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FATE AND DECOMPOSITION OF PIPE COATING MATERIALS IN ABANDONED PIPELINES

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1.0 EXECUTIVE SUMMARY

Executive Summary

The history and composition of pipeline coating materials were reviewed. The fate of the buried pipeline coatings was assessed with respect to *in-situ* abandonment. Leachates from the pipeline coatings and their degradation and fate were considered. Based on information from leaching studies in the literature, it was determined that leaching from the coatings has been occurring since the pipeline was originally buried. Consequently, the lower molecular weight, water soluble, easily leachable components have probably all been removed some time ago. Leaching from coal tar and asphalt coatings occurs at a slower rate. These coating materials may have retained the higher molecular weight polyaromatic hydrocarbons (PAHs) which can continue to be leachable post-abandonment. It is recognized that the PAH molecules are toxic and that coating materials containing these molecules would pose more concern for abandoned pipelines. If leaching of PAHs occurs these molecules have low solubility in water and high affinity for organic carbon. This means that if leached, they will be sorbed to soil carbon and will not migrate with soil water or to groundwater. Furthermore these molecules can be biodegraded by soil microorganisms. Consequently their contribution to health and environmental risk of abandoned pipelines will be low and will be no greater than risks posed by pipelines containing these materials currently in operation.

2.0 INTRODUCTION

In-situ abandonment of pipelines after useful service lifetime has passed is viewed as a potential alternative to excavation and removal (1, 2). Several conditions for abandonment have been outlined depending on soil types, terrain and proximity to water bodies (1). It has been suggested that the materials from degrading pipeline materials may pose an environmental or health risk. This was recognized as an area which lacked sufficient information and was pinpointed as a candidate for future investigation (1). The objective of this project is to acquire scientific information about the decomposition products of pipeline coating materials to enable the soil and groundwater contamination risks associated with abandonment to be understood and managed.

3.0 LITERATURE SEARCH METHODS

For this literature review, the following procedures were used. The database of Science Direct was searched using the strategy:

Pipelines AND coating* (Abstract, title, keywords) AND degrade* (All Fields).

The database of Engineering Village was searched using the strategy:

Coatings (Controlled Term) AND Pipelines (Controlled Term) AND degradation (Subject, Title, Abstract).

The databases of Google AND Google Scholar were searched using the following phrases:

“Pipeline coating” AND degradation

“Microbial degradation” AND “Pipeline coating”

“Microbial corrosion” AND Pipelines AND coatings.

More direct searches of Google and Google Scholar used the following strategy:

“Pipeline coatings components” AND solubility AND migration

“Pipeline coatings composition” AND behavior AND buried

Leachates, leachables from pipeline coatings

Leachates, leachables from coal tar, asphalt, epoxy, etc.

Microbial growth on leachates, leachables from coal tar, epoxy, etc.

Microbial degradation of individual components of pipeline coatings

Finally the Material Safety Data Sheets (MSDS and SDS) for each coating type were reviewed to identify human and environmental toxicity issues. Also the environmental toxicity of individual components of pipeline coatings was reviewed.

4.0 DISCUSSION

4.1 HISTORY AND COMPOSITION OF PIPELINE COATINGS

Buried pipelines are used to transport primarily gas and oil and sometimes their refined products. Because the pipelines are buried, they must be protected from water, salts, microbes and soil stress which can contribute to corrosion or pipe damage and eventually to pipeline failure. One means of protection for the buried pipelines is to coat them which will protect them from the damaging effects of the underground environment. The architecture of the buried pipeline consists of the steel pipe itself which is then covered with a series of coating materials installed based on soil conditions and the decisions of the pipeline owner.

The earliest coating materials consisted of coal tar and asphaltic materials in a matrix of fibrous materials like asbestos, fiberglass or even burlap (hessian) (3, 4). As technology developed some coatings were made of plastic materials including polyvinyl chloride. This material was later found to lose its plasticizer and was thus superseded by polyethylene coatings. The architecture of buried pipelines evolved to include a chemically treated pipe which was then covered with a layer of primer followed by an adhesive backed by polyethylene layer (Figure 1). Currently, sometimes up to three layers of polyethylene were used (5).

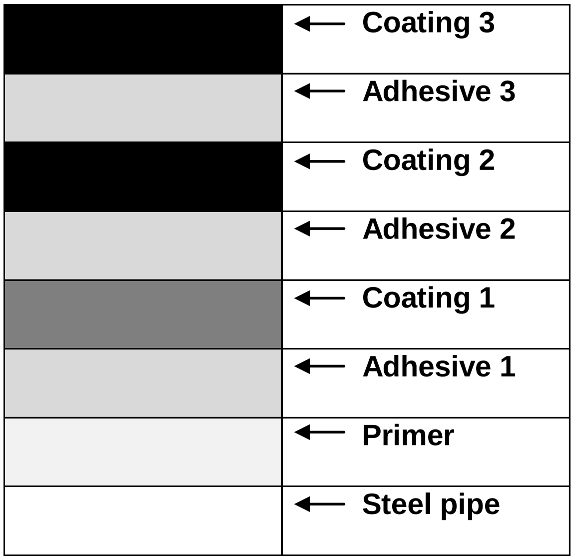


Figure 1. A representation of steel pipe and the different layers that may constitute the coating

In the 1970s and 1980s there was increased use of fusion bonded epoxy as a coating material. Today fusion bonded epoxy and polyethylene are the major coating types. A timeline tracing the evolution of pipeline coating composition is shown in Figure 2.

