field in particular, the well production life is estimated to decline by an average of 45% per year. This includes new wells, where the production decline is significantly greater for the first year, and established wells. In contrast, conventional fields decline on average 2–5% per year. So after fracturing, an individual well produces significant oil, which rapidly declines with time, necessitating new wells be drilled and existing wells to be stimulated in order to maintain production levels. The break-even cost for drilling and fracturing in the Bakken Formation is approximately USD$60 per barrel, considerably less than for processes such as SAGD and CSS, which are approximately USD$100 per barrel for new projects due to capex costs (the breakeven point for existing facilities is approximately USD$40 per barrel).

During early well production, produced water – the water that is produced alongside the oil and natural gas – may include many of the injection chemicals described above. This water is a mixture of injection water (fracturing fluids) and water that was naturally present in the reservoir. The water phase is stripped from the oil, and it declines in quantity with time. It does not make economic sense to have gas and water separator facilities for a field that is producing relatively small amounts of water, so following the initial back-flow of fracturing fluids, the mobile facilities are taken off-site. However, the injection fluids can be produced over the life of the well, often as an emulsion (water droplets suspended in oil). Reservoir water may also be produced. One of the largest uncertainties regarding oil produced through hydraulic fracturing is the nature of the water produced; it may be rich in VFA's, contain considerable hydrogen sulfide, or may contain fracture-stimulation acids. Water may settle out over time and accumulate in the tank car. It is currently believed, by the author and all

of the engineers included in the industry survey, that this is the main source of water found in rail tank cars.

Supporting evidence comes from a US Federal Railroad Administration open letter to the American Petroleum Institute (July 29 2013), which stated:

> FRA's [Federal Railroad Administration's] review of the OTMA [One-Time Move Approval] data also indicates an increasing number of incidents involving damage to tank cars in crude oil service in the form of severe corrosion of the internal surface of the tank, man way covers, and valves and fittings. A possible cause is contamination of the crude oil by materials used in the fracturing process that are corrosive to the tank car tank and service equipment.[12]

No further information on the nature of the corrosion was given. The FRA were contacted regarding clarification, but no response was forthcoming.

As described above, oil can only be produced by hydraulic fracturing if the reservoir contains sufficient natural gas. Once the reservoir is tapped, the expansion of this gas drives oil toward the production well, which produces oil, gas and water. One of the key economic benefits of hydraulic fracturing is that the economic barrier to market – the cost of starting production from a new field – is considerably less than for conventional oil fields. This has permitted a great number of new companies to start up and purchase leases for mineral rights. However, the facilities and often the necessary expertise are not always present for dealing with the produced fluids. In addition to anecdotal evidence regarding excessive water in the tank cars, video

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[12]https://www.fra.dot.gov/eLib/Details/L04717

evidence is available of 'live' oil, vigorously degassing, having been loaded into a tank car. This gas was primarily natural gas and carbon dioxide. This point is intended to highlight the operational nature of the fracturing industry; 'live' oil is potentially explosive and it is imperative that the natural gas be removed from the crude oil before shipping. The fact that it had not been correctly processed is ultimately an act of wanton negligence stemming from a lack of facilities or expertise.

In 2013, Enbridge detected lethal quantities of hydrogen sulfide (1200 ppm) in the gas phase of a holding tank containing Bakken crude.[13] This resulted in Enbridge requesting and being granted the right to reject oil containing greater than 5 ppm hydrogen sulfide in the oil phase. Whilst this related to use of a pipeline, it both demonstrates that significant souring has occurred in the Bakken Formation, and one explicit reason for invoking the tariff was to protect workers at an affiliated downstream rail facility.

These two points are explicitly mentioned because it has proven difficult to understand the composition and variability in gases in Bakken crude, and subsequently, within the tank car. This is important from a corrosion perspective, as both hydrogen sulfide and carbon dioxide can play a major role in corrosion. It appears that tank car facilities do not routinely include analysis of the oil, nor the gas composition of the tank head space. Indeed, the presence and quantity of water residing in tank cars is another unknown. Workers connect the necessary tubing to the bottom outlet valve (BOV), or lower it into the car, and start pumping. As the tubing is opaque, water is transferred further into the system where it is presumably

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[13]http://www.ferc.gov/EventCalendar/Files/20130606172210-IS13-273-000.pdf

accumulated and separated as appropriate. It was only due to the diligence of a single engineer, who requested the collection of the first few gallons of tested tank cars, that we are aware that tank cars frequently contain considerable water and are subjected to internal corrosion, although the significance of the corrosion is as yet unknown (it may be superficial). He found that the loaded tank car always produced clear water followed by emulsion, then the oil itself.

3.2.4   Water Accumulation in Tank Cars

One observation resulting from the industry survey was that the edge of the rusted steel is typically 12" from the 6 o'clock position of the tank car body. These 'tide' marks delineate the edge of the accumulated water. A straight shell 58' long tank car, with an internal diameter of 110" has a 110,000 litre, (29,000 US gallon) capacity. The edge of the corrosion corresponds to a water volume of approximately 400 litres (100 US gallons), and a water depth of just over one inch. If the tank car has a 5% outage (head space), then the water phase corresponds to 0.4%, by volume, of the transported fluid.

