



**ENVIRONMENTAL FATE AND BEHAVIOUR OF  
ANIONIC POLYACRYLAMIDES IN OIL SANDS  
TAILINGS MANAGEMENT: A STATE OF  
KNOWLEDGE SYNTHESIS**

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**Prepared for:**

**Alberta Innovates**  
**Attn: Mark Donner**  
250 Karl Clark Road NW  
Edmonton, AB, T6N 1E4

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## LIST OF CONTRIBUTORS

This report was prepared by the following:

- Jerry Vandenberg, B.Sc., M.Sc., P.Chem.  
Report Author  
Vandenberg Water Science Ltd.
- Daniel Smith, B.Sc., M.Env.Sc.  
Report Author  
Intrinsic Corp.
- Bart Koppe, B.Sc., PBD (Tox)  
Report Author and Senior Review  
Intrinsic Corp.

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# ENVIRONMENTAL FATE AND BEHAVIOUR OF ANIONIC POLYACRYLAMIDES IN OIL SANDS TAILINGS MANAGEMENT: A STATE OF KNOWLEDGE SYNTHESIS

## EXECUTIVE SUMMARY

### Background

Anionic polyacrylamide (PAM) compounds are polymeric flocculants that are applied in many industries, including oil sands mines, for the purification and management of water and solids. At oil sands mines, PAM flocculants are applied to fluid tailings to accelerate and improve consolidation and to clarify supernatant water, processes that are important for water recycling and reclamation.

Historically, the environmental risk of PAM was thought to be relatively low because the polymer is very large and non-toxic and would be strongly bound to soil particles, while the residual monomer and other degradation products are highly biodegradable and unlikely to persist in the environment. Abundant literature suggests that PAM itself poses little to no toxicological risk as an amendment in oil sands tailings. PAM sorbs strongly to soil and is unlikely to be transported to human or ecological receptors. Even if PAM were transported, it is not bioavailable or toxic. It is widely applied in many industrial and personal products with no apparent adverse health effects.

To test these assumptions, this literature review compiled the state of knowledge regarding the use of anionic PAM in tailings management at Alberta oil sands mines and the potential environmental consequences of PAM and its byproducts. The review was based primarily on peer-reviewed literature, with secondary sources including government reports, conference proceedings, academic theses, company tailings plans, Material Data Sheets, websites and interviews with academic researchers and industry experts.

### Analytical Methods

In theory, numerous analytical methods exist for the separation, identification and quantification of PAM in oil sands tailings and other media such as sediments, soils and wastewater; in reality, the accuracy and reproducibility of these methods is limited due to the characteristics of the PAM being analyzed and the characteristics of the sample matrix. Available literature does not present a commercial analytical method applicable to oil sands tailings, and there is currently no standard method for detecting low concentrations of PAM in aqueous solutions with various environmental impurities. Analysis of PAM in oil sands tailings or oil sands process water is challenging for two main reasons: (1) the compounds vary widely in terms of chemical properties; and (2) they are highly adsorptive within a complex matrix of OSPW and tailings.

### PAM Degradation

PAM is applied to tailings at all operating oil sand mines. Full-scale application follows decades of evaluation at smaller scales including laboratory and pilot-scale field trials. Tailings are treated to become either terrestrial landforms or aquatic substrates at closure.

Biodegradation of PAM may occur within the tailings matrix where PAM is abundant and stably bound until degraded. Long-term sorption of PAM to the tailings matrix may present opportunities for microbial communities to adapt to metabolize the molecule after other sources of carbon or nitrogen are depleted.

Studies generally suggest that while nitrogen appears to be readily metabolized from PAM under a wide range of conditions, carbon tends to be used only when labile carbon sources have been depleted. This suggests that PAM degradation in oil sands tailings may be incomplete or absent in fresher tailings where labile sources of carbon (such as solvents) are present, but could become more pronounced in the future as these compounds are depleted. Literature from many non-oil sands applications and three oil sands tailings ponds suggests the following:

1. Microbes are able to degrade PAM to use nitrogen under anaerobic and aerobic environments.
2. Microbes are able to degrade PAM to use carbon under limited circumstances. The PAM backbone is relatively recalcitrant, and microbes are likely to use more available electron donors that may be present before they adapt to using PAM.
3. Acrylamide is generally not a detectable byproduct of PAM degradation, and residual acrylamide is rapidly removed through biodegradation.

Biodegradation is the most common mechanism of PAM degradation. Mechanical, thermal and photodegradation may be relevant for short periods during handling and placement, but are not likely to persist after tailings have been placed and covered with soil or water.

### **Factors Affecting Degradation**

Several factors can affect the rate and degree of PAM degradation. The degree of hydrolyzation can influence degradation, especially regarding deamination. Molecular weight affects degradation, with higher molecular weight being less degradable. Microbial communities and oxidation-reduction potential of tailings deposits will affect degradation, with aerobic environments typically promoting faster degradation. Degradation is also increased under neutral pH and high temperatures. Considering these factors, PAM degradation in oil sands tailings is likely to be slow in most of the deposit, but may be more prominent in geochemically active zones such as near the surface of the deposit.

### **Degradation Rates and Products**

During biodegradation of PAM, deamination of acrylamide subunits within PAM results in the release of nitrogen in the form of ammonia or ammonium and the conversion of acrylamide subunits in PAM to acrylic acid subunits. Once PAM has become completely deaminated, the remaining carbon backbone is polyacrylic acid or polyacrylate, depending on environmental pH. Thus, degradation products formed via deamination are polyacrylate and ammonium or polyacrylic acid and ammonia.

Based on laboratory studies and information derived from other industries, PAM degradation products arising from chain scission are generally limited to lower molecular weight polymers, and volatile fatty acids and their intermediates. No compelling evidence exists to indicate that acrylamide or acrylic acid would accumulate as a degradation product of PAM in oil sands treated tailings.

### **Environmental Transport and Exposure**

Due to the characteristics that lend PAM its flocculating properties, anionic PAM is strongly adsorbed to soil and clay mineral surfaces, which limits its mobility in soil and leaching potential to groundwater. Anionic PAM adsorption to soil is rapid and irreversible. Therefore, PAM is not likely to migrate from tailings to groundwater or surface water systems.

Fugitive dust from dry tailings is a documented issue in mine waste management at oil sands and other mines. The application of PAM to tailings is likely to reduce the amount of fugitive dust from a dry tailings deposit compared to a deposit that has not been amended with PAM as PAM has been used in other applications to control dust. Based on findings from several agricultural studies, deposition of dust containing PAM is not considered to be a significant health risk. Site-specific data from dry tailings applications would be required to assess the presence of PAM and its degradation products in dust.

Based on its solubility, acrylamide contained in leachate from tailings could be transported by aqueous phase migration to groundwater and then downgradient via advective groundwater flow to a receiving waterbody. However, this transport would likely be mitigated by two factors. First, the degradation rate of acrylamide is high, so acrylamide is likely to be degraded before reaching environmental receptors. Second, the hydraulic conductivity of PAM-amended tailings is very low, so the total mass load associated with the leachate is also likely to be very low. Based on these considerations, acrylamide is unlikely to be detected along surface or groundwater pathways downgradient of tailings deposits.

Environmental (non-toxicological) implications of PAM deposition and degradation were considered in terms of nutrient enrichment, change in pH and generation of greenhouse gases. None of these processes were deemed to pose significant environmental risks.

### Thresholds

Anionic PAM is considered non-toxic to humans and other mammalian species; exposure to PAM is well tolerated. Similarly, anionic PAMs are generally assumed to be non-toxic to fish and freshwater invertebrates. The low toxicity is likely due to the high molecular weight of PAM. No environmental guidelines were found for PAM in North America.

The toxicity of acrylamide to humans is reasonably well established, and human health guidelines exist in some jurisdictions for soil and water for both acrylamide and acrylic acid. Acrylamide is thought to be a human carcinogen, though at exposure levels well in excess of those anticipated for PAM-treated tailings. No environmental guidelines were found for acrylamide or acrylic acid.

Ammonia is known to be toxic to aquatic species at environmentally relevant concentrations, and aquatic guidelines exist in several jurisdictions. The toxicity and bioavailability of ammonia vary according to pH and temperature. Ammonia is considered to have low toxicity to humans in drinking water.

### Monitoring

Challenges associated with analyzing PAM are well documented. While there may be good reasons to measure PAM from a geotechnical or economic perspective, the low environmental risk of PAM itself suggests that developing methods to analyze PAM in oil sands tailings would be a low priority. Instead, monitoring efforts should be focussed on three potential pathways where the risk is thought to be low but uncertain: (1) PAM exposure through fugitive dust; (2) release of acrylamide from recently placed deposits; and, (3) long-term release of ammonia from deposits.

Although the risk of PAM exposure through fugitive dust is considered low, testing the dust, including whether PAM is a component of dust, from drying tailings may be warranted to confirm this. Based on the results from similar applications, testing is likely to show that PAM provides a net benefit for dust control.

There is no evidence that acrylamide accumulates through PAM degradation in tailings; however, it may be present as a residual monomer in commercial formulations. In addition, PAM-treated tailings are likely to have initially higher hydraulic conductivity and pore water release. Therefore, acrylamide monitoring in groundwater or surface waters should focus on the recently-placed deposit. If significant quantities of acrylamide are not detected in the initial release of water, they are unlikely to be detected thereafter.

Conversely, ammonia is more likely to be generated over the long term through deamination. Therefore, ammonia should be monitored in seepage waters or tailings release waters until it can be shown that degradation is not occurring or that insignificant quantities of water are seeping from tailings deposits. Ammonia may serve as an early indicator of PAM degradation.

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# Environmental Fate and Behaviour of Anionic Polyacrylamides in Oil Sands Tailings Management: A State of Knowledge Synthesis

## 1.0 INTRODUCTION

### 1.1 Purpose and Scope

Anionic polyacrylamide (PAM) compounds are polymeric flocculants that are applied in many industries, including oil sands mines, for the purification and management of water and solids. At oil sands mines, PAM flocculants are applied to fluid tailings to accelerate and improve consolidation and to clarify supernatant water processes that are important for water recycling and reclamation.

As part of mine reclamation, treated tailings pore water and supernatant water will be actively or passively transported to the receiving environment. Therefore, the environmental transport and transformation mechanisms of PAM, including degradation to daughter products and release of residual acrylamide, must be understood to manage the materials during operations and closure. Historically, the environmental risk of PAM was thought to be relatively low because the polymer is very large and non-toxic and is strongly bound to soil particles, while the residual monomer and other degradation products are highly biodegradable and unlikely to persist in the environment. To test these assumptions, this literature review compiled the state of knowledge regarding the use of anionic PAM in tailings management at Alberta oil sands mines and the potential environmental consequences of PAM and its byproducts.

The review was based primarily on peer-reviewed literature. Where certain information was not available in published literature, other sources of information such as government reports, conference proceedings, academic theses, company tailings plans, Material Data Sheets, websites and interviews with academic researchers and industry experts were referenced. Wherever publicly available information was insufficient to describe a given topic, knowledge gaps were identified at the conclusion of this report. Given that some of the subsections within this report relate to entire fields of study (e.g., geotechnical performance of tailings, soil erosion), references are provided to other review documents that cover those topics more comprehensively.

To obtain provincial regulatory approval, tailings plans for oil sands operations must include “ready-to-reclaim” criteria for the safe storage of tailings under Directive 85 (Alberta Energy Regulator 2017), as well as environmental criteria under Environment Protection and Enhancement Act approvals (Alberta Government 2000). This literature review supports the latter requirement by evaluating environmental and health risks associated with PAM, including its degradation products.

### 1.2 Chemistry of PAM and Flocculation

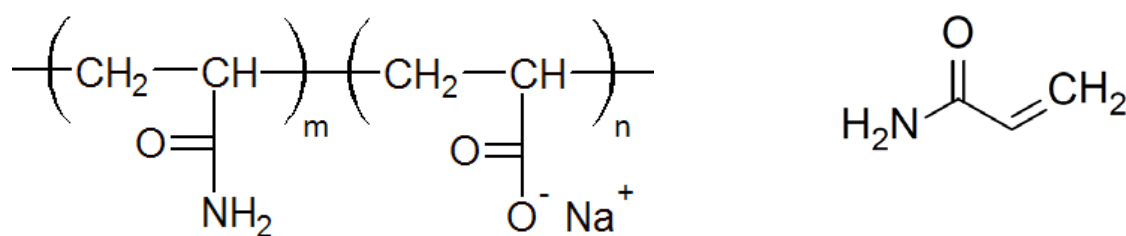
The term PAM is applied generically to hundreds of different polymer compounds that include a repeating acrylamide plus acrylate backbone (Figure 1-1) as the monomer (Sojka et al. 2007; Xiong et al. 2018a). Strictly speaking, a pure PAM compound is non-ionic; however, many variations of the polymer are created commercially to obtain specific chemical properties and behaviours.

These water-soluble compounds are mainly linear chains, although the chains may be coiled or curved in response to ambient electrolytes (Sojka et al. 2007). The molecular weight of PAM is generally high, ranging from  $10^5$  to  $10^7$  g/mol (Xiong et al. 2018a).

Flocculent properties of PAM are related to its large size and charge. The high-molecular-weight, charged PAM attract multiple particles to each molecule, forming a bridge between otherwise suspended particles. The bridge overcomes electrostatic repulsion, leading to solid-water separation and accelerated sedimentation rates (Heath et al. 2006). The polymer bridge may be fragile, so application to oil sands tailings must balance the energy and turbulence needed to fully mix the applied polymer with the need to produce and maintain stable flocs. The bridge strength (and thus flocculation efficiency) is affected by multiple characteristics of the polymer, such as molecular weight and charge density (Sojka et al. 2007; Guezennec et al. 2015a).

Anionic PAM is negatively charged due to the inclusion of a carboxylic, sulfonate or other anionic functional group. Anionic PAM may be formed through the copolymerization of acrylamide with acrylic acid or by the hydrolysis of non-ionic PAM. A common synthesis method for anionic PAM is to hydrolyze the non-ionic polymer with caustic soda, creating hydrolyzed PAM. PAM can be hydrolyzed to varying degrees to affect the proportion of carboxylate functional groups, which in turn affects acidity and anionicity. The charge of a given formulation is dependent upon ambient pH, with most PAM remaining ionic above pH of 6 and tending to be protonated below pH of 4 (Barvenik 1994). Sulfonic anionic PAMs can be created by sulfomethylation to remain anionic at lower pH (Huang et al. 2001), though these are not required for use in mainly neutral to alkaline oil sands process water (OSPW) (Allen 2008; Vedoy and Soares 2015a). Synthesis pathways for PAM are described elsewhere (Barvenik 1994; Huang et al. 2001; Bolan et al. 2020).

This review is limited to anionic PAM, which is the only documented form of PAM used to treat oil sands tailings. Anionic PAM is the most widely used form of PAM in many industries because of its relatively low toxicity compared to other forms (Biesinger et al. 1976; Sojka et al. 2007). Unless otherwise specified, the term PAM is used hereafter to refer to anionic or hydrolyzed PAM, which includes many specific polymer compounds. The overarching term includes the commercial compounds that are listed in Section 3.0 for the applications where such information is publicly available. Note however that none of the environmental processes described in Section 3.0 are specific to a given compound, as the literature does not contain enough detail to differentiate the environmental fate of any given commercial formulation compared to the broader class of PAM.



**Figure 1-1 Chemical structure of polyacrylamide (left) and acrylamide (right)**

### 1.2.1 **Presence of Acrylamide**

While the desired compound in commercial flocculant formulations is anionic PAM, the formulations include trace amounts (0.05% to 0.1%) of the residual monomer acrylamide (prop-2-enamide; Figure 1-1) from the synthesis of PAM (Guezennec et al. 2015a). Although present in much smaller quantities, acrylamide is a probable carcinogen and neurotoxin (Tepe and Çebi 2019) and is therefore the subject of most public concern related to the use of PAM in oil sands and other industrial applications.

### 1.3 **Other Industry Uses of PAM**

PAM is widely used in other industries and household products. The most common uses are summarized in the following subsections.

PAM has many uses, including water treatment, soil stabilization, cosmetic applications, and food packaging.

#### 1.3.1 **Agriculture – Soil Conditioning and Erosion Control**

PAM is widely applied to agricultural soils to provide multiple benefits, including stabilization of soil structure that limits both wind and water soil erosion, increasing the infiltration capacity of soil and limiting the loss of nutrients (Seybold 1994; Barvenik 1994; Sojka et al. 2007). As a result of these direct benefits to soil conditions, the use of PAM improves the quality of agricultural runoff by reducing the amount of surface runoff and associated constituent loadings of nutrients, sediment, bacteria and pesticides, and in doing so improves water and nutrient conservation rates (Sojka et al. 2007).

Early reviews of PAM in agricultural applications suggested low environmental and health risk due to the stability and low toxicity of PAM within the soil matrix (Seybold 1994; Barvenik 1994). These reviews were completed because, at the time, PAM appeared to be a promising amendment to improve agricultural yield and protect against erosion, but its use was limited due to a lack of understanding of environmental impacts. A later review (Sojka et al. 2007) confirmed the safety of PAM as an agricultural amendment after its use had become widespread.

PAM may be applied by dosing furrow or sprinkler irrigation water to spread the polymer with dosing rates in the range of 10 mg/L or 1 to 7 kg/ha (Kay-Shoemaker et al. 1998a; Sojka et al. 2007). PAM dosing rates were listed as high as 308 and 615 mg/L for using PAM as a soil conditioner to reduce soil erosion and nitrogen loss (Watson et al. 2016).

#### 1.3.2 **Water Treatment – Flocculation**

Anionic PAM is one of the most widely used chemicals in the water treatment industry, including for the treatment of drinking water, storm runoff, sewage and industrial wastewaters. It is used to flocculate and settle particles to create a clarified supernatant (Zhu et al. 1996; Lee et al. 2014; Shatat et al. 2019). In many cases, the PAM is applied primarily to remove clay particles that do not otherwise self-settle within reasonable retention times, and it is also used to remove particulate metals and residual hydrocarbons (Lee et al. 2014). It is generally used as a coagulant aid along with alum, polyaluminum chloride, ferric sulfate or another coagulant. Settled solids form sludges which are then concentrated by mechanical means such as centrifuge or filter press to further separate water and reduce the solid waste volume. When used in conjunction with ferric sulfate, PAM removed over 80% of residual oil from oilfield-produced water (Mousa and Al-Hasan 2017). These are waters that are brought to the surface

during oil production and are typically contaminated with salts and organic compounds. More recently, anionic PAM has been applied to remove microplastics from water (Ma et al. 2019).

The use of PAM itself is considered safe for the treatment of drinking water, and public concern and dosing thresholds are related to residual acrylamide. Dosage of PAM is typically low (0.01 to 0.5 mg/L) in drinking water treatment applications (Kurenkov et al. 2002) and may be set to maintain effluent levels below acrylamide thresholds that vary by jurisdiction. In contrast, dosage rates for treating oilfield-produced water and other non-potable water were up to 3 mg/L (Mousa and Al-Hasan 2017).

### **1.3.3      *Drilling and Hydraulic Fracturing – Viscosity Enhancer and Friction Reducer***

PAM is used for various purposes in the upstream oil industry. In addition to the use of PAM for treating oilfield-produced water (Lee et al. 2014; Mousa and Al-Hasan 2017), PAM is also used as a friction reducer in hydraulic fracturing operations (Xiong et al. 2018b). The polymer is added to drilling fluids to reduce the overall friction of the fluids and drill equipment. Dosage rates for these applications range from approximately 20 to 700 mg/L (Xiong et al. 2018b). Additionally, PAM is applied as a viscosity enhancer as part of enhanced oil recovery (Sabhapondit et al. 2003) with dosage rates as high as 500 to 3000 mg/L (Thomas et al. 2012; Xiong et al. 2018a). PAM has been found to mechanically and chemically degrade in these environments (Xiong et al. 2018b, a), albeit at notably higher pressure and temperature than present at oil sands tailings deposits.

### **1.3.4      *Cosmetics – Multiple Uses***

PAM is used for many purposes in cosmetics, including as binders, emulsifiers, foam-builders, film-builders, lubricants and thickeners (Cosmetic Ingredient Review Expert Panel 2005; Duis et al. 2021). They are used in thousands of topical products including makeup, shampoo, soap and lotion. PAM is used in sunscreen lotions to retain the lotion on skin.

PAM is present at concentrations of 0.05% to 2.8% in cosmetics (Cosmetic Ingredient Review Expert Panel 2005). Scientific reviews concluded that the polymer itself was non-toxic and too large to penetrate skin, but the acrylamide monomer was indicated as a potential concern (Cosmetic Ingredient Review Expert Panel 2005).

### **1.3.5      *Food – Clarification and Packing***

PAM is used for food production for clarifying juices, similar to the clarification of drinking water. Use of PAM for this purpose is approved by the US FDA at up to 10 mg/L, provided the residual acrylamide monomer in the polymer mixture does not exceed 0.2% by weight. PAM is also used in food packing materials (Mroczek et al. 2015).