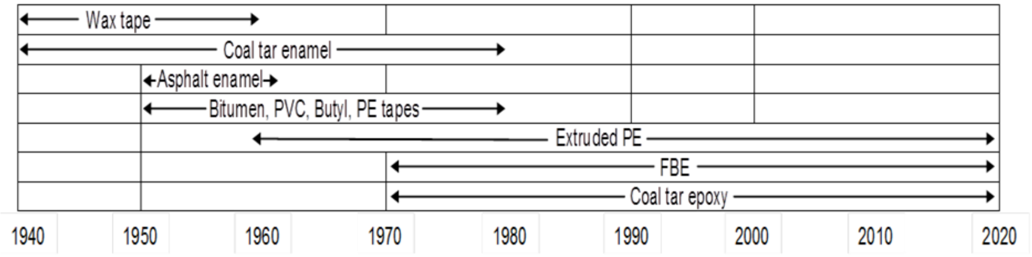


Figure 2. Historical evolution of pipeline coatings and their use

4.2 PIPELINE COATINGS COMPOSITION

4.2.1 Asbestos

Asbestos is a naturally occurring silicate mineral. Some members of this family include chrysotile $(Mg_3(Si_2O_5)(OH)_4$, Amosite, CAS No. 12172-73-5 $(Fe_7Si_8O_{22}(OH)_2$, Crocidolite, CAS No. 12001-28-4 $(Na_2Fe^{2+}{}_3Fe^{3+}{}_2Si_8O_{22}(OH)_2$ and there are other forms. Asbestos is composed of fibers that possess the characteristics of strength and fire resistance which render it suitable for a pipeline coating material. It does not contain organic molecules to cause additional concerns. Asbestos has traditionally been used in combination with asphalt or coal tar.

4.2.2 Asphalt/Bitumen

Asphalt is a dark brown to black, cement-like semisolid or solid or viscous liquid produced by the non-destructive distillation of crude oil during petroleum refining. In Europe it is more commonly referred to as bitumen. The exact chemical composition of asphalt is dependent on the chemical nature of the original crude petroleum and the manufacturing process used. Crude petroleum consists mainly of aliphatic compounds, cyclic alkanes, aromatic hydrocarbons, polycyclic aromatic compounds (PAHs) which may contain metals like iron, nickel, and vanadium. The proportions of these chemical components can vary greatly because of significant differences in crude petroleum from oil field to oil field or even at different locations in the same oil field. However, the chemical nature of the asphalt does not change unless thermal cracking occurs.

By weight most asphalts contain 79–88% carbon, 7–13% hydrogen, traces to 8% sulfur, 2– 8% oxygen, and traces to 3% nitrogen. The chemical composition of asphalts is in Table 1.

Table 1. Chemical composition of asphalts analysed by gas chromatography – mass spectrometry*

Compound class	Fraction in various asphalts				
	A	B	C	D	E
Hydrocarbons:					
Alkanes	++	+	+	-	-
Alkenes/cycloalkanes	++	+	+	-	-
Benzenes, C2 – C8	++	+	-	-	-
Indanes, C0 – C4	++	+	-	-	-
Indenes, C0 – C3	++	+	-	-	-
Naphthalenes, C0–C5	++	+	-	-	-
Biphenyls, C0–C2	++	+	-	-	-
Fluorenes, C0–C3	++	+	-	-	-
Anthracenes/phenanthrenes, C0–C4	++	+++	+	-	-
Pyrenes/fluoranthenes, C0–C2	-	++	+	-	-
Chrysenes/benzo[a]anthracenes, C0–C2	-	-	+	-	-
Sulfur-containing compounds:					
Benzothiophenes, C0–C9	++	+	-	-	-
Dibenzothiophenes/naphthothiophenes, C0–C4	++	+++	+	-	-
Tricarbocyclic fused-ring thiophenes, C0–C1	-	-	+	-	-
Oxygen-containing compounds:					
Benzofurans, C0–C2	-	+	-	-	-
Dibenzofurans, C0–C2	-	+	-	-	-
Acetophenones, C0–C3	-	+++	++	+	+
Fluorenones, C0–C3	-	+	++	-	-
Dihydroindenones, C0–C4	-	++	++	+	+
Cycloalkenones, C6–C11	-	+	+++	+	+
Dihydrofuranones	-	-	+	++	-
Isobenzofuranones, C0–C3	-	-	+	++	-
Phenols, C0–C4	-	-	-	+	-
Naphthols, C0–C2	-	-	-	+	-
Furanones, C1–C3	-	-	-	+	-
Alkanones, C8–C22	-	-	-	++	+
Alkanoic acids, C5–C14	-	-	+	++	+++
Benzoic acids, C0–C4	-	-	-	-	+
Nitrogen-containing compounds:					
Carbazoles, C0–C4	-	-	-	+	-

Oxygen- and sulfur-containing compounds: Hydroxybenzenethiols, C0 –C4	-	-	+	-	-

*Taken from reference 6. A,B,C,D, E are different asphalt sources

4.2.3 Coal Tar

Coal tar is produced as a by-product when coal is carbonized to make coke or gas. Distillation of coal tar produces coal tar creosotes as a distillation product, and coal-tar pitch as a distillation residual. Coal tars are viscous and slightly soluble in water, while coal-tar pitches can be semi-solid to solid. These are complex mixtures containing over 400 identified compounds including hydrocarbons, phenols and heterocyclic compounds. The composition and properties of a coal tar (and coal tar pitch derived thereof) depend mainly on the temperature of carbonization and, to a lesser extent, on the nature of the coal used as feedstock.

In general, coal tars are only slightly soluble in water and are composed of complex combinations of hydrocarbons, phenols, and heterocyclic oxygen, sulfur, and nitrogen compounds.