Whilst the transport of oil by tank cars does not specify limits to the amount of water, for oil pipelines such tariffs do exist. In Canada, the maximum 'basic sediment and water' (BS&W), which includes the free water phase, emulsified water and sediments, is 0.5% by volume, although sources in the industry claim that the actual BS&W is typically significantly less than the tariff limit. These tariffs serve both quality and corrosion prevention purposes. Producers of conventional and heavy crude oils typically prepare the oil for pipeline transport. Where tank cars are used, to meet supply requirements or for access to other consumers, the oils likely meet this tariff. For oils pro-

duced through hydraulic fracturing, where the most likely means of transport is via tank cars, there is no need to meet this requirement. The simple calculation of 0.4% BS&W by volume for tank cars suggests that water production, whilst perhaps significantly higher than the historical average, is not excessively high. Whilst not having any water present is the best safeguard against corrosion, in a tank car, there are several aspects that exacerbate the risks of corrosion when water is found:

1. Water accumulates within tank cars between cleanings, regardless of the methods for emptying the tank car.[14] Similarly, whether the tank car be straight shell, or sloping bottom design (where the two shell halves are welded together at an angle, so the lowest point of the tank car is in the centre where the bottom outlet valve is situated), thin layers and beads of water do not move readily; they adhere to the steel. Simple experiments, conducted with steel cut from a domestic heating oil tank, under kerosene, demonstrated that beads of water did not migrate until the steel was angled in excess of $10°$. Publicly-available designs for sloping bottom tank cars stated an angle of 1/4" per foot; $1.2°$. In a pipeline, any separated water is swept down the pipe by the flowing oil, and cannot accumulate in significant amounts.

2. The calculation presented above is based on empirical observations from a single source. It is entirely conceivable that tank cars might be carrying considerably less water on average, and that corrosion might be due to relatively rare events. One such

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[14]The majority of crude service tank cars are emptied using a bottom-out valve, although lowering of a tube through the roof of the tank car is not uncommon.

example could be early-life production from a new well that may contain both water, but also fracturing proppant, acids, etc. This might introduce water to a limited number of tank cars before the water cut wanes to insignificant levels. However, with so many wells being fractured between 2000 and 2014, this could account for the perceived increase in corrosion.

3. As described earlier, molecular oxygen is a highly corrosive chemical species that can drive corrosion. In a pipeline, oxygen is excluded. In a tank car, this is not possible, and is at its most extreme in the empty return condition. Oxygen-based corrosion is discussed in detail below.

3.3   The Corrosion Cell

The stability of different chemical species are defined by the 'reduction potential', which is a measure of how easily atoms can acquire electrons in water, i.e. the process of reduction. For a species M, this can be described by

$$\text{M}^{x+} + \text{xe}^- \rightleftharpoons \text{M}^{y+} + \text{ye}^- \tag{1}$$
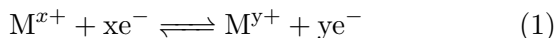
where x and y are integers. This is a 'half cell reaction'; electrons are released or consumed, depending on the direction of reaction (left or right), but for a full reaction, there are no left-over electrons as two or more sets of reactions are combined. If a metal is corroding, the reaction moves from the right to the left ($y = 0$), releasing electrons and an ion: $\text{M} \longrightarrow \text{M}^{x+} + \text{xe}^-$. This is the 'anodic' reaction and the metal is being oxidised. The liberated electrons must be consumed somewhere else, and this occurs through the 'cathodic', reduction reaction (left to right in reaction 1) for a chemical species in the water phase.

Examples of this cathodic reaction include the reduction of hydrogen ions (more commonly described as protons): $H^+ + e^- \longrightarrow \frac{1}{2} H_2$.

Similar in concept to electronegativity, the reduction potential is not just a measure of how easily an electron is attracted to an atom, but includes the interactions with water molecules, which, as was already described, can stabilise ions in solution. The reduction potential does not describe the availability of a chemical species (concentration), nor the speed with which it reacts, only the driving force for reaction.

Half cell reactions can be ranked by their reduction potentials under standard conditions (all ion concentrations are 1 mol/L, including H^+, i.e. pH = 0, at 25 °C at 1 atmosphere pressure). As half-cell reactions cannot be measured individually, reactions are compared against the hydrogen reaction using a Standard Hydrogen Electrode (SHE). The potential difference is given in Volts. Several select values are presented in Table 1. The more positive the potential, the more strongly the reaction moves to the right-hand side (the cathodic reaction). Conversely, the lower the standard reduction potential, the more readily the reaction moves to the left-hand side (the anodic reaction).

For corrosion to occur, both anodic and cathodic reactions happen simultaneously – this is termed the 'corrosion cell'. Crucially, both occur on the same surface (although they can be spatially distant), and, because electrons flow readily in the metal, the reactions occur at almost exactly the same potential, at some point between the two half cell reaction potentials. This 'mixed electrode potential' means that both half-reactions have been pulled away from their non-reacting state. The exact value of the mixed potential depends on numerous parameters, such as the types of half cell reactions occurring, concentration of cathodic re-

$\mathbf{R}^n$	Element	Half cell reaction	E
1	Gold	$Au^{3+} + 3\,e^- \rightleftharpoons Au$	+1.52
2	Oxygen	$O_2 + 4\,H^+ + 4\,e^- \rightleftharpoons 2\,H_2O$	+1.23
3	Iron	$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77
4	Hydrogen	$2\,H^+ + 2\,e^- \rightleftharpoons H_2$	0.00
5	Iron	$Fe^{3+} + 3\,e^- \rightleftharpoons Fe$	-0.04
6	Iron	$Fe^{2+} + 2\,e^- \rightleftharpoons Fe$	-0.44
7	Water	$2\,H_2O + 2\,e^- \rightleftharpoons H_2 + 2\,OH^-$	-0.83
8	Sodium	$Na^+ + e^- \rightleftharpoons Na$	-2.71

Table 1: Selected standard reduction potentials ($\mathbf{E}$), for reactions ($\mathbf{R}^n$) as measured against the Standard Hydrogen Electrode (SHE), under standard conditions.

actants in solution, surface area, cleanliness of surface, and so on. The differences in potential between the individual half cell reactions and the mixed potential are described by 'overpotentials'. If an overpotential for a half cell reaction is positive, the oxidation reaction occurs; if it is negative, the reduction reaction occurs. A schematic is presented in Figure 2.

