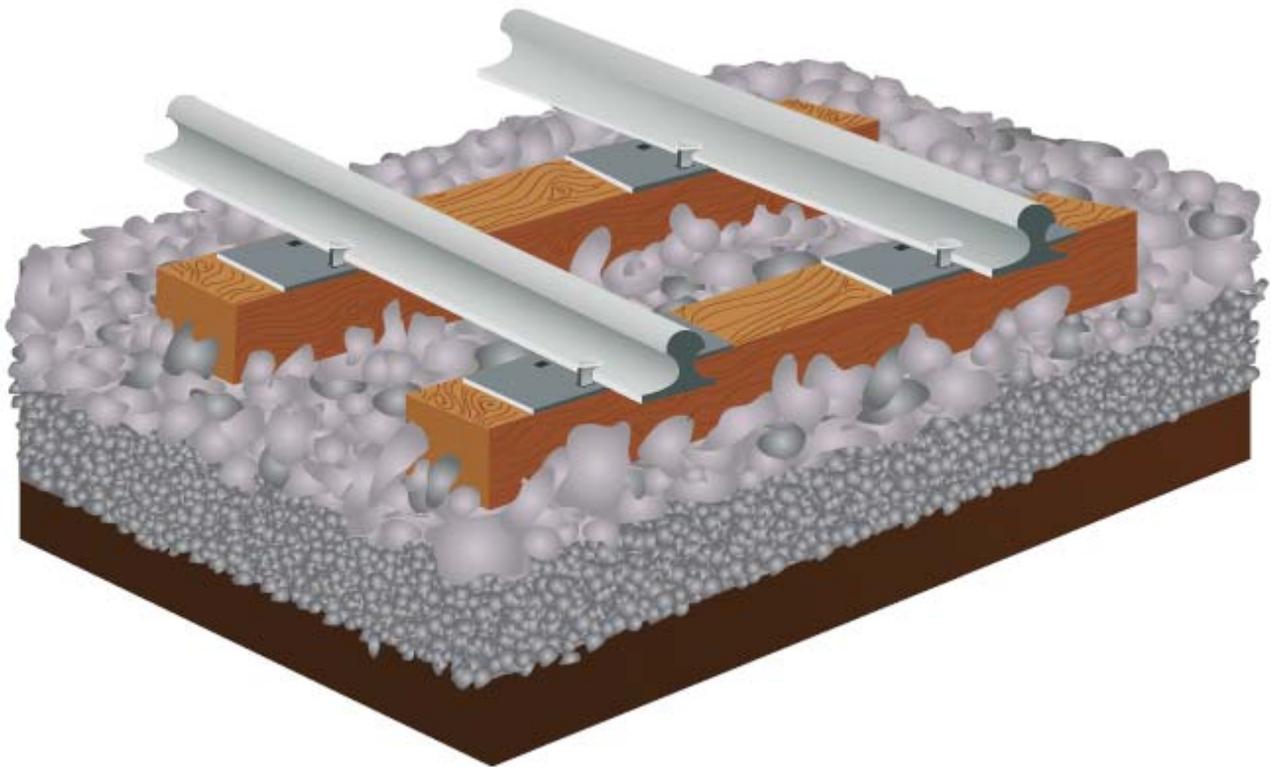


TECHNICAL BACKGROUNDER: LOW CARBON FUELS

Guidelines for the Safe and Beneficial Use of Mixed Fossil & Biomass Fuel Sources in the Cement Industry,
with a Focus on Railroad Ties,



March 15, 2012

Prepared by A.J. Chandler & Associates Ltd. with contributions from Lafarge

Reviewed by Ted Grandmaison, Queen's University

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Executive Summary

Lafarge has been engaged in a program called Cement 2020 that aims to improve the sustainability of the cement industry using Lafarge's Bath Cement plant, located west of Kingston, Ontario, as a case study. Through this program, and a multi-stakeholder approach, a Protocol was developed in 2011 to pre-screen cement kiln fuels to ensure that they meet the environmental and social criteria necessary for sustainability. Those that met these criteria (collectively deemed "low carbon fuels") and were also economical were recommended for additional testing and review. Under the precautionary principle, the need for a deeper technical review of one of these fuels in particular, railway ties, was identified. A.J Chandler & Associates was engaged to undertake this review and prepare a report. Many of the findings and recommendations of this report are applicable to the other low carbon fuel types.

The report outlines the historical and current uses and characteristics of railway ties, particularly those at the end of the tie's service life of 30-50 years. The cement industry requires significant thermal energy to produce clinker, the intermediate product prior to cement. There are not enough Canadian ties replaced each year to supply the Canadian cement industry's full fuel needs but this material can offset part of the fuel requirements. Railway ties tend to have heating values much higher than other forms of used wood and, as such, they represent a promising source of fuel.

The elevated higher heating value arises from the presence of the creosote in the railway ties. Creosote has a long history of use in wood preservation and greatly extends the service life of the tie. Creosote is most commonly derived from the distillation of coal; extensive physical and chemical analyses of creosote are presented in the report. Creosote is comprised of a large variety of complex organic compounds including poly aromatic hydrocarbons. Incorporating creosote as part of the kiln fuel, requires the same application of combustion engineering principles that are necessary to ensure that any fuel is used safely.

In order to determine the engineering requirements to ensure safe use, the results of previous testing at cement plants and industrial boilers, where railway ties are in successful use, were directly or indirectly reviewed. The report also presents a brief survey of combustion principles.

The report concludes that railway ties can be used safely to fuel cement plants and 11 recommendations are made (see page 42) to promote the conditions that ensure the safe use of both railway ties and other low carbon fuels – in actual practice. The report adopts the precautionary principle by reviewing the available science first and then recommending field testing prior to seeking the necessary regulatory approvals needed for their permanent use. A summary of test results is provided in the table below.

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Overview of Test Results

Process	Temperatures (°C)	Residence Times (Seconds)	Results	Government Permits
"Burn Barrel"	370-740	<< 1	Unacceptable, Emissions 1500- 3800x higher than incinerators	Prohibited
Wood Fired Industrial Boiler	920-1100	2.5-3	No increase in emissions	Permitted
Coal Fired Industrial Boiler	1100	3	Lower emissions	Permitted
Cement kilns	1450	4-16	Expecting same or lower emissions	Permitted (seeking test permit at Bath)

The report was prepared by A.J. Chandler & Associates with contributions from Lafarge Canada and others. The reports relied upon are provided with references including internet references where feasible. It has been reviewed by Dr. Ted Grandmaison, Professor Emeritus, Department of Chemical Engineering, Queen's University. See the back page for more information about the author and other contributors.

Introduction

As part of the Cement 2020 program, funded in part by the Asia Pacific Partnership and Natural Resources Canada, Lafarge commenced two parallel but inter-related tasks in the spring of 2011. The first was to seek proposals from the local business community for cleaner, sustainable, local fuels to replace the coal and petroleum coke in use by the cement industry. The second was to work with a multi-stakeholder task force to establish protocols for the assessment of candidate fuels to determine their relative sustainability (“greenness”). One of the proposals for a replacement fuel was from a First Nations owned company that had a contract to manage used railway ties from a major railway company operating in Eastern Canada. Other replacement fuels proposed include: construction & demolition wood-based materials; pre-consumer materials; and post-consumer/post-diversion surplus materials – all of which have been assessed for their suitability as a fuel in the cement industry.

A task force assembled by Lafarge under the auspices of the Cement 2020 project had created a draft Green(er) Fuel Protocol (for more on the Protocol and selected fuel types, refer to Appendix B) to assess the merits of various fossil fuel alternatives. The Protocol was initially developed without reference to any specific candidate fuel in order to ensure that it was a dispassionate and transparent assessment of all potential fuels. When the Protocol was later used to assess a variety of alternative fuels, including railroad ties, it indicated that many of these fuels would likely constitute greener alternatives than the current fuels. The preliminary evaluations require further validation, but they serve to define areas needing further study. The potential benefits of one fuel, railway ties, suggested that it merited a deeper review based upon the benefits identified during the preliminary review:

1. Being comprised of 85% wood, 15% fossil fuel derived substances, railroad ties have a higher heating value than many biomass fuels, virgin or non-virgin, and under existing carbon trading protocols the 85% biomass content would be considered greenhouse gas (GHG) neutral. As such, railway ties were considered to handily meet the low carbon fuels criteria (see page 9 for a definition of low carbon fuels).
2. Railroad ties can be delivered to a railway siding equipped processing site on or near Lafarge’s Bath plant site thereby taking advantage of a lower environmental footprint transportation mode and minimizing truck traffic.
3. Landfilling of railway ties results in the emissions of methane, a potent GHG. Using the ties in place of virgin coal and other fossil fuels should result in a net reduction in GHG emissions **beyond** the neutral emission of GHG associated with the biomass fraction noted earlier. At least one Life Cycle Assessment¹ has been completed and concluded that using ties as fuel will provide significant GHG benefits as compared to landfill.
4. Analytical data indicates that, compared to coal, the railway ties are lower in non-combustible constituents of concern (eg trace metals). Thus, in addition to lower GHG emissions, other emissions should be lowered.

¹ Smith, Stephen and Chris Bolin, 2010. Creosote-Treated Ties, End-of-Life Evaluation,, February 18, 2010. Available at http://www.rta.org/Portals/0/Documents/Research%20Paper%20&%20Articles/RTA%20Sponsored%20Research/Creosote%20Tie%20Evaluation%20Article%20_4_.pdf

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5. Development of a local, processing business creates local employment with the potential that this employment may extend, particularly in this case, to more underemployed sectors.
6. The 15% fossil fuel component of railway ties is derived from coal, a fuel already in use at the Bath cement plant. The experience using coal suggests that the fossil fuel component will perform well in the system.
7. Railway ties are an economical fuel source and the savings can justify investment in a new, separate fuel delivery system at the cement plant – a delivery system that can be used in the future for multiple low carbon fuel stocks including those with a less favourable economics.
8. Replacement of imported fuels with Canadian/Ontario fuels increases the value the cement plant provides to its broader community while enhancing the plant's own economic viability. For example, as the plant expands its use of local, low carbon fuels on a permanent basis, assuming the success of the proposed demonstration program, it ensures the viability of the 3rd party supply, separation, processing, and transportation infrastructure that would be created. Use of the local, low carbon fuel by a large energy user will provide the economies of scale that will enable other, smaller fuel users to be supplied as well.

The use of a biomass fuel at Lafarge's Bath Cement Plant, located west of Kingston, was demonstrated in a trial conducted in October, 2010. The results of that testing indicated that biomass fuels are feasible and desirable for the sustainability of the Bath cement plant. While the Green Fuel Protocol and the biomass trial suggested that railway ties could be used successfully as a low carbon fuel, the task force urged that the precautionary principle be followed through additional testing of the use of railway ties prior to permanently adopting ties as a fuel source. Further, feedback from the Community Liaison Committee requested additional information about the use of railway ties to enable them to inform the local community. The committee wanted the information so that they would be more capable of participating in the review of the use of ties as fuel. Specifically, and anticipating the primary source of questions expected from the community, the Committee wished to learn more about creosote and its performance in a cement kiln. It was the Committee's opinion that many of the recommendations and conclusions that could apply to the use of railway ties would also apply to other mixed fuels such as construction & demolition wood.

Lafarge approached A.J. Chandler & Associates Ltd. to review the known science and policy papers regarding the use of railway ties.

There were a number of objectives for the report including:

- Providing basic, background information about railway ties;
- Describing the conditions necessary to ensure efficient combustion, particularly with respect to railway ties;
- Reviewing available results from the use of railway ties at other facilities to corroborate the initial findings of the Green(er) Fuel Protocol and to identify information that would indicate against their use;
- Reviewing the findings from the 2010 biomass demonstration at Lafarge, Bath as they might be applicable to other low carbon fuels;
- Reviewing the existing policies governing the disposal or re-use of railway ties in various jurisdictions; and, developing recommendations on the safe, beneficial use of railway ties in the cement industry.

Energy Use in Cement Production

The cement industry uses vast amounts of energy in cement kilns to convert raw materials such as limestone and clay into an intermediate product known as “clinker” which is discharged from the kiln. After leaving the kiln, clinker is cooled, ground to a fine powder and blended with gypsum to form Portland Cement. The high temperatures required for the clinker forming chemical reactions are achieved by the combustion of fuels in the kiln. As the carbon and hydrogen present in the fuel are oxidized to carbon dioxide [CO₂] and water vapour, energy is released. Depending upon the particular cement process, between 3,000 and 6,500 MJ of fuel supplied energy is required to produce a tonne of clinker. Most kilns are fired with coal although many operators blend coal with petroleum coke and to a lesser extent natural gas or oil.

All fuels, with the possible exception of natural gas, contain substances that are not completely converted to gaseous constituents when burned. These materials, categorized as ash, remain after the fuel is consumed, much like the residue in a fireplace. In the cement kiln, **virtually all ash present in the fuel, or for that matter in the raw materials, becomes incorporated into the clinker**².

A notable exception in the referenced table is mercury. As a semi-volatile metal, mercury is liberated from the kiln in vapour form, and may be released from the stack if not removed in the air pollution control system. Coal typically contains 0.17 ppm of mercury³ as do the other raw materials introduced into the process. Some dust also escapes the kiln and is captured in the air pollution control system. This material, known as cement kiln dust, [CKD], is partially recirculated to the process⁴ with the balance being discarded to maintain the appropriate chemistry in the kiln.

Coal, oil and natural gas are categorized as fossil fuels. Burning large quantities of fossil fuel contributes to CO₂ emissions that add to greenhouse gas [GHG] emissions. The cement industry is a large contributor to world-wide CO₂ emissions with typically 40% of the emissions resulting from fossil fuel combustion and 50% from the chemical reactions in the kiln (i.e. calcination of limestone). The GHG emissions include CO₂, N₂O and CH₄ resulting from the combustion of carbon-based fuels in the cement kiln and other onsite combustion equipment. It should be noted that N₂O and CH₄ emissions are 1000 times lower than CO₂ emissions when burning most solid fuels, so the emphasis in this report is on CO₂ as the major GHG component. The cement



Artist's rendering showing the flame inside a typical cement kiln. The Bath plant kiln is 18`in diameter and 655`long.

² Lafarge Cement and Hyndman & Associates, 2011. Lafarge Biomass Demonstration Project Summary Report. See §4.1.2 Metals Balance Table 2. Available at http://www.cement2020.com/sg_userfiles/Lafarge_Biomass_Demonstration_Summary_Report_2011.pdf

³ Tewart, Susan J., Linda J. Bragg, and Robert B. Finkelman, 2005. Mercury in U.S. Coal—Abundance, Distribution, and Modes of Occurrence. Issued by the U.S. Geological Survey as Fact Sheet 095-01 Available at: <http://pubs.usgs.gov/fs/fs095-01/fs095-01.pdf>

⁴ Since 2010, all of the CKD collected at the Bath Cement Plant is re-circulated to the kiln process.

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kiln is the most significant GHG source on site. The direct CO₂ emission intensity, [kg CO₂ per MJ of energy input], of fuels depends upon the carbon content of the fuel. This varies by both the type of fuel and the geologic origin of that fuel. The major fuel used in the kiln is coal. Bituminous coals range from 62 – 83% carbon depending upon the grade and source. Conversely, biomass fuels generally have between 45 - 50% carbon⁵.

To improve the sustainability of the cement industry– and specifically the GHG aspects of cement operations – operators search for low carbon fuels that can reduce emissions and also improve the economics of their operations. Clearly, using locally derived biomass fuel has the potential to reduce CO₂ emissions. Typically biomass fuels are ultimately derived from:

- Woody forest residue, fuelwood, mill residues, short rotation crops; silviculture; and,
- Non-woody agricultural crops, crop residue, processing residues.

Definitions

Virgin biomass fuel, in the Cement 2020 project context, refers to biomass derived directly from plant and forest sources that is used as a fuel source. *Non-virgin biomass fuel* refers to cases where the biomass is first used as a product and, at the end of its useful life, is made available as a fuel source. The term *low carbon fuels* is intended to describe fuels that, while they may have fossil fuel derived components, are predominantly comprised of biomass, virgin, and non-virgin, and/or have other characteristics that ultimately lower the carbon footprint/carbon emissions the fuel. While there are other forms of biomass fuels such as animal waste and sewage sludges, the focus in this phase of the Cement 2020 project is on the fuels identified above.

⁵ Schlesinger, W.H. 1991. Biogeochemistry, an Analysis of Global Change. New York, USA, Academic Press. As cited in <http://www.fao.org/forestry/8758/en/>.

Low Carbon Fuels – the Railway Tie Example

Based on the findings of the Energy Farm project and the Cement 2020 project⁶, it is technically possible to obtain purpose grown virgin biomass sufficient to meet the individual needs of the Bath Cement plant. However, this approach has limitations. The lower fuel quality of this biomass fuel limits the maximum co-fire rate to approximately 20%. There are lingering questions about the potential land use changes that would be necessary to grow sufficient biomass. Furthermore, biomass fuels cannot be purpose grown at an affordable price for the foreseeable future, and particularly not at a price that would attract capital investment in processing and fuel delivery systems at an energy user's site.

One source of low carbon fuel that may prove beneficial for the cement industry is used railway ties. Environment Canada⁷ estimated that there were over 100 million railroad ties in service in Canada in 1999 and suggests that 1.4 million new ties are put into service each year. This amounts to approximately 147,000 m³ of ties being produced each year. Allowing for only limited expansion of rail lines a large portion of these new ties are likely replacements for ties removed from service each year. A decade old estimate⁸ suggested that 1.45 million m³ of treated wood wastes could be accommodated in Canadian cement kilns. A more current estimate can be based upon 2008 Canadian operating data⁹ which indicates that the average amount of energy used in the Canadian cement industry was 3.7 GJ/tonne of clinker produced. The energy available¹⁰ from railway ties is approximately 15.5 GJ/m³ based upon data presented later in this report. If the estimated 1.4 million ties replaced all the current fuel in a kiln, over 600,000 tonnes of clinker could be produced. This represents a small fraction of the total annual energy needed by the industry.

The railroad ties used in Canada are treated with a mixture of creosote and heavy oil to preserve the wood and ensure an operational life of 25 – 30 years. This coating leads to concerns about any material that it is used to treat, not to mention the fact that treated ties have an odour that becomes more pronounced in the warmer months of the year. Given the concerns about creosote treated wood, a guidance document¹¹ was created by Environment Canada. The document contains several recommendations that severely restrict the use of these materials after their intended function has ceased.