Table 2 Table 8. Categories of various components and contents in the coal tar*

Categories	Composition	Content (%)
Aliphatics	Paraffin hydrocarbons	9.998
	Alkene	7.341
Aromatics	Benzene and its derivatives	7.997
	Naphthalene and its derivatives	10.738
	Phenanthrene, anthracene and their derivatives	6.963
	Indene and its derivatives	0.755
	Fluorene and its derivatives	0.461
	Pyrene and its derivatives	0.492
Oxygenic compounds	Alcohols	0.774
	Phenols,	8.493
	Aldehyde, ketone	1.589
	Acid, ester	2.754
	Furan and its derivatives	0.809
	Pyran and its derivatives	0.041
Nitrogenous compounds	Pyridine and its derivatives	1.015
	Indole and its derivatives	0.409
	Quinoline and its derivatives	1.053
	Aniline and its derivatives	0.503
	Nitrile and its derivatives	0.431
	Phenazine and its derivatives	0.089
	Carbazole and its derivatives	0.094
Sulfuric compounds	Thiophene and its derivatives	0.010
Unknown	Unknown	0.929
Total		63.728

*Taken from reference 7 and 8.

4.2.4 Asphaltic or Coal Tar Coatings Containing Polychlorinated Biphenyls (PCBs)

There are oblique references to PCBs in pipeline coating materials – namely asphaltic materials (9, 10). Since instructions for handling such materials have been published by at least one government agency (9), it would appear to be a real phenomenon. It is believed that asphalt coatings containing PCBs were in use until the 1970s (10). Therefore in-situ abandonment of pipelines built between 1940 and 1970s will have to consider PCBs as a contaminant. The basic structure of PCB is shown in Figure 3. Each carbon atom in the biphenyl molecule (except the alpha carbon atoms) can be the site of attachment of a chlorine atom resulting in a total of 209 possible PCB isomers or congeners. Increasing the number of chlorines in the molecule increases the durability and toxicity of the PCB.

Because the PCB oils were not used in all applications or on all jobs, PCBs will not be found in all coal tar coatings. Intermittent positive results may be found in one area sampled or positives may find PCBs throughout the pipeline.

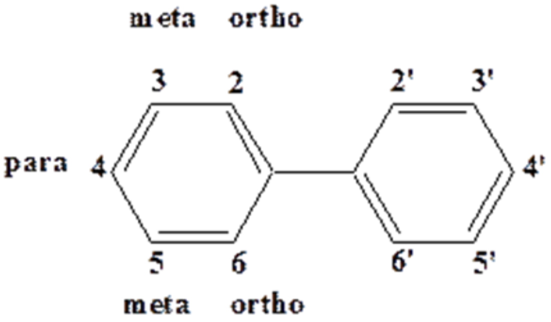


Figure 3. The structure of PCB

4.2.5 Polyethylene

Polyethylene is used as a primary coating material and as a repair coating when pipeline defects are excised and/or repaired. Polyethylene is a thermoplastic polymer of ethylene (Figure 4). It has a high molecular weight (average molecular weight = 100,000 Daltons or grams/mole) and may be flexible or rigid. This polymer is not soluble in water. This material is fairly inert and does not break down or decompose readily. Strong oxidizing agents like UV radiation or ozone can break the polyethylene chain to release smaller molecular weight units.

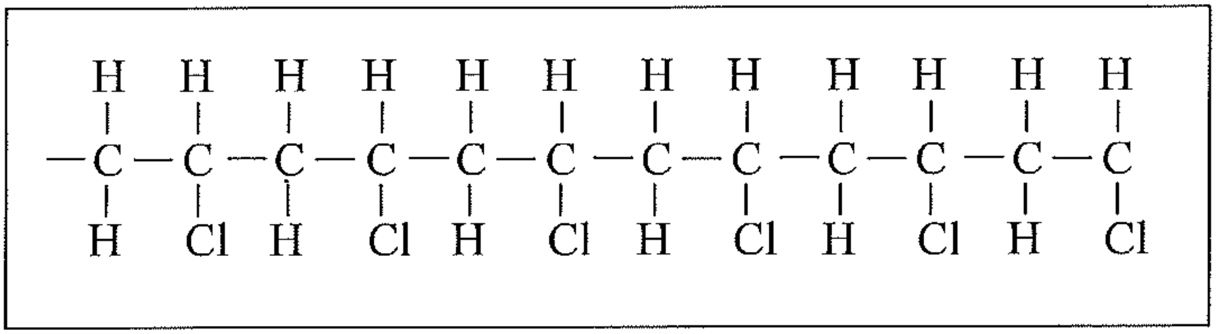
$$CH_3 – CH_2 – (CH_2 – CH_2)_n – CH_2 – CH_3$$

Figure 4. Structure of polyethylene

Polyethylene is attached to the pipe by adhesives or mastics which form a sticky bond between the pipe and the polyethylene coating or between the polyethylene and the original coating when repairs are made

4.2.6 Polyvinyl Chloride

Polyvinyl chloride is a thermoplastic polymer of vinyl chloride and is a rigid plastic (Figure 5). When used for pipeline coatings it is made more flexible by the addition of plasticizers such as phthalates (Figure 6). Polyvinyl chloride is no longer used as a pipeline coating. There may be some old pipelines in existence where this coating was used originally and observations in the past have shown that this material is subject to water leaching and loss of the phthalates under this condition in the field has led to coating failure (11, 12).



$$\begin{array}{cccccccccccccccccccccccc} & \mathrm{H} && \mathrm{H} && \mathrm{H} && \mathrm{H} && \mathrm{H} && \mathrm{H} && \mathrm{H} && \mathrm{H} && \mathrm{H} && \mathrm{H} && \mathrm{H} && \mathrm{H} \\ & | && | && | && | && | && | && | && | && | && | && | && | \\ - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} \\ & | && | && | && | && | && | && | && | && | && | && | && | \\ & \mathrm{H} && \mathrm{Cl} && \mathrm{H} && \mathrm{Cl} && \mathrm{H} && \mathrm{Cl} && \mathrm{H} && \mathrm{Cl} && \mathrm{H} && \mathrm{Cl} && \mathrm{H} && \mathrm{Cl} \end{array}$$

Figure 5. Structure of polyvinyl chloride (lower figure)