Metallic gold (reaction 1), for instance, is so stable that it is not corroded by oxygen, hence the term 'noble metal'; gold is one of the few elements to be found naturally in its metallic state. On the other hand, sodium (reaction 8) is so keen to lose its electron that it can split water and generate hydrogen gas: $2\,Na + 2\,H_2O \longrightarrow 2\,Na^+ + H_2 + 2\,OH^-$. It can also react with H^+ to form H_2, and O_2 to form H_2O. Whilst these latter reactions have a much greater overpotential, and there is therefore a greater driving force for these reactions to happen, the concentrations of protons in a strong acid, and dissolved oxygen (2.5×10^{-4} mol/L at 25 ℃) are much less that that of water itself (55.5 mol/L). This serves to re-iterate the point that there must be a thermodynamic driving force for corrosion to occur, but

Individual reactions

$2H_2O \rightarrow O_2 + 4e^- + H^+$

$\overline{O_2 + 4e^- + H^+ \rightarrow 2H_2O}$

Mixed potential

Negative overpotential
leads to reduction:
cathodic reaction

$2Fe + O_2 + 4H^+ \rightarrow 2Fe^{2+} + 2H_2O$

Positive overpotential
leads to oxidation:
anodic reaction

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

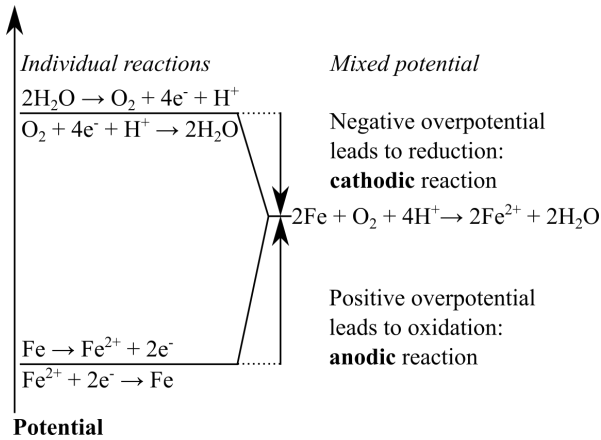$\overline{Fe^{2+} + 2e^- \rightarrow Fe}$

Potential

Figure 2: Schematic describing the corrosion cell from a thermodynamic viewpoint for oxygen (O) and iron (Fe). If the system was under standard conditions, as described in the text, then the individual reaction equilibria would be at the reduction potential values given in Table 1. At potentials above these lines, oxidation occurs; below the line, species are reduced. During corrosion, oxygen and iron half cell reactions combine. The iron is oxidised due to the positive overpotential, and the oxygen, reduced, due to the negative overpotential.

the *rate* at which it occurs is determined by the speed of reaction (kinetics) and the availability of reactants. This primer considers the factors necessary for corrosion to occur, but doesn't consider the factors that determine how fast it would be. To do so would require better knowledge of the internal tank car environment.

Considering materials that are specific to tank cars, there is, simplistically, only one element of interest; iron. Tank cars for oil service are typically constructed with ASTM SA516 Grade 70 steel, or AAR TC 128 Grade B, both of which are in excess of 96% iron by weight. Whilst the exact composition and the microstructure can have significant effects on materials performance in more extreme environments, for tank car corrosion, this approximation is valid.

Compared to gold or sodium, the behaviour of iron is more complex. It can be oxidised to Fe^{2+} (ferrous) and Fe^{3+} (ferric) depending on the species available to fulfil the cathodic reaction. As demonstrated in Table 1, iron cannot split water to generate hydrogen as the mixed potential would not provide a positive overpotential. It can, however, react with protons: $Fe + 2\,H^+ \rightleftharpoons Fe^{2+} + H_2$ (reactions 6 and 4). Theoretically, iron can be oxidised to Fe^{3+}, but the overpotential is too small, and the reaction is complex due to the hydrogen atoms requiring two electrons and iron liberating three. In the presence of oxygen, however, iron can be oxidised to Fe^{3+} (half cell reaction 5), although in practice Fe^{2+} and related oxide species are formed at the metal surface, and are subsequently oxidised to Fe^{3+} in a later step (half cell reaction 3). This can be described by $2\,Fe + O_2 + 4\,H^+ \longrightarrow 2\,Fe^{2+} + 2\,H_2O$.

As both anodic and cathodic reactions must happen simultaneously, and there is plenty of available iron ready to be oxidised, it is the cathodic reaction that controls the

speed with which the steel corrodes. The rate at which oxygen reaches the steel surface depends on the concentration in the water and the mass transfer of oxygen to the tank shell inner surface, which is controlled by diffusion, convection and mass transport as well as geometrical considerations such as depth of the water layer for replenishment. Similarly, the reduction of protons to form hydrogen is also limited by the availability of protons on the metal surface. At pH 7 (neutral), the concentration of hydrogen ions is 1×10^{-7} mol/L, considerably less than that of oxygen in naturally aerated water (see above).

> Key Point 3: The cathodic reaction determines the overall speed of corrosion.

In addition to the anodic and cathodic reactions occurring on the same surface, they must occur in the same (connected) fluid. This is because both half cell reactions change the composition of ions in solution. As the fluid cannot carry an overall charge, the whole process must result in no net change. This is why corrosion inside a tank car or pipeline is unaffected by the conditions occurring outside, and vice versa.