⁶ Lafarge Canada, Bath Plant, Sustainable Ventures Inc. and Hyndman & Associates Inc. 2011. Renewable Fuels for Cement Manufacturing - A Review of Activities Undertaken to Assess Energy Crop Biomass Fuel Production for Use in Lafarge's Bath Plant (2008-09). Draft for Public Comment available at: http://www.cement2020.com/sg_userfiles/Lafarge%20Energy%20Farm%20Report%20Final%20Draft%20for%20Comment%20Nov%2014%202011.doc

⁷ Environment Canada, 1999. Strategic Options for the Management of CEPA-Toxic Substances from the Wood Preservation Sector. Available at: <http://www.ec.gc.ca/Publications/B6EDB2D6-DAEA-415F-BBF3-EC5C689075E9/p60.pdf>

⁸ WRAP, 2007. Options and Risk Assessment for Treated Wood Waste. Written by: TRADA Technology & Enviros Consulting Ltd. Published by: The Waste & Resources Action Programme, June 2005. Available at: http://www.wrap.org.uk/downloads/Options_and_Risk_Assessment_for_Treated_Wood_Waste.bcbea09f.2237.pdf cites discussion of limitations for chromium in clinker and suggests that this could limit input to 10-15% of the energy demand in a kiln - Cooper, P. A. 2003. A review of issues and technical options for managing spent CCA treated wood. Proceedings of the AWPA Annual Meeting, AWPA, Boston, Massachusetts, April 27th-29th. Bernardin, 1995 is also cited suggesting that Canadian kilns could accommodate 1.45 million m³ of CCA TWW.

⁹ Cement Association of Canada, 2011. 2010 Canadian Cement Industry Sustainability Report. Available at: <http://www.cement.ca/images/stories/ENGLISH%20FINAL%202010%20SD%20Report%20Mar17.pdf>

¹⁰ This example assumes a tie provides 21.5 – 22.8 MJ/kg of energy and is approximately 0.105 m³ in volume. Thus 9.5 ties provide 1 m³ of fuel, and weighs about 700 kg resulting in 15 – 16 GJ/m³.

¹¹ Environment Canada, 2004. INDUSTRIAL TREATED WOOD USERS GUIDANCE DOCUMENT Guidance for the Industrial Treated Wood User Concepts to include in an Environmental Management System concerning the use of Wood treated with CCA (chromated copper arsenate), ACA (ammoniacal copper arsenate), ACZA (ammoniacal copper zinc arsenate), Creosote and Pentachlorophenol. EPS 2/WP/7 E

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The wood should not be used in residential interiors, nor where it may become a component of food or animal feed. It should be kept out of contact with drinking water. It should not be burned. One must conclude that this last recommendation is specifically targeted at low temperature, open burning of treated wood since the document also incorporates measures suggesting the energy can be recovered as a beneficial use of end-of-life ties. In fact, the guidance suggests that the waste hierarchy should be applied: reuse - recycle - energy recovery - disposal. Since ties have a very limited re-use potential the last two alternatives represent the most likely disposition for the ties. The document notes that in 2000 12% of railway ties were disposed in landfills. Over the intervening years landfill capacity and additional concerns about the nature of the material have caused many landfills to reject these materials. This leaves energy use as the preferred alternative.

The guidance document states that pulp and paper mills in Prince George and Trois-Rivières have approval to accept creosote treated wood for use in their power boilers. Two co-generation systems in Williams Lake and Lytton BC also accept creosote treated wood and some creosote treated wood is shipped to co-generation facilities in the US. The St. Lawrence Cement facility in Joliette QC is permitted to accept all types of treated wood.

With the availability of end of life railway ties, and the apparent acceptability of their use, at least in some jurisdictions, the questions become:

- What are the potential effects including benefits of using railroad ties in a cement kiln?
- What is the best method of verifying the anticipated effects?
- What guidelines can be applied to maximise their effective use?

To answer these questions it is necessary to examine the material that is being considered as a fuel: its origin, availability, and nature along with the potential effects of converting this material to energy in various systems, including cement kilns. These issues are addressed in the following sections.

Railroad Ties – The History and Nature of their Use

Most of us have seen transportation systems that run on steel rails and if you have examined the rail bed closely you will see that the rails are fastened to a structural support system that spread the loads into the surrounding soil. Since the earliest days of railway building the structural support members were manufactured from wood. At various times over the last 100 years various alternatives to timber ties have been tried, not always successfully, suggesting that, for the foreseeable future, timber will be used to support the rails.

Magee¹² notes that railway track consists of two lines of rails supported by tie plates, ties and ballast, as illustrated in Figure 1. The rails must resist the contact pressure of the wheels and be stiff enough to distribute the wheel load over several ties but must also be capable of flexing under load and to resist fatigue failures. Tie plates, essentially a steel plate that reduces abrasion on the tie and helps hold the correct separation between the rails (gage), sit in an area of the tie that has been notched to allow the plate placement. The tie plates have tabs to position the rail and are affixed to the ties with spikes.

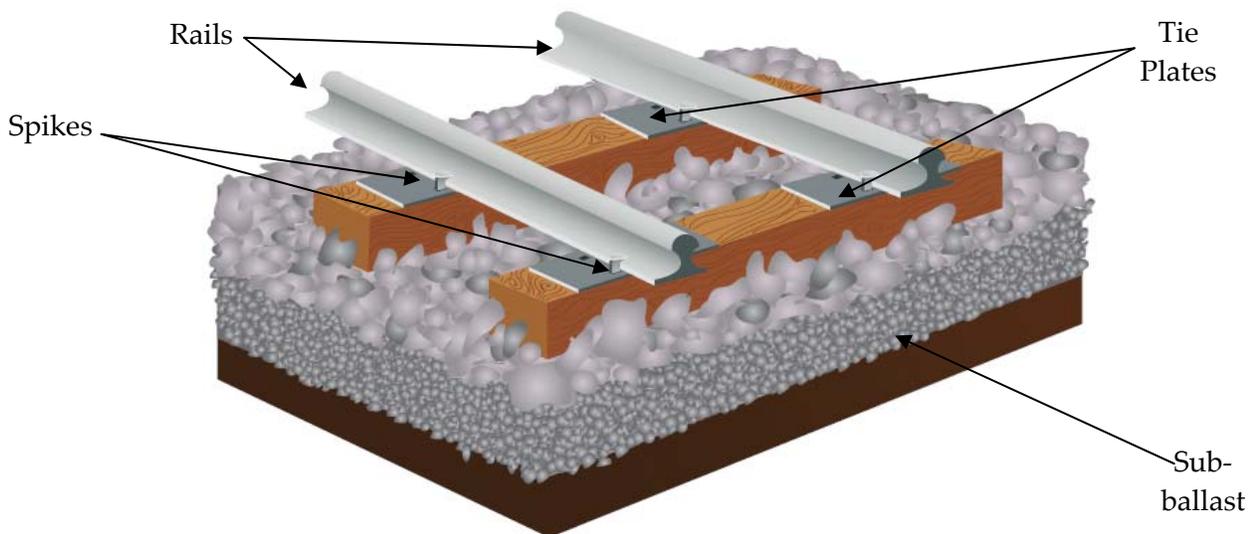


Figure 2 Schematic of Railroad Tie Installation with Rails, Tie Plates, Ties, and Ballast Shown

The rails are spiked to the tie through holes in the plate. The ties sit on a layer of top ballast laid over the sub-ballast. The sub-ballast is a 30 cm layer of finer rock, which is compacted on the earthen roadbed for the rail line. This layer allows drainage of the rail line and the top ballast and prevents the subgrade soil from penetrating the top ballast. Top ballast, a 30 cm layer of hard crushed rock which is angular in nature and thus will not shift covers the sub-ballast and the ties are set on this layer. After the ties are set in place, the level of the top ballast is raised to within 5 cm of the top of the ties, limiting their ability to shift during use.

¹² Magee, G.M., 1968. Rail Transportation Engineering. In Standard Handbook for Civil Engineers, F.S. Merritt Editor. McGraw Hill, New York.

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The ties on main line tracks are 7" x 9" [18 cm x 23 cm nominally] and 8'-6" [2.59 m] long. Thus each tie has a volume of 3.763 ft³ [0.105 m³] although slightly smaller and shorter ties may be used for yard tracks. The ties are sawn from the heartwood of the tree which, Magee suggests, is less desirable for lumber but more desirable for ties. The preferred species of wood, in order of preference, are: oak, gum, pine and fir. The specific gravity of wood is directly related to its strength characteristics. Of course, the specific gravity also has an influence on the heating value of wood. Literature values¹³ suggest that air dried oak, with 22% moisture, has a calorific value of 5560 Btu/lb [12.93 MJ/kg] or about 43% that of typical bituminous coal. Oak has a specific gravity of 0.7 suggesting that the average tie contains 73.5 kg of wood.

It is helpful to understand how much wood is used to lay 1 km of mainline track. The ties are installed on 49.5 cm centres or about 2 for every meter of track, implying that replacing the ties for 1 km of track would require 2020 ties, or 148.5 tonnes of wood. This quantity of wood was readily available when the railways were being built in North America; however untreated ties used for early railway lines had an average useful service life of only 5.5 years¹⁴. The most common type of failure is related to decay of the wood by fungi which deteriorates the wood structure and leads to crushing in the tie plate area. Research¹⁵ has determined that 43-44% of ties fail due to decay. Other causes include: being cut by the tie plate 18-20%; splitting 16-18%; and, 14-16% by spike killing.

There are numerous factors that contribute to the failure of a railway tie. These mechanisms¹⁶ include:

- Weathering such as temperature cycling, water, and freeze-thaw cycles;
- Biological mainly from fungal rot;
- Stress due to abrasion and compression by the ballast, impact compression and impact bending due to vertical rail loads, and spike loading due to lateral rail loads;
- Incompatibility factors such as chemical degradation due to rusting metal and acidic salts, and physical degradation caused by particulate matter between the tie plate and the tie;
- Use factors including the volume of traffic and the weight of the traffic, the quality and frequency of maintenance, the track geometry including curves and number of ties per kilometre, and accidents due to derailment or spills, or dragging equipment.

Some of these factors can be addressed by preserving the wood before it is installed in the rail bed. Increasing the life of the crossties by improving durability is economically important because not only does it save timber resources, but it reduces the amount of money spent on replacing ties.

¹³ U.S Dept. Agr. Bull. 753, The Use of Wood as Fuel listed in Chemical Engineer's Handbook, 1973 McGraw Hill, New York. A reference for Table 9-8.

¹⁴ Webb, D.A., 2005. The Tie Guide Handbook for Commercial Timbers Used by the Crosstie Industry. Prepared for the Railway Tie Association. Available at: <http://www.rta.org/Portals/0/Documents/Tie%20Basics/TieGuide%20Revised%209%2005.pdf>

¹⁵ American Railway Engineering Association: Report of Committee 3, 1977. Tie and Wood Preservation. Bulletin 661 as referenced in Zaremski, Allan, Examining Wood Tie Failure. A paper available on the RTA.org website. <http://www.rta.org/Portals/0/Documents/Research%20Paper%20&%20Articles/Dr.%20Allan%20Zaremski%20Papers/EXAMINING%20WOOD%20TIE%20FAILURE.PDF>

¹⁶ Chow, P., S.L. Lewis, and A.J. Reinschmidt, 1987. Effects of Natural and Accelerated Aging on Oak Crossties. A paper in the Proceedings of the American Wood Preserves Association, referenced in Zaremski, Allan, Examining Wood Tie Failure.

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Ties are prepared in a multi stage process. The rough sawn timber is shipped to a treatment plant where the ties are prepared for use by adding anti-splitting devices, seasoning the wood, machining and preserving. The anti-splitting devices are inserted into the end of the ties before seasoning. These devices are either fluted dowels, or pieces of steel formed into the shape of an “S” or a “C” embedded in the ends of the tie. Seasoning, or drying, reduces the moisture content of the wood and allows better penetration of a preservative. After seasoning, the ties are machined to accommodate the tie plates and drilled to take the spikes that will be used to hold the plates and the rails. The ties are then preserved.

Wood preservation commenced in the mid-1800s. Initially crossties were treated with a water-borne solution of mercuric chloride with copper sulfate and zinc chloride solutions also being used. It quickly became evident that these salt solutions could be leached from the wood if there was any water flow around the wood. By combining zinc chloride and creosote the leaching effects were reduced, however this approach was abandoned in the mid-1930s. Full cell creosote treatment processes started to be developed in the 1860s with the first pressure treating of wood being undertaken in 1875 in Mississippi. Various other processes developed in the ensuing years to address limitations in the early methods and to ensure that the maximum amount of preservative was placed into the wood. The processes evolved to the development of the empty cell processes that essentially coats the cell walls but leaves little free preservative in the wood. This reduced the consumption of creosote and lowered the cost of treatment.

Further cost reductions were achieved by diluting the creosote with coal tar, water-gas tar a by-product of town’s gas production, and heavy petroleum materials. Over the years, the use of coal tar in this way fell into disfavour; and manufactured town’s gas was replaced by natural gas limiting the availability of water gas tars. The result is that creosote is generally mixed with heavy petroleum products today. Two other types of oil-borne preservatives: pentachlorophenol [PCP] and copper naphthenate are used in some locales. These preservatives are thought to be more effective in warmer climates where there is a high wood decay rate. PCP preservatives are used for utility poles in Canada, but its use is declining, due to use restrictions, and being replaced by ammoniacal copper zinc arsenate which is applied as a water-based solution. A mixture of heavy petroleum and creosote is the only preservative system used by Canadian railways¹⁷.

Treating crossties with creosote extends the average service life of ties to in excess of 30 years. Data available on the Rail Tie Association (RTA) website suggests that mechanical failures are the main reason ties need to be replaced on mainline routes. As would be expected, the higher the traffic volume is on the track, the earlier failures will occur. Ties on branch lines and sidings can last up to 50 years in Canada although in some parts of the US rot sets in and destroys the ties before they reach that age. Since the wood to replace these crossties can be grown during the service life of the ties, crossties are supportive of a renewable timber resource.

¹⁷ Webb, D.A., 2005. The Tie Guide Handbook for Commercial Timbers Used by the Crosstie Industry. Prepared for the Railway Tie Association. Available at: <http://www.rta.org/Portals/0/Documents/Tie%20Basics/TieGuide%20Revised%209%2005.pdf>

Creosote and its Compounds

Based on the detailed chemical analysis provided in the Appendix, creosote is a liquid that contains a wide range of organic compounds. It is manufactured from the coal tars that are generated during the production of the coke used in the manufacture of steel. The coal tar created by the coking process is heated to temperatures up to 400°C thereby releasing vapours. These vapours are condensed and the resulting liquid is creosote. Creosote is brownish-black/yellowish-dark green in colour and has an oily feel. It has a characteristic sharp odour. Being derived from coal, the exact makeup of any particular batch of creosote will vary with the coal source, and the temperatures used in the distillation process. Typically creosote is a mixture of several hundred chemicals, but there are only a limited number that are found in concentrations exceeding 1%. Up to 90% of the mix can consist of polycyclic/polynuclear aromatic hydrocarbons [PAH]. Creosote can be used as a fuel as it will ignite at 500°C and when combusted will supply 29 MJ/kg of energy. This is more than 2.2 times the heat that can be derived from a kg of air dried oak (22% moisture) as noted earlier.

There are naturally occurring sources of PAHs released to the environment including forest fires, volcanic eruptions, diagenesis (chemical changes in soil and sediments), and biosynthesis (changes in living cells to more complex forms). Human activities, however, are considered to be a major source of PAH contamination¹⁸. PAHs are created during the incomplete combustion of hydrocarbon materials ranging from gasoline and oil in automobiles to coal in power plants¹⁹. It should be noted that the better the combustion process, the less likely it will be to release PAHs as products of incomplete combustion. Cement kilns, as discussed later in this document, provide the type of combustion environment that minimizes PAH releases.

Pressure treating wood with creosote results in creosote being retained in the wood. The American Wood Preservers Association standard UC4²⁰ for crosstie treatment suggests that the amount of creosote solution retained in the tie should vary by the species of timber from 96 kg/m³ for Jack, Red and Lodgepole pine to 128 kg/m³ for southern pine and Douglas Fir. Oak and hickory are in the middle of the range at 112 kg/m³. If the average tie is 0.105 m³ in volume, 10 – 13 kg of creosote solution would be expected to be found in a new tie.

After the tie is put into service various changes take place. The result is that the end of use tie can have a different composition of the preservative than that found in freshly treated wood and the relative concentration of the different compounds will be different than that found in typical creosote. Investigations were completed in various jurisdictions to assess the potential impacts of both the in-use effects of creosote treated ties and the anticipated effects from the re-use of ties after they are removed from the rail line. Samples of wood treated with creosote were placed in 4.2 litre glass cells through which air at various temperatures, 20-38°C, was blown²¹. The air leaving the cell was sampled to assess which compounds had been released. The experiments at normal ambient temperature showed that the PAH with the lowest boiling point, naphthalene, accounted for 75% of the volatile compounds in the test chamber air even though naphthalene comprised only

¹⁸ CCME (Canadian Council of Ministers of the Environment), 2008. Canadian Soil Quality Guidelines for Carcinogenic and Other Polycyclic Aromatic Hydrocarbons (Environmental and Human Health Effects). Scientific Supporting Document. 218 pp. Available at http://www.ccme.ca/assets/pdf/pah_sogg_ssd_1401.pdf

¹⁹ National Research Council, 1994, Alternatives for ground water cleanup: Washington, D.C., National Academies Press, 315 p.

²⁰ Webb, D.A., 2005. The Tie Guide Handbook for Commercial Timbers Used by the Crosstie Industry.

²¹ Ingram, Leonard L. and Kimberley Tarlton, 2005. Effect of physical properties of pentachlorophenol and creosote components on vaporization from treated wood: Review of prior data. Forests Products Journal Vol. 55 No. 6 86-89

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10.5% of the solution used to treat the wood. The more non-volatile compounds in creosote were not identified in the air samples. There was an expected effect of increased release of compounds at elevated temperatures. Cooper et al.²² notes that there were fewer PAHs in the weathered wood confirming the observations in the previous study.

The loss of these compounds from the treated wood was also studied by Brooks²³ who notes that the typical initial loss rate is 30-40 ug PAH/cm²/day in new wood decreases to 3-5 ug PAH/cm²/day at 25 years of age. Furthermore, Brooks suggests that the PAHs lost in this manner are degraded by chemical and photo-oxidation processes and metabolized by microbes. Even though there are losses, he concluded that the compounds migrating out of the railway ties are retained in the ballast on the roadbed and not mobilized into the surrounding environment. Kohler et al.²⁴ suggest that railway ties may emit 5 kg of creosote over their life with 2 and 3 ring PAHs predominating the losses. The UNEP review of creosote provides some data on the range of concentrations of creosote compounds in weathered ties. That data is provided in Table A-3 in the Appendix and includes results for samples collected in both Europe and Canada.

In the last couple of decades there have been a number of studies concerning the use of creosote as a wood preservative. These studies have led to restrictions on the use of creosote by the general public, and recommendations concerning the reformulation and use of creosote compounds. One of the more recent studies provided a comprehensive analysis of the socio-economic benefits of creosote as a preservative for crossties used in Europe. In Europe²⁵ the content of benzo(a)pyrene [B(a)P] in the creosote is an important factor in governing usage. Three different types of preservatives were used: a heavy oil and creosote mixture for ties which can have up to 500 mg/kg of B(a)P however in 2003 that was lowered to 50 mg/kg; a light oil mix with low B(a)P content 5 – 50 mg/kg used on poles; and, a medium oil mix with low B(a)P and the low and high boiling fractions separated. Given that the study found a range of potential health effects related to creosote, end of life railway ties have been designated for special handling in Europe. This is similar to the restrictions recommended in Canada²⁶.