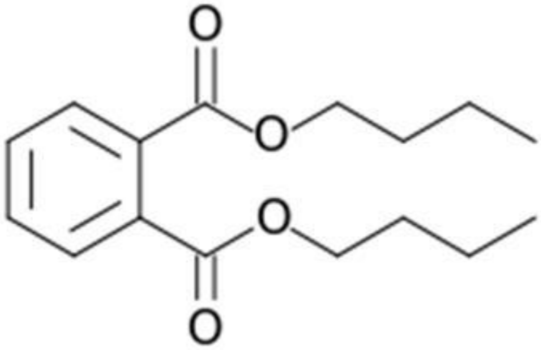


Figure 6. The structure of butyl phthalate

4.2.7 Polyisobutylene, Butyl rubber

Polyisobutylene or butyl rubber has a structure somewhat similar to polyethylene, except that each second carbon atom in the polymer chain is bonded to two methyl (CH3) side groups (Figure 7). Polyisobutylene is a thermoplastic material that has not been used extensively as a pipeline coating material in the past but there are some references to its use after the year 2000 primarily in adhesives and mastics (13).

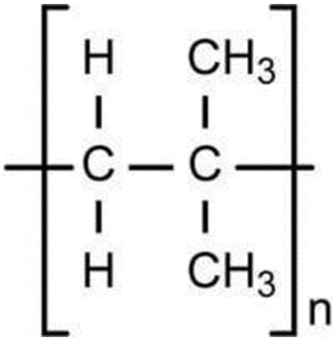


Figure 7. Structure of polyisobutylene

4.2.8 Polyurethane

Polyurethane is a polymer formed by reacting a di- or polyisocyanate with a polyol (Figure 8). For polyurethanes used for coating materials the aromatic di-isocyanate is replaced with an aliphatic or cycloaliphatic isocyanate in the synthesis reaction. Most poluyrethane coatings are thermosetting materials.

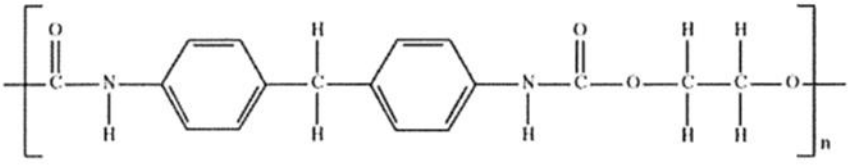
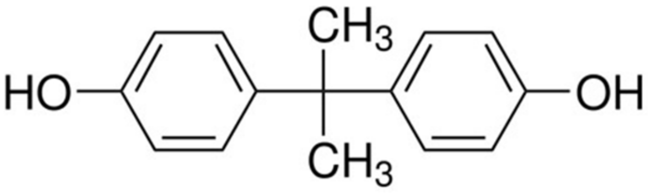


Figure 8. Structure of a polyurethane

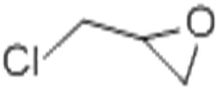
4.2.9 Fusion Bonded Epoxy

Fusion bonded epoxy coatings are made from a polymer consisting of bis-phenol A and epichlorohydrin (Figure 9). This polymer coating is applied electrostatically to the pipe as a powdered mixture which is then heated to a high temperature. The epoxy flows over the pipe surface and then hardens to fill all the crevices in the surface resulting in a tight bond with the steel pipe. They are thus thermoset coatings. Fusion bonded epoxy coatings are available as stand-alone coatings as well as a component in multi-layer coating systems. Other types of base resin (e.g. bisphenol F) also may be used in fusion bonded formulations to obtain various specified properties.

Bisphenol A



Epichlorohydrin



Structure of unmodified Bisphenol A type epoxy prepolymer

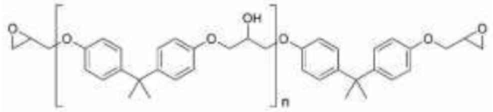


Figure 9. Components of fusion bonded epoxy

4.3 LEACHABILITY OF COMPONENTS FROM PIPELINE COATING MATERIALS

There is a concern that objectionable materials may be leached or may migrate from deteriorating pipeline coatings under abandonment. Herein are considered the materials that might leach from coatings.

4.3.1 Asbestos

Asbestos is not water soluble and so there should be no components that could leach from asbestos in coatings and migrate through soil via the soil water. Asbestos is a mineral so it does not contain organic molecules to cause additional concerns. However, asbestos can pose a health risk as it is classified as a human carcinogen and is the only known causative agent of mesothelioma, a cancer of the lining of the chest and abdomen (14). Abandoned pipelines with asbestos coating should not raise concerns about asbestos so long as they remain buried.

4.3.2 Asphalt/Bitumen

The components of asphalt are high molecular weight polyaromatic compounds (Table 1). As such they tend to have low water solubility which means that they will have low water leachability.

Four roofing asphalt samples did not leach any of 29 tested polyaromatic hydrocarbons (PAHs) and of six paving asphalt samples tested two contained detectable amounts of naphthalene and phenanthrene but both were below the drinking water limits of 0.015 mg/L (15). Leaching tests on reclaimed asphalt samples did not reveal the presence of 16 priority pollutant PAHs (16); PAH concentrations in leachate water from 210 asphalt samples were below the European limits of 0.1 µg/L for potable water (17).

Studies performed by NOVA Chemicals showed that leaching behaviours from asphalts are probably complex. Water leaching caused weight loss, probably due to loss/migration of soluble hydrocarbon from asphalt coatings but also water is absorbed by the asphalt and causes it to crack and break (18). Unfortunately in that report there was no analysis of the water to detect the presence of leachable components.

Asphalt leaching studies reported a 40% decrease in the leaching rate of total organics from asphalt over a 30 day period . The predicted half-lives of small molecular weight molecules like xylenes and toluene were 9 – 29 days while that of a larger molecule like the PAH, naphthalene, was 178 days (19).