As a component of food itself, acrylamide is most commonly generated by high-temperature cooking of starches such as potatoes (Eriksson 2005; US EPA 2010; ATSDR 2012). For example, the median concentration of acrylamide measured in French fries and potato chips ranges from 0.178 to 0.6 mg/kg, with maximum measured concentrations above 3.7 mg/kg (US EPA 2010).

### 1.3.6 Other Uses

The first reported use of PAM was in the 1940s to stabilize road surfaces and in the 1950s as soil conditioners (Seybold 1994). Today, other uses for PAM include biomedical applications (Bolan et al. 2020), analytical chemistry, laundry detergent (Duis et al. 2021), textile applications, chemical grouting, friction reduction, adhesives, and viscosity enhancements (Barvenik 1994). In the metal mining industry, PAM is used as a flocculent for mineral recovery in the milling process of several ores and for treatment of mine waste such as phosphate slimes, uranium leach residue, cyanide leach residue and coal refuse (Huang et al. 2001), as well as for conventional water treatment of mine waters prior to discharge to the environment. In the paper manufacturing process, PAM is used to dewater the cellulose pulp and improve overall fibre structure (Huang et al. 2001).

## 2.0 METHODS

A search was conducted to identify peer-reviewed literature on the environmental fate and behaviour of anionic PAM in oil sands tailings management. The literature search was conducted in Google Scholar and Web of Science using combinations of the primary and secondary search terms listed in Table 2-1. Search terms operators varied depending on the search engine used.

**Table 2-1 Search Terms**

<i>Primary Search Terms</i>	<i>Secondary Search Terms</i>
<ul style="list-style-type: none"> <li>• Polyacrylamide</li> <li>• “Anionic polyacrylamide”</li> <li>• “Hydrolyzed polyacrylamide”</li> <li>• “Acrylamide polyelectrolyte”</li> </ul>	<ul style="list-style-type: none"> <li>• Environment*</li> <li>• Degradation</li> <li>• Biodegradation</li> <li>• Persistence</li> <li>• Uptake</li> <li>• Accumulation</li> <li>• Bioaccumulation</li> <li>• Persistence</li> <li>• Fate</li> <li>• Transport</li> <li>• REDOX</li> <li>• Tox*</li> <li>• Risk Assessment</li> </ul>

Following these initial searches, hand-searching was conducted to identify additional primary literature. This hand-searching involved review of papers recommended by key journal websites, publications by study authors, and the citations from papers relevant to the review.

As there is a lack of peer-reviewed literature that is directly applicable to environmental fate of PAM in oil sands tailings management (Cossey et al. 2021), literature was not limited to oil sands tailings applications but included relevant information from PAM usage in other applicable industries (e.g., agriculture, waste management, water treatment, oil well development).



For completeness, a separate search was conducted to identify supplemental information on acrylamide when it was determined to be relevant and necessary to characterizing human health and environmental risks associated with PAM use. This search was conducted in a similar targeted manner as the PAM search.

Retrieved literature was reviewed according to a predetermined hierarchy, with peer reviewed scientific literature and government agency guidance documents and reports considered first. Subsequently, other sources of information such as conference proceedings, theses, company tailings plans and Material Data Sheets were considered in the absence of peer reviewed or authoritative government information.

Additionally, interviews were conducted with academic researchers and industry experts involved in oil sands tailings management or environmental sciences to identify emerging research on the fate and behaviour of PAM or any publicly available industry reports that would contain relevant information. The individuals who provided information are listed in Section 5.0.

### **3.0 FINDINGS**

#### **3.1 Analytical Methods**

##### **3.1.1 Polyacrylamide**

Analysis of PAM is well studied, and descriptions of available analytical methods, including their advantages and limitations are presented in reviews (Taylor and Nasr-E 1994; Huang et al. 2001; de Rosemond and Liber 2002; Lu and Wu 2003a; Wang 2016; Joshi and Abed 2017). In theory, numerous analytical methods exist for the separation, identification and quantification of PAM in oil sands tailings and other media such as sediments, soils and wastewater; in reality, the accuracy and reproducibility of these methods is limited due to the characteristics of the PAM being analyzed and the characteristics of the sample matrix. Available literature does not present a commercial analytical method applicable to oil sands tailings, and there is currently no standard method for detecting low concentrations of PAM in aqueous solutions with various environmental impurities (Swift et al. 2015). Analysis of PAM in oil sands tailings or oil sands process water (OSPW) is challenging for two main reasons: (1) the compounds vary widely in terms of chemical properties; and (2) they are highly adsorptive within a complex matrix of OSPW and tailings. Challenges in developing efficient and reliable analytical methods to characterize PAM flocculants in environmental media has limited the ability to study the environmental impact and ecological balances of PAM flocculant use (Guzzo and Guezennec 2015).

PAM includes compounds with highly variable properties tailored to meet specific requirements in treating oil sands tailings. It can have different charges, charge densities, molecular weights, and monomer compositions (Vedoy and Soares 2015a; Cossey et al. 2021). Depending on the ratio of monomers involved or the degree of hydrolysis, the degree of anionicity can vary between 0% and 100%; however, a charge density between approximately 22% and 30% is considered ideal for oil sands tailings (Gregory and Barany 2011; Vedoy and Soares 2015a; Cossey et al. 2021). Furthermore, anionic PAM used as flocculants commonly have extremely high molecular weights ranging from 1 to 30 million g/mol (Soares and Motta 2018; Xiong et al. 2018a). An anionic PAM with a given molecular weight will also have a range of polymer chain lengths, which is referred to as the molecular weight distribution. Commercial flocculants can have large molecular weight distributions which are especially hard to measure for high-

molecular weight polymers (Vedoy and Soares 2015a). All these factors contribute to the difficulty in quantifying and characterizing PAM concentrations.

The high degree of adsorptivity of PAM and the complex sample matrices involved in oil sands tailings significantly complicate quantification and characterization of PAM (Beazley 1985; Taylor and Nasr-E 1994; de Rosemond and Liber 2002; Sojka et al. 2007; Wang 2016). Tailings may contain various solids including fine silt and clay particles, dissolved ions, dissolved and particulate metals and metalloids, petroleum hydrocarbons and unrecovered bitumen, surfactants, solvents, and other organic compounds (Allen 2008; Dompierre et al. 2016; Lindsay et al. 2019; Cossey et al. 2021) which may interfere with the measurement of polymer concentrations.

Several methods exist which remove PAM from the particles to which it is adsorbed for analysis. Standard solvents for PAM separation include acetone and alcohols (Huang et al. 2001), which precipitate PAM and separate it from organic compounds and ions that remain in the water or solvent, including organic acids and acrylamide. However, the effectiveness of PAM desorption and the accuracy of the determination of analytes has been called into question (Sojka et al. 2007; Entry et al. 2008). In soils, the strong chemical reactions required to extract PAM from soil for analysis can modify the PAM being analyzed and influence other organics in the sample matrix that may interfere with quantification of PAM (Sojka et al. 2007). Oil sands tailings would presumably pose similar or additional challenges related to matrix effects compared to agricultural soils.

### **3.1.2 Acrylamide**

Unlike PAM, analytical methods for detecting, measuring and monitoring acrylamide, its metabolites and other biomarkers of exposure are well established. Many analytical methods used for environmental samples are used as standard methods of analysis and approved by various agencies such as the United States Environmental Protection Agency (US EPA) and the National Institute for Occupational Safety and Health (NIOSH). The Agency for Toxic Substances and Disease Registry (ATSDR) provides a summary of the standard methods of analysis for acrylamide as well as methods that modify established standards to obtain lower detection limits and/or to improve accuracy and precision (ATSDR 2012). Two methods for acrylamide detection include: (1) a reversed-phase high performance liquid chromatography (HPLC)-ultraviolet (UV) absorption procedure which can achieve a detection limit of 5 µg/L; and, (2) an assay of dibromopropionamide, a bromination product of acrylamide, which, when coupled with HPLC, has been used to detect acrylamide at concentrations as low as 0.2 µg/L in natural and polluted surface waters, sewage and China clay works effluents (ATSDR 2012). Nonetheless, when selecting an analytical method, consideration must be given to the complex sample matrices involved in oil sands tailings which may interfere with some methods.

### **3.1.3 Degradation Products**

Several methods exist for indirectly measuring the degradation of PAM. When selecting a method to assess PAM degradation or when interpreting degradation results from published literature (as in Section 3.3), it is important to consider differences in the methods by which degradation is measured, as different methods may yield very different degradation rates (Gaytán et al. 2021). These differences are relevant to interpreting the degradation of PAM described in Section 3.3. Because of these differences, reliable quantification of the degradation of PAM is challenging, and it is often unclear if degradation leads to mineralization, breakdown

into intermediate compounds, or simply size reduction of the polymer (Nyyssölä and Ahlgren 2019).

For example, some analytical methods are based only on PAM side-groups, such as the starch-cadmium-iodine method, which measures deamination of PAM rather than the degradation of the polymer's carbon backbone. Since these side groups are cleaved as a first step in the biodegradation of PAM, degradation rates based on deamination may overestimate initial biodegradation. Nyyssölä et al. (2019) note that PAM degradation evaluated solely by the starch-cadmium-iodine method are misleading. Studies that report PAM degradation or removal efficiencies based on this method indicate the degree to which PAM has been deaminated and not a degree of mineralization or breakdown into smaller polymer chains.

In contrast, an analytical method measuring total carbon content or utilizing  $^{14}\text{C}$ -labeled PAM might yield markedly lower biodegradation rates given that the carbon backbone of PAM is much more recalcitrant to biodegradation (Nyyssölä and Ahlgren 2019; Gaytán et al. 2021).

### **3.2 Polyacrylamide Application to Oil Sands Tailings**

Various commercial formulations of PAM are applied to oil sands tailings. The polymer is applied to fine tailings fractions such as mature fine tailings (MFT), fluid fine tailings (FFT) and froth treatment tailings (FTT). It can be applied in-line and combined with other chemical amendments such as coagulants, and it may be combined with mechanical mixing or thickening processes.

Commercial polymers include a residual fraction of acrylamide. The residual amount is a small fraction of the PAM, normally cited as 0.05 to 0.1%. Other compounds such as coagulants may be added with the PAM; however, these compounds are outside of the scope of this review.

#### **3.2.1 Oil Sands Tailings**

The Athabasca Oil Sands Region hosts the world's third largest oil reserves, with about 165 billion barrels of proven reserves (Alberta Energy 2018). Where ore is within 75 m of surface, it is economically mineable using conventional open-pit mining techniques. Approximately 20% of Alberta's oil sands are planned to be extracted by open pit mining.

Oil sands ore comprises a mixture of sand, silt, clay, water and 8% to 14% bitumen (Gosselin et al. 2010). Bitumen is extracted from the ore by the Clark Hot Water Process, which entails mixing it with warm caustic water to create a froth (Masliyah et al. 2008). The resulting slurry is separated by gravity by settling the solids and skimming the froth to remove bitumen. Water is recycled through the process and co-disposed with tailings as OSPW.

Tailings are placed in above-ground tailings ponds during mining of the first pit; subsequently, they are progressively backfilled into mined-out pits for the remainder of a mine's operations. While the coarse tailings fraction readily settles from the slurry, residual fluid tailings remain in suspension for years to decades. The residual fine tailings fraction has posed challenges to reclamation since the inception of Alberta's oil sands industry in 1967 (Fine Tailings Fundamentals Consortium 1995).

Problems associated with FFT include residual toxicity (Marentette et al. 2015a, b; Morandi et al. 2015, 2017, 2020; Bartlett et al. 2017; Li et al. 2017; White and Liber 2018), inability to create a trafficable landform (Hyndman et al. 2018), inability to revegetate the surface, waterfowl



attraction, aesthetics, risk of tailings dam failure, water quality, and removal of productive land to create tailings ponds. Solving most of these challenges entails separating the solids from fluids for safe, permanent disposal. Various methods of fluid-tailings separation and disposal have been researched over the past five decades (Sobkowicz 2012).

Each oil sands mine has variations in ore and waste characteristics, extraction technologies, process aids, solvents, and other factors which lead to tailings streams with different physical and chemical composition at each operation. Oil sands tailings are described more fully elsewhere (Kasperski and Mikula 2011; Cossey et al. 2021). For the purposes of this literature review, fine tailings refer to three main tailings types that are dosed with PAM for reclamation: MFT, FFT and FTT. Specific tailings types that are treated with PAM at each operation are listed in Section 3.2.3. However, as no studies have evaluated environmental or health risks of specific PAM-treated oil sands tailings, this review focuses on tailings properties (such as oxidation-reduction potential and moisture) rather than tailings type.

In addition to differences in tailings generation, tailings deposition and mine closure strategies also vary. PAM-treated tailings may be deposited into open pits or dedicated disposal areas (DDAs) during operations and remain in place after mine closure and reclamation. Permanent disposal options for tailings can be grouped into two main categories: (1) subaqueous disposal in pit lakes; and, (2) accelerated densification methods to create terrestrial landforms. Terrestrial methods evaluated by oil sands companies and researchers include combinations of chemical amendments, atmospheric drying and mechanical densification such as centrifugation (Sobkowicz 2012). Terrestrially reclaimed tailings will be covered with reclamation soils and vegetation during mine closure. Aquatic reclamation of PAM-treated tailings is currently being evaluated at field scale by Suncor in its Lake Miwasin project (COSIA 2020).

### **3.2.2 PAM Technology Development**

All oil sands mines are currently evaluating or commercially applying PAM to enhance densification of tailings. Operators and researchers are applying the technology at various scales including laboratory columns, small field trails, pilot-scale deposition, and in one case, full-scale deposition in a DDA.

Full-scale deposition follows two decades of research into various dewatering strategies involving PAM. PAM has been evaluated as an amendment to accelerate dewatering of oil sands composite tailings and fluid tailings since 2000, with early experiments evaluating the use of non-ionic, cationic and anionic PAM (Sworska et al. 2000; Matthews et al. 2002; Franks et al. 2008). In the lab, water recovery from tails was shown to be accelerated by using various commercial mixtures of PAM through flocculation, with variable performance dependent upon the molecular weight, dosage and charge density of the PAM formulation.

In 2012, a Tailings Roadmap was commissioned to evaluate the potential of all commercially available and conceivable technologies for oil sands tailings reclamation (Sobkowicz et al. 2013). Various formulations of PAM were evaluated in combination with mechanical separation. Related technologies included in-line flocculation combined with atmospheric drying, poldering or thin-lift dewatering. Field trails were conducted by Suncor, Syncrude and Shell. At the time, deposition of PAM-treated tailings was envisioned over several square kilometers per summer, with rapid dewatering resulting in supernatant that could be collected and maintained within closed-circuited operations.

Research between 2012 and 2021 (Alamgir et al. 2012; Nik 2013; Beier et al. 2013; Farkish and Fall 2013; Beier 2015; Johnston et al. 2016; Mizani 2016; Mizani et al. 2017; Fisseha 2020; Igbinedion 2020) focused on geotechnical properties such as rheology and thixotropy of tailings, but did not document the fate and transport of supernatant water, groundwater seepage, or its chemical constituents. The Tailings Roadmap noted that “*The environmental impacts of polymers and their degradation products needs to be fully understood before their widespread use*” (Sobkowicz 2012).

The requirement to couple flocculation with physical or atmospheric drying processes stems from the limitation of PAM to effectively flocculate particles smaller than 44 µm (Vedoy and Soares 2015a). For this reason, Vedoy and Soares (2015a) evaluated alternative polymers for oil sands tailings flocculation. Their review paper provides a description of polymer flocculation and drying methods of oil sands tailings. They noted that “*long term environmental impact of residual polymers that remain in the sediments should be studied*” (Vedoy and Soares 2015a).

The evaluation of different polymer formulations continues as the material properties, commercial formulations and understanding of flocculation evolves (Vedoy and Soares 2015b; Li et al. 2021). Dewatering performance is affected by many factors, such as tailings composition (size, pH, clay content, sodium adsorption ratio), polymer formulation and dosage rate, co-dosage with coagulant (including order of dosage), mixing impeller type, speed and duration (Li et al. 2021).

### **3.2.3 Current Application to Oil Sands Tailings**

Current PAM usage by each oil sands mine is described in the mine’s Annual Fluid Tailings Management Report that is filed with the Alberta Energy Regulator to meet the requirements of Directive 85, as cited below. Mines are grouped by company since they tend to share tailings research, development, and treatment technologies.

#### **3.2.3.1 Canadian Natural**

At the Horizon Mine, Canadian Natural generates non-segregated tailings (NST) to manage fine tailings, which is a recombined stream of fine and coarse tailings along with CO<sub>2</sub> injection that is intended to capture fines (Canadian Natural 2021a). As part of technology development, enhanced NST is generated by injecting PAM in-line just prior to tailings deposition. Recent trials have used Kemira E-4993, SNF NRG 3320 and SNF NRG 3340. In related column tests, polymer dosage was 70 g/tonne solids.

At Muskeg River Mine, fine tailings are treated with PAM and deposited subaerially in thin lifts to become terrestrial landforms in a process known as Atmospheric Fines Drying (AFD). Water is evaporated from the tailings, and the dried tailings are transported to final deposition cells. Canadian Natural also uses centrifuges and has experimentally treated fluid tailings with PAM in Geotubes to create terrestrial landforms (Canadian Natural 2021b).

#### **3.2.3.2 Imperial Oil**

At Imperial Oil’s Kearl Mine, thickened tailings are produced by flocculating flotation tailings and fluid tailings in a thickener with PAM and re-flocculating the stream using a secondary chemical injection of PAM. The approved PAM polymers for both the thickening and secondary injection are currently FLOPAM™ A3338, FLOPAM™ A3332, SNF FLOPAM NRG 5320 and Kemira E4993.

Imperial has also carried out multi-phase field trials of inline flocculation of fine tailings at the Kearl Mine. The objectives of the various phases included; 1) comparing the performance of fluid tailings treated either with a single polymer (PAM) or with an enhanced chemistry which consist of PAM, a coagulant and colloidal silica, 2) assessing different deposition strategies, including co-deposition with CST, and 3) testing the technology using different source materials. Pond water chemistry, which would include tailings supernatant water, was monitored and modelled but not detailed in the annual report.

### **3.2.3.3**      **Suncor**

Suncor developed the polymer assisted, thin-lift drying technology termed Tailings Reduction Operations (TRO) in 2010, then transitioned plans to subaqueous disposal in a process known as Permanent Aquatic Storage Structure (PASS) in 2018. In PASS, tailings are treated in-line with PAM and a coagulant before being placed in a pit. Coagulants include ferric sulfate and alum. After deposition, PASS tailings are covered with a water cap for permanent storage. PASS tailings have been demonstrated at a pilot scale in Lake Miwasin since 2018 and are currently being deposited on a commercial scale in DDA3 (Suncor 2021).

Syncrude applies polymer injection for fine tailings management at both the Mildred Lake and Aurora North mines using multiple approaches. FFT are dredged from tailings ponds, injected with PAM and centrifuged to form a cake, then transported and placed as a cake deposit. This process has been carried out at commercial scale since 2015.

Syncrude also employs accelerated dewatering of flocculated tailings through pre-treatment with coagulant and in-line flocculation with a dynamic mixer followed by subaerial deposition with ditching and atmospheric drying. The coagulant may be comprised of Flue Gas Desulphurization solids or gypsum. This process has been developed in three phases of field pilots since 2009 (Syncrude 2021).