> Key Point 4: A corrosion cell involves two currents. The first is electrical – the flow of electrons, released through oxidation, through the metal to the site of the cathodic reaction. The second is ionic – both anodic and cathodic currents produce and consume ions and these processes must occur in the same fluid and result in no net change in charge.

The two main cathodic reactions that dominate steel corrosion have already been mentioned: oxygen and hy-

drogen reduction. Let us consider these reactions a little further.

For tank cars carrying crude oil, water and no hydrogen sulfide, oxygen is the most likely culprit for causing corrosion.[15] Kinetically, the cathodic reaction is very fast, and as soon as oxygen reaches the steel surface under the water layer it is consumed. As already described, the reaction rate is determined by the availability of oxygen. As oxygen in the water layer is depleted, it is replenished by oxygen that is dissolved in the crude oil. As a rough approximation, at 50 ℃, oils carry between 6 (for heavy oils) and 22 (for light crudes) times more oxygen than the water.[16] As oxygen transfers from the oil to the water phase, so too it must move from the gas space above the oil, into the oil itself. The migration of oxygen to the bottom of the tank car is likely to be slow as the diffusivity (the rate of transmission through the fluid) is low. Whilst it has not been studied specifically, the oxygen-driven corrosion rate is likely to be low for full tank cars. As the temperature is increased from ambient, the diffusivity and surface-availability of oxygen increases and corrosion rate increases too. To counter this effect, the solubility of oxygen in water and oil decreases significantly with increasing temperature: at 100 ℃, the solubility of oxygen in water is close to zero. Taking these two effects into account, the corrosion rate increases with increasing temperature until it peaks and declines toward zero with further-increasing temperature.

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[15]Oxygen and hydrogen sulfide are not found together for any great length of time, as they react: $O_2 + 2\,H_2S \longrightarrow 2\,H_2O + 2\,S$. If there is sufficient oxygen and time, the hydrogen sulfide in crude oil can be fully consumed, although this is unlikely to happen in practice. The elemental sulfur can then undergo numerous other reactions, typically ending as sulfate, SO_4^{2-}.

[16]Battino R. (ed), (1981), Solubility data series. Oxygen and ozone, vol 7. Pergamon Press, Oxford, p 519.

The peak value, for flowing pipes, typically lies between 50 and 80 °C. This implies that for tanks carrying heavy crude, that are heated in excess of 100 °C to facilitate loading and unloading, and are insulated to retain heat during transport, the availability of oxygen will be very limited and the corrosion rate might be significantly less than at ambient temperature.
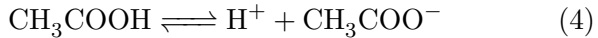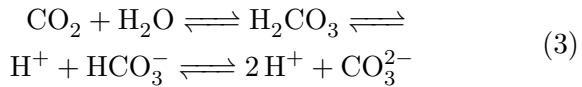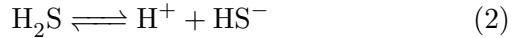
For empty tank cars with accumulated water, the corrosion rate will be significantly higher. The oxygen does not have far to travel to transition from the gas space, through a thin layer of oil (if still present) into the water phase. It is therefore most likely that it is the empty tank cars on the return journey from refinery to oil field that suffer the greatest corrosion.

> Key Point 5: Oxygen-driven corrosion is at its greatest in empty tank cars that have thin layers of accumulated water at the bottom.

During the cathodic reaction ($O_2 + 4\,H^+ + 4\,e^- \longrightarrow 2\,H_2O$) protons are consumed. This causes the solution to gradually become more alkaline and may even cause a change in the nature of corrosion products. However, the composition of the accumulated water is heavily dependent upon the transfer of species from the oil and air, which contribute to the availability of protons.

The hydrogen cathodic reaction ($2\,H^+ + 2\,e^- \longrightarrow H_2$) consumes protons that are available in the water phase. This reaction may be much slower than the oxygen cathodic reaction, but the concentration of protons can be many times higher than that of oxygen, with contributions from free protons in solution (H^+), but also protons from other chemical species. In particular, crude oils can carry hydrogen sulfide, carbon dioxide (which is also present in air) and volatile fatty acids. These species can all exist in

the gas phase (where hydrogen sulfide can be dangerous to tank car personnel), in the oil and in the water phase. Because water is polar and can support ionic charges, these species can also dissociate; releasing protons that can be used in the corrosion cell, as follows:

$$H_2S \rightleftharpoons H^+ + HS^- \tag{2}$$

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons$$
$$H^+ + HCO_3^- \rightleftharpoons 2\,H^+ + CO_3^{2-} \tag{3}$$

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^- \tag{4}$$

These reactions are *not* electrochemical as there is no transfer of electrons. They therefore occur spontaneously in the solution, not just at the metal surface. As these equilibria all include H^+, the water composition – the concentrations of the individual species – is dependent upon the pH (which is defined as the concentration of free protons), and vice versa. For instance, pure water left to equilibrate with air will absorb carbon dioxide, some of which combines with water to form carbonic acid (H_2CO_3), further dissociating to form bicarbonate (HCO_3^-) and protons. The concentration of protons thus increases, and the pH drops from 7.0 to approximately 5.5. The extent to which the pH changes depends upon the nature of the equilibrium, the temperature, the concentrations of the gaseous species and the consumption of protons through corrosion. This can be modelled, but again, only for well-defined systems. The un-dissociated species can also react on the steel surface directly: $2\,H_2CO_3 + Fe \longrightarrow Fe^{2+} + 2\,HCO_3^-$. Suffice to say that if H_2S, CO_2 or acetic acid are present in the oil, then they will partition into the water phase and increase the corrosion rate of the steel.