In Europe, the 1999 Landfill Directive²⁷ actively encouraged a ban on landfilling biodegradable waste and encouraged treatment of such materials before landfilling. The Directive defines treatment as physical, thermal, chemical or biological processes that change the characteristics of the waste to reduce its volume or hazardous nature. This has prompted the interest in the effects of treating used railway ties in Europe. While the Canadian guidance document suggests that recycling can be employed but restricts potential uses of

²² Cooper, Paul, Tony Ung, Jean-Paul Aucoin, and Chris Timusk, 1996. The Potential for Re-Use of Preservative Treated Utility Poles Removed from Service. *Waste Management & Research*, (1996) 14. 263-279

²³ Brooks, K.M. 1997. Literature Review, Computer Model and Assessment of the Potential Environmental Risks Associated with Creosote Treated Wood Products Used in Aquatic Environments. In Goyette and Brooks (1999) *Creosote Evaluation: Phase II, Sooke Basin Study – Baseline to 535 Days Post Construction – 1995-1996*. A report prepared for Environment Canada, Pacific and Yukon Region.

²⁴ Kohler M., Künniger T., Schmid P., Gujeer E., Crockett R., Wolfensberger M., 2000. Inventory and Emission Factors of Creosote, Polycyclic Aromatic Hydrocarbons (PAH), and Phenols from Railroad Ties Treated with Creosote. *Environmental Science and Technology*, 34 pp 4766-4772.

²⁵ Mayer, Ingo, Christelle Ganne-Chédeville, Julien Ropp, Urs von Arx, Frédéric Pichelin, 2010. Thermal Decontamination of Railway Sleepers for Recycling. World Conference on Timber Engineering, Paper 454 Available at: http://www.ewpa.com/Archive/2010/june/Paper_454.pdf

²⁶ Environment Canada, 2004. INDUSTRIAL TREATED WOOD USERS GUIDANCE DOCUMENT

²⁷ European Union, 1999. Council Directive 1999/31/EC of 26 April 1999 on the Landfill of Waste. In the Official Journal of the European Communities L 182/1 16.7.1999

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creosote treated timber, it does encourage recycling in terms of energy recovery and notes that cement kilns offer an opportunity to recover the energy. Since Canada currently does not have a landfill ban such as that in the EU, the guidance also notes that disposal in a landfill is a viable alternative for the non-recyclable treated wood.

Energy Recovery

During the preparation and preservation processes, moisture is driven from the wood so the pores can be filled with creosote. Moreover, during use, the residual moisture in the wood evaporates and the used tie becomes drier than kiln dried hardwood (8% moisture) resulting in an increase in the heating values of the timber. Freeman et al.²⁸ report the characteristics of treated crossties, as shown in Table 1, in comparison to other potential fuels. The heating values in the table reflect the added energy of the creosote and the reduced moisture content compared to typical wood.

As noted above, pentachlorophenol [PCP] has been used to treat wooden telephone poles in Canada, and the data for wood treated with this chemical is included in Table 1. The data in the table indicates that PCP treated wood contains 10 times the amount of chlorine found in creosote treated wood. This is an important consideration when evaluating the effectiveness of energy recovery systems. For instance, there are limitations to the chlorine content of the feed materials²⁹ of a cement kiln to maintain the appropriate chemistry for the finished cement products. In fact, this limitation on chlorine content is one of the reasons for disposal of cement kiln dust rather than reintroducing this material to the kiln. By far, the preferred treated wood for cement kiln use would be creosote treated railway ties.

Notably, the ignition temperature for creosote treated wood is 50 – 100°C higher than that of untreated timber according to a reference in the UNEP³⁰ study. This is likely because the proportion of volatile carbon in the creosote treated timber is lower than untreated wood, a difference seen in Table 1. It is the volatile material leaving the wood upon being heated that leads to ignition of the timber under most circumstances. However, other authors³¹ suggest that there is some uncertainty in the definition of an appropriate ignition temperature for wood. For energy recovery systems, the actual ignition temperature of the tie is likely of little importance since the tie will need to be prepared by shredding before use in most combustion systems. Shredded ties will have a significantly different behaviour than whole ties.

The table indicates that there is considerable energy available in end of use railway ties and that the sample heating values are 30% higher than switchgrass. The Environment Canada guidance document notes that energy recovery from ties occurs at several facilities in Canada, including two pulp mills (Prince George BC and Trois-Rivières, QC), one cement kiln, (Joliette, QC) and two co-generation facilities (Williams Lake, and Lytton, BC). In all cases ties are mixed with the base fuel used in the facility. These uses meet the stated goal

²⁸ Freeman, M., W. O'Dowd, P. Goldberg, S. Plasynski and G. Walbert, 2000. Pilot Scale Cofiring Results of Treated Woods and Other Biomass Fuels for Coal-Fired Boiler Applications. Available at: <http://www.nrbp.org/papers/012.pdf>

²⁹ The degree of tolerance of chlorine in cement kilns varies depending on the specifics of the raw material mix in use at the plant.

³⁰ ITC (1990) Information about coal-tar creosote for wood preservation. Prepared by Tar Industries Services (TIS) for International Tar Conference, Paris, March, pp. 1–79. As referenced in the UNEP Creosote Chemical Assessment Document 62.

³¹ Babrauskas, V., 2001. Ignition of Wood: A Review of the State of the Art, pp. 71-88 in *Interflam 2001*, Interscience Communications Ltd., London.

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of recovering energy in industrial boilers or co-generation facilities, however, from an environmental point of view, the cement kiln application may offer a better solution. Cement kilns use vast quantities of energy as noted earlier, and account for significant greenhouse gas emissions, so replacing fossil fuels with the biomass in the end of use railway tie not only is useful for energy recovery but serves to lower greenhouse gas emissions from the process.

Table 1: Comparison of Analysis of Treated Wood and Other Biomass

	Creosote Treated Wood	PCP Treated Wood	Switch Grass
Proximate %			
Moisture	5.62	5.01	8.77
Volatile Matter	83.54	88.4	71.68
Fixed Carbon	9.56	6.06	11.2
Ash	1.28	0.53	6.95
Ultimate, dry %			
Hydrogen	6.16	7.28	6.02
Carbon	55.83	56.8	46.21
Sulphur	0.16	0.07	0.11
Nitrogen	0.23	0.18	0.94
Oxygen	36.27	34.29	39.1
Chlorine	0.08	0.82	0.04
Ash	1.35	0.56	7.62
Heating Value			
MJ/kg as recd	21.47	21.94	16.37
MJ/kg dry	22.75	23.1	17.94
Composition			
lb Ash/MMBtu	1.39	0.56	11.9
lb Cl/MMBtu	0.08	0.83	0.05
lb S/MMBtu	0.16	0.07	0.14
lb N/MMBtu	0.24	0.17	0.61

Proposals to burn any “waste” material tend to create concerns that are expressed by members of the community surrounding the facility even when the specific fuel being considered is expected to result in lower emissions. Such concerns are typically related to the potential for changes in air emissions from an existing facility, or increases in air emissions related to new facilities. In some communities there is a tolerance for using waste wood as a fuel because it is generally seen as being a lower risk for emissions than any other waste material. A distinction was made between clean wood and treated wood³² in a 1990 Ontario guideline. The guideline applied more stringent emission limits from treated wood combustors to limit the release of metal species or organic compounds. More recently O.Reg. 347 defined wood waste by including all types of wood except preservative treated materials and any wood with a plastic or other laminate attached. It also specifically excludes upholstered items. That Regulation also requires that removable metal fittings be removed from wood before charging. O.Reg. 347 defines a woodwaste combustor site as one that uses woodwaste to recover energy and provides exemptions for such sites under certain circumstances. Railway

³² Ontario Ministry of the Environment, 1990. Interim Design and Review Guidelines for Wood Fired Combustors. Issued by the Approvals Branch, August 30, 1990. Publication 4376e.

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ties and most of the other low carbon fuels do not fall under the woodwaste definition but under the all-encompassing “municipal waste” definition.

In a response to a report that encouraged the sustainable use of biomass from forests, Miller³³ suggested that there was a need to consider the beneficial use of treated wood for the development of energy. The author alludes to the clean versus treated wood distinction suggesting that perceptions are that clean fuel will not create emission concerns whereas treated wood might release undesirable compounds. He makes the very important point that **any wood can create undesirable emissions, if the wrong conditions are present, and treated wood can be burned in a satisfactory manner under the right conditions.** This is a theme that is evident in many jurisdictions. It is necessary to ensure that appropriate combustion conditions exist, emission controls are in place, and that appropriate regulations govern the manner in which any combustion is conducted.

Definitions

Combustion, in this report, refers to the exothermic oxidation of carbon-containing fuels into carbon dioxide, water, and heat in engineered, controlled systems. Open burning refers to uncontrolled fires such as campfires, wood fireplaces, and other similar low efficiency systems.

The ban on open burning of preservative treated wood in the Environment Canada report referenced earlier responds to the inability to meet these requirements when burning such material in an open fire. The author and other contributors to this report concur with the ban on open burning of treated woods.

In Ontario the use of natural gas for heating systems in homes, offices and factories is generally considered to be of low risk, explaining recent changes in the requirements for approval of these systems. Natural gas is a uniform fuel that contains few contaminants and can be reliably burned in purpose built systems. The same reliability and uniform emission levels can be achieved from more complex fuels if systems are optimised to ensure good performance.

Since creosote contains PAHs, and PAHs are compounds that have been deemed to require special procedures it may be natural to think that the combustion of PAH containing wood will lead to high emissions of PAHs and eventual environmental degradation and health effects. However, the US EPA’s Emission Factor documentation for wood combustion³⁴ notes a wide range of PAH’s can be present in the exhaust of wood residue boilers and another section of AP42 shows considerable PAH emissions from fireplaces and wood stoves. This should not be surprising because the tars that condense in fireplace flues are known to be a potential hazard. Replacing open burning with carefully controlled combustion of treated woods addresses these very concerns. Taken one step further, the nature of the cement kiln combustion system is such that the destruction of organic compounds such as PAHs would be expected to be much better in the kiln with its higher temperatures and longer residence times.

³³ Miller, Jeffrey T., 2010. Letter re Proposed Biomass Regulations from Treated Wood Council to Massachusetts Department of Energy Resources. Available at: <http://www.env.state.ma.us/eea/doer/biomass/comments-oct21-2010/Treated%20Wood%20Council.pdf>

³⁴ US EPA, 2003. AP42 Section 1.6, Wood Residue Combustion in Boilers available at: <http://www.epa.gov/ttn/chief/ap42/ch01/final/c01s06.pdf>

Review of Lab Scale Combustion Tests

Research has been conducted into the behaviour of creosote, wood, and creosote treated wood to determine how these materials react during thermal destruction³⁵. These data are helpful in developing an understanding of what is likely to occur during the combustion of these materials in the cement manufacturing context. Reviewing the results of earlier experience prior to developing a test program at a cement kiln site is an excellent means of implementing the precautionary principle. The laboratory tests can help identify the conditions needed for efficient, safe combustion prior to validating the results at a larger scale.

The experiments involved heating samples of all three materials from ambient temperature to 1000°C at a rate of 10 K³⁶ /minute in two different environments: a combination of argon/air; and a pure argon one. During this testing weight loss, thermogravimetry, and differential thermal analyses were conducted. Coupled with a mass spectrometer that allowed qualitative analysis of the compounds released during the process, the testing provides information on thermal degradation. Combustion experiments were also conducted in a laboratory apparatus that was heated and held at various temperatures while a flow of synthetic air was maintained through the chamber. The gases released were collected to ascertain which low and high volatility organic compounds were generated at the various temperatures.

In an argon environment oxygen is eliminated and thus the chemical changes are not influenced by the oxidation reactions that occur in normal combustion processes when materials are heated. In the argon environment, thermogravimetric experiments on the creosote treated wood showed a 2 step degradation process, one endothermic (the material heats up) at 80°C and one exothermic (heat is released) at 340°C. When an argon/oxygen atmosphere was used there were two additional exothermic steps, at 390°C and 440°C. No further degradation occurs at temperatures above 500°C. The authors attribute the first step to drying of the wood. The exothermic step in the 300-340°C range was non-oxidative decomposition as the treated wood lost moisture, carbon dioxide and hydrocarbons. Carbon dioxide was the main product of the continued degradation at higher temperatures. By comparison, tests with untreated wood produced similar results with the exception that there was only one oxidative step suggesting that creosote was degrading separately from the wood in the treated sample. Testing of creosote alone shows endothermic steps at 220 and 280°C attributed to the evaporation of the lower boiling point compounds, and an exothermic reaction at 540°C when the creosote was oxidized to carbon dioxide and water.

When the samples were tested at various temperatures no highly volatile compounds were trapped in the activated carbon tubes, indicating that they were not produced. The XAD tubes collected aldehydes, phenols and polyaromatic and heteroaromatic compounds. Analysis of the XAD tubes produced a qualitative list of compounds summarized in Table A-4 in the Appendix. For each component tested (untreated wood, creosote, and treated wood) qualitative identification of compounds in the atmosphere of the chamber was completed for each temperature condition. This procedure allowed the researchers to associate the degradation products of the treated wood with either the wood or creosote. As might be expected the compounds identified when creosote was degraded were similar to those of pure creosote listed in the Appendix. This is not surprising

³⁵ Becker, L. G. Matuschek, D. Lenoir, and A. Kettrup, 2000. Thermal degradation of wood treated with creosote. *Journal of Analytical and Applied Pyrolysis*, 57(2001) 15-36.

³⁶ One degree Kelvin [K] is equivalent to one degree Celsius [C].in quantity.

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since the experiment was effectively another distillation of the material created by fractional distillation. The list of compounds associated with the untreated wood was much shorter and the compounds were, for the most part, different than those identified with creosote. The treated wood degradation process identified many substances common to those in the two components – wood and creosote both produced semi-volatile organic compounds.

The XAD tubes were also used to quantify 12 compounds: Phenol, Naphthalene, Quinoline, Acenaphthene, Dibenzofurane, Fluorene, Phenanthrene, Fluoranthene, Pyrene, 1,2-Benzanthracene, Triphenylene, Benzo(a)pyrene for each of the three sample types at each temperature. With the exception of phenol and dibenzofurane, the release rates in mg/g from untreated wood samples were all below analytical detection limits. As might be expected the treated wood release rates were higher than the untreated wood, but much lower than those for pure creosote. This is to be expected because the amount of creosote in the samples would be expected to be significantly lower than the amount of creosote introduced into the apparatus.

The authors conclude that treated wood can be destroyed by thermal processes but they caution that some polyaromatic hydrocarbons may be released in the process. They caution that the combustion system must ensure that the hydrocarbons are destroyed thoroughly – suggesting that this will require **temperatures well above 600°C**. Furthermore, they note that appropriate particulate emission controls should be used.

These data provide an indication of what would be expected to occur were ties to be used for energy recovery in a boiler or industrial furnace. The question remains, will these processes thoroughly combust these compounds? This question can be addressed in two ways, a consideration of the basic organic destruction mechanisms in a combustion system, and a review of test data from systems where treated wood was destroyed.

Cement Industry Energy Recovery

A number of jurisdictions distinguish between incineration (a means of disposal, even when the waste heat is used for electricity production) and energy recovery. Manufacturing facilities that are using a virgin fuel resource as their energy source are recognized as preferred options for the re-use of otherwise unwanted energy containing materials. It is also acknowledged that not all energy containing materials may be suitable for energy recovery and so disposal methods may still be required.

Much research has taken place into the effective, safe incineration of a variety of materials and this science can be relied upon to guide energy recovery facilities to ensure that they provide similar, if not superior, levels of safety. Some of this science is provided in this report. However, cement plants are unique in that they typically operate at temperatures and residence times far in excess of that in place for incineration processes. Further, the emissions from fossil fuels are replaced if not reduced by co-firing with cleaner low carbon fuels and so no new emissions tend to result. Ash present in fuels of all kinds, when matched to the clinker needs, can represent a useful or at least innocuous component of cement providing additional value from the material being used as fuel. In other processes this ash material can represent a waste that requires disposal.

Finally, while incinerators are built to dispose of waste, manufacturing facilities exist to make a product. Should a better option become available for a particular surplus fuel product, manufacturing facilities will continue to seek out fuel sources whereas incinerators depend on long term commitments to provide waste materials to justify capital investments. This can lead to barriers to the development of preferred waste management strategies; barriers which do not arise with energy recovery options.

The Combustion Process

Organic Reaction Principles

As noted above, Becker et al. suggest that good combustion control is necessary to ensure appropriate oxidation of the organic materials. Combustion control must compensate for:

- the natural variability in fuel quality; and,
- the controlling factors governing the rate of chemical reactions.

There are numerous ways the designer of a furnace can choose to control the combustion process depending upon the nature of the use of the fuel. In the following paragraphs the basic principles of the reactions that convert fuels, consisting of carbon and hydrogen, to energy and combustion products are discussed. Specific aspects of cement kiln combustion controls are also explained.

Typically with homogeneous fuels, such as oil and natural gas, combustion control is relatively easy, hence the relatively unnoticed operation of the heating systems in homes. As fuels become more variable the combustion control process becomes more complex. For example, coal fires systems must compensate for changes in coal quality resulting in varying levels of ash, and fixed and volatile carbon, or in biomass which can have a range of moisture levels that will influence combustion and the available heat from the fuel; or in the extreme, the heterogeneous nature of household solid waste.

These variables must be addressed and the operators of any industrial furnace must understand how to keep the operation at a steady level, despite these variations, and achieve the best performance. This is doubly important in a

cement kiln where the clinker production process can be upset by some of these changes and the resulting product would be unacceptable for use. That noted, it is also important to recognise that when biomass, or treated wood waste is introduced into a cement kiln these materials

Cement Process Note

In the cement kiln context, control of fuel variability – whether traditional fossil fuels such as coal or local, low carbon – is of added importance as the stability of the clinker process is paramount. Cement makers are highly committed to ensuring that neither their product quality nor the stability of their process is detrimentally affected by altering fuels.

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would typically only form a portion, up to 30%, of the overall energy input to the system. Thus the potential for upsets induced by fuel variations will be limited.

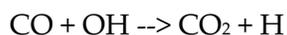
Each component of a complex fuel has inherent energy content and this must be matched with sufficient oxygen to ensure proper combustion. The ideal blend of oxygen and fuel ensures that there is just sufficient oxygen available to accomplish the conversion of carbon and hydrogen in the fuel to carbon dioxide and water vapour. In actual practice, the need to control temperatures in the system to achieve the desired performance or to protect portions of the combustion system from high temperatures means that there is usually excess oxygen in the system. In conventional combustion systems that use fuels with varying characteristics, the designer might choose to introduce large quantities of fuel to the combustion chamber so the variation is averaged out. Alternatively, the amount of air added to the system could be varied; lowered to address fuel with less available energy or raised to compensate for higher energy input. The third common approach would be to vary the amount of fuel added to the system so that steady state operation is maintained.