### **3.2.4**      ***Dosing rates***

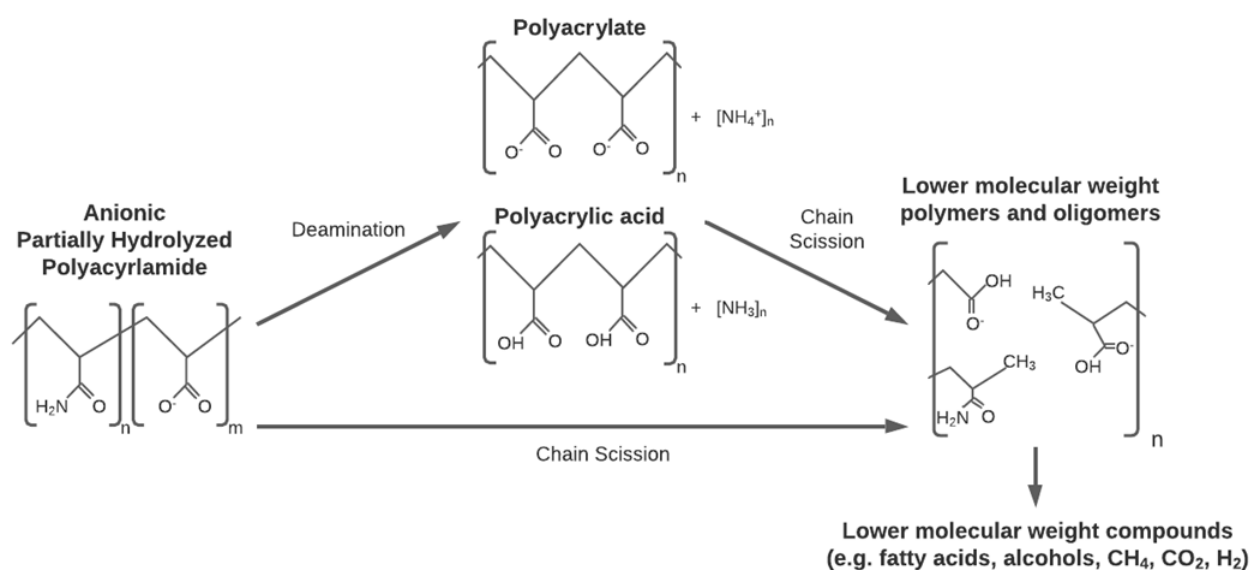
The dosage rate of PAM in oil sands tailings will affect its dewatering performance (Vedoy and Soares 2015b; Li et al. 2021), but more importantly for this study it will affect the total amount of PAM and acrylamide present in tailings. Dosage rates are currently being optimized at both laboratory and field scale, so there is no single dosage rate that can be used to characterize all oil sands tailings applications. However, a dosage range of 1 kg to 1.5 kg PAM per tonne of solids within fluid tailings is derived from the annual tailings reports listed above and the published studies that follow. This dosage rate is considered optimum for oil sands fluid tailings (Zhang et al. 2021), though both lower and higher rates also can be optimal under different conditions (Lister et al. 2020; Sasar et al. 2021), and lower rates are applied to other tailings types.

In laboratory studies, PAM dosage rates for oil sands tailings have varied by orders of magnitude. For example, PAM solutions were prepared at 0.45 wt% by dissolving PAM in OSPW, then the solutions were dosed for different durations to achieve overall dosages of 700 to 2,400 g PAM per tonne of tailings solid (Li et al. 2021). Optimum dosage concentrations for various formulations of PAM are listed as 5 to 50 mg/L in various experimental studies (Li et al. 2005, 2009; Vedoy and Soares 2015a). In experiments using 20-L pails for mixing PAM and tailings, PAM was added at approximately 800 to 1,000 mg/L (Mizani 2016) and 4,000 mg/L (Fisseha 2020) to conduct various settling tests for two separate PhD theses.

The dosing concentration of 1,000 mg/L is therefore considered an approximate value to gain a general sense of quantities applied, with the understanding that optimization will result in variable dosages for each tailings deposit. Given the most recent estimate of 1,270 Mm<sup>3</sup> of total fluid tailings (Alberta Energy Regulator 2020), the total amount of PAM applied to oil sands tailings could be thousands of tonnes.

### 3.3 Degradation Mechanisms and By-Products

The following subsections outline the main degradation mechanisms for PAM based on literature from other industries. While degradation is often thought of as the complete breakdown of complex compounds into inert chemical forms such as carbon dioxide and nitrogen gas, it more commonly entails the partial breakdown of compounds into smaller fragments or functional groups of the original compound. A general chemical pathway of degradation of PAM is provided in Figure 3-1.



**Figure 3-1 Potential Polyacrylamide Degradation Pathways**

Few studies have directly measured the degradation of PAM and generation of byproducts in oil sands tailings. Based on PAM degradation research from other commercial applications, degradation of PAM in tailings is expected to occur primarily via biological, photolytic and mechanical pathways, while other reviews have suggested degradation may also occur via thermal and chemical (e.g. free-radical induced) degradation. The mechanisms are presented in expected order of prominence based on the literature.

#### 3.3.1 Biodegradation

Biodegradation is the breakdown of compounds by biological organisms such as bacteria and fungi; it is the most common type of PAM degradation. Biodegradation of PAM mainly occurs through two main processes: cleavage of polymer side groups (i.e., deamination of the polymer, releasing nitrogen compounds) and breaking of the polymer carbon backbone (chain scission, creating fragment hydrocarbon compounds) (Sang et al. 2015; Nyssölä and Ahlgren 2019; Gaytán et al. 2021).

The enzymatic reactions and metabolic pathways involved in the biodegradation of PAM have not been studied in relation to oil sands tailings. However, they are described in studies from other commercial applications (Joshi and Abed 2017; Nyssölä and Ahlgren 2019; Gaytán et al. 2021).

### 3.3.1.1 Studies of Oil Sands Tailings

Degradation and use of PAM as a nutrient in oil sands tailings has been measured in three studies. The first study (Haveroen et al. 2005) measured the degradation of Magnafloc LT27AG ( $8 \times 10^6$  g/mol, 29% charge density) and release of nitrogen in laboratory microcosms. This polymer was being evaluated for use in thickening MFT to create thickened tailings (TT), so the study was designed to understand whether it could also stimulate methanogenesis in the TT deposit. At the time, it was not clear whether PAM could be used as a sole nitrogen source under anaerobic conditions. In this study, benzoate and acetate were provided as a labile carbon source and inoculated with microbial consortia from three sources: Syncrude MFT and TT, and a domestic sewage sludge. Initial results indicated that PAM as a nitrogen source did not affect methane generation, indicating that the inoculum used contained sufficient nitrogen to support methanogenic activities. After an initial addition and depletion of labile carbon, samples were serially transferred to reduce ambient nitrogen concentrations, and PAM was added as the sole nitrogen source. Whereas control microcosms that lacked PAM did not further metabolize the labile carbon, PAM-amended samples did so and generated methane. The researchers concluded that microbes present in tailings ponds were able to anaerobically use PAM as a sole nitrogen source through deamination of PAM amide groups, but they were not able to use PAM as a carbon source.

A second study involving bacteria isolated from oil sands tailings investigated whether persistent methanogenic activity in tailings ponds was fuelled by nitrogen fixation or PAM as a nitrogen source (Collins et al. 2016). This study was conducted on MFT from the Muskeg River Mine, in which methanogenesis had been observed even though the tailings were nitrogen limited. They applied Magnafloc LT27AG in laboratory microcosms under anaerobic conditions using citrate as a readily metabolized carbon source. Citrate is a readily metabolized carbon source that was used as a process aid at the Muskeg River Mine. Methane production rates were found to be similar in samples with and without PAM, which suggested that PAM was not used as a nitrogen source, even in this nitrogen limited environment. Instead, the source of nitrogen to support methanogenesis was attributed to nitrogen fixation. The authors attributed differences compared to Haveroen et al. (2005) as possibly due to different microbial communities in Muskeg River Mine versus Syncrude tailings, different carbon sources in microcosms, higher dosages of PAM by Haveroen et al. (2005), or the serial transfers that removed all other sources of nitrogen. Deamination of PAM was not examined in this study due to technical limitations.

Li (2010) evaluated the degradation of PAM in Muskeg River Mine tailings and concluded that microbes did not use PAM as a carbon or nitrogen source, though that analysis was less focused on PAM than the studies conducted by Haveroen et al. (2005) and Collins et al. (2016).

While Haveroen et al. (2005) and Collins et al. (2016) came to opposite conclusions after conducting fairly similar laboratory experiments, different oil sands tailings ponds have many other differences that will make microcosm studies difficult to generalize (Foght et al. 2017). For example, while Collins (2013) found that Muskeg River Mine tailings were nearly devoid of inorganic nitrogen, and other studies have found low levels of nitrogen in tailings pond water (Fedorak et al. 2002; Penner and Foght 2010; Stasik and Wendt-Potthoff 2014), Syncrude tailings contain higher concentrations of ammonia (Dompierre et al. 2016) as a result of



desulfurization residuals in tailings water. Many other differences exist within different tailings ponds, depending on: ore and tailings mineralogy; sulfide mineral content; extraction methods, additives and solvents; tailings reclamation and treatment technology; microbial consortia; tailings depositional history; and other factors (Saidi-Mehrabad et al. 2013; Stasik et al. 2014; Kuznetsov et al. 2015; Foght et al. 2017; Lindsay et al. 2019; Cossey et al. 2021). Thus, it seems unlikely that specific findings from one microcosm study of one tailings pond would be generalizable to all oil sands tailings.

### 3.3.1.2 Non-Oil-Sands Studies Examining Deamination

Deamination is the removal of the amide functional group ( $\text{NH}_2$ ) from PAM. Deamination of PAM is most widely studied in the context of biodegradation, although there is evidence that deamination can also occur via other mechanisms as discussed below. Deamination of PAM by microbes is generally thought to occur when the microbes are nitrogen-limited and able to cleave off the amide group to support their metabolic processes. Therefore, deamination is generally studied by observing the ability of microbes to use PAM as a sole nitrogen source, which is an indirect measure of their ability to degrade the compound by cleaving the nitrogen functional group.

In the absence of more labile nitrogen sources, PAM biodegradation involves amidase-catalysed deamination of PAM to produce ammonia and, if all amide groups are removed, polyacrylate. In doing so, bacteria are able to utilize the liberated ammonia as a nitrogen source for growth (Gaytán et al. 2021). The enzymatic removal of PAM side groups has been demonstrated in numerous studies investigating the biodegradation of PAM under both aerobic and anaerobic conditions (Nyyssölä and Ahlgren 2019; Gaytán et al. 2021).

While hydrolyzed PAM (HPAM) and PAM are similar and are expected to yield similar degradation products, PAM contains more amide groups than HPAM; the higher the degree of hydrolysis of HPAM, the fewer amide groups and the more carboxylic groups the polymer will contain. Thus, PAM has a higher nitrogen content than HPAM and may act as a more nitrogen-dense source for bacteria.

In an oilfield setting, degradation of PAM and release of ammonia was studied using bacterial cultures in soil extracts (Gruła et al. 1994). This study indicated that PAM can serve as the sole nitrogen source under both aerobic and anaerobic conditions, and that the PAM stimulated growth of sulfate reducing bacteria.

### 3.3.1.3 Non-Oil-Sands Studies Examining Chain Scission

Due to the length of carbon chains and the strength of the carbon-carbon bonds in PAM and polyacrylate, the polymer carbon backbones are recalcitrant to degradation (Gaytán et al. 2021). However, chain scission has been shown to occur, often to a limited extent, via biodegradation by various bacterial cultures. Chain scission results in smaller molecules being formed; nonetheless, the weight of evidence suggests that acrylamide monomers are not released via the degradation of PAM under environmental conditions.

The biodegradation studies discussed in this section investigated the use of PAM as a carbon source for microbial growth. In these studies, an observed reduction in molecular weight or evidence of bacterial growth when PAM is present as a sole carbon source indicate that the carbon chain was being broken. While some studies found that PAM was not used as a carbon source, this may have been attributed to more labile carbon sources in the test media which

would support bacterial growth. Other studies confirmed that PAM could be used as a sole carbon source under aerobic (Wen et al. 2010; Bao et al. 2010; Yu et al. 2015; Song et al. 2017, 2019, 2020; Berdugo-Clavijo et al. 2019) and anaerobic (Song et al. 2017, 2020; Hu et al. 2018) conditions. Some of these studies also provided evidence of co-metabolism, where low concentrations of alternate carbon sources were able to increase PAM degradation (Wen et al. 2010; Song et al. 2019).

Polyacrylate is formed from complete deamination of PAM. Polyacrylate is also a long-chain molecule that is recalcitrant to biodegradation. Many studies investigating the degradation of PAM under different environmental conditions are reported in current reviews and assessments (Dell'Ambrogio et al. 2019; Gaytán et al. 2021); however most of these studies involve small-molecular-weight polyacrylates and oligomer derivatives (500-530,000 g/mol) or cross-linked superabsorbent polyacrylate polymers and fertilizer coatings.

Several studies have examined the biodegradation of the carbon backbone in outdoor agricultural settings. At least four studies (Wilske et al. 2014; Bai et al. 2015; Liang et al. 2018, 2019) show that degradation of polyacrylate is slow. In agricultural soil, a mineralization rate of 0.12% to 0.24% in 6 months is reported for crosslinked superabsorbent polyacrylic polymer used as a soil appendment to increase water retention (Wilske et al. 2014). Another study on the degradation of a polyacrylate fertilizer coating in agricultural soil found that the coating weight was reduced by 1.77% after 12 months (Liang et al. 2018). However, this rate is likely attributed not only to biodegradation, but to a combination of mechanisms such as mechanical and photolytic degradation due to the agricultural study environment. Similar results were found in another agricultural field study which found that polyacrylate fertilizer coatings experienced a weight loss between 1.46% and 1.69% after 12 months (Liang et al. 2019). The biodegradation and mineralization of two linear polyacrylate polymers (219,500 and 530,400 g/mol) were also investigated in agricultural soil (Bai et al. 2015).

Song et al. (2019) tested the ability of bacteria isolated from soil contaminated with oilfield-produced water to biodegrade HPAM ( $2.2 \times 10^7$  g/mol, 10% charge density). Incubation in a mineral salt medium resulted in 56% of the deamination of HPAM (starch-cadmium-iodine method) after 7 days of incubation under optimum conditions ( $(\text{NH}_4)_2\text{SO}_4$  at 1668 mg/L, 24°C and pH=8.19). Total organic carbon removal was also observed over time and the molecular weight of PAM decreased, indicating that cleavage of the carbon backbone was also occurring. The effect of crude oil presence was also investigated on the degradation of HPAM in this study. It was found that addition of crude oil, at concentration <0.5% increased HPAM removal rates as the organic compounds within crude oil could be used as carbon sources for co-metabolism. At higher crude oil concentrations, the HPAM degradation rate decreased, possibly due to the toxic effects of some of the constituents in crude oil.

#### 3.3.1.4 Non-Oil-Sands Studies Examining Both Deamination and Chain Scission

Many studies in agricultural, wastewater, oilfield and other settings have examined both deamination and chain scission. These studies generally suggest that while nitrogen appears to be readily metabolized from PAM under a wide range of conditions, carbon tends to be used only when labile carbon sources (electron donors) have been depleted (Caulfield et al. 2002; Dai et al. 2014, 2015). This suggests that PAM degradation in oil sands tailings may be incomplete or absent in fresher tailings where labile sources of carbon (such as solvents) are present but could become more pronounced in the future as these compounds are depleted.

In an agricultural soil study, Kay-Shoemake et al. (1998a) studied the ability of indigenous aerobic soil bacteria to use anionic PAM as a nitrogen and/or carbon source. Soil samples from PAM-treated and untreated irrigation furrows were spiked with PAM ( $1-2 \times 10^7$  g/mol, 18% charge density), acrylamide or acrylic acid (0.05% final concentration) and supplemented with either  $\text{NH}_4\text{NO}_3$  as a nitrogen source or acetate and mannitol as a carbon source. Soil bacteria could utilize PAM as a nitrogen source but not as a carbon source, while acrylamide could serve as the sole source of both carbon and nitrogen, and acrylic acid could serve as the sole carbon source. The use of PAM for nitrogen was believed to be due to extracellular bacterial amidase activity which generates  $\text{NH}_4^+$  as a nitrogen source and not due to abiotic mechanisms. Use of PAM by soil bacteria as a nitrogen source but not a carbon source indicates that PAM may ultimately be degraded to long chain polyacrylate; however, polyacrylate was not measured in this study.

In a subsequent study, Kay-Shoemake et al. (1998b) measured amidase activity in agricultural soils from either PAM-treated or untreated fields. They found that bacteria could produce PAM-specific amidase, which was not produced when other sources of nitrogen were provided, and that this amidase activity was inducible in the presence of PAM. The degree of amidase activity was evaluated by measuring free  $\text{NH}_4^+$  available in the soil sample. In soil samples from PAM-treated agricultural fields, PAM-specific amidase activity was higher ( $14.86 \pm 14.0$  mg  $\text{NH}_4^+$  released per gram of soil) versus activity in untreated soil ( $1.02 \pm 2.3$  mg  $\text{NH}_4^+$  released per gram of soil).

Two bacterial strains isolated from uncontaminated soil were able to utilize PAM ( $2 \times 10^6$  g/mol) as a sole source of carbon and nitrogen (Nakamiya and Kinoshita 1995). This study found that soil bacteria could biodegrade about 15-20% of the available total organic carbon and reduce the average molecular weight of PAM to  $0.5 \times 10^6$  g/mol after 27 hours of incubation.

Two bacterial strains isolated from domestic wastewater sludge were evaluated for their ability to degrade PAM ( $0.5-1.6 \times 10^7$  g/mol) under aerobic conditions (Yu et al. 2015). With PAM as the sole nutrient source, PAM degradation was reported to be 31.1% in 7 days. Compounds were measured by Fourier transform infrared (FT-IR) spectroscopy, comparing sidechain functional group changes before and after degradation, indicating that part of the amide groups of PAM had been hydrolyzed and converted to carboxyl groups. The effect of temperature and pH on PAM degradation was also evaluated and, under optimal conditions (pH 7.2, 39°C), PAM degradation reached 45%. Glucose added as a supplemental carbon source further improved PAM degradation and microbial growth. Molecular weight changes were measured via gel-filtration chromatography, which revealed that small molecular oligomer derivatives were formed, indicating that scission of the PAM carbon backbone had occurred and was associated with the biodegradation of PAM. High-performance liquid chromatography (HPLC) conducted before and after degradation revealed an initial profile with peaks for PAM and residual acrylamide. After 7 days of incubation, the area of the PAM peak was reduced, and the acrylamide peak was no longer present; residual acrylamide was completely degraded, and PAM degradation did not result in an accumulation of acrylamide.

Biodegradation of HPAM ( $2.17 \times 10^7$  g/mol) was investigated in a bioreactor study that compared degradation products following either aerobic or anaerobic treatment (Song et al. 2017). HPAM was fed through four separate upflow blanket reactors at concentrations of 100 and 200 mg/L, with a hydraulic residence time of 2 days in each reactor. Aerobic reactors were run at 25°C and 40°C and anaerobic reactors were run at 35°C and 55°C. In all cases, HPAM removal was low (9-17%), with anaerobic degradation exhibiting slightly higher removal efficiency. The average molecular weight of PAM decreased to approximately one third of its initial values, from



$2.17 \times 10^7$  g/mol to between  $3.76 \times 10^6$  g/mol and  $5.87 \times 10^6$  g/mol after treatment. This indicates that PAM was degraded in all reactors to a certain extent, and the degradation was believed to be due to both amide group removal and carbon chain scission (Song et al. 2017).

In a subsequent study (Song et al. 2020) by the same research group, molecular weight changes were compared between a low ( $1.4 \times 10^6$  g/mol) molecular weight HPAM and the high molecular weight PAM from the Song et al. (2017) study. Under aerobic conditions, the molecular weight of the low-molecular-weight PAM was reduced from  $1.4 \times 10^6$  g/mol to  $6.45$ - $7.42 \times 10^5$  g/mol while the high-molecular-weight PAM was reduced from  $2.2 \times 10^7$  g/mol to  $3.76$ - $5.87 \times 10^6$  g/mol. These results indicate that smaller chain PAM are more easily hydrolysed under aerobic conditions, but carbon chain cleavage was still limited.

In a bioreactor study, Liu et al. (2012), found that under aerobic conditions, PAM could be utilized as a sole nitrogen and carbon source by well-acclimated PAM-degrading granules. An analysis of intermediate PAM degradation products was conducted and found that PAM was initially degraded through hydrolysis of amide side groups. As the amide groups were hydrolyzed to release ammonia, ammonia concentrations initially increased until bacteria started utilizing them as a nutrient source after approximately 24 hours, after which nitrogen concentrations decreased rapidly. The main intermediate product identified was a low-molecular-weight polyacrylate comprised of seven acrylic acid monomers. No acrylamide was detected.

Several studies have examined PAM degradation in oilfield-produced waters. Two strains of bacteria isolated from oilfield-produced waters were tested for their ability to biodegrade HPAM ( $2 \times 10^7$  g/mol, 23% charge density) as the sole carbon and/or nitrogen source in an aerobic growth medium (Bao et al. 2010). The amide group from PAM was found to be readily cleaved and used as a nitrogen source under nitrogen-limited conditions. In the nitrogen-limited culture, HPAM removal efficiency was 36.3% over 7 days at 40°C. In the carbon- and carbon-plus-nitrogen-limited cultures, PAM was found to be partially used as a carbon source (removal efficiency 14.7% and 13.6%, respectively). These results suggest that HPAM is better utilized as a nitrogen source, but that HPAM could be utilized as a carbon source to a limited extent. HPLC analysis indicated that no acrylamide monomers were produced, but a new peak was detected after degradation, which the authors believed to correspond to polyacrylate, although the identity of this compound was not confirmed (Bao et al. 2010). The starch-cadmium-iodine method was used to measure HPAM removal efficiencies, so biodegradation rates may have been overestimated.