A note of warning: Traditionally, the corrosivity of water is considered to be directly related to the pH, the measure of acidity. As demonstrated above, this is not strictly true, and it is necessary to have a full water analysis before an informed opinion can be made regarding the risks associated with the accumulated water. An overview of sample collection procedures is given in the Appendix.

3.4   Corrosion Products

The reactions described above have been given for relatively simply circumstances: metallic iron in an acidic solution, where the Fe^{2+} is the stable species. The iron cations remain dissolved in the water and the bare steel is free to corrode at a stable rate. In the majority of cases relating to tank cars, this is likely not the case. The expectation is that the accumulated water will be only slightly acidic, close to neutral, and may even be slightly alkaline if considerable corrosion has occurred.

Under alkaline conditions, the oxygen and hydrogen cathodic reactions are described by the dissociation of water itself, as there are few free protons available. The oxygen reduction half cell reaction becomes: $O_2 + 2\,H_2O + 4\,e^- \rightleftharpoons 4\,OH^-$. The hydrogen reduction reaction becomes: $2\,H_2O + 2\,e^- \rightleftharpoons H_2 + 2\,OH^-$.

A number of corrosion products can be formed depending on the cathodic reactions – which determine the mixed potential – and the pH of the solution. It is possible to create behavioural maps, where the dominant stable species is identified. These maps are called 'Pourbaix' diagrams, after their creator Marcel Pourbaix. The Pourbaix diagram for iron is presented in Figure 3. The x-axis is pH, and the y-axis, the electrochemical potential, relative to a standard hydrogen electrode.
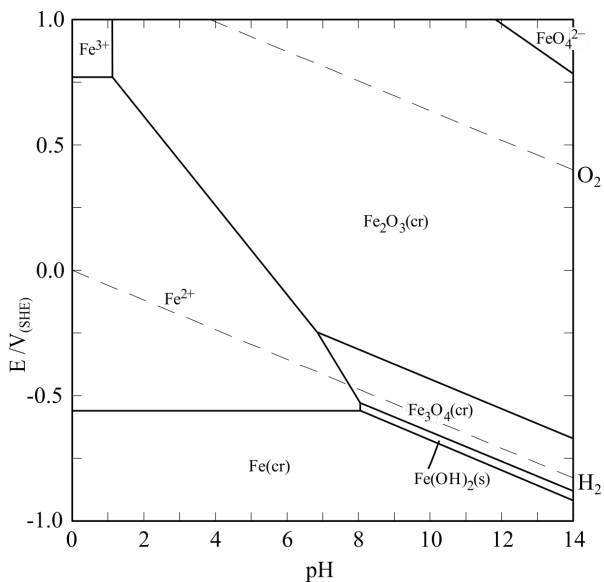
Figure 3: Pourbaix diagram for 0.001 mol/L iron at 25 ℃. Abbreviations: (cr) crystalline, (s) solid. Where no phase of state is provided (Fe^{2+}, Fe^{3+}, FeO_4^{2-}), the species is soluble (i.e. non-protective).

The diagram includes two diagonal dashed lines. These are labelled on the right-hand side as oxygen and hydrogen, and represent the equilibrium potentials for these reactions for 1 atmosphere pressure (reactions 2 and 4, respectively, in Table 1). These are essentially guidelines that permit the user to determine the likely outcome of a corrosion reaction. At potentials above the oxygen line, water is oxidised to form molecular oxygen (O_2). Such conditions should not occur in a tank car. Below this line, O_2 is reduced to form water. Air contains 20.9% oxygen, a fifth of the amount used to determine the line in the diagram. For water that is in equilibrium with air, the oxygen reduction potential will be slightly lower than the line on the diagram, but this difference is usually not significant. If oxygen is not present in the system at all (i.e. there is excess hydrogen sulfide present) then the line should be ignored. For hydrogen, electrochemical potentials above the line indicate that H_2 is being oxidised. Under naturally occurring conditions, and this includes tank cars, molecular hydrogen would not be expected to be present at all. Below the hydrogen line, protons are consumed and the metal oxidised.

Turning to the iron itself, the bottom region, labelled 'Fe(cr)' is metallic iron. If the environment results in a potential and pH point within this region, iron is the most stable form; metallic iron will not corrode, and iron cations in solution will be reduced to metallic iron. Above this region lies Fe^{2+}, where the ferrous ion dissolves in the water.

Under alkaline pH's, iron oxides and hydroxides form on the metal surface. With hydrogen reduction as the cathodic reaction, $Fe(OH)_2$ (ferrous hydroxide) is formed via reaction with water: $Fe + 2\,H_2O \longrightarrow Fe(OH)_2 + H_2$. Protons are consumed in the cathodic reaction and lost from the water through the formation and dispersion of hydrogen gas bubbles, but the hydroxide ions bind onto

the iron and there is no net change in the solution pH. At slightly higher potentials, Fe_3O_4, known as magnetite, is formed, primarily through reaction with oxygen. Containing one Fe^{2+} and two Fe^{3+} ions, magnetite is formed in a multi-step reaction between neighbouring iron-containing complexes, that link together and eject protons and water molecules. $Fe(OH)_2$ can also present. The resulting solid is quite protective and the corrosion rate of the steel should be low as the corrosion product acts as a barrier between the steel and the water. Similarly, at higher potentials, Fe_2O_3, haematite, is formed. This is also protective although to a lesser extent than magnetite as it can be porous and brittle.