4.3.3 Coal Tar

Analysis of roofing tar found PAHs similar to those present in asphalt (Table 2). Leachable components from coal tar were almost entirely all PAHs (19). In laboratory studies leaching rates of specific compounds showed little change over a 30 day period. This indicated that at the PAH components were held more strongly in coal tar than in asphalt and that it would take a longer time to deplete the coal tar of these components (Table 3). Calculated half life for naphthalene in the coal tar was 1,267 days while that of phenanthrene was 146 days (19).

Table 3. Leaching rate of selected components from coal tar*

Component	Leaching rate (µg/L/day)	
Component	T = day 1	T = day 30
Naphthalene	32	31
Acenaphthylene	0.3	0.1
Fluorine	11.8	11.8
Phenanthrene	43.4	37.8
Dibenzithiophene	2.9	1.7
Total leachate concentration	184	161

*Data taken from reference 19.

4.3.4 PCBs Present in Asphaltic or Coal Tar Coatings

PCBs have low water solubility and so would be expected to have low leachability from asphaltic and coal tar coatings. It is expected that PCBs in a hydrocarbon matrix will be retained by the hydrocarbon with little migration to the aqueous phase. A study of PCBs in asphalt road surface samples reported that PCB was concentrated in the binder at 1.76 – 1.81 mg/kg concentrations but at 55 µg/kg in the pavement and at 28 – 95 µg/kg in soil beneath the pavement (20). This work did not attempt to correlate the presence of other organics from the road with the location or concentration of the PCB in the soil. A study of soil contaminated with hydrocarbon and PCB found that vertical and lateral migration of PCB correlated with migration of the hydrocarbon through the soil. There was no incidence of PCB in the absence of the hydrocarbon (21).

4.3.5 Polyethylene

Potential leachables from polyethylene include solvents entrained in the material during manufacture, additives of antioxidants and processing agents used to preserve the lifespan and the effectiveness of use respectively. Water-extractables from polyethylene pipeline coatings have been shown to support microbial growth and sulfate reducing activity (11, 12). Gas chromatography - mass spectral analysis was not performed to identify individual components that could support microbial growth.

Fatty acids and their esters were extractable in water and in solvents while amides such as erucamide and antioxidants such as the sterically hindered phenolic, Irganox 1010, were not (28). Additionally, it was noted these water-leachable materials are present in polyethylene at ppm levels and do not constitute a major proportion of the product (22).

4.3.6 Polyvinyl Chloride

The solvents methyl isobutyl ketone, methyl isoamyl ketone, and toluene were major components of leachates from vinyl coatings (19). Benzylbutyl phathalate which is a plasticizer used to make the material supple and malleable was also found in leachate.

4.3.7 Polyisobutylene, butyl rubber

Reported leachables from polyisobutylene include aromatic and alkane species whose composition varied with the type of material. Non halogenated butyl products leached butylbenzene and other phenylalkanes. Brominated butyl products leached PAHs and benzothiazoles. Concentrations of butylbenzene and phenylalkane in leachates were 0.9 µg/L and 9.7 µg/l respectively (23).

4.3.8 Polyurethane

Toluenediamine or methylenedianilene were identified as leachables from polyurethane depending on the raw materials used to make the polymer i.e. whether made from toluene diisocyanate or methylene diphenyl diisocyanate (24). These two chemicals are highly water soluble their adsorption coefficient which are the logs of the ratios between their concentration in the soil and the concentration in the aqueous phase at adsorption equilibrium (log Koc) at 1.56 and 1.59 respectively, suggest that they will leach to water rather than be sorbed to soil organic carbon, and could be mobile in the aqueous phase. However, they are biodegradable and over the life of the pipelines they have most likely leached from the coatings (25).

4.3.9 Fusion Bonded Epoxy

The major leachable chemicals from epoxy pipeline coatings included primarily the solvents methyl isobutyl ketone, and *ortho*-, *meta*- and *para*-xylene. These solvents may be present in the epoxy from the manufacturing process but are quickly leached from the coating and their content may be reduced by 77% after 30 days in water (19).

4.4 PERSISTENCE AND FATE OF LEACHED MATERIALS

4.4.1 Asbestos

There are no materials expected to be leached from asbestos itself. As a mineral, asbestos will persist in the location of the buried pipeline.

4.4.2 Asphalt/Bitumen and Coal Tar

The PAHs present in asphalt, bitumen and coal tar have low water solubility. They also have high affinity for soil organic matter based on log Koc values in the range of 4..4 – 6.0. This means that they will tend to stay in the coating material. The minute amounts that could dissolve in soil water will tend to be sorbed to soil particles and will not migrate appreciably with ground water. A study of a coal tar contaminated site found the bulk of the PAHs was located in the original release location. There was some migration with surface and groundwater flow but concentrations were in the range of 0.04 – 3.7 µg/g and these concentrations were up to 3 orders of magnitude less than present at the original release location where the bulk of the contamination was located (26).

PAH molecules are subject to biodegradation by soil microorganisms under both aerobic and anaerobic conditions (27, 28, 29, 30, 31, 32). Initial steps of degradation of hydrocarbon molecules is conversion to an alcohol and then a carboxylic acid before mineralization to carbon dioxide and water (30).

4.4.3 PCBs Present in Asphaltic or Coal Tar Coatings

Like PAHs, PCBs have low water solubility in the nanogram to microgram per litre range . In the absence of a liquid hydrocarbon to dissolve and mobilize them, PCBs will remain with the asphalt or coal tar matrix. Like PAHs, minute amounts that might dissolve in water but the high adsorption constant (Log Koc = 6.4 – 8) suggests the PCBs will sorb to soil particles and will not migrate appreciably. Soil microorganisms can biodegrade PCBs over time albeit quite slowly. Biodegradation rates will depend on the PCB concentration, the presence of other hydrocarbon, the level of chlorination of the PCB, the microbial species present and the prevalence of aerobic or anaerobic conditions (33, 34, 35). Half-lives may vary from years to decades. Recent work has reported accelerated biodegradation of PCBs by microorganisms found in the root zone of certain pine and willow trees (33).