Anaerobic biodegradation of HPAM ( $3 \times 10^6$  g/mol, 20% charge density) was also investigated in long-term methanogenic enrichment cultures from oilfield-produced water (Hu et al. 2018). In this study, HPAM as the sole source of either nitrogen or carbon was incubated with bacteria cultured from oilfield-produced water for 328 days. A notable increase in ammonium concentration in the nitrogen-limited test indicated that PAM was being deaminated. Based on gas production (total, methane, and carbon dioxide) in both nitrogen- and carbon- limited tests, degradation was believed to be occurring with HPAM being used as either a nitrogen or carbon source.

Another study tested whether PAM ( $1.6 \times 10^7$  g/mol) could be utilized as a sole carbon source by two strains of bacteria isolated from activated soil and sludge from an oilfield (Wen et al. 2010). They measured degradation using the starch-cadmium-iodine method. This method measures the extent of deamination and does not necessarily indicate degradation of the carbon chain. In a liquid media, PAM was tested at concentrations of 50, 100, 250, 500, 750 and 1,000 mg/L as

the sole carbon source, and degradation was measured after 96 hours of incubation. PAM degradation (deamination) rates decreased with increasing initial PAM concentration, with 70% removal efficiency after 96 hours at 50 mg/L but only 14% removal with an initial PAM concentration of 1,000 mg/L. Higher initial PAM concentrations resulted in higher PAM concentrations remaining after 96 hours of incubation, but the ratio between utilized (degraded) PAM and initial PAM decreased with increasing initial PAM concentration. Wen et al. (2010) attributed this to bacteria only being able to degrade a fixed amount of PAM, which was consistent with previous work by Nakamiya and Kinoshita (1995).

In a separate experiment as part of the same study (Wen et al. 2010), the effect on the PAM degradation as a result of adding glucose was tested to assess co-metabolism. At low glucose concentrations, PAM removal increased as the additional glucose was thought to support increased bacterial growth, leading to higher levels of enzymes available to degrade the PAM; however, at higher glucose concentrations, PAM degradation decreased as bacteria preferentially used glucose as a carbon source. Thus, even at low concentrations, other carbon sources such as glucose, can be used as a co-metabolism substrate with PAM. FT-IR spectrogram analysis after degradation revealed that the PAM amide groups had been cleaved from the polymer chain, but that no acrylamide had been produced. Again, it is noteworthy that the starch-cadmium-iodine method was used to measure HPAM removal which may overestimate overall PAM biodegradation (Nyssölä and Ahlgren 2019).

In addition to (or in combination with) biodegradation, scission of the carbon chain may occur by other mechanisms, including photolytic, mechanical and free-radical processes.

### **3.3.2 Photodegradation and Free Radical Degradation**

Free radical degradation is the breakdown of PAM by a series of chemical reactions that lead to the formation atoms or molecules with unpaired electrons. Photodegradation is the breakdown of PAM by electromagnetic radiation, and is a subset of free radical degradation.

Photodegradation of PAM resulting in carbon chain scission is reported in literature with numerous studies showing that sunlight or UV irradiation can result in the reduced chain length of PAM (El-Mamouni et al. 2002; Caulfield et al. 2002, 2003; Woodrow et al. 2008; Guezennec et al. 2015a). However, in the context of oil sands tailings, photodegradation would only be a plausible mechanism where PAM is directly exposed to solar radiation. Thus, photodegradation would only be expected to occur at the surface of a tailings deposit before it is covered with reclamation soils or water.

A study on the chemical degradation of high molecular weight PAM ( $1 \times 10^7$  g/mol) used in hydraulic fracturing investigated the effects of oxygen, temperature, pressure, and salinity on PAM degradation (Xiong et al. 2018b). Peak molecular weight of PAM was found to decrease almost two orders of magnitude, from  $1 \times 10^7$  g/mol to  $2 \times 10^5$  g/mol. The degree of degradation was not dependent on pressure or salinity but increased at elevated temperature and in the presence of dissolved oxygen. The dependence on temperature and oxygen led the authors to conclude that free-radical-induced chain scission was responsible for the degradation. This theory was supported by previous work by Gröllmann and Schnabel (1982), who found that the presence of free radicals can also result in the oxidative main chain degradation of PAM into radical and non-radical polymer fragments.

### 3.3.3 *Mechanical and Thermal Degradation*

Mechanical degradation is the breakdown of PAM by direct forces such as mixing and shearing, and thermal degradation is the breakdown of PAM as a result of heat exposure. Mechanical and thermal degradation of PAM are possible during transport, dosing, mixing and placement of the tailings. Therefore, tailings must be carefully dosed and mixed to avoid degrading or overdosing the polymer. Mechanical and thermal degradation of PAM have mainly been observed in much more turbulent and heated environments, as described below, and are less likely to occur after tailings have been placed.

Mechanical degradation may occur through various processes such as freeze/thaw cycles or as a result of hydrodynamic shearing during mixing, pumping or filtration (Caulfield et al. 2002; Nyyssölä and Ahlgren 2019). A more extreme case of these conditions is observed in hydraulic fracturing, which involved high pressures and flow velocities that impart a high degree of mechanical stress on PAM solutions. A study focussed on the mechanical degradation of PAM under strain conditions that would be experienced during hydraulic fracturing found that the peak molecular weight of PAM decreased from  $1 \times 10^7$  g/mol to  $7 \times 10^5$  g/mol (Xiong et al. 2020). Degraded PAM with molecular weights  $< 1 \times 10^6$  g/mol experienced only minimal further degradation following repeated passes through the test system. Study results indicated that when considering only mechanical degradation during hydraulic fracturing, the molecular weight distribution of PAM is reduced due to greater degradation of the larger PAM polymer chains and preferential mid-chain scission of PAM.

In a similar study of mechanical degradation, an enhanced oil recovery PAM solution ( $1.8 \times 10^7$  g/mol; 28% charge density) was tested at various shear rates (Mansour et al. 2014). Degradation was measured by assessing changes in viscosity. Low to medium shear rates that might be experienced during enhanced oil recovery applications caused a small degree of degradation (5-20%), with no further degradation above a certain shear point.

At elevated temperatures (95°C), PAM has been shown to partially hydrolyze with approximately 10% of amide groups converted to carboxylic acid residues after 10 days (Caulfield et al. 2003). Amide groups can thermally hydrolyze to carboxyl groups at lower temperatures (68°C-78°C) (Uranta et al. 2018b, a). In an investigation of PAM under operational conditions for enhanced oil recovery, the degree of hydrolysis of PAM ( $5-6 \times 10^6$  g/mol, non-ionic) in brine and deionized water was evaluated at various temperatures (50-90°C) for 30 days. The degree of hydrolysis increased with increasing temperature and occurred in both brines and deionized water, although to a lesser extent in deionized water (Uranta et al. 2018a). These results are consistent with previous work (Muller et al. 1980; Muller 1981).

PAM is generally thermally stable at temperatures relevant to tailings such that treatment alone is not likely to result in chain scission. A review by Xiong et al. (2018a) concluded that thermal degradation is unlikely to occur in environmental applications, although temperature may influence the rate of chemical and photolytic degradation. A review by Caulfield et al. (2002) suggested that PAM only begins to undergo thermal degradation at temperatures  $> 200^\circ\text{C}$ .

### 3.3.4 *Other Degradation Mechanisms*

Aside from the biological hydrolyzation/deamination of PAM discussed in the previous section, other mechanisms for the deamination of PAM have been investigated. However, these are likely of low relevance to oil sands tailings.

Both acid-catalyzed and alkaline-catalyzed hydrolysis of PAM have been investigated. Under weakly acidic conditions (pH 4), the degree of hydrolysis is increased as compared to at pH 7 (Muller et al. 1980; Caulfield et al. 2002). In another study, PAM ( $\sim 3.7 \times 10^6$  g/mol) and HPAM ( $\sim 6.3 \times 10^6$  g/mol) exposed to high concentrations of hydrochloric acid (1% and 10%) first underwent deamination via acid-induced hydrolysis prior to chain scission (Pei et al. 2016).

Conversely, nucleophilic addition of hydroxide to the amide carbonyl group on PAM results in deamination; however, this form of hydroxylation slows as the proportion of amide group on the PAM chain falls below 30% (Caulfield et al. 2002).

Chain scission may also occur under acidic conditions, following the hydrolysis of amide groups on PAM (Pei et al. 2016). PAM ( $\sim 3.7 \times 10^6$  g/mol) and HPAM ( $\sim 6.3 \times 10^6$  g/mol) exposed to high concentration hydrochloric acid (1% and 10%) first underwent deamination via acid-induced hydrolysis followed by chain scission. PAM molecular weight slowly decreased by approximately 13% (1% HCl) to 42% (10% HCl) after 100 hours, whereas HPAM was rapidly reduced in molecular weight by 34% (1% HCl) and 48% (10% HCl) within 1 hour and did not degrade further during the 100 hour incubation (Pei et al. 2016).

### **3.3.5 Summary of Findings on Degradation**

The individual studies on PAM degradation, as well as related literature reviews (EU RAR 2002a; Caulfield et al. 2002; Guezennec et al. 2015a; Joshi and Abed 2017; Nyssölä and Ahlgren 2019) suggest the following three points:

1. Microbes are able to degrade PAM to use nitrogen under anaerobic and aerobic environments. While they are able to use PAM as a nitrogen source in oil sands tailings ponds, they do not always do so. The reasons for microbes using PAM as a nitrogen source in one pond but not another are not known, but are generally thought to be driven by nitrogen-limited conditions.
2. Microbes are able to degrade PAM to use carbon under limited circumstances. The PAM backbone is relatively recalcitrant, and microbes are likely to use more available electron donors that may be present before they adapt to using PAM (e.g., solvents). Therefore, carbon enrichment from PAM degradation is unlikely in the short-term, though the long-term fate of the carbon is not known.
3. Acrylamide is not a detectable byproduct of PAM degradation, and residual acrylamide is consistently and rapidly removed through biodegradation.

Although only three studies of PAM degradation have been conducted on oil sands tailings samples, the findings of these studies supported these points where applicable.

## **3.4 Factors Affecting Degradation**

Understanding the factors that promote or inhibit degradation can be used to safely treat and store PAM-amended tailings. Factors that are identified in studies are discussed below.

### **3.4.1 PAM Formulation**

Different PAM formulations have been shown to degrade at different rates and to different extents. As discussed previously, Bai et al. (2015) found that polyacrylates, the deaminated

carbon backbones of PAM that retain large carbon chain lengths, are biodegraded (mineralization measured via  $^{13}\text{CO}_2$  efflux) more slowly than those with shorter chains in agricultural soils. Both polymers tested (219,500 and 530,400 g/mol) had low rates of degradation (1.85% and 0.91%) after 149 days, respectively. In this study, the average molecular weight of the larger polymer exhibited approximately half of the degradation (0.91%) of the smaller polymer (1.85 %) after 149 days. This indicates that carbon chain length can affect degradation rates of these polymers. The polymers studied by Bai et al. (2015) are much smaller than the PAMs typically used in oil sands tailings but would be representative of polymer lengths that could be present following the degradation of PAM.

In a review of studies evaluating the inherent biodegradability of low-molecular-weight polyacrylic acids (1,000 to 215,000 g/mol), removal rates were also found to be dependent on molecular weight (Duis et al. 2021). Biodegradation was found to be responsible for polymer removal of low molecular weight polymers (<1,000-2,000 g/mol) and sorption resulted in the loss of larger molecular weight polymers.

Another study investigating the ability of microbes to utilize both PAM and HPAM (25-30% charge density) as a nitrogen or carbon source by microbes isolated from oilfield-produced water and activated wastewater sludges found that the degree of hydrolyzation of PAM can affect degradation (Berdugo-Clavijo et al. 2019). Under nitrogen-limited conditions, both microbial cultures showed a metabolic preference for HPAM over PAM based on  $\text{CO}_2$  production; however, a greater degree of deamination was observed for PAM (22%-34%) as compared to HPAM (13%-20%). This is likely due to the greater number of amide groups available on PAM as compared to HPAM. Under carbon-limited conditions,  $\text{CO}_2$  production, as an indirect measure of microbial growth, was very limited, whereas the bacteria from oilfield-produced water cultures produced significantly more  $\text{CO}_2$ . These results indicate that different degrees of hydrolyzation can influence degradation and highlight the importance of different bacterial communities and ambient conditions on PAM and HPAM degradation.

### 3.4.2 **Microbial Communities**

Bacterial community composition can affect the degradation of PAM. As demonstrated by Kay-Shoemake et al. (1998b), certain bacteria produce PAM-specific amidase in the presence of PAM. Additionally, evidence of co-metabolism of PAM has also been demonstrated in studies of bacteria isolated from oilfield-produced water (Wen et al. 2010; Song et al. 2019). Many studies have investigated the ability of various bacteria strains to degrade PAM, and a strong correlation has been found between some bacteria and PAM degradation. These include *Bacteroidetes*, *Firmicutes*, *Proteobacteria*, *Spirochaetes*, *Synergistetes*, and *Thermotogae* phyla, and *Bacillus*, *Trichococcus*, *Brooklawnia*, *Pseudomonas*, and *Methanosaeta* genera (Cossey et al. 2021), most of which have been identified in oil sands tailings (Foght et al. 2017).

Fungal degradation of polyacrylic acids has been reported in literature (Joshi and Abed 2017; Nyssölä and Ahlgren 2019; Gaytán et al. 2021); however, these studies investigate insoluble cross-linked superabsorbent polyacrylic or PAM polymers and not the soluble PAM or HPAM relevant to tailings treatment. Studies by Sutherland et al. (1997), Stahl et al. (2000) and Cameron et al. (2000) found that white-rot fungus (*Phanerochaete chrysosporium*) can use these crosslinked polymers as a carbon or nitrogen source under nutrient limited conditions. The lignin-degrading enzyme system of this fungus involves extracellular peroxidases and other enzymes which appear to depolymerize and solubilize the crosslinked polymers, leading to increased mineralization over that of soil bacteria alone (Sutherland et al. 1997; Stahl et al. 2000; Cameron et al. 2000). Due to the differences between the polymers used in these studies



and those used in treating tailings, the significance of these findings is uncertain in the context of treated tailings landforms. Additionally, the ligninolytic ability described is limited to few taxa of fungi (Pointing 2001), and their presence in oil sands tailings is uncertain. In terms of breaking the carbon-backbone of PAM or polyacrylate in the context of oil sands tailings, this process is not likely given that it would require the appropriate fungal communities and the extracellular enzymes they produce in an aerobic environment (J. Foght, personal communication, September 7, 2021), which is not the case with oil sands tailings.

### **3.4.3 pH**

PAM degradation is also affected by pH. Bacterial communities that have been shown to degrade PAM tend to prefer a neutral pH; however, various optimal ranges have been described between a pH of 5.5 to 8 (Chen et al. 2013; Yu et al. 2015). Investigation of acid-catalyzed and alkaline-catalyzed hydrolysis of PAM have also demonstrated that under weakly acidic conditions (pH 4), PAM hydrolysis is increased as compared to at neutral pH (Muller et al. 1980; Caulfield et al. 2002). An anaerobic fermentation study found that optimal conditions for PAM degradation were achieved by supplementing the fermentation with proteins and carbohydrates at an alkaline pH of 9.0. At this pH, the relative abundance of bacteria with the ability to biologically hydrolyse PAM was increased (Dai et al. 2015). The effect of pH likely depends on the microbial communities present and the enzymes they produce which hydrolyze PAM. Oil sands tailings are generally neutral to alkaline (Dompierre et al. 2016; Foght et al. 2017), though some tailings such as FTT have the potential to produce acidic conditions (Kuznetsov et al. 2015; Lindsay et al. 2019).

### **3.4.4 Temperature**

In general, PAM hydrolysis increases with increasing temperatures tested between 50°C and 90°C, and this effect is greater under highly saline conditions as compared to deionized water or in the presence of dissolved iron and oxygen (Ryles 1988; Caulfield et al. 2003; Seright and Skjevraak 2015; Uranta et al. 2018b, a). Yu et al. (2015) investigated the effect of temperature and pH on PAM degradation, and found that at temperatures above 40°C PAM degradation decreased, and that optimal conditions for degradation were pH 7.2 at 39°C. Tailings landforms may be warmer than natural landforms by approximately 10°C, depending on the depth, time of year and age of deposit (Ramos-Padrón et al. 2011; Dompierre and Barbour 2017). While biodegradation could be increased, thermal effects on chemical PAM degradation at these temperatures are unlikely to be significant as they are well below the temperatures shown to cause high rates of degradation.

### **3.4.5 Oxidation-Reduction**

Studies have demonstrated the importance of oxidation-reduction in the chemical degradation of PAM (Xiong et al. 2018a). The presence of electron donors (normally labile carbon such as residual solvents or process aids, in the context of oil sands tailings) may affect the degradation of PAM by promoting co-metabolism, as described in Section 3.3.1. The presence of electron acceptors such as oxygen,  $\text{SO}_4^{2-}$  and  $\text{Fe}^{3+}$  has also been shown to lead to higher biodegradation rates (Zhao et al. 2016, 2019a, 2020; Zhang et al. 2018); rates are typically higher with increasing oxygen content in aerobic vs. anaerobic conditions.

Cycling of iron and other electron acceptors is complex and affects multiple properties of oil sands tailings geochemistry and microbiology (Stasik and Wendt-Potthoff 2014; Stasik et al. 2014) beyond PAM degradation, especially near the tailings-water or tailings-atmosphere interface. Nonetheless, the majority of tailings deposits below the interface are anaerobic (Dompierre et al. 2016; Foght et al. 2017; Cossey et al. 2021), which will tend to lead to slower degradation.

### 3.5 Products Formed

Degradation pathways for PAM and polyacrylate are well described in literature (Caulfield et al. 2002; Dai et al. 2015; Joshi and Abed 2017; Nyssölä and Ahlgren 2019; Gaytán et al. 2021); however there is a lack of published information on the extent of PAM degradation in treated oil sands tailings and therefore little is known about the degradation products that may be formed (Cossey et al. 2021).

Based on laboratory studies and information derived from other industries, PAM/polyacrylate degradation products arising from chain scission are generally limited to lower molecular weight polymers (i.e., smaller chain PAM or polyacrylate), and volatile fatty acids (e.g. acetic acid, butyric acid and propanoic acid) and their intermediates (e.g. acetyl-coenzyme A and pyruvate) (Hu et al. 2018; Nyssölä and Ahlgren 2019; Gaytán et al. 2021). No compelling evidence exists to indicate that acrylamide would be formed as a degradation product of PAM in oil sands treated tailings.

The lack of acrylamide formation through degradation is supported by numerous studies (Kay-Shoemake et al. 1998b; Ver Vers 1999; Wen et al. 2010; Bao et al. 2010; Liu et al. 2012; Yu et al. 2015; Sang et al. 2015); however, most studies have been conducted under aerobic conditions and commonly with other potential sources of carbon for microbes to utilize. Exceptions to these findings do exist. For instance, in a study by Caulfield et al. (2003) testing the stability of PAM under thermal and irradiation conditions found that a small amount of acrylamide could be released following UV irradiation, albeit at an intensity much more energetic than the wavelengths of sunlight (Guezennec et al. 2015a). Additionally, a study of PAM biodegradation in dewatered sewage sludge using an anaerobic digestion reactor found that acrylamide was produced at up to 500 µg/g of total solids in the reactor (Dai et al. 2014). In this study, acrylamide accumulated over the initial 18 days incubation in the reactor before accumulation stopped and it was believed that microbes in the reactor started to consume acrylamide, deaminating it to acrylic acid.

Deamination of acrylamide subunits within PAM involves the hydrolyzation of the acrylamide amide groups into carboxylic groups and release of nitrogen in the form of ammonia or ammonium. By converting the amide groups to carboxylic groups, the acrylamide subunits are converted to acrylic acid molecules within the PAM chain, which increases the charge density of the polymer as it becomes more hydrolyzed. Once PAM has become completely deaminated, the remaining carbon backbone is polyacrylic acid or polyacrylate. The molecular ionization of these products is controlled by environmental pH. At higher pH (>6), most acrylic acid subunits of the polymer are anionic (thus, polyacrylate), whereas at lower pH (<4) acrylic acid subunits are more likely to be protonated (thus, polyacrylic acid) (Barvenik 1994). The degradation products formed via deamination are polyacrylate and ammonium or polyacrylic acid and ammonia (Nyssölä and Ahlgren 2019; Gaytán et al. 2021), but not acrylamide.

Evidence for the release of acrylamide or acrylic acid monomers during the degradation of PAM or polyacrylate under environmental conditions is limited and somewhat inconsistent in

literature. One research group found that acrylamide was released from a PAM-based thickening agent due to temperature and photolytic effects representative of natural agricultural environments (Smith et al. 1996, 1997). However, aspects of these studies, including the PAM product used and how it was dissolved, the experimental study design, as well as the study results and interpretation have all been called into question. Reviewers suggested that the PAM product used was not fully dissolved in the test solution and residual acrylamide monomer within the product was slowly released over time (Kay-Shoemake et al. 1998a; Ver Vers 1999; Caulfield et al. 2003; Guezennec et al. 2015a).