The Pourbaix diagram describes the most stable species only, not all the species that are present. Similarly, it indicates the reactions that occur at the metal surface, and also describes the equilibrium conditions. In a tank car with a thin stagnant layer of water, the oxygen concentration can vary significantly with depth, from the shallow edge to the maximum depth at the 6 o'clock position. As the mixed potential depends on the concentration of the cathodic species different corrosion products may be formed at different locations. As the environment changes, for instance, when the tank car is emptied and oxygen availability increases, corrosion products can also change.

If hydrogen sulfide is present, then corrosion products can include various iron sulfides, even under acidic conditions. Iron sulfides can exacerbate corrosion in the absence of oxygen, as the corrosion product is highly conductive and the proton reduction reaction can happen faster than on oxide-covered steel.

3.5   Uniform Corrosion

We have discussed the mechanics of the corrosion cell on an atomic level; but how does the corrosion product actually look? It can take several forms, the most common of which is 'uniform' corrosion, which means that the surface looks much the the same all over. The anodic and cathodic reactions occur all over the surface. In an acidic solution, the anodic process typically does not result in a corrosion product as the ferrous cations are stabilised in solution. The iron surface can have a bright grey matte surface, which discolours rapidly when dried.

Where corrosion products are formed, at higher potentials and pH, they act as a barrier to the cathodic reaction. Over time, the uniform corrosion rate decreases as the corrosion layer builds up. This corrosion may be unsightly, especially in the presence of excess oxygen forming $Fe(OH)_3$ which is the classic orange rust, but is not necessarily a cause for concern. The iron hydroxides occupy significantly more solution volume than the original metal did. Whilst it may appear that there is significant corrosion product in solution, it may have originated from only a small amount of corrosion. Similarly, uniform corrosion can result in blackened surfaces under conditions of oxygen limitation; this could be the beneficial protective magnetite. One advantage of uniform corrosion it that it leaves 'tide marks' which enable calculation of the quantity of water held in the tank.

The key to uniform corrosion is that the corrosion penetration rate, the length of time required for the shell to corrode through, might be sufficiently slow as to require decades, as it occurs evenly everywhere. Unfortunately, it does not account for the pitting described by engineers in the industry survey. This, instead is likely due to under

deposit corrosion.

3.6   Under Deposit and Crevice Corrosion

Under deposit corrosion occurs where material sits on the steel surface. Examples include sludges, sediments (included detached corrosion products), sand, physical objects, and microbial biofilms. There remains a small layer of water between the steel and the deposit, but because of the constricted geometry, the water chemistry can be considerably different from the bulk solution. Crevice corrosion is similar to under deposit corrosion in that, between two components, there is a volume of fluid with restricted connection to the bulk solution. For instance, submerged screw threads can contain water and allow corrosion to occur. Oxygen within these spaces can be depleted, and the pH can rise through proton consumption. For this reason, the cathodic reaction does not occur under the deposit or in the crevice at the same rate as on adjacent steel surfaces. However, the steel can still corrode. The cathodic current is provided by the steel around the deposit/crevice and the anodic process, rather than occurring uniformly over the surface, is concentrated under the deposit or in the crevice. In essence, the localised corrosion is protecting the steel around it. From an industry perspective under deposit corrosion is a significant concern because it is unpredictable and can result in accelerated localised corrosion that can perforate the tank shell. Whether or not crevice corrosion occurs depends on the tank car design and materials selection choices.

3.7   Galvanic Corrosion

Galvanic corrosion can occur when dissimilar metals are connected, both electrically and through a common solu-

tion. The different metals/alloys have different reduction potentials. As with the half cell reactions discussed earlier, a mixed potential, comprising all possible half-cell reactions, is reached. The material with the lowest potential is held at a positive overpotential and corrodes. The more noble metal/alloy can provide a surface that is much more active for the cathodic reaction than the corroding metal when alone. For instance, in the galvanic coupling of stainless and carbon steel, the stainless material behaves as the cathodic surface. Because it forms only very thin surface oxides (the 'stainless' refers to a thin layer of chromium oxide – too thin to see, but dense enough to prevent the iron underneath from rusting), oxygen can be rapidly reduced and the carbon steel corroded. In a manner similar to under deposit corrosion, corrosion occurs at a fixed site, as close to the more noble metal as possible. In a tank car, this may arise from use of stainless steel components in the tank shell. As these fixtures are at the top of the tank, galvanic corrosion is most likely to occur if there is condensation on the interior surface. This is most likely for non-insulated tanks, and could result in leakage at the fitting connection.

3.8   Microbiologically-Influenced Corrosion

Water that has accumulated in tank cars can be infected by microorganisms, such as bacteria, archaea and fungi. These microbes require water to live in, carbon to consume for both energy and multiplication, and chemical species such as oxygen or sulfate, for respiration. Given the wide variety of microbes, their metabolic requirements and responses, and environments to which they are suited, microbiologically-influenced corrosion (MIC) is a relatively new and complex field.

Many microbes, given a suitable environment, produce biofilms. These can take the appearance of slime or biological fluff. The biofilm serves numerous purposes, including providing a degree of protection against dangerous chemicals in the environment such as biocides (poisons); acting as a primitive external digestive system; and facilitating communication (quorum sensing) and gene exchange between microbes. The biofilm also permits many different types of microbes to thrive in close proximity. Each biofilm can be considered a city, with a thriving and diverse population that adapts as it grows and the environment around it changes.