4.4.4 Polyethylene

Polyethylene coating on buried pipelines are expected to remain inert and unchanged. Exposure to the ultraviolet region of sunlight can cause oxidation of the polymer and reduction of the molecular size. Work performed by NOVA Chemicals succeeded in oxidizing polyethylene under the oxidizing influence of ozone and created a subset of molecules with a molecular weight of 10,000 compared to the molecular weight of the starting material being of 100,000. An abandoned buried pipeline is unlikely to experience conditions of exposure to high sunlight or ozone to effect such changes. Additives in polyethylene include fatty acids and fatty acid esters. The presence of fatty acids, like decanoic acid, which have Log Koc = 2.2 – 2.6 and solubility of 61.8 mg/L suggests that they could leach from polyethylene and enter soil moisture where they could migrate somewhat. Conversely higher molecular weight fatty acids, like octadecanoic acid, are slightly soluble in water (in the range of 0.6 – 1 mg/L) with a log Koc of 4.06 – 4.71 which suggests that it will bind to soil matter and not migrate. Additionally these materials will be biodegraded if they encounter soil microorganisms. Converting alkane molecules to fatty acids are early steps in their biodegradation by microorganisms (36, 37).

4.4.5 Polyvinyl Chloride

Polyvinylchloride is a large molecule which is not water soluble. Pipeline coatings of polyvinylchloride should remain inert. However, polyvinylchloride is fairly brittle and plasticizers have been incorporated in formulations in order to make it more malleable. A common plasticizer is dibutylphthalate (Figure 6). Evidence from pipeline excavations has shown that over time the plasticizer has leached out of the coating leaving it brittle and cracked leading to coating failure. Phathalates that have leached out of polyvinyl chloride coatings can migrate to soil and the groundwater. However, phthalates can be biodegraded by soil and sediment organisms under both aerobic and anaerobic conditions (38).

4.4.6 Polyisobutylene, Butyl Rubber

Polyisibutylene is sprayed onto the pipeline surface as a liquid after which it dries and cures into a solid coating. Pipeline coatings made of this material will remain inert. Solvents used in their manufacture and application or additives may be leachable from the finished product. Reported leachables include butylbenzene, phenylalkane and benzothiazole (39). These are expected to be biodegradable.

4.4.7 Polyurethane

The polyurethane chain is a composed of polyester linkages. Over time the coating of the abandoned pipeline could succumb to esterase enzymes which will break the chains (24, 40). This will take some time since polyurethane is a large molecule and cannot be taken inside the microbial cell where most degrading enzymes are located. Consequently such enzymes will have to be actively excreted by the organisms or be released when cells die.

Reported leachates from polyurethane include toluene diamine and methylene dianilene. These have been reported to exponentially decline in products after manufacture (33) and believed to be biodegradable (41). Consequently, their continued presence in abandoned pipelines that have been in use for over 50 years is questionable.

4.4.8 Fusion Bonded Epoxy

Leachates of solvents including xylenes and methyl isobutyl ketone from fusion bonded epoxy have been noted (AWWA). They are not expected to persist and over 50 years of the pipeline’s usage will have been leached by the time of abandonment. Leaching studies showed that their content may be reduced by 77% after 30 days in water (19).

4.5 TOXIC EFFECTS AND RELATIVE TOXICITY

There are some toxicity and health and safety concerns associated with pipeline coating materials.

4.5.1 Asbestos

Asbestos is classified as a human carcinogen. It is a fibrous material and inhalation of the fibers is viewed as causative agent of mesothelioma, a cancer of the lining of the chest and abdomen (14). As long as the abandoned pipelines with asbestos coating remain buried, there should not be an issue. However, the owner of the pipeline should be aware of location of coatings containing asbestos.

4.5.2 Asphalt/Bitumen and Coal tar

In asphalt and coal tar, the components of concern are PAH compounds. These chemicals are expected to be leached from coating materials over a long period of time and may still be present in the coatings at abandonment. The PAHs are all of concern but anthracene, chrysene, benzo(a)anthracene and benzo(a)pyrene were selected for focus as the most toxic representatives. For Benzo(a) pyrene as a representative PAH, 308 ppm in food over a period of 10 days caused birth defects. With mice 923 mg/kg in food over a period of several months caused problems in the liver and blood (42). The provisional environmental PAH limits recommended by the Canadian Council of Ministers of the Environment are 0.6, 6.2, 6.2 and 61.5 mg/L for Benzo(a)pyrene, benzo(a)anthracene, chrysene and anthracene, respectively (17). Relative toxicity ratings for Benzo(a)pyrene, benzo(a)anthracene, chrysene and anthracene, are 1, 0.013 – 0.145, 0.001 – 0.145 and 0.01 respectively (17).

4.5.3 PCB in Asphalt and Coal Tar

For PCBs present in asphalt and coal tar coatings, PCBs are recognized by the US EPA as a possible human carcinogen. PCBs cause cancer in other mammals plus other effects that affect the immune system, the reproductive system, the nervous system and the endocrine system. With respect to exposure limits Drinking Water Standards Maximum Contaminant Level Goal (MCLG): zero mg/L, Maximum Contaminant Level (MCL): 0.0005 mg/L, Health Advisory Level (HAL) for a child: none (43)

4.5.4 Polyethylene

Polyethylene is chemically inert. The leachable additives in polyethylene including fatty acids, and fatty acid esters. These chemicals may be skin irritants but they do not cause cancer nor are they hepatoxic. For the C18 fatty acid, stearic acid, the oral LD50 is 2,000 mg/kg in rats. For decanoic acid the LD50 is 10,000 mg/kg (44, 45).