This finding aligns with the general focus on the residual acrylamide content of PAM by regulatory agencies, rather than acrylamide release due to PAM degradation. According to the European Chemicals Bureau, while the potential for acrylamide release from PAM needs to be considered, the breakdown of PAM's backbone to form acrylamide is energetically unfavourable and unlikely to occur. Based on this observation, in the European Union Risk Assessment Report (EU RAR) on acrylamide, the only source of acrylamide considered available for release from PAM is the residual unpolymerized acrylamide present in the commercial PAM (EU RAR 2002a)

Woodrow et al. (2008) found that acrylamide could be released in an agricultural setting. In this study, a linear anionic PAM product ( $2.09 \times 10^7$  g/mol) in aqueous solution was subjected to natural or artificial sunlight and various concentrations of ferric sulfate due to the relative abundance and common occurrence in natural waters, and its tendency toward redox cycling and free radical chemistry. Acrylamide was only formed at acidic to neutral pH and the amount formed was directly related to the  $\text{Fe}^{3+}$  concentration (range: 0.022 to 4.43 mg/kg  $\text{Fe}^{3+}$ ) and the irradiation duration. Low iron concentrations or alkaline pH (~8) prevented the formation of acrylamide (Woodrow et al. 2008). Finally, anaerobic degradation of PAM has not been as widely investigated and may be more likely to produce acrylamide (Nyyssölä and Ahlgren 2019). Bioreactor studies investigating anaerobic digestion of anionic PAM have found that acrylamide was produced during PAM degradation (Zhao et al. 2019b; Akbar et al. 2020). Although these reactor studies may not be representative of typical environmental conditions, they illustrate that acrylamide may be formed under certain conditions relevant to treated tailings (i.e., treated tailings in thin lifts exposed to sunlight or anaerobic conditions within capped treating tailings deposits).

### **3.6 Degradation Rates**

#### **3.6.1 Polyacrylamide**

Although numerous studies report on the degree of PAM or polyacrylate removal over time in laboratory testing or bioreactor studies, the test conditions are generally not representative of environmental conditions. Furthermore, different analytical methods (e.g., starch-cadmium-iodine test vs. total organic carbon) may produce different degradation rate estimates or measure different degrees of degradation. Thus, the literature is often not clear about whether reported polymer degradation leads to size reduction of the polymer, intermediate compounds, or mineralization. Therefore, it is difficult to interpret degradation rates or make comparisons among rates from different studies.

In the literature reviewed, few degradation rates for overall PAM degradation were reported under environmental conditions. A general degradation rate of 10% has been repeatedly cited as encompassing degradation through both biotic and abiotic processes (Barvenik 1994; Entry et al. 2002, 2008; Sojka et al. 2007; Song et al. 2018; Dell'Ambrogio et al. 2019). The reference



that is ultimately cited for this value is Azzam et al. (1983); however, the original publication did not analyze the degradation of PAM. Additionally, the focus of that work was on PAM generated by reactions with spent nuclear fuel and applied as a gel to sand in the Sinai desert. Thus, even if the study did generate a site-specific degradation rate, it could not be generalized to the anionic PAMs used in the treatment of oil sands tailings under different microbial, geochemical and environmental conditions.

PAM is considered persistent (not readily biodegradable) in the environment in Safety Data Sheet (SDS) classifications for identified anionic PAM products used in oil sands tailings treatment. These include:

- EXPN E-4993SK (Kemira 2020)
- NRG 5320 (SNF 2018a)
- FLOPAM A 3332 (SNF 2015)
- FLOPAM A 3338 (SNF 2018b)
- Magnafloc LT27AG (BASF 2017)

The degree of biodegradability does not need to be fully characterized for the purposes of an SDS, so the information contained in these documents is of limited use in understanding long-term environmental risk. For example, the classification for biodegradability may be based simply on whether or not the product meets a certain threshold such as >70% biodegradability according to the established test protocols (e.g., CO<sub>2</sub> Evolution Test/OECD Test Guideline 301B/28 d or Closed Bottle test/OECD Test Guideline 301D/28 d).

Nonetheless, some reviews include tabulated summaries of degradation rates and the conditions under which they were achieved (Joshi and Abed 2017; Zhao et al. 2019a; Gaytán et al. 2021). A summary of degradation rates presented by Gaytán et al. (2021) is reproduced in Table 3-1. This table includes rates for PAM and polyacrylic acid polymers.

**Table 3-1 Summary of PAM degradation rates reported in literature**

<b>Original Compound (molecular weight)</b>	<b>Biodegradation rates (method)</b>	<b>Time Period</b>	<b>Reference</b>
Linear anionic PAM (1,000,000-2,000,000 g/mol)	0.7-2 mg/kg of ammonia-N and 10-36.7 mg/kg of nitrate-N production (Ammonia-N-specific electrode, Nitrate-N UV Spectroscopy)	5 days	(Kay-Shoemake et al. 1998a)
Anionic, linear PAM (1,000,000-2,000,000 g/mol)	20% (N removed. Acid Hydrolysis)	5 days	(Kay-Shoemake et al. 1998b)
Hydrolyzed PAM (20,000,000 g/mol)	29-42% (PAM removal efficiency. SCI)	7 days	(Bao et al. 2010)
PAM (16,000,000 g/mol)	74-76% (PAM removal efficiency. SCI)	5 days	(Wen et al. 2010)
PAM (NP)	86.64% (PAM hydrolysis. SCI)	17 days	(Dai et al. 2015)
HPAM (22,000,000 g/mol)	89.8% (SCI) 32.9% (total organic carbon)	>20 days	(Sang et al. 2015)
PAM (17,000,000-22,000,000 g/mol)	47.2, 56.8% (PAM removal efficiency. SCI)	5 days	(Yu et al. 2015)
HPAM (22,000,000 g/mol)	55.93% (HPAM removal rate. SCI)	7 days	(Song et al. 2019)

<b>Original Compound (molecular weight)</b>	<b>Biodegradation rates (method)</b>	<b>Time Period</b>	<b>Reference</b>
HPAM (NP)	40.5% (SCI), 38.9% (total organic carbon) (PAM removal efficiency)	49 days	(Zhao et al. 2019b)
<sup>14</sup> C-cross-linked PAA & PAA/PAM (NP)	Cross-linked PAA: ~5%. Cross-linked PAA/PAM: ~3% ( <sup>14</sup> CO <sub>2</sub> production. LSS)	70-80 days	(Sutherland et al. 1997)
<sup>14</sup> C-cross-linked PAA & PAA/PAM (NP)	PAA/PAM: 7.3%; PAA: 0.95% in soil microcosms ( <sup>14</sup> CO <sub>2</sub> production. LSS)	76 days	(Stahl et al. 2000)
<sup>14</sup> C-cross-linked PAA & PAA/PAM (NP)	PAA/PAM: 0.67%; PAA: 3.6% in peroxidase induced cultures ( <sup>14</sup> CO <sub>2</sub> production. LSS)	90 days	(Stahl et al. 2000)
<sup>14</sup> C-cross-linked PAA & PAA/PAM (NP)	PAA/PAM: 1.5%; PAA: 6% in CDH induced cultures ( <sup>14</sup> CO <sub>2</sub> production. LSS)	30 days	(Stahl et al. 2000)
<sup>14</sup> C-cross-linked PAA & PAA/PAM (NP)	Cross linked PAA: 0.6%, cross linked PAA/PAM: 0.7% ( <sup>14</sup> CO <sub>2</sub> production. Scintillation Spectroscopy)	80 days	(Cameron et al. 2000)
<sup>14</sup> C-PAA & PAM/phenolic compounds (~80,000-500,000 g/mol)	27-67% MW decrease	48 days	(Mai et al. 2004)
<sup>14</sup> C-PAA & PAM/phenolic compounds (~80,000-500,000 g/mol)	0.8-3.2% <sup>14</sup> CO <sub>2</sub>	100 days	(Mai et al. 2004)
PAA (1,000; 2,000; 4,500 g/mol)	2-7.4% BOD/ThOD (O <sub>2</sub> consumption. (JIS K102))	10 days	(Kawai 1993)
PAA (4,500 g/mol)	8.1% ( <sup>14</sup> CO <sub>2</sub> production. NP)	28 days	(Freeman and Bender 1993)
PAA (4,500 g/mol)	15.6% ( <sup>14</sup> CO <sub>2</sub> production. NP)	45 days	(Freeman and Bender 1993)
Sodium acrylate oligomer with butyl thioether (NP)	69% decrease (Total organic carbon analysis)	14 days	(Hayashi et al. 1993)
Oligomers, PAA (1,000; 2,000; 4,500 g/mol)	Oligomers: 70-75%, PAA: 10-30% (CO <sub>2</sub> production. Modified Sturm Test (OECD 301B))	28 days	(Freeman et al. 1996)
Monomers, dimers, oligomers, PAA (Oligomers: 500; 700 g/mol, PAA: 1,000; 2,000 and 4,500 g/mol)	Monomer, dimer: 100%, Oligomers: 70-80%, PAA: 12-40% (CO <sub>2</sub> production. Modified Sturm Test)	32 days	(Larson et al. 1997)
Cross-linked PAA (>500,000 g/mol)	7.6% ( <sup>14</sup> CO <sub>2</sub> production. LSS)	100 days	(Cook et al. 1997)
Cross-linked PAA (NP)	0.12-0.82% (Remaining <sup>13</sup> C of initial weight. Wavelength-scan cavity ring-down spectroscopy)	6 months	(Wilske et al. 2014)
Linear <sup>13</sup> C-PAA (219,000-530,000 g/mol)	0.91-1.85% (Remaining <sup>13</sup> C of initial weight.)	149 days	(Bai et al. 2015)

<b>Original Compound (molecular weight)</b>	<b>Biodegradation rates (method)</b>	<b>Time Period</b>	<b>Reference</b>
	Wavelength-scan cavity ring-down spectroscopy)		
PAA coating component (NP)	0.5 mg/mL-1 (CO <sub>2</sub> production. Modified Sturm Test)	21 days	(Vargas-Suárez et al. 2019)

Adapted from Gaytán et al. (2021).

LSS = Liquid Scintillation Spectrometry; NP = not provided; PAA = polyacrylic acid; PAM = polyacrylamide, SCI = starch-cadmium-iodine.

### 3.6.2 Polyacrylic Acid/Polyacrylate

Since polyacrylic acid or polyacrylate is the carbon-backbone that makes up PAM following deamination, degradation rates are expected to be similar to those reported for PAM in instances where degradation is a measure of chain scission and not deamination. Polyacrylic acids are not readily biodegradable (Duis et al. 2021).

In a human and environmental risk assessment on polycarboxylates used in detergents, HERA (2014) presents degradation rates based on CO<sub>2</sub> evolution for a variety of polyacrylic acid molecular weights up to 10,000 g/mol in domestic activated sludge, river water, sediment and soil. Degradation rates for 10,000 g/mol polyacrylic acid were 17% CO<sub>2</sub> after 90 days in activated sludge, 7% in 135 days in river water, 12% after 135 days in sediment (with river water), and 5% after 165 in sludge-treated soil (HERA 2014).

### 3.6.3 Acrylamide & Acrylic Acid

The biodegradation of acrylamide has been extensively studied with several decades of research on the fate and behaviour of acrylamide in natural environments amended with PAM (Shanker et al. 1990; Guezennec et al. 2015a, b). In the event that PAM monomers, acrylamide or acrylic acid, were to be produced via degradation, it is well established that these compounds are readily biodegradable (EU RAR 2002a, b; Environment Canada and Health Canada 2009); except for acrylamide at high concentrations (>2 mg/L), where degradation is inhibited by toxicity to microorganisms (Environment Canada and Health Canada 2009).

Acrylamide biodegradation is known to occur in soils, sediments, wastewater and hydrosystems (e.g., natural waterbodies or irrigation canals), and in both aerobic and anaerobic environments. While acrylamide degradation is known to be rapid, actual degradation rates under environmental conditions may vary, depending on acrylamide concentration, temperature, microbial composition and lag time from exposure to the start of microbial degradation (Guezennec et al. 2015a).

Degradation rates summarized by Environment Canada and Health Canada (2009) indicate that acrylamide is completely degraded in water within 28 days at concentrations up to 2 mg/L, and ~80% degraded in 20 hours if inoculated or 100 hours without inoculation. In soil, acrylamide half lives were between 18 and 96 hours, depending on soil and acrylamide concentration (25-500 mg/kg). In the European Union risk assessment report on acrylic acid (EU RAR 2002b), the following rate constants are assumed: 0.047 day<sup>-1</sup> in surface water and soil, and 0.0023 day<sup>-1</sup> in sediment, corresponding to approximately 15-day and 30-day half lives, respectively.

### 3.7 Environmental Transport

Environmental transport describes how a chemical can move from its source through environmental media such as water, land, and air. Along its transport pathway, the chemical may be retained through sorption or other processes that retard its movement. This section describes the likely transport pathways and mechanisms for PAM and its products through an oil sands mine from a tailings deposit to environmental receptors.

The pathways evaluated are shown in Figure 2-1 and Figure 2-2. Possible pathways for PAM and its products to reach the environment include:

- Groundwater transport from terrestrial or aquatic landforms
- Aerial transport through fugitive dust from terrestrial landforms
- Direct release to surface waters from aquatic landforms

Limited information is published that specifically evaluates the transport of PAM and its degradation products in oil sands tailings. Therefore, information about PAM has been drawn from other industries, especially agriculture, and put into the context of oil sands mines based on region-specific and sector-specific studies of the landscape and its properties. The reliance on agricultural literature likely provides a conservative estimate of PAM mobility in oil sands tailings, because agricultural fields are subject to continual tilling and irrigation compared to a tailings landform, where rehandling of material is minimized.

#### 3.7.1 Polyacrylamide and Polyacrylate

Due to the characteristics that lend PAM its flocculating properties, anionic PAM is strongly adsorbed to soil and clay mineral surfaces, which limits its mobility in soil and leaching potential to groundwater (Guezennec et al. 2015a). It is expected that the strong binding of PAM to the minerals and clay fractions in agricultural fields would also occur with the clay fractions of oil sands tailings.

PAM and polyacrylate are strongly bound to tailings after deposition and are not expected to migrate through surface runoff or groundwater

In agricultural applications, PAM becomes concentrated in the upper portions of soil profiles because of its high affinity for clay mineral surfaces in soil (Sojka et al. 2007). Oil sands tailings, in contrast, would be dosed in-line as part of deposition, so the PAM would be more consistently applied throughout the landform compared to an agricultural field.

Anionic PAM has been used for soil stabilization and conditioning and has been studied for decades (Seybold 1994). As described in several reviews (Seybold 1994; Sojka et al. 2007; Guezennec et al. 2015a), numerous studies have investigated or reviewed the adsorption of PAM from aqueous media onto clay and mineral surfaces. So, although PAM is highly water soluble, it adsorbs to solids through several mechanisms (e.g., electrostatic, hydrogen, and chemical bonding, and by displacement of inner solvation-sphere water molecules), and can form cation or polymer bridges between particles due to its negative charge and large size of anionic PAM molecules used for flocculation (Seybold 1994; Guezennec et al. 2015a).

Although the degree of adsorption is dependent on PAM conformation and water and soil/mineral properties, anionic PAM adsorption is rapid and irreversible (Nadler et al. 1992;

Deng et al. 2006; Sojka et al. 2007; Chen 2020). In a variety of agricultural soil studies using anionic PAMs of a similar molecular weight and charge density as those used in oil sands treatment (10-15 million g/mol; ~20-40% charge density), it was found that PAM did not penetrate deeply into soil (<20 cm) (Nadler et al. 1994; Lu and Wu 2003b) and was strongly adsorbed, with little to no desorption, especially after soil drying (Malik et al. 1991; Nadler et al. 1992; Lentz et al. 2002). This is generally attributed to the large polymer chain lengths and high number of adsorption sites along PAM molecules, and thus this behaviour may be restricted to large molecular weight PAMs (Sojka et al. 2007). In addition, the less coiled the polymer chain (generally in PAM with a charge density of 20%), and the greater the chain length, the greater the adsorption of PAM (Malik and Letey 1991; Seybold 1994).

Adsorption of PAM to soil was described by Langmuir sorption isotherms (Lu et al. 2002). Soil texture, the organic matter content in soil and the presence of dissolved salts all influenced the extent of PAM sorption to soil. Soils with high levels of organic matter had lower sorption affinities, whereas soils with high clay or silt content and low organic matter had increased sorption. This effect was attributed to a reduction of accessible sorption sites between the polymer and inorganic mineral surfaces. Additionally, PAM sorption increased with increased total dissolved salt concentrations. In particular,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  cations were found to be most effective in increasing sorption, especially in soils with finer textures.

Conversely, PAMs with smaller chain lengths have higher mobility than the higher-molecular-weight PAM used in oil sands tailings management. PAMs with lower molecular weights generally penetrate soil pores more readily and act to stabilize soils to a greater depth than larger molecular weight PAMs (Sojka et al. 2007). This implies that the presence of degraded PAM chains with lower molecular weights could lead to increased mobility in the environment (Xiong et al. 2018a).

Lower-molecular-weight PAMs (15-16 mg/mol; charge densities of 7%, 20% and 50%) have been evaluated in the context of optimizing soil-PAM interactions for erosion control at construction sites (McLaughlin et al. 2014). This study confirmed that PAM sorption to soil is described by Langmuir sorption isotherms. Retardation factors for PAM transport through soil were greater than 2,300, indicating a strong retardation of dissolved PAM into soil. With the soil acting as a strong sorbent for the applied PAM, leaching was highly limited. Thus, even with markedly smaller chain PAMs than those used in oil sands tailings management, (0.015-0.016 g/mol vs up to  $2 \times 10^7$  g/mol), PAM tends to adsorb to soil surfaces and is not likely to leach under typical conditions (McLaughlin et al. 2014).

Polyacrylates and polyacrylic acids are expected to react similarly to PAM in tailings and the environment. As with PAM, these polymers strongly adsorb to activated sludge, soil particles, and other solids (HERA 2014; Duis et al. 2021). When released into the environment, they are almost completely immobile due to their sorption to solids (ECETOC 1993). Once adsorbed to soil, desorption and elution to surface water or groundwater is unlikely unless the polymer is first degraded to smaller more mobile fragments. When evaluating removal of polyacrylic acids in waste water treatment, removal of low-molecular-weight polymers (<1,000-2,000 g/mol) is largely due to biodegradation, whereas sorption results in the loss of larger molecular weight polymers (Duis et al. 2021). Also similar to PAM, the presence of divalent cations such as  $\text{Ca}^{2+}$  increase sorption of polyacrylic acid. If sufficient  $\text{Ca}^{2+}$  exists to bind with PAM, it may lead to precipitation in waste water treatment plants or in natural waters (HERA 2014; Duis et al. 2021).

The studies from agricultural settings and PAM-amended sludge suggest that PAM and polyacrylate will be strongly bound to tailings after deposition and will not migrate through



surface runoff or groundwater. Therefore, the only viable pathway for PAM to enter the environment from tailings is through wind erosion.

Fugitive dust from dry stack tailings is a well known issue in mine waste management (Csavina et al. 2012) and fugitive dust in general is an issue at oil sands mines (Jautzy et al. 2013). Dust is a plausible transport mechanism of PAM during the placement and drying of tailings, especially for atmospheric dried tailings. Based on studies from other settings, the application of PAM to tailings is likely to reduce the amount of fugitive dust

At operating mines, the only potential pathway for PAM to enter the environment from tailings is through wind erosion, although PAM has been proven to be effective in controlling dust.

from a tailings deposit compared to a dry deposit that has not been amended with PAM. PAM has been used in other applications to control dust, such as military encampments, helicopter-landing areas, roadways (Sojka et al. 2007) and mine haul roads (Kashi et al. 2020) and bauxite tailings (Ding et al. 2020). While PAM is likely to be effective in reducing dust from dry oil sands tailings, there is no published data to confirm this. Given the prominence of fugitive dust emissions from oil sands operations in general (Wang et al. 2015), monitoring the dust, including whether PAM is a component of dust, from drying tailings may be warranted to confirm this. Based on the results from similar applications, monitoring is likely to confirm that PAM provides a net benefit for dust control. At any rate, once the deposits are covered by vegetation or water, this transport mechanism would no longer apply.

### 3.7.2 Acrylamide

Unlike PAM, acrylamide is highly mobile in soil and water. It does not significantly sorb to soil and can readily migrate through the soil column and groundwater. Acrylamide has a low estimated log  $K_{oc}$  value of 1.02 and experimental log  $K_{ow}$  value of -0.67 (Environment Canada and Health Canada 2009). Acrylamide has a higher mobility in sandy soils compared to in fine-texture clay soils (Lande et al. 1979; ATSDR 2012; Guezennec et al. 2015a).