Two particular broad types of MIC are of concern as far as tank cars are concerned. The first occurs in accumulated water within tank cars that are aerobic (i.e. there is no H_2S in the water or oil). In the presence of oxygen, lighter oil components and organic species such as volatile fatty acids can be rapidly consumed. As with the electrochemical reactions described earlier, there are two half-reactions: the reduction of oxygen and the oxidation of carbon-based species, ultimately to carbon dioxide. The biofilms locate themselves at the position in the water phase best suited to their needs: floating at the top, at the water / oil interface. Here, microbes can access oil directly, and have the greatest availability of water-soluble species and oxygen as these chemicals diffuse from the oil. These types of biofilms are largely transparent and fluffy in appearance, and can be up to a centimetre in depth. These biofilms can cause localised corrosion where they touch the steel surface at the bottom of the tank. This can be due to a biofilm sinking or where the water layer is sufficiently thin that the biofilm is both at the water / oil interface *and* in contact with the steel. Because the microbes in the biofilm are continually consuming oxygen, the steel in contact with the biofilm

water is in contact with oxygen-depleted fluid. Indeed, in more extreme cases, biofilms commonly exist with oxygen-consuming microbes in the outer regions, and anaerobic microbes, that can function only in the absence of oxygen, thriving deeper within the biofilms. Nevertheless, the steel directly under the biofilm is not exposed to oxygen in the same way the rest of the tank steel is, creating an oxygen concentration cell: steel under the biofilm can behave anodically, and the surface beside, cathodically. This is a type of 'under deposit corrosion', as described earlier, and can be exacerbated by local changes in water chemistry at the biofilm / steel interface, due to microbial activity.

The second type of MIC involves sulfate-reducing bacteria (SRB). These anaerobic microbes only thrive in water that is free of oxygen, require sulfate (SO_4^{2-}) in the water phase (it is present in low concentrations in potable water, at a much higher concentration in seawater, and exists in the formation water of many, although not all, oil reservoirs), and also water-soluble organic molecules, typically VFA's, such as acetic and propanoic acid. Thermodynamically, it is difficult to consume oil directly with sulfate reduction, so these microbes favour consuming organic acids. These acids may be present in oil produced through fracking, and in more conventional wells, but heavy oil reservoirs, that have already been biologically degraded, contain no such VFA's. The SRB consume the available carbon sources, producing carbon dioxide, reducing the sulfate to hydrogen sulfide. The hydrogen sulfide is an end-product and has negligible effect on the microbes. Both the carbon dioxide and the hydrogen sulfide can increase localised corrosion by acidifying the local water chemistry, i.e. within the biofilm on the steel surface.

In addition to suitable carbon sources, microbes can only thrive below temperature thresholds, above which they

are forced into stasis or die. A common temperature limit for microbes that are also active under ambient conditions lies between 45 and 55 °C. These microbes are termed 'mesophiles', in contrast to 'thermophiles' that are both less common and require consistently higher temperatures to thrive. From an oil tank car perspective, loading of heavy oil that has been heated in excess of 100 °C might be found to sterilise the tank car, or at least prevent microbial activity; certain microbes in distress can form spores that withstand harsh environments. These spores can then re-establish microbial colonies when the environment becomes favourable, although it can takes days to weeks for the spores to re-establish themselves.

As with corrosion that does not involve microbes, if there is no water, there is no problem. Where there is water, the microbes can establish, and once a tank car has been infected, they are hard to remove even with vigorous cleaning. The only note of caution to be sounded regarding MIC, is that without data to demonstrate that it is actually a problem to begin with, it is not possible to determine a mitigation strategy for corrosion. Tank car inspectors are asked to be vigilant, and to record what they find. If possible, microbial analysis of settled tank car water could yield significant insight into the likelihood of MIC within rail tank cars.

4 Recommendations

The arguments outlined above are based on an understanding of the oil production industry, a knowledge of corrosion, a broad literature and internet search, and what little anecdotal evidence was supplied during the rail car industry survey. This process has highlighted two primary chemicals for concern. The first is hydrogen sulfide, which is

likely to be sporadically present in tank cars, can play a significant role in increasing corrosion and is potentially lethal to personnel. The second is water; without it, there would be no corrosion at all.

In order to refine understanding of tank car corrosion, it is necessary to test laden tank cars for hydrogen sulfide in the head space (analysis can be done on-site with a hand-held monitor), and correlate the results with the source of the oil. Water samples should be obtained for analysis, although as the water can accumulate over numerous trips, its composition cannot be directly linked with the transported oil. One participant in the industry survey suggested that collection of the first few gallons from the bottom outlet valve always included water. Analysis of this water for pH, oxygen concentration, volatile fatty acids, microbial activity, etc., permits determination of the corrosivity of the water. Finally, inspection of tank cars after cleaning, specifically to identify localised corrosion at the tank bottom, measure tide marks caused by uniform corrosion and inspection of roof-mounted fixtures for galvanic corrosion, will enable Transport Canada to understand the severity of internal corrosion. It is highly recommended that Transport Canada staff participate or contribute toward the collection of this data. Whilst the responses during the industry survey ranged from grave concern over internal corrosion to indifference, insufficient evidence was forthcoming to make a judgement on whether or not internal corrosion is a major source of concern, whether the problem is getting worse when compared to changes in the tank car population, and if hydraulic fracturing plays a significantly different role to conventional oil production or not.

If this information is obtained and points to corrosion concerns, it may be possible to make recommendations to

the industry such as:

- Use of lined tank cars for early-production hydraulically fractured wells, which may have a high water cut that is also corrosive.

- Partial lining of the bottom third of tank cars as a cost reduction, if head space condensation corrosion is not a concern.

- Best practice regarding tank cleaning and inspection frequency.

5 Acknowledgements

A Toxicity of Hydrogen Sulfide

Hydrogen sulfide gas, H_2S, is colourless, heavier than air (vapour density = 1.19), flammable (4.3% lower explosive limit – 46% upper explosive limit) and extremely toxic. In small concentrations, it has a rotten egg smell and causes eye and throat irritation. At higher concentrations H_2S can deaden your sense of smell and cause permanent brain damage and death. The concentration at which H_2S is considered immediately dangerous to life and health (IDLH) is 100 ppm. The symptoms of exposure are presented in Table 2.