4.5.5 Polyvinylchloride

The phthalates in polyvinylchloride coatings are leachable to soil and water. They can alter gene expression acting as a pseudoestrogen. They are toxic in humans if oral exposure greater than average daily intake (ADI) of 0.2 mg/kg/day dibutylphthalate (46)

4.5.6 Polyurethane

Fully reacted polyurethane polymer is chemically inert. No exposure limits have been established in the U.S. by OSHA (Occupational Safety and Health Administration) or ACGIH (American Conference of Governmental Industrial Hygienists). It is not regulated by OSHA for carcinogenicity.

The leachate from polyurethane, toluene diamine, when fed at 50 and 100 ppm to inbred, barrier-raised F344 rats for 2 years caused an increase in the occurrence of hepatic and mammary tumors (47). EPA has classified toluene-2,4-diamine as a Group B2, a probable human carcinogen and assigned an oral cancer slope factor of 3.2 (mg/kg/d) (48).

The other leachable from polyurethane, methylene dianiline, also causes cancer. The US Occupational Health and Safety Administration (OSHA) has set exposure limits of 10 parts per billion for an 8 hour time weighted average and a short time exposure limit of 100 parts per billion (49).

4.5.7 Polyisobutylene, Butyl Rubber

There is not much information available for butylbenzene as a representative phenylalkane or for benzothiazole (36, 50). The Safety Data Sheets note that little toxicity data is available. While the US EPA’s DRINKING WATER STANDARDS AND HEALTH ADVISORIES TABLE does not include benzothiazole, it does include butylbenzene but there are no units or values for this compound in the list (51).

4.5.8 Fusion Bonded Epoxy

Methyl isobutyl ketone is leachable from fusion bonded epoxy. No reported instances of carcinogenicity were found for this compound but effects in liver, blood and kidney were reported (52) The American Conference of Governmental Industrial Hygienists established a Threshold Limit Value with a Time weighted Average of 200 ppm for Biological Exposure Index.

4.5.9 Relative Toxicity Rating of Pipeline Coating Materials

The relative toxicity of coating materials at abandonment is based on the nature of the toxic leachable component as well as its leachability, its toxic effects, and/or exposure limits. The data from leaching studies has shown that the toxic components of most pipeline coatings are readily leachable. Therefore at abandonment there will be little, if any, of these leachable components left in the coatings. Only the PAHs found in the asphalt and coal tar coatings, and possibly PCBs added to such materials, are expected to be still present by the time of abandonment. This is due to the fact that PAHs and PCBs have low water solubility and high affinity for the carbon matrix of the coating material.

PAHs were rated for their toxicity by relative toxicity (53). The relative toxicity ratings of PAHs are as follows:

Benzo(a)pyrene = 1

Benzo(a)Anthracene = 0.013 – 0.145

Anthracene = 0.01

Chrysene = 0.001 – 0.0044

Since benzo(a)pyrene was rated most toxic, if it is present in the coating material, then that material is considered the most toxic. The amount of benzo(a)pyrene present in individual coating materials will account for its toxicity. A comparison of the PAHs present in coal tar and in asphalt found the levels in coal tar to be 1000 times greater than in asphalt. For example the level of benzo(a)pyrene in coal tar pitch was 18,100 mg/kg while in asphalt the level was 3.2 – 5.3 mg/kg (54). Therefore the concentration of PAHS and of benzo(a)pyrene coatings pipeline coatings made from coal tar and coal tar epoxies would be considered the most toxic and the most worthy of concern followed by the asphalt coatings. For other coating materials, while they may contain toxic constituents, most will have leached or migrated out of the coating by the time of abandonment. In partial support of this is the observation of leaching of the phthalate ester plasticizers from polyvinyl chloride films where they were used to make the plastic malleable and pliable (55).

The summary information on the composition, leachability and toxicity of the pipeline coating materials is collected in Table 4.

Coating material	**Composition**	**Leachable component of concern**	**Water solubility (mg/L)**	**Potential for transport in groundwater Log K_{oc} Calculated or (measured)**	**Toxic effects on humans or wildlife**	**Relative toxic ranking**	**Environmental Limits**
Asbestos	Asbestos fibers	–	Insoluble	–	Asbestosis; mesothelioma	–	
Asphalt	High molecular weight hydrocarbon	PAHs Anthracene Chrysene Benzo(a)anthracene Benzo(a)pyrene	4.34E-02 1.60E-03 1.60E-03 9.40E-03	4.371 5.599 5.841 5.986 From reference 56	308 parts per million (ppm) of PAHs (specifically benzo (a) pyrene) in food for 10 days (short term exposure) caused birth defects. Mice exposed to 923 ppm of benzo (a) pyrene in food for months caused problems in the liver and blood. From reference 42	Anth = 0.01 Chr = 0.001 – 0.0044 BAA = 0.013 – 0.145 BAP = 1 From reference 53	Anthracene, Benzo(a)pyrene 0.015 µg/L for aquatic life From reference 53
Coal tar	High molecular weight hydrocarbon	PAHs Anthracene Chrysene Benzo(a)anthracene Benzo(a)pyrene	4.34E-02 1.60E-03 1.60E-03 9.40E-03	4.371 5.599 5.841 5.986 From reference 56	308 parts per million (ppm) of PAHs (specifically benzo (a) pyrene) in food for 10 days (short term exposure) caused birth defects. Mice exposed to 923 ppm of benzo (a) pyrene in food for months caused problems in the liver and blood. From reference 42	Anthracene = 0.01 Chrysene = 0.001 – 0.0044 Benzo(a)Anthracene = 0.013 – 0.145 Benzo(a)pyrene = 1 From reference 53	Anthracene, Benzo(a)pyrene 0.015 µg/L for aquatic life From reference 53
PCBs present in asphaltic or coal tar coatings	Coal tar, high molecular weight hydrocarbon; PCBs	PCBs PAHs (See asphalt and coal tar above)	2.7E-12 -4.2E-10	6.4 – 8.0	PCBs are recognized by the US EPA as possible human carcinogen. PCBs cause cancer in other mammals; other effects include the immune, reproductive system, nervous system and endocrine systems.		Drinking Water Standards MCLG: zero mg/L MCL: 0.0005 mg/L HAL(child): none From reference 43
Polyethylene	Linear polymer	Fatty acid and fatty acid esters	C10 fatty acid: 2.2 – 2.6 C18 fatty acid: 0.6 – 1.0	C10: 4.07 – 4.71 C18: 4.708	C10 LD50 for rat = 10,000 mg/kg C18, LD50 for rat = 2,000 mg/kg		
Polyvinyl chloride	Polymer of vinyl chloride + additive of phthalic acid derivative	Dibutyl phthalate	11.2 mg/L	3.14 – 4.17	Can alter gene expression acting as a “pseudo estrogen”		Oral exposure ADI 0.2 mg/kg/day DBP