The mobility of acrylamide in soils has not been extensively studied as most literature focussed on acrylamide biodegradation, which is the dominant factor affecting the fate of acrylamide in the environment (Guezennec et al. 2015a). A study that investigated the leaching potential of acrylamide in various soil types found that acrylamide was mobile in all soils, but most mobile in loamy fine sand and least mobile in silt clay (Lande et al. 1979). In another study, sterilized river water was spiked with acrylamide and incubated with different substrates (kaolinite clay, montmorillonite clay, peat, activated carbon, cation exchange resin, anion exchange resin and hydrophobic resin) under aerobic conditions for 168 hours. No acrylamide was lost in the tests with montmorillonite, kaolinite, anionic, cationic or hydrophobic resins, indicating that no sorption had occurred. While some acrylamide was lost in the peat, this was attributed to biodegradation. Activated carbon was found to adsorb acrylamide to a limited extent (Brown et al. 1980).

The fate and transport of acrylamide was investigated in the environment surrounding an aggregate quarry in France that used a PAM-based flocculant. At this quarry, aggregate required washing to remove fine particles, and the wash water was recycled (Touzé et al. 2015). To recycle this wash water, it was collected in a closed loop liquid-solid separation system and treated with PAM flocculants to improve the efficiency of the liquid-solid separation. Unlike oil sands tailings, these settling basins were relatively permeable so that water freely seeped into the surrounding environment. Residual acrylamide contained in the commercial PAM flocculant was found in the quarry's water circuit (0.41 to 5.66  $\mu\text{g/L}$ ) and at lower concentrations within downgradient groundwater and a nearby pond (0.01 to 0.08  $\mu\text{g/l}$ ). This study indicated that

residual acrylamide from PAM-based flocculants can lead to the release of acrylamide to the environment if not managed (Touzé et al. 2015).

Based on its solubility, acrylamide contained in leachate from tailings could be transported by aqueous phase migration to groundwater and then downgradient via advective groundwater flow to a receiving waterbody. However, this transport would likely be mitigated by two factors. First, the degradation rate of acrylamide is high, as noted in Section 3.6.3. Based on this degradation rate alone, acrylamide is likely to be degraded before reaching environmental receptors. Second, the hydraulic conductivity of PAM-amended tailings is very low, on the order of  $10^{-9}$  m/s depending on tailings composition, PAM dosing, deposit age, deposit height and other factors (Roshani et al. 2018; Wilson et al. 2018). Consequently, the total volume of leachate and therefore the total mass load associated with the leachate is also likely to be very low. Based on these considerations, acrylamide is unlikely to be detected along surface or groundwater pathways downgradient of tailings deposits. A further consideration is that acrylamide is only likely to be present as the residual amount from the commercial formulation (<0.5%), and not as a byproduct of PAM degradation.

Acrylamide is unlikely to be detected in surface water or groundwater pathways downgradient of tailings deposits.

Volatilization from surface water or soil surfaces is considered an unimportant fate process based on the moderate vapour pressure and Henry's Law constant of acrylamide. Therefore, aerial transport of acrylamide is not considered to pose significant risks.

### 3.7.3 **Acrylic Acid**

The mobility of acrylic acid is expected to be similar to that of acrylamide. Acrylic acid does not strongly sorb to soils and will almost exclusively (99%) partition into water, where it will distribute according to groundwater flow. Acrylic acid is essentially non-volatile (EU RAR 2002b). That said, the same mitigating factors for acrylamide would also apply to acrylic acid, so seepage to downgradient receptors is not considered likely to be significant.

### 3.7.4 **Ammonia**

The fate and behaviour of ammonia in the environment is well established, as it is a ubiquitous constituent of potential concern in mining, municipal and agricultural effluent and runoff. In surface waters, ammonia acts as both a toxicant and a nutrient depending on its form, concentration and receiving environment.

Ammonia is bound to soil via several mechanisms. As such, it is poorly mobile in soil; however, once in groundwater, ammonia will move with the groundwater flow. In general, adsorption of ammonia increases with increasing organic-matter content of soil and decreases with increasing pH (ATSDR 2004).

Ammonia has a pKa of 9.25, which means that at lower pH it exists primarily in the form of ammonium ion ( $\text{NH}_4^+$ ) and at higher pH it exists primarily as ammonia ( $\text{NH}_3$ ). As such, ammonia has high solubility at lower pH and is more volatile at higher pH. In surface waters, volatilization plays an important role in the fate of ammonia (Environment Canada and Health Canada 2001). The rate of volatilization of ammonia from surface water increases with increasing pH and temperature (ATSDR 2004).

As noted in Section 3.3.1, deamination is a potential mechanism in PAM-amended tailings, and it may represent the first step along the degradation pathway. Therefore, the potential exists for ammonia generation and release to the environment. Given its properties, ammonia could be transported by groundwater from aquatic or terrestrial landforms or by surface water if released to a pit lake. Potential exposure pathways and monitoring are discussed in the following sections.

### 3.8 Exposure Pathways

Exposure pathways describe how chemicals may reach people and ecological receptors including plants, fish, and other wildlife or biological organisms. If there is no plausible mechanism for exposure or the potential for exposure is insignificant, risks of adverse effects would not occur. Alternately, operable exposure pathways, or pathways by which exposure may occur, do not necessarily indicate that adverse effect will occur, as potential effects depend on a number of factors including the toxicity of the chemical and the concentration or dose to which a receptor is exposed. An operable pathway, therefore, is an indication of a potential exposure that may be relevant and could be monitored in a site-specific setting. In this section, the potential for exposure of various ecological reporters and people (workers and non-worker area users) to PAM, its residual monomers and degradation products are discussed.

As described in Section 3.7, with the possible exception of fugitive dust emissions, transport of PAM and polyacrylate from treated tailings is not considered likely, and there is limited potential for exposure to PAM or polyacrylate in either terrestrial or aquatic environments. Degradation products such as acrylamide and acrylic acids are also not expected to occur in receiving environments given that they are not expected to be produced in large amounts, the hydraulic conductivity of PAM-amended tailings is very low and these compounds are readily biodegradable in the environment. Conversely, given that deamination is an expected step in the degradation of PAM, there is potential for greater ammonia generation in PAM-amended tailings and release to the environment over the long term, including after mine closure. Therefore, people and ecological receptors potentially may be exposed to ammonia through surface water.

Dust in the context of oil sands mines has been extensively studied (Wang et al. 2015, Ahad et al. 2021), albeit not with a focus on PAM exposure. Given that the tailings in question are treated with PAM as a flocculant, and many studies have shown that doing so stabilizes soil and reduces erosion (Barvenik 1994, Guezennec et al. 2015b), production of dusts or particulate from flocculated tailings is expected to be limited. However, during operations, tailings deposition may produce particulate matter if tailings are deposited in thin lifts or surface beaches to facilitate evaporative dewatering. Since this process would involve PAM-treated tailings being thinly spread along the ground to dry, there may be potential for some dust to form during the drying process. This is potentially more likely given that photolytic degradation of PAM is known to result in chain scission, which can reduce the polymer's molecular weight and reduce its flocculating ability. Accordingly, emission of fugitive dust from terrestrial drying of PAM-amended tailings is considered a plausible pathway by which people and ecological receptors may be exposed to PAM and its degradation products or residual monomers. Following reclamation, the soil cap that would cover treated tailings would eliminate this pathway.

Should measurable amounts of PAM or its degradation products or residual monomers be detected in dust, sampling of soil from areas with dust deposition would indicate if dust was contributing to concentrations of PAM and related chemicals in other media. Given that PAM is



widely applied directly to agricultural soils (Seybold 1994; Barvenik 1994; Sojka et al. 2007), unacceptable risks from potential deposition of dust onto other media is not expected. Site-specific data from dry tailings applications would be required to confirm these findings.

Further discussion of ecological and human exposure pathways is presented below.

### 3.8.1 Ecological Exposure Pathways

As described above, ecological receptors may be exposed to PAM, its degradation products and residual monomer through fugitive dust emissions during oil sands mine operations. Following reclamation, terrestrial treated tailings landscapes are planned to be covered with a soil cap that is sufficiently thick to prevent ecological contact (root zone contact and terrestrial invertebrates). Ammonia is the only degradation product that may be expected to migrate through groundwater into a receiving waterbody or be released from porewater directly into an aquatic landform (pit lake) where ecological receptors may be exposed through direct contact or drinking water.

Only ammonia could potentially migrate through groundwater into a receiving waterbody.

Given that ecological receptors may subsequently contribute to human exposure (e.g., consumption of wild plants, fish or game), the potential for biological uptake and accumulation of PAM and its degradation products is discussed below.

#### 3.8.1.1 Uptake and Bioaccumulation in Plants and Animals (Terrestrial and Aquatic)

Biological uptake is the transfer of substances from the environment into plants or animals by either passive (e.g., diffusion across a concentration gradient) or active (e.g., diet) means. Limited information was identified on the uptake and accumulation of PAM and polyacrylate; however, uptake of large molecular size compounds is generally limited. In order for uptake to occur, substances must first cross biological membranes such as respiratory (e.g. fish gills), dermal or intestinal barriers (Barron 1990; Müller and Nendza 2007). Although there is no clear molecular size cut-off for uptake and bioconcentration to occur (Arnot et al. 2007; Müller and Nendza 2007), it is generally accepted that molecules with molecular weights >700 g/mol will not be absorbed or bioconcentrated by fish (European Commission 2008). Compounds are also unlikely to be taken up by plants at >390 g/mol (Lamshoeft et al. 2018). It has been demonstrated in rats that ingestion of radio-labelled PAM (molecular weight not reported) was not absorbed (Stephens 1991). According to the European Food Safety Authority, 1,000 g/mol may be considered a cut-off value for absorption of polymers and oligomers via the gastrointestinal tract (EFSA 2016). Furthermore, the bioavailability of PAM is strongly reduced in aqueous solution because PAM binds to suspended particles (Buczek et al. 2017). Given these findings and that the molecular weight of the PAMs used in tailings treatments are more than four orders of magnitude larger than these approximate thresholds, uptake of these compounds into biota is not expected.

PAM and acrylamide are not expected to accumulate in plants or animals.

Acrylamide is also of little concern in regard to uptake and accumulation. PAMs are widely used in agricultural applications such as a thickening agent for pesticides, irrigation water additive to minimize soil erosion and promote water retention, and PAM may be used as a medium for hydroponically grown crops. This provides compelling evidence that accumulation of acrylamide is not a concern in plants. Bologna et al. (1999), investigated the residual acrylamide in PAM in

bean, sugar beet, corn and potato crops grown in soil treated with PAM to reduce soil erosion (Bologna et al. 1999). In all cases, acrylamide was below the 10 ppb limit of quantification (Bologna et al. 1999). Further, plant samples soaked in acrylamide-spiked water revealed reduced acrylamide concentrations over time. The more biologically active crops (corn and beans) had a faster reduction in acrylamide concentration as compared to the less biologically active mature potato and sugar beet crops (Bologna et al. 1999). This indicates that even if acrylamide were to be present in plants, it would be rapidly broken down and be unlikely to persist. Similar findings are reported elsewhere (Castle et al. 1991; Barvenik 1994).

According to Environment Canada and Health Canada (2009), acrylamide has a low potential to bioaccumulate in the environment based on experimental and modelled  $\log K_{ow}$  values of  $-0.67$  and  $-0.81$ , respectively. Several studies have investigated bioconcentration factors (BCFs) in fish, with various regulatory agencies considering BCF values for aquatic organisms to be  $<1$  to  $<2$  L/kg (EU RAR 2002a; Environment Canada and Health Canada 2009; ATSDR 2012). This is well below the bioaccumulation criterion (BCF or bioaccumulation factor  $\geq 5,000$  L/kg) set out in Canada's *Persistence and Bioaccumulation Regulations* (Government of Canada 2000). Thus, acrylamide is not expected to accumulate in aquatic organisms.

No experimental information on the bioaccumulation of acrylic acid was identified. Based on the  $\log K_{ow}$  of 0.46, an estimated BCF of 0.49 L/Kg indicates little potential for bioaccumulation (EU RAR 2002b).

The uptake of ammonia in the environment is well understood and described in literature and by regulatory agencies (Environment Canada and Health Canada 2001; ATSDR 2004). Ammonia is a key intermediate in the nitrogen cycle and occurs naturally in the environment. As ammonia is continually recycled in the environment as a macronutrient, bioaccumulation is not a relevant mechanism (ATSDR 2004).

### **3.8.2 Human Exposure Pathways**

As with ecological receptors, people may be exposed to PAM, its degradation products and residual monomer through fugitive dust emissions, although this exposure is expected to be limited. Additionally, there is potential for exposure to ammonia through surface water. Human exposure pathways are discussed separately below.

#### **3.8.2.1 Dust Inhalation**

As discussed above, the application of PAM to tailings is likely to reduce the amount of fugitive dust from a tailings deposit compared to a non-PAM-treated dry deposit; nonetheless, during the drying of tailings in terrestrial landforms, fugitive dusts present a pathway by which people may be exposed. These exposures would be more likely for on-site workers than off-site area users given differences in proximity to terrestrial landforms during mine operation. Following reclamation, the soil cap that would cover treated tailings will eliminate the possibility of impacted fugitive dusts.

#### **3.8.2.2 Direct Contact (Dermal Contact and Incidental Ingestion) with Treated Tailings**

Oil sands mines are actively managed landscapes with rigid engineering controls and requirements for personal protective equipment (PPE). As such, direct human exposure to PAM-treated tailings is generally not expected during operations. Following reclamation, treated

tailings are covered with either a soil cap or pit lake, thereby eliminating the potential for direct contact with treated tailings.

### 3.8.2.3 Direct Contact (Dermal Contact and Incidental Ingestion) with Other Media and Ingestion of Drinking Water

Exposure to PAM and its degradation products or residual monomers via direct contact with soil, surface water or sediment would require migration of these chemicals from terrestrial or aquatic landforms, or through deposition of fugitive dusts. As discussed above, this pathway is unlikely for these chemicals.

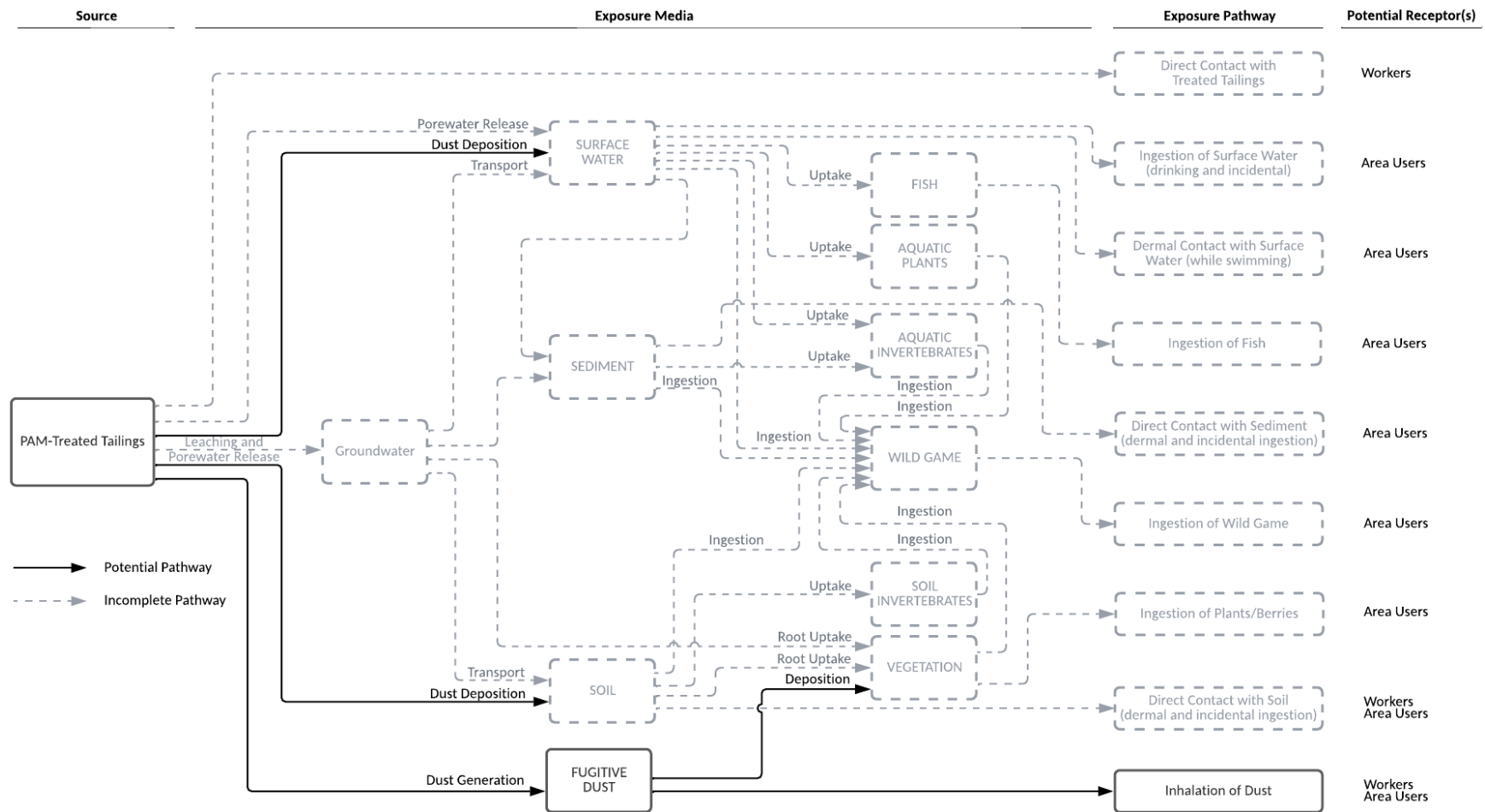
Ammonia has a greater potential for generation in PAM-amended tailings and is mobile in the environment. As such, over the long-term, ammonia could seep from tailings (terrestrial or under a pit lake) and migrate with groundwater towards a receiving waterbody or be released from porewater directly into the water cap of pit lakes where exposure may occur. People may directly contact water in the downstream environments or pit lakes through recreational and traditional activities and use surface water as a source of drinking water.

### 3.8.2.4 Ingestion of Fish, Wild Game, Plants and Berries

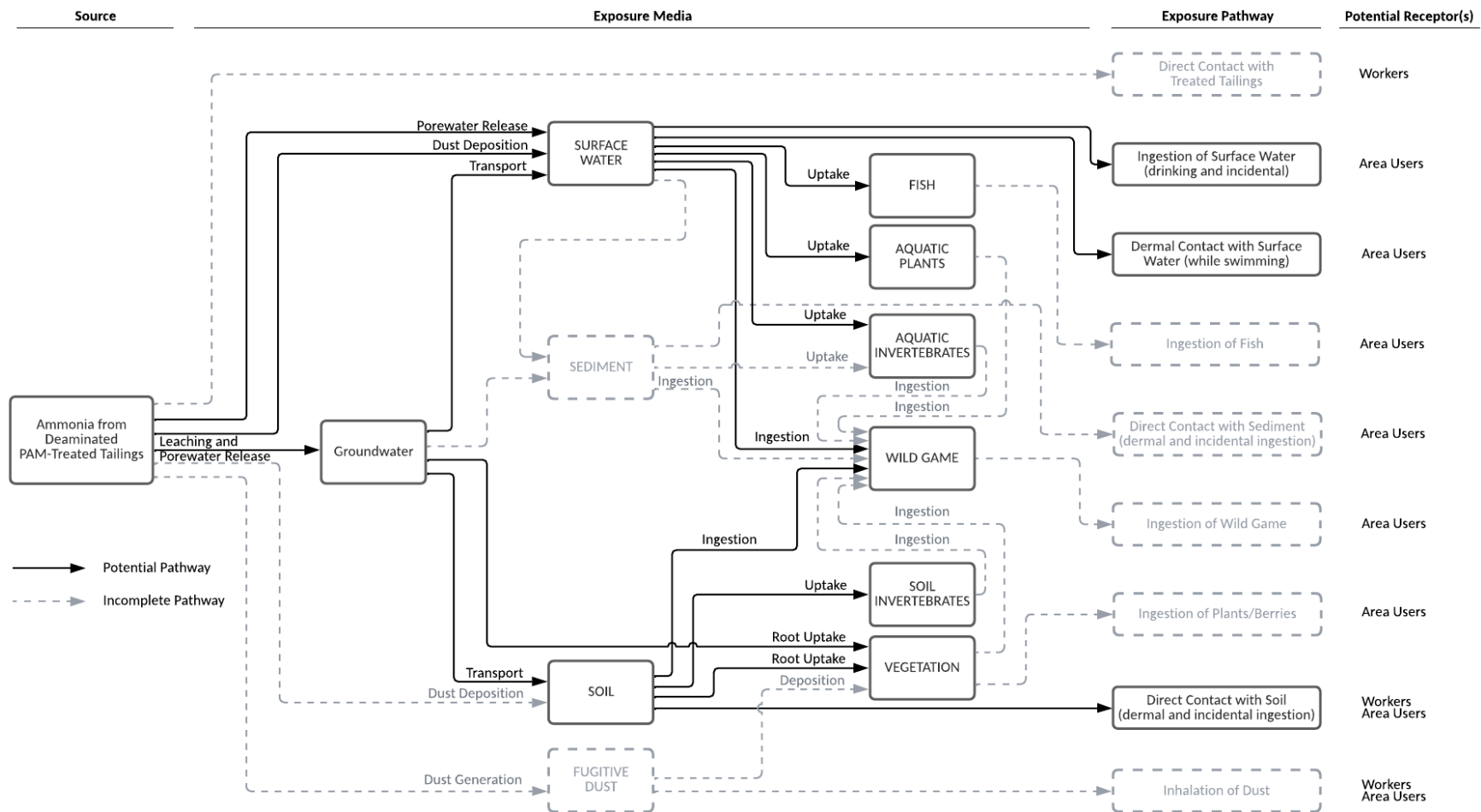
As discussed in 3.8.1, with the possible exception of ammonia, there is limited opportunity for exposure of fish, wildlife and plants to PAM and its degradation products and no uptake or accumulation of these compounds is expected. Any deposition of dusts onto plants is not expected to contribute significantly to human exposure as washing of harvested plants is common practice and agricultural applications have indicated low risk.