Concentration (ppm)	Possible Health Effects
<1	Detectable by smell
1 – 10	No known adverse effects for most people
10 – 20	Potential eye irritation
20 – 200	Eye and respiratory tract irritation and loss of smell. Headache and nausea
200-500	Above effects, but sooner and more severe. Loss of breathing and death within hours
500-700	Affects the central nervous system. Loss of reasoning, loss of balance, unconsciousness and breathing to stop within minutes
>700	Immediate loss of consciousness. Permanent brain damage and death if not rescued immediately

Table 2: Health effects due to exposure to hydrogen sulfide.

B Internal Inspection

In order to identify the likelihood and severity of localised corrosion, tank cars could be inspected following cleaning.

This provides staff the opportunity to enter a safe tank car environment and inspect for:

1. Localised corrosion. Replica moulds of the localised corrosion can be taken using stiff plasticine with spray-on release agent. This permits accurate measurement of the corrosion depth and surface area in a more convenient setting.

2. Tide marks, in particular at the mid-way point of the tank; this is indicative of the depth of accumulated water, and many tide marks are likely to be present.

3. Evidence of crevice or galvanic corrosion where fittings, such as the bottom outlet valve or the vacuum prevention valve, penetrate the tank shell.

4. Evidence of surface corrosion at the 12 o'clock position, in the gas space; potentially caused by water condensation and acid gases.

When photographing internal tank car corrosion, include a ruler in the photograph for scale.

Prior to entering the tank car, the internal atmosphere must be analysed as the tank car is an enclosed space. The standard practice is to use an explosion-proof multi-gas monitor that incorporates a pump. Attached to the pump is a length of tubing which is lowered into the tank car, permitting the user to remain in a safe location whilst sampling. The monitor must be capable of detecting oxygen (which must be in excess of 19.5% before entry), residual hydrogen sulfide and flammable organics (limits of which are set by Federal and Provincial legislation). The monitor must also be tested against a calibration gas before use (at least once daily), to confirm correct operation. Entry to the tank car must comply with enclosed space protocols and legislation, to be prepared beforehand. This may

include (but not be limited to) a buddy system, winching gear, personal monitors, purifying respirators (for residual fumes), etc.

C   Analysis of the Gas Space

Laden tank cars provide the opportunity for analysis of the gas space above the oil, using the same multi-gas monitor required to confirm the safety of the cleaned tank car prior to entry.

D   Water Collection Procedures

When sampling for accumulated water within loaded tank cars, it is important to extract the water without contaminating it with air or debris. Water can be collected at the bottom outlet outlet valve, or can be collected from the tank bottom by means of a weighted length of tubing and a syringe, from an open hatchway. This latter approach can also be used to determine the approximate depth of water settled in the tank car. If sampling through the hatch-way, it is important to confirm the safety of the gas space (in terms of hydrogen sulfide and noxious organics) as described above. Whilst there are many types of water analysis that can be conducted, the main groups of analysis are as follows:

1. Microbes

2. Dissolved gases (oxygen and hydrogen sulfide)

3. Dissolved organics (such as volatile fatty acids)

4. Inorganic species (such as sulfate and chloride)

There are generally only two bottle types available – glass and plastic. The advantage of glass is that it is gas impermeable, and the advantage of plastic is that is is more durable than glass, although is permeable to gas such as oxygen. It is not uncommon that analytical laboratories provide procedures for clients to follow, in order to obtain and store samples correctly. These procedures may be more specific than the broad overview outlined in Table 3.

Preservatives are as follows:

Preservative A : 4 drops of $2 \, mol \, dm^{-3}$ zinc acetate per 100 mL.

Preservative B : $6 \, mol \, dm^{-3}$ sodium hydroxide. Warning: solution is highly caustic – avoid contact with skin and eyes. Add to solution drop-wise until pH is greater than 9.

Many of these analyses can be conducted on-site using field kits. For instance, water-dissolved hydrogen sulfide can be detected colourimetrically and quantified using a supplied colour wheel. However, field analyses are sometimes susceptible to interference from other chemical species; laboratory analysis permits pre-treatment of the water samples to minimise this interference, although this is not always practical – dissolved oxygen is typically measured on-site, for instance. Also, the analyses result in hazardous chemical waste that must be disposed of properly; this is easier in a laboratory setting.

Microbial analyses can include cultivating the microbes or extracting and inspection of the DNA for community analysis.

Personal protective equipment (PPE) should be worn at all times when using chemicals. This includes gloves, safety glasses and protective clothing.

Analysis	Bottle	Size	Preserv.	Hold time	Notes
Microbial analysis	g, p	100 mL	none	48 hours	bottles must be sterilised. No headspace. Store <4 °C.
Dissolved oxygen	g	300 mL	none	15 min.	Winkler bottle, filled to overflowing before capping. Analyse immediately.
Dissolved hydrogen sulfide	g, p	100 mL	A & B	48 hours	Store <4 °C
Dissolved organics	g	100 mL	B	48 hours	No headspace. Store <4 °C
Inorganic species	g, p	100 mL	none	28 days	Store <4 °C
pH (acidity)	n/a	30 mL	n/a	15 min.	Analyse immediately. Easiest to use universal paper.

Table 3: Overview of collection details for various analyses. pH measurements can be taken prior to adding preservatives to dissolved hydrogen sulfide and organics samples. Abbreviations: g, glass; p, plastic (polyethylene). Adapted from 'Standard Methods for the Examination of Water & Wastewater, American Public Health Association'.