The operational reality of adjusting fuel flow or air flow to the furnace is that these changes are interrelated to some extent. Gas flow in the furnace should be sufficiently high so that turbulence levels are maintained and the air is fully mixed with the volatile gases generated during the burning process. These situations must be controlled because the thermal destruction of organics is not a simple process.

There are many intermediate steps involved in the oxidation of long chain hydrocarbon materials to the ultimate products of complete combustion, namely carbon dioxide (CO₂) and water (H₂O). Generally, it is agreed that the reaction starts as gasification of the fuel as it is exposed to air while being heated in the combustion environment. The amount of air in contact with the fuel and the degree of agitation of the fuel controls the rate of gas generation. The gases that leave the fuel are rich in carbon monoxide and hydrogen and contain many unburned gaseous hydrocarbons, as Becker and his colleagues identified in the creosote and wood experiments discussed earlier. When provided with additional air these gases will burn readily. In many furnaces additional air is introduced to ensure that there is sufficient oxygen to allow the process to go to completion.

Complete combustion will result in the conversion of all the carbon and hydrogen entering the furnace to CO₂ and water vapour. This is the ideal condition, but even for a fuel as simple as natural gas, it is not uncommon to find unburned methane in the exhaust stream of large furnaces. Most systems have some traces of organic materials escaping the combustion zone.

Combustion and the conversion of hydrocarbons to carbon dioxide and water vapour requires numerous chemical reactions including the creation of carbon monoxide. Carbon monoxide (CO) is the most refractory, or difficult to oxidize, species in the oxidative chain from hydrocarbon to carbon dioxide and water. The oxidation of CO to CO₂ is accomplished much faster in the presence of hydrogen. Miller and Fisk³⁷ suggest the dominant reaction in the chain is:



The concentration of hydroxyl radicals [OH] is thus very important to the reaction. Hydroxyl radicals will also react with hydrocarbons in the system and this reaction is faster than the reaction between CO and OH. This means that it is necessary to consume all the hydrocarbons in the system before the system can maximize the

³⁷ Miller, J.A. and G.A. Fisk, 1987. Combustion Chemistry. C&EN Aug. 31, 1987; pp22-48.

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conversion of CO to CO₂. It follows that high levels of CO in the exhaust generally correlate with higher levels of residual hydrocarbons, evidence of the rate-limiting steps in the reaction.

If excessive air is present in the furnace, the combustion temperature and the concentration of hydroxyl radicals are reduced. In turn, the organics react with the OH radicals and the CO oxidation does not occur. Conversely, insufficient air can lead to pockets of fuel rich gas that lack sufficient oxygen to oxidize the CO. It is possible to establish an appropriate range for the concentration of oxygen in any system. Operation in this zone minimizes the release of CO and thus also minimizes trace organic releases. The establishment of this range is most important because, once determined for a system, it can be used to ensure that the system is operating at its most efficient level.

Good combustion conditions leading to reduced organic emissions are those that:

- ensure complete mixing of the fuel and the air;
- maintain high temperatures in the presence of sufficient oxygen; and,
- prevent the formation of quench zones or low temperature pathways that would allow partially-reacted solids or gases to exit from the combustion chamber.

These design conditions must be combined with good operating conditions to ensure that the performance is maintained and organic constituents are reduced to the basic elements. As noted by McKay³⁸ it is particularly important to prevent the generation of soot in the system, because soot consists of carbon, and as noted in the discussion of creosote manufacture, carbon is a major portion of the tars that contain a wide range of chemical compounds, some of which are associated with environmental and potential health concerns. An example of poor combustion is illustrated by the picture above³⁹. These compounds are broadly classified as products of incomplete combustion [PICs] and these are discussed later in this document. Also, as explained below, soot formation in a cement kiln process that is producing quality cement is a practical impossibility.

Cement Process Note

In the cement kiln context, control of oxygen levels is primarily aimed at monitoring and controlling fuel consumption rather than as a driver of combustion efficiency. High combustion efficiency is expected to result from the same process conditions as lead to the production of high quality cement.



Shown above, an offshore gas flare functioning with poor combustion controls

³⁸ McKay, Gordon, 2002. Dioxin characterisation, formation and minimisation during municipal solid waste (MSW) incineration: review. Chemical Engineering Journal 86 (2002) 343–368. Available at: http://www.seas.columbia.edu/earth/wtert/sofos/mckay_dioxin-formation_2002.pdf.

³⁹ Pagot, P.R., 2002. "Cold and Hot Model Investigation of Flow and Mixing in a Multi-Jet Flare", Ph.D. Thesis, Department of Mechanical Engineering, Queen's University, Kingston, ON.

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In contrast to the soot generated under poor combustion conditions, the picture on the next page shows a well controlled combustion system taken by the same researcher. Note the absence of black soot around the perimeter of the flame, and the presence of a blue flame near the burner. The blue-colored flame emerges when the amount of soot decreases and the emissions from excited molecular radicals become dominant.

While combustion control is generally designed to address the full oxidation of organic compounds, adjusting combustion conditions can also influence the downstream partitioning of inorganic materials in the furnace. For instance, higher temperatures can volatilize inorganics from the solid phase. Apart from a brief discussion below, no further discussion of the relationships between combustion and trace metals emissions from furnaces is contained in this report; the reader is referred to other documents for a detailed discussion on those contaminants⁴⁰.

The conditions that lead to a reduction in organic emissions can also cause an increase in the generation of oxides of nitrogen [NO_x]. The formation of NO_x is attributed to two primary mechanisms: the oxidation of the fuel nitrogen to NO_x; and the combination of nitrogen and oxygen in combustion air at high temperatures, the thermal NO_x portion. The conversion of fuel nitrogen to NO_x is dependent upon the local oxygen availability to volatile species, the amount of fuel-bound nitrogen and the chemical structure. The thermal NO_x reaction is strongly temperature dependent because it is formed by the combination of radicals of the two species. It has been shown that the conversion of fuel nitrogen can range from 5% to 50%, largely controlled by the extent of mixing and the content of oxygen.



Shown above, a 500 kW model flare operating with good fuel-air mixing conditions

⁴⁰ Chandler, A.J., 2003. Background Study on the Incineration of Hazardous Waste. Final Draft of A Report to ENVIRONMENT CANADA to complete Contract Number K2237-2-0006. Prepared by A.J. Chandler & Associates Ltd. Toronto. March

Combustion in the Cement Kiln Context

In a cement kiln, minimizing heat loss is important and excess air levels are maintained as low as reasonably possible. This results in the operator needing to use other methods to control combustion if the fuel quality varies. This control starts with the careful preparation of the fuels. By ensuring that a highly uniform fuel, which allows for easy and complete combustion, is used the potential for upsets is reduced. To achieve the desirable uniform fuel, solid fuels such as coal or petcoke are pulverized and ground. The fineness of the pulverised fuel is important because if it is too fine the flame temperatures can get too high, and if it is too coarse poor combustion will result. If the nature of the fuel differs, say in the volatility or volatile content, the size of the materials must be adjusted. By reducing the size of the fuel, the material can be made more homogeneous and variations in the process are limited. Furthermore, the process of size reduction serves to mix the fuel components further reducing variability.

As noted earlier, low carbon fuel substitution in the kiln is only expected to partially reduce the amount of coal (and petroleum coke) used in the process. Since the coal and the low carbon fuel are unlikely to have similar combustion characteristics the first step in controlling performance is to ensure that the low carbon fuels are well mixed with the other fuels, either in the feed preparation stage or by introducing the fuels through separate channels in the burner assembly each with their own feed control to allow suitable mixing in the flame zone. This will minimise the effects of variation in the properties of the low carbon fuel, or at the very least decrease the effect of fuel differences.

Typically, coal/coke is injected into the kiln through such a multi-channel burner which is the primary fuel source to the kiln. This burner produces the main flame which has a temperature around 2,000°C. The length of the flame is adjustable to optimize the process. The length and shape of the flame are controlled by the addition of primary air which comprised 10 – 15% of the total combustion air in the kiln. The rate at which fuel is added to the kiln is the principal means of controlling the temperature in the system. As conditions in the kiln change, the fuel feed rate can be adjusted to maintain the stable operation needed for good clinker production.

It should be noted that the combustion process discussed in the previous section is typical of non-cement kiln configurations where the fuel is on a grate and the process proceeds as air is added under the grate so it can pass through the fuel and the grate moves to agitate the fuel and exposed fresh surfaces. In the main cement kiln flame, the fuel is burned while suspended in the gases of the flame thus being constantly mixed with the air and ensuring optimal combustion performance. In the atmosphere of the kiln, oxygen must be present to facilitate the clinker reactions and thus there is oxygen available for the complete burning of the gases.

The importance of tight control of the combustion process for clinker production results in a process that is much more capable of destroying organic components in the fuel than many conventional boilers. Moreover, as will be seen later, these reactions are influenced by temperature – and the high temperatures of the flame zone in the kiln, coupled with long residence times, ensures excellent conversion of fuel carbon and hydrogen to CO₂ and water vapour.

Assuming the combustion control system of the kiln is set up to maintain stable operation, chemical kinetics and thermodynamics govern eventual destruction of organic compounds. These processes are discussed in the next section. Influence of Thermal Dynamics and Kinetics

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The organic reactions that occur inside a furnace are complex. Indeed, in hazardous waste incinerators, where there has been more study of these mechanisms, researchers⁴¹ have looked at both the rate of destruction of principal organic hazardous compounds [POHCs] and the formation and destruction of products of incomplete combustion [PICs]. Both these mechanisms play a role in the eventual emissions of organic contaminants from combustion devices. These reactions involve the decomposition of molecules by different mechanisms and the potential reactions that occur between the fragments created during the decomposition and create new products.

The University of Dayton report suggests that POHC destruction involves four classes of mechanisms:

1. concerted molecular elimination;
2. bond fission;
3. bimolecular radical attachment; and,
4. surface catalyzed decomposition.

Similar mechanisms govern PIC formation:

1. concerted molecular elimination of stable molecules;
2. complex radical-molecule pathways;
3. radical-radical (atom) and radical-molecule association reactions; and,
4. surface catalyzed synthesis.

The different reactions for POHCs and PICs can occur in different zones of the combustion systems. The first mechanism in each group dominates the pre-flame zone where temperatures are between 200 and 1000°C. The 2nd and 3rd POHC mechanisms and the 2nd PIC mechanism dominate at higher temperatures found in the flame and post flame zones. The remaining mechanisms dominate in the cool down zones in the systems. The cooler zones can be found in the Air Pollution Control [APC] system or the stack. Of course, the nature and quantity of byproduct emissions depends upon the nature of the combustion process in the furnace and the elemental and molecular chemical composition of the feed.

When considering cement kilns fired with coal or petroleum coke the fuel can be classified as fairly uniform. Employing biomass can introduce more variation in the fuel, but since it is unlikely that the energy provided by the biomass will be much more than 15-30% of the total input, variability will not be that significant. The size of the fuel particles in the furnace can influence the reaction rates in the system because a larger fuel particle will degrade at a slower rate than will a finer fuel particle.

When considering the release of organics from the kiln, there are two possibilities for emissions: 1) flow through or pass through emissions; and, 2) formation of the compounds as products of incomplete combustion [PICs] from the combustion of other organic compounds. The first mechanism addresses the potential for destruction in the system if the compounds are present in the fuel stream; the second reflects the potential for compound formation during the combustion process.

⁴¹ University of Dayton. Assessing the Origin and Emissions of Products of Incomplete Combustion from Waste Incineration, Environmental Sciences and Engineering Group, University of Dayton Research Institute. Available at: <http://www.udri.udayton.edu/enviroscience/Incineration%20Archive/IncinerabilityDocument.pdf>

Flow Through Emissions

In the past, it has been suggested that the emissions of certain compounds from combustion processes was related to the concentration of these compounds in the feed stock to the process. Thus, to have “flow through” emissions of PAHs in a cement kiln, the material must be present in the fuel. Moreover, it would have to be present in sufficient quantities to affect air emissions. As mentioned earlier, creosote has large quantities of PAHs so there is a potential for flow through if these compounds are not subjected to the appropriate conditions. (It should be recognized that this is different from generating PAHs from the other fuels used in the system which is discussed in the next section.) For flow through to exist, the compounds of concern must survive the combustion process. The question becomes how likely is that to occur?

It follows that the thermal stability of a given organic compound under the predominant combustion conditions within a cement kiln will determine the potential for flow through emissions. The Dayton report referenced above states:

“Calculations and experimental observations have shown that the emissions of undestroyed, residual [organic chemicals] are kinetically, not thermodynamically controlled. Thus, under the assumption that heterogeneous reactions are insignificant and mass transport is not-rate limiting, organic chemical destruction in incinerators is controlled by gas phase chemical kinetic factors including temperature, reaction atmosphere and residence time.”

If one is to define the potential for pass through it is important to identify the temperature, reaction atmosphere and residence time of flue gases in the combustion system. The next step is to compare the chemical properties of compounds of concern such as boiling point, flash point and auto-ignition temperatures to the specified operating temperatures of the combustion process under consideration.

In many jurisdictions there are regulatory requirements for certain types of combustion devices, particularly those used for thermal treatment of wastes. For instance, in Ontario, MSW incinerators are required to meet minimum flue gas temperatures for a specific duration, 1,000°C and 1 second. Temperatures within the fuel bed or burning zone of an MSW incinerator can exceed 1,100°C⁴². The CERF dry bottom pulverized coal combustion system, used for testing treated wood samples, simulates a utility power boiler with a radiant section operating at temperatures from 980 – 1,370°C with residence times from 0.5 to 3 seconds depending upon firing rate⁴³. Typical conditions in a cement kiln have 2,000°C temperatures in the flame zone and the clinker reaching 1,450°C before being discharged from the kiln. Even in the pre-calciner, temperatures are in the 1,000 – 1,200°C range. Most importantly, gas residence times in a cement kiln are typically more than 5 seconds at temperatures above 1,000°C. In the Bath cement plant, the residence time above 1000 °C is reported to be around 10 seconds.

It was shown by Becker et al. that the creosote in the treated wood was released at temperatures below 800°C suggesting that in most combustion systems it would be expected that no PAH compounds would be present in the residues from the grate. Once in the vapour phase, the organic compounds would be subject to thermal decomposition due to pyrolysis (independent of oxygen concentration), and oxidation (dependent on oxygen

⁴² International Ash Working Group (IAWG). *Municipal Solid Waste Incinerator Residues*, Elsevier Publishers, ISBN 0-444-82563-0, 1997.

⁴³ O'Dowd, W.J., H.W. Pennline, M.C. Freeman, E.J. Granite, R.A. Hargis, C.J. Lacher, A. Karash, 2006. A technique to control mercury from flue gas: The Thief Process. *Fuel Processing Technology*, 2006.

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concentration and susceptibility of the compound to oxygen attack). Most industrial furnaces operate with excess air levels that ensure that there is more oxygen present in the furnace than needed to combine with the hydrogen and carbon being burned in the process. MSW incinerators in Ontario are mandated to operate in excess of 6% oxygen in their flue gases representing an excess air level of 41%. Most of these systems operate at 10% oxygen and a corresponding 90% excess air, while achieving the necessary flue gas retention times of greater than 1 second, or in the case of the European regulation, 2 seconds. Pulverized coal boilers operate with excess air levels between 15 and 20% thereby maintaining an oxidizing atmosphere. Cement kilns require an oxidizing atmosphere for clinker production however, as noted earlier, to control energy usage the oxygen level in the firing process is maintained in the range of 3%. Under these excess oxygen circumstances it would be expected that virtually all volatile and semi-volatile organic compounds which enter the flame zone of an industrial furnace or incinerator would be destroyed. However, a small fraction may circumvent the flame zone, while another small fraction may be caught up in pyrolytic pockets or eddy currents of flue gas which might inhibit full oxidative decomposition or destruction of the compounds. This applies to all fuels that may be in use.

The Dayton report used pyrolysis kinetic parameters to calculate thermal stability rankings for some pure organic compounds based upon the estimated mean temperature needed to achieve 99% destruction efficiency (T_{99} @ 2 sec \pm 10°C). Note these are destruction levels independent of the oxygen levels in the system. The experimentally derived 99% pyrolysis related destruction temperatures for 3 of the compounds quantitatively measured in the Becker experiments are available in Table 13 of the Dayton report: naphthalene 1,070°C; benzo(a)pyrene 1,025°C; and phenol 775°C. Thus it can be concluded that, if these compounds are exposed to their T_{99} for 2 seconds, even in fuel rich situations, they should be destroyed to a level that they would not be detectable during sampling. The T_{99} values for naphthalene and b(a)p are higher than temperatures one might expect downstream of the flame zone in an MSW incinerators and one might expect to measure these compounds in the exhaust if they were introduced in the feed. *However in furnace with higher temperatures and longer residence times one would expect that any naphthalene or benzo(a)pyrene will be destroyed.*

The Dayton report provides first order oxidation kinetic parameters for a limited number of compounds. Unfortunately, none of the compounds in Table 14 of that report are identified in Becker's list of compounds quantified in his experiments; however, benzene is listed in both tables. As with the pyrolytic ranking table the oxidation parameters include a T_{99} temperature. The important observation that can be made is that while the pyrolysis T_{99} for benzene is 1150°C, the oxidative T_{99} for benzene found in the literature ranges from 700 – 760°C. *This suggests that, if there is excess oxygen present, benzene will be reduced to negligible levels at temperatures much lower than required in the absence of oxygen.* Other data in the report shows this to be consistent with findings for other compounds.

These data, combined with the operating conditions in cement kilns, suggest that PAH destruction should be at least 99%, as long as temperatures in the system exceed 1,000°C. This implies that if introduced into the kiln, the closer the point of introduction is to the burner end of the kiln the better. Even if the materials were introduced further down the kiln where temperatures are still in excess of 1,000°C, it would be reasonable to assume that only a very small proportion of the PAH loading in the waste might flow through the kiln and be emitted to the atmosphere. **It can be concluded that there is no scientific or practical basis for suggesting that flow through emissions of PAHs will occur in the cement kiln process context.**

Products of Incomplete Combustion

Recognizing that other, more persistent, organic chemicals can be formed as products of incomplete combustion [PICs] in furnaces, the potential for formation of PAHs as PICs must also be examined. Of the 4 mechanisms mentioned earlier, the most predominant pathways for PIC formation are the complex radical-molecule pathways, and the radical-radical and radical molecule association reactions. The most studied PIC formation mechanism is the surface catalyzed synthesis reaction generally associated with the catalyzed oxidation or de-novo synthesis formation of PCDD/PCDF compounds⁴⁴.

The laboratory databases cited in the University of Dayton report suggest that chlorinated compounds are most likely to be associated with the generation of naphthalene or phenols as a PIC. With the exception of pentachlorophenols, it is highly unlikely that chlorinated organic compounds will be present in kiln feed, suggesting that it is unlikely that naphthalene or phenols will be formed, much less survive in the aggressive thermal oxidative environment of the kiln. Since, pentachlorophenols are widely used as a fungicide treatment for some wood products, there is a possibility that some of this material could be mixed with treated railway ties and be present in the treated wood stream. These may act as a potential source of PAHs and chlorinated species in the flue gas of a cement kiln.