## **3.8.3 Exposure Pathway Summary**

Based on the environmental transport of PAM and its residual monomers and degradation products, plausible exposure pathways exist for these chemicals in fugitive dust and through release of ammonia into receiving waterbodies. On this basis, two separate conceptual models for exposure pathways are presented below, one for PAM and its degradation products or residual monomers as driven by fugitive dusts (Figure 3-2) and a separate model to illustrate potential exposures to ammonia driven primarily by groundwater transport and releases to surface water, as well as fugitive dusts (Figure 3-3). The focus of these figures is on potential human exposures; however, ecological receptors such as invertebrates, plants, wildlife, and fish are evaluated and included in the context of their potential contribution to human exposure (i.e., as potential exposure media).



**Figure 3-2 Conceptual Model of Potential Exposure Pathways for PAM and its Degradation Products**



**Figure 3-3 Conceptual Model of Potential Exposure Pathways for Ammonia**



### 3.9 Health and Risk-Based Thresholds

The potential toxicity of PAM and its principal breakdown products (polyacrylate, acrylic acid, acrylamide and ammonia) is described below. Where available, regulatory health- and environmental-based guidelines are presented.

PAM and polyacrylate exhibit low toxicity due to their chemical inertness and large molecular size (Dell'Ambrogio et al. 2019). In an evaluation of the potential environmental risks associated with polymer-amended thickened tailings deposits, Kindzierski (2001) notes that “anionic polyacrylamide is considered to exhibit low toxicity to ecological and mammalian systems” and “although adverse ecological and human health effects are reported in literature for acrylamide, the quantities and exposure conditions necessary to elicit these effects are not expected to be present associated with anionic polyacrylamide use in the oil sands”. Kindzierski (2001) also states that acrylic acid exhibits low acute toxicity to humans through the oral pathway (drinking water, soil ingestion, etc.) and that algae are the most sensitive group of aquatic organisms to acrylic acid, although as noted above, the likelihood of acrylic acid reaching surface waters is low.

PAM exhibits low toxicity to aquatic and mammalian systems.

The following reference sources were reviewed for environmental quality guidelines for PAM, acrylamide, polyacrylate, acrylic acid and ammonia:

- Alberta Tier 1 and Tier 2 Soil and Groundwater Remediation Guidelines
- Alberta Environmental Quality Guidelines for Surface Water in Alberta
- Canadian Council of Ministers of the Environment (CCME) Canadian Environmental Quality Guidelines
- British Columbia Ministry of the Environment and Climate Change Strategy (BC ENV) Contaminated Sites Regulations Standards
- BC ENV Approved Water Quality Guidelines: Aquatic Life, Wildlife and Agriculture
- US EPA Ecological Soil Screening Levels
- US EPA Regional Screening Levels

Brief toxicity summaries are provided for compounds that have no environmental quality guidelines.

#### 3.9.1 **Polyacrylamide**

There are no environmental quality guidelines available for PAM in the reviewed sources.

##### 3.9.1.1 Human Health

Anionic PAM is considered non-toxic to humans and other mammalian species (Kindzierski 2001). For this reason, toxicological assessments of PAM have focused on its breakdown products, like acrylamide.

PAM is commonly used in cosmetic formulations at concentrations ranging from 0.05% to 2.8% (Cosmetic Ingredient Review Expert Panel 2005). The associated safety assessments indicate that exposure to PAM is well tolerated. In subchronic oral toxicity studies, rats and dogs exposed to PAM at doses up to 464 mg/kg body weight per day showed no signs of toxicity. Similarly, in two-year chronic oral toxicity studies where rats and dogs were fed diets containing up to 5% PAM there was no evidence of significant adverse effects (Cosmetic Ingredient Review Expert Panel 2005).

In his screening evaluation and risk assessment of PAM, Kindzierksi (2001) makes note of the compound's high acute LD<sub>50</sub> values by the oral and dermal routes (>5 g/kg) and the overall absence of significant adverse effects in chronic oral toxicity studies. PAM is not a reproductive or development toxicant, nor is it carcinogenic (Cosmetic Ingredient Review Expert Panel 2005). According to Stephens (1991), human epidemiological studies have demonstrated no association between occupational exposure to PAM and tumours.

### 3.9.1.2 Ecological

Duis et al. (2021) note that in aquatic toxicity tests, anionic homo- and copolymers of acrylic acid (PAM) showed no to low toxicity. Similarly, results from limited toxicity tests with sediment and soil organisms showed no toxicity.

According to Dell'Ambrogio et al. (2019), one of the most important factors that influences PAM's toxicity to aquatic organisms is its ionic state, with toxicity increasing with increasing charge density. While cationic polymers bind strongly to fish gills, which have a negative surface charge, the same is not the case for anionic PAMs. Anionic PAMs are generally assumed to be non-toxic to fish and freshwater invertebrates (Dell'Ambrogio et al. 2019). The mode of action for crustaceans appears to be mechanical, resulting in physical entrapment.

Acharya et al. (2010) reported a no-observable-effect-concentration (NOEC) of 0.5 mg/L and lowest-observable-effect-concentration (LOEC) of 1 mg/L for growth in *Daphnia magna* continuously exposed to anionic PAM. When measuring effects on reproduction, the NOEC and LOEC were 5 mg/L and 10 mg/L, respectively. Acharya et al. (2010) observed that the flocculent increased water viscosity which inhibited the ability of *Daphnia* to move and filter food.

In his review of the aquatic toxicity of anionic PAM, Kindzierski (2001) states that exposures of fathead minnows, rainbow trout, yellow perch and bluegills to 1,000 mg/L for five days or 100 mg/L over 90 days resulted in no adverse effects. The low toxicity to fish is likely due to the high molecular weight of PAM - the size of the molecules prevents them from being transported across biological membranes.

Dell'Ambrogio et al. (2019) used the available aquatic toxicity data to derive a predicted-no-effect-concentration (PNEC) for water. Of the aquatic species, they identified a lowest chronic threshold for *Daphnia magna* of 0.5 mg/L. Dell'Ambrogio et al. (2019) divided that NOEC by an "assessment factor" of 10 to calculate a PNEC of 0.05 mg/L.

Following their review of available literature, Dell'Ambrogio et al. (2019) note that anionic PAM are generally not toxic to plants.

Less information is available on the toxicity of anionic PAM to soil organisms. Dell'Ambrogio et al. (2019) states that the effects of PAM on soil microorganisms are variable, at times both decreasing and increasing soil microbial biomass. However, the data are limited to the extent that a NOEC (or LOEC) cannot be established.

### 3.9.2 Acrylamide

Available environmental quality guidelines for acrylamide are summarized in Table 3-2. Human health-based soil quality and surface water quality guidelines are available from British Columbia and the United States Environmental Protection Agency; there are no ecological-based environmental quality guidelines available for acrylamide.

**Table 3-2 Environmental Quality Guidelines – Acrylamide**

Source	Human Health				Ecological			
	Soil (mg/kg)	Groundwater (mg/L)	Surface Water (mg/L)	Sediment (mg/kg)	Soil (mg/kg)	Groundwater (mg/L)	Surface Water (mg/L)	Sediment (mg/kg)
Alberta	-	-	-	-	-	-	-	-
CCME	-	-	-	-	-	-	-	-
BC	3 / 6 <sup>(a)</sup>	-	0.0001 <sup>(b)</sup>	-	-	-	-	-
US EPA	0.24 <sup>(c)</sup>	-	0.00005 <sup>(d)</sup>	-	-	-	-	-

Notes:

“-“ = no guideline available

- Generic numerical soil standard for residential / natural wildlands
- For drinking water, based on 2015 US EPA “Regional Screening Levels” for tapwater
- Residential soil
- For drinking (tap) water

#### 3.9.2.1 Human Health

The toxicity of acrylamide is reasonably well established. Much of the health information relates to the presence of acrylamide in foods. The Government of Canada assessed acrylamide under its Chemicals Management Plan, after which it updated its risk management strategy for acrylamide in food to “ensure that Canadians’ exposure to acrylamide is as low as possible” (Government of Canada 2021). While exposure to very high levels of acrylamide has been shown to cause cancer in experimental animals, there is no conclusive evidence that lower levels of acrylamide typically seen in diets cause cancer in humans (Government of Canada 2021).

In its comprehensive toxicological profile for acrylamide, the Agency for Toxic Substances and Disease Registry describes the following potential health effects associated with exposure to high levels of acrylamide (ATSDR 2012):

- Nervous system effects such as muscle weakness, numbness in the extremities, unsteadiness. However, most people are not exposed to high enough levels to cause these effects.
- Reduced ability of male animals to produce offspring. Again, these effects are unlikely to occur at levels at which people are exposed.
- Several cancer types in laboratory animals, although it remains unknown if acrylamide causes cancer in humans.

These non-carcinogenic effects occur at concentrations well in excess of the established toxicity reference values discussed below. Although the specific mechanisms whereby acrylamide induces tumours in laboratory animals are not well understood, the U.S. EPA, International

Agency for Research on Cancer (IARC) and the National Toxicology Program (NTP) all concluded that acrylamide is likely to be carcinogenic to humans.

The U.S. EPA developed a reference dose (RfD) for oral exposure of 0.002 mg/kg bw/day based on degenerative nerve changes in rats. The RfD is an estimate of a daily oral exposure to the human population (including sensitive subgroups) that is expected to be without an appreciable risk of deleterious effects during a lifetime (US EPA 2010).

The U.S. EPA RfD is based on a chronic study where male and female F344 rats (90/sex/treatment group) were exposed to 0, 0.01, 0.1, 0.5, or 2.0 mg/kg/day of acrylamide mixed in drinking water for up to 2 years. Animals were sacrificed at 6, 12 and 18 months. Light microscopy of peripheral nerve sections showed degenerative changes, with nerve degeneration graded as very slight, slight, moderate, or severe. Microscopy revealed male rats exposed for 3 and 6 months had increased incidences of axolemma invaginations in the tibial branch of the sciatic nerve and male and female rats exposed for 2 years had increased prevalence of “moderate” to “severe” nerve degeneration. A NOAEL of 0.5 mg/kg/day and a LOAEL of 2.0 mg/kg/day was identified. Benchmark dose modelling was used to determine a benchmark dose lower confidence limit (BMDL) of 0.27 and 0.49 mg/kg/day for males and females, respectively. The male BMDL of 0.27 mg/kg/day was chosen as the point-of-departure (POD) and was used to derive a human equivalent dose (HED) BMDL of 0.053 mg/kg/day. A cumulative uncertainty factor of 30 was applied to account for intraspecies variability (10) and interspecies variability (3).

The U.S. EPA has concluded that acrylamide is carcinogenic by a mutagenic mode of action. Using tumour data recorded for the same study that formed the basis of the oral RfD, the U.S. EPA calculated an oral slope factor of  $0.5 \text{ (mg/kg/day)}^{-1}$ , which equates to a risk-specific dose (RsD) of 0.00002 mg/kg bw/day at a 1 in 100,000 cancer risk. Significant increases in tumours of the mammary glands, central nervous system, oral tissues and uterus were identified in exposed females relative to controls. In males, a significant increase in the incidence of adrenal pheochromocytomas and central nervous system tumours were observed.

The World Health Organization has a drinking water quality guideline for acrylamide of 0.0005 mg/L (WHO 2017). The basis of the guideline derivation is combined mammary, thyroid and uterine tumours observed in female rats in a drinking water study using the linearized multistage cancer model. WHO (2017) notes that, in general, the maximum authorized dose of polymer as a coagulant used in the treatment of drinking water is 1 mg/L. At a monomer content of 0.05%, this corresponds to a maximum theoretical concentration of 0.0005 mg/L. The U.S. EPA drinking (tap) water criterion for acrylamide is the same as the WHO guideline.

### 3.9.2.2 Ecological

There are no ecological-based environmental quality guidelines available for acrylamide from the referenced sources.

As is the case for human exposure, concern regarding the aquatic environment is not simply for PAM exposure but also for the more toxic acrylamide monomer. The U.S. EPA (1985) reported acrylamide LC<sub>50</sub> values for several aquatic species. The 24-, 48-, and 96-h flow-through LC<sub>50</sub> values for harlequin fish (*Rasbora heteromorpha*) were 460, 250, and 130 mg/L, respectively. The 24- and 96-h static LC<sub>50</sub> values for goldfish (*Carassius auratus*) were 460 and 160 mg/L, respectively. According to Kindziarski (2001), the most sensitive freshwater species appears to be bluegill sunfish (*Lepomis macrochirus*) with a 96-hour LC<sub>50</sub> of 100 mg/L. In terms of aquatic

invertebrates, the water flea (*Daphnia magna*) appears to be the most sensitive with a 48-h LC<sub>50</sub> of 98 mg/L and a 24-h LC<sub>50</sub> of 230 mg/L. These levels are much higher than anticipated for PAM-treated tailings residuals.

In their screening assessment, Environment Canada and Health Canada (2009) provide select empirical data for the aquatic invertebrate and fish toxicity of acrylamide (see Table 3-3).

**Table 3-3 Aquatic Invertebrate and Fish Toxicity of Acrylamide**

Test Organism	Type of test	Endpoint	Value (mg/L)
<b>Aquatic Invertebrates</b>			
Algae ( <i>Selenastrum capricornutum</i> )	Acute (72 h)	EC <sub>50</sub>	33.8
Daphnids ( <i>Daphnia magna</i> )	Acute (48 h)	LC <sub>50</sub>	160
		EC <sub>50</sub>	98
Midge larvae ( <i>Paratanytarsus parthenogenetica</i> )	Acute (48 h)	LC <sub>50</sub>	410
		EC <sub>50</sub>	230
Opossum shrimp ( <i>Mysidopsis bahia</i> )	Acute (48 h)	LC <sub>50</sub>	109
	Acute (96 h)		78
American oyster larvae ( <i>Crassostrea virginica</i> )	Acute (48 h)	EC <sub>50</sub>	153
<b>Fish</b>			
Goldfish ( <i>Carassius auratus</i> )	Acute (24 h)	LC <sub>50</sub>	460
	Acute (96 h)		160
Stinging catfish ( <i>Heteropneustes fossilis</i> )	Acute (24 h)	LC <sub>50</sub>	104
	Acute (96 h)		86
Fingerling rainbow trout ( <i>Salmo gairdneri</i> )	Acute (24 h)	LC <sub>50</sub>	300
	Acute (48 h)		210
	Acute (72 h)		170
	Acute (96 h)		162
Rainbow trout ( <i>Salmo gairdneri</i> )	Acute (96 h)	LC <sub>50</sub>	110
Fathead minnow ( <i>Pimephales promelas</i> )			120
Bluegill ( <i>Lepomis macrochirus</i> )			100
Rainbow trout ( <i>Salmo gairdneri</i> )	Acute (96 h)	EC <sub>50</sub>	88
Fathead minnow ( <i>Pimephales promelas</i> )			86
Bluegill ( <i>Lepomis macrochirus</i> )			85

Source: Environment Canada and Health Canada (2009)

The data suggests that acrylamide is moderately acutely toxic to aquatic invertebrates and fish. However, Environment Canada and Health Canada (2009) note that, based on available ecotoxicological data, acrylamide does not appear to cause significant harm to aquatic organisms at low concentrations in species relevant to the Canadian environment, including Alberta's oil sands region. As an example, for relevant aquatic species, acute LC<sub>50</sub> and EC<sub>50</sub> ecotoxicity values range from 33.8 mg/L for a freshwater alga to 410 mg/L for midge larvae. Environment Canada and Health Canada (2009) identified the lowest reported EC<sub>50</sub> value of 33.8 mg/L as a critical toxicity value (CTV), which was then used to estimate a PNEC. An attenuation factor of 100 was applied to the CTV to account for uncertainty regarding the potential for chronic effects (i.e., lack of data on chronic effects), culminating in a PNEC of 0.338 mg/L.

The toxic effects of acrylamide on terrestrial plants were summarized in EURAR (2002a) and NICNAS (2002), which indicates that an acrylamide concentration in soil of 10 mg/kg may result



in a slight effect on plant growth. No effects on seed germination were observed at that concentration.

Environment Canada and Health Canada (2009) concluded that acrylamide does not meet the persistence or bioaccumulation criteria set out in the *Persistence and Bioaccumulation Regulations*.

### 3.9.3 Polyacrylate

There are no environmental quality guidelines available for polyacrylate in any of the reviewed sources.

Limited toxicological data are available for polyacrylate. However, as is the case for PAM, polyacrylates are generally thought to exhibit low toxicity due to their chemical inertness and large molecular size (Dell’Ambrogio et al. 2019). Due to their large molecular size, polyacrylates are unable to cross biological membranes.

In their review of the ecotoxicological effects of polyacrylate, Dell’Ambrogio et al. (2019) conclude there are insufficient toxicological data available to develop ecotoxicological thresholds.

### 3.9.4 Acrylic Acid

Available environmental quality guidelines for acrylic acid are summarized in Table 3-4. British Columbia and the US EPA have soil and water quality guidelines for the protection of human health for acrylic acid. There are no human health-based guidelines available from Alberta or CCME, nor are there any ecological based guidelines available from any of the regulatory agencies.

**Table 3-4 Environmental Quality Guidelines – Acrylic Acid**

Source	Human Health				Ecological			
	Soil (mg/kg)	Groundwater (mg/L)	Surface Water (mg/L)	Sediment (mg/kg)	Soil (mg/kg)	Groundwater (mg/L)	Surface Water (mg/L)	Sediment (mg/kg)
Alberta	-	-	-	-	-	-	-	-
CCME	-	-	-	-	-	-	-	-
BC	8,000 / 15,000 <sup>(a)</sup>	-	2 <sup>(b)</sup>	-	-	-	-	-
US EPA	99 <sup>(c)</sup>	-	0.0021 <sup>(d)</sup>	-	-	-	-	-

Notes:

“-“ = no guideline available

- a. Generic numerical soil standard for residential / natural wildlands
- b. For drinking water
- c. Residential soil
- d. For drinking (tap) water

Acrylic acid exhibits low acute toxicity to humans through oral exposure pathways such as drinking water and soil ingestion (Kindzierski 2001).

Acute and long-term aquatic tests indicate that algae are most sensitive to the effects of acrylic acid. Acute EC<sub>50</sub> values for fish are higher than those identified for algae but similar to those for *Daphnia*.

The European Union Risk Assessment Report presents an aquatic PNEC for acrylic acid of 0.003 mg/L (EU RAR 2002b). This is based on the lowest EC<sub>10</sub> value for the algae *Scenedesmus subspicatus* (0.03 mg/L), which was subsequently divided by an uncertainty factor of 10 to derive the PNEC.

The European Union Risk Assessment Report also presents a PNEC for soil, based on a soil respiration test (respiration inhibition of natural soil microflora). After 28 days of exposure at an acrylic acid concentration of 100 mg/kg, the respiration rate of the soil microflora was unaffected. The European Union Risk Assessment Report (EU RAR 2002b) applied an uncertainty factor of 1,000 to derive a PNEC of 0.1 mg/kg.

### 3.9.5 Ammonia

No human-health-based environmental quality guidelines are available for ammonia; however, the regulatory agencies do provide guidelines for the protection of aquatic life. The water quality guidelines for ammonia vary according to pH and temperature, with the toxicity increasing (guideline decreasing) as pH and temperatures increase. See Alberta 2018 Environmental Quality Guidelines for Alberta Surface Waters, CCME water quality guideline for protection of aquatic life, or US EPA national recommended aquatic life criteria for additional information. In British Columbia, the aquatic life guideline varies for total ammonia according to pH only. Additional information is presented in the BC Contaminated Sites Regulation generic numerical water standards (Schedule 3.2).