							Health Canada estimated a tolerable daily intake of 0.0625 mg/kg body weight/day estimated total average daily intakes of dibutyl phthalate for the various age groups in the Canadian population range from 1.9 to 5.0 µg/[kg (b.w.)·d]
Polyisibutylene	Butyl rubber	PAHs (See asphalt above) Butyl benzene Phenyl alkane benzothiazole	 11.8 mg/L insoluble Low solubility	 3.9 3.9 2.47	Butylbenzene: No information available Benzothiazole: Oral LD50 in mouse = 900 mg/kg; Intraperitoneal LD50 in mouse = 100 mg/kg		
Polyurethane	Polymer containing polyester linkage	Toluene diamine Methylene dianilene		1.56 1.59	Both cause cancer.		EPA assigned toluene diamine an oral cancer slope factor of 3.2 mg/kg/day. NIOSH recommends that workers not breathe air containing more than 0.03 mg/m3 during a 10 hour workday
Fusion bonded epoxy	Epoxy polymer made from bis-phenol A and epichlorohydrin.	Xylenes, methylisobutylketone		Estimated Log Koc = 11. also noted that it will readily vaporize.	Methyl isobutyl ketone not carcinogenic but may affect liver, blood and kidneys.		American Conference of Governmental Industrial Hygienists established a Threshold Limit Value with a Time weighted Average of 200 ppm for Biological Exposure Index
Primer, adhesive used with polyethylene, epoxy and PVC coatings	Butyl rubber Saturated aliphatic hydrocarbon		See butyl rubber above Insoluble	See butyl rubber above	See butyl rubber above	See butyl rubber above	See butyl rubber above

Table 4. Summary Matrix of Pipeline Coating Materials

5.0 CONCLUSION

Pipelines have been in place for over 50 years with no evidence or complaints of adverse effects of coating materials. Abandonment of pipelines in place with no maintenance means that the pipe and its coatings are subject to degradation under environmental forces. The pipes are buried so there will be no effects from sunlight and its attendant UV radiation. The buried conditions will mean that the environment of the pipeline could be a combination of aerobic and anaerobic depending on the season and the available rainfall. Any degradation that occurs has probably been ongoing already over the life of the pipeline and may accelerate marginally over time. However, it is expected that microbes in the vicinity would degrade the materials that could leach from the pipeline coatings.

The PAHs and other aromatic molecules as well as alkane molecules found in pipeline coatings have been reported to biodegrade effectively under aerobic conditions (28, 30) and under anaerobic conditions using sulfate (27, 31) or nitrate (28, 29) as electron acceptors. The question is how much biodegradable material is left on the pipe after 50 years of service. Since water leaching of organics has been shown to occur with pipeline coatings, the same phenomenon has been ongoing from the coatings to soil and soil moisture over the life of the pipeline. Based on leaching rates observed in laboratory studies (19), leachable toxic components will have been depleted form coating materials. Only the asphalts and tars are likely to have retained PAHs because their leaching rates are so much slower.

Leaching rates will also be impacted by the amount of leachable material in the coating material initially. The higher content of PAHs in coal tar pitch compared to asphalt (54) points to coal tar as the more toxic coating material.

In summary, by the time a pipeline is abandoned after approximately 50 years of service, the following are expected to apply:

- Lower molecular weight hydrocarbons will have leached from coating materials.
- Higher molecular weight hydrocarbons (i.e. PAHs) may still be present in coating materials.

- Higher molecular weight hydrocarbons have low solubility in water and will remain attached to other hydrocarbons on coating or within coating matrix.

- Because of low water solubility and high affinity for organic carbon, higher molecular weight hydrocarbons will tend to sorb to soil organic matter in the locality of the abandoned pipeline.

- The hydrocarbons that are leached from pipeline coating materials will tend to biodegrade over a long time period. Degradation intermediates are not expected to accumulate as they are leached.

6.0 RECOMMENDATIONS

1. The amount of leachable material still left in pipeline coatings at abandonment should be confirmed by sampling and analysis. A protocol should be developed for sampling in terms of pipeline coating material and the soil environment of the buried pipeline. Ideally soil sampling location should be within 30 cm below the pipe at the 6 o'clock position of the pipeline. Extraction of the soil and analysis of the extract could be based on EPA methods.
2. It has been reported that PCBs were included in coatings manufactured in the period 1940s – 1970s. Asphalt and coal tar coatings from pipelines built in that era should be analysed for the presence of PCBs when plans are made to abandon those pipelines.
3. Samples obtained from pipeline digouts should be catalogued as to composition and age. These samples should be analysed for residual composition and subjected to leachate tests to determine rates of release of residual components. A database of such information would be an asset in responding to criticisms of in-situ pipeline abandonment.

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