The preceding paragraphs suggest that the presence of chlorine, or chlorinated compounds in the kiln could contribute to the production of PICs. However, chlorine is present in coal and in the raw materials introduced into the cement making process, but results indicated that it has little effect on emission levels. The Bath plant has conducted emission testing in 2002, 2004, 2006, and 2010 and in all cases PCDD/F levels are below the limit of quantification suggesting that kiln conditions limit the potential for formation of these compounds. The Bath facility strives to control chlorine inputs to limit detrimental effects on the cement quality. Even though limited quantities of chlorinated compounds could be introduced into the kiln, data suggest that high temperatures and residence times limit the potential for chlorinated PIC formation.

To develop an appreciation of the significance of the potential PAH formation as PICs from treated wood combustion, it is helpful to review test data collected at various types of thermal treatment systems.

The authors of the University of Dayton study suggest that much of the emission data should be considered anecdotal since a full characterization of the waste feed streams was not available in all cases. Clearly, if the feed streams vary, it is likely that the substances found in the stack gasses could vary not only in their composition but in their concentration. That said, it is notable that equilibrium calculations of by-product concentrations are frequently less than the detection limits available to those measuring such emissions. Based upon the calculations, one would not expect to find these compounds unless the destruction process was kinetically limited. The presence of measurable quantities of PAHs suggests that different thermal treatment systems might have different emission concentrations even if they were fed identical waste streams. These could occur because there may be zones of lower temperatures due to quenching, reduced residence time due to non-ideal flow situations or unswept areas of the furnace where fuel rich situations exist, or limitations in microscale mixing due to the size and configuration of the furnace.

⁴⁴ Schwarz, G., L. Stieglitz and W. Roth. Formation Conditions of Several Polychlorinated Compound Classes on Fly ash of a Municipal Waste Incinerator, Organohalogen Compounds - Vol. 3, Dioxin 90, Ecoinforma Press, 1990.

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In summary, the data suggest that it is possible to have PAHs emitted from thermal treatment systems as PICs that are the result of the decomposition of specific materials in the feed. Depending upon where in the system these decomposition products form, they could be destroyed. The exact concentration found in a specific furnace is likely to relate to that furnace and its combustion conditions, suggesting that testing is appropriate. For this reason, the next section reviews the available test data related to combustion of treated wood wastes.

Trace Metal Behaviour In the Cement Kiln

In a cement kiln some of the dynamics of trace metal behaviour are different because, in some kiln processes, the exhaust from the kiln(s) is used to heat the incoming materials and in the process ash constituents are transferred to the clinker and ultimately combined into the cement product. In the case of the Bath plant, flue gases are not used this way but test results show that these metals are sequestered in the clinker at a high rate due to the inherent characteristics of the process (see Table 4, Page 41). As pointed out earlier, the one inorganic species that does not behave in this manner is mercury. Due to the temperatures in the kiln and the volatility of mercury a large portion of the mercury present in the fuel and other raw materials escapes from the system.

As noted earlier, the average content of mercury in US coals was found to be on the order of 170 parts per billion [ppb]. It is important to note that the mean value varies by the geographic region where the coal was mined. The range of average mercury concentrations from different regions varied from 70 to 240 ppb. During the 2010 Biomass Demonstration program the mercury concentration in the coal was 71 ppb⁴⁵. It would not be surprising to find analyses over a particular coal seam could see the range in a particular deposit having similar ranges \pm half the average value.

Mercury is present in wood in trace amounts. This is attributable to root uptake from soil and deposition of airborne mercury to leaves, buds and bark⁴⁶. If the coal was to be replaced by railway ties, the question becomes what would happen to the mercury emissions from the kiln process. While no specific mercury in railway ties data was located, a study to assess the mercury content of wood fuels was completed in 2004⁴⁷. The researchers found that there is a difference between the mercury content of different parts of the tree: the bark contains on average 37 ppb of mercury, whereas the stem wood, used for the railway tie, averaged 2.3 ppb of mercury. If coal averages 70 ppb any coal replaced by railway ties would result in a reduction of nearly 30 times in the concentration of mercury in that portion of the fuel. Lafarge conducted some testing of chipped railway ties and report a mercury concentration of 15.9 ppb, or about 78% lower than the coal used during the 2010 demonstration program. Even with a lower energy value per tonne of railway ties, **the mercury input to the kiln would be reduced, and the emissions would decrease.**

⁴⁵ However, Lafarge reports that previous coal shipments have ranged from 70-250 ppb consistent with the literature results.

⁴⁶ Massachusetts DEP, 1996. Toxics & Hazards: Mercury in Massachusetts An Evaluation of Sources, Emissions, Impacts and Controls Chapter 3 Mercury Sources, Emission Monitoring and Source Release Estimates. <http://www.mass.gov/dep/toxics/stypes/hgch3c.htm>

⁴⁷ Mentz, K., J. Pinkerton, and J. Louch, 2005. Potential mercury and hydrochloric acid emissions from wood fuels, *Forest Products Journal*, 55(2): 46-50. Available at: http://goliath.ecnext.com/coms2/gi_0199-3756522/Potential-mercury-and-hydrochloric-acid.html

Full Scale Test Data from Treated Wood Combustion Studies

Published test data can be divided into 3 categories:

- laboratory furnace tests such as those conducted by Becker et al. (discussed above);
- speciality testing in pilot scale furnaces used for combustion research; and,
- compliance testing at North American facilities attempting to obtain approval to use treated wood as a fuel substitute.

A fourth category is anecdotal data reported on the basis of other testing programs where the actual test data were not available for review.

Pilot Scale Testing

A European study, conducted in Germany⁴⁸, used a 1:4 mix of treated wood with untreated wood in three different furnaces that were designed to have efficient burn-out of the fuel. The first furnace was a 2 stage system with pre-oven, boiler and fluidised bed degassing reactor. The second was a solid fuel gasifier with a pre-drying section. The third was a grate firing system with a pre-connected shaft furnace. The units ranged in size from 35 kW to 6 MW output. While the tests involved a number of different preservatives, only those reported for creosote treated wood are discussed here. The main result is a comparison between measured emissions for the 1:4 treated wood fuel and untreated wood fuel firing situations. The furnaces were monitored with CEMs for oxygen, carbon monoxide, carbon dioxide, oxides of nitrogen, and hydrocarbons with an FID. PCDD/F, chromium, copper, chlorine, boron and fluorine were also monitored. No specific analysis of PAHs was conducted on the exhaust gas streams.

Typical oxygen levels in the furnaces were reported to be in the range of 11 – 12.5% indicating the presence of an oxidizing environment. Performance was reported to be hampered by the moisture content of the untreated wood. When the moisture content exceeded 25%, the combustion became more irregular leading the study team to conduct all the reported experiments using pre-dried wood. Gas temperatures in the first furnace was 1000-1050°C with the boiler temperature being 400-450°C, in the second the gasifier temperature was 1100-1250°C and the exhaust gas was in the range of 200-240°C. The authors report that combustion was very good for the creosote treated wood tests although the total hydrocarbons measured by FID were up to 7.7 mg/m³ compared to untreated wood levels of up to 3.1 mg/m³. The CO levels, sometimes used as an indicator of combustion efficiency, when testing the creosote treated wood were lower than when burning untreated wood. NO_x levels show no significant change with treated wood. Another indication of the improvements in combustion with the creosote treated wood was that these were the only tests in the whole series where PCDD/F levels from furnace 2 were below 0.1 ng/m³, the European emission limit. **The authors conclude that the emissions of organic and inorganic components are the same order of magnitude regardless of whether treated or untreated wood is fired.**

⁴⁸ Salthammer, T., H. Klipp, R.-D. Peek, and R. Marutzky, 1994. Emissions from the Combustion of Wood Treated with Organic and Inorganic Preservatives. A paper at the 25th Annual Meeting of the International Research Group on Wood Preservation. Available at: <http://www.bfafh.de/inst4/43/irg/1994/IRG%2094-50019.pdf>

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A U.S. research study⁴⁹ conducted at a government research facility was designed to provide data for utility permitting applications for the use of biomass in pulverised coal-fired utility boilers. The Department of Energy recognised that this approach offered an opportunity to increase renewable energy generation and reduce greenhouse gas emissions. PCP and creosote treated wood were co-fired for the testing that included a comprehensive assessment of air toxics, including dioxins, furans, polycyclic aromatic hydrocarbons (PAH), heavy metals (Hg, Sb, As, Cd, Cr, Co, Pb, Ni, and Se), formaldehyde and other volatile organic compounds, HCl, and particulates. Testing was completed **upstream** of the air pollution control system so the values represent uncontrolled emissions from the furnace (without air pollution control system reductions), with a co-firing rate of 10% of the heat input provided by the treated wood. The baseline fuel for the furnace is bituminous coal. Recognizing that the particle size for treated wood would not be the same size as pulverised coal in the boiler, studies were completed prior to the testing to determine the appropriate size for the treated wood to minimise carryover of glowing particles (sparklers) in the gas stream and carbon in the fly ash. This testing was aimed at limiting overgrinding of the wood. Tests were conducted with 20% total excess air, thereby ensuring oxygen in the furnace, and a furnace exit temperature of 1100°C. Velocities in the radiant section of the furnace provide up to 3 seconds residence time. Three sets of tests were conducted at each condition with the results averaged for presentation.

The results of these tests showed that treated wood had a higher volatility than the coal and this resulted in a changed flame root position in the furnace. This relocation was thought to have contributed to lower NO_x emissions when burning the treated wood. SO₂ also dropped due to lower sulphur levels in the wood. Lower CO and total hydrocarbon levels were noted with treated wood firing and because the treated wood has a lower ash content than coal, the particulate concentration in the emissions were reduced. Aldehydes and ketones were not significantly different from the baseline runs. The total PAHs released during combustion of creosote treated wood were reduced from the baseline values largely because the only compound that was found above the detection level was naphthalene whereas 2-methylnaphthalene was found in the baseline testing. Total PCDD/F was an order of magnitude lower than the baseline results when the creosote treated wood was fired.

The authors conclude that the results clearly indicate that treated woods can be successfully cofired with pulverised coal with respect to the emissions of air toxics. Indeed, as the authors note, the emission factors with treated wood were “actually somewhat lower than the baseline pulverised coal testing”.

Demonstration Testing

Stantec report the results of comparison testing at a Canadian wood fired co-generation facility⁵⁰. The study was completed for the TransCanada Power’s Williams Lake BC power plant to determine the emissions associated with burning creosote-treated rail ties. The facility is a wood fired co-generation site designed to use wood waste from local sawmills. Emissions from baseline tests at 100% normal wood waste firing rate were compared to testing while burning 100% rail ties. Sampling was conducted for various PAH, dioxin and

⁴⁹ Freeman, M.C., W.J. O’Dowd, T.D. Brown, R.A. Hargis, Jr., R. A. James, S. I. Plasynski, G.F. Walbert, A.F. Lowe, and J.J. Battista, Jr., 2000. Pilot-Scale Air Toxics R&D Assessment of Creosote-Treated and PCPTreated Wood Cofiring for Pulverized Coal Utility Boiler Applications. Biomass & bioenergy., ISSN: 09619534, Vol: 19, Issue: 6, Date: December, 2000, Pages: 447-456 Available at: <http://www.netl.doe.gov/technologies/coalpower/cctc/cctdp/bibliography/misc/pdfs/haps/2002-710.pdf>

⁵⁰ Stantec, 2009. Letter to BC Ministry of Environment, Thompson Region re: BC MOE Information Request Related to VOC, PAH, and Dioxin-Furan Emissions Available at: <http://savekamloops.ca/Docs/Attachment%20E.pdf>

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furan compounds, with the results being submitted to the BC Ministry of Environment. In a summary of the sampling results the PAH emissions from the substituted fuel testing were essentially unchanged however the dioxin and furan concentrations increased. Unfortunately, the summarized data for PCDD/F was quoted in the incorrect units, and while the levels appear to have increased by a factor of 3 times, the reported values 1–3 pg TEQ/m³ are so far below the effective quantitation limit [LoQ], 32 pg TEQ/m³, established by Environment Canada⁵¹, that the data should be considered to be in the noise range and the difference to be insignificant. In a second report issued by Norske Canada⁵² that references the same testing, the Williams Lake facility is noted to operate at 1100°C with a residence time of 2.5-3 seconds. The exhaust is treated with multiclones and an ESP. The Norske reports states that there were no changes in emissions of particulate, trace metals, dioxins and furans or PAHs however there was an increase in chlorophenol, SO₂ and HCl. Based upon this testing the Williams Lake facility permit was amended to allow railroad tie burning.

Permit Testing

Holzman and Atkins⁵³ provide data collected at three relatively large 20-50 MW wood fired power plants with spreader stoker type boilers and high efficiency electrostatic precipitator particulate control devices. Railroad ties were burned in the three units at 25-50%, 20% and 10% feed rates. The results are summarized in Table 2 at emission rates in lb/MMBtu. There appears to be little difference in the emission rates when ties are added to the fuel mix.

⁵¹ Environment Canada, Accessed 25 Jan 2012. <http://www.ec.gc.ca/toxiques-toxics/Default.asp?lang=En&n=C5039DE5-1&xml=02C78FC6-535B-4681-8931-0E84B26D7023>

⁵² Norske Canada, 2003. Crofton Division, #4 Power Plant – Alternative Fuels Trial Plan. A report submitted to BC MoE by Graham Kissack, Director, Environment. Available at: <http://www.croftonair.org/images/stories//alt-fuels-trial.pdf>

⁵³ Holzman, M.I. and R.S. Atkins, 1995. Emissions from Combustion of Treated Wood Fuel and Tires in Industrial Boilers. A paper 95-PR137.03 presented at the 1995 AWMA Annual Conference, San Antonio, Texas. Available at: <http://miholzman.com/resources/Emissions%2Bfrom%2BCombustion%2Bof%2BTreated%2BWood%2BAWMA%2B95-RP137.03.pdf>

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Table 2 Summary Emission Rates for End of Life Railway Tie Fuel Addition [lb/MMBtu]

Parameter	Facility 1		Facility 2		Facility 3	
	Base	25-50%	Base	20%	Base	10%
Firing Rate [MMBtu/hr]	339	339	711	681	286	295
PM	1.68E-03	1.31E-03	2.63E-02	2.80E-02		
NO _x	1.44E-01	1.22E-01	2.06E-01	2.07E-01	1.96E-01	2.00E-01
CO	2.65E-01	5.21E-01	4.50E-01	4.04E-01	2.66E-01	1.39E-01
SO ₂	2.54E-03	4.07E-02			2.00E-03	4.30E-02
THC	3.62E+03	5.72E-03			5.07E-03	3.62E-03
2,3,7,8 TCDD	7.80E-11	3.51E-11	1.66E-12	3.66E-12		
Acetaldehyde	7.57E-05	2.54E-05	5.11E-04	1.54E-04		
Acrolein			1.65E-04	5.74E-05		
Benzene	2.45E-04	1.55E-04	2.15E-04	2.40E-04		
benzo(a)anthracene	BDL	BDL	2.73E-07	2.62E-07		
B(A)P	BDL	BDL	2.96E-07	3.21E-07		
chlorophenols			1.94E-05	2.11E-05		
chlorobenzenes			1.19E-05	1.26E-05		
chrysene/triphenylene	BDL	BDL	2.98E-07	3.08E-07		
naphthalene			7.05E-06	3.28E-06		
phenol			2.27E-05	4.58E-06		
dioxins			BDL	BDL		
furans			BDL	BDL		

The authors concluded that the results demonstrate that these materials could be burned in an environmentally safe manner in conventional boilers.

In a stack test program⁵⁴, at a 30,000 lb/hr biomass boiler in Mississippi, emissions were measured when a mix of 50/50 creosote treated wood and pentachlorophenol treated wood was fired in the boiler at two different firing rates 20.33 MMBtu/hr and 47.92 MMBtu/hr. The test report does not mention any air pollution control devices on the exhaust. Samples of the fuel feed were tested during the program to allow calculation of the “Destruction & Removal Efficiency” [DRE] of pentachlorophenol and creosote compounds in the process based upon the quantity of these materials in the exhaust stream. The report shows an average DRE under low fire conditions of 99.9971% and this rose to 99.9984% during high fire conditions. The test results indicate that the main PAH released from the stack was naphthalene, which agrees with that compound’s relative ranking on the T₉₉ values reported earlier. In Miller’s letter⁵⁵ referenced earlier, additional information on PAH emissions for untreated fuel firing is provided. Table 4 in the letter indicates generally higher PAH emission rates for those compounds measured in the untreated wood testing than with the treated wood being fired. The exception was naphthalene where the treated testing results were 1.22 times the untreated wood results. For the other six compounds measured in both tests, the difference was up to 3 orders of magnitude lower with the treated wood testing. Miller suggests that this behaviour occurs because the treated wood waste is

⁵⁴ Smith, S.T. 1996. Stack Testing Report, Koppers Industries Ltd., Grenada Plant, Tie Plant, MS. Submitted to the Mississippi DEQ, May 6, 1996. Available on the Mississippi DEQ web site.

⁵⁵ Miller, Jeffrey T., 2010. Letter re Proposed Biomass Regulations from Treated Wood Council to Massachusetts Department of Energy Resources. Available at: <http://www.env.state.ma.us/eea/doer/biomass/comments-oct21-2010/Treated%20Wood%20Council.pdf>

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generally drier than green biomass, and the presence of the creosote in the wood increases the heating value of the fuel so it burns hotter than “clean” biomass.

Anecdotal Reports

In this section, the results of various tests are reported on the basis of the comments in the referenced document. Without being able to review copies of the actual test reports, the comments and conclusions in the cited documents could not be verified.

The Norske report referenced above suggests that Northwood Pulp in Prince George BC has permission to burn 10% railway ties in their hog fuel power boilers that operate at 920°C with a 3 second residence time. It is stated that approval followed trials that included testing by Environment Canada that concluded that the system was suitable to achieve virtual destruction of chlorophenols and PCDD/F. Testing showed 99.99% DRE for chlorophenols. The Norske report also notes that Blandin Paper in Minnesota was re-permitted in 1997 to burn up to 15% railway ties.

Morrell⁵⁶ cites three authors who discussed combustion of creosote treated wood at a 1992 conference on life cycle assessment of treated wood. The author implies that the referenced papers suggest that the destruction of creosote was relatively simple given the high temperatures involved. Morrell notes that the authors indicate that burning wood treated with other preservatives can increase emissions of various contaminants. In fact, he concludes that because of the limitations caused by the other treatment system, the use of combustion for disposal would likely be limited to only the creosote treated wood that represents 15-20% of the treated wood in service.

Cooper⁵⁷ also notes the same conclusion, creosote treated wood can be used in cement kilns without restriction, but cites a 1995 paper by St. Lawrence Cement employee, Bernardin, given at a Life Cycle Assessment Conference that suggests that up to 13 kg of CCA treated wood could be used for the manufacture of a tonne of cement. The WRAP publication⁵⁸ cites similar limits on the use of CCA treated wood waste in Europe, but also notes that France was burning 40,000 tonnes of creosote treated wood waste in cement kilns in 2005. Zandersons et al.⁵⁹ suggest that they found references indicating that small scale furnaces at greenhouses burning treated wood had higher emissions of hydrocarbon, suggesting the need for better controls. They note that burning creosote treated wood to replace fossil fuels will reduce greenhouse gas emissions. They cite the work of Freeman and note that high temperatures and good combustion control eliminates higher emissions.

⁵⁶ Morrell, J.J., 2004. Disposal of Treated Wood. A paper in the Proceedings of Conference on the Environmental Impacts of Preservative Treated Wood, held at the Florida Centre for Environmental Solutions, Gainesville. Available at: http://ccaresearch.org/Pre-Conference/document/FI_Env_Cent_Treated_Wood_Proceedings2.pdf

⁵⁷ Cooper, P.A., 1999. Future of Wood Preservation in Canada – Disposal Issues. A paper presented at the 20th Annual Conference of the Canadian Wood Preservation Association. Vancouver. Available at: http://www.forestry.toronto.edu/treated_wood/future.pdf

⁵⁸ WRAP, 2007. Options and Risk Assessment for Treated Wood Waste. Written by: TRADA Technology & Enviros Consulting Ltd. Published by: The Waste & Resources Action Programme, June 2005. Available at: http://www.wrap.org.uk/downloads/Options_and_Risk_Assessment_for_Treated_Wood_Waste.bcbea09f.2237.pdf

⁵⁹ Zandersons, J., A. Zhurinsh and E. Someus, 2006. Prospects for Co-Firing of Clean Coal and Creosote-treated Waste Wood at Small Scale Power Stations. THERMAL SCIENCE Vol 10,3 PAGES [109 - 118]

Conclusions from Test Data

Most of the test data indicates that under carefully controlled combustion conditions creosote treated wood will not give rise to higher emissions. All the confirmed testing referred to in this section was undertaken in furnaces that were typically used for waste wood combustion, except for the one pulverized coal boiler. All the systems considered achieved temperatures in excess of 920°C but none appear to have gas residence times at this temperature that exceed 3 seconds. In contrast, the typical cement kiln has higher operating temperatures and longer residence times suggesting that combustion outcomes should be much better in the cement kiln. This has been confirmed in other studies⁶⁰ of waste firing in cement kilns where it is noted that “no statistically significant increase in emission rates were observed when the waste fuel (as opposed to coal) were burned.”

The test data reviews clearly show a range of different types of combustion systems with favourable emissions results when burning creosote treated wood. These agree with the earlier discussion on the importance of temperature and residence time in limiting the release of PICs. No direct references to open burning of railway ties were found in the literature, other than the noted ban on open burning in the Environment Canada publication. Some understanding of why that ban is suggested is available in a review of open burning test results published by the US EPA⁶¹. These tests simulated open burning of waste in burn barrels, an arrangement that facilitated gathering of emissions data. During the tests the maximum bed temperature varied from 370 – 740°C and while no gas residence time was reported it would be expected to be fairly short <1 second. The report suggests that PAH emissions from the combustion system were on the order of 1500 – 3800 times greater than one might find in a typical incinerator. This is an indicator of relatively poor combustion performance.

Two wood fired boilers tested burning creosote treated wood in western Canada had 920 – 1100°C temperatures in the combustion zone with residence times between 2.5 and 3 seconds. These showed no increase in emissions of PAHs when the ties were added at rates between 10% and 100% of normal feed rates.

For the coal fired boiler co-firing tests from the US DoE the boiler had an operating temperature near 1100°C and a residence time estimated to be in the 3 second range. The authors note that when firing 10% creosote treated wood with the coal, the PAH emissions were lower than those seen with coal firing alone.

For a cement kiln, the clinker must achieve 1450°C and to do this the gas temperatures approach 2800°C at the hot end of the kiln. The total gas residence time in these systems varies from 4 second to 16 seconds. The US EPA in reviewing cement kiln operation⁶² suggests that organics are efficiently destroyed when fed into the hot end of the kiln and destruction removal efficiency data confirms this. In fact they go on to state that failures to meet destruction removal efficiency targets in kilns are extremely rare and typically caused by design limitations. The test data reported in the literature confirms this performance.

⁶⁰ Branscome, M., Westbrook, W., Mournighan, R., Bolstad, J., and Chehaske, J., 1985. Summary of testing at cement kilns co-firing hazardous waste. In BREF, 2005. Waste treatments. Available at: <http://eippcb.jrc.es/pages/FAactivities.htm>

⁶¹ Lemieux, P.M. 1997. Evaluation of Emissions from the Open Burning of Household Waste in Barrels, Vol. 1. Technical Report, U.S. Environmental Protection Agency (EPA-600/R-97-134a), (NTIS PB98-127343), Research Triangle Park, NC, November

⁶² US EPA, 2001. Risk Burn Guidance for Hazardous Waste Combustion Facilities. Office of Solid Waste and Emergency Response. Prepared by Region 4, Atlanta, Georgia as EPA530-R-01-001. Available at: <http://www.epa.gov/osw/hazard/tsd/td/combust/pdfs/burn.pdf>. Reference is from §4.5.

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A simple comparison of these combustion situations is provided in Table 3.

Table 3 Overview of Test Results

Process	Temperature (°C)	Residence Time (Seconds)	Results	Government Permits
"Burn Barrel"	370-740	<< 1	Unacceptable, Emissions 1500- 3800x higher than incinerators	Prohibited
Wood Fired Industrial Boiler	920-1100	2.5-3	No increase in emissions	Permitted
Coal Fired Industrial Boiler	1100	3	Lower emissions	Permitted
Cement kilns	1450	4-16	Expecting same or lower emissions	Permitted (seeking test permit at Bath)

Conclusion: Using End of Life Railway Ties in Cement Manufacturing

As noted in the introduction, the cement industry's kilns use a tremendous amount of energy to convert the raw materials to clinker. The IPPC BREF⁶³ notes that the theoretical energy use for the burning process (chemical reactions) is about 1700 to 1800 MJ/tonne clinker. The actual fuel energy use for different kiln systems ranges from 3000 to 6000 MJ/tonne clinker with Canadian facilities consuming an average of 3700 MJ/tonne of clinker. The predominant energy source is coal which has a heating capacity of 15 - 27 MJ/kg. Coal can be blended with petroleum coke which typically has a higher heating value of 28 MJ/kg. If the blend averaged 25 MJ/kg, Canadian facilities will average 150kg of the mix for every tonne of clinker produced. By contrast, creosote treated wood with moisture levels on the order of 5% has reported calorific values on the order of 19-22 MJ/kg (Freeman and Zandersons references). It would thus take approximately 5 Mg of railway ties to replace 4 Mg of the blended coal/coke mix. The referenced moisture content of treated wood is quoted in other references, Miller and Holzmann, note that moisture could be in the 20 – 26% range which lowers the calorific value as received to 13.9-15.8 MJ/kg. By contrast green wood has a net calorific value of 10 MJ/kg. If the treated wood contains higher levels of moisture the amount of treated wood required to replace the energy equivalent of coal would rise.

Converting creosote treated wood to energy in a cement kiln represents a recycling of materials that can no longer perform their intended function and thus would fit with the hierarchy of waste disposal alternatives. The biomass in the ties is renewable so the energy recovery would classify as a renewable fuel, and with its use there would be an attendant decrease in the greenhouse gas production rate in the kiln. The timber used in cross ties can be reproduced during the service life of the tie thus it would be sustainable. Most importantly, since the PAHs in cross ties present concerns with respect to their re-use, the preferred alternative for post service is disposal. While disposal in a landfill will lead to the eventual degradation of the tie in the landfill and the release of methane, a potent greenhouse gas, the net effect of burning the treated cross ties will be a substantial reduction in the potential for greenhouse gas emissions from the tie materials.

This report has concentrated on the organic compounds that are present in creosote treated ties. These compounds will be destroyed in the kiln. Inorganic contaminants, metals such as cobalt, magnesium, copper, etc. are not destroyed in the kiln but the chemistry in the system will segregate most of these materials to the product stream. As demonstrated in the October, 2010 biomass demonstration program⁶⁴, the partitioning factors (the amount of input metals sequestered in the clinker) are typically very high (see Table 4 below). Only limited quantities of these metals will be emitted in the exhaust stream regardless of which fuel is used. Inorganics are also found in coal at levels that depend largely upon the origin of the coal.

Mercury is an exception in that it is in vapour form at the temperatures inherent in cement manufacturing (and similarly for industrial boilers) and is only partly sequestered into clinker. Data suggests that the wood used for railway ties could have a 30 times lower mercury concentrations than coal, which would be expected to lower mercury emissions when railway ties replace coal as a kiln fuel.

⁶³ IPPC, 2005. BREF Reference Document on Best Available Techniques in the Cement and Lime Manufacturing Industries. Integrated Pollution Prevention and Control (IPPC). December. Available at: http://eippcb.jrc.ec.europa.eu/reference/brefdownload/download_CLM.cfm

⁶⁴ Lafarge Biomass Demonstration Project Summary Report, May 24, 2011 available at http://www.cement2020.com/sg_userfiles/Lafarge_Biomass_Demonstration_Summary_Report_2011.pdf

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Table 4 Partitioning Factors for metals during biomass cofiring

	Inputs		Outputs		
	(Coal/Coke)/biomass (90:10)	Raw mix	Stack Emissions	Clinker by difference	Partitioning Factors
	grams/h	grams/h	grams/h	grams/h	%
Arsenic	32.6	774.2	0.425	806	99.947%
Antimony	3.4	161.9	0.576	165	99.651%
Barium	529.7	18,792.0	1.819	19320	99.991%
Beryllium	3.4	56.3	0.032	60	99.946%
Cadmium	1.7	42.2	0.291	44	99.338%
Chromium	565.2	15,413.7	0.798	15978	99.995%
Lead	129.2	4,997.1	9.129	5117	99.822%
Mercury	1.0	5.4	3.022	3	52.848%
Silver	3.4	42.2	0.241	45	99.473%
Thallium	0.8	8,234.7	3.864	8232	99.953%
Selenium	13.5	739.0	1.345	751	99.821%
Nickel	129.6	1,794.7	0.866	1924	99.955%
Cobalt	26.0	506.8	0.126	533	99.976%
Copper	186.8	1,998.8	43.808	2142	97.996%
Manganese	10,122.3	267,451.6	N/M		
Vanadium	16.1	2,111.5	0.279	8582	99.997%
Zinc	629.2	7,953.2	18.556	4317	99.572%

*Partitioning Factors were calculated by using the average of 3 runs from the stack test results (measured on Oct 5, 6, 7 2010) and the input metal concentrations (coal/coke was a composite sample from Oct 6 and the biomass were average results from samples taken over Oct 5, 6, and 7th, 2010). The Raw mix was a composite sample from Oct 6, 2010.

The best surrogate data for predicting what might happen in the kiln if treated wood was substituted for coal is the Freeman et al. data from the pulverised coal boiler where substituting 10% creosote treated wood resulted in a decrease in the inorganic emission rate from 10–50% depending upon the element⁶⁵. Zandersons et al. report the metals concentration in charcoal created from thermally treated wood in comparison to a control sample of pine. Arsenic, chromium, cobalt, and iron were noted to have increased while copper, zinc, lead and cadmium levels decreased. They attribute the increased concentrations to the wear of the rails and wheels on the railway, and suggest that the decrease in zinc may be due to the trees having grown in different soils. The arsenic level, while noted, was not commented on but could also be due to uptake from soil.

⁶⁵ The only element that did not respond in this manner was mercury but with only a 3% change in the emission rate this data is hardly conclusive.

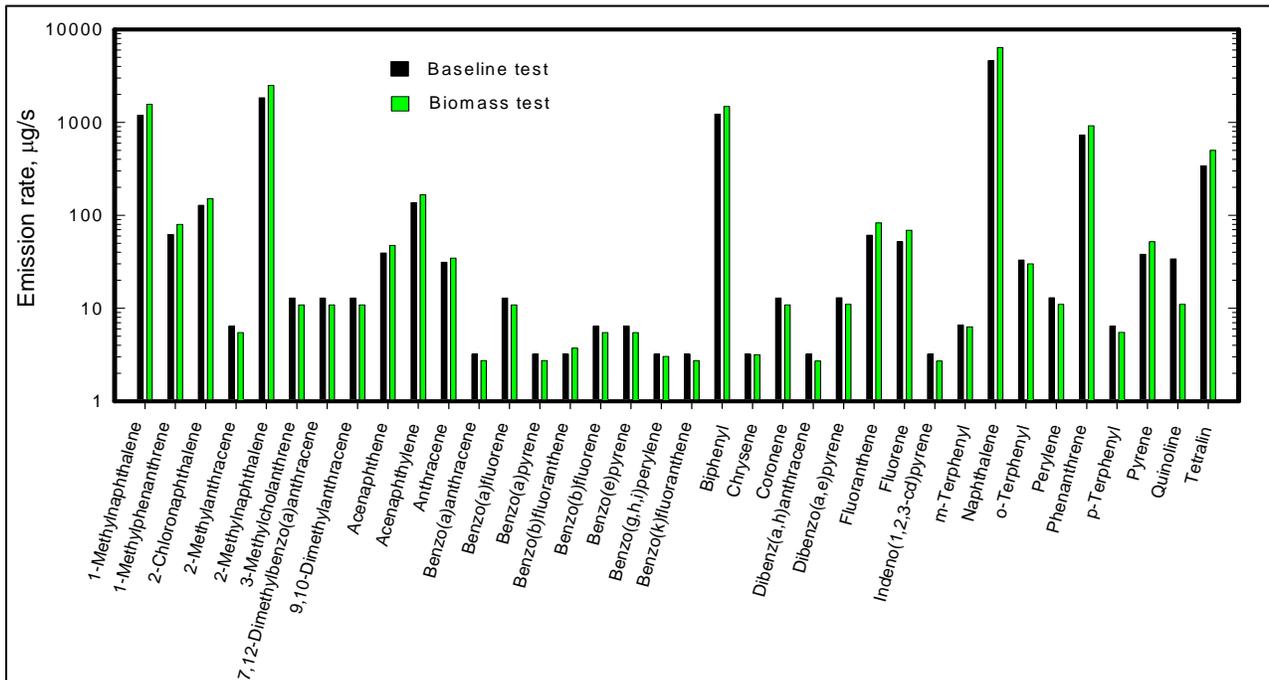
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Salthammer et al. noted an increase in chromium and copper emission rates from the two stage furnace but no difference in the gasifier exhaust. They concluded however that, since the values did not change by an order of magnitude, there was no significant change. In a report on a slow pyrolysis study, the authors compare chromium, copper and arsenic contents of treated and untreated wood⁶⁶ showing chromium to be lower, copper higher and arsenic measurable in the treated sample and BDL in the untreated sample. It can be concluded on the basis of these data that it is unlikely that significant changes will occur in emissions of inorganics from the kiln, particularly for chromium and iron which will likely form part of the clinker.

Probably the most relevant testing data pertaining to a Canadian cement kiln burning treated wood waste is that from the Joliette facility. To date, the author has been unable to locate a copy of those testing reports. In the absence of that data, should Lafarge wish to proceed with the use of creosote treated wood in the kiln at Bath, a test program should be developed. That program should include some initial operation of the facility to ensure that combustion conditions in the kiln are not disturbed by the introduction of the wood. Testing should measure emission rates for all the pertinent organic compounds and metallic species with and without the treated wood be charged to the kiln.

In 2010, Lafarge conducted tests of PAH emissions ($\mu\text{g/s}$) for both a baseline case and with approximately 9% co-fire of virgin biomass. **In all cases all emission levels were <1% of the Ontario Ministry of Environment regulations.** Further, there wasn't a significant difference between the baseline and biomass results (simple random variation measured). Results show expected behaviour with larger emissions noted for naphthalene (the most rudimentary PAH). Across the spectrum of PAH compounds there is a wide range of emission rates from barely detectable levels up to measureable amounts.

Figure 2: PAH Results from the 2010 Baseline and Virgin Biomass Source Emission Tests



⁶⁶ Zhurnish, A., J. Zandersons, and G. Dobeles, 2005. Slow Pyrolysis studies for Utilization of Impregnated Waste Timber Materials. *J. Anal. Appl. Pyrolysis*, 74 (2005) 439-444.

Recommendations and Guidelines

1. Based on previous tests and the operation conditions in cement plants, railway ties can be used as safe and effective substitutes for typical fossil fuels such as coal and petroleum coke. Furthermore, there is a good expectation that their use will improve the facility's emissions. It is recommended that this conclusion be subjected to statistically based comparison testing for PAHs and metals.
2. Pyrolytic destruction temperatures for PAHs in treated wood waste should be in excess of 1100 C for a minimum of 2 seconds. Since this minimum is intrinsically far exceeded when cement plants are producing clinker, cement kilns are highly suitable for firing with railway ties.
3. Biomass containing fuels should be as dry as possible to improve their performance in the kiln. When dry sources of biomass are shredded, efforts should be made to cover or otherwise contain the shredded product. Railway ties, where practical, should be kept in covered storage to control moisture levels and odour. When shredding railway ties, and during subsequent handling, organic control respirators are recommended for equipment operators.
4. Chlorinated compounds are present in many fuels, traditional and non-traditional, as well as the raw materials typically used to make cement. When present at levels above a kiln specific limit, chlorine can result in the need to dispose or otherwise use cement kiln dust and/or it can lead to the risk of process instability. Care should be taken to monitor fuel chlorine levels, alongside other feed materials, to ensure that the use of the fuel does not produce unwanted effects.
5. A maximum particle size specification should be established for solid fuels. Ash characteristics should be assessed to ensure that cement quality requirements are met.
6. Magnetic separators should be used to keep spikes and plates from entering and damaging shredding equipment from railway ties and other tramp metals that may be present in other low carbon fuels.
7. When long aspect ratio splinters become problematic, secondary screening may be required by fuel processors to ensure uninterrupted fuel supply (eg plugged feed lines) at the fuel user site. Pneumatic conveyance pipelines should be equipped with long-sweep elbows and cleanout locations. The fuel delivery system should be placed as close to the combustion process as possible.
8. To the degree practical, fuels should be consistently mixed and shredded to minimize differences between fuel deliveries.
9. Inspection programs at supplier sites and other quality control measures should be implemented to ensure that no untested new material types are inadvertently added to the fuel mix.
10. Carbon trading systems will require precise and comprehensive accounting and recordkeeping and may require analytical data as evidence of biomass proportions. Consideration should be given to additional sampling and process measurements that can assist in the support of the furtherance of science.
11. Results of testing should be subject to QA/QC reviews, statistical analysis, and reviewed by a multi-stakeholder executive panel, and made public.

APPENDIX A: Chemistry

Materials in this section represent detailed lists of compounds identified in creosote and creosote treated wood, and data concerning the physical properties of these compounds. The tables also provide a list of the compounds found in the various experiments conducted by Becker et al. as referenced in the main text.

The Chemistry of Creosote

Creosote is derived from various tars. Coal tar creosote⁶⁷ is a brownish-black/yellowish-dark green oily liquid with a characteristic sharp odour, obtained by the fractional distillation of crude coal tars. The approximate distillation range is 200-400°C.

Tars are formed as products of the incomplete combustion of wood or coal that creates soot and tarry smoke. Wood tars are the materials that can cause concern in the flues of wood stoves or wood fireplaces. There is a difference between creosotes distilled from wood tars, and used in pharmaceutical preparations, and coal tar creosote. Wood tar creosotes contain methyl ethers of phenol; whereas, coal tar creosotes contain naphthalenes and anthracenes. Coal tars are by-products of steel manufacturing and the production of coal tar products may vary depending on demand for steel⁶⁸. Since coal tar creosotes are used for wood preservation it is appropriate to look at their characteristics in more detail. Wood tar creosotes are not discussed further in this document.

The origin of the coal influences the chemical composition of coal tar creosote. Moreover, the distillation process can vary in different locations thereby affecting the concentration of the components in the mix. Indeed, creosote is a mixture of several hundred chemicals but only a limited number of them are found in concentrations exceeding 1%. The UNEP document, referenced above, notes that there are 6 major classes of compounds in coal tar creosote:

1. Aromatic hydrocarbons: including Polyaromatic Hydrocarbons (PAHs), alkylated PAHs (non-heterocyclic PAHs can constitute up to 90% by weight) and BTEX (benzene, toluene, ethyl benzene and xylene);
2. Tar acids/Phenolics: phenols, cresols, xylenols, and naphthols (tar acids 1-3% by weight, phenolics 2-17% by weight);
3. Tar bases/nitrogen contained heterocycles: indole, quinoline, isoquinoline, carbazole; acridine; and benz(a)acridine (tar bases 1-3% and nitrogen containing heterocycles 4.4-8.2% by weight);
4. Aromatic amines: aniline, aminonaphthalenes, diphenyl amines, aminofluorenes, and aminophenanthrenes as well as cyano-PAHs, benzacridine and its methyl-substituted congeners;
5. Sulphur-containing heterocycles: benzothiophenes and their derivatives (1-3% by weight); and,
6. Oxygen-containing heterocycles: dibenzofuran (5-7.5%).

⁶⁷ UNEP, 2004. Concise International Chemical Assessment Document 62, Coal Tar Creosote. Available at <http://www.inchem.org/documents/cicads/cicads/cicad62.html>.

⁶⁸ ATSDR, 2002. Toxicological Profile for Wood Creosote, Coal Tar Creosote, Creosote, Coal Tar, Coal Tar Pitch and Coal Tar Pitch Volatiles. U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry. Available at: <http://www.atsdr.cdc.gov/substances/toxsubstance.asp?toxid=18>

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A summary of reported chemical concentrations is listed in Table A-1. The references for the table can be found in the UNEP document. Creosote has a density of 1.00 – 1.17 g/cm³ at 25°C with an ignition temperature of 500°C. While coal tars have a higher heating value [HHV] in excess of 38 MJ/kg, the creosote distilled from the tar is reported to have a HHV of 29 MJ/kg⁶⁹.

The physical properties of some of the components of creosote are also summarised in the UNEP document. Table A-2 was adapted from Table 5 in the UNEP document. These properties, particularly the boiling point and vapour pressure can influence the destruction of creosote in various potential disposal scenarios for wood preserved with creosote. From the perspective of “in use” environmental effects of creosote treated wood, the solubility of the creosote material in water is important as it relates to the potential for it to leach from treated wood into the environment. Creosote is considered to be immiscible in water by the US EPA whereas it is classed as slightly soluble according to data in the UNEP reference. The individual compounds in creosote possess a wide range of aqueous solubility as seen in the right column of Table A-2. The PAH compounds with three or more aromatic rings have a solubility of less than 1 mg/litre however BTEX and other compounds show solubility levels that are orders of magnitude higher.

Various authors report that weathered creosote treated wood has a different range of compounds than freshly treated wood. Cooper et al.⁷⁰ notes that the mix of compounds in the creosote extracted from aged poles after service was substantially different than that found in fresh creosote. There were fewer PAHs in the weathered wood and lower relative concentrations of the volatile and water soluble compounds such as naphthalene, quinolone and methylnaphthalenes. Given that creosote is composed of products distilled from coal tars at temperatures from 200 – 400°C it should not be surprising that experiments⁷¹ run at normal ambient temperature ranges 20-38°C showed that creosote treated wood released volatile compounds. The PAH with the lowest boiling point, naphthalene, accounted for 75% of the volatile compounds in the test chamber air even though naphthalene comprised only 10.5% of the solution used to treat the wood. The more non-volatile compounds in creosote were not identified in the air samples. Brooks⁷² notes that the typical initial loss rate is 30-40 ug/cm² of PAH for new wood decreasing to 3-5 ug/cm² at 25 years of age. The author notes that the PAHs lost in this manner are degraded by chemical and photo-oxidation processes and metabolized by microbes. Even though there are losses, the author concluded that the compounds migrating out of the railway ties are retained in the ballast on the roadbed and not mobilized into the surrounding environment. Kohler et al.⁷³ suggest that railway ties may emit 5 kg of creosote over their life. The 2 and 3 ring PAHs predominate the losses.

⁶⁹ Stephen Smith and Chris Bolin, Creosote-Treated Ties End-of-Life Evaluation. Available at : http://www.rta.org/Portals/0/Documents/Research%20Paper%20&%20Articles/RTA%20Sponsored%20Research/Creosote%20Tie%20Evaluation%20Article%20_4_.pdf

⁷⁰ Cooper, Paul, Tony Ung, Jean-Paul Aucoin, and Chris Timusk, 1996. The Potential for Re-Use of Preservative Treated Utility Poles Removed from Service. Waste Management & Research, (1996) 14. 263-279

⁷¹ Ingram, Leonard L. and Kimberley Tarlton, 2005. Effect of physical properties of pentachlorophenol and creosote components on vaporization from treated wood: Review of prior data. Forests Products Journal Vol. 55 No. 6 86-89

⁷² Brooks, K.M. 1997. Literature Review, Computer Model and Assessment of the Potential Environmental Risks Associated with Creosote Treated Wood Products Used in Aquatic Environments. In Goyette and Brooks (1999) Creosote Evaluation: Phase II, Sooke Basin Study – Baseline to 535 Days Post Construction – 1995-1996. A report prepared for Environment Canada, Pacific and Yukon Region.

⁷³ Kohler M., Künniger T., Schmid P., Gujeer E., Crockett R., Wolfensberger M., 2000. Inventory and Emission Factors of Creosote, Polycyclic Aromatic Hydrocarbons (PAH), and Phenols from Railroad Ties Treated with Creosote. Environmental Science and Technology, 34 pp 4766-4772.

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The UNEP review of creosote provides some data on the range of concentrations of creosote compounds in weathered ties. That data is provided in Table A-3. It is important to note that a range of values are reported for 27 samples collected in western Canada, but the target list of substances was restricted to the less volatile species. The Canadian study was done to supplement work completed in the early 1990s assessing the toxicity of treated wood as part of the Priority Substances List under the Canadian Environmental Protection Act (CEPA).

One report about creosote treated crossties in Europe notes that in 2008 a comprehensive analysis of the socio-economic benefits of creosote as a preservative was initiated. In Europe⁷⁴ the content of benz(a)pyrene [B(a)P] in the creosote is an important factor in governing usage. Three different types of preservatives were used: a heavy oil and creosote mixture for ties which can have up to 500 mg/kg of B(a)P however in 2003 that was lowered to 50 mg/kg; a light oil mix with low B(a)P content 5 – 50 mg/kg used on poles; and, a medium oil mix with low B(a)P and the low and high boiling fractions separated. Given the range of potential health effects related to this compound, railway ties have been designated for special handling in Europe. Thermal or biological treatment processes have been developed in Europe to dispose of these materials. These recommendations go a step further than those in Canada⁷⁵ which recommend that ties be sent for energy recovery and failing that, ties should be disposed in landfills.

Experimental Data from a Thermogravimetric Study

The main text discusses the research of Becker and his colleagues. These experiments examined what happened to samples of wood, treated wood, and creosote as it was heated in different atmospheres. Samples of the air inside the test apparatus were taken and both qualitative and quantitative analysis was completed. These data show the types of compounds released as the samples were heated. The results for the treated wood samples clearly show the combined effects of the degradation of the two components in the system, wood and creosote. A comparison of the qualitative results is provided in Table A-4. For each material, at each temperature, the compounds found in the samples are denoted by the X in the box.

⁷⁴ Mayer, Ingo, Christelle Ganne-Chédeville, Julien Ropp, Urs von Arx, Frédéric Pichelin, 2010. Thermal Decontamination of Railway Sleepers for Recycling. World Conference on Timber Engineering, Paper 454 Available at: http://www.ewpa.com/Archive/2010/june/Paper_454.pdf

⁷⁵ Environment Canada, 2004. INDUSTRIAL TREATED WOOD USERS GUIDANCE DOCUMENT

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Table A-1 Creosote Chemical Analyses from the UNEP Chemical Assessment Document

	Chemical analysis (weight %)							
	(A)	(B)	(C)	(D)	(E)	(F)	(G)	(H)
Aromatic hydrocarbons								
Indene					0.6	0.43	0.87	
Biphenyl	0.8*/1.6	2.1	1-4	0.8 ^c	1.3	1.45	4.1	
<i>PAHs</i>								
Naphthalene	1.3/3.0*	11	13-18	7.6	12.9	12.32	11.4	
1-Methylnaphthalene	0.9*/1.7		12-17	0.9 ^c	2.2	3.29	8.87	
2-Methylnaphthalene	1.2*/2.8	3	12	2.1 ^c	4.5	7.51	11.5	
Dimethylnaphthalenes	2.0*/2.3	5.6			1.6	3.42	5.16	
Acenaphthylene					0.2	0.15	0.1	
Acenaphthene	9.0*/14.7	3.1	9	8.3 ^c	5.8	12.51	5.86	
Fluorene	7.3/10.0*	3.1	7-9	5.2 ^c	4.6	5.03	6.33	
Methylfluorenes	2.3/3.0*				3.1			
Phenanthrene	21*	12.2	12-16	16.9 ^c	11.2	10.21	6.7	1-3.3
Methylphenanthrenes	3.0*				3.1	0.45	0.54	
Anthracene	2.0*		2-7	8.2 ^d	1.7	0.9	0.8	0.4-1.2
Methylanthracenes	4.0*	5.9						
Fluoranthene	7.6/10.0*	3.4	2-3	7.5 ^c	4.6	4.41	2.27	0.2-2.2
Pyrene	7.0/8.5*	2.2	1-5	5.3 ^c	3.7	2	1.13	0.1-1.5
Benzofluorenes	1.0/2.0*	3.4			2.2			
Benz[<i>a</i>]anthracene					0.5	0.26	0.17	
Benzo[<i>k</i>]fluoranthene					0.22			0.16-0.3
Chrysene	2.6/3.0*	2.2	1 ^e		0.5-1.0	0.21	< 0.05	
Benzo[<i>a</i>]pyrene				0.43 ^c	0.2	<0.1	<0.05	0.02-0.16
Benzo[<i>e</i>]pyrene					0.2			
Perylene					0.1			
Tar acids / phenolics								
Phenol					0.24	0.56	0.24	
<i>o</i> -Cresol					0.1		0.2	
<i>m</i> -, <i>p</i> -Cresol					0.24	2.31	0.6	
2,4-Dimethylphenol					0.12	0.59	0.48	
Naphthols					0.12			
Tar bases / nitrogen-containing heterocycles								
Indole				2 ^d				
Quinoline			1	2.0 ^d	0.59	0.58	0.89	
Isoquinoline				0.7 ^d	0.18	0.3	0.59	
Benzoquinoline				4 ^d	0.29	0.05	0.5	
Methylbenzoquinoline				0.3 ^d				
Carbazole		2.4		3.9 ^d	0.7	0.53	0.22	
Methylcarbazoles				2 ^d				
Benzocarbazoles				2.8 ^d	0.1			
Dibenzocarbazoles				3.1 ^d				
Acridine				2 ^d	0.2	1.5	0.12	
Aromatic amines								
Aniline				0.05 ^d	0.21			
Sulfur-containing heterocycles								
Benzothiophene				0.3 ^c	0.4	0.3	0.5	
Dibenzothiophene					1	0.78	0.73	
Oxygen-containing heterocycles / furans								
Benzo-furan						< 0.1	< 0.1	
Dibenzofuran	5.0*/7.5	1.1	4-6	3.9 ^c	3.7	6.14	5.59	
Other not specified components					23.1			

NOTES:

- a Adapted from Heikkilä (2001).
b (A) Lorenz & Gjovik (1972); with asterisk (*) from a literature survey; without asterisk, own measurements of main components in an AWP standard creosote.
(B) Nestler (1974); six creosotes, four unspecified, and two fulfilled the US federal specifications I and III.
(C) Andersson et al. (1983); Rudling & Rosen (1983); creosote used in the impregnation of railway ties.
(D) Wright et al. (1985).
(E) ITC (1990); AWP standard creosote P1 (AWPA P1).
(F) Nylund et al. (1992); sample of German creosote; about 85 compounds were identified.
(G) Nylund et al. (1992); sample of former Soviet creosote; about 85 compounds were identified.
(H) Schirmberg (1980); three different creosote samples, all fulfilling the British standard BS 144/73/2.
c Concentration in PAH fraction.
d Concentration in nitrogen compound fraction.
e Includes triphenylene.

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Table A-2 Physical Properties of Components of Creosote from the UNEP Chemical Assessment

Compound	Chemical formula	Relative molecular mass	Boiling point (°C)	Vapour pressure (Pa, 25 °C)	Log K_{ow}	Exp. ^a log K_{tw}	Aqueous solubility (mg/litre @ 25°C)
Aromatic hydrocarbons							
Benzene	C ₆ H ₆	78.1 ^b	80 ^b	12 700 ^c	2.12 ^b		1780 ^b
Toluene	C ₇ H ₈	92.1 ^d	111 ^d	3700 ^c	2.69 ^e		515 ^e
Ethylbenzene	C ₈ H ₁₀	106.2 ^d	136 ^d	1240 ^c	3.13 ^e		152 ^e
<i>p</i> -Xylene	C ₈ H ₁₀	154.2 ^d	254 ^d	1180 ^c	3.18 ^e		215 ^e
Indene	C ₉ H ₈	116.2 ^d	182 ^d	160 ^f	2.92 ^g	3.68	insoluble ^h
Biphenyl	C ₁₂ H ₁₀	154.2 ^d	254 ^d	0.7 ^f	3.16–4.17 ^h		7.5 ^d
PAHs							
Naphthalene	C ₁₀ H ₈	128.2 ⁱ	218 ⁱ	10.4 ⁱ –12.3 ^c	3.37 ^e	4	31 ^{e,i}
1-Methylnaphthalene	C ₁₁ H ₁₀	142.2	242 ^j	8.3 ^c	3.87 ^e		28 ^e
2-Methylnaphthalene	C ₁₁ H ₁₀	142.2 ^d	241 ^d	9.0 ^c	3.97 ^g	4.76	24.6 ^h
2,6-Dimethylnaphthalene	C ₁₂ H ₁₂	156.2 ⁱ	263 ⁱ	20.4 ⁱ	4.35 ^h		2 ⁱ
Acenaphthylene	C ₁₂ H ₁₂	152.2 ^d	280 ^d	0.89 ^j	4.07 ^d		3.9 ^j
Acenaphthene	C ₁₂ H ₁₀	154.2 ⁱ	279 ⁱ	0.29 ^j	3.93 ⁱ	5.07	3.9
Fluorene	C ₁₃ H ₁₀	166.2 ⁱ	295 ⁱ	8.0 × 10 ⁻²¹	4.18 ^e	4.52	4.64 ^k ; 1.9 ^{e,i,l}
Phenanthrene	C ₁₄ H ₁₀	178.2 ⁱ	340 ⁱ	1.6 × 10 ⁻²¹	4.57 ^e		1.1 ^e
Anthracene	C ₁₄ H ₁₀	178.2 ⁱ	342 ⁱ	8.0 × 10 ⁻²¹	4.5 ⁱ		73 ⁱ
Fluoranthene	C ₁₆ H ₁₀	202.3 ⁱ	375 ⁱ	1.2 × 10 ⁻²¹	5.22 ⁱ		260 ⁱ
Pyrene	C ₁₆ H ₁₀	202.3 ⁱ	393 ⁱ	6.0 × 10 ⁻²¹	5.18 ⁱ		135 ⁱ
Chrysene	C ₁₈ H ₁₂	228.3 ⁱ	448 ⁱ	8.4 × 10 ⁻²¹	5.91 ⁱ		0.002 ⁱ
Benzo[<i>a</i>]pyrene	C ₂₀ H ₁₂	252.3 ⁱ	496 ⁱ	7.3 × 10 ⁻²¹	6.50 ⁱ		0.0038 ⁱ
Dibenzo[<i>a,h</i>]anthracene	C ₂₂ H ₁₄	278.4	524 ⁱ	2.0 × 10 ⁻¹⁰¹	6.50 ⁱ	5.80 ⁱ	0.0005 ⁱ
Phenolics							
Phenol	C ₆ H ₆ O	94.1 ^b	182 ^b	61 ^c	1.46 ^b		93 000 ^b ; 88360 ^e ; 67 000 ^m
<i>o</i> -Cresol	C ₇ H ₈ O	108.1 ^d	191 ^d	37 ^c	1.98 ^e		26 000 ^g
<i>m</i> -, <i>p</i> -Cresol	C ₇ H ₈ O	108.1 ^d	202 ^d	22 ^c /16 ^c	1.96/2.01 ^d		24 000 ^m ; 22 700/ 21 500 ^l
2,4-Dimethylphenol	C ₈ H ₁₀ O	122.2 ^d	212 ^d		2.35 ^e ; 2.42 ^d		8795 ^e
Nitrogen-containing heterocycles							
Pyrrrole	C ₄ H ₅ N	67 ^b	131 ^b		0.75 ^b		58 800 ^b
Indole	C ₈ H ₇ N	117 ^b	254 ^b		2.00 ^b		1875 ^b
Quinoline	C ₉ H ₇ N	129 ^b	238 ^b		2.03 ^b	4.2	6300 ^b ; 60 000 ^{d,l,m}
Isoquinoline	C ₉ H ₇ N	129 ^b	243 ^b		2.08 ^b		4500 ^b
Benzoquinoline	C ₁₃ H ₉ N	179.2 ^d			3.54 ^b		
Acridine	C ₁₃ H ₉ N	179 ^b	346 ^b		3.4 ^b	3.36	46.5 ^b
Benz[<i>c</i>]acridine	C ₁₇ H ₁₁ N	229 ^g					
Carbazole	C ₁₂ H ₉ N	167 ^b	355 ^b		3.29 ^a ; 3.71 ^b	4.01	1.2 ^b ; 0.91 ^k
Aromatic amines							
Aniline	C ₆ H ₇ N	93 ^g	184 ^g	65 ^g	0.90 ^g		36 ^g
Sulfur-containing heterocycles							
Thiophene	C ₄ H ₄ S	84 ^b	84 ^b	8400 ^f	1.81 ^b		3600 ^b
Benzo[<i>b</i>]thiophene	C ₈ H ₆ S	134 ^b	221 ^b	26 ^g	3.12 ^b	3.7	130 ^b
Dibenzothiophene	C ₁₂ H ₈ S	184 ^b	332 ^b	0.26 ^g	4.38 ^a ; 5.45 ^b	5.45	1.0 ^b ; 0.53 ^k
Oxygen-containing heterocycles / furans							
Furan	C ₄ H ₄ O	68 ^d	31.3 ^d	80 300 ^c	1.34 ^e		28 600 ^g ; 10 000 ^d
Benzo[<i>f</i>]furan	C ₈ H ₆ O	118 ^b	174 ^b		2.67 ^b	2.96	100–1000 (18 °C) ^g
Dibenzofuran	C ₁₂ H ₈ O	168 ^b	285 ^b		4.12 ^b ; 4.31 ^e	4.74	4.75 ^b ; 3.1 ^k

NOTES:

- a Rostad et al. (1985); experimental log tar/water partition coefficient.
- b Johansen et al. (1998).
- c Rippen (1999).
- d Verschueren (1996).
- e Broholm et al. (1999a).
- f At 20 °C; Auer-Technikum (1988).
- g ChemFinder.com Database & Internet Searching (<http://www.chemfinder.com>).
- h Hansch & Leo (1979).
- i Data on PAHs taken from IPCS (1998); details on other PAHs to be found there; solubilities from Mackay & Shiu (1977).
- j BUA (1990).
- k Lu et al. (1978).
- l Raven & Beck (1992); calculated from relation of Shiu et al. (1988).
- m Sundström et al. (1986).
- n IPCS (1995).
- o Bleeker et al. (1998).
- p At 20 °C; Mackay et al. (1982).

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Table A-3 Compounds Found in Old Railway Ties (UNEP Chemical Assessment document)

Compound	Concentrations (mg/kg shavings)		
	Germany ^a (n = 5) ^b	Canada ^c (n = 27)	
	range	range	mean
Acenaphthene	44–973	139–5600	1410
Acenaphthylene		n.d. ^d –42	11
Anthracene		273–5300	1170
Benzo[a]anthracene		167–2110	599
Benzo[a]fluoranthene	22–419		
Benzo[b]fluoranthene	+ [j]: 307–2316	82–948	421
Benzo[k]fluoranthene	100–1930	52–811	310
Benzo[ghi]perylene		28–339	142
Benzo[e]pyrene	30.8–1300		
Benzo[a]pyrene	43.8–1573	86–656	342
Cyclopenta[def]phenanthrene	418–3917		
Chrysene	+ triph: 266–12 950	220–2260	681
Dibenzo[a,h]anthracene		n.d.–187	64
Fluoranthene	833–23 067	481–7820	2560
Fluorene	58–1849	178–4910	1420
Indeno[1,2,3-cd]pyrene	322–354	18–389	193
Naphthalene	6.4–392		
Phenanthrene	+ anth: 1005–19 892	654–13 500	3720
Perylene	32–231		
Phenylanthracene	101–2140		
Pyrene	553–11 683	356–5110	1670
Dibenzofuran	23–990		
Dibenzothiophene	22–1420		
Quinoline	7.8–30.5		
Phenols (phenol, mono-, di-, trimethylphenols)	0.48–37.8		
1-Naphthol	0.8–5.1		
4-Phenylphenol	0.5–7.7		

Notes: a Rotard & Mailahn (1987).

b Three samples from sleepers installed in playgrounds, one sample from closed railway sleepers, one sample from discarded sleepers provided as firewood (with maximum concentrations in the playground sleepers); anth = anthracene; [j] = benzo[j]fluoranthene; triph = triphenylene.

c Gurprasad⁷⁶ et al. (1995).

d n.d. = not detected

⁷⁶ Gurprasad N, Sproull J, Chau D, Constable M (1995) Polycyclic aromatic hydrocarbons in creosote impregnated waste materials from across Western Canada. *International Journal of Environmental Analytical Chemistry*, 60:95–99.

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Table A-4 Qualitatively Determined Thermolysis Products (From Becker et al., 2001)

Compound	Untreated Wood			Creosote			Treated Wood		
	400°C	600°C	800°C	400°C	600°C	800°C	400°C	600°C	800°C
C4H6O butenal	x								
C5H10O, e.g. methylbutanal	x	x	x				x		
C5H4O2, e.g. furfural	x						x		
C5H8O3, e.g. levulinic acid	x								
C5H6O2, e.g. furanmethanol							x		
m/z=84, z.B C4H8N2 or C2H4N4	x						x		
Butenal							x		
C5H6O2, e.g. cyclopentandione							x		
C5H6O3, e.g. dihydromethylfurandione	x						x		
C6H6O2, e.g. pyrocatechol or methylfurfural	x						x		
C6H10O, e.g. methylenpentanone	x								
Ethylbenzene				x	x	x			
Xylene				x	x	x			
C5H8N2				x	x	x			
Ethynylbenzene				x	x	x			
C8H8, e.g. styrene				x	x	x		x	x
C8H12N2O, e.g. methoxymethylethylpyrazin							x		
C8H8O3, e.g. hydroxymethoxybenzaldehyde							x		
C8H16, e.g. octene	x								
C6H8N2O, e.g. methoxymethylpyrimidine	x								
C7H8O2, e.g. guaiacol or methylprocatechol	X								
C8H10O, e.g. dimethylphenol			x						
C8H10O2, e.g. methylguaiacol or ethyl-pyrocatechol	x								
C8H8O3, e.g. hydroxymethoxybenzaldehyde	x								
C10H16				x	x	x			
Benzaldehyde						x		x	x
C9H12, e.g. ethylmethylbenzene				x	x				
C9H12, e.g. trimethylbenzene				x	x	x			
Phenol	x	x	x	x	x	x	x	x	x
Isocyanobenzene						x		x	
Benzofurane		x	x	x	x	x		x	x
Guaiacol							x		
C7H6O2						x			
C9H10, e.g. propenylbenzene				x	x	x			
C9H8, e.g. propinylbenzene				x	x	x			
Cresol		x	x	x	x	x		x	x
Methylbenzaldehyde						x			
C9H8O, e.g. methylbenzofurane						x			
C10H10					x	x			
Naphthalene		x	x	x	x	x	x	x	x
Benzothiophene				x	x	x			
Quinoline				x	x	x	x	x	x
C11H14				x	x				
Isoquinoline				x	X	x			
C11H10, e.g. methylnaphthalene	x	x		x	x	x	x	x	x
C11H10, e.g. 1-ethyliden-1H-indene				x					x
Methylbenzothiophene					x	x			
C10H9N (3 peaks), e.g. methylquinoline				x	x				
C10H12O2, e.g. methoxypropenylphenol							x		
C11H10, e.g. 1-ethyliden-1H-indene					x	x			
Dihydromethoxy-naphthalene						x			
Ethyl- und dimethylnaphthalene					x				
C12H12, e.g. 2,5-cyclohexadien-1-yl-benzene									x
C12H12, e.g. ethyl- und dimethylnaphthalene (4 peaks)				x			x	x	x
C10H9N, e.g. methylquinoline				x		x			
Peak with m:z-124			x						
Methylantracene								x	
4H-cyclopenta[def]phenanthrene							x	x	x
Cyclopenta[def]phenanthrenone									x
Ethenylnaphthalene or biphenyl				x	x	x	x	x	x
C12H10, e.g. biphenyl						x			
C12H8 acenaphthylene or biphenylene				x	x	x	x	x	x
C12H12, e.g. ethyl- or dimethylnaphthalene				x	x	x			
Acenaphthene	x	x		x	x	x	x	x	x
C13H12, e.g. methyl-biphenyl				x	x				
Naphthalenecarbonitrile				x	x				
Dibenzofurane	x	x	x	x	x	x	x	x	x

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Compound	Untreated Wood			Creosote			Treated Wood		
	400°C	600°C	800°C	400°C	600°C	800°C	400°C	600°C	800°C
Fluorene				x	x	x	x	x	x
Methylfluorene (3 peaks)						x			
Fluorene-9-one						x		x	x
Dibenzothiophene				x	x	x	x	x	x
Phenanthrene				x	x	x	x	x	x
Anthracene				x	x	x	x	x	x
C12H9N, e.g. 9H-carbazole or 5H-indeno[1,2-6]pyridine				x	x	x	x	x	x
C13H9N, e.g. acridine or phenanthridine				x	x	x			
Methyldibenzothiophene						x			
Trimethylnaphthalene (4 peaks)				x	x	x			
C13H14, e.g. methylethyl-naphthalene				x					
C13H12 (3 peaks)				x	x	x	x		
C13H10O, e.g. xanthene						x			
C13H10O (3 peaks), e.g. methyldibenzofurane or 9H xanthene					x	x	x	x	x
C14H12 (4 peaks), e.g. 9,10 dihydro-phenanthrene or -anthracene or methyl-9H-fluorene				x	x		x		
C15H12 (3 peaks) e.g. methylphenanthrene or -anthracene or phenylindene				x	x	x	x	x	x
C15H9N, e.g. acenaphthopyridine				x					
4H-cyclopenta[def]phenanthrene				x	x	x			
Methylcarbazole					x	x			
Phenyl-naphthalene				x	x	x	x	x	x
C16H14, dimethyl- or ethylphenanthrene or -anthracene				x	x	x			
Cyclopenta[def]phenanthrenone						x			
Fluoranthene				x	x	x	x	x	x
Pyrene				x	x	x	x	x	x
C16H10									x
C16H12, e.g. 9-ethenyl-anthracene					x	x			
C16H12, e.g. dihydro-pyrene				x	x	x			
C16H10O (2 peaks), e.g. hydroxypyrene or benzo[b]naphtho[2,3-d]furan				x	x	x	x	x	x
C17H14, e.g. phenylmethyl-naphthalene				x	x		x		
C18H16						x			
C17H12 (2 peaks), e.g. 11H-benzofluorene or methylpyrene				x	x	x	x	x	x
C18H14 (3 peaks), e.g. dimethylpyrene				x	x	x			
Pyrenecarboxaldehyde						x			
C17H16O, e.g. 7H-Benz[de]anthracen-7-one					x				
C16H10S, benzo[b]naphthothiophene				x	x	x	x	x	x
Benzo[ghi]fluoranthene				x	x	x	x	x	x
m:z-229, probably benzo[a]acridine				x	x	x			
m:z-230, probably 7H-Benz[de]anthracen-7-one						x			
C19H14, e.g. methyltriphenyl				x	x				
1,2-Benzanthracene				x	x	x	x	x	x
Triphenylene				x	x	x	x	x	x
C18H12, e.g. chrysene							x	x	
C18H12, e.g. benzophenanthrene				x	x	x			
C19H14, e.g. methylchrysene							x		
C19H14 (3 peaks), e.g. methylbenzanthracene or methylchrysene				x	x	x			
C16H11N, e.g. benzocarbazole				x	x	x			
C20H14, e.g. binaphthalene or phenylanthracene				x	x	x			
3 peaks with C20H12, e.g. benzofluoranthene or perylene				x	x	x	x	x	x
Benzo[a]pyrene				x	x	x	x		x
C21H16				x	x	x			

Appendix B: Selection of Low Carbon Fuels

In March of 2011 as part of the Cement 2020 project, funded in part by the Asia Pacific Partnership, a “Request For Information (RFI)” was issued to the business community. The goal of the RFI was to ask prospective local business partners to identify fuel sources that would meet each of the three interrelated “Triple Bottom Line” criteria of sustainability. A particular emphasis was placed on low carbon fuel sources that would allow the Bath Cement plant to reduce its net carbon emissions amongst other emissions. Fifteen proposals were received that outlined the characteristics of the fuel sources, the tonnages available on an annual basis, and a rationale as to why they would be considered “greener” than current fuels. Project co-investigators had earlier made the important point that no fuel is perfectly “green” but fuels may be “greener” than other fuel choices.

An important part of the “social” bottom line is to bring partner stakeholders into the decision making process. This process was carried out through a multi-stakeholder task force which had as its task the development of a “Greener Fuel Protocol”. This protocol answers the question, how do we grade or assess the relative “greenness” of a fuel choice? The economics of the fuel choice were assessed separately. The team kicked off its work with a tour of the Bath cement plant and an introduction to the manufacture of cement and pollution control and fuel use in the cement plant context. The Task Force met over the summer and early fall of 2011 to determine what factors are important to consider and identified 6 categories for evaluation:

1. **Fuel Supplier:** Does the supplier of the fuel conduct its operations in a sustainable manner (or is it prepared to adopt better practices in order to be considered a suitable fuel supplier)? A number of discrete elements were listed in the assessment to produce a total score.
2. **Fuel User:** Very similar to the fuel supplier section, the same approach was adopted for the fuel user.
3. **Greenhouse gases:** Consideration of the carbon footprint of the fuel from its production, processing, transportation, and additional processing and other effects at the fuel user site. A percentage reduction was used to score this section.
4. **Air Emissions:** This section begins with a screening evaluation to identify which air pollution elements merit the closest scrutiny. It acknowledges the technical underpinnings of cement plant operations (i.e. which fuel characteristics have the most significant effects on air emissions from the facilities.) A score is produced.
5. **Other Environmental Aspects:** Water use, potential for transportation effects (e.g. a spill), resource consumption, other benefits (e.g. waste diversion), and other aspects. A score is produced.
6. **Social Aspects:** Consideration of the potential for local economic development, educational opportunities, technology development and potential for technical expertise export, and other aspects. A score is produced.

The candidate fuels, on a preliminary basis, were screened using the draft tool. Those fuels that met the economic criteria AND were successful through the Greener Fuel Protocol assessment were put forward for additional scrutiny. Consistent with the precautionary principle, the Task Force and the Lafarge Bath Plant’s Community Liaison Committee both recommended that demonstration testing be carried out prior to their permanent use at the Bath Cement plant. Additional public consultation in November, 2011 bore

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out the wisdom of this precautionary approach. In the specific case of railway ties, it was further recommended that additional research be carried out to validate their expected efficacy as a fuel source – which was completed through the development of this report. Also, since many of the fuel contain fossil derived materials mixed with virgin biomass – but typically at lower concentrations than is the case with railway ties – this report was partially prepared with these other fuels in mind.

Many of the fifteen proposals were screened out due to their cost structure or their need for costly drying. Indeed one of the major obstacles identified to the use of biomass and biomass containing fuels is the need to construct a separate feed system and the implicit requirement to justify this capital investment from the fuel savings. In the absence of carbon costing systems, not expected to take full effect until 2020 or later, and noting that virgin biomass fuels are higher in cost and lower in quality than fossil fuels, capital investment is not warranted. However, capital investment in a fuel processing and feed infrastructure is merited for the other low carbon fuels selected and this also serves to provide the necessary infrastructure for many of the other fuel sources when their cost structure becomes affordable.

Some fuel sources were “screened out” pending additional research or future changes. For example, studies were considered that showed that the use of “auto fluff” produces higher CO_{2e} emissions than the reference fuels (coal, petcoke) when considered from a life cycle basis. “Auto fluff” is what remains when the metal from an automobile is removed. There are other potential benefits (eg waste diversion) associated with the use of “auto fluff” but it did not meet the low carbon fuel definition and was deferred for further review at a later time. Other fuels, such as sewage derived biosolids, were deferred due to anticipated social acceptance concerns. Also biosolids require processing into a fuel form and this requires investment by municipalities and the desire to move ahead with low carbon fuels in 2012-2015 suggested that other fuel sources be developed first.

Some possible fuel supplies would depend on the simultaneous development of other economic activities. An example of this is the use of hemp hurd. As a sole product it is not economical to produce hemp hurd, the portion of the hemp stalk remaining after the fibre is removed; but it may be an economical source should a fibre decortification plant be built that can produce large scale supplies of fibre for a variety of markets. However, as noted above, construction of a feed system using readily available, economically priced low carbon fuels will prepare the Bath plant to receive hemp hurd should a hemp fibre business be developed.

One additional fuel source arises from the torrefaction of biomass (including some low carbon fuels) which acts to raise the heating value of the material to close to that of coal. This results in the potential to increase the co-fire rates to levels higher than the 30% expected to be achievable with the low carbon fuels suggested in the phase of the Cement 2020 program. Lafarge is working with various partners who are developing novel torrefaction processes and should they be successful in producing test quantities of this type of fuel the Bath plant hopes to test this promising fuel source in addition to the others identified.

The fuel sources that were “screened in” are listed in the table below.

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Table B-1 Feedstock description

Type of feedstock	Description
Construction & demolition (C&D) debris	<p>1) A renewable biomass product generated from C&D sites, mainly composed of wood.</p> <p>2) Graded based on their contents of unwanted materials (e.g. rocks, wallboard, metal, etc) and particles sizes (from very fine to 10 inches).</p> <p>3) The control of moisture content, ash quality and fuel particle size also affects the use of C&D debris as a fuel.</p>
Railway ties	<p>1) A special example of C&D</p> <p>2) Ties are typically 85% wood and 15% coal-derived creosote</p>
Pre-consumer, post diversion materials	Essentially non-recyclable, mixed (biomass, biomass/fossil) materials from manufacturers, including coffee chaff, off-spec materials, etc.
Post-consumer, post diversion materials	Essentially non-recyclable materials from recycling companies. Examples are paper coffee cups, cardboard cast offs, etc.
Asphalt shingles	Derived from bitumen, screened to remove aggregates, lower CO _{2e} emissions than coal.
Torrefied biomass	Torrefaction is a process that increases biomass energy density and enhances its hydrophobic properties. Testing depends on its availability from a 3 rd party.

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The work was reviewed by Edward W. Grandmaison, Ph.D., P.Eng. Professor Emeritus, Chemical Engineering, Queen's University in Kingston, ON. As an academic at Queen's University since 1979, his research interests have included Transport phenomena, Turbulent mixing in jets, flames and flares, Low NOX combustion for industrial furnaces, and Energy efficiency in industrial furnace operations. During his time at Queen's University he as served as Associate Head, Chemical Engineering, 2008-2011; Chair, Undergraduate Studies, Chemical Engineering, 1996-1998, 2002-2011; Operations Committee, Curriculum, Faculty of Applied Science 2000-2001; and many other senior administration and research roles. Dr. Grandmaison is a Member and Fellow (FCIC), Canadian Society for Chemical Engineering, and a Member of the Order of Engineers of Quebec (ing.) and the Combustion Institute (International and Canadian), an associate Member, American Flame Research Committee.

Lafarge contribution to this work came from Robert Cumming, MASC, P.Eng, Environment & Public Affairs Manager at the Lafarge facility in Bath, Ontario and Sam Fujimoto, BASc, Senior Process Engineer based out of Lafarge's Technical Services facility in Montreal, P.Q. Mr Cumming has been the Senior Project Manager for the Energy Farm Project (2007-2010) and the Cement 2020 Project with over 23 years of experience in environmental engineering. Mr. Fujimoto has over 28 years of cement process engineering experience specializing in the use of non-traditional fuels and environmental process engineering.