In 2013, Health Canada published a supporting document for the ammonia drinking water quality guideline. In that document, Health Canada (2013) states that “it is not considered necessary to establish a health-based guideline for ammonia, based on its low toxicity at concentrations found in drinking water.” For that reason, when considering the potential impact associated with ammonia stemming from the use of anionic PAM, the focus should be on ecological effects, as opposed to human effects.

The complexity of the nitrogen cycle, influencing conditions (pH and temperature) and behaviour of ammonia makes it difficult to determine the fate of ammonia in the aquatic environment (CCME 2010). However, the aquatic toxicity of ammonia is well understood. In water, an equilibrium exists between unionized ammonia (NH<sub>3</sub>) and ionized ammonia (NH<sub>4</sub><sup>+</sup>), as described in Section 3.7.4. The proportion of NH<sub>3</sub> vs. NH<sub>4</sub><sup>+</sup> is most dependent on the pH and temperature of the aqueous solution. Raising the pH or temperature will increase the unionized ammonia (NH<sub>3</sub>) concentration in the solution. Because of its ability to diffuse across biological membranes, unionized ammonia is known to be more toxic to freshwater aquatic life than ionized ammonia.

The aquatic toxicity of ammonia is described in the CCME (2010) Canadian Water Quality Guidelines for the Protection of Aquatic Life summary report and the US EPA (2013) Aquatic Life Ambient Water Quality Criteria for Ammonia – Freshwater. While there is considerable information available on the toxicity of ammonia on fish, less information is available on the potential effects on aquatic invertebrates and benthic organisms. However, the information that is available suggests that fish are most sensitive to the potential effects of ammonia.

### **3.10 Environmental (non-toxicological) Consequences**

While the potential toxicological effects of PAM and its degradation products were evaluated above, the placement of large amounts of PAM in the landscape may carry environmental implications beyond toxicity. As PAM is comprised of carbon, hydrogen, oxygen and nitrogen, its degradation products are evaluated in terms of environmental effects of each of these elements. The potential (non-toxicological) environmental implications of PAM degradation include: (1) nutrient enrichment of the downstream aquatic environment (2) change in pH; and, (3) biogenic greenhouse gas generation.

#### **3.10.1 Carbon and Nitrogen Enrichment**

Nitrogen and carbon are macronutrients in aquatic systems; as such, excess inputs of either element could cause changes to the ecosystem in the receiving aquatic environment. If produced through PAM degradation, dissolved organic carbon and ammonia could be transported to receiving waters via groundwater from terrestrial tailings or to the water column in pit lakes. At the tailings-water interface, nitrifying bacteria could convert the ammonia to nitrate (Saidi-Mehrabad et al. 2013), and either form of nitrogen could be taken up within the water column or discharged to downstream watercourses (Figure 3-3). In the environment, uptake of ammonia is well understood (Environment Canada and Health Canada 2001; ATSDR 2004). It is continually recycled in the environment as a macronutrient, where in plants and animals it is metabolised or assimilated to promote growth (ATSDR 2004).

Organic carbon, ammonia, nitrate and other forms of nitrogen have been extensively monitored in the Athabasca River and its tributaries for decades (Scrimgeour and Chambers 2000; Glozier et al. 2009, 2018; Hebben 2009; Seitz et al. 2013; Culp et al. 2020, 2021; Arciszewski and McMaster 2021). Organic carbon is naturally high in the region, with muskeg-type waters draining to most tributaries in the region. Nitrogen concentrations are moderately high, with contributions from sources upstream of oil sands developments such as agriculture, pulp mills and municipal effluent, as well as aerial emissions of nitrogen from oil sands operations. To date, oil sands developments have not affected river concentrations of organic carbon or nitrogen, with the only change in nutrients attributed to phosphorus from Fort McMurray's municipal effluent (Glozier et al. 2018; Arciszewski and McMaster 2021; Culp et al. 2021).

In this environmental setting, additional inputs of carbon and nitrogen are not likely to cause adverse impacts to the environment, as the PAM degradation and transport (described in Section 3.3 to 3.7) would be very slow and the relative flux of carbon and nitrogen concomitantly low. Nonetheless, as there is no publicly available data to confirm this low rate, monitoring is suggested (see Section 4.0).

#### **3.10.2 Change in pH**

Hydrogen and oxygen will primarily be attached to various carbon compounds or released as water molecules. However, protons may be consumed or released through the degradation of PAM, depending on the pathway and ultimate reaction products. Therefore, potential changes in pH are considered.

Degradation of PAM could have the potential to alter the pH of tailings pore water by affecting the balance of protons involved in redox reactions and by creating intermediate products that are weak acids or bases (including carbon dioxide). This is a theoretical concern based on

stoichiometry of the reactions involved that was not evaluated in most of the supporting literature, including the studies that examined PAM degradation in oil sands tailings.

Only two of the reviewed studies stated the change in pH during degradation. In aerobic degradation of oil field PAM, the pH fluctuated as low as 5.6 and high as 9.3 depending on timing and co-dosing with glucose, with the glucose-dosed cultures having the lowest pH (Al-Moqbali et al. 2018). Similar findings were reported in an aerated tank designed for biodegradation, with neutral to alkaline conditions except where the tank had been dosed with glucose, which caused pH to decline to 6.2 (Sang et al. 2015).

Changes in pH will depend on acids and bases produced in PAM degradation, but are unlikely to be significant in most oil sands tailings, as tailings pore water and oil sands process waters in general have high alkalinity with high concentrations of base cations and carbonates (Allen 2008; Dompierre et al. 2016; Foght et al. 2017). The exception to high alkalinity may be oxidative weathering of FTT, which may contain sulfide minerals and therefore could become acidic over time (Kuznetsov et al. 2015; Lindsay et al. 2019), depending on overall acid-base balance. As noted by Cossey et al. (2021), acid generating potential in FTT can be mitigated by disposing of those tailings under a water cap, as practiced regularly by the hard rock mining industry (Verburg et al. 2009; ARCADIS 2015; McCullough et al. 2020).

Given these site-specific conditions of oil sands tailings, change in pH due to PAM placement and degradation is not likely to pose environmental risks.

### **3.10.3 Greenhouse Gas Generation**

As noted in Section 3.3, the main forms of carbon that are generated from breakdown of PAM include various intermediate organic compounds that, from the non-toxicological perspective, will comprise total and dissolved organic carbon. Complete oxidation or reduction of the intermediate compounds would generate carbon dioxide or methane.

Li (2010) evaluated the effects of tailings amendments, including PAM (Hyperfloc® Af 246), on methanogenic potential of Muskeg River Mine MFT in microcosms. Li concluded that PAM did not affect methanogenesis except as it pertains to the physical characteristics of the bubbles produced, which is likely due to PAM effects on the solid matrix, not the bubble contents. However, the microcosms that were dosed with PAM were also amended with the much more labile citrate, which could have been preferentially utilized by microbes instead of the PAM. The other studies that evaluated PAM degradation in oil sands tailings (Haveroen et al. 2005; Collins et al. 2016) also reported a lack of methanogenic potential from PAM. Nonetheless, it is difficult to draw sector-wide conclusions about long-term methanogenic potential from these studies because bioavailable carbon and nutrients were added to cultures in all three microcosms. Furthermore, while microcosm studies are well suited to evaluate and compare changes in single variables and to answer specific questions, they lack environmental realism that is required to understand complex processes at large temporal and spatial scales (McCullough and Vandenberg 2020) that are relevant to oil sands tailings ponds.

Methanogenesis has been observed in several oil sands tailings ponds as a result of the long-term degradation of residual hydrocarbons in tailings pore water (Siddique et al. 2006, 2007, 2011, 2012; Li 2010; Penner and Foght 2010; Saidi-Mehrabad et al. 2013; Mohamad Shahimin et al. 2016, 2021; Mohamad Shahimin and Siddique 2017). Methanogenesis has been attributed to the biodegradation of some compounds that can be found in tailings such as

diluent, solvents and remaining bitumen. In all likelihood, microbes present in oil sands tailings could eventually adapt to metabolize PAM and its products?

Non-oil sands studies have shown that PAM can be degraded to intermediate organic carbon compounds, which could presumably be further reduced to methane or oxidized to carbon dioxide, given enough time and depletion of other carbon sources. The carbon backbone of PAM limits the rate at which smaller carbon compounds may be formed. Scientific evidence suggests that chain scission may occur more readily in the presence of white-rot fungus under aerobic conditions; however, the presence of this fungus in oil sands tailings is uncertain and most treated tailings deposits are anaerobic. As such, fungal degradation of PAM in treated tailings deposits is considered unlikely.

While there appears to be no conclusive answer to whether PAM could be ultimately degraded to greenhouse gases, the process would likely be extraordinarily slow, taking several decades to begin (based on the methanogenesis observed in oil sands tailings ponds) and likely centuries to unfold. If produced, greenhouse gases would then need to escape the low-permeability tailings, further slowing their release to the atmosphere. The environmental risk of greenhouse gas production, therefore, seems low in the context of overall greenhouse gas emissions from oil sands mines.

## 4.0 KEY FINDINGS AND RECOMMENDATIONS

### Background

Anionic polyacrylamide (PAM) compounds are polymeric flocculants that are applied in many industries, including oil sands mines, for the purification and management of water and solids, among other uses. At oil sands mines, PAM flocculants are applied to fluid tailings to accelerate and improve consolidation and to clarify supernatant water processes that are important for water recycling and reclamation.

Historically, the environmental risk of PAM was thought to be relatively low because the polymer is very large and non-toxic and would be strongly bound to soil particles, while the residual monomer and other degradation products are highly biodegradable and unlikely to persist in the environment. Abundant literature suggests that PAM itself poses little to no toxicological risk as an amendment in oil sands tailings. PAM sorbs strongly to soil and is unlikely to be transported to human or ecological receptors. Even if PAM were transported, it is not bioavailable or toxic. It is widely applied in many industrial and personal products with apparently no adverse effects.

To test these assumptions, this literature review compiled the state of knowledge regarding the use of anionic PAM in tailings management at Alberta oil sands mines and the potential environmental consequences of PAM and its byproducts. The review was based primarily on peer-reviewed literature, with secondary sources including government reports, conference proceedings, academic theses, company tailings plans, Material Data Sheets, websites and interviews with academic researchers and industry experts.

### Analytical Methods

In theory, numerous analytical methods exist for the separation, identification and quantification of PAM in oil sands tailings and other media such as sediments, soils and wastewater; in reality, the accuracy and reproducibility of these methods are limited due to the characteristics of the PAM being analyzed and the characteristics of the sample matrix. Available literature does not present a commercial analytical method applicable to oil sands tailings, and there is currently no



standard method for detecting low concentrations of PAM in aqueous solutions with various environmental impurities (Swift et al. 2015). Analysis of PAM in oil sands tailings or oil sands process water is challenging for two main reasons: (1) the compounds vary widely in terms of chemical properties; and, (2) they are highly adsorptive within a complex matrix of OSPW and tailings.

Several methods exist for indirectly measuring the degradation of PAM. However, because of differences in the methods, reliable quantification of the degradation of PAM is challenging, and it is often unclear if degradation leads to mineralization, breakdown into intermediate compounds, or simply size reduction of the polymer (Nyyssölä and Ahlgren 2019).

### **PAM Degradation**

PAM is applied to different tailings types at all operating oil sand mines. Full-scale application follows decades of evaluation at smaller scales including laboratory and pilot-scale field trials. Tailings are treated to become either terrestrial landforms or aquatic substrates at closure.

Biodegradation of PAM may occur within the tailings matrix where PAM is abundant and stably bound until degraded. Long-term storage of PAM may present opportunities for microbial communities to adapt to metabolize the molecule after other sources of carbon or nitrogen are depleted.

Studies generally suggest that while nitrogen appears to be readily metabolized from PAM under a wide range of conditions, carbon tends to be used only when labile carbon sources have been depleted. This suggests that PAM degradation in oil sands tailings may be incomplete or absent in fresher tailings where labile sources of carbon (such as solvents) are present, but could become more pronounced in the future as these compounds are depleted. The literature from many non-oil sands applications and three oil sands tailings ponds suggest the following:

1. Microbes are able to degrade PAM to use nitrogen under anaerobic and aerobic environments. While they are able to use PAM as a nitrogen source in oil sands tailings ponds, they do not always do so. The reasons for microbes using PAM as a nitrogen source in one pond but not another are not known, but are generally thought to be driven by nitrogen-limited conditions.
2. Microbes are able to degrade PAM to use carbon under limited circumstances. The PAM backbone is relatively recalcitrant, and microbes are likely to use more available electron donors that may be present before they adapt to using PAM. Therefore, carbon enrichment from PAM degradation is unlikely in the short-term, though the long-term fate of the carbon is not known.
3. Acrylamide is generally not a measurable byproduct of PAM degradation, and residual acrylamide is rapidly removed through biodegradation.

Biodegradation is the most common mechanism of PAM degradation. Mechanical, thermal and photodegradation may be relevant for short periods during handling and placement, but are not likely to persist after tailings have been placed and covered with soil or water.

### **Factors Affecting Degradation**

Several factors can affect the rate and degree of PAM degradation. The degree of hydrolyzation can influence degradation, especially regarding deamination. Molecular weight affects

degradation, with higher molecular weight being less degradable. Microbial communities and oxidation-reduction potential of tailings deposits, factors that are interdependent, will affect degradation, with aerobic environments typically promoting faster degradation. Degradation is also increased under neutral pH and high temperatures. Considering these factors, PAM degradation in oil sands tailings is likely to be slow in most of the deposit, but may be more prominent in geochemically active zones such as near the surface of the deposit.

### **Degradation Rates and Products**

During biodegradation of PAM, deamination of acrylamide subunits within PAM results in the release of nitrogen in the form of ammonia or ammonium and the conversion of acrylamide subunits in PAM to acrylic acid subunits. Once PAM has become completely deaminated, the remaining carbon backbone is polyacrylic acid or polyacrylate, depending on environmental pH. Thus, degradation products formed via deamination are polyacrylate and ammonium or polyacrylic acid and ammonia.

Although numerous studies report on the degree of PAM or polyacrylate removal in laboratory testing or bioreactor studies, the test conditions are generally not representative of environmental conditions. Furthermore, different analytical methods may produce different degradation rate estimates or measure different degrees of degradation. Thus, the literature is often not clear about whether reported polymer degradation leads to size reduction of the polymer, intermediate compounds, or mineralization. Degradation of PAM is often incomplete, with partial degradation occurring over weeks to months.

On the other hand, degradation rates for acrylamide are well known from many years of study in different settings. Half-lives for acrylamide vary depending on ambient conditions but may be on the order of hours to days. Despite uncertainty in the PAM degradation rates, it is well established that PAM degrades much more slowly than acrylamide.

Based on laboratory studies and information derived from other industries, PAM degradation products arising from chain scission are generally limited to lower molecular weight polymers, and volatile fatty acids and their intermediates. No compelling evidence exists to indicate that acrylamide or acrylic acid would accumulate as a degradation product of PAM in oil sands treated tailings.

### **Environmental Transport and Exposure**

Due to the characteristics that lend PAM its flocculating properties, anionic PAM is strongly adsorbed to soil and clay mineral surfaces, which limits its mobility in soil and leaching potential to groundwater. Anionic PAM adsorption to soil is rapid and irreversible. Therefore, PAM is not likely to migrate from tailings to groundwater or surface water systems.

Fugitive dust from dry tailings is a documented issue in mine waste management at oil sands and other mines. The application of PAM to tailings is likely to reduce the amount of fugitive dust from a dry tailings deposit compared to a deposit that has not been amended with PAM as PAM has been used in other applications to control dust. Based on findings from several agricultural studies, deposition of dust is not considered to be a significant health risk. Site-specific data from dry tailings applications would be required to confirm these findings.

Based on its solubility, acrylamide contained in leachate from tailings could be transported by aqueous phase migration to groundwater and then downgradient via advective groundwater flow to a receiving waterbody. However, this transport would likely be mitigated by two factors. First, the degradation rate of acrylamide is high, so acrylamide is likely to be degraded before reaching environmental receptors. Second, the hydraulic conductivity of PAM-amended tailings

is very low, so the total mass load associated with the leachate is also likely to be very low. Based on these considerations, acrylamide is unlikely to be detected along surface or groundwater pathways downgradient of tailings deposits.

Environmental (non-toxicological) implications of PAM deposition and degradation were considered in terms of nutrient enrichment, change in pH and generation of greenhouse gases. None of these processes were deemed to pose significant environmental risks.

### Thresholds

Anionic PAM is considered non-toxic to humans and other mammalian species; exposure to PAM is well tolerated. Similarly, anionic PAMs are generally assumed to be non-toxic to fish and freshwater invertebrates. The low toxicity is likely due to the high molecular weight of PAM. No environmental guidelines were found for PAM in North America.

The toxicity of acrylamide to humans is reasonably well established, and human health guidelines exist in some jurisdictions for soil and water for both acrylamide and acrylic acid. Acrylamide is thought to be a human carcinogen, though at exposure levels well in excess of levels anticipated in PAM-treated tailings. No environmental guidelines were found for acrylamide or acrylic acid.

Ammonia is known to be toxic to aquatic species at environmentally relevant concentrations, and aquatic guidelines exist in several jurisdictions. The toxicity and bioavailability vary according to pH and temperature. Ammonia is considered to have low toxicity to humans in drinking water.

### Monitoring

Challenges associated with analyzing PAM are well documented. While there may be good reasons to measure PAM from a geotechnical or economic perspective, the low environmental risk of PAM itself suggests that developing methods to analyze PAM in oil sands tailings would be a low priority. Instead, monitoring efforts should be focussed on three potential pathways where the risk is thought to be low but uncertain: (1) PAM exposure through fugitive dust; (2) release of acrylamide from the initial deposit; and, (3) release of ammonia from long-term deposits.

Although the risk of PAM exposure through fugitive dust is considered low, monitoring the dust, including whether PAM is a component of dust, from drying tailings may be warranted to confirm this. Based on the results from similar applications, monitoring is likely to show that PAM provides a net benefit for dust control.

Acrylamide is not likely to be produced through PAM degradation, but it may be present as a residual monomer in commercial formulations. In addition, PAM-treated tailings are likely to have initially higher hydraulic conductivity and pore water release. Therefore, acrylamide monitoring in groundwater or surface waters should focus on the initial deposit. If significant quantities of acrylamide are not detected in the initial release of water, they are unlikely to be detected thereafter.

Conversely, ammonia is more likely to be generated over the long term through deamination. Therefore, ammonia should be monitored in seepage waters or tailings release waters until it can be shown that degradation is not occurring or that insignificant quantities of water are seeping from tailings deposits. Ammonia may serve as an early indicator of PAM degradation.

## Study Limitations

Tailings ponds are complex geomicrobiological settings with highly site-specific conditions; the factors affecting PAM degradation will vary widely within each deposit. Despite a large volume of research on closely related topics such as the geotechnical properties of PAM treated tailings, the geomicrobiology of oil sands tailings, and the breakdown of PAM in other industries, there are few directly related studies on the breakdown of PAM in oil sands tailings. Any application of the findings and recommendations in this report should be considered in the context of the specific conditions of a given tailings landform.

Likewise, chemicals that are dosed along with PAM, such as alum, gypsum and other coagulants may carry environmental implications but are outside the scope of this study. Sulfur-containing coagulants or residual organics may affect degradation rates in ways that were not evaluated in the cited literature, which is based largely on agricultural applications. Such co-dosing should be considered on a site-specific basis.

The toxicity of the PAM by-products is reasonably well understood, with regulatory-endorsed thresholds/guidelines available for acrylamide and ammonia. As noted by Environment Canada and Health Canada (2009), there is an overall lack of chronic toxicity studies that consider the effects of long-term exposure of acrylamide on aquatic life. As well, limited ecotoxicological information is available for acrylic acid. Although the European Union developed both aquatic and terrestrial PNECs for acrylic acid, those “guidelines” are based on limited toxicological datasets.

## Closing

In summary, the literature review confirmed that the risks to the environment, including toxicological and non-toxicological risks, posed by PAM are low. PAM is expected to be strongly retained within the soil matrix. Degradation is likely to be very slow, on the order of decades, and is due primarily to deamination. If chain scission occurs to the carbon backbone, it is likely also very slow and expected to only generate fragment carbon chains or fatty acids with low toxicity.

Future tests can be considered to confirm the conclusion of this report that the overall risk of PAM from oil sands tailings applications to the environment is low. Such tests may consider pathways such as: (1) PAM release through fugitive dust; (2) residual acrylamide release from recently placed deposits; and, (3) ammonia release through long-term deamination